A. THE PREPARATION OF DILUTE, DRY, NONAQUEOUS SOLUTIONS OF MOLECULAR IODINE INOCULATED WITH IODINE-131.

^{131}I and

B. THE DISTRIBUTION OF MOLECULAR IODINE BETWEEN CYCLOHEXANE AND AQUEOUS SOLUTIONS.

BY

GARET E. VAN DE STEEG

B.S. Marquette University, 1962

DISSERTATION

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
in the Graduate School of
The University of New Mexico
Albuquerque, New Mexico
June, 1968

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DISCLAIMER

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Garet E. Van De Steeg, Ph.D

Department of Chemistry

The University of New Mexico, 1968

A. The preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131 has been investigated. The dilute, dry, nonaqueous solutions of molecular iodine were inoculated with iodine-131 via the isotopic exchange of iodine atoms between iodine-131 activity adsorbed on a platinum surface and the molecular iodine in solution. This procedure permits the preparation of dilute, dry solutions of molecular iodine, in a number of nonaqueous solvents, which are inoculated with appropriate amounts of iodine-131 without introducing any known or measurable impurities into the solution, without affecting the iodine concentration, without changing the chemical nature of the dissolved iodine and without introducing into the solutions iodine-131 species which behaved in a manner other than that expected of molecular iodine. Another procedure, whereby the dilute, dry, nonaqueous solutions of molecular iodine were inoculated with iodine-131 via the isotopic exchange of iodine atoms between iodide-131 adsorbed on the surface of preformed silver iodide precipitates and molecular iodine in solution, was investigated briefly; this procedure, however, was not as satisfactory as the procedure, just described, employing the use of platinum.

B. The distribution of iodine between cyclohexane and aqueous solutions was investigated. The distribution coefficient was found to be dependent on the pH and ionic strength of the aqueous phase, the initial concentration of iodine in the cyclohexane, the duration of the mixing process for the cyclohexane - iodine - aqueous system and the purity of the cyclohexane. However, when very high purity cyclohexane was used the dependence of the distribution coefficient on the pH of the aqueous phase, the initial concentration of iodine in the cyclohexane and the duration of the mixing process for the cyclohexane - iodine - aqueous system was decreased. Iodine-131 species, which did not behave as molecular iodine, iodide or hypoiodite, were observed in both the cyclohexane and aqueous phases of the two-phase reaction mixture after 24 hours or more mixing time. A mechanism, encompassing reactions between iodine and impurities originally present in the cyclohexane, is proposed to explain the observed behavior of the distribution coefficient.

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ABBREVIATIONS AND SYMBOLS

F = formal

M = molar

N = normal

D = distribution coefficient

*p*H = negative log of the hydrogen ion activity

u = ionic strength

g = grams

ml. = milliliter

cc. or cm^3 = cubic centimeter

° = degrees centigrade

* = iodine-127 labeled with iodine-131

[ ] = molar quantities

K = equilibrium constant

% = percent

rpm = revolutions per minute

mm. = millimeter

cm = centimeter

λ = microliter

Ppt = precipitate

hr. = hour

C_6H_{12} = cyclohexane

PART A

THE PREPARATION OF DRY, DILUTE, NONAQUEOUS SOLUTIONS OF MOLECULAR IODINE INOCULATED WITH IODINE-131

A.I. INTRODUCTION

Preliminary work on the subject of the distribution of iodine between nonaqueous solvents and aqueous solutions indicated that it would be necessary to develop a procedure for the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with appropriate amounts of iodine-131.

Initially, the dilute, dry, nonaqueous solutions of molecular iodine were inoculated with iodine-131 via the isotopic exchange of iodine atoms between iodide-131 adsorbed on the surface of preformed silver iodide precipitates and the molecular iodine in solution. The development of this procedure was not pursued to a significant extent, however, because the yield of iodine-131 in the nonaqueous iodine solutions was only about 10 percent of the initial starting activity and because of the mechanical problems encountered when working with an active, finely divided silver iodide precipitate; for example, the dry, finely divided precipitate could easily be dislodged by an air current and scattered around the laboratory.

Subsequently, a different approach was undertaken. A number of investigators had reported that under certain conditions, carrier-free iodine-131 activity is almost quantitatively adsorbed from aqueous solutions by platinum (1, 2, 3, 4, 5, 6 and 7). Therefore, an investigation into the inoculation of dilute, dry, nonaqueous solutions of molecular iodine with iodine-131, via isotopic exchange with iodine-131 activity adsorbed on a platinum surface, was undertaken. This investigation led to a successful procedure whereby iodine solutions in a number of nonaqueous solvents could be inoculated with iodine-131 without introducing any known or measurable impurities into the solution, without affecting the iodine concentration, without changing the chemical nature of the dissolved iodine and without introducing into the solutions iodine-131 species which behaved in a manner other than that expected of molecular iodine.

A.II. EXPERIMENTAL

A.II.a. General Procedures, Reagents and Materials

Two procedures were investigated for use in the activation of dry, dilute, nonaqueous solutions of molecular iodine. One procedure involved preformed silver iodide precipitates whose surface was made active with adsorbed iodide-131. The other procedure employed platinum foil which had iodine-131 activity adsorbed on its surface.

The term "adsorption" used in this chapter refers to the following:

1. For silver iodide precipitates; uptake of carrier-free iodine-131 by preformed silver iodide precipitates via adsorption on the surface of the precipitate and/or isotopic exchange with iodide ions in the crystal lattice.
2. For platinum foil;
   a. uptake of carrier-free iodine-131 activity by platinum foil via adsorption on the surface of the foil, or,
   b. uptake of carrier-free iodine-131 activity by iodinated platinum foil via adsorption on the surface of the foil and/or isotopic exchange with iodine previously adsorbed onto the surface of the foil.

Iodination is that process whereby iodine-127 is adsorbed onto the surface of the foil by exposure of the foil to a nonaqueous solution of molecular iodine.

Except where noted, procedures were usually carried out in the presence of ordinary fluorescent lighting. The exclusion of light, where noted, was accomplished by wrapping the entire reaction vessel in aluminum foil after the reactants had been added. Except where noted, no attempt was made to maintain the reactants at a constant temperature during the experiments; all reactions were performed at room temperature (22 ± 2°) with the exception of one instance where the temperature was 50°.

Water

All water used in this research was prepared in the following manner. Ordinary distilled water was redistilled from alkaline permanganate in an all-Pyrex system and stored in Pyrex vessels capped with 24/40 female Pyrex joints.

Perchloric Acid

Analytical reagent grade perchloric acid (Mallinckrodt) was fumed for one hour in an open platinum crucible at 160° (8). Prepurified nitrogen gas (Matheson) was passed directly from the tank through the acid during the heating, fuming and cooling process. Upon cooling, the fumed nitrogen-treated acid was immediately diluted with about twice its volume of water. The concentration of the dilute acid was determined by titration with standard sodium hydroxide.

Nitrobenzene

Reagent grade nitrobenzene (Baker) was fractionally distilled, from alumina, in the dark, under vacuum through a 20-plate Oldershaw column according to the procedure of Lin (9).

Iodine

Analytical reagent grade iodine (Mallinckrodt) was resublimed under vacuum and, then stored in a desiccator over anhydrous calcium sulfate.

Cyclohexane, Methanol and Carbon Tetrachloride

Eastman Spectro Grade cyclohexane and methanol and Spectro Grade carbon tetrachloride (Matheson, Coleman and Bell) were used without further purification.

Radioiodine

The radioactive iodine used was carrier-free iodide-131 obtained in a slightly basic sulfite solution from Oak Ridge National Laboratories (ORNL). Stock solutions of carrier-free iodide-131 were prepared by removing microliter amounts of the radioactive solution from the original container and inoculating freshly prepared. 1.00×10^{-3} $\underline{F}$ sodium sulfite. These stock solutions were used immediately after preparation.

Other Reagents

All other reagents were of analytical reagent grade and used without further purification.

Glassware

All glassware was constructed of borosilicate glass (Pyrex or Kimax) and, in the case of centrifuge tubes, volumetric flasks and Erlenmeyer flasks, were fitted with ground-glass stoppers. All volumetric glassware was of Class A tolerance.

Glassware was cleaned by immersion in chromic acid for at least 12 hours. The glassware was then rinsed with ordinary distilled water, followed by a thorough rinsing with water distilled from alkaline permanganate, covered with aluminum foil and dried in an oven at 110°. The possibility of radiochemical contamination by adsorbed iodine-131 activity was resolved by monitoring all counting tubes and reaction vessels after cleaning.

Centrifugation

Centrifugations were performed in an International Clinical Centrifuge at 2000 to 3000 rpm.

Counting Procedures

A Nuclear Chicago Model 132 single channel analyzer in conjunction with a Nuclear Chicago DS-5 Na(Tl) well-type scintillation probe was used to detect the gamma activity of the iodine-131. Samples were prepared and counted in 15 x 125 mm. calibrated Pyrex test tubes.

The test tubes were calibrated by filling them to a predetermined height (corresponding to a volume of approximately 10.5 ml.) with an iodide-131 solution and counting. Those tubes which gave the same counting rate within an expected standard deviation of ± 0.6 percent were used for counting. All liquid samples were diluted to the standard counting-height and counted to within an expected standard deviation of ± 1.0 percent. Counting rates were not corrected for variations in solution densities: Kahn (10) has reported that over the range of 0.88 to 1.04 grams/ml. the change in counting rate due to self-absorption is negligible.

As indicated in Figure A.6 it was necessary to count activity on the platinum foils. Rather than dissolving the foils in aqua regia and counting the solution, the foils were placed directly in empty counting tubes and counted. The counting rate ratio, activity on foil activity in solution, was determined by comparing the counting rate of the iodine-131 activity on a platinum foil with the counting rate of the solution produced by dissolving the active foil in aqua regia. This ratio was found to be 2.31 ± 0.01. In the dissolution of an active foil in aqua regia, at room temperature, over 4 hours, at least 99 percent of the adsorbed iodine-131 was recovered.

As indicated in Figures A.1 through A.5, it was necessary to count the activity on the silver iodide precipitates. The silver iodide precipitates were dissolved in a potassium cyanide solution and counted.

The Preparation of Dilute, Dry, Nonaqueous Solutions of Molecular Iodine

A 1.00×10^{-2} F molecular iodine solution was prepared by adding the prescribed amount of iodine crystals to a 100-ml. volumetric flask and immediately diluting to the mark with the dry, nonaqueous solvent. This solution was stored in the presence of light for up to one month and constituted the solution from which the more dilute solutions of iodine were prepared. In the case of nitrobenzene solutions of molecular iodine, the solutions were prepared and stored in the dark. The more dilute solutions of molecular iodine were prepared by further dilution of aliquots of the 1.00×10^{-2} F iodine solution. The iodine crystals were weighed on a Mettler H-16 balance to ± 10 micrograms. Initially, aliquots of the 1.00×10^{-2} F iodine solutions were periodically titrated so that the iodine concentration would be accurately known. It was found, however, that over a period of one month, no change in the concentration of the iodine was detected.

A.II.b. The Preparation of Dilute, Dry, Nonaqueous Solutions of Molecular Iodine Inoculated with Iodine-131 by Isotopic Exchange with Iodine-131 Activity Adsorbed on Silver Iodide Precipitates

The procedures used to investigate various aspects of the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131 by isotopic exchange with iodine-131 activity adsorbed on the surface of preformed silver iodide precipitates are summarized in Figures A.1 to A.5 and described below.

A.II.b.1. Activation of Silver Iodide Precipitate Five ml. of aqueous 1.00×10^{-3} F potassium iodide and 0.2 ml. of 1.00×10^{-2} F perchloric acid were placed in a 10-ml., Pyrex, centrifuge tube and mixed. This was followed by the addition of 0.1 ml. of 0.100 F silver nitrate. The contents of the tube were stirred mechanically for several minutes by means of a Pyrex rod rotated at about 100 rpm. After stirring, the tube was stoppered and centrifuged. The aqueous layer was then drawn off by means of a capillary pipette and discarded. This procedure produced 1.175 mg. of silver iodide. Subsequently, the precipitates in the centrifuge tubes were treated using one of the five following procedures.

In procedure A, the silver iodide precipitate was washed twice with 5-ml. portions of 1.00×10^{-2} F perchloric acid, washed once with acetone and dried in an oven for 0.5 hour at 140° (see Figure A.1).

In Procedure B, the silver iodide precipitate was washed twice with 5-ml. portions of 1.00×10^{-2} F perchloric acid, aged for 12 hours while wet, washed once with acetone and dried in an oven for 0.5 hour at 140° (see Figure A.2).

In procedure C, the silver iodide precipitate was washed twice with 5-ml. portions of water (see Figure A.3).

In procedure D, the silver iodide precipitate was washed twice with 5-ml. portions of water, washed three times with 2-ml. portions of absolute ethanol and dried in an oven for 0.25 hour at 110° (see Figure A.4).

In procedure E, the silver iodide precipitate was washed once with 5 ml. of absolute ethanol and dried for several hours at room temperature in a vacuum desiccator (see Figure A.5).

These procedures were carried out in the centrifuge tubes. Each precipitate was washed by introducing the washing solution into the centrifuge tube and stirring the contents by bubbling air through the solutions for one minute, utilizing a capillary pipette with a rubber bulb at one end. The tube and its contents was then stoppered and centrifuged, and the liquid phase drawn off using a capillary pipette. The tube containing the silver iodide was capped with aluminum foil rather than with the stopper before placing in the oven to dry.

The dry, preformed silver iodide was activated by introducing into the cooled centrifuge tube one ml. of a stock solution of iodide-131 of known specific activity. The mixture was stirred either

1. mechanically for 3 minutes by means of a Pyrex rod which was rotated at about 100 rpm., or,
2. by passing 50 $cm.^3$ of air through the mixture for one minute.

Subsequently, the tube and its contents was stoppered, centrifuged, the aqueous phase drawn off with a capillary pipette and counted.

The active silver iodide precipitate in the centrifuge tube was treated using one of the five following procedures.

In procedure F, the active silver iodide precipitate was washed twice with 5-ml. portions of 1.00 x 10^{-2} $\underline{F}$ perchloric acid (see Figure A.1).

In procedure G, the active silver iodide precipitate was washed twice with 2.5-ml. portions of 1.00 x 10^{-2} $\underline{F}$ perchloric acid, washed once with acetone and dried in an oven for 0.5 hour at 140° (see Figure A.2).

In procedure H, the active silver iodide precipitate was washed twice with 2-ml. portions of water and dried in oven for 0.5 hour at 140° (see Figure A.3).

In procedure I, the active silver iodide precipitate was washed three times with 1-ml. portions of absolute ethanol and dried in an oven for 0.25 hour at 110° (see Figure A.4).

In procedure J, the active silver iodide precipitate was washed once with 2 ml. of absolute ethanol, washed once with 2 ml. of cyclohexane and dried for several hours at room temperature in a vacuum desiccator (see Figure A.5).

The washings involved introducing the washing solution into the centrifuge tube and stirring the contents by bubbling air through the solution for one minute, using a capillary pipette with a rubber bulb at one end. The tube and its contents was then centrifuged and the liquid phase drawn off using a capillary pipette. The tube containing the silver iodide was capped with aluminum foil rather than with the stopper before placing in the oven to dry.

<u>A.II.b.2. Activation of Nonaqueous Iodine Solution</u> The isotopic exchange between the active, dry, silver iodide precipitates and molecular iodine in cyclohexane was studied using the following procedure.

Five ml. of a 1.00×10^{-4} $\underline{F}$ molecular iodine-cyclohexane solution was added to the active silver iodide precipitate in the centrifuge tube. The mixture was then stirred using one of the three following procedures.

In procedure K, cm^3. of air was passed through the mixture, utilizing a capillary pipette as the delivery tube.

In procedure L, nitrogen gas was passed through the mixture for one minute utilizing a capillary pipette as the delivery tube.

In procedure M, nitrogen gas was passed through the mixture for 15 minutes utilizing a capillary pipette as the delivery tube. The tube and its contents was centrifuged and the cyclohexane phase was drawn off using a capillary pipette. The precipitate was then washed once with one ml. of cyclohexane, the tube centrifuged and the cyclohexane drawn off. The cyclohexane wash was combined with the iodine-cyclohexane solution and the whole counted. The silver iodide precipitate was dissolved in aqueous potassium cyanide and counted.

The percent exchange was calculated from the activity which remained in the silver iodide and the activity detected in the iodine-cyclohexane solution.

A.II.c. The Preparation of Dilute, Dry, Nonaqueous Solutions of Molecular Iodine Inoculated with Iodine-131 by Isotopic Exchange with Iodine-131 Activity Adsorbed on Platinum Foil

The procedures used to investigate various aspects of the preparation of dilute, dry, nonaqueous solutions of molecular iodine, inoculated with iodine-131 by exchange with iodine-131 activity adsorbed on the surface of a platinum foil are summarized in Figures A.6, A.7 and A.8 and described below.

A.II.c.1. Activation of Platinum Foil The following procedures were used in the pretreatment of the platinum foil prior to its activation with iodine-131. Platinum foil, 0.0625 mm. thick, was cut into 0.5 x 1.5 cm. strips. These strips were pretreated in the various manners described below and, then, in all instances, washed five times with water and stored under water in a glass-stoppered vessel until ready for use. The strips were subsequently supported on a nichrome spiral, heated to redness for one minute in the hottest portion of a Meeker burner flame and, then, either iodinated or placed directly in the reaction vessel.

Pretreatment A consisted of immersing the foils in concentrated nitric acid for 16 hours at room temperature.

Pretreatment B consisted of placing the foils in concentrated nitric acid for 16 hours at room temperature and, then, treating with aqua regia at room temperature for one minute.

In pretreatment C, the foils were immersed in concentrated nitric acid at room temperature for 16 hours followed by immersion in aqua regia for five minutes at room temperature.

In pretreatment D, the foils were treated with aqua regia at room temperature for five minutes.

Iodination consisted of placing the pretreated foils in a cyclohexane solution of inactive molecular iodine (usually 1.00×10^{-4} F) for a specific time (usually 16 hours) at room temperature in the presence of ordinary fluorescent laboratory light. The foils were then rinsed five times with cyclohexane and dried in an oven for 0.5 hours at 110°.

The following procedure was used to investigate the adsorption of iodine-131 activity by platinum foil (see Figure A.6).

Five ml. of an aqueous reaction mixture was transferred to a reaction vessel; 50 to 500 microliters of the iodide-131 stock solution of known specific activity was then added. Pretreated platinum foil (No. 1) was then introduced into the solution which had been mixed and the whole stirred for a given time. Foil No. 1 was subsequently washed with three one-ml. portions of water and, then, counted (count No. 1); count No. 2 represented the total activity present in the reaction mixture and the water washes subsequent to the removal of foil No. 1. The percent activity adsorbed by the foil and the total percent recovery were calculated from these data. Initially, 15 x 125 mm. Pyrex test tubes served as reaction vessels. The reaction mixtures were stirred mechanically with a Pyrex rod which was rotated at about 100 rpm. Subsequently, glass-stoppered 10-ml. Erylenmeyer flasks were used as reaction vessels. The reaction mixtures were stirred magnetically; the magnetic stirring bar consisted of a 0.1 x 0.5 cm. piece of iron wire sealed in a small piece of Pyrex tubing. The platinum foil, bent in the shape of a square-U, was placed on its side in the reaction vessel in order to expose the maximum amount of surface to the reaction mixture.

A.II.c.2. Activation of Nonaqueous Iodine Solution at Room Temperature

The following procedure was used to investigate the isotopic exchange of the iodine-131 activity, adsorbed on the platinum foil, with dilute, dry, nonaqueous solutions of molecular iodine (see Figure A.6). The platinum foil (No. 1) was activated for one hour, placed in a reaction vessel and dried in an oven for 2 hours at 110°. No detectable amount of activity was volatilized from the foil during the drying operation. Five ml. of a dry nonaqueous solution of inactive molecular iodine was added to the reaction vessel containing foil No. 1 and the whole stirred for a predetermined time.

This isotopic exchange procedure was also used in connection with other nonaqueous solvents with the following exceptions;

1. the inactive iodine solutions were freshly prepared, and,
2. the exchange process in nitrobenzene was carried out in the dark.

The percent exchange was calculated from the activity which remained on foil No. 1 (count No. 3) and the activity detected in the iodine solution (count No. 4).

A.II.c.3. Adsorption of Iodine onto Platinum Foil For very dilute (less than or equal to 10^{-4} $\underline{F}$ iodine) nonaqueous solutions of molecular iodine, it is important to know whether the initial concentration is decreased via adsorption on the platinum foil during the exchange process. Such information was obtained by immersing the platinum foil (foil No. 2) in the activated nonaqueous solution for a given time. The decrease in the iodine concentration was calculated from the activity on foil No. 2 and in the solution (see Figure A.7).

A.II.c.4. Activation of Nonaqueous Iodine Solution of 50° The following procedure was used to study the exchange, at 50°, of iodine atoms between iodine-131 adsorbed on a platinum foil and molecular iodine dissolved in cyclohexane. A 50-ml. round-bottomed flask with a 4-inch neck, ending in a 19/38 ground-glass joint, served as a reaction vessel. Twenty-five ml. of a dilute solution of molecular iodine in cyclohexane was transferred to the flask which was then loosely stoppered with a ground-glass joint. The flask was then immersed in a constant temperature (50° ± 0.25°) glycerine bath for 10 minutes to allow the contents to attain thermal equilibrium. A dry active foil, bent in the shape of a square-U, was then added to the flask and the whole stirred with a small Pyrex-covered magnetic stirring bar at about 100 rpm. The foil was removed periodically by means of a glass rod and counted. At the conclusion of the experiment, 10 ml. of the cooled iodine solution was counted; the percent recovery ranged from 100 to 102 percent, indicating little loss of solvent during the activation of the iodine solution.

A.II.c.5. Iodine-Solvent Reactions Clearly, it is important to know whether the presence of platinum in the nonaqueous iodine solutions would catalyze the formation of organic iodine compounds with either the solvent itself or impurities in the solvent. It was arbitrarily assumed that any iodine activity not extracted by aqueous sulfite was a measure of the formation of these organic iodine compounds. The procedure employed to detect the presence of nonextractable compounds of iodine is outlined in Figure A.8 and described below.

Five ml. of nonaqueous molecular iodine solution was transferred to each of two reaction vessels. An activated iodinated platinum foil (see Figure A.6) was then introduced into each solution and the contents of the vessels stirred magnetically for 2 hours. The platinum foil was subsequently removed from one of the vessels, a 0.5-ml. sample of the nonaqueous iodine solution taken from each vessel for analysis, and the stirring continued. Additional 0.5-ml. samples of the nonaqueous iodine solutions were removed from the vessels at specified time intervals and analyzed. The analysis consisted of treating the samples of the nonaqueous iodine solutions with aqueous sulfite, washing the nonaqueous phase with water, and determinating the percentage of activity which remained behind in the nonaqueous solvent by counting both the aqueous sulfite phase plus the water wash and the nonaqueous phase.

The effect of ordinary fluorescent laboratory light on the formation of these nonextractable iodine compounds was investigated with a procedure identical to that just described and outlined in Figure A.8 with two exceptions; both platinum foils were allowed to remain in the iodine solutions throughout the duration of the experiment, and, one of these solutions, beginning with the activation step, was kept continuously in the dark.

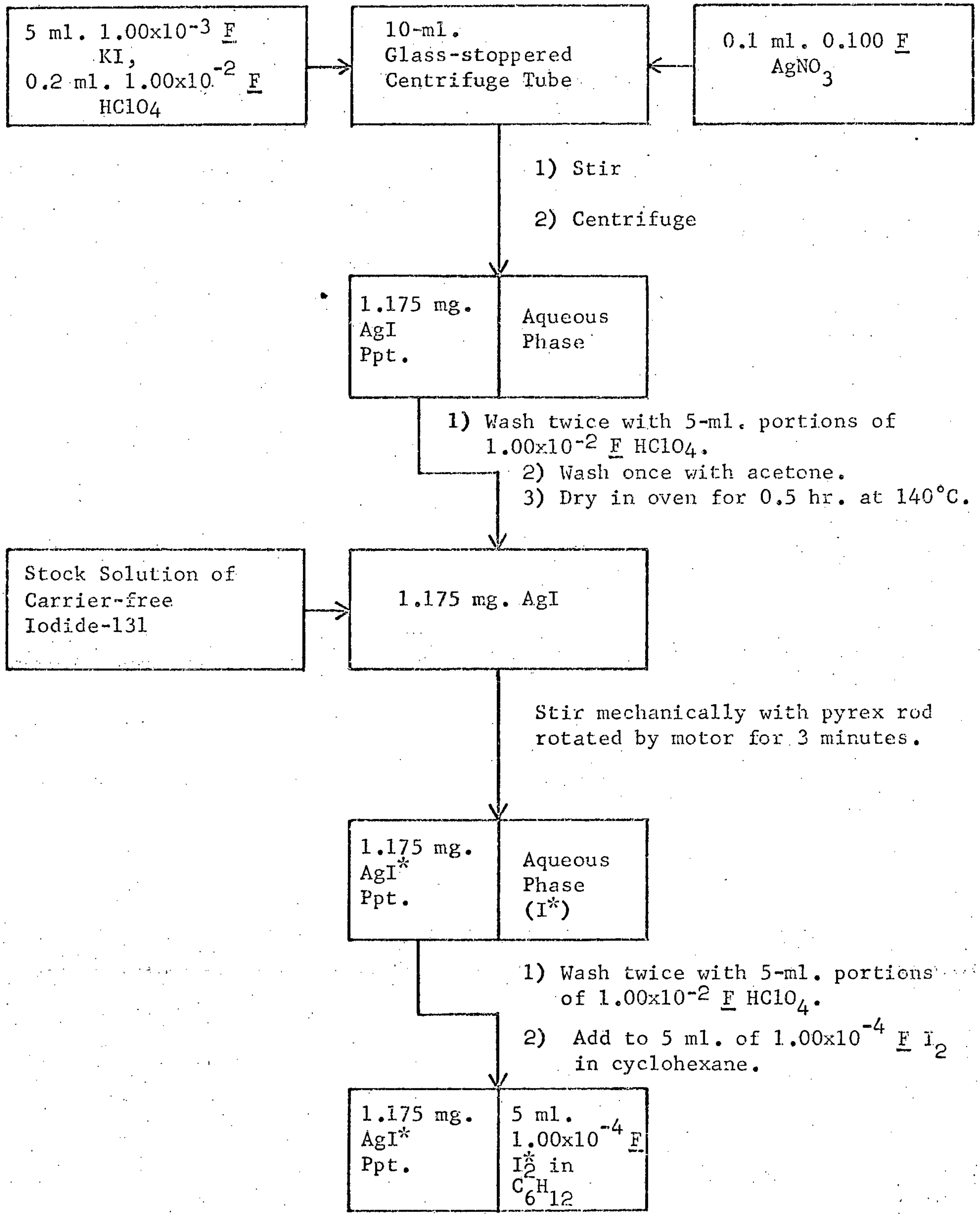


Figure A.1. Procedure used to investigate the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131.

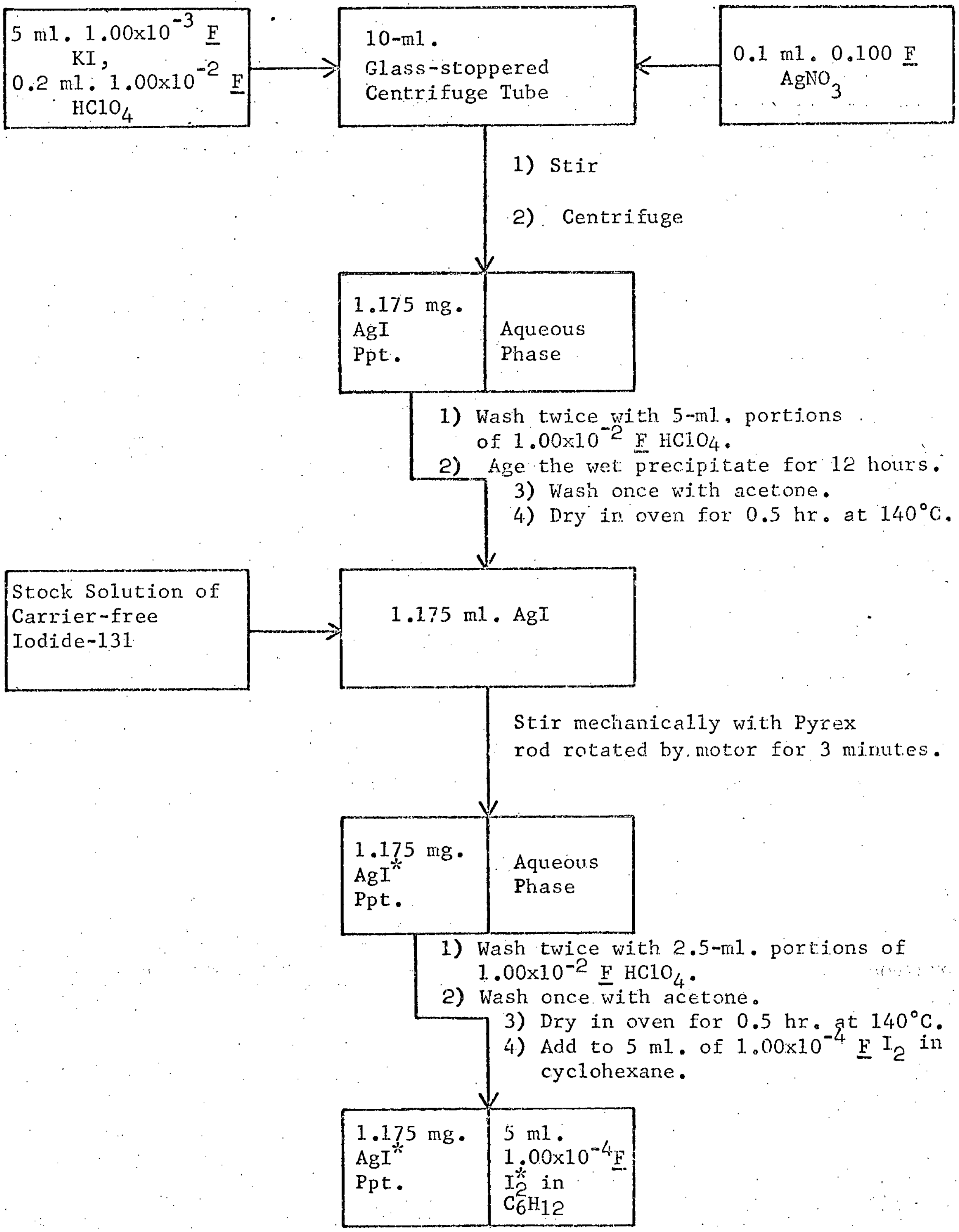


Figure A.2. Procedure used to investigate the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131.

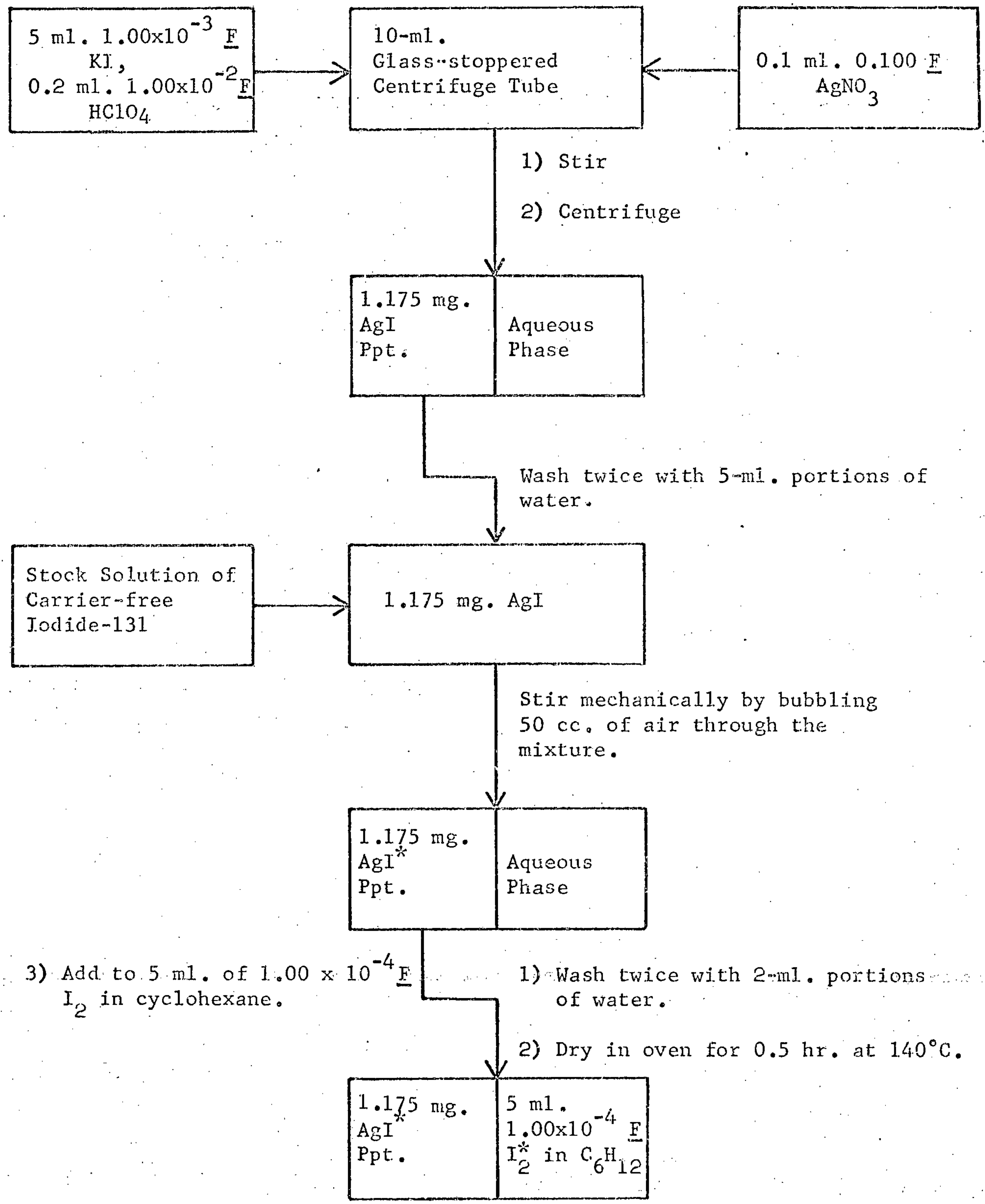


Figure A.3. Procedure used to investigate the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131.

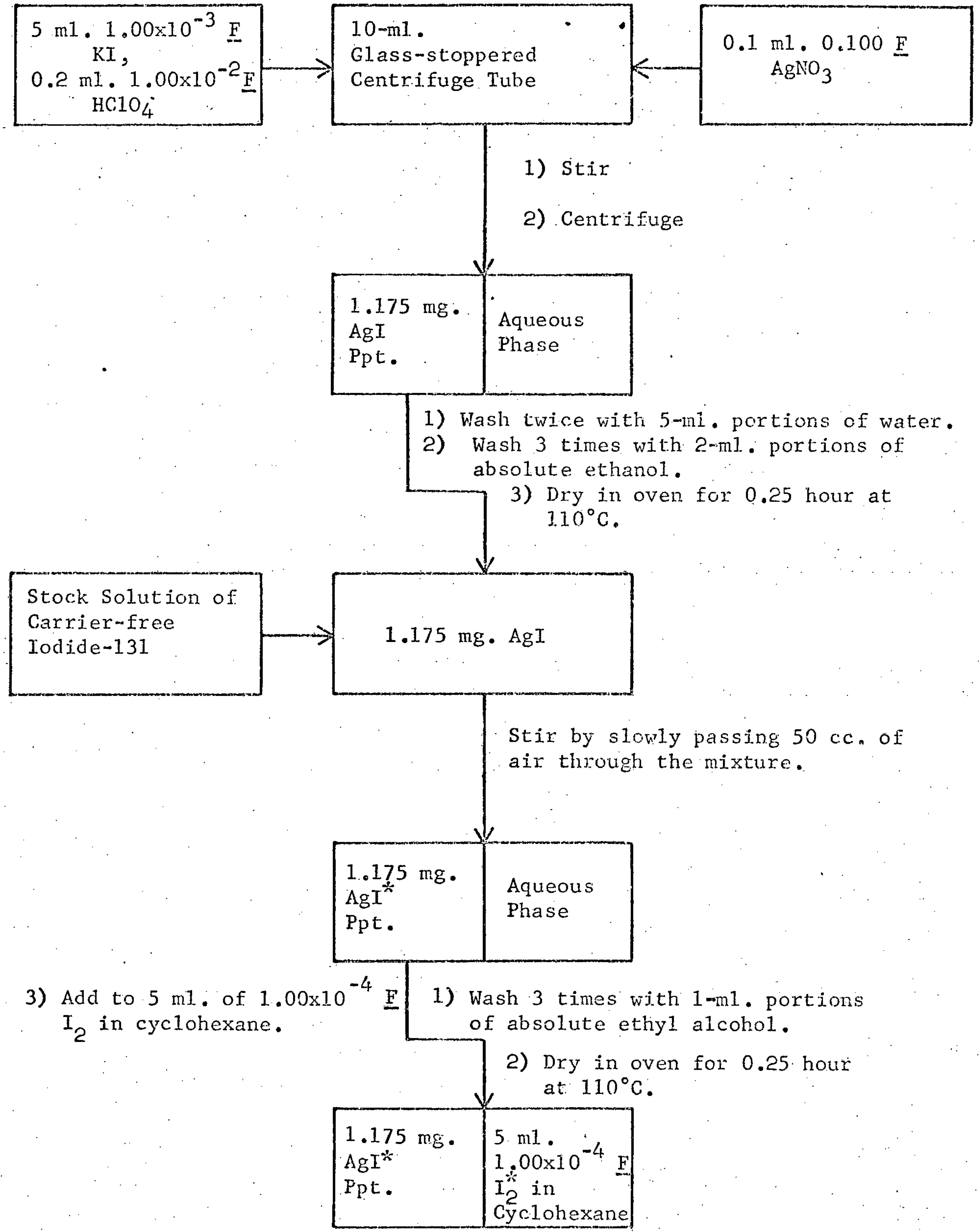
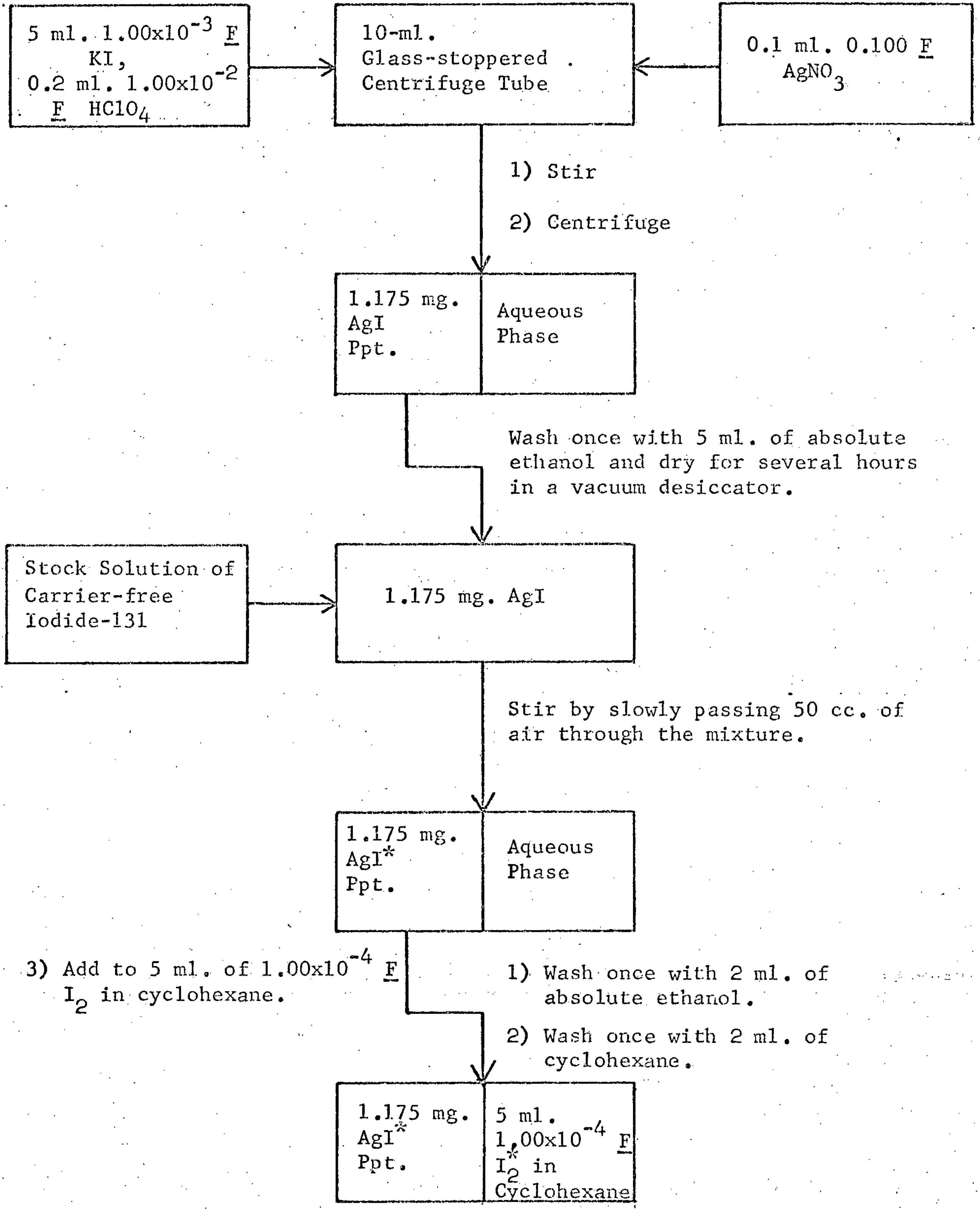


Figure A.4. Procedure used to investigate the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131.



Figute A.5. Procedure used to investigate the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131.

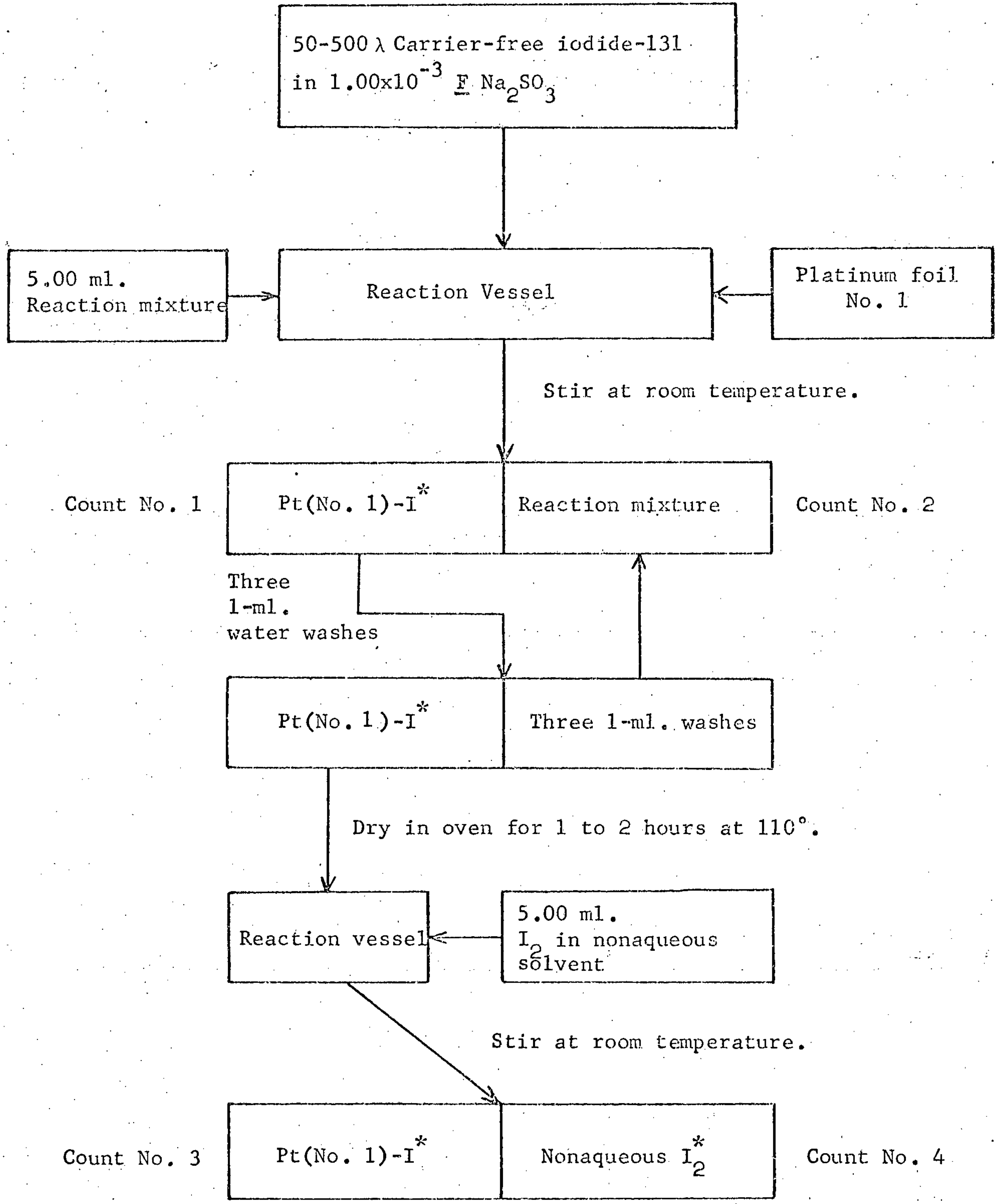
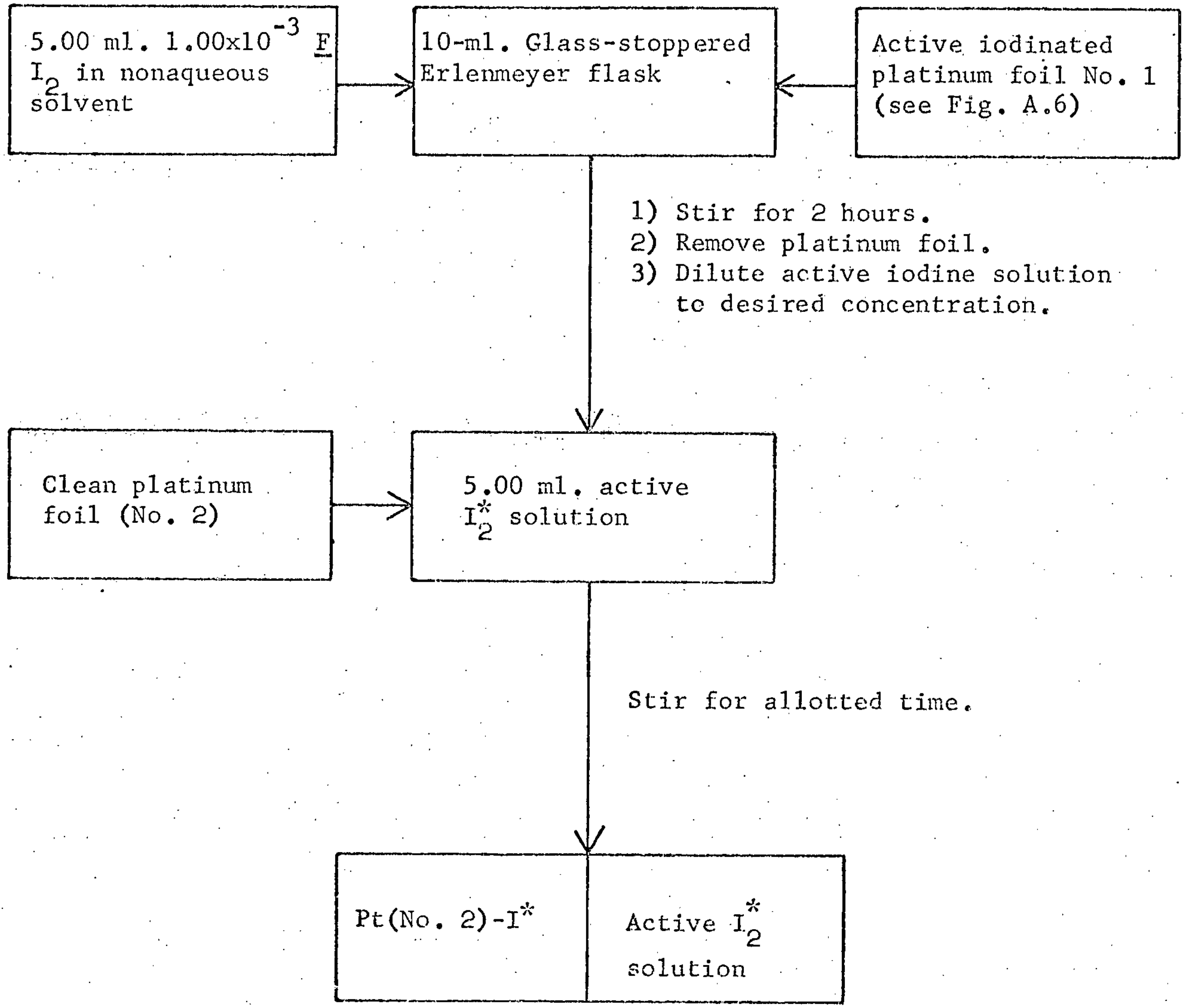


Figure A.6. Procedure used to investigate the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131.



1) The foil is removed periodically, counted, and returned to the solution.

2) At the end of the experiment both the foil and the solution are counted.

Figure A.7. Procedure used to investigate the adsorption of active molecular iodine on a clean platinum foil.

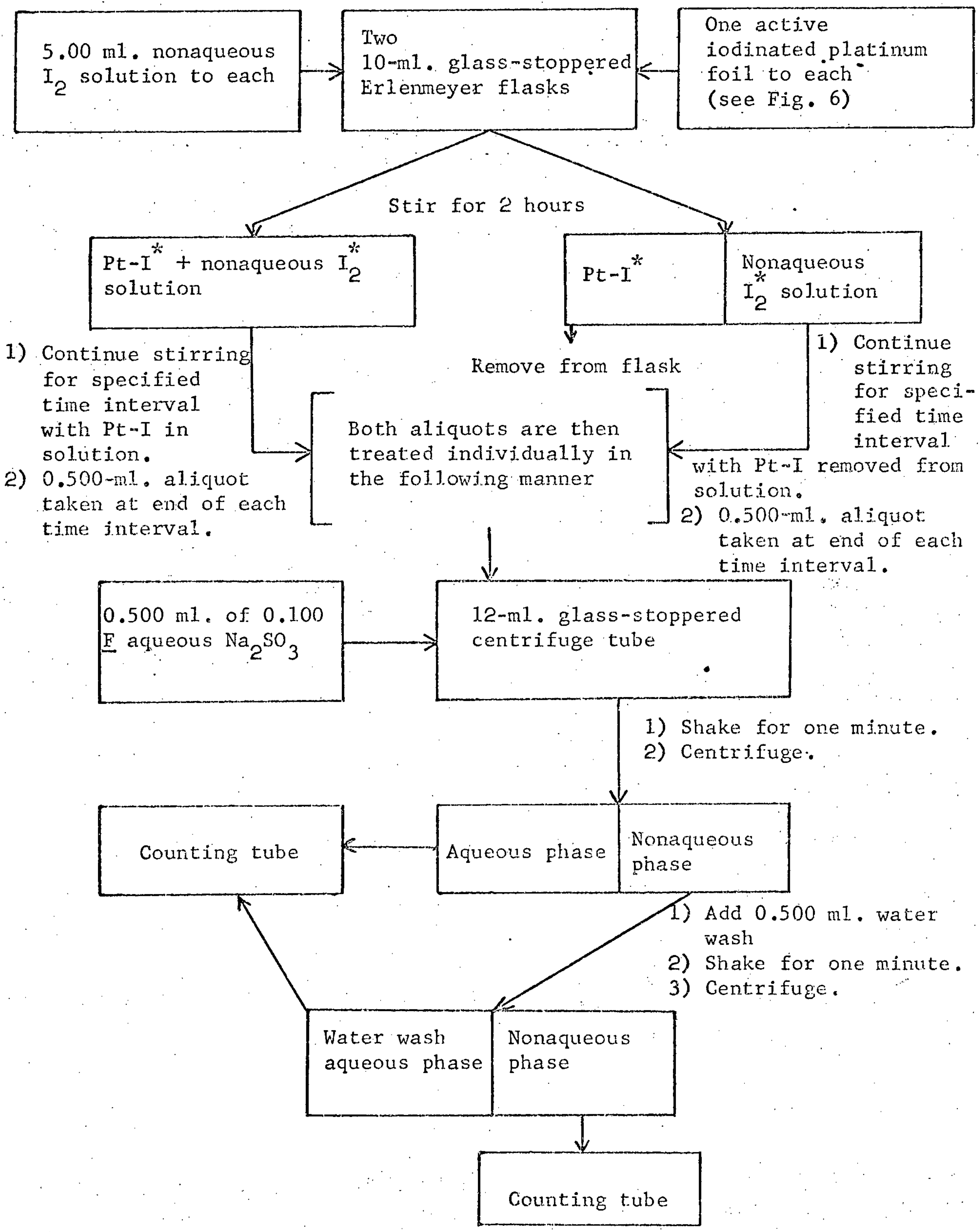


Figure A.8. Procedure used to investigate the effect of light and platinum on the stability of dry nonaqueous solutions of molecular iodine.

A.III. RESULTS AND DISCUSSION

The results of the investigation of the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131 are summarized in Table A.1 through A.23 and Figures A.9 through A.12. The results of activation experiments using preformed silver iodide precipitates inoculated with iodide-131 are summarized in Tables A.1 to A.5. The results of activation experiments using platinum foil inoculated with iodine-131 activity are summarized in Tables A.6 to A.23 and Figures A.9 to A.12.

The term "adsorption" refers to the following:

1. For silver iodide precipitates; uptake of carrier-free iodine-131 activity by preformed silver iodide precipitates via adsorption on the surface of the precipitate and/or isotopic exchange with iodide ions in the crystal lattice.
2. For platinum foil;
   - a. uptake of carrier-free iodine-131 activity by platinum foil via adsorption on the surface of the foil, or,
   - b. uptake of carrier-free iodine-131 activity by iodinated platinum foil via adsorption on the surface of the foil and/or isotopic exchange with iodine atoms previously adsorbed onto the surface of the foil.

Iodination is that process whereby iodine-127 is adsorbed onto the surface of platinum foil by exposure of the surface of the foil to a nonaqueous solution of molecular iodine.

A.III.a. Adsorption of Carrier-Free Iodine-131 Activity by Preformed Silver Iodide Precipitates, from Aqueous Solutions, and the Subsequent Exchange Between the Adsorbed Iodide-131 and Molecular Iodine in Cyclohexane (1.00×10^{-4} F)

The results of the investigation of the preparation of dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131 via isotopic exchange with iodide-131 adsorbed on silver iodide precipitates are summarized in Tables A.1 through A.5

Table A.1 summarizes the preliminary results obtained with a wet silver iodide-iodide-131 precipitate (see Figure A.1). Seventy-nine percent of the activity initially used was found in the silver iodide precipitate and 35 percent of the activity initially used exchanged with the molecular iodine in the cyclohexane solution.

Tables A.2 through A.5 summarize the results obtained when using a dry silver iodide-iodide-131 precipitate to inoculate the cyclohexane-molecular iodine solution with iodine-131.

Table A.2 summarizes the results obtained when the experimental procedure outlined in Figure A.2 was used. It is of interest to note that those precipitates aged for 12 hours in water carried the greatest amount of the carrier-free iodide-131 and, subsequently, gave the greatest exchange with the molecular iodine; moreover, those precipitates which were not aged or which were aged in 5.00×10^{-3} <u>F</u> silver nitrate carried less of the carrier-free iodide-131 and subsequently exchanged less with the molecular iodine. It is interesting to note that the percent of iodide-131 adsorbed divided by the percent exchange is essentially a constant.

The results in Table A.3 were obtained when the experimental

Table A.1

Adsorption of Carrier-Free Iodide-131 by a Preformed Silver Iodide Precipitate, from an Aqueous Solution, and the Subsequent Exchange between the Adsorbed Iodide-131 and Molecular Iodine in Cyclohexane (1.00×10^{-4} $\underline{F}$).[a,b,c,d]

Age of the AgI, hours	Iodide-131 adsorbed, %[e]	Exchange, %[e]
0	79	35

[a] The adsorption was carried out for 3 minutes, at room temperature, in the presence of light.

[b] The exchange was carried out for one minute, at room temperature, in the presence of light.

[c] The procedure used is outlined in Fig. A.1.

[d] In all instances the recovery of activity was essentially quantitative.

[e] Percent of activity initially used.

Table A.2

Adsorption of Carrier-Free Iodide-131 by Dry Preformed Silver Iodide Precipitates, from Aqueous Solution, and the Subsequent Exchange between the Adsorbed Iodide-131 and Molecular Iodine in Cyclohexane (1.00 x 10^{-4} F).[a,b,c,d]

Age of the AgI, hours	Iodide-131 adsorbed, %[e]	Exchange, %[e]
0	37	12
0	52	16
12[f]	63	22
12[f]	77	22
12[g]	34	9.0

[a] The adsorption was carried out for 3 minutes, at room temperature, in the presence of light.

[b] The exchange was carried out for one minute, at room temperature, in the presence of light.

[c] The procedure used is outlined in Fig. A.2.

[d] In all instances the recovery of activity was essentially quantitative.

[e] Percent of activity initially used.

[f] The inactive silver iodide precipitates were aged in water.

[g] The inactive silver iodide precipitate was aged in 5.00 x 10^{-3} F silver nitrate.

Table A.3

Adsorption of Carrier-Free Iodide-131 by Dry Preformed Silver Iodide Precipitates, from Aqueous Solution, and the Subsequent Exchange between the Adsorbed Iodide-131 and Molecular Iodine in Cyclohexane (1.00×10^{-4} F).[a,b,c,d]

Age of the AgI, hours	Iodide-131 adsorbed, %[e]	Exchange, %[e]
0	53	1.9
0	55	1.6
0	61	3.0
0	74	3.8
16[f]	51	5.5
16[f]	52	2.5

[a] The adsorption was carried out for one minute, at room temperature, in the presence of light.

[b] The exchange was carried out for one minute, at room temperature, in the presence of light.

[c] The procedure used is outlined in Fig. A.3.

[d] In all instances the recovery of activity was essentially quantitative.

[e] Percent of activity initially used.

[f] The inactive silver iodide precipitate was aged in water.

procedure outlined in Figure A.3 was used. Although aging the inactive silver iodide precipitates in water did not increase the carrying of the carrier-free iodide-131 (see Table A.2), it did increase the exchange between the iodide-131 adsorbed on the precipitate and the molecular iodine in the cyclohexane. However, the values observed for the isotopic exchange were, in all cases, very low.

Tables A.4 and A.5 summarize the results observed when employing the experimental procedures outlined in Figures A.4 and A.5 respectively. There does not appear to be a significant effect attributable to the aging of the inactive silver iodide precipitate.

The following observations summarize the findings of this investigation.

1. Washing the inactive wet silver iodide precipitates with acetone or ethanol caused the precipitates to become granular (11).
2. The procedures summarized in Figures A.2, A.4 and A.5 resulted in more exchange between the iodide-131 on the silver iodide precipitates and molecular iodine in cyclohexane than did the procedures summarized in Figure A.3. Presumably, this is due washing the inactive and/or active silver iodide precipitates with acetone or ethanol which enhanced the exchange.
3. Aging the inactive silver iodide precipitates in water may increase the exchange between the iodide-131 on the precipitates and molecular iodine in cyclohexane.
4. The use of a vacuum desiccator to dry the inactive and/or active silver iodide precipitates, at room temperature, may enhance the adsorption and/or exchange of the iodide-131.

Table A.4

Adsorption of Carrier-Free Iodide-131 by Dry Preformed Silver Iodide Precipitates, from Aqueous Solution, and the Subsequent Exchange between the Adsorbed Iodide-131 and Molecular Iodine in Cyclohexane (1.00×10^{-4} F).[a,b,c,d]

Age of the AgI, hours	Iodide-131 adsorbed, %[e]	Exchange %[e]
0	47	1.0
0	47	13

[a] The adsorption was carried out for one minute, at room temperature, in the presence of light.

[b] The exchange was carried out for one minute, at room temperature, in the presence of light.

[c] The procedure used is outlined in Fig. A.4.

[d] In all instances the recovery of activity was essentially quantitative.

[e] Percent of activity initially used.

Table A.5

Adsorption of Carrier-Free Iodide-131 by Dry Preformed Silver Iodide Precipitates, from Aqueous Solution, and the Subsequent Exchange between the Adsorbed Iodide-131 and Molecular Iodine in Cyclohexane (1.00×10^{-4} F).[a,b,c]

Age of the AgI, hours	Iodide-131 adsorbed, %[d]	Exchange %[d]
0[e]	50	8
0[e]	60	11
0[e,f]	69	9
0[f,g]	71	9
4[e,f,h]	61	7
4[f,g,h]	90	11

[a] The adsorption was carried out for one minute, at room temperature, in the presence of light.

[b] The procedure used is outlined in Fig. A.5.

[c] In all instances the recovery of activity was essentially quantitative.

[d] Percent of activity initially used.

[e] The exchange was carried out for one minute, at room temperature, in the presence of light.

[f] The inactive and active silver iodide precipitates were dried, at room temperature, in a vacuum desiccator.

[g] The exchange was carried out for 15 minutes, at room temperature, in the presence of light.

[h] The inactive silver iodide precipitate was aged in acetone.

Table A.6

Adsorption of Carrier-Free Iodine-131 Activity by Platinum Foil,[a] from Aqueous Solutions, at Room Temperature, Over 0.5 and 2 Hours.[b,c]

Composition of reaction mixture[d,e]	Iodine-131 activity adsorbed, %[f,g]	
	Over 0.5 hour	Over 2 hours
1.00×10^{-3} $\underline{F}$ Na_2SO_3	1.0	13
1.00×10^{-3} $\underline{F}$ Na_2SO_3 1.00×10^{-3} $\underline{F}$ $HClO_4$	39	99
1.00×10^{-3} $\underline{F}$ Na_2SO_3 0.100 $\underline{F}$ $HClO_4$	77	99

[a] The platinum foils were subjected to pretreatment A.

[b] The procedure used is outlined in Fig. A.6; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] The Oak Ridge Iodide-131 solution was, in all instances, less than 2 weeks old.

[e] The stock solution (see Fig. A.6) was, in all instances, less than 48 hours old.

[f] It is noteworthy that the reaction vessels were found to contain only a negligible amount of activity after removal of the foils and reaction mixtures, followed by 3 water washes.

[g] A different activated foil was used for each value.

Table A.7

Adsorption of Carrier-Free Iodine-131 Activity by Platinum Foil,[a] from Aqueous Solutions, at Room Temperature, Over 0.5, 1 and 2 Hours.[b,c]

Composition of reaction mixture[d,e]	Iodine-131 activity adsorbed, %[f,g]		
	Over 0.5 hour	Over 1 hour	Over 2 hours
1.00×10^{-5} $\underline{F}$ Na_2SO_3	32	-	78
1.00×10^{-5} $\underline{F}$ Na_2SO_3 1.00×10^{-3} $\underline{F}$ $HClO_4$	84	-	91
1.00×10^{-5} $\underline{F}$ Na_2SO_3 0.100 $\underline{F}$ $HClO_4$	85	-	92
1.00×10^{-5} $\underline{F}$ Na_2SO_3 1.00 $\underline{F}$ $HClO_4$	-	94 96	-

---

[a] The foils were subjected to pretreatment A.

[b] The procedure used is outlined in Fig A.6; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] The Oak Ridge iodide-131 solution was, in all instances, less than 2 weeks old.

[e] The stock solution (see Fig. A.6) was, in all instances, less than 48 hours old.

[f] It is noteworthy that the reaction vessels were found to contain only a negligible amount of activity after removal of the platinum foils and reaction mixtures, followed by 3 water washes.

[g] A different activated foil was used for each value.

No further investigation into the use of preformed precipitates with adsorbed iodide-131 as agents for inoculating dilute, dry, nonaqueous solutions of molecular iodine was undertaken. In view of recent findings published in the literature (1 through 7), it was decided that metal foils, principally platinum, could be more advantageous for activating dilute, dry, nonaqueous solutions of molecular iodine because of several factors.

1. The metal foils should not be significantly permeable to iodide-131 and, hence, more activity would be present on the surface of the foil so that isotopic exchange with molecular iodine in nonaqueous solutions could more readily occur.
2. The possibility of introducing contaminants into the nonaqueous, dilute, dry, molecular iodine solutions would be decreased.
3. The possibility of molecular iodine reacting with the activating agent would be lessened.
4. Better overall activity yields could be possible.

A.III.b. The Preparation of Dilute, Dry, Nonaqueous Solutions of Molecular Iodine Inoculated with Iodine-131 via Isotopic Exchange with Iodine-131 Activity Adsorbed on Platinum Foil

A.III.b.1. Activation of Platinum Foil The results of the studies of the adsorption of iodine-131 activity by platinum foil from dilute sodium sulfite and dilute sodium sulfite-perchloric acid solutions are summarized in Tables A.6, A.7, A.8, A.9, A.10, A.11 and A.12. In all instances the experiments were carried out in the presence of ordinary laboratory fluorescent light.

The results in Tables A.6 and A.7 indicate that the percent adsorption of iodide-131 increased with a decrease in the sodium sulfite concentration and an increase in the perchloric acid concentration. Also, the percent adsorption increased with time and was generally greater than 90 percent over 2 hours from acidic solutions. In these experiments the percent recovery, based on the activity initially present in the stock solutions of iodide-131, ranged from 98 to 100 percent. Consistently, the best results were achieved with a sodium sulfite concentration of 1.00×10^{-5} F and an acid concentration of 1.00×10^{-3} F or greater.

The results in Tables A.8 and A.9 indicate that aging the stock solution of iodide-131 or the active acidic sulfite reaction mixture had little affect on the adsorption of iodine-131 activity. However, the percent activity adsorbed was significantly less than expected (see Tables A.6 and A.7). In this connection, it is noteworthy that different shipments of Oak Ridge iodide-131 were used for Tables A.6 and A.7 and Tables A.8 and A.9.

The results in Table A.10 demonstrate that the percent adsorption of carrier-free iodine-131 activity by iodinated platinum foil was virtually the same as that observed for platinum foil (see Tables A.6, A.7, A.8 and A.9) and essentially complete after 0.5 hour. Iodination consisted of immersing a platinum foil (which had been subjected to pretreatment A) in 1.00×10^{-4} F molecular iodine in cyclohexane for a given length of time (usually 16 hours or greater), washing the foil with cyclohexane and, subsequently, drying in an oven for one hour at 110°. The shipment of Oak Ridge carrier-free iodide-131 used to obtain

Table A.8

The Effect of the Age of the Stock Solution on the Adsorption of Carrier-Free Iodine-131 Activity by Platinum Foil.[a,b,c,d]

Age of the stock solution, hours	Iodine-131 activity adsorbed, %[e]
0[f]	64
	66
	67
	67
	69
24[f]	55
	64
	80
42[f]	61
	77
	85

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[a] The composition of the reaction mixture was: 1.00×10^{-3} $\underline{F}$ Na_2SO_3, 0.100 $\underline{F}$ $HClO_4$. The reaction mixtures were prepared just prior to use.

[b] The foils were subjected to pretreatment A. Adsorption took place at room temperature over 0.5 hour.

[c] The procedure used is outlined in Fig A.8; light was present.

[d] In all instances the recovery of activity was essentially quantitative.

[e] These numbers represent maximum values because the foils were counted in water-washed reaction vessels which may have contained adsorbed activity. Such adsorption, however, was previously found to be negligible (see Table A.6, note d).

[f] The Oak Ridge solution, which represents a different shipment from that used in Tables A.6 and A.7, was less than one week old. The stock solutions were aged in aluminum-capped counting tubes.

Table A.9

The Effect of the Age of the Reaction Mixtures[a] on the Adsorption of Carrier-Free Iodine-131 Activity by Platinum Foil.[b,c,d,e]

Age of reaction mixture, hours	Iodine-131 activity adsorbed, %[f]
20.5[g]	58 62
30[g]	61 68

[a] The composition of the reaction mixture was: 1.00×10^{-3} $\underline{F}$ Na_2SO_3, 0.100 $\underline{F}$ $HClO_4$.

[b] The stock solutions were prepared just prior to use.

[c] The foils were subjected to pretreatment A. Adsorption took place at room temperature over 0.5 hour.

[d] The procedure used is outlined in Fig. A.6; light was present.

[e] In all instances the recovery of activity was essentially quantitative.

[f] These numbers represent maximum values because the foils were counted in water-washed reaction vessels which may have contained adsorbed activity. Such adsorption, however, was previously found to be negligible (see Table A.6, note d).

[g] The Oak Ridge solution was the same as in Table A.8, but was 2 weeks old. The reaction mixtures were aged in 12-ml. glass-stoppered centrifuge tubes.

Table A.10

Adsorption of Carrier-Free Iodine-131 Activity by Iodinated Platinum Foil[a] at Room Temperature.[b,c,d]

Activation time, hours	Adsorption, %
0.25	44
0.50	84 92 94
1.0	84

[a] The foils were subjected to pretreatment A, immersed in 1.00 x 10^{-4} F molecular iodine in cyclohexane for 16 hours, washed with cyclohexane and, subsequently, dried in the oven for one hour at 110°.

[b] The procedure used is outlined in Fig. A.6; light was present.

[c] The composition of the reaction mixture was: 1.00 x 10^{-5} F Na_2SO_3, 1.00 x 10^{-3} F $HClO_4$.

[d] In all instances the recovery of activity was essentially quantitative.

the results in Table A.10 was the same as that used to obtain the results in Tables A.8 and A.9. With subsequent shipments of Oak Ridge carrier-free iodide-131, the iodinated foils adsorbed about 93 percent of the activity. Generally, adsorption of activity for both iodinated and noniodinated platinum foils significantly decreased, often to values as low as 50 percent, when the stock solutions were prepared from shipments of Oak Ridge carrier-free iodide-131 kept 6 weeks or longer.

The data in Table A.11 demonstrate that the percent carrier-free iodine-131 activity adsorbed by iodinated foils decreased with a decrease in the iodination time, but was independent of the concentration of the iodinating solution over the range of 1.00×10^{-3} to 1.00×10^{-5} F molecular iodine in cyclohexane.

The results of experiments designed to study the percent adsorption of carrier-free iodide-131 from acidic solutions containing hydrogen peroxide are summarized in Table A.12. It is seen that although the presence of a moderate amount of hydrogen peroxide (2×10^{-2} F) caused the percent adsorption to decrease, small quantities of hydrogen peroxide (2×10^{-3} F) had no significant affect.

A.III.b.2. Adsorption of Iodine onto Platinum Foil It is necessary to know the extent of the loss of iodine from solutions, via adsorption on the platinum foil, during the activation process since adsorption of small quantities of iodine could lead to a decreased and uncertain concentration of the molecular iodine in a dilute solution. The results of experiments designed to determine the decrease in

2

Table A.11

Adsorption of Carrier-Free Iodine-131 Activity by Platinum Foil which was Iodinated[a] for Varying Times and at Various Iodine Concentrations.[b,c,d,e]

Time of iodination, hours	Iodine concentration in iodinating solution, F	Adsorption, %
2	1.00×10^{-4}	52[f] 59[f]
2	1.00×10^{-4}	57[g] 73[g]
24	1.00×10^{-3}	90[h] 91[h]
24	1.00×10^{-4}	91[h] 91[h]
24	1.00×10^{-5}	92[h] 91[h]

[a] The foils were subjected to pretreatment A, immersed in molecular iodine in cyclohexane for the predetermined time, washed with cyclohexane and, subsequently, dried in an oven for one hour at 110°.

[b] The procedure used is outlined in Fig. A.6; light was present.

[c] The composition of the reaction mixture was: 1.00×10^{-5} F Na_2SO_3, 0.100 F $HClO_4$.

[d] The foils were activated for one hour at room temperature.

[e] In all instances the recovery of activity was essentially quantitative.

[f] The Oak Ridge solution was 60 days old.

[g] The Oak Ridge solution was 12 days old and a different shipment from that used for notes f and g.

[h] The Oak Ridge solution was one month old.

Table A.12

Adsorption of Carrier-Free Iodine-131 Activity by Platinum Foil and Iodinated Platinum Foil from Solutions Containing Hydrogen Peroxide.[a,b,c]

Hydrogen peroxide concentration, F	Adsorption, %[d]	
	I[e]	II[e]
2.00×10^{-3}	92	91
	88	64
2.00×10^{-2}	55	20
	60	36

[a] The procedure used is outlined in Fig. A.6; light was present.

[b] The composition of the reaction mixture was: 1.00×10^{-5} F Na_2SO_3, 0.100 F $HClO_4$, H_2O_2 at the two given concentrations.

[c] In all instances the recovery of activity was essentially quantitative.

[d] The adsorption was carried out for one hour at room temperature.

[e] The experiments differed as follows:

I. The foils were subjected to pretreatment A.

II. The foils were subjected to pretreatment A, immersed in molecular iodine in cyclohexane (1.00×10^{-4} F) for 24 hours, washed with cyclohexane and, subsequently, dried in an oven for one hour at 110°.

Table A.13

Adsorption of Molecular Iodine-(127 and 131) on Platinum Foil[a] from Cyclohexane at Room Temperature.[b,c]

Time of Adsorption, hours	Moles of Iodine adsorbed ($\times 10^{10}$) per cm^2. of Pt. I[d]	II[d]	III[d]
0.5	2.3	1.7	0.8
	2.0	1.6	0.5
1	2.9	2.7	0.9
	2.8	1.8	0.8
2	3.4	4.1	1.1
	3.3	2.1	0.5
4	3.7	5.7	1.4
	3.7	2.3	0.6
8	5.7	8.0	1.5
	4.0	2.5	0.7

[a] The size of the platinum foil was 0.50 x 1.50 x 0.00625 cm.; the area of each foil was 1.5 cm^2.

[b] The procedure used is outlined in Fig A.7 and described in the text; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] The adsorption was carried out with 5 ml. of a cyclohexane solution of molecular iodine made active by activating for 2 hours at room temperature with an active iodinated foil. The concentrations of molecular iodine in the cyclohexane solutions were:

I. 1.00×10^{-5} F.
II. 1.00×10^{-6} F.
III. 1.00×10^{-7} F.

iodine concentration during the activation process are given in Table A.13. It was observed that adsorption of iodine increased with increased with increasing time. Additional experiments, not included in Table A.13, were carried out to determine the amount of iodine adsorbed on a platinum foil immersed in 1.00 x 10^{-4} F molecular iodine in cyclohexane, over relatively long periods of time. After 16 hours this value was observed to be 1.00 x 10^{-9} mole of iodine per cm^2 of platinum foil. Because increasing the time to 72 hours did not result in further adsorption, it was concluded that the foregoing value represented the saturation value of the foil. This value was in good agreement with those reported by other investigators (3, 4, 5 and 8) and with the value calculated from atomic radii of platinum and iodine assuming a monolayer of iodine and a real surface area twice the apparent surface area. From the data in Table A.13 it is possible to calculate an expected loss of iodine during activation with noniodinated foils. For example, a loss of approximately 6 percent of the iodine present in 5 ml. of a 1.00 x 10^{-6} F molecular iodine solution would be expected over a 2-hour activation period. However, by using active foils which had been iodinated for 16 hours or more in 1.00 x 10^{-4} F molecular iodine, to achieve saturation, the loss of iodine is virtually eliminated.

A.III.b.3. Desorption of Adsorbed Iodine from Platinum by Solvents

Experiments were carried out to determine the loss of adsorbed iodine to the solvent during the activation of dilute solutions of iodine with active iodinated foils. The activation procedure outlined in Fig. A.6

was followed with the exception that the active iodinated foil was added to 5 ml. of pure nonaqueous solvent. The results summarized in Table A.14 demonstrate the importance of checking each solvent for its ability to remove iodine from active iodinated platinum foils. A large percentage loss, however, does not necessarily eliminate the possibility of using a particular solvent. For example, nitrobenzene solutions of iodine could be activated without any significant change in the concentration of the iodine provided the initial amount of iodine contained in the solution was on the order of 5 x 10^{-7} moles or greater.

The values given in Table A.14 for the fractional loss of iodine-131 activity from an active, iodinated, platinum foil in all probability represent maximum values for the fractional loss of iodine (127 and 131) from the foil. This arises from the fact that it is possible that the specific activity of the desorbed iodine was greater than the specific activity of the iodine originally present on the active, iodinated, platinum foil. The converse of this, however, does not appear to be probable; that is, the specific activity of the desorbed iodine was less than the specific activity of the iodine originally present on the active, iodinated, platinum foil thereby causing the values given in Table A.14 to represent minimum values for the fractional loss of iodine (127 and 131) from the foil. These conclusions are based on the following reasoning.

1. Molecular iodine, in the nonaqueous solvents mentioned (nitrobenzene, benzene, cyclohexane and carbon tetrachloride), undergoes rapid isotopic exchange with iodine-131 adsorbed on

an iodinated platinum foil (see Tables A.17 and A.21). Hence, if the iodine-127 is desorbed as molecular iodine the specific activity of the iodine in the solution and on the foil would be similar.

2. Only a very small amount (approximately one percent) of the iodine-131 in a cyclohexane-iodine solution, inoculated with iodine-131 by using an active, iodinated, platinum foil did not behave as molecular iodine (see Tables A.22 and A.23). Hence, if iodine-127 is desorbed from a foil in a chemical state other than molecular iodine, it does not undergo measurable isotopic exchange with iodine-131 on the foil or in solution over 3 hours. Evidence listed in Part B (The Distribution of Iodine Between Aqueous Solutions and Cyclohexane) indicates that if iodine-127 is desorbed from an active, iodinated, platinum foil in a chemical state other than molecular iodine, it does not undergo measurable isotopic exchange with molecular iodine tagged with iodine-131 over 2 weeks. This is based on the following evidence;

   a. the distribution coefficient (D), where

   $$D = \frac{\text{concentration of I-atoms (I-131) in nonaqueous phase}}{\text{concentration of I-atoms (I-131) in aqueous phase}}$$

   for iodine between cyclohexane and acidic aqueous solutions is independent of the age of the cyclohexane-iodine solutions, inoculated with iodine-131 by using an active, iodinated, platinum foil, over 2 weeks, and,

   b. the magnitude of the distribution coefficient for an initial iodine concentration in cyclohexane of 1.00 x 10^{-3} F and 1.00 F sulfuric acid, is independent of whether active, iodinated, platinum foils or active, noniodinated, platinum foils were used.

3. Spot checks on the desorption of carrier-free iodine-131 activity, adsorbed onto noniodinated platinum foils, by nitrobenzene, benzene, methanol and cyclohexane, over 2 hours, showed that less than one percent of the activity appeared in the nonaqueous solvent. Hence, the nonaqueous solvents do not readily cause the desorption of carrier-free iodine-131 activity from a noniodinated platinum foil.

Therefore, the results indicate that the values given in Table A.14 for the fractional loss of iodine-131 activity from an active, iodinated, platinum foil represent maximum values for the fractional loss of iodine (127 and 131) from the foil.

A.III.b.4. Exchange between Iodine-131 on Platinum Foil and Iodine in Nonaqueous Solution at Room Temperature The data in Tables A.15 and A.16 indicate that the percent exchange of iodine in cyclohexane with noniodinated active platinum foils was essentially independent of time over the range of 0.25 to 2.5 hours. Aging of these foils at room temperature decreased the percent exchange.

The percent exchange was greater for iodinated foils than for noniodinated foils (see Tables A.15 and A.16). In a subsequent experiment it was observed that aging an active iodinated foil at room temperature over 4 hours decreased the exchange from the expected value of 45 percent to 30 percent.

Table A.14

Iodine Removed from Active Iodinated Platinum Foils[a] by Various Organic Solvents.[b,c]

	Iodine-131 removed, %			
	Time, hours			
Solvent	1	2	19.1	20.5
Nitrobenzene[d]	45	50	66	-
Nitrobenzene[e]	-	-	-	64
Benzene[f]	0.01	0.01	1.5	-
Benzene[g]	-	-	-	4.1
Cyclohexane	0.01	0.01	0.36	-
Carbon Tetrachloride	-	-	-	1.0
	2.5	4.1	11	-
Methanol	25	35	34	-
	18	19	29	-

[a] The foils were subjected to pretreatment A, iodinated for 16 hours in 1.00×10^{-4} F molecular iodine in cyclohexane, washed and, then, dried in an oven for one hour at 110°. They were then activated in 1.00×10^{-3} F Na_2SO_3 and 0.100 F $HClO_4$ for one hour, washed and dried in an oven for 2 hours at 110°. The foils were then used immediately. Light was present during this procedure.

[b] In all instances the recovery of activity was essentially quantitative.

[c] Light was present during the desorption studies.

[d] Untreated nitrobenzene was pretreated by allowing it to stand for one week with 1.00×10^{-3} moles of iodine per liter in it, reducing the iodine with aqueous sulfite dried over alumina and distilled under vacuum through a 20-plate Oldershaw column; all operations were performed in the dark (9).

[e] Untreated nitrobenzene was treated according to the procedure given on p. 15.

[f] This benzene was Phillips Research Grade.

[g] This benzene was Mallinckrodt AR Grade.

Table A.15

Exchange between Molecular Iodine in Cyclohexane (1.00×10^{-4} F) and Iodine-131 Adsorbed on Platinum Foil,[a] at Room Temperature.[b,c]

Exchange time, hours	Exchange, %[d] I[e]	II[e]	III[e]
0.25	30	12	33
0.50	18	4.7	32
	19	-	-
1.0	22	5.6	37
	25	-	-
2.0	-	23	46
2.5	28	-	-

[a] The foils were subjected to pretreatment A.

[b] The procedure used is outlined in Fig A.6; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] A different activated foil was used for each value.

[e] The experiments differed as follows:
I. The foils were activated just prior to use.
II. The foils were activated, and then, allowed to age in the atmosphere, at room temperature, in ordinary laboratory light, for 60 hours, prior to use.
III. The inactive foils were iodinated in 1.00×10^{-4} F molecular iodine in cyclohexane for 16 hours, at room temperature, in ordinary laboratory light. The foils were then activated and used immediately.

Table A.16

Exchange between Molecular Iodine in Cyclohexane (1.00×10^{-6} F) and Iodine-131 Adsorbed on Platinum Foil,[a] at Room Temperature.[b,c]

Exchange time, hours	Exchange, %[d] I[e]	II[e]
0.25	-	13
0.50	4.6	16
1.0	5.0	21
2.0	2.4	21

[a] The foils were subjected to pretreatment A.

[b] The procedure used is outlined in Fig. A.6; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] A different foil was used for each value.

[e] The experiments differed as follows:
I. The foils were activated just prior to use.
II. The inactive foils were iodinated in 1.00×10^{-4} F molecular iodine in cyclohexane for 16 hours, at room temperature, in ordinary laboratory light. The foils were then activated and used immediately.

A comparison of the data in Table A.15 with those in Table A.16 reveals that decreasing the iodine concentration in cyclohexane from 1.00×10^{-4} F to 1.00×10^{-6} F decreased the percent exchange for both iodinated and noniodinated foils.

Inasmuch as the usual iodination time was 16 to 24 hours, it was of interest to determine the effect of decreasing the iodination time on the percent exchange of the iodine-131 on a foil and iodine in cyclohexane. The data in Table A.17 indicate that reducing the iodination time to 2 hours had little affect on exchange, which was found to be 40 to 45 percent over an iodination time of 16 to 24 hours (see Table A.15): the low values for the 1.00×10^{-4} F iodinating solutions, with 24-hour iodination time, given in Table A.17, are atypical. The data in Table A.17 also indicate that the percent exchange over 2 hours with active foils, which had been iodinated over 24 hours, was found to be independent of the concentration of the iodinating solutions which ranged from 1.00×10^{-3} F, to 1.00×10^{-5} F in molecular iodine. Two experiments indicated that measurable exchange occurred over 15 seconds with active foils which had been iodinated for 24 hours in 1.00×10^{-5} F iodine.

The data in Table A.18 demonstrate that the addition of hydrogen peroxide to the active aqueous reaction mixture (see Figure A.16) did not alter the percent exchange when noniodinated foils were used; however, with iodinated foils the percent exchange decreased (see Table A.15).

Tables A.19, A.20 and A.21 summarize the results of exchange experiments in nitrobenzene, benzene, methanol, cyclohexane and carbon tetrachloride. Tables A.19 and A.20 indicate that the percent

Table A.17

Exchange between Molecular Iodine in Cyclohexane (1.00×10^{-4} F) and Iodine-131 Adsorbed on Platinum Foil,[a] which was Iodinated over Two Different Intervals, at Various Iodine Concentrations, at Room Temperature.[b,c]

Time of Iodination, hours	Time of exchange	Exchange, %[d,e] I	II	III
2	2 hours	-	40	-
		-	41	-
2	2 hours[f]	-	39	-
		-	46	-
24	15 sec.	-	-	7
		-	-	26
24	2 hours	14	10	24
		26	24	26

---

[a] The foils were subjected to pretreatment A, immersed in molecular iodine in cyclohexane for the allotted time and, subsequently, dried in an oven for one hour at 110°.

[b] The procedure used is outlined in Fig. A.6; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] A different foil was used for each value.

[e] The experiments differed as follows:

I. The concentration of the iodinating solution was 1.00×10^{-3} F in molecular iodine.
II. The concentration of the iodinating solution was 1.00×10^{-4} F in molecular iodine.
III. The concentration of the iodinating solution was 1.00×10^{-5} F in molecular iodine.

[f] The age of the Oak Ridge solution was 10 days. (The other results were obtained using an Oak Ridge solution which was 5 weeks old.)

Table A.18

Exchange between Molecular Iodine in Cyclohexane (1.00×10^{-4} F) and Iodine-131 Adsorbed,[a] from Solutions Containing Hydrogen Peroxide, on Platinum Foil.[b,c]

Hydrogen peroxide, F	Exchange, %[d] I[e]	II[e]
2.00×10^{-3}	21	20
	26	29
2.00×10^{-2}	21	29
	31	39

[a] The composition of the reaction mixture was: 1.00×10^{-5} F Na_2SO_3, 0.100 F $HClO_4$, H_2O_2 at the two given concentrations.

[b] The procedure used is outlined in Fig. A.6; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] The exchange was carried out for 2 hours at room temperature. (See Table A.12 for the associated adsorption data.)

[e] The experiments differed as follows:
I. The foils were subjected to pretreatment A.
II. The foils were subjected to pretreatment A, immersed in molecular iodine in cyclohexane (1.00×10^{-4} F) for 24 hours, washed with cyclohexane and, subsequently, dried in an oven for one hour at 110°.

Table A.19

Exchange between Molecular Iodine in Nitrobenzene and Iodine-131 Adsorbed on Platinum Foil,[a] at Room Temperature, in the Absence of Light.[b,c]

Time, hours	Exchange, %[d,e] 2.00×10^{-5} $\underline{F}$ I_2	2.00×10^{-4} $\underline{F}$ I_2	2.00×10^{-3} $\underline{F}$ I_2	2.00×10^{-2} $\underline{F}$ I_2
0.5	-	-	-	26
1.0	3.8	5.4	21	33
1.5	-	-	-	38
2.0	-	-	-	42
2.8	-	-	-	47
4.1	-	-	-	51
5.0	9.4	10	37	-
9.8	-	-	-	60
11.0	10	15	49	-
23.3	-	-	-	69
24.0	23	28	58	-
48.0	-	-	-	74
59.0	-	-	-	76
71.0	-	-	-	78
72.0	-	-	68	-
96.0	-	-	70	-

[a] The foils were subjected to pretreatment A.

[b] The procedure used is outlined in Fig. A.6.

[c] In all instances the recovery of activity was essentially quantitative.

[d] A different foil was used for each iodine solution; after a specified time the foil was removed, counted, and then returned to the reaction vessel, etc.

[e] The foils were activated just prior to use.

Table A.20

Exchange between Molecular Iodine in Benzene (1.00 x 10^{-2} F) and Iodine-131 Adsorbed on Platinum Foil,[a] at Room Temperature.[b,c]

Exchange time, hours	Exchange, %[d,e]
0.5	23
1.0	31
1.5	37
2.0	42
2.8	49
4.1	53
5.2	55
6.2	58
9.8	61
23.3	64
35.5	67
48.0	70
59.0	72
71.0	74

[a] The foil was subjected to pretreatment A.

[b] The procedure used is outlined in Fig. A.6; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] After a specified time the foil was removed, counted, and then returned to the reaction vessel, etc.

[e] The foil was activated just prior to use.

Table A.21

Exchange between Molecular Iodine in Nonaqueous Solvents (1.00×10^{-4} $\underline{F}$) and Iodine-131 Adsorbed on Iodinated Platinum Foils,[a] at Room Temperature, over 2 hours.[b,c]

Solvent	Exchange, %[d]
Methanol	49 52
Benzene	51 66
Nitrobenzene	39 63
Cyclohexane	35 47
Carbon Tetrachloride	38 46

[a] The platinum was subjected to pretreatment A, immersed in molecular iodine in cyclohexane (1.00×10^{-4} $\underline{F}$) for 24 hours, washed with cyclohexane, and, subsequently, dried in an oven for one hour at 110°. The foils were then used immediately.

[b] The procedure used is outlined in Fig. A.6; light was present except during the exchange in nitrobenzene.

[c] In all instances the recovery of activity was essentially quantitative.

[d] A different foil was used for each value.

Table A.22

The Effect of Platinum Foil[a] on the Stability of Molecular Iodine Solutions in Cyclohexane, in the Presence of Ordinary Laboratory Light, at Room Temperature.[b,c]

Time, hours	Iodine concentration, F	Activity not extracted by Na_2SO_3, %[d]	
		Pt present[e]	Pt absent
0	1.00×10^{-3}	1.0	2.6
2	1.00×10^{-3}	1.5	2.2
6.75	1.00×10^{-3}	2.2	3.0
0	1.00×10^{-5}	9.6	6.8
3	1.00×10^{-5}	2.3	2.5
16.5	1.00×10^{-5}	3.9	6.5

[a] The foil was subjected to pretreatment A, immersed in molecular iodine in cyclohexane (1.00×10^{-4} F) for 24 hours, washed with cyclohexane and, subsequently, dried in an oven for one hour at 110°. The foil was then activated for 2 hours at room temperature (see Fig. A.6, foil #1).

[b] The procedure used is outlined in Fig. A.8; light was present.

[c] In all instances the recovery of activity was essentially quantitative.

[d] A different foil was used for each value.

[e] The foil was the same foil that was used to activate the solution.

Table A.23

The Effect of Light on the Stability of Molecular Iodine Solutions in Cyclohexane, at Room Temperature, in the Presence of Platinum Foil.[a,b,c]

Time, hours	Iodine concentration, F	Activity not extracted by Na_2SO_3, %[d,e] Light present	Light absent[f]
1.0	1.00×10^{-3}	0.80	0.14
3.0	1.00×10^{-3}	1.3	0.33
1.0	1.00×10^{-5}	0.87	0.54
3.0	1.00×10^{-5}	1.1	0.62

[a] The foil was subjected to pretreatment A, immersed in molecular iodine in cyclohexane (1.00×10^{-4} F) for 24 hours, washed with cyclohexane and, subsequently, dried in an oven for one hour at 110°. The foil was then activated for 2 hours at room temperature (see Fig A.6, foil #1).

[b] The procedure used is outlined in Fig. A.8.

[c] In all instances the recovery of activity was essentially quantitative.

[d] A different foil was used for each value.

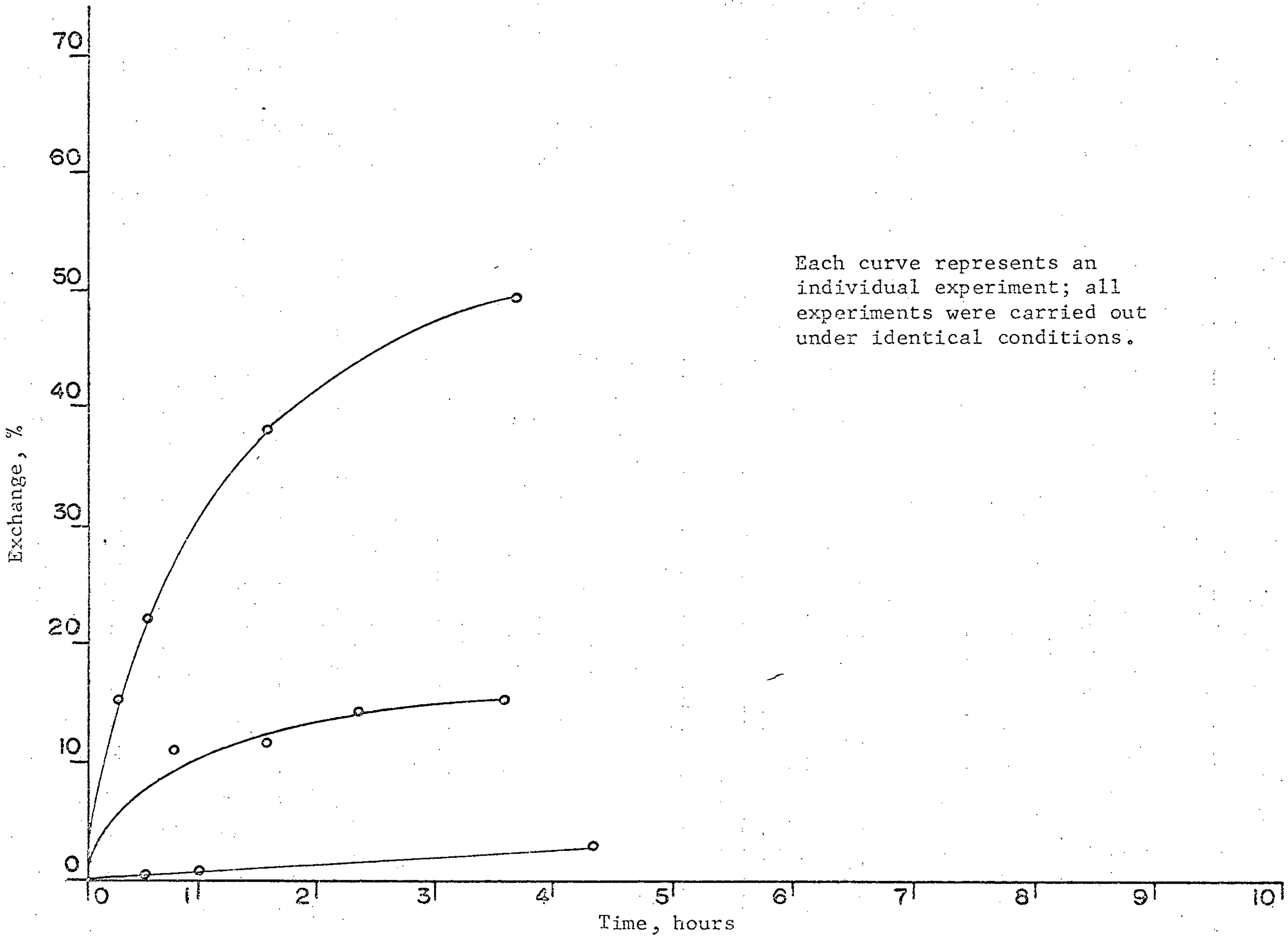
[e] The foil was the same foil that was used to activate the solution.

[f] Light was excluded by wrapping the reaction vessel in aluminum foil.

exchange between active noniodinated foils and 1.00 x 10^{-2} F molecular iodine in nitrobenzene and benzene are virtually the same. Table A.19 further indicates that the percent exchange increases with increasing iodine concentration and time. On the other hand, the percent exchange between active iodinated foils and 1.00 x 10^{-2} F iodine, in the aforementioned solvents is essentially independent of the solvent (see Table A.21).

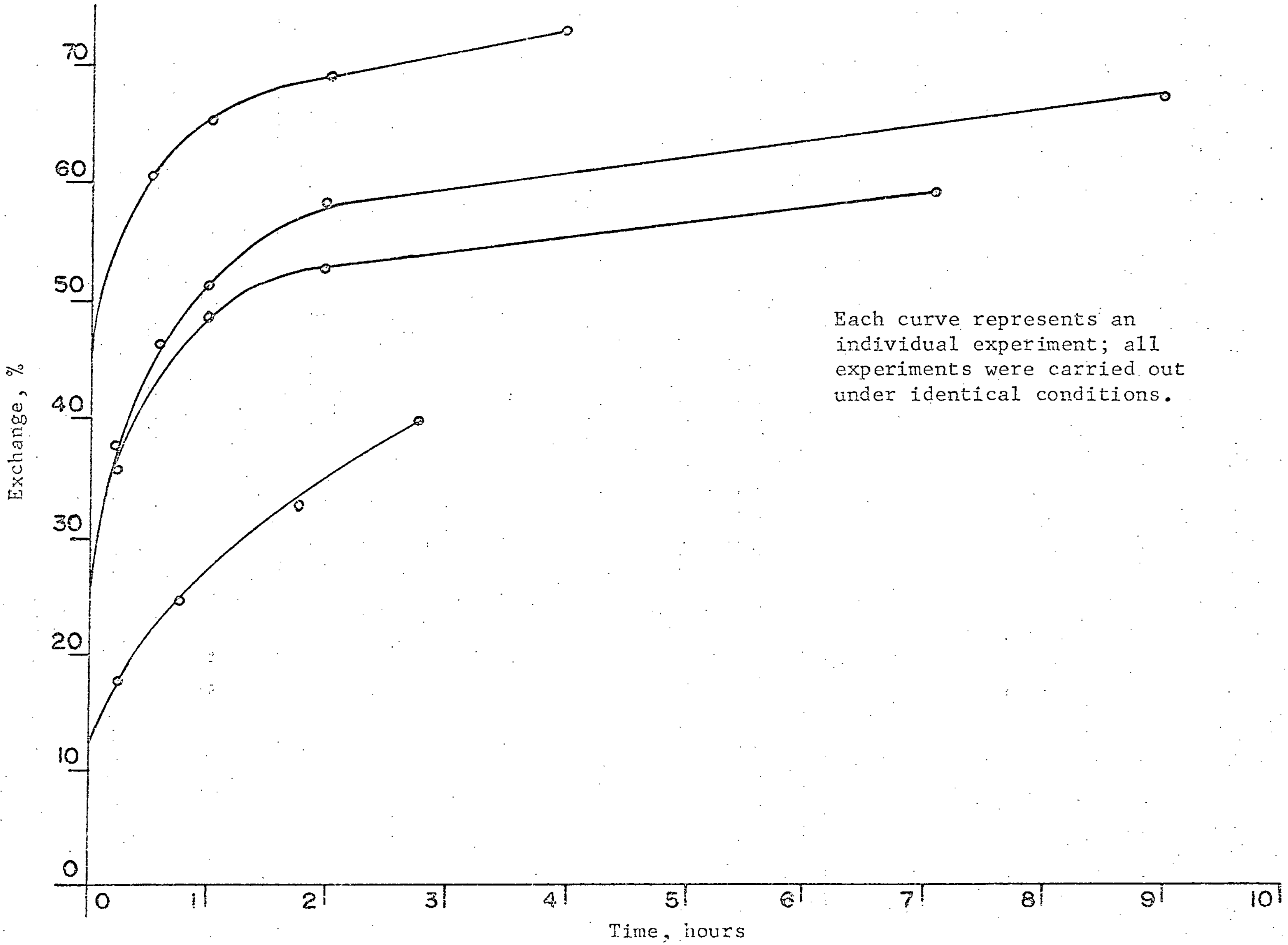
<u>A.III.b.5. Iodine-Solvent Reactions</u>. It was thought possible that platinum foil, in the presence of light, could catalyze the formation of organic iodine compounds with either the solvent itself or impurities in the solvent during activation of the nonaqueous iodine solutions. Although the data in Tables A.22 and A.23 show that a small fraction of the activity in the nonaqueous solutions was not extractable with aqueous sulfite, there was no well-defined trend with regard to the absence or presence of platinum either in the dark or in the presence of light.

<u>A.III.b.6. Exchange between Iodine-131 on Platinum Foil and Iodine in Nonaqueous Solvent at 50°</u>. The dependence of the percent exchange at 50°, on the reaction time and pretreatment of the foils, is summarized in Figures A.9, A.10, A.11 and A.12. In general, the percent exchange between iodine-131 on platinum foils and iodine in cyclohexane at 50° was greater than the percent exchange at room temperature. The rate of exchange generally decreases significantly after about 2 hours. Because of the wide variations in the plots of data obtained from identical experiments (see Figures A.14, A.5 and A.7), the relative effectiveness of any one of the pretreatments cannot be assessed.



Each curve represents an individual experiment; all experiments were carried out under identical conditions.

Figure A.9. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment A) and 1.00×10^{-4} F molecular iodine in cyclohexane, at 50°.



Each curve represents an individual experiment; all experiments were carried out under identical conditions.

Figure A.10. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment B) and 1.00x 10^{-4} F molecular iodine in cyclohexane, at 50°.

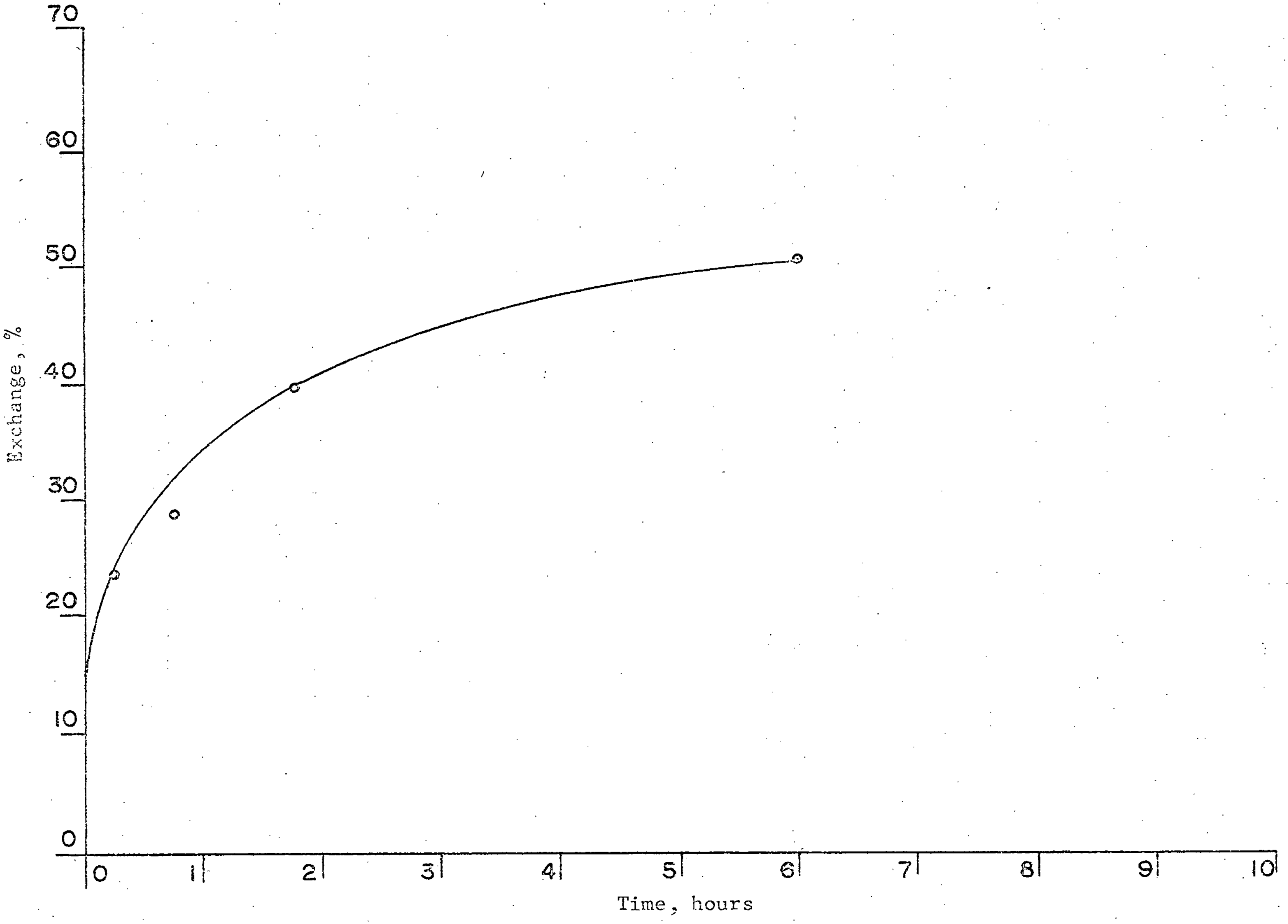
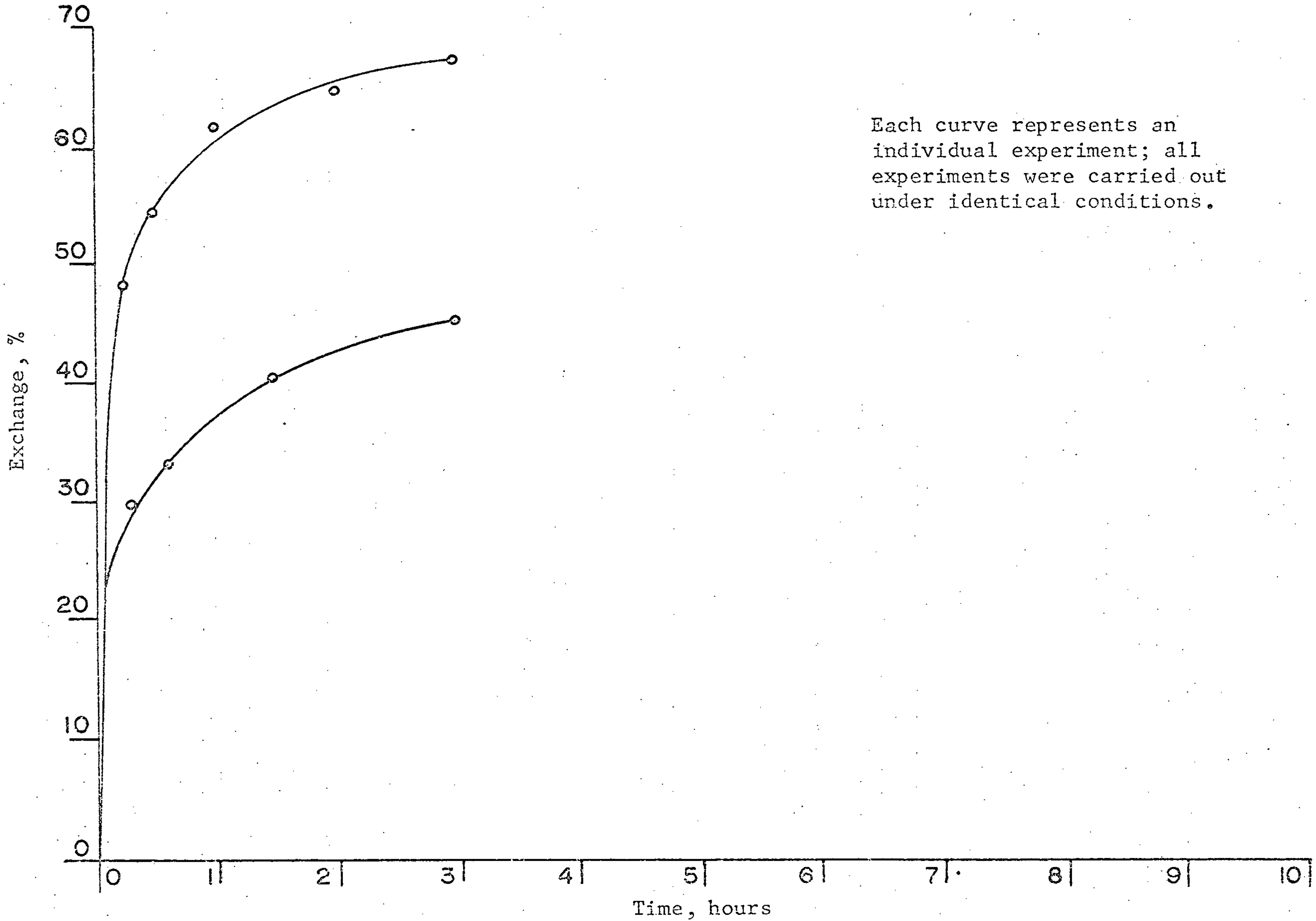


Figure A.11. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment C) and 1.00×10^{-4} $\underline{F}$ molecular iodine in cyclohexane, at 50°.



Each curve represents an individual experiment; all experiments were carried out under identical conditions.

Figure A.12. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment D) and 1.00×10^{-4} F molecular iodine in cyclohexane, at 50°.

A.IV. SUMMARY

It has been demonstrated that dilute, dry, nonaqueous solutions of molecular iodine inoculated with iodine-131 may be prepared via two processes; namely, the isotopic exchange between inactive iodine in nonaqueous solutions and iodine-131 activity adsorbed on either platinum foils or silver iodide precipitates.

The following procedure was found to be the most suitable for the inoculation of dry nonaqueous solutions of molecular iodine with iodine-131.

1. Iodinate a platinum foil, which has been subjected to pretreatment A, for 16 to 24 hours employing a nonaqueous solution of molecular iodine, where the iodine concentration is equal to or greater than 1.00×10^{-4} F, and dry the foil in an oven for 0.5 to 2 hours at 110°.
2. Immerse the iodinated foil in an acidic solution (pH approximately equal to 1) of carrier-free iodine-131 activity and stir for 0.5 to 2 hours.
3. Wash the activated foil with water and dry in an oven for one to 2 hours at 110°.
4. Immerse the dried active foil in the nonaqueou solution of molecular iodine to be activated and stir for one to 2 hours at room temperature.
5. The nonaqueous solvent used should be checked for the extent to which the solvent removes iodine-131 activity from the active iodinated foil.

6. The active nonaqueous iodine solution should be checked for the fraction of activity in the active solution which is not extracted by aqueous sodium sulfite, aqueous potassium iodide and aqueous sodium hydroxide.

Step No. 5 increases in importance as the concentration of the desired iodine solutions decreases because the loss of iodine-131 activity to pure solvent indicates that the concentration of iodine in a dilute (less than or equal to 1.00 x 10^{-6} moles of iodine in the solution) nonaqueous solution may be increasing during the activation procedure. (In this connection, it is noteworthy that iodinated foils will not remove iodine from nonaqueous solutions.) This decrease in the iodine concentration (see step No. 5) may be obviated by changing the procedure in the following manner.

7. Reduce the activation time for the iodine solutions to approximately one minute (see step No. 4).
8. Reduce the size of the platinum foil.

In an alternate procedure a noniodinated platinum foil, which had been subjected to pretreatment A, is used and steps No. 2, 3, 4 and 6 are followed. In a dilute (less than 1.00 x 10^{-6} moles of iodine in the solution) iodine solution steps No. 7 and 8 should also be followed because theuse of this alternate procedure will cause a decrease in the concentration of iodine in the solution to be activated.

In preparing very dilute (less than or equal to 1.00 x 10^{-9} moles of iodine in the solution) solutions of iodine inoculated with iodine-131 it would be advisable to activate a more concentrated solution, by one of the two procedures just described, and diluting to the desired concentration.

Generally, using ORNL carrier-free iodide-131 shipments less then 30 days old, the overall activity yields were about 40 percent when the iodine concentrations were greater than or equal to 1.00×10^{-4} F. When ORNL carrier-free iodide-131 shipments were as old as 60 days, the overall activity yields were often as low as 20 percent with iodine concentrations greater than or equal to 1.00×10^{-4} F.

Although activation of a nonaqueous iodine solution at 50° results in slightly higher yields, this small advantage may be offset by the troublesome possiblities of volatilization of iodine and/or solvent and reactions between the solvent and the molecular iodine.

REFERENCES

1. Breiter, M. W., "Voltammetric Study of Halide Ion Adsorption on Platinum in Perchloric Acid Solutions," Electrochim. Acta 8, 925 (1963).

2. Chang, Chau-ting and Chien-chang Lin, "Preparation of Carrier-free Iodine-131 with Adsorption Method. (II) Sorption of Iodine on Platinum Metal Surface," A1j-12, Proc. of the 5th. Japan Conference on Radioisotopes, May 21, 1963, Tokyo.

3. Lin, Chien-chang, Chau-ting Chang and Si Jung Yeh, "Preparation of Carrier-free I-131 with Adsorption Method," J. Atomic Energy Soc. Japan 5, No. 3, 187 (1963).

4. Osteryoung, R. A. and F. C. Anson, "Behavior of the Iodide-Iodine Couple at Platinum Electrodes," Anal. Chem. 36, 975 (1964).

5. Schwabe, K. "Untersuchung Über Die Anionenadsorption Mit Hilfe Markierter Ionen," Electrochim. Acta 6, 223 (1962).

6. Schwabe, K. and W. Schwenke, "Untersuchungen Über Anionenadsorption An Metalloberflächen In Abhängigkeit Vom Potential," Electrochim. Acta 9, 1003 (1964).

7. Tóth, G., "Production of Carrier-free I-131 from Telluric Acid by an Adsorption Method," J. Inorg. and Nucl. Chem. 19, 186 (1961).

8. Reynolds, M. S., Thesis submitted for degree of Doctor of Philosophy, University of New Mexico, Albuquerque, N. M. (1966).

9. Lin, Chien-chang, Thesis submitted for degree of Doctor of Philosophy, University of New Mexico, Albuquerque, N. M. (1968).

10. Kahn, M., Thesis submitted for degree of Doctor of Philosophy, Washington University, St. Louis, Mo. (1950).

11. Kahn, M., A. J. Freedman, R. D. Feltham and N. L. Lark, "Counting Techniques for Chlorine-36," Nucleonics 13, 58 (1955).

PART B

THE DISTRIBUTION OF MOLECULAR IODINE BETWEEN CYCLOHEXANE AND AQUEOUS SOLUTIONS.

B.I. INTRODUCTION

Generally, the chemical behavior of iodine at low concentrations (less than 1 x 10^{-5} F) cannot be predicted by extrapolation of the known macro chemistry of iodine (12, 13 and 14). Previous studies of the distribution of iodine, at low concentrations, between an aqueous phase and a nonaqueous phase have revealed that the distribution coefficient, D[1], decreases with a decrease in the total iodine concentration more readily than would be predicted from the macro chemistry of iodine. The work reported here is concerned with the distribution of molecular iodine between a nonaqueous phase and aqueous solutions.

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[1] $D = \frac{\text{concentration of I-atoms(I-131) in nonaqueous phase}}{\text{concentration of I-atoms(I-131) in aqueous phase}}$

B.I.a. The Distribution of Iodine Between the Two Phases of an Aqueous-Nonaqueous System

In 1950 Kahn (12) reported that the distribution coefficient for iodine between benzene and dilute sulfuric acid (pH = 1.3) decreased with a decrease in the initial iodine concentration in the benzene phase. He observed that more iodine appeared in the aqueous phase than would be expected from the known macro chemistry of iodine. For example, for an initial iodine concentration in the benzene phase of 1.9×10^{-2} F the experimentally determined distribution coefficient is 379, and for an initial iodine concentration in the benzene phase of 1.9×10^{-4} F the experimentally determined distribution coefficient is 304. Other investigators have since reported on this anomolous chemical behavior of iodine.

In 1953 Katzin (15) reported on the determination of the equilibrium constant for the reaction,

$$H_2O \cdot I_2 = H_2OI^+ + I^-$$

by spectrophotometric methods. He reported that the equilibrium constant increased with decreasing iodine concentration. Reid and Mulliken (16), in 1954, reported that similar results were observed when studying the spectra of dilute solutions of iodine in pyridine. Their spectrophotometric investigations showed that, at low concentrations, the ratio of $[I_3^-] / [Py \cdot I_2]$ increased rather than decreased as would be expected.

In 1956 Good and Edwards (17) reported on a study of the distribution of iodine between aqueous solutions at various pH and carbon disulfide where the initial concentration of iodine in the carbon disulfide was varied over the range 10^{-1} to 10^{-6} F. They reported that more iodine appeared in the aqueous phase than could be accounted for on the basis of the known chemistry of iodine. This discrepency increased as the total iodine concentration decreased and as the time of contact between the two phases increased. They accounted for this discrepency by postulating a reaction (or reactions) between the iodine and unknown impurities present in the aqueous phase which caused excess iodine to appear in the aqueous phase. In 1957 Wille and Good (18) reported on the distribution of iodine between carbon tetrachloride and aqueous solutions at various pH where the initial concentration of iodine in the carbon tetrachloride phase was varied over the range 10^{-1} to 10^{-5} F. They also observed excess iodine appearing in the aqueous phase and that this excess iodine increased with increasing time of contact between the two phases and decreasing iodine concentration.

In 1957 Wolfenden (19), in a spectroscopic study of the slow development of triiodide ion in aqueous solutions of iodine, concluded that the slow formation of triiodide ion was due mainly to reduction of the aqueous iodine by traces of dust and not to the slow hydrolysis of a water-iodine complex ($I_2 \cdot H_2O$).

B.I.b. Reactions and Equations Involved in the Distribution of Iodine Between the Two Phases of an Aqueous-Nonaqueous System (20)

The following reactions are involved in the partitioning of molecular iodine between nonaqueous solvents and aqueous solutions, where the bracketed quantities refer to molar quantities.

1. $I_{2\ \text{aq.}} \xrightarrow{K_1} I_{2\ \text{nonaq.}}$

$$K_1 = \frac{[I_2]\ \text{nonaq.}}{[I_2]\ \text{aq.}}$$

2. $I_{2\ aq.} + H_2O \underset{}{\overset{K_2}{\rightleftharpoons}} H^+ + I^- + HIO$

$$K_2 = \frac{[H^+][I^-][HIO]}{[I_2]\ aq.}$$

3. $I_{2\ aq.} + H_2O \overset{K_3}{\rightleftharpoons} H_2OI^+ + I^-$

$$K_3 = \frac{[H_2OI^+][I^-]}{[I_2]\ aq.}$$

4. $I_{2\ aq.} + [I^-] \overset{K_4}{\rightleftharpoons} [I_3^-]$

$$K_4 = \frac{[I_3^-]}{[I_2]\ aq.\ (I^-]}$$

5. $3I_{2\ aq.} + 3H_2O \xrightarrow{K_5} IO_3^- + 5I^- + 6H^+$

$$K_5 = \frac{[IO_3^-][I^-]^5[H^+]^6}{[I_2]^3\ aq.}$$

6. $HIO \xrightarrow{K_6} H^+ + IO^-$

$$K_6 = \frac{[H^+][IO^-]}{[HIO]}$$

7. $IO^- + I^- + H_2O \xrightarrow{K_7} I_2OH^- + OH^-$

$$K_7 = \frac{[I_2OH^-][OH^-]}{[IO^-][I^-]}$$

8. $IO^- + I^- \xrightarrow{K_8} I_2O^=$

$$K_8 = \frac{[I_2O^=]}{[IO^-][I^-]}$$

9. $I_2 + \text{Imp} \xrightarrow{K_9} 2I^- + \text{Imp}'$

Where Imp is an impurity coming from either phase and Imp' is the chemically changed form of that impurity.

At 25° the values for the equilibrium constants for reactions 1 through 7 are:

$K_1 = 80$ for cyclohexane and 1.00 F sulfuric acid (this value will be different for other nonaqueous solvents) (this work);

$K_2 = 5.40 \times 10^{-13}$ (21);

$K_3 = 1.2 \times 10^{-11}$ (22);

$K_4 = 768$ (23);

$K_5 = 4 \times 10^{-48}$ (24);

$K_6 = 2.3 \times 10^{-11}$ (25);

$K_7 = 0.13$ (25).

For reaction 8, at low pH the reaction lies far to the left, and, reaction 9 simply indicates the possibility of a reaction between iodine and unidentified impurities. Only reactions 1, 2, 3 and 4 are important for systems of low pH (pH less than or equal to 3), low iodine concentration and high purity. No net reduction or oxidation occurs during a hydrolysis reaction and as a consequence of the stoichiometry of equations 1 through 4 it follows that

$$[\text{HIO}] + [\text{H}_2\text{OI}^+] = [\text{I}^-] + [\text{I}_3^-]$$

If it is assumed that only molecular iodine has an appreciable solubility in the nonaqueous phase of the two phase (aqueous-nonaqueous) system then

$$D = \frac{2 \text{ mole } I_2 \text{ / liter nonaqueous solvent}}{\text{mole I atoms / liter aqueous solvent}}$$

where D is the distribution coefficient. Then

$$D = \frac{2\,[I_2]\text{ nonaq.}}{2\,[I_2]\text{ aq.} + [HIO] + [H_2OI^+] + [I^-] + 3\,[I_3^-]}$$

Substitution of expressions for $[HIO]$, $[H_2OI^+]$ and $[I_3^-]$ into the last equation yields

$$D = \frac{2\,[I_2]\text{ nonaq.}}{\frac{2\,[I_2]\text{ nonaq.}}{K_1} + \frac{[I_2]^{\frac{1}{2}}\text{ nonaq.}}{K_1}\left[\frac{K_2}{[H^+]} + K_3\right]^{\frac{1}{2}}\left[\left[1 + K_4\frac{[I_2]\text{ nonaq.}}{K_1}\right]^{\frac{1}{2}} + \left[1 + K_4\frac{[I_2]\text{ nonaq.}}{K_1}\right]^{-\frac{1}{2}} + \left[1 + 3\,K_4\frac{[I_2]\text{ nonaq.}}{K_1}\right]\right]}$$

From this equation D can be calculated for various iodine and acid concentrations. If there are further reactions taking place due to impurities, as has been suggested by other workers (17 and 19), these will, in all probability, yield a lower distribution coefficient than that which would be calculated by using the equation given and, indeed, this does seem to be the case.

B.I.c. Scope of This Work

The distribution coefficient, D, for iodine between cyclohexane and aqueous solutions was studied. The initial concentration of iodine in the cyclohexane ranged from 1.00×10^{-2} to 1.00×10^{-5} F. The composition, ionic strength and pH of the aqueous solutions were varied, as was the purity of the cyclohexane and aqueous solutions. The distribution coefficient was found to decrease with

1. a decrease in the initial concentration of molecular iodine in cyclohexane,
2. a decrease in the ionic strength of the aqueous phase,
3. a decrease in the acidity of the aqueous phase,
4. an increase in the time of contact between the two phases, and,
5. an increase in the impurity level of the cyclohexane.

Anomolous fractions have been detected in both phases. The concentration of these fractions increased with

1. an increase in the time of contact between the two phases,
2. an increase in the acidity of the aqueous phase, and,
3. an increase in the impurity level of the cyclohexane.

These fractions were most prominent in the aqueous phase but were detectable in the cyclohexane phase as well.

B.II. EXPERIMENTAL

B.II.a. General Procedures and Equipment

Exclusion of Light

All operations were performed in the absence of light except where specifically noted. A fifteen-watt, shielded, incandescent light bult, placed fifteen feet from the working area, provided the illumination necessary to perform all operations. Vessels containing solutions to be stored and vessels in which extended-time reactions were taking place were securely wrapped with aluminum foil.

Maintenance of Constant Temperature

A constant-temperature bath was maintained, initially, at 28.0° ± 0.1°, and, subsequently at 24.9° ± 0.1°. All vessels containing solutions to be stored and vessels in which extended-time reactions were taking place were kept in the constant-temperature bath. Centrifuge tubes to be used in the one-minute studies were placed in a dry, glass tube, suspended in the constant-temperature bath and brought to temperature prior to use.

Glassware

All glassware was constructed of borosilicate glass (Pyrex or Kimax); centrifuge tubes, Erlenmeyer flasks and volumetric flasks were fitted with ground-glass stoppers. All volumetric glassware was of class-A tolerance.

Cleaning of Glassware

Glassware was cleaned by immersion in chromic acid for at least 12 hours. The glassware was then rinsed with ordinary distilled water, followed by a thorough rinsing with water distilled from alkaline permanganate, capped with aluminum foil and dried in an oven at 110°.

The possibility of radiochemical contamination by adsorbed iodine-131 was resolved by monitoring all counting tubes and reaction vessels after cleaning.

Centrifugation

Centrifugations were performed in an International Clinical Centrifuge at 2,000 to 3,000 rpm.

Counting Procedures

A Nuclear Chicago Model 132 single-channel analyzer in conjunction with a Nuclear Chicago DS-5 Na(Tl) well-type scintillation probe and a Hewlett Packard Model 5201L single-channel analyzer with a Hewlett Packard Model 5551A high-voltage supply in conjunction with a Nuclear Chicago DS-5 Na(Tl) well-type scintillation probe were used to detect the gamma activity of the iodine-131. Liquid samples were prepared and counted in 15 x 125 mm., calibrated, Pyrex test tubes.

The test tubes were calibrated by filling them to a predetermined height (corresponding to a volume of approximately 10.5 ml.) with an iodine-131 solution and counting. Those tubes which gave the same counting rate within an expected standard deviation of ± 0.6 percent were used for counting. All liquid samples were diluted to the standard counting-height and counted to within an expected standard deviation of ± 1.0 percent. Counting rates were not corrected for variation in solution densities: Kahn (12) has reported that over the range of 0.88 to 1.04 g/ml. the change in counting rate due to self absorption is negligible.

B.II.b. Reagents

Water

Water used in this research was prepared in the following manner.

Ordinary distilled water was redistilled from alkaline permanganate in an all-Pyrex system and stored in Pyrex vessels capped with 24/40 female Pyrex joints.

Perchloric Acid

Analytical reagent grade perchloric acid (Mallinckrodt) was fumed for one hour in an open platinum crucible at 160° (14). Prepurified nitrogen gas (Matheson) was passed directly from the tank through the acid during the heating, fuming and cooling process. Upon cooling, the nitrogen-treated acid was immediately diluted with about twice its volume of water. The concentration of the dilute acid was determined by titration with standard sodium hydroxide.

Iodine

Analytical reagent grade iodine (Mallinckrodt) was resublimed under vacuum and, then, stored in a desiccator over anhydrous calcium sulfate.

Cyclohexane

Four types of cyclohexane were used and a description of each is given below.

1. Eastman Spectro Grade cyclohexane was used without further purification and is referred to in the text as "untreated." This cyclohexane was stored in a brown bottle in the presence of light. Private correspondence with Eastman Kodak Company revealed that the most probable impurities in their Spectro Grade cyclohexane were isoheptanes; specifically, 2,4-dimethylpentane and 3,3-dimethylpentane.
2. Eastman Spectro Grade cyclohexane, referred to in the text as "treated," was treated according to the following procedure.

Two-hundred-fifty milliliters of cyclohexane was placed in a 500-ml. round-bottom flask with a 24/40 female joint. Sufficient iodine was added to the flask to make the resulting solution 1×10^{-3} F in iodine and this was followed by the addition of one ml. of a 1×10^{-3} F iodine solution in cyclohexane containing iodine-131 at a known specific activity. The flask was fitted to a reflux condenser, the solution refluxed for 48 hours and, then, allowed to cool. An excess of aqueous sodium sulfite was added to the cooled contents of the flask, the mixture refluxed for 8 hours to reduce the iodine to iodide, and, then, cooled. Subsequently, a 10-ml. sample of the cyclohexane was removed for counting to ascertain whether removal of the iodine-131, by reduction with aqueous sulfite, was quantitative. (It is noteworthy that no iodine-131 could be detected in the cyclohexane.) Then, the aqueous phase remaining in the flask was drawn off by means of a pipette, calcium hydride was added to the flask and the mixture refluxed for 16 hours to remove the last traces of water and dry the cyclohexane. The cooled, dry cyclohexane was transferred to a clear volumetric flask and stored in the presence of ordinary fluorescent light.

3. Phillips Research Grade cyclohexane was used without further purification and was stored in the dark. The Phillips Petroleum Company's catalog of hydrocarbons indicates that small quantities of isoheptanes are present in their Research Grade cyclohexane.

4. Primary Standard Grade cyclohexane obtained from James Hinton, 358 Chicago Avenue, Valparaiso, Florida, was used without furthur purification and was stored in the dark. Private correspondence with James Hinton revealed that he purifies his cyclohexane in the following manner, and I quote.

> I repeatedly filter cyclohexane through a three-foot column of silica gel activated with nitric acid, then heated at 200 degrees for several hours. The starting material is better than 99%. This material is observed in the ultraviolet to establish that less than 0.01% unsaturates are present (estimate 0.001%).
>
> This is zone refined at a very slow zone pass until the MELTING POINT OF THE IMPURE FRACTION IS THE SAME AS THE MELTING POINT OF THE PURE FRACTION TO 0.01 degrees.
>
> It is then observed fluorometrically.
>
> While numerous batches have been observed by gas chromotography, no impurities have ever been detected. However, I believe this approach to be inherently unsuitable for impurity observation since the melting point may be low, yet no impurities observed in some cases.
>
> I advertise 99.98% because the melting point is very difficult to observe absolutely .... no doubt because of the low heat of fusion.
>
> The material is dried over molecular sieve 5A to less than 0.01% water, and can be dried to less than 0.001% water.

Cyclohexene, 2-methyl-2-pentanol, 2-methyl-2,4-pentanediol and 2,4-dimethylpentane

Cyclohexene (Hinton 99.4%), 2-methyl-2-pentanol (Hinton 99.9%), 2-methyl-2,4-pentanediol (Hinton 99.9%) and 2,4-dimethylpentane (Phillips Research Grade) were used without further purification.

Radioiodine

The radioactive iodine employed was carrier-free iodide-131 obtained in a slightly basic sulfite solution from Oak Ridge National Laboratory. Stock solutions of carrier-free iodide-131 were prepared by removing microliter amounts of the radioactive solution from the original container and inoculating freshly prepared aqueous 1.00 x 10^{-3} F sodium sulfite. These stock solutions were used within 5 minutes after preparation.

Nitrogen and Oxygen

Prepurified nitrogen (Matheson) and oxygen (Linde) were passed through a concentrated sulfuric acid bubbler.

Ozone

Ozone was generated according to the procedure of Bonner (26).

Other Reagents

All other chemicals were of analytical reagent grade and used without further purification.

Preparation of Cyclohexane Solutions of Inactive Molecular Iodine

The dilute cyclohexane solutions of inactive molecular iodine were prepared by dilution of a 1.00 x 10^{-2} F stock solution of iodine in cyclohexane which had been stored in the presence of ordinary fluorescent laboratory light for as long as one month. However, the dilute cyclohexane solutions of molecular iodine were stored in the absence of light in glass-stoppered, Pyrex, volumetric flasks wrapped in aluminum foil and suspended in a constant-temperature bath.

It is noteworthy that no chemical difference could be detected between dilute cyclohexane solutions made from the above stock solution or dilute cyclohexane solutions made by dilution of a 1.00 x 10^{-2} F stock solution of iodine which had been prepared and stored in the dark for as long as one month. It is equally noteworthy that no chemical difference could be detected between dilute cyclohexane solutions of iodine made from stock solutions which were freshly prepared or dilute cyclohexane solutions which were made from stock solutions which were stored in the light or dark for one month. These conclusions are based on the observation that the value of the distribution coefficient of iodine between cyclohexane and aqueous solutions, at low concentrations of iodine, was independent of whether the stock solutions of 1.00×10^{-2} $\underline{F}$ iodine were stored in the dark or in the light over periods as long as one month.

Preparation of Cyclohexane Solutions of Molecular Iodine Inoculated with Iodine-131

The dilute cyclohexane solutions of molecular iodine inoculated with iodine-131 were prepared according to the following methods.

1. The dilute (10^{-2} to 10^{-5} $\underline{F}$) cyclohexane-iodine solutions were shaken with a small quantity, on the order of 0.001 ml., of the original Oak Ridge National Laboratory aqueous carrier-free iodide-131. The system was centrifuged and the active cyclohexane-iodine solution pipetted from the centrifuge tube.
2. A small quantity of the original Oak Ridge National Laboratory aqueous carrier-free iodide-131, on the order of 0.001 ml., was washed with one ml. of cyclohexane to remove any cyclohexane soluble iodine species present. The active aqueous solution was then shaken with a quantity of a dilute (10^{-2} to 10^{-5} $\underline{F}$) cyclohexane solution of molecular iodine in a centrifuge tube. The system was then centrifuged and the active cyclohexane solution removed by means of a capillary pipette.
3. A small quantity, on the order of 0.001 ml., of the original Oak Ridge National Laboratory aqueous carrier-free iodide-131 was introduced into the aqueous phase of the two-phase cyclohexane-

iodine-aqueous system to be studied.

4. The dilute (10^{-2} to 10^{-5} F) cyclohexane solutions of molecular iodine were inoculated with iodine-131 by the platinum foil procedure described in Part A. Carrier-free iodide-131 was adsorbed, from an acidic aqueous solution, onto a platinum foil whose surface had been previously saturated with adsorbed iodine-127. The active foil was dried and immersed in a dry cyclohexane solution of molecular iodine for at least 2 hours; activation of this solution took place via isotopic exchange.

B.II.c. Distribution Procedures

The procedures used to investigate various aspects of the distribution of iodine between cyclohexane and aqueous solutions, employing iodine-131 as tracer, are summarized in Figures B.1 through B.6 and described below.

B.II.c.1. Zero-Time Distribution

The following procedure was used to investigate the zero-time distribution of molecular iodine between cyclohexane and aqueous solutions (see Figure B.1) where the initial concentration of iodine in cyclohexane ranged from 1.00×10^{-2} to 1.00×10^{-5} F. Five milliliters of an aqueous solution was pipetted into a 10-ml., glass-stoppered, Pyrex, centrifuge tube. This was followed by the addition of one ml. of the cyclohexane-iodine solution of known specific activity. The stopper was wet, the vessel stoppered and shaken for one minute. The vessel was centrifuged for one minute and, then, aliquots were taken from each phase for counting. It is noteworthy that increasing the shaking time to 2, 3 or 5 minutes did not alter the values of the distribution coefficients.

Moreover, no activity was detected on the stopper or walls of the centrifuge tube after the contents had been removed.

B.II.c.2. The Dependence of the Distribution on the Mixing Time

The following procedure was used to investigate the distribution of iodine between cyclohexane and aqueous solutions, where the initial concentration of iodine ranged from 1.00 x 10^{-2} to 1.00 x 10^{-5} F, with respect to the time the two phases were in contact (see Figure B.2). Ten milliliters of an aqueous solution was pipetted into a 25-ml. glass-stoppered, Kimax, Erlenmeyer flask. This was followed by the addition of 5 ml. of the cyclohexane-iodine solution of known specific activity. The reaction vessel was then stoppered, wrapped in aluminum foil to exclude light, placed in a constant-temperature bath and stirred magnetically, using a Pyrex covered magnetic stirring bar, for a given length of time. In early experiments, at the end of the mixing time the reaction vessel was removed from the constant-temperature bath and allowed to sit for several minutes while the phases separated. Then, aliquots were taken from each phase for counting and the remaining contents of the flask discarded. In later experiments, aliquots, representing the same fraction of each phase, were taken for counting, the vessel stoppered, rewrapped with foil, returned to the constant-temperature bath and stirred magnetically for a given time before additional aliquots were taken.

The degree of separation of the two phases upon standing was checked against centrifugation using the following two procedures.

1. A sample from each phase was placed in different centrifuge tubes, centrifuged for one minute and aliquots of each sample

taken for counting.

2. Two milliliters of the aqueous phase and one ml. of the cyclohexane phase was placed in the same centrifuge tube, shaken for one minute, centrifuged for one minute and aliquots of each phase taken for counting.

In all instances, the distribution coefficient was the same for a particular reaction mixture indicating that adequate separation of the phases occurred. However, in later experiments procedure 1 was used. The results of using procedure 2, in conjunction with the data given in the Tables, show that adequate mixing of the two phases occurred using magnetic stirrers.

B.II.c.3. Detection of Iodine-131 Fractions in the Cyclohexane Phase

The distribution coefficient for iodine between cyclohexane and aqueous solutions decreased with decreasing iodine concentration and increasing time of the mixing process. It was of interest, therefore, to ascertain the disposition of iodine-131 in the cyclohexane phase after it and the aqueous phase had been mixed. In order to detect the iodine-131 fractions in the cyclohexane phase it was necessary to perform experiments, separate from the measurement of the distribution coefficient, where the volume of the cyclohexane phase was increased. The chemical nature of the iodine-131 species in the cyclohexane phase was studied where the initial concentration of iodine in the cyclohexane was either 1.00×10^{-3} $\underline{F}$ or 1.00×10^{-5} $\underline{F}$ and the duration of the mixing process was either one minute or 24 hours or more. The experimental procedures used are described below.

The following procedure (see Figure B.3) was used to study the chemical nature of the iodine species in the cyclohexane phase where the initial iodine concentration in the cyclohexane was either 1.00×10^{-3} F or 1.00×10^{-5} F; the two phases were shaken manually for one minute in the absence of light. Four-milliliter aliquots of the aqueous and cyclohexane-iodine solutions were pipetted into a 10-ml., glass-stoppered, Pyrex, centrifuge tube. The stopper was wet, the vessel stoppered, shaken for one minute and centrifuged for one minute. One-milliliter aliquots were taken from the cyclohexane phase and added to each of three centrifuge tubes. One centrifuge tube contained 5 ml. of freshly prepared aqueous 0.100 F sodium sulfite with 0.5 millimole of sulfuric acid added, another centrifuge tube contained 5 ml. of freshly prepared aqueous 0.100 F sodium iodide and the other centrifuge tube contained 5 ml. of aqueous 0.100 F sodium hydroxide. The stoppers were wet, the vessels stoppered and shaken for one minute. Then, the vessels were centrifuged and the whole of each phase taken for counting. Quantitative separation and removal of each phase from the centrifuge tube was accomplished in the following manner: all but about 0.01 ml. of the aqueous phase was removed by means of a capillary pipette, the vessel was centrifuged to bring down the aqueous phase adhering to its walls, and the remaining aqueous phase removed.

The following extraction procedure (see Figure B.4) was used to investigate the chemical nature of the iodine species in the cyclohexane phase, where the initial concentration of iodine in the cyclohexane was either 1.00×10^{-3} F or 1.00×10^{-5} F; the two phases were stirred for at least 24 hours in the absence of light. Five milliliters each of the aqueous and cyclohexane-iodine solutions were pipetted into a 25-ml., glass-stoppered, Kimax, Erlenmeyer flask. The vessel was stoppered, wrapped in aluminum foil, placed in a constant-temperature bath and stirred magnetically using a Pyrex-covered magnetic stirring bar. After a specified time the vessel was removed from the constant-temperature bath and allowed to stand for several minutes so the two phases could separate. Four milliliters of the cyclohexane phase was transferred to a centrifuge tube. After centrifugation one-ml. aliquots were taken from the cyclohexane phase and added to each of three centrifuge tubes. One centrifuge tube contained 5 ml. of freshly prepared aqueous 0.100 F potassium iodide, another centrifuge tube contained 5 ml. of freshly prepared 0.100 F sodium sulfite with 0.5 millimole of sulfuric acid added and the other centrifuge tube contained 5 ml. of aqueous sodium hydroxide. The stoppered centrifuge tubes were shaken for one minute, centrifuged and the whole of each phase taken for counting. Quantitative separation and removal of each phase was accomplished in the following manner: all but about 0.01 ml. of the aqueous phase was removed by means of a capillary pipette, the vessel centrifuged to bring down the aqueous phase adhering to its walls, and the remaining aqueous phase removed.

B.II.c.4. Detection of Iodine-131 Fractions in the Aqueous Phase

During the studies of the distribution of iodine between cyclohexane and aqueous solutions the distribution coefficient was found to decrease with decreasing iodine concentration and increasing time of the mixing process. Therefore, a study was made of the chemical nature of the iodine-131 fractions in the aqueous phase. In order to detect the iodine-131 species in the aqueous phase it was necessary to perform experiments separate from the measurement of the distribution coefficient so that there was sufficient aqueous phase to work with. The disposition of iodine-131 in the aqueous phase was studied in the manner described below.

The following extraction procedure (see Figure B.5) was used to investigate the chemical nature of the iodine species in the acidic aqueous phase where the initial concentration of iodine in the cyclohexane was either 1.00 x 10^{-3} or 1.00 x 10^{-5} F; the two phases were stirred for at least 24 hours in the absence of light. Ten milliliters of an aqueous solution (see Figure B.5) was added to a 25-ml., glass-stoppered, Kimax, Erlenmeyer flask. This was followed by the addition of 5 ml. of a cyclohexane-iodine solution of known specific activity. The flask was stoppered, wrapped in aluminum foil, placed in a constant-temperature bath and stirred magnetically with a Pyrex-covered magnetic stirring bar. After a specified time (at least 24 hours) the flask was removed from the constant-temperature bath and allowed to stand for several minutes so that the two phases could separate. Nine milliliters of the aqueous phase and 4 ml. of the cyclohexane phase were removed from the flask, transferred to individual centrifuge tubes and centrifuged. One-milliliter aliquots of each phase were then taken for counting in order to determine the distribution coefficient of iodine-131. Another one-ml. aliquot was taken from the centrifuge tube containing the cyclohexane phase, placed in a centrifuge tube containing 5 ml. of the original solution A (see Figure B.5) and subjected to the procedure outlined in Figure B.1. This gave a value for the distribution coefficient for a cyclohexane-iodine solution, which had been in contact with an acidic aqueous solution B (see Figure B.5) for one day or more, and a fresh acidic aqueous solution. Two milliliters of the aqueous phase B (see Figure B.5) was added to a 10-ml., glass-stoppered, Pyrex, centrifuge tube containing 2 ml. of cyclohexane. The centrifuge tube was stoppered, shaken for one minute and centrifuged. Then, the aqueous phase was quantitatively removed and transferred to a centrifuge tube containing 2 ml. of a 1.00 x 10^{-2} F cyclohexane-iodine solution and the cyclohexane phase was quantitatively transferred to a centrifuge tube containing 2 ml. of 0.100 F aqueous sodium iodide. Quantitative separation and removal of each phase from a centrifuge tube was accomplished in the following manner: all but about 0.01 ml. of the aqueous phase was removed by means of a capillary pipette, the vessel centrifuged to bring down the aqueous phase adhering to the walls of the vessel, and the remaining aqueous phase removed. The two centrifuge tubes, each containing two phases, were stoppered, shaken for one minute and centrifuged. Subsequently, one milliliter of each phase from each tube was removed for counting.

B.II.c.5. Detection of Iodine-131 Fractions in the Original Cyclohexane-Iodine Solutions

The following procedure (see Figure B.6) was used to investigate, via extraction analysis with aqueous sodium hydroxide, the chemical nature of the iodine in various active stock cyclohexane-iodine solutions in the absence of light. Five milliliters of an aqueous 0.100 F sodium hydroxide solution was placed in a 10-ml., glass-stoppered, Pyrex, centrifuge tube. This was followed by the addition of one ml. of an iodine-cyclohexane solution of known specific activity. The stopper was wet, placed in the tube, the whole shaken for one minute and centrifuged. Four milliliters of the aqueous phase and 0.5 ml. of the cyclohexane phase were removed for counting.

B.II.c.6. The Effect of Oxygen, Ozone and Hydrogen Peroxide on the Distribution

The procedures used to investigate the effect of the presence of oxygen, ozone and hydrogen peroxide on the distribution of iodine between cyclohexane and aqueous solutions are the same as those used to study the zero-time distribution (see pp. 82 and 83 and Figure B.1) and the dependence of the distribution on the mixing time (see pp. 83 and 84 and Figure B.2). The initial concentration of the iodine in the cyclohexane was either 1.00×10^{-3} F or 1.00×10^{-5} F. Aqueous solutions, 1.00 F in sulfuric acid, were treated according to the following methods.

1. Oxygen gas was passed through the solution for one hour at a moderate rate and in the dark.
2. Nitrogen gas was passed through the solution for one hour at a moderate rate and in the dark.
3. A mixture of ozone and oxygen gases was passed through the solution for one hour at a moderate rate and in the presence of light.
4. The solution was made 1.00×10^{-3} F in hydrogen peroxide by the addition of an appropriate amount of 30 percent hydrogen peroxide solution.

B.II.c.7. The Effect of Organic Impurities on the Distribution

The distribution coefficient for iodine between cyclohexane and 1.00 F sulfuric acid had been found to decrease with decreasing iodine concentration and increasing time of the mixing process. The magnitude of the decrease of the distribution coefficient was found to be significantly less when very high purity (Hinton Primary Standard grade) cyclohexane was used rather than Eastman Spectro Grade cyclohexane. It was of interest, therefore, to add certain impurities to very high purity (Hinton Primary Standard grade) cyclohexane and note their effect on the distribution coefficient.

The procedure used to investigate the effect of the presence of organic impurities on the distribution of molecular iodine between cyclohexane and 1.00 F sulfuric acid is summarized in Figure B.1. The initial concentration of molecular iodine in cyclohexane was either 1.00×10^{-3} F or 1.00×10^{-5} F. Five milliliters of 1.00 F sulfuric acid and one ml. of the cyclohexane-iodine solutions were added to a 10-ml., glass-stoppered centrifuge tube: this was followed by the addition of 0.01 ml. of the impurity to the cyclohexane phase. The resulting impurity concentrations were approximately 0.1 molar. The centrifuge tube was stoppered, shaken for one minute and centrifuged. Four milliliters of the aqueous phase and 0.5 ml. of the cyclohexane phase were then taken for counting.

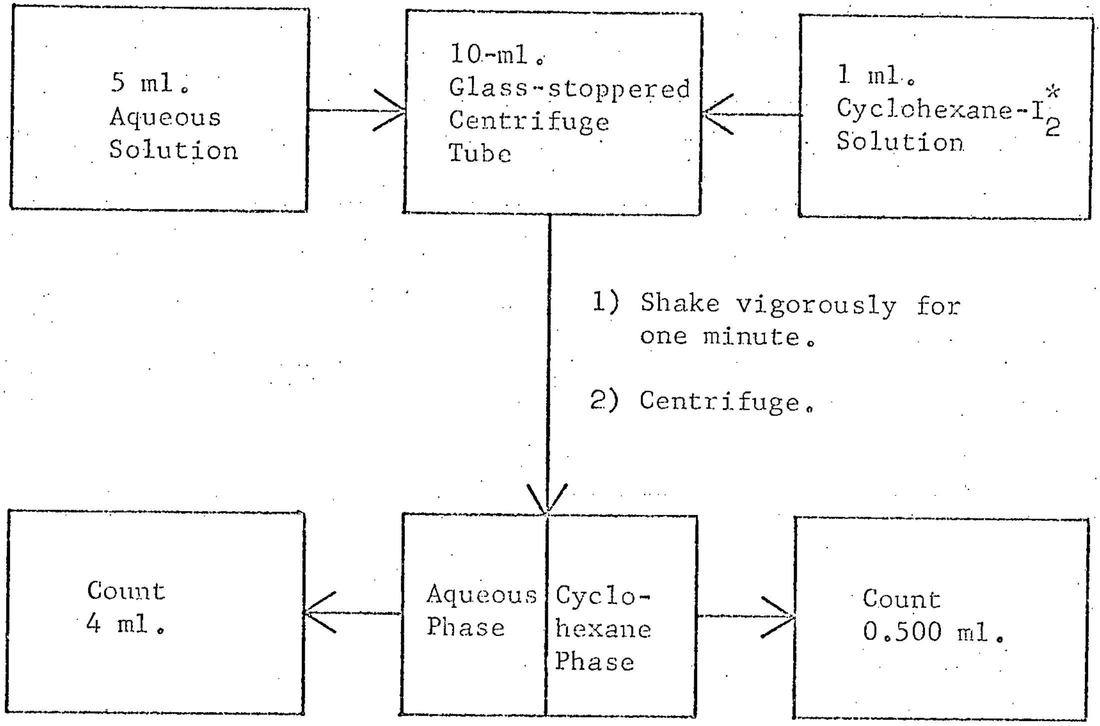


Figure B.1. This procedure was used to investigate the zero-time distribution of molecular iodine between cyclohexane and aqueous solutions.

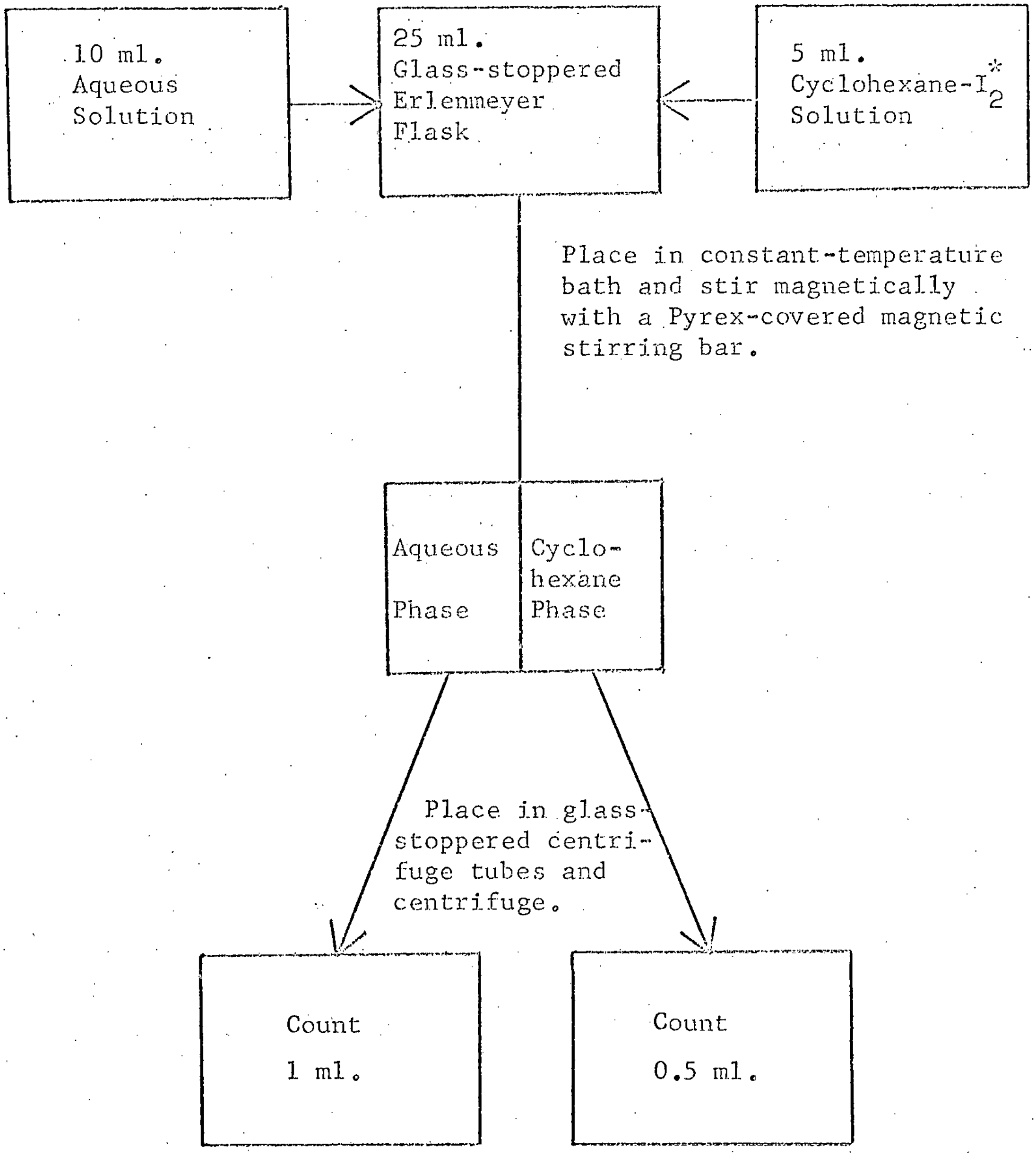


Figure B.2. This procedure was used to investigate the distribution of molecular iodine between cyclohexane and aqueous solutions, in the absence of light, with respect to the time the two phases were in contact.

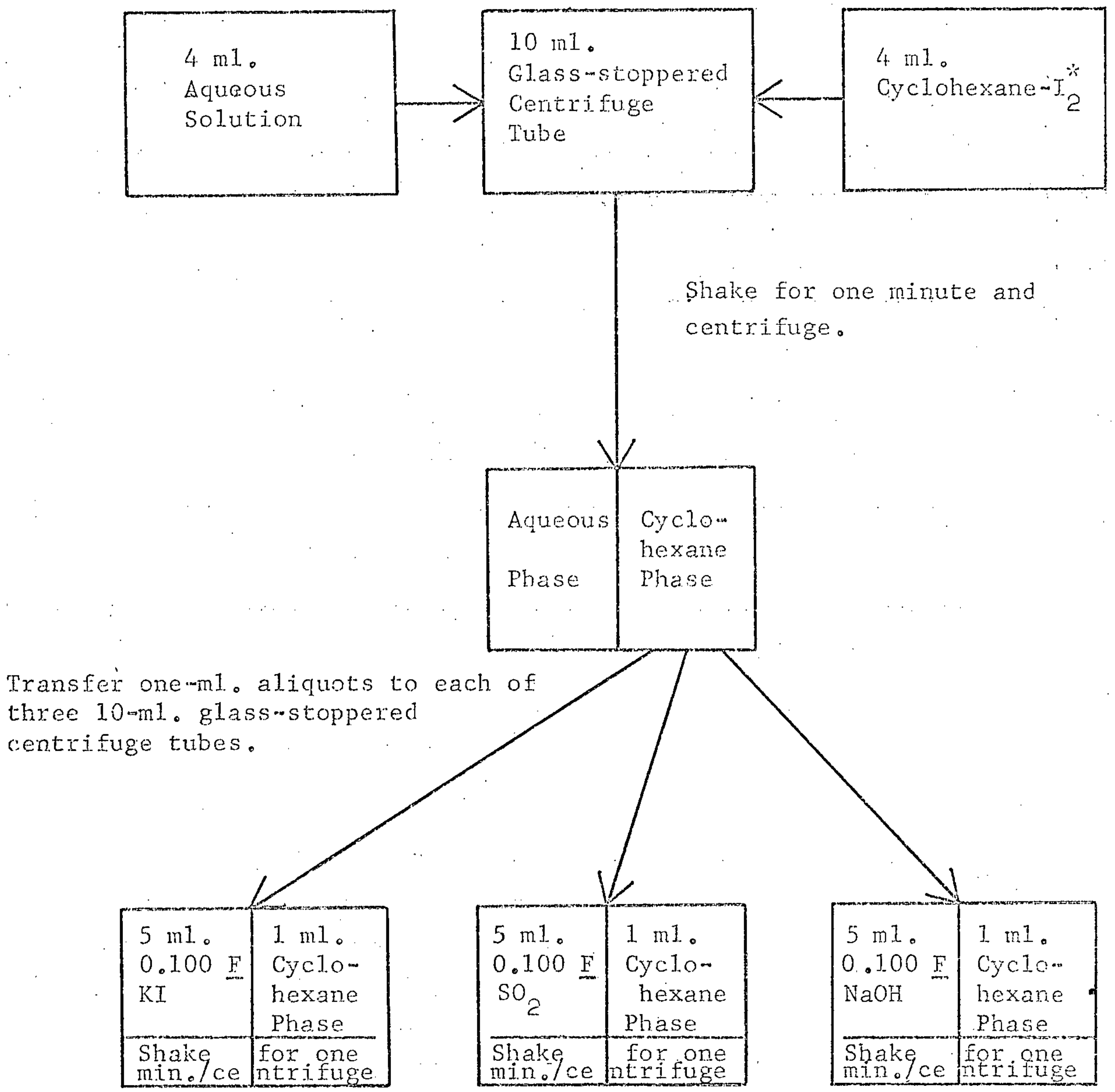
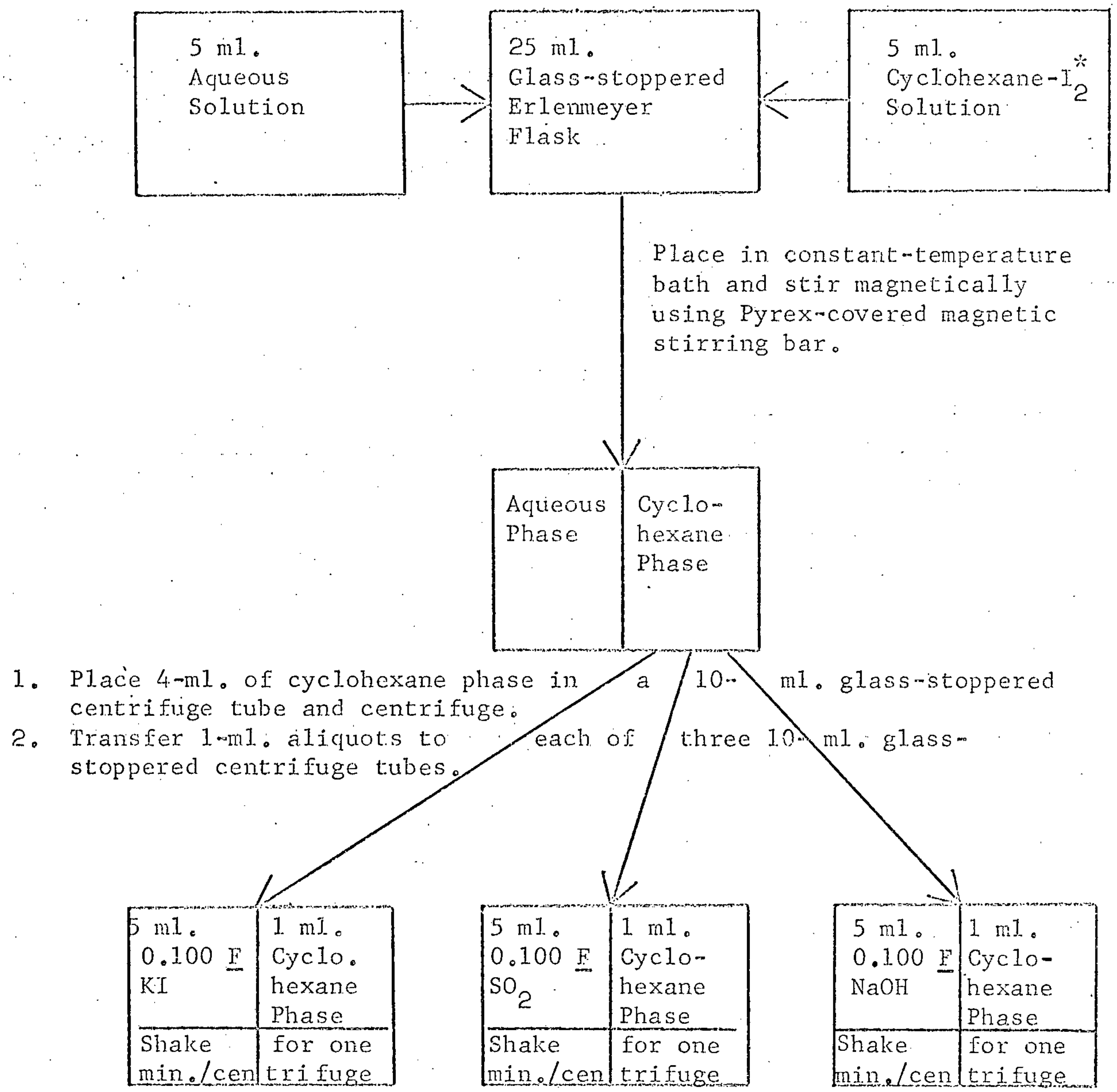


Figure B.3. Procedure used to investigate the chemical nature of the iodine in the cyclohexane phase after extraction for one minute with an aqueous solution. All operations were carried out in the absence of light.



Place in constant-temperature bath and stir magnetically using Pyrex-covered magnetic stirring bar.

1. Place 4-ml. of cyclohexane phase in a 10-ml. glass-stoppered centrifuge tube and centrifuge.
2. Transfer 1-ml. aliquots to each of three 10-ml. glass-stoppered centrifuge tubes.

Figure B.4. Procedure used to investigate the chemical nature of the iodine in the cyclohexane phase after extraction for at least 24 hours with an aqueous solution. All operations were carried out in the absence of light.

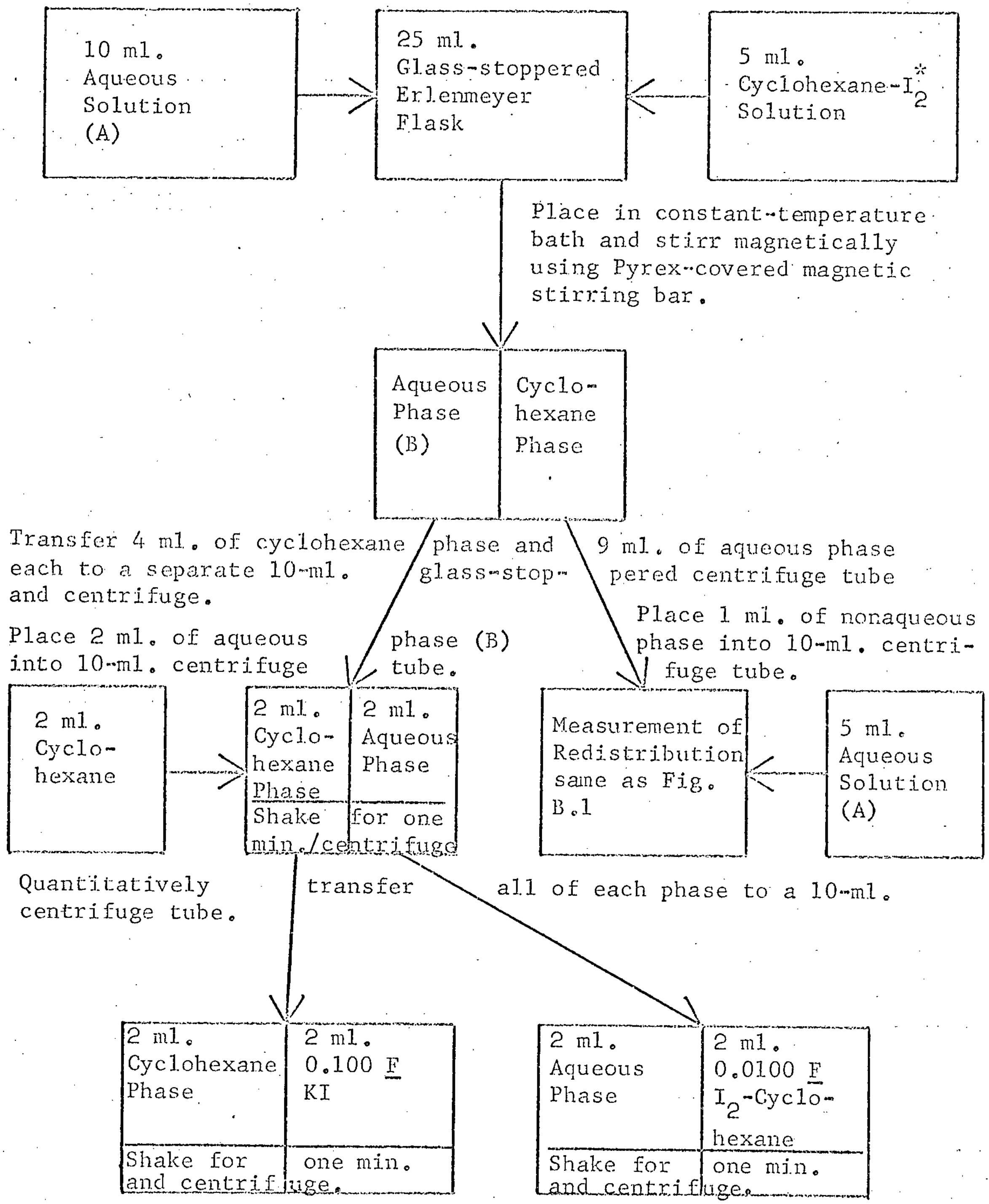


Figure B.5. Procedure used to investigate the chemical nature of the iodine in the acidic aqueous phase after extraction for at least 24 hours with a cyclohexane solution of iodine. All operations were carried out in the absence of light.

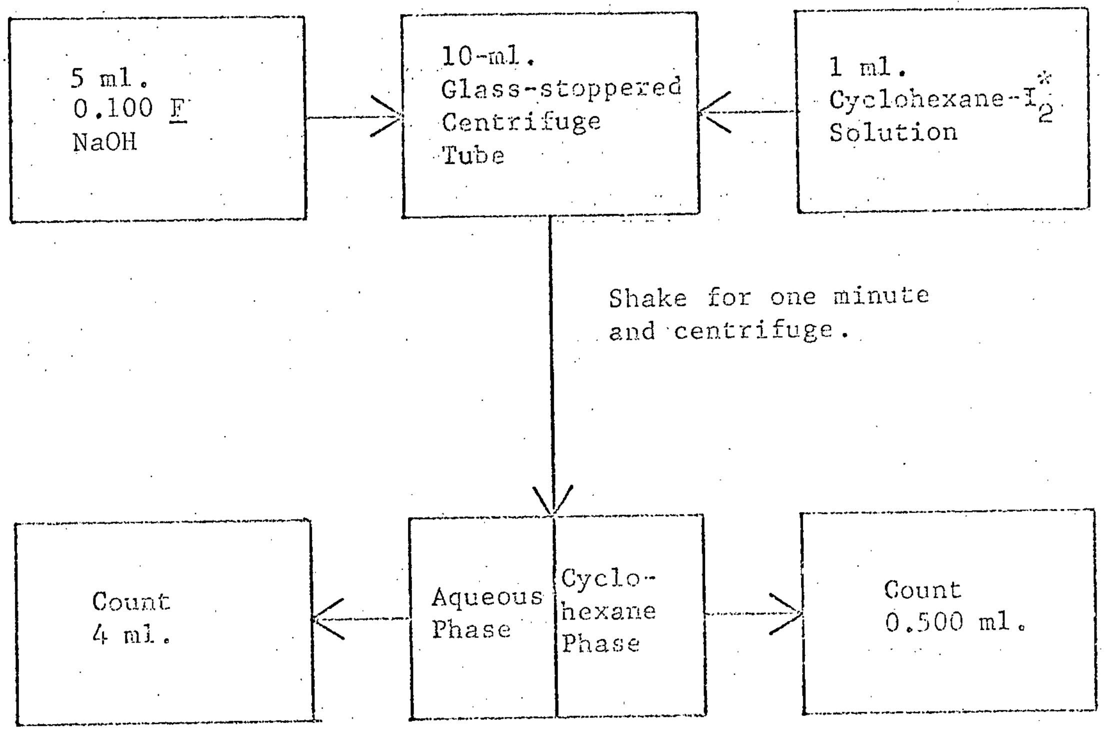


Figure B.6 This procedure was used to investigate the chemical nature of the iodine in freshly prepared cyclohexane-I_2^* solutions with cyclohexane obtained from various sources. This procedure was carried out in the absence of light.

B.III. RESULTS

The results of the investigation of the distribution coefficient, D, for iodine, where

$$D = \frac{\text{concentration of I-131 atoms in cyclohexane}}{\text{concentration of I-131 atoms in aqueous phase}},$$

are summarized in Tables B.1 through B.33

B.III.a. The Distribution of Iodine Between Cyclohexane and Aqueous 0.100 F Perchloric Acid

The results of studies of the distribution coefficient for iodine between dilute cyclohexane-iodine solutions and aqueous perchloric acid are summarized in Tables B.1 through B.7.

B.III.a.1. The Effect of the Age of the Cyclohexane-Iodine Solutions on D

The results of studies of the dependence of the distribution coefficient on the age of the cyclohexane-iodine solutions are summarized in Tables B.1 through B.4. The cyclohexane-iodine solutions were aged in volumetric flasks suspended in a constant-temperature bath; one-milliliter aliquots were removed at various times and subjected to the procedure outlined in Figure B.1. Tables B.1 and B.2 indicate that for 1.00×10^{-3} F iodine in cyclohexane the distribution coefficient is independent of the age of the cyclohexane-iodine solution, over one week, and whether the cyclohexane-iodine solution was aged in the dark or in the presence of ordinary laboratory fluorescent light. In more dilute cyclohexane-iodine solutions, namely 1.00×10^{-4} F and 1.00×10^{-5} F in iodine, there is a small decrease in the distribution coefficient for cyclohexane-iodine solutions aged in the presence or absence of light

Table B.1

The Dependence of D on the Age of Cyclohexane-Iodine Solutions Aged, at 28.0°, in the Presence or Absence of Light: the Aqueous Phase was 0.100 F Perchloric Acid.[a,b,c,d,e]

Age of Cyclohexane-I_2 solution, hours	Distribution coefficient, D	
	Light present	Light absent
0	64	62
16	61	61
40	63	63
44	57	59
69	60	62
112	63	61
136	60	61
160	58	60
185	62	61

[a] The procedure used is outlined in Fig. B.1; the cyclohexane-I_2 solution was aged in the presence (or absence) of light, as noted.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 1 (see p. 81).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-2} F.

[e] In all instances the recovery of activity was essentially quantitative.

Table B.2

The Dependence of D on the Age of Cyclohexane-Iodine Solutions Aged, at 28.0°, in the Presence or Absence of Light: the Aqueous Phase was 0.100 F Perchloric Acid.[a,b,c,d,e]

Age of cyclohexane-I_2 solution, hours	Distribution coefficient, D	
	Light present	Light absent
0	62	64
16	62	62
40	58	59
44	52	49
69	58	58
112	60	59
136	59	59
160	59	60
185	64	66

[a] The procedure used is outlined in Fig. B.1; the cyclohexane-I_2 solution was aged in the presence (or absence) of light, as noted.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 1 (see p. 81).

[d] The initial concentration if I_2 in cyclohexane was 1.00×10^{-3} F.

[e] In all instances the recovery of activity was essentially quantitative.

Table B.3

The Dependence of D on the Age of Cyclohexane-Iodine Solution Aged, at 28.0°, in the Presence or Absence of Light: the Aqueous Phase was 0.100 F Perchloric Acid.[a,b,c,d,e]

Age of cyclohexane-I_2 solution, hours	Distribution coefficient, D	
	Light present	Light absent
0	49	51
25	49	49
45	49	45
73	47	49
121	48	48
164	45	44
171	42	45

[a] The procedure used is outlined in Fig. B.1; the cyclohexane-I_2 solution was aged in the presence (or absence) of light, as noted.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 1 (see p. 81).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-4} F.

[e] In all instances the recovery of activity was essentially quantitative.

Table B.4

The Dependence of D on the Age of Cyclohexane-Iodine Solution Aged, at 28.0°, in the Presence or Absence of Light: the Aqueous Phase was 0.100 F Perchloric Acid.[a,b,c,d,e]

Age of cyclohexane-I_2 solution, hours	Distribution coefficient, D Light present	 Light absent
0	31	31
25	30	29
45	32	29
73	23	19
121	15	15
164	23	22
171	21	22

[a] The procedure used is outlined in Fig. B.1; the cyclohexane-I_2 solution was aged in the presence (or absence) of light, as noted.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 1 (see p. 81).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-5} F.

[e] In all instances the recovery of activity was essentially quantitative.

over one week (see Tables B.3 and B.4).

B.III.a.2. The Dependence of D on the Time of Mixing the Two Phases

The results of the studies of the dependence of the distribution coefficient on the mixing time between the two phases in the system are summarized in Tables B.5 and B.6. The distribution coefficient decreased with time for both the 1.00 x 10^{-3} F and 1.00 x 10^{-4} F iodine solutions, with the largest decrease occurring during the first 22.5 hours. The decrease of the distribution coefficient with time for the 1.00 x 10^{-3} F and 1.00 x 10^{-4} F iodine, as is demonstrated by comparing Table B.2 with Table B.5 and Table B.3 with Table B.6, is not caused by the method of activation nor aging effects in the cyclohexane-iodine system alone, but rather is due to some factor introduced by the aqueous phase.

B.III.a.3. The Dependence of D on the Method of Activation of the Cyclohexane-Iodine Solutions

The distribution coefficient for iodine between cyclohexane and aqueous 0.100 F perchloric acid was also dependent on the method of activation of the dilute cyclohexane-iodine solution when Methods 1, 2 and 3 were used (see Table B.7).

Table B.5

The Dependence of D on the Time of Mixing of the Two Phases, at 28.0°: the Aqueous Phase was 0.100 F Perchloric Acid.[a,b,c,d,e]

Reaction time, hours	Distribution coefficient, D[f]
0	44 , 45
22.4	20 , 19
46.5	22 , 22
70.5	29 , 28
90	25 , 26
115	20 , 19

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 1 (see p. 81).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-3} F.

[e] In all instances the recovery of activity was essentially quantitative.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.6

The Dependence of D on the Time of Mixing of the Two Phases, at 28.0°: the Aqueous Phase was 0.100 F Perchloric Acid.[a,b,c,d,e]

Reaction time, hours	Distribution coefficient, D[f]
0	28 , 30
22.5	11 , 11
46.5	4.6, 4.7
70.5	2.4, 2.4
90	2.3, 2.3
115	7.6, 7.6

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 1 (see p.81).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-4} F.

[e] In all instances the recovery of activity was essentially quantitative.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.7

The Dependence of D on the Method of Activating the Reaction Mixture at 28.0°: the Aqueous Phase was 0.100 F Perchloric Acid.[a,b,c]

Initial $[I_2]$ in cyclohexane, F	Method of activation	Distribution coefficient[d]
1.00×10^{-3}	Method 1	64
1.00×10^{-4}	Method 1	51
1.00×10^{-5}	Method 1	31
1.00×10^{-3}	Method 2	15, 18
1.00×10^{-4}	Method 2	8.3, 11
1.00×10^{-3}	Method 3	42
1.00×10^{-4}	Method 3	24
1.00×10^{-5}	Method 3	5.3

[a] The procedure used is outlined in Fig. B.1; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] In all instances the recovery of activity was essentially quantitative.

[d] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

B.III.b. The Distribution of Iodine Between Cyclohexane and Sulfuric Acid and Potassium Sulfate - Sulfuric Acid Mixtures

The results summarized in Tables B.8 through B.33 were obtained with cyclohexane solutions which had been activated by Method 4. This method was found to be of significant value in that:

1. It allowed the preparation of dry, active cyclohexane solutions of iodine.
2. The iodine-131 in the active cyclohexane-iodine solutions behaved as molecular iodine.
3. The activation procedure did not change the concentration of the molecular iodine in the cyclohexane where the initial concentration of iodine in cyclohexane ranged from 10^{-2} to 10^{-7} F.
4. The distribution coefficient was not dependent on the age of the dilute, dry, active cyclohexane-iodine solution over a period of 2 weeks (see Table B.8).

B.III.b.1. The Dependence of D on the Ionic Strength of the Aqueous Phase

A brief study of the effect of ionic strength, u, upon the distribution of iodine was undertaken and the results are summarized in Table B.9. Although the results are not conclusive, the distribution coefficient appears to be dependent on the ionic strength of the aqueous phase. For this reason, all future work was performed at constant ionic strength; the arbitrarily chosen value for $u = 1.00 \pm 0.01$ was used in compounding the aqueous solutions.

Table B.8

The Dependence of D on the Age of the Active, Dilute Cyclohexane-Iodine Solutions.[a,b,c,d]

Age of cyclohexane-iodine solutions, days	Distribution coefficient, D[e] iodine concentration, F	
	1.00×10^{-3}	1.00×10^{-5}
1	68, 67	6.1, 6.2
3	69, 68	--
6	69, 68	--
13	--	6.1, 6.2
15	63, 61	--

[a] The procedure used is outlined in Fig. B.1; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The aqueous phase was 1.00 F sulfuric acid.

[e] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution treated identically.

Table B.9

The Dependence of D on the Ionic Strength of the Aqueous Phase at 24.9°.[a,b,c,d] The Initial Concentration of Iodine in Cyclohexane was 1.00×10^{-3} F.

Composition of aqueous phase	Distribution coefficient, D
1.00×10^{-4} F H_2SO_4	57
pH = 3.7[e]	59
$u = 2.5 \times 10^{-4}$	
0.340 F K_2SO_4	83
brought to a pH = 3.4[e]	82
with H_2SO_4	
u = 1.7	

[a] The procedure used is outlined in Fig. B.3; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] In all instances the recovery of activity was essentially quantitative.

[e] The pH was measured with a Beckman Model C pH meter.

B.III.b.2. The Dependence of D on the Time of Mixing of the Two Phases

The results of studies of the dependence of the distribution coefficient on the time of mixing the cyclohexane-iodine and aqueous 1.00 F sulfuric acid phases are summarized in Tables B.10, B.11, B.15, B.16, B.17, B.18, B.19, B.20 and B.21 and Figures B.7, B.9, B.10, B.11 and B.12. The dependence of the distribution coefficient on the time of mixing the cyclohexane-iodine and 0.340 F potassium sulfate, brought to a pH of 2.7 with sulfuric acid, is summarized in Tables B.13, B.14 and B.15 and Figure B.8. These results demonstrate that for all the cyclohexanes used the distribution coefficient decreases with decreasing iodine concentration and increasing duration of the mixing process. The rate of the decrease of the distribution coefficient decreases with increasing duration of the mixing process.

The zero-time distribution coefficients were essentially the same when treated Eastman Spectro Grade or Hinton Primary Standard grade cyclohexanes were used: on the other hand, the zero-time distribution coefficients were considerably less when untreated Eastman Spectro Grade cyclohexane was used.

The decrease of the distribution coefficients with increasing duration of the mixing process was less when using treated Eastman Spectro Grade or Hinton Primary Standard grade cyclohexanes than when untreated Eastman Spectro Grade cyclohexane was used.

The addition of varying amounts of airborne impurities to the aqueous phase did not have any appreciable effect on the distribution coefficients, either for the zero-time or after 4 or 24 hours of mixing of the two phases.

The results summarized in Tables B.10 through B.15 were obtained using untreated Eastman Spectro Grade cyclohexane. The results summarized in Tables B.16 and B.17 were obtained using treated Eastman Spectro Grade cyclohexane. The results summarized in Tables B.18 and B.19 were obtained using Hinton Primary Standard grade cyclohexane. And, the results summarized in Tables B.20 and B.21 were obtained using an aqueous solution containing varying amounts of added airborne impurities and Hinton Primary Standard grade cyclohexane.

In some instances, the percent recovery of iodine-131 was low (see Tables B.10 through B.15). The loss of activity is attributed to volatilization of iodine-131 species. This conclusion is based on the fact that the reaction vessels and stirring bars were monitored for activity which may have been adsorbed on the walls of the vessel and stirring bar; no residual activity was found in the reaction vessel or on the stirring bar. The reaction vessels and stirring bars were monitored for iodine-131 by placing them on the NaI crystal of a scintillation detector; the sensitivity of this procedure for iodine-131 adsorbed anywhere on the reaction vessel or stirring bar was such that 0.1 percent of the activity initially present in the reaction vessel could be detected. Also, spot checks were made where the reaction vessel and stirring bar were washed with chromic acid and the chromic acid wash counted to detect any iodine-131 adsorbed by the reaction vessel or stirring bar; no activity was ever found. However, the purity of the cyclohexane was demonstrated to be an important factor in the loss of iodine-131 by volatilization from the reaction mixtures; the reaction mixtures made with the purer cyclohexane lost less activity over 24 hours than those reaction mixtures made with untreated Eastman Spectro Grade cyclohexane (see Tables B.10 through B.19).

3

Table B.10.

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Run	Mixing time, hours	Distribution coefficient, D[f]	Recovery of activity,%
	0	69, 68	100, 99
	1	50, 56	96, 97
1	6	11, 27	89, 98
	22.8	-- 17	-- 94
	44	-- 14	-- 92[g]
	9.5	29, 30	94, 95
2	23	19, 20	93, 93
	47	17, 17	92[g], 93[g]

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cylohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-3} F.

[e] The aqueous phase was 1.00 F sulfuric acid.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

[g] The reaction vessels and stirring bars were washed with chromic acid in order to detect adsorbed activity; no adsorption was found.

Table B.11

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D[f]	Recovery of activity, %
0	40 , 41	97, 98
0	43 , 45	101, 100
1	19 , 17	96, 95
5	6.9, 6.3	93, 89
18.8	2.7, 2.7	80, 78
24.5	2.5, 2.4	78, 76
47	2.3, 2.2	76, 75
116.8	2.4, 2.2	77[g], 74[g]

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00 x 10^{-4} F.

[e] The aqueous phase was 1.00 F sulfuric acid.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

[g] The reaction vessels and stirring bars were washed with chromic acid in order to detect adsorbed activity; no adsorption was found.

Table B.12

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D[f]	Recovery of activity, %
0	6.1, 6.2	100, 100
1	5.6, 2.3	93, 93
9.5	2.5, 2.5	76, 76
23	1.4, 1.6	76, 74
47	1.7, 1.7	74[g], 72[g]

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-5} F.

[e] The aqueous phase was 1.00 F sulfuric acid.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

[g] The reaction vessels and stirring bars were washed with chromic acid in order to detect adsorbed activity; no adsorption was found.

Table B.13

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D[f]	Recovery of activity, %
0	76, 78	100, 100
1	--, 84	--, 96
9.5	65, 57	97, 95
23	54, 51	97, 98
47	48, 47	95, 99

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cylohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-3} F.

[e] The aqueous phase was 0.340 F potassium sulfate at a pH of 2.7.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.14

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing Time, hours	Distribution coefficient, D[f]	Recovery of activity, %
0	63, 66	95, 98
1	47, 47	98, 97
6	27, 28	96, 96
22.8	17, 16	94, 93
44	13, 12	93, 92
67	11, 8.3	91, 89

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-4} F.

[e] The aqueous phase was 0.340 F potassium sulfate at a pH of 2.7.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.15

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D[f]	Recovery of activity, %
0	30, 24	97, 99
1	43, 46	97, 97
9.5	9.6, 10	88, 90
23	1.8, 2.7	65, 75
47	0.6, 1.1	47[g], 63[g]

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was untreated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-5} F.

[e] The aqueous phase was 0.340 F potassium sulfate at a pH of 2.7.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

[g] The reaction vessels and stirring bars were washed with chromic acid in order to detect adsorbed activity; no adsorption was found.

Table B.16

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D	Recovery of activity, %
0	78	102
4	61	100
24	51	98

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was treated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-3} $\underline{F}$.

[e] The aqueous phase was 1.00 $\underline{F}$ sulfuric acid.

Table B.17

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D	Recovery of activity, %
0	48	99
4	16	100
24	5.5	96

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was treated Eastman Spectro Grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-5} <u>F</u>.

[e] The aqueous phase was 1.00 <u>F</u> sulfuric acid.

Table B.18

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D[f]	Recovery of activity, %
0	81, 78	99, 99
4	70, 65	100, 100
24	57, 60	104, 102

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was Hinton Primary Standard grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-3} F.

[e] The aqueous phase was 1.00 F sulfuric acid.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.19

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e]

Mixing time, hours	Distribution coefficient, D[f]	Recovery of activity, %
0	39 , 40	100, 99
4	8.4, 6.8	98, 99
24	3.5, 3.3	90, 92
24.25[g]	1.7	83
25.5[h]	0.28	61

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was Hinton Primary Standard grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00 x 10^{-5} F.

[e] The aqueous phase was 1.00 F sulfuric acid.

[f] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

[g] The reaction mixture was exposed to ordinary laboratory light for 15 minutes after 24 hours reaction time in the dark.

[h] The reaction mixture was exposed to ordinary laboratory light for 1.5 hours after 24 hours reaction time in the dark.

Table B.20

The Dependence of D on the Amount of Airborne Impurities in the Aqueous Phase at 24.9°.[a,b,c]

The Aqueous Phase was 1.00 F Sulfuric Acid.

Initial $[I_2]$ in cyclohexane, F	Amount of airborne impurities present[d]	Distribution coefficient, D	Recovery of activity, %
1.00×10^{-3}	I	75	100
	II	78	99
	III	78	100
	IV	80	100
	V	79	101
1.00×10^{-5}	I	41	99
	II	45	100
	III	47	99
	IV	46	99
	V	36	99

[a] The procedure used is outlined in Fig. B.1; light was excluded.

[b] The cyclohexane used was Hinton Primary Standard grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

Table B.20 (cont.)

[d] The experiments differed as follows:

I. Unfiltered air was drawn through water for one hour prior to using the water in making the 1.00 F sulfuric acid.

II. Unfiltered air was drawn through water for 2 hours prior to using the water in making the 1.00 F sulfuric acid.

III. Unfiltered air was drawn through water for 4 hours prior to using the water in making the 1.00 F sulfuric acid.

IV. Unfiltered air was drawn through water for 8 hours prior to using the water in making the 1.00 F sulfuric acid.

V. Unfiltered air was drawn through water for 24 hours prior to using the water in making the 1.00 F sulfuric acid.

Table B.21

The Dependence of D on the Time of Mixing at 24.9°.[a,b,c,d,e,f]

Reaction time, hours	Distribution coefficient, D	Recovery of activity, %
0	76	99
4	59	100
24	49	104

[a] The procedure used is outlined in Fig. B.2; light was excluded.

[b] The cyclohexane used was Hinton Primary Standard grade.

[c] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[d] The initial concentration of I_2 in cyclohexane was 1.00×10^{-3} F.

[e] The aqueous phase was 1.00 F sulfuric acid.

[f] Unfiltered air was drawn through water for 24 hours prior to using the water in making the 1.00 F sulfuric acid.

B.III.b.3. The Disposition and Characterization of the Iodine-131 in the Cyclohexane and Aqueous Phases of the Two-Phase Reaction Mixtures

The aqueous and cyclohexane phases of the two-phase reaction mixture were subjected to extraction procedures (see p. 84) in order to characterize the disposition of iodine-131 in each phase. The reaction mixtures were similar in composition to those used to study the dependence of the distribution coefficient on the mixing time (see p. 83). Three one-ml. aliquots of the cyclohexane phase were subjected to extraction with aqueous 0.1 F sodium iodide, aqueous acidic 0.1 F sodium sulfite and aqueous 0.1 F sodium hydroxide (see Tables B.23 through B.27): each one-ml. aliquot was subjected to one of the foregoing extractions. These extractions yielded the percentage of iodine-131 in the cyclohexane phase which isotopically exchanged with, or was reduced by, aqueous iodide, was reduced by aqueous acidic sulfite and extracted into aqueous hydroxide.

One two-ml. aliquot of the aqueous phase was extracted first with cyclohexane and secondly with 0.01 F iodine in cyclohexane; the cyclohexane, from the first extraction, was then extracted with 0.1 F sodium iodide (see Tables B.28, B.29 and B.30). These extractions yielded the percentage of iodine-131 in the aqueous phase which was soluble in cyclohexane and isotopically exchanged with aqueous iodide, soluble in cyclohexane but did not isotopically exchange with aqueous iodide, not soluble in cyclohexane but isotopically exchanged with iodine in cyclohexane, and neither soluble in cyclohexane nor isotopically exchangeable with iodine in cyclohexane.

Table B.22

Iodine-131 Species Present in Freshly Prepared Active Cyclohexane-Iodine Solutions at 24.9°.[a,b]

Brand of cyclohexane	Initial $[I_2]$ in cyclohexane, F	Activity extracted into 0.1 F NaOH %[c,d]
Untreated Eastman	1.00×10^{-3}	98
Spectro Grade	1.00×10^{-5}	84
Phillips	1.00×10^{-3}	91
Research Grade	1.00×10^{-5}	68
Hinton	1.00×10^{-3}	100
Primary Standard	1.00×10^{-5}	99

[a] The procedure used is outlined in Fig. B.6; light was excluded.

[b] The cyclohexane-I_2 solutions were prepared by

1) Dissolution of the crystalline I_2 in cyclohexane over 12 hours to prepare the 1.00×10^{-2} F stock cyclohexane-I_2 solution.
2) Dilution of the stock cyclohexane-I_2 solution.
3) Activation of the dilute cyclohexane-I_2 solution over 8 hours via Method 4 (see p. 82).

Table B.23

Iodine-131 Species Present in the Cyclohexane Phase after One-Minute Contact Time with 1.00 F Sulfuric Acid at 24.9°.[a,b]

Iodine-131 species in untreated Eastman Spectro Grade cyclohexane	Activity, % [c,d] Initial $[I_2]$ in cyclohexane, F 1.00×10^{-3}	1.00×10^{-5}
Extracted into 0.1 F NaI	100	99
Extracted into acidic 0.1 F Na_2SO_3	100	99
Extracted into 0.1 F NaOH	98	95

[a] The procedure used is outlined in Fig. B.3; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

[d] Percent of activity in the cyclohexane phase after the one-minute contact time.

Table B.24

Iodine-131 Species Present in the Cyclohexane Phase after One-Minute Contact Time with 0.340 F Potassium Sulfate at a pH of 2.7 at 24.9°. [a,b]

Iodine-131 species in untreated Eastman Spectro Grade cyclohexane	Activity, % [c,d] Initial $[I_2]$ in cyclohexane, F 1.00×10^{-3}	 1.00×10^{-5}
Extracted into 0.1 F NaI	99.7	99.0
Extracted into acidic 0.1 F Na_2SO_3	99.7	99.0
Extracted into 0.1 F NaOH	97.0	97.0

[a] The procedure used is outlined in Fig. B.3; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

[d] Percent of activity in the cyclohexane phase after the one-minute contact time.

Table B.25

Iodine-131 Species Present in the Cyclohexane Phase after Thirty-eight Hours Contact Time with 1.00 F Sulfuric Acid at 24.9°.[a,b]

Iodine-131 species in untreated Eastman Spectro Grade cyclohexane	Activity, % [c,d,e] Initial $[I_2]$ in cyclohexane, F 1.00×10^{-3}	1.00×10^{-5}
Extracted into	96	38
0.1 F NaI	96	40
Extracted into acidic	97	67
0.1 F Na_2SO_3	97	67
Extracted into	98	98
0.1 F NaOH	98	98

---

[a] The procedure used is outlined in Fig. B.4; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantiative.

[d] Percent of activity in the cyclohexane phase after the 38-hours contact time.

[e] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.26

Iodine-131 Species Present in the Cyclohexane Phase after Thirty-eight Hours Contact Time with 0.340 F Potassium Sulfate at a pH of 2.7 at 24.9°.[a,b]

Iodine-131 species in untreated Eastman Spectro Grade cyclohexane	Activity, %[c,d,e] Initial $[I_2]$ in cyclohexane, F 1.00×10^{-3}	1.00×10^{-5}
Extracted into	99.4	74
0.1 F NaI	100	80
Extracted into	100	87
acidic 0.1 F Na_2SO_3	100	95
Extracted into	96	94
0.1 F NaOH	95	91

[a] The procedure used is outlined in Fig. B.4; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

[d] Percent of activity in the cyclohexane phase after the 38-hours contact time.

[e] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.27

Iodine-131 Species Present in the Cyclohexane Phase after Twenty-four Hours Contact Time with 1.00 F Sulfuric Acid at 24.9°.[a,b]

Iodine-131 Species in Hinton Primary Standard grade cyclohexane	Activity, % [c,d,e] Initial $[I_2]$ in cyclohexane, F	
	1.00×10^{-3}	1.00×10^{-5}
Extracted into 0.1 F NaI	100	95
	100	98
Extracted into acidic 0.1 F Na_2SO_3	100	97
	100	97
Extracted into 0.1 F NaOH	100	97
	99	97

---

[a] The Procedure used is outlined in Fig. B.4; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

[d] Percent of activity in the cyclohexane phase after a 24-hour contact time.

[e] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.28

Iodine-131 Species Present in the 1.00 F Sulfuric Acid after Thirty-four Hours Mixing Time with 1.00×10^{-5} F Iodine in Untreated Eastman Spectro Grade Cyclohexane at 24.9°.[a,b,c]

Iodine-131 species in the sulfuric acid phase	Activity, % [c,d,e]	
	Cyclohexane Phase	Aqueous Phase
Extracted with cyclohexane, back-extracted with 0.1 F NaI	6	22
	6	21
Not extracted with cyclohexane but back-extracted with 10^{-2} F I_2 in cyclohexane	68	4
	69	4

[a] The procedure used is outlined in Fig. B.5; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

[d] Percent of activity in the sulfuric acid after 34-hours mixing time.

[e] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.29

Iodine-131 Species Present in the 0.340 F Potassium Sulfate at a pH of 2.7 after Thirty-four Hours Contact Time with 1.00×10^{-5} Iodine in Untreated Eastman Spectro Grade Cyclohexane at 24.9°.[a,b]

Iodine-131 species in the sulfuric acid phase	Activity, % [c,d,e]	
	Cyclohexane Phase	Aqueous Phase
Extracted with cyclohexane, back-extracted with 0.1 F NaI	4	57
	4	63
Not extracted with cyclohexane but back-extracted with 10^{-2} F I_2 in cyclohexane	32	6
	28	6

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[a] The procedure used is outlined in Fig. B.5; light was excluded.

[b] The cyclohexane-I_2 solutions was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

[d] Percent of activity in the potassium sulfate phase after 34-hours mixing time.

[e] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.30

Iodine-131 Species Present in the 1.00 F Sulfuric Acid after Twenty-four Hours Mixing Time with Iodine in Hinton Primary Standard Grade Cyclohexane at 24.9°.[a,b]

Iodine-131 species in the 1.00 F sulfuric acid phase	Activity, % [c,d,e]			
	Initial $[I_2]$ in cyclohexane, F			
	1.00×10^{-3}		1.00×10^{-5}	
	Cyclohexane phase	Aqueous phase	Cyclohexane phase	Aqueous phase
Extracted with cyclohexane, back-extracted with 0.1 F NaI	7	63	3	4
	1	72	3	4
Not extracted with cyclohexane but back-extracaed with 10^{-2} F I_2 in cyclohexane	27	4	85	8
	27	0	85	7

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[a] The procedure used is outlined in Fig. B.5; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

Table B.30 (contd)

[d] Percent of activity in the sulfuric acid after 24-hours mixing time.

[e] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Untreated Eastman Spectro Grade Cyclohexane The foregoing extraction analysis indicated that:

1. For one-minute mixing time between 1.00×10^{-3} F iodine in untreated Eastman Spectro Grade cyclohexane and 1.00 F sulfuric acid or 0.340 F potassium sulfate, brought to a pH of 2.7 with sulfuric acid, at least 98 percent of the iodine-131 present in the cyclohexane phase behaved as molecular iodine (see Tables B.23 and B.24).
2. For one-minute mixing time between 1.00×10^{-5} F iodine in untreated Eastman Spectro Grade cyclohexane and 1.00 F sulfuric acid or 0.340 F potassium sulfate, brought to a pH of 2.7 with sulfuric acid, approximately 5 percent of the iodine-131 in the cyclohexane phase did not behave as molecular iodine (see Tables B.23 and B.24).
3. For a 38-hour mixing time between 1.00×10^{-3} F iodine in untreated Eastman Spectro Grade cyclohexane and 1.00 F sulfuric acid or 0.340 F potassium sulfate, brought to a pH of 2.7 with sulfuric acid, approximately 4 percent of the iodine-131 in the cyclohexane phase did not behave as molecular iodine (see Tables B.25 and B.26).
4. For a 38-hour mixing time between 1.00×10^{-5} F iodine in untreated Eastman Spectro Grade cyclohexane and 1.00 F sulfuric acid or 0.340 F potassium sulfate, brought to a pH of 2.7 with sulfuric acid;
    a. approximately 60 percent and 25 percent, respectively, of the iodine-131 in the cyclohexane phase did not behave as

molecular iodine towards isotopic exchange with aqueous iodide (see Tables B.25 and B.26),

b. approximately 33 percent and 10 percent, respectively, of the iodine-131 in the cyclohexane phase did not behave as molecular iodine towards reduction with aqueous acidic sulfite (see Tables B.25 and B.26),

c. in both instances, over 90 percent of the iodine-131 in the cyclohexane phase extracted into aqueous hydroxide (see Tables B.25 and B.26),

d. 4 to 6 percent of the iodine-131 in the aqueous phase extracted into cyclohexane but did not back-extract into either cyclohexane or a cyclohexane-iodine solution (see Tables B.28 and B.29).

e. 4 to 6 percent of the iodine-131 in the aqueous phase did not extract into either cyclohexane or a cyclohexane-iodine solution (see Tables B.28 and B.29).

The results for 1.00×10^{-5} F iodine in cyclohexane indicated that at least two chemically distinct forms of iodine-131, other than molecular iodine, were present in the cyclohexane phase after 24 hours or more mixing time with an acidic aqueous phase; one species is reduced by aqueous acidic sulfite and extracts into aqueous hydroxide but does not undergo isotopic exchange with aqueous iodide, and another species is neither reduced by aqueous acidic sulfite or aqueous iodide nor undergoes isotopic exchange with aqueous iodide but is extracted into aqueous hydroxide.

The results for 1.00×10^{-5} F iodine in cyclohexane also indicate that the aqueous phase, after 24 hours or more mixing time with a cyclohexane phase, contained at least two chemically distinct forms of iodine-131 which do not behave as iodide, hypoiodite or iodine. One of these species of iodine-131 was soluble in cyclohexane but did not undergo isotopic exchange with aqueous iodide, and the other species of iodine-131 was insoluble in cyclohexane and did not undergo isotopic exchange with molecular iodine in cyclohexane.

The results of studies with 1.00×10^{-3} F iodine in cyclohexane indicate that a small percentage (less than 4 percent) of the iodine-131 in the cyclohexane phase did not behave as molecular iodine.

Hinton Primary Standard Grade Cyclohexane The experiments just described were repeated using 1.00 F sulfuric acid and very high purity (Hinton Primary Standard grade) cyclohexane (see Tables B.27 and B.30). The extraction analyses gave the following results.

1. For a 24-hour mixing time between 1.00×10^{-3} F iodine in cyclohexane and 1.00 F sulfuric acid;
   a. greater than 99 percent of the iodine-131 in the cyclohexane phase behaved as molecular iodine (see Table B.27),
   b. approximately 70 percent of the iodine-131 in the aqueous phase extracted into cyclohexane but 4 percent did not back-extract into aqueous iodide (see Table B.30) and,
   c. approximately 3 percent of the iodine-131 in the aqueous phase did not extract into a cyclohexane-iodine solution (see Table B.30).
2. For a 24-hour mixing time between 1.00×10^{-5} F iodine in cyclohexane and 1.00 F sulfuric acid;
   a. 95 to 98 percent of the iodine-131 in the cyclohexane phase behaved as molecular iodine (see Table B.27),

b. approximately 7 percent of the iodine-131 in the aqueous phase extracted into cyclohexane but 3 percent did not back-extract into aqueous iodide (see Table B.30), and,

c. approximately 8 percent of the iodine-131 in the aqueous phase did not extract into a cyclohexane-iodine solution (see Table B.30).

These results indicate that for 1.00×10^{-5} F iodine in cyclohexane there is a considerable decrease in the amount of iodine-131 species, which do not behave as molecular iodine, in the cyclohexane phase of the two-phase reaction mixture, when Hinton Primary Standard grade cyclohexane is used, as opposed to the results found when using untreated Eastman Spectro Grade cyclohexane.

B.III.b.4. The Dependence of D on the Purity of the Cyclohexane and Aqueous Solutions

Airborne Impurities. Varying amounts of airborne impurities were added to 1.00 F sulfuric acid to determine whether these impurities are, in part, responsible for either the decrease in the distribution coefficient with decreasing iodine concentration or the decrease in the distribution coefficient with increasing duration of the mixing process. The results of these studies are summarized in Tables B.21 and B.22. These results indicate that there is no apparent correlation between the amount of airborne impurities present in the aqueous phase and either the initial distribution coefficient (see Tables B.19, B.20 and B.21) or the decrease of the distribution coefficient with time (see Tables B.19, B.20 and B.21).

Redistribution Studies Previous studies reported here have indicated that much of the observed anomolous behavior of the distribution coefficient for iodine may be attributed to impurities in the cyclohexane which react with iodine in the presence of an acidic aqueous phase. Studies of the dependence of the distribution coefficient on the time of mixing of the two phases indicated that the reaction, or reactions, between iodine and the impurities go to completion within 24 hours (i.e., the distribution coefficient is essentially a constant for mixing times of 24 hours or more). If these reactions free the cyclohexane-iodine solution from impurities then a constant distribution coefficient should result when this "purified" cyclohexane-iodine solution and a fresh acidic aqueous solution are mixed.

Several experiments were performed where the distribution coefficient for iodine, which had been in contact with an acidic aqueous phase for 24 hours or more, was remeasured using a fresh portion of the same aqueous solution. The results of this investigation are summarized below.

1. For 1.00×10^{-3} $\underline{F}$ iodine in untreated Eastman Spectro Grade cyclohexane and 1.00 $\underline{F}$ sulfuric acid;
    a. the distribution coefficient was 70 after a one-minute mixing time,
    b. the distribution coefficient was 15 after 34-hours mixing time, and,
    c. the distribution coefficient was 62, using fresh 1.00 $\underline{F}$ sulfuric acid and the cyclohexane-iodine solution which had been mixed with 1.00 $\underline{F}$ sulfuric acid for 34 hours

(see 1-b), after a one-minute mixing time.

2. For 1.00×10^{-3} F iodine in untreated Eastman Spectro Grade cyclohexane and 0.340 F potassium sulfate, brought to a pH of 2.7 with sulfuric acid;
    a. the distribution coefficient was 77 after a one-minute mixing time,
    b. the distribution coefficient was 51 after 34-hours mixing time, and,
    c. the distribution coefficient was 73, using fresh 0.340 F potassium sulfate at a pH of 2.7 and the cyclohexane-iodine solution which had been mixed with 0.340 F potassium sulfate at a pH of 2.7 for 34 hours (see 2.b), after a one-minute mixing time.
3. For 1.00×10^{-3} F iodine in Eastman Spectro Grade cyclohexane, which had been treated by refluxing with 20 F potassium hydroxide for 3 days and, then, distilling (off of the potassium hydroxide solution), and 1.00 F sulfuric acid;
    a. the distribution coefficient was 74 after a one-minute mixing time,
    b. the distribution coefficient was 25 after 24-hours mixing time,
    c. the distribution coefficient was 59, using fresh 1.00 F sulfuric acid and the cyclohexane-iodine solution which had been mixed for 24 hours with 1.00 F sulfuric acid (see 3-b), after a one-minute mixing time, and,
    d. the distribution coefficient was 41, using fresh 1.00 F

sulfuric acid and the cyclohexane-iodine solution which had been mixed for 24 hours with 1.00 F sulfuric acid (see 3-b and 3-c), after 24-hours mixing time.

4. For 1.00 x 10^{-5} F iodine in Eastman Spectro Grade cyclohexane, which had been treated by refluxing with 20 F potassium hydroxide for 3 days and, then, distilling (off of the potassium hydroxide solution), and 1.00 F sulfuric acid;
   a. the distribution coefficient was 28 after a one-minute mixing time,
   b. the distribution coefficient was 1.1 after 24-hours mixing time,
   c. the distribution coefficient was 18, using fresh 1.00 F sulfuric acid and the cyclohexane-iodine solution which had been mixed for 24 hours with 1.00 F sulfuric acid (see 4-b), after a one-minute mixing time, and,
   d. the distribution coefficient was 4.8, using fresh 1.00 F sulfuric acid and the cyclohexane-iodine solution which had been mixed for 24 hours with 1.00 F sulfuric acid (see 4-b and 4-c), after 24-hours mixing time.

These results indicate that although the remeasured distribution coefficient decreased over a 24-hour mixing time (see 3-c, 3-d, 4-c and 4-d), the decrease is less than that found over the initial 24-hour mixing time (see 3-a, 3-b, 4-a and 4-b).

Stability of Cyclohexane-Iodine Solutions In order to determine the stability of dilute solutions of molecular iodine in cyclohexane the following experiments were performed. Cyclohexane-iodine solutions,

1.00×10^{-3} F and 1.00×10^{-5} F in iodine, inoculated with iodine-131, were prepared using untreated Eastman Spectro Grade cyclohexane, Phillips Research Grade cyclohexane and Hinton Primary Standard grade cyclohexane. These solutions were extracted with aqueous 0.1 F sodium hydroxide. The activity remaining in the cyclohexane phase after the extraction was considered a measure of the impurity level of the cyclohexane. For 1.00×10^{-3} F and 1.00×10^{-5} F iodine in untreated Eastman Spectro Grade cyclohexane, 1.6 and 16 percent of the iodine-131, respectively, did not extract into the aqueous hydroxide; for 1.00×10^{-3} F and 1.00×10^{-5} F iodine in Phillips Research Grade cyclohexane, 9.0 and 31.7 percent of the iodine-131, respectively, did not extract into the aqueous hydroxide; for 1.00×10^{-3} F and 1.00×10^{-5} F iodine in Hinton Primary Standard grade cyclohexane , 0.2 and 1.1 percent of the iodine-131, respectively, did not extract into the aqueous hydroxide. In each instance, the cyclohexane-iodine solutions were 48 hours old; 24 hours was required to prepare the 1.00×10^{-2} F stock cyclohexane-iodine solution and 24 hours was required to inoculate the dilute cyclohexane-iodine solutions with iodine-131 using Method 4. The dilute, active, cyclohexane-iodine solutions were stored in the dark in a constant-temperature bath at 24.9°. These results reaffirm the previously given results (see Tables B.23, B.24, B.25, B.26 and B.27) which indicate the presence of impurities in the cyclohexane which react with molecular iodine.

Effect of Oxygen, Ozone and Hydrogen Peroxide on D The results of studies of the effect of oxygen, ozone and hydrogen peroxide on the distribution coefficient for iodine between Hinton Primary Standard grade

Table B.31

The Dependence of D on the Presence of Oxygen, Ozone and Hydrogen Peroxide in the 1.00 F Sulfuric Acid Phase at 24.9°.[a] The Initial Concentration of Iodine in the Hinton Primary Standard Grade Cyclohexane was 1.00×10^{-3} F.[b]

Composition of the aqueous phase	Mixing time, hours	Distribution coefficient, D[c,d]
1.00 F H_2SO_4	0	76 , 78
+ Nitrogen[e]	4	60 , 58
	24	43 , --
1.00 F H_2SO_4	0	71 , 75
+ Oxygen[f]	4	28 , 60
	24	15 , 23
1.00 F H_2SO_4	0	68 , 78
+1.00×10^{-3} F H_2O_2	4	58 , 61
	24	48 , 49
1.00 F H_2SO_4	0	7.4, 9.0
+ Ozone[g]		

---

[a] The procedures used are outlined in Fig. B.1 and B.2; light was excluded.

[b] The cylohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

Table B.31 (cont.)

[d] In all instances the recovery of activity was essentially quantitative.

[e] Nitrogen gas was passed through the 1.00 F H_2SO_4 for one hour.

[f] Oxygen gas was passed through the 1.00 F H_2SO_4 for one hour.

[g] A mixture of ozone and oxygen gas was passed through the 1.00 F H_2SO_4 for one hour.

Table B.32

The Dependence of D on the Presence of Oxygen, Ozone and Hydrogen Peroxide in the 1.00 F Sulfuric Acid Phase at 24.9°.[a] The Initial Concentration of Iodine in the Hinton Primary Standard Grade Cyclohexane was 1.00×10^{-5} F.[b]

Composition of the aqueous phase	Mixing time, hours	Distribution coefficient, D[c,d]
1.00 F H_2SO_4 + Nitrogen[e]	0	23 , 24
	4	8.4, 5.5
	24	4.4, 2.7
1.00 F H_2SO_4 + Oxygen[f]	0	8.7, 28
	4	3.8, 25
	24	1.8, 13
1.00 F H_2SO_4 + 1.00×10^{-3} F H_2O_2	0	58 , 58
	4	8.6, 7.3
	24	3.4, 3.5
1.00 F H_2SO_4 + Ozone[g]	0	2.3, 2.5

[a] The procedures used are outlined in Fig. B.1 and B.2; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

Table B.32 (cont.)

[d] Two reaction mixtures were prepared from the same cyclohexane-I_2 solution and treated identically.

[e] Nitrogen gas was passed through the 1.00 F H_2SO_4 for one hour.

[f] Oxygen gas was passed through the 1.00 F H_2SO_4 for one hour.

[g] A mixture of ozone and oxygen gas was passed through the 1.00 F H_2SO_4 for one hour.

cyclohexane and aqueous solutions 1.00 F in sulfuric acid are summarized in Tables B.31 and B.32. These results indicate that there is no apparent effect attributable to the presence of oxygen or hydrogen peroxide; the presence of ozone greatly decreased the distribution coefficient, presumably through the formation of iodate, and visibly reduced the color intensity of the cyclohexane phase of the reaction mixture. When the aqueous phase of the reaction mixture containing ozone was shaken with 10^{-2} F iodine in cyclohexane none of the activity extracted into the cyclohexane. It is noteworthy, however, that the values for the distribution coefficient in the presence of oxygen or nitrogen are lower than those found previously (see Tables B.18 and B.19). This lowering of the distribution coefficient may be attributed to an impurity in the gas stream which either passed through or came from the concentrated sulfuric acid bubbler which was placed between the gas tank and the aqueous 1.00 F sulfuric acid which was being treated with the gas. Subsequent distribution experiments using a 1.00 F sulfuric acid aqueous phase made from concentrated sulfuric acid, through which nitrogen, taken directly from the tank, was passed for 24 hours, and a cyclohexane-iodine solution using Hinton Primary Standard grade cyclohexane, however, yielded values for the distribution coefficient similar to those found in Tables B.18 and B.19.

Impurities in Cyclohexane   Previously given results, see Tables B.10 through B.31, have shown that the zero-time distribution coefficient for iodine is lower when untreated Eastman Spectro Grade cyclohexane is used than when treated Eastman Spectro Grade or Hinton Primary Standard grade cyclohexanes are used. It was of interest,

Table B.33

The Dependence of D on the Presence of Trace Organic Impurities in the Cyclohexane-Iodine Solutions at 24.9°.[a,b] The Aqueous Phase was 1.00 F Sulfuric Acid.

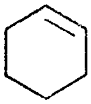
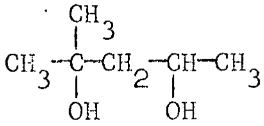
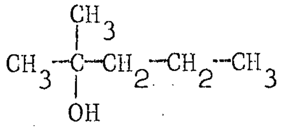
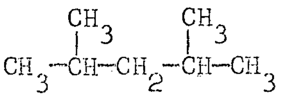
Composition of cyclohexane phase	Initial $[I_2]$, F	Distribution coefficient, D^c
Hinton cyclohexane	1.00×10^{-3}	70
	1.00×10^{-5}	60
Hinton cyclohexane + 1% cyclohexene 	1.00×10^{-3}	50
	1.00×10^{-5}	21
Hinton cyclohexane + 1% 2-methyl-2,4-pentanediol  $CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2-\underset{OH}{CH}-CH_3$	1.00×10^{-3}	73
	1.00×10^{-5}	54
Hinton cyclohexane + 1% 2-methyl-2-pentanol  $CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2-CH_2-CH_3$	1.00×10^{-3}	37
	1.00×10^{-5}	14

Table B.33 (cont.)

Composition of cyclohexane phase	Initial $[I_2]$, F	Distribution coefficient, D^c
Hinton cyclohexane + 1% 2,4-dimethylpentane  $CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_3$	1.00×10^{-3}	73
	1.00×10^{-5}	41

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[a] The procedure used is outlined in Fig. B.1; light was excluded.

[b] The cyclohexane-I_2 solution was activated by Method 4 (see p. 82).

[c] In all instances the recovery of activity was essentially quantitative.

[d] This value for D was atypical; the usual value for D was 80.

therefore, to speculate as to the possible impurities present in the untreated Eastman Spectro Grade cyclohexane which could cause the zero-time distribution coefficient to be lower than the values found when using the purer cyclohexanes. Four "impurities" were chosen for investigation: cyclohexene, 2-methyl-2-pentanol, 2-methyl-2,4-penanediol and 2,4-dimethylpentane. 0.01 ml. of the "impurity" was added to one ml. of the cyclohexane-iodine phase of the reaction mixture; the aqueous phase was 1.00 F sulfuric acid and the initial iodine concentration in the Hinton Primary Standard grade cyclohexane was either 1.00×10^{-3} F or 1.00×10^{-5} F. The results, summarized in Table B.33, indicate that the unsaturated compound (cyclohexene) and the tertiary alcohol (2-methyl-2-pentanol) reduced the measured distribution coefficient; the diol (2-methyl-2,4-pentanediol) and the alkane (2,4-dimethylpentane) did not affect it.

B.III.b.5. The Dependence of D on Light and Radiation

Effect of Light It is well-known that light can have a significant effect upon the chemistry of iodine. For this reason all operatings, except where specifically noted otherwise, were carried out in the dark. A spot-check was made to determine the effect, if any, of ordinary laboratory fluorescent light on the two-phase reaction mixture. A reaction mixture comprised of 1.00×10^{-5} F iodine in Hinton Primary Standard grade cyclohexane and 1.00 F sulfuric acid was stirred, in the dark, for 24 hours to determine the dependence of the distribution coefficient on the time of mixing. At the completion of the 24-hour mixing time one-ml. aliquots were removed from each phase and counted. The reaction vessel and its contents was then allowed to stand in the light and without being stirred. After 0.25 and 1.5 hours had elapsed one-ml. aliquots were removed from each phase and counted. The results, given in the last two entries of Table B.19 indicate that light significantly decreased the distribution coefficient.

Effect of Radiation It is noteworthy that, although the amount of iodine-131 used in the experiments varied over the range of from 0.025 to 0.5 microcuries per milliliter of cyclohexane-iodine solution, no effect attributable to the radiation could be detected.

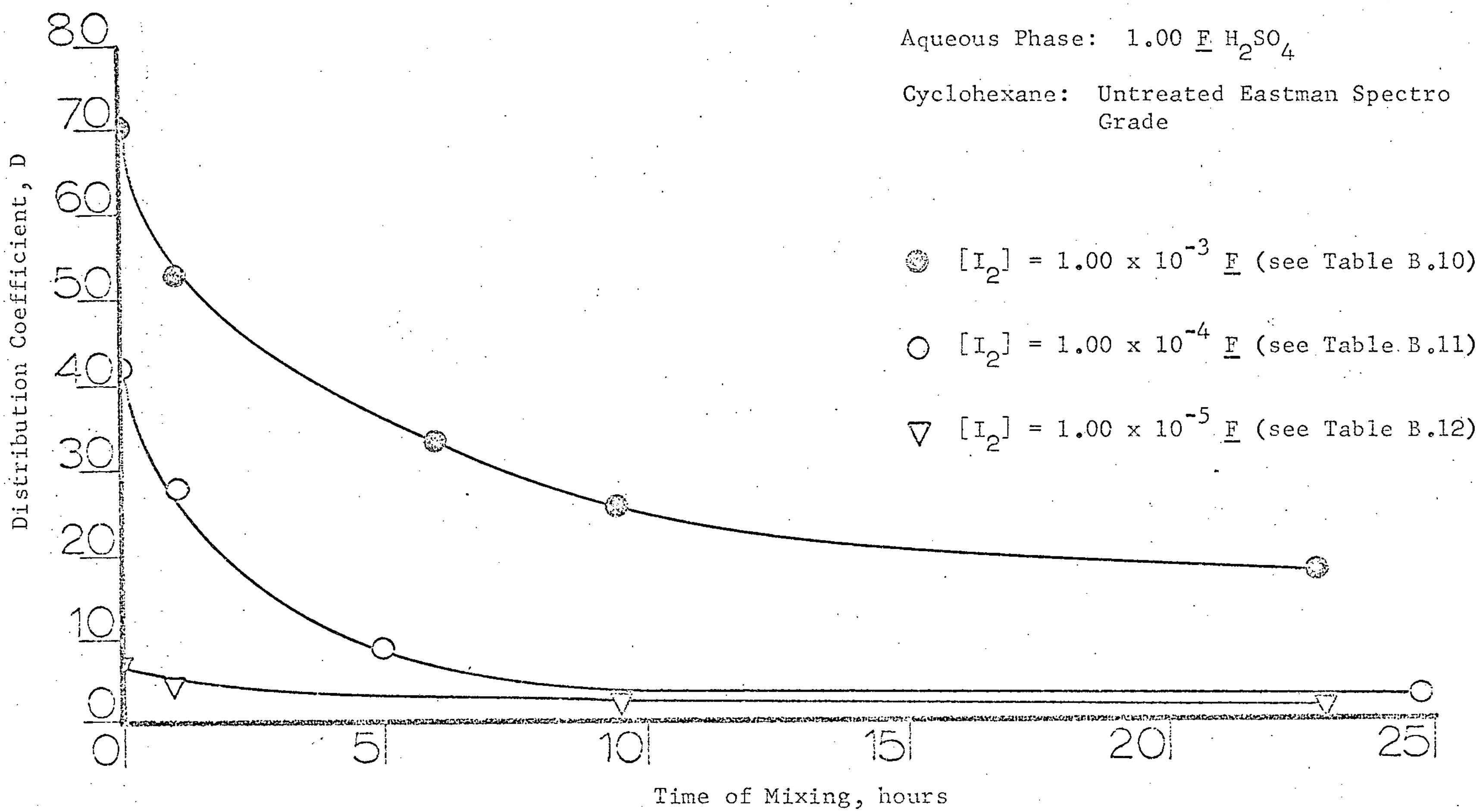


Figure B.7. The Decrease in D with the Time of Mixing at 24.9°.

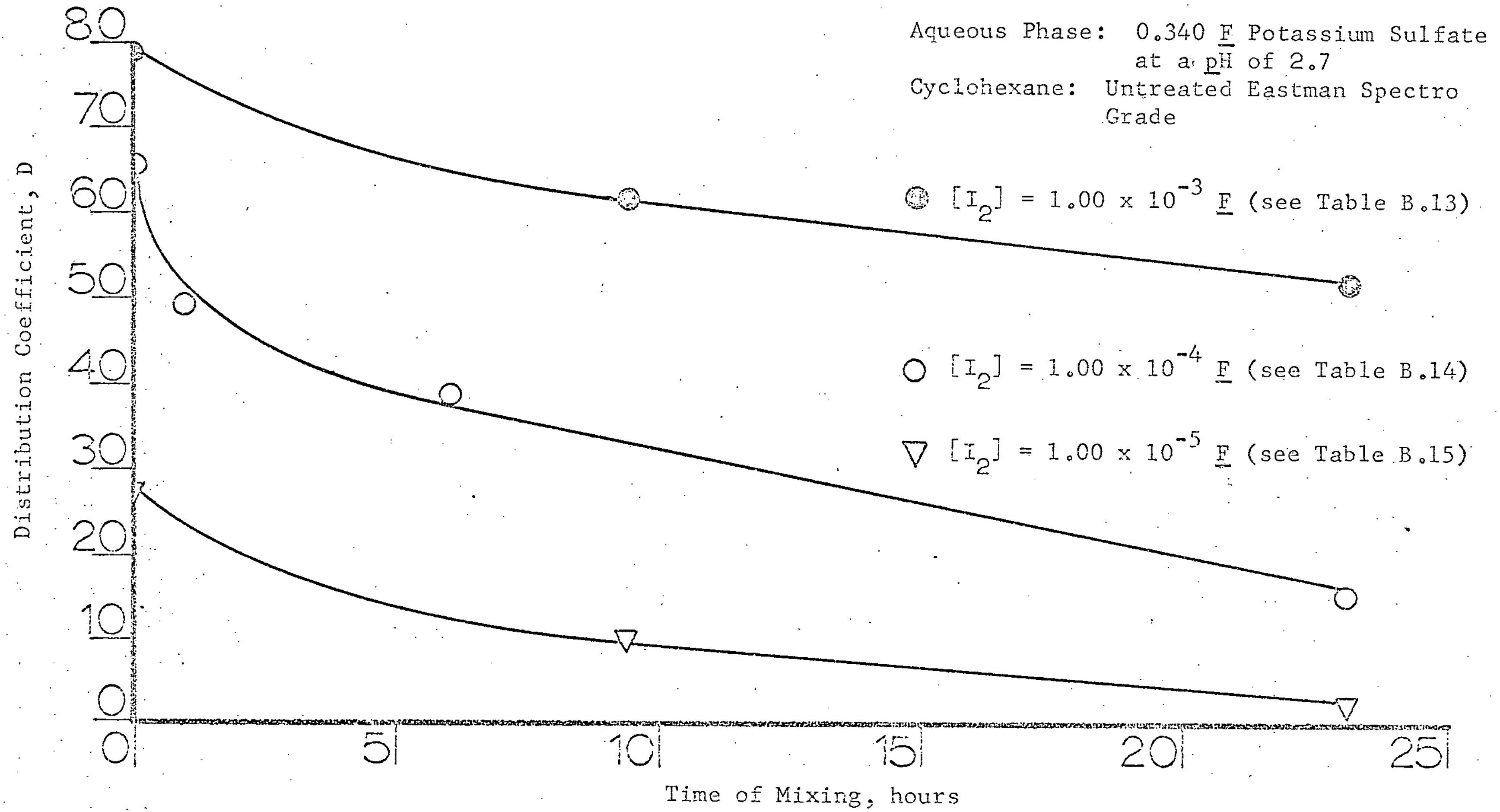


Figure B.8. The Decrease in D with the Time of Mixing at 24.9°.

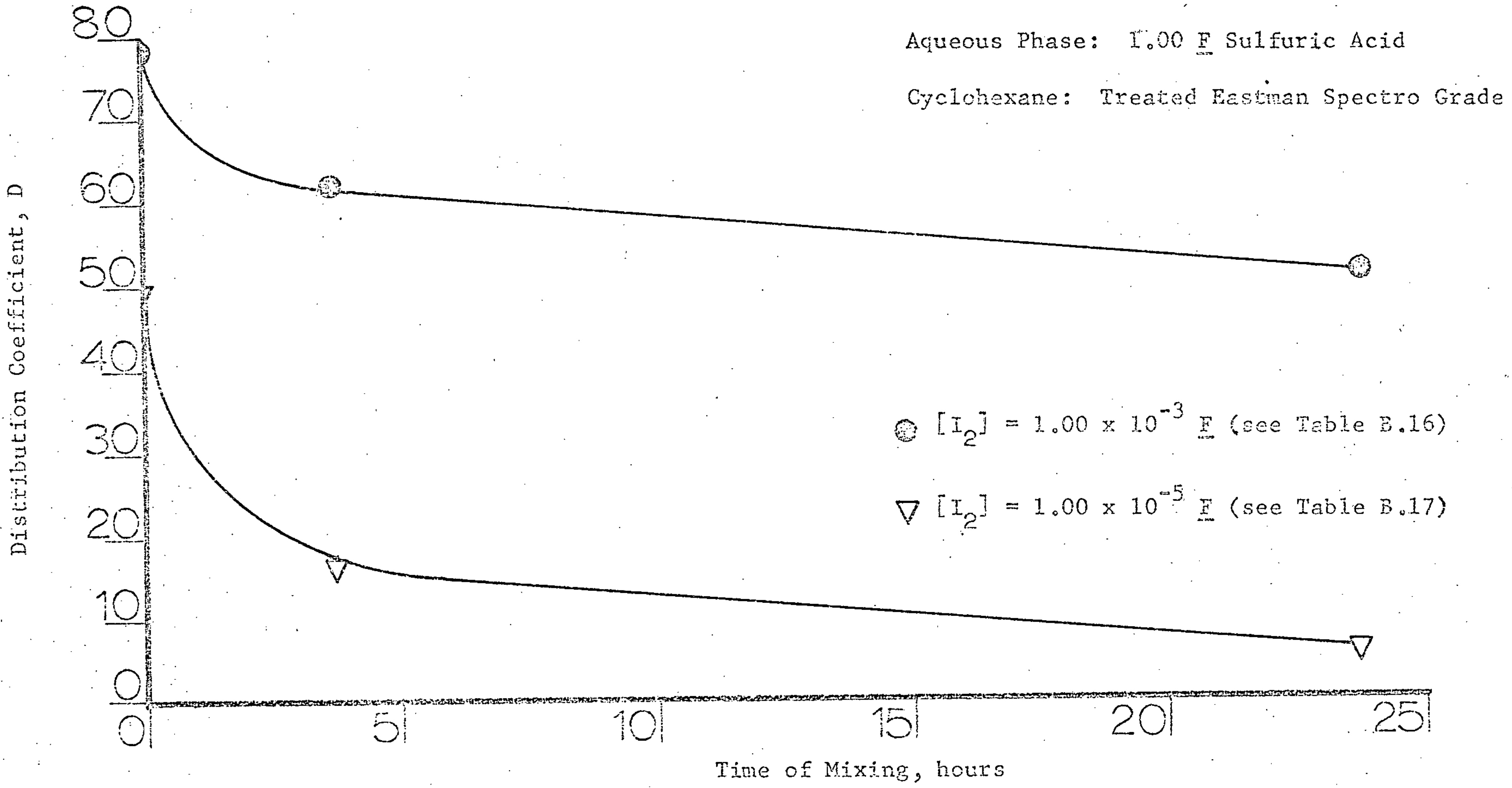


Figure B.9. The Decrease in D with the Time of Mixing at 24.9°.

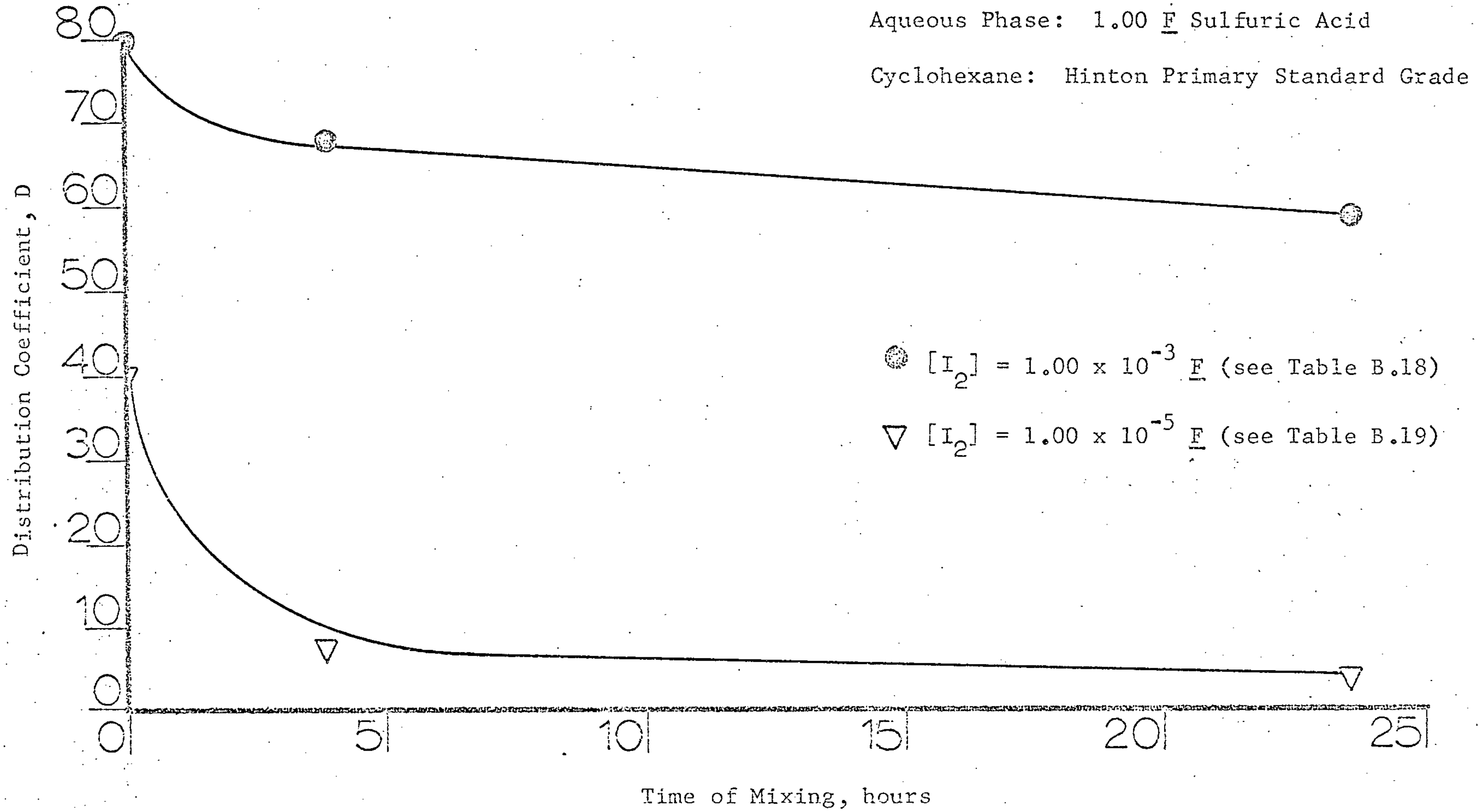
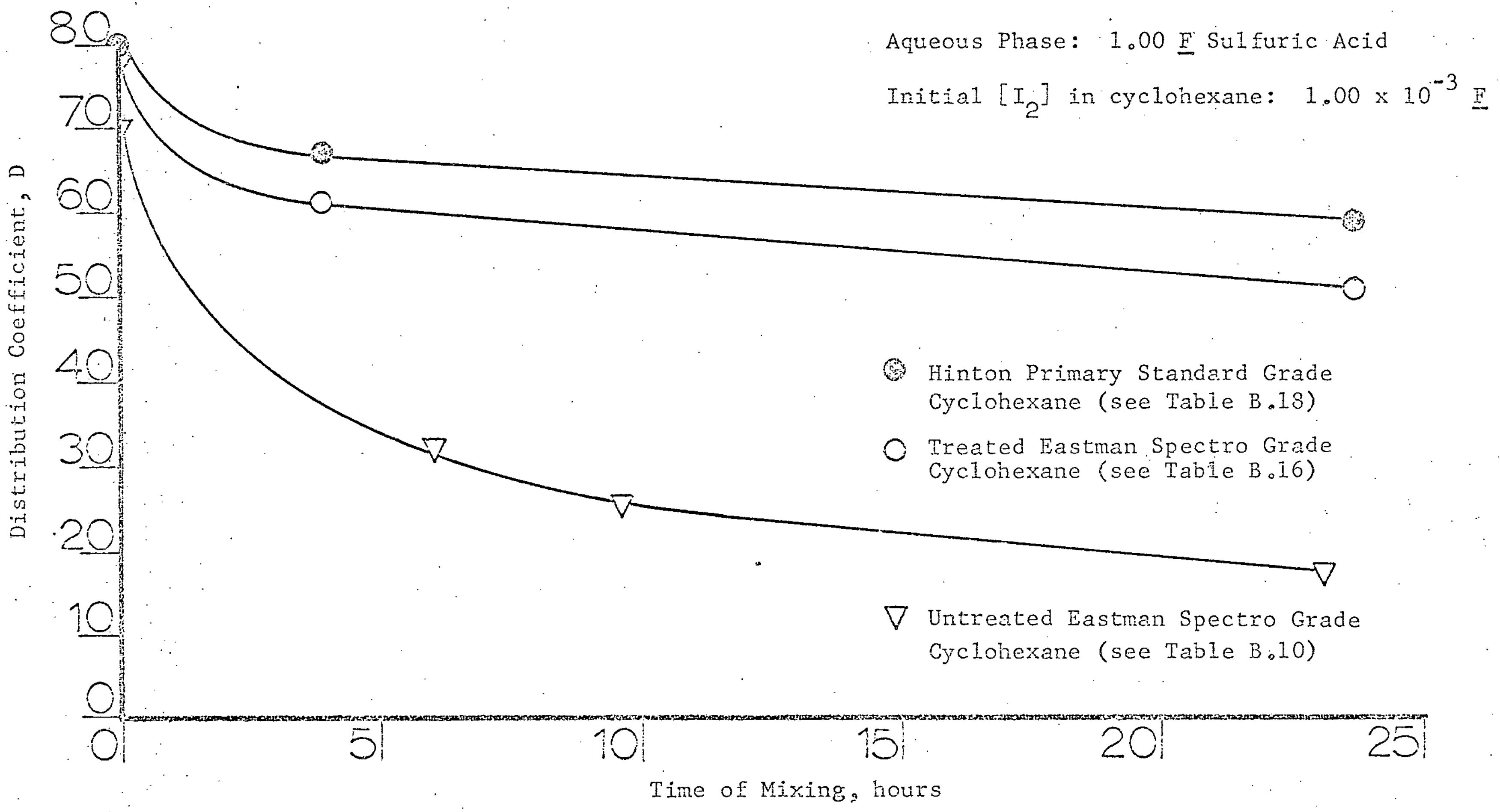


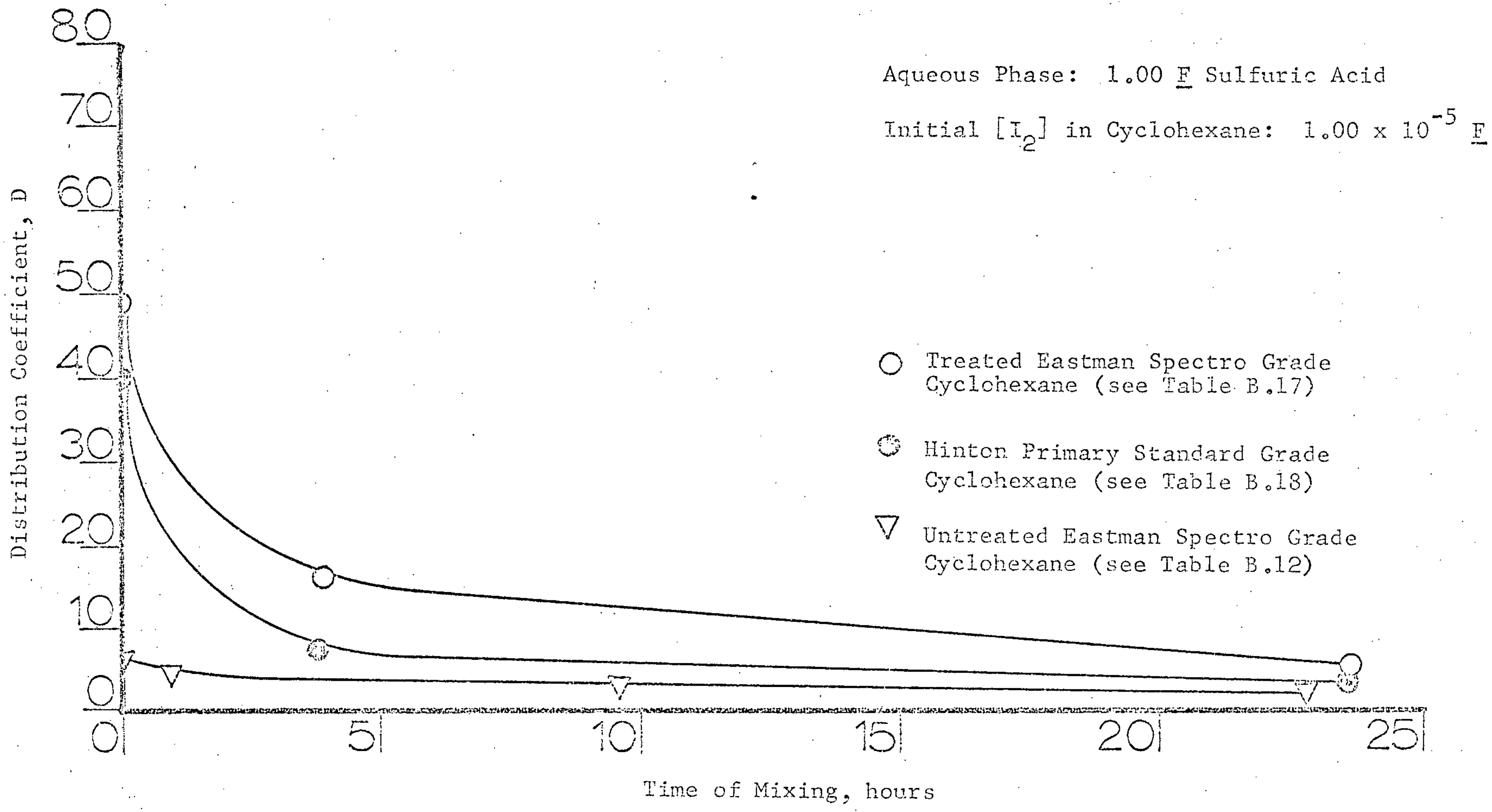
Figure B.10. The Decrease in D with the Time of Mixing at 24.9°.



Aqueous Phase: 1.00 F Sulfuric Acid

Initial $[I_2]$ in cyclohexane: 1.00×10^{-3} F

Figure B.11. The Dependence of D on the Purity of the Cyclohexane and the Time of Mixing at 24.9°.



Aqueous Phase: 1.00 F Sulfuric Acid

Initial $[I_2]$ in Cyclohexane: 1.00×10^{-5} F

Figure B.12. The Dependence of D on the Purity of the Cyclohexane and the Time of Mixing at 24.9°.

B.IV. DISCUSSION

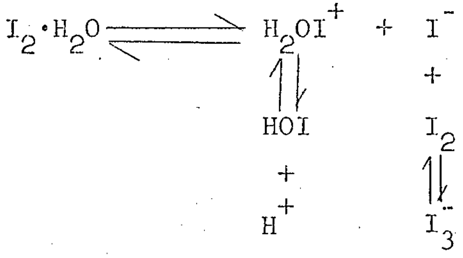
B.IV.a. A Brief Summary of the Previous Work Concerning the Distribution of Iodine Between Nonaqueous Solvents and Aqueous Solutions

In 1950 Kahn (12) reported that the distribution coefficient, D, for iodine between benzene and dilute sulfuric acid (pH = 1.3) decreased with a decrease in the initial iodine concentration in the benzene phase. He reported that more iodine appeared in the aqueous phase than would be expected from the known macro chemistry of iodine. For example, for an initial iodine concentration in the benzene phase of 1.0×10^{-2} F the experimentally determined distribution coefficient was 379, and for an initial iodine concentration in the benzene phase of 1.0×10^{-4} F the experimentally determined distribution coefficient was 304. Kahn explained this decrease in the distribution coefficient with decreasing iodine concentration by postulating the presence of an impurity in the aqueous phase which reacted with molecular iodine to form a benzene-insoluble iodine species. The concentration of the impurity in the aqueous phase was estimated to be 5×10^{-7} M. However, Kahn did not mention the possibility of an impurity originating in the nonaqueous solvent contributing to the decrease in the distribution coefficient with decreasing iodine concentration.

In 1956 Good and Edwards (17) reported on a study of the distribution of iodine between aqueous solutions at various pH and carbon disulfide where the initial concentration of iodine in the carbon disulfide was varied over the range 10^{-1} to 10^{-6} F. They also reported that more iodine appeared in the aqueous phase than could be accounted for on the basis of the known chemistry of iodine. This discrepency increased as the total iodine concentration decreased and as the time of mixing of the two phases increased. Good and Edwards attempted to account for this discrepency by postulating a reaction (or reactions) between iodine and unknown impurities in the aqueous phase which caused excess iodine to appear in the aqueous phase. However, Good and Edwards did not mention the possibility of an impurity originating in the nonaqueous solvent contributing to the decrease in the distribution coefficient.

In 1957 Wille and Good (18) reported on the distribution of iodine between carbon tetrachloride and aqueous solutions at various pH where the initial concentration of iodine in the carbon tetrachloride phase was varied over the range 10^{-1} to 10^{-5} F. They also reported excess iodine appearing in the aqueous phase and that this excess iodine increased with increasing mixing time of the two phases and decreasing iodine concentration. Wille and Good accounted for these discrepencies by postulating the following mechanism.

> "...the first initial activity in the water layer is due to the partition of iodine and to reactions between iodine and water.

> $$I_{2(CCl_4)} \rightleftharpoons I_{2(H_2O)} \qquad (1)$$
>
> $$I_2 + H_2O \rightleftharpoons I_2\cdot H_2O \qquad (2)$$
>
> At low concentrations reaction (2) would lie far to the right. To calculate the exact effect of this reaction on the distribution coefficient, the equilibrium constant would have to be known. However, the effect of this reaction would be seen at all pH values, which corresponds to the data obtained. Secondly, the slow rise in activity of the aqueous phase with time could be caused by the following dissociation of the water-iodine complex.
>
> 
>
> $$\begin{tikzcd} I_2\cdot H_2O \arrow[r, shift left] & H_2OI^+ \arrow[l, shift left] \arrow[d, shift left] & + & I^- \\ & HOI \arrow[u, shift left] & & + \\ & + & & I_2 \arrow[d, shift left] \\ & H^+ & & I_3^- \arrow[u, shift left] \end{tikzcd} \qquad (3)$$
>
> This equilibrium would be pH dependent due to the decomposition of H_2OI^+. Thus the equilibrium concentrations of HOI and I_3^- should decrease with a decrease in pH" (18).

This mechanism, postulated by Wille and Good, is in error. First, reaction (2) would be independent of the total iodine concentration. Second, the previous theoretical discussion of the distribution coefficient (see p. 70 through 73) fully considers the contribution of reaction (3) to the observed distribution coefficient and demonstrates that this contribution is negligible.

It is of interest to compare some of the experimental techniques employed by Good and Edwards (17) and Wille and Good (18), which were the same in both instances, with those of this author. First, Good and Edwards (17) and Wille and Good (18) reported that the distribution coefficient decreased for mixing times of from one to 5 minutes; this author, however, has reported that the distribution coefficient is a constant for mixing times of from one to 5 minutes. Presumably, this dependence of the distribution coefficient on the mixing time for short mixing times, as reported by Good and Edwards (17) and Wille and Good (18), is due to insufficient mixing between the two phases of the system. Second, Good and Edwards (17) and Wille and Good (18) reported that, although they removed aliquots from both phases during an experimental run, (to keep the ratio of the volumes in the two phases constant) they only counted the iodine-131 activity in the aliquot removed from the aqueous phase. This author, however, found it necessary to count aliquots from both phases as activity was often volatilized out of the reaction vessels.

In 1961 Brewer, Simonson and Tong (27) reported on a study of the distribution of iodine between carbon tetrachloride and 10^{-5} $\underline{N}$ sulfuric acid where the initial concentration of iodine in the carbon tetrachloride was varied over the range 0.073 to 0.013 $\underline{F}$. Brewer, et al., reported that their "distribution ratios" (which they define as "...ratio of concentration in carbon tetrachloride to concentration in water...") decreased predictably from 91.1 to 89.8 as the initial concentration of the iodine in the carbon tetrachloride decreased from 0.073 to 0.013 $\underline{F}$. They used an apparatus of their design, "a vapor phase equilibrator," for their distribution studies. This apparatus transferred the iodine from the carbon tetrachloride solution to the aqueous solution via the vapor phase and thereby eliminated direct contact between the two liquid phases. Brewer, et al., concluded that the low values reported for the "distribution ratio" by other investigators was due to "...varying emulsification of some of the CCl_4 phase in the aqueous phase" (27).

However, the report by Brewer, et al., is somewhat incomplete with respect to the following topics.

1. The initial concentration of iodine in the carbon tetrachloride is sufficiently high (0.073 to 0.013 F), and the iodine concentration range sufficiently small based on the work by Kahn (12), Good and Edwards (17), Wille and Good (18) and this author, that it is doubtful if an investigator could, within experimental error, discern any dependence of the distribution coefficient on the iodine concentration.
2. The total iodine concentration could have been significantly decreased by dissolution of the iodine in the saturated sodium nitrate solutions which were used to pump the iodine-containing vapor around the system. No mention of this possibility was made by Brewer, et al.
3. The contention of Brewer, et al., that varying emulsification of the carbon tetrachloride in the aqueous phase could be responsible for the observed decrease in the distribution coefficient with decreasing iodine concentration cannot possibly explain the decrease of the distribution coefficient with decreasing iodine concentration as observed by other investigators (12, 17, 18 and this work).
4. There was a complete lack of references to the work on the distribution of iodine performed by Kahn (12), Good and Edwards (17) or Wille and Good (18) and, also, the related work performed by Kennedy (28), Katzin (15) or Wolfenden (19).

B.IV.b. A Brief Summary of the Previous Work Concerning Topics Related to the Distribution of Iodine Between Nonaqueous Solvents and Aqueous Solutions

In 1949 Kennedy (28) reported on a study of "The Hydrolysis of Iodine and a Reaction with 'Proponal'"; he investigated the inhibition of the iodide-iodate reaction,

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O ,$$

by small concentrations of n-propanol and the decolorization of aqueous acidic solutions of iodine in the presence of iodate and n-propanol. Kennedy reported that, "The kinetic studies (of the iodide-iodate reaction) in acid solution give good evidence for the existance of a species not before reported, I_2OH^-. This substance is analogous to I_3^-........" (28).

In 1953 Katzin (15), in a spectroscopic study of iodine in oxygenated solvents and the dissociation of iodine in aqueous solutions, reported that triiodide slowly developed in the solutions of iodine in either water or one of the lower alcohols of four carbons or less. Katzin attributed the slow formation of triiodide in the alcohols to the presence of impurities in the alcohol which reduced iodine to iodide.

In 1957 Wolfenden (19), in a spectroscopic study of the slow development of triiodide in aqueous solutions of iodine, concluded that the slow formation of triiodide was due mainly to reduction of the aqueous iodine by traces of dust and not to the slow hydrolysis of a water-iodine complex ($I_2 \cdot H_2O$).

B.IV.c. This Work

The distribution coefficient, D, for iodine between cyclohexane and aqueous solutions was studied where the initial concentration of iodine in cyclohexane ranged from 1.00×10^{-2} to 1.00×10^{-5} F. The composition, ionic strength and pH of the aqueous solutions were varied, as was the purity of the cyclohexane and aqueous solutions.

B.IV.c.1. The Distribution of Iodine Between Cyclohexane and 0.100 F Perchloric Acid

The distribution coefficient for iodine between cyclohexane and 0.100 F perchloric acid was studied where the initial concentration of iodine in cyclohexane ranged from 1.00×10^{-2} to 1.00×10^{-5} F. The distribution coefficient, D, behaved in the following manner.

1. D decreased with a decrease in the initial concentration of iodine in the cyclohexane.
2. D decreased with an increase in the time of mixing between the two phases.
3. D was independent of the age of the cyclohexane-iodine solution (with the exception of the 1.00×10^{-5} F iodine solution where slight aging effect was noted).
4. D was independent of the presence, or absence, of ordinary fluorescent light.
5. D varied with the method used for inoculating the cyclohexane-iodine solution with iodine-131.

The investigation of the distribution coefficient for iodine between cyclohexane and 0.100 F perchloric acid was terminated and the investigation started anew where sulfuric acid and sulfuric acid-potassium sulfate mixtures were used for the aqueous phase. It was decided to change the composition of the aqueous phase from perchloric acid to sulfuric acid because of the results of Reynolds (14) which indicated the presence of impurities, which react with iodine, in perchloric acid.

B.IV.c.2. The Distribution of Iodine Between Cyclohexane and Sulfuric Acid or Sulfuric Acid - Potassium Sulfate Mixtures

The distribution coefficient for iodine between cyclohexane and sulfuric acid or sulfuric acid - potassium sulfate mixtures was studied where the initial concentration of iodine in cyclohexane ranged from 1.00×10^{-3} to 1.00×10^{-5} F.

Zero-Time Studies The results of studies of the distribution coefficient for iodine between cyclohexane and aqueous solutions, where the two phases are mixed for one minute, are summarized below.

1. Time of Mixing: It was demonstrated that the distribution coefficient was independent of the time of mixing of the two phases where the mixing time varied from one-half to 5 minutes. The two phases were mixed by vigorously shaking the glass-stoppered centrifuge tube in which they were contained. These results are in contradiction to those reported by Good and Edwards (17) and Wille and Good (18); they reported that, over a similar range of mixing times, the distribution coefficient decreased as the mixing time increased. This discrepancy is undoubtedly ascribable to the more thorough mixing of the two phases with vigorous hand-shaking, which was employed by this author and also Kahn (12), as compared to the mechanical shaker, suspended in a constant temperature bath, as employed

by Good and Edwards (17) and Wille and Good (18).

2. Iodine Concentration: The distribution coefficient decreased with a decrease in the initial concentration of iodine in the cyclohexane; the initial concentration of iodine in cyclohexane ranged from 1.00 x 10^{-3} to 1.00 x 10^{-5} F. These results are similar to those reported by other investigators (12, 17 and 18). This decrease in the distribution coefficient with decreasing iodine concentration cannot be explained on the basis of the known macro chemistry of iodine.

3. Age of Cyclohexane-Iodine Solutions: It was demonstrated that the distribution coefficient was independent of the age of either the inactive or active cyclohexane-iodine solutions up to two weeks old.

4. Composition of Aqueous Phase: The distribution coefficient increased as the pH of the aqueous phase increased from that of 1.00 F sulfuric acid to that of 0.340 F potassium sulfate (at a pH of 2.7), at constant ionic strength (u = 1.0), and, as the ionic strength increased from 2.5 x 10^{-4} to 1.7, at constant pH (pH = 3.55 ± 0.15). This increase in the distribution coefficient with increasing pH, at constant ionic strength, is in contradiction to the results reported by Good and Edwards (17) and Wille and Good (18). However, they did not mention what the exact composition of their aqueous solutions were and, therefore, no direct comparison between this investigator's results and those of Good and Edwards', or Wille and Good's, is possible.

5. Purity of the Cyclohexane: The distribution coefficient increased with increasing purity of the cyclohexane.

The distribution of iodine between cyclohexane and aqueous solutions was studied using three cyclohexanes; untreated Eastman Spectro Grade, treated Eastman Spectro Grade and Hinton Primary Standard grade. For an initial concentration of iodine in cyclohexane of 1.00×10^{-3} F the Hinton Primary Standard grade cyclohexane gave the highest value for the distribution coefficient (D = 80), the treated Eastman Spectro Grade cyclohexane gave the next highest value for the distribution coefficient (D = 77) and the untreated Eastman Spectro Grade cyclohexane gave the lowest value for the distribution coefficient (D = 68). For an initial concentration of iodine in cyclohexane of 1.00×10^{-5} F the treated Eastman Spectro Grade cyclohexane gave the highest value for the distribution coefficient (D = 48), the Hinton Primary Standard grade cyclohexane gave the next highest value for the distribution coefficient (D = 40) and, again, the untreated Eastman Spectro Grade cyclohexane gave the lowest value for the distribution coefficient (D = 6). Although the absolute purity of the treated Eastman Spectro Grade cyclohexane is unknown, the indications are, with regards to impurities which lower the distribution coefficient for iodine, that its purity is similar to Hinton Primary Standard grade cyclohexane.

Distribution experiments were not carried out with Phillips Research Grade cyclohexane since it was found to react with molecular iodine.

The distribution coefficient decreased if certain selected impurities were added to the cyclohexane phase of the two-phase reaction mixture. The addition of one percent, by volume, of cyclohexane and 2-methyl-2-pentanol decreased the distribution coefficient, whereas the addition of one percent, by volume, of 2,4-dimethylpentane and 2-methyl-2,4-pentanediol had no effect upon the distribution coefficient.

6. Aqueous Impurities: The distribution coefficient was observed to be dependent on the presence of certain impurities in the aqueous phase. Ozone decreased the distribution coefficient, presumably through the formation of iodate, whereas hydrogen peroxide increased the distribution coeficient. However, saturating the aqueous phase with either nitrogen or oxygen had no effect upon the distribution coefficient. Likewise, the addition of airborne impurities to the aqueous phase did not affect the distribution coefficient.

Time Studies The results of studies of the distribution coeficient for iodine between cyclohexane and aqueous solutions, where the two phases are mixed for up to 38 hours, are summarized below.

1. Mixing Time: The distribution coefficient decreased with increasing duration of the mixing process up to approximately 24 hours. These results are compatible with those reported by Good and Edwards (17) and Wille and Good (18); they reported that the distribution coefficient decreased with increasing duration of the mixing process over a period of 2 hours.
2. Composition of Aqueous Phase: The distribution coefficient

decreased more rapidly with increasing mixing time when the composition of the aqueous phase was changed from 0.340 F potassium sulfate at a pH = 2.7 to 1.00 F sulfuric acid; the ionic strength, u = 1.0, was the same for both aqueous phases. The addition of nitrogen or oxygen to the 1.00 F sulfuric acid did not affect the values observed for the distribution coefficient over a mixing time of 24 hours. The addition of hydrogen peroxide did not affect the values observed for the distribution coefficient at 4 and 24 hours mixing time although hydrogen peroxide increased the values observed for the initial (zero-time) distribution coefficient.

3. Purity of the Cyclohexane: The distribution coefficient decreased more rapidly with increasing mixing time as the purity of the cyclohexane decreased.

4. The Characterization of Activity in the Cyclohexane Phase: The iodine-131 activity in the cyclohexane phase was characterized employing an extraction procedure. The procedure used yielded the percentage of iodine-131 in the cyclohexane phase which isotopically exchanged with, or was reduced by, aqueous iodide, was reduced by aqueous acidic sulfite or extracted into aqueous hydroxide.

For a one-minute mixing time between 1.00 x 10^{-3} and 1.00 x 10^{-5} F iodine in untreated Eastman Spectro Grade cyclohexane and the aqueous phase (1.00 F sulfuric acid or 0.340 F potassium sulfate at a pH of 2.7) 99 and 95 percent of the iodine-131, respectively, in the cyclohexane phase, behaved as molecular iodine.

For a 38-hour mixing time between 1.00×10^{-3} F iodine in untreated Eastman Spectro Grade cyclohexane and the aqueous phase (1.00 F sulfuric acid or 0.340 F potassium sulfate at a pH of 2.7) 96 percent of the iodine-131 activity in the cyclohexane phase behaved as molecular iodine.

For a 38-hour mixing time between 1.00×10^{-5} F iodine in untreated Eastman Spectro Grade cyclohexane and 1.00 F sulfuric acid and 0.340 F potassium sulfate (pH = 2.7);

a. approximately 60 and 25 percent, respectively, of the iodine-131 activity in the cyclohexane phase did not extract into aqueous iodide,

b. approximately 33 and 10 percent, respectively, of the iodine-131 activity in the cyclohexane phase did not extract into aqueous acidic sulfite, and,

c. in both instances, over 90 percent of the iodine-131 activity in the cyclohexane phase extracted into aqueous hydroxide.

These results for 1.00×10^{-5} F iodine indicated that at least two chemically distinct forms of iodine-131 activity, other than molecular iodine, were present in the untreated Eastman Spectro Grade cyclohexane phase after 38-hours mixing time with an acidic aqueous phase; one species is reduced by aqueous acidic sulfite and extracts into aqueous hydroxide but does not under go isotopic exchange, or reduction, with aqueous iodide, and, another species which is neither reduced by aqueous acidic sulfite nor aqueous iodide nor undergoes isotopic exchange with aqueous iodide but is extracted into aqueous hydroxide.

For a 24-hour mixing time between 1.00 x 10^{-3} and 1.00 x 10^{-5} F iodine in Hinton Primary Standard grade cyclohexane and 1.00 F sulfuric acid 98 percent and 99 percent, respectively, of the iodine-131 activity in the cyclohexane phase behaved as molecular iodine. These results show that for 1.00 x 10^{-5} F iodine in cyclohexane there is a considerable decrease in the amount of iodine-131 species which do not behave as molecular iodine in the cyclohexane phase of the two-phase reaction mixture when Hinton Primary Standard grade cyclohexane is used as opposed to the results observed when untreated Eastman Spectro Grade cyclohexane was used.

5. Characterization of Activity in the Aqueous Phase: The aqueous phase of the two-phase reaction mixture was subjected to an extraction procedure in order to characterize the iodine-131 activity. The procedure used yielded the percentage of iodine-131 activity in the aqueous phase which was soluble in cyclohexane and isotopically exchanged with aqueous iodide, soluble in cyclohexane but did not isotopically exchange with aqueous iodide, not soluble in cyclohexane but isotopically exchanged with iodine in cyclohexane, and, neither soluble in cyclohexane nor isotopically exchangeable with iodine in cyclohexane.

For a 38-hour mixing time between 1.00 x 10^{-5} F iodine in untreated Eastman Spectro Grade cyclohexane and 1.00 F sulfuric acid and 0.340 F potassium sulfate (pH = 2.7); 28 and 64 percent, respectively, of the iodine-131 activity in the aqueous phase extracted into cyclohexane but, in each instance, 5 percent did not back-extract into aqueous iodide, and in each instance, approximately 5 percent of the iodine-131 activity in the aqueous phase did not extract into a cyclohexane-iodine solution. These results for 1.00×10^{-5} $\underline{F}$ iodine indicate that the aqueous phase, after 38-hours mixing time, contained at least two chemically distinct forms of iodine-131 activity which did not behave as iodine, iodide or hypoiodite. One of these species of iodine-131 activity was soluble in cyclohexane but did not undergo isotopic exchange, or reduction, with aqueous iodide, and, the other species of iodine-131 activity was insoluble in cyclohexane and did not undergo isotopic exchange with molecular iodine in cyclohexane.

For a 24-hour mixing time between 1.00×10^{-3} $\underline{F}$ iodine in Hinton Primary Standard grade cyclohexane and 1.00 $\underline{F}$ sulfuric acid approximately 70 percent of the iodine-131 activity in the aqueous phase extracted into cyclohexane but 4 percent did not back-extract into aqueous iodide, and approximately 3 percent of the iodine-131 activity in the aqueous phase did not extract into a cyclohexane-iodine solution.

For a 24-hour mixing time between 1.00×10^{-5} $\underline{F}$ iodine in cyclohexane and 1.00 $\underline{F}$ sulfuric acid approximately 7 percent of the iodine-131 activity in the aqueous phase extracted into cyclohexane but 3 percent did not back-extract into aqueous iodide, and, 7 percent of the iodine-131 activity in the aqueous phase did not extract into a cyclohexane-iodine solution.

6. Airborne Impurities: Varying amounts of airborne impurities were added to 1.00 F sulfuric acid to determine whether these impurities are, in part, responsible for the decrease in the distribution coefficient for iodine with either decreasing iodine concentration or increasing duration of the mixing process. The results indicate that there is no apparent correlation between the amount of airborne impurities present in the aqueous phase and the decrease in the distribution coefficient with either decreasing iodine concentration or increasing mixing time. These results contradict those of Wolfenden (19) who, in 1957, reported on a spectroscopic study of the slow development of triiodide in aqueous solutions of iodine; he concluded that the slow formation of triiodide was due mainly to reduction of the aqueous iodine by traces of dust. However, the results reported here do not preclude the possibility of a reaction between dust and iodine being a factor in the slow formation of triiodide.

7. Redistribution Studies: Studies of the dependence of the distribution coefficient on the time of mixing of the two phases indicate that the reaction, or reactions, go to completion within 24 hours (i.e. the distribution coefficient is essentially a constant for mixing times of 24 hours or more). If these reactions free the cyclohexane-iodine solutions from impurities then a constant distribution coefficient for iodine should be observed when this "purified" cyclohexane-iodine solution and a fresh acidic aqueous phase are mixed. Several

experiments were performed where the distribution coefficient for iodine, which had been in contact with an acidic aqueous phase for 24 hours or more, was remeasured using a fresh portion of the same aqueous solution. For an initial iodine concentration in cyclohexane of 1.00×10^{-3} or 1.00×10^{-5} F and an acidic aqueous phase the initial zero-time and remeasured zero-time distribution coefficients were essentially the same for a given iodine concentration and composition of the aqueous phase. The cyclohexane was either untreated Eastman Spectro Grade or Eastman Spectro Grade which had been treated by refluxing with 20 F potassium hydroxide for 3 days and, then, distilled and the acidic aqueous phase was either 1.00 F sulfuric acid or 0.340 F potassium sulfate at a pH of 2.7. However, the remeasured 24-hour distribution coefficients were observed to be two to four times larger than the initial 24-hour distribution coefficients. These results indicate that the reaction, or reactions, which cause the distribution coefficients to decrease with increasing duration of the mixing process do not completely free the cyclohexane-iodine phase of reactive impurities after 24 hours of mixing. Likewise, the treatment of the cyclohexane with hydroxide apparently does not affect the values observed for the distribution coefficient.

B.IV.d. A Mechanism to Explain, in Part, the Discrepencies in the Distribution of Iodine between Cyclohexane and Aqueous Solutions

Any mechanism proposed to explain the discrepencies in the distribution of iodine between cyclohexane and aqueous solutions must be consistent with the following brief summary of the results.

1. The distribution coefficient decreases with a decrease in the initial concentration of iodine in cyclohexane.
2. The distribution coefficient increases when the composition of the aqueous phase is changed from 1.00 F sulfuric acid to 0.340 F potassium sulfate (at a pH = 2.7). The ionic strength of these two solutions is 1.0.
3. The distribution coefficient increases with an increase in the purity of the cyclohexane.
4. The distribution coefficient decreases as the time of mixing of the two phases of the reaction mixture increases.
5. Iodine-131 species, which do not behave as molecular iodine, iodide or hypoiodite, were observed in both the aqueous and nonaqueous phases of the reaction mixture after 24 or more hours mixing time.
6. The distribution coefficient for iodine in cyclohexane, which had been in contact with an acidic aqueous phase for 24 hours, was remeasured using a fresh portion of the same aqueous solution. The remeasured zero-time distribution coefficients were found to be virtually the same as the initial zero-time distribution coefficients when the remeasured zero-time distribution coefficients were corrected for the change in the concentration

of iodine in the cylohexane after the 24-hour mixing time. Also, the remeasured 24-hour distribution coefficients were found to be approximately two to four times larger than the initial 24-hour distribution coefficients.

The following general reaction is proposed to partially explain the six aforementioned discrepencies in the distribution of iodine between cyclohexane and aqueous solutions.

$$I_2 + Imp + H_2O + H^+ \overset{slow}{\rightleftharpoons} I_{aq} + I_{nonaq} + Imp' \; [1]$$

where I_2 = molecular iodine in either the aqueous phase, the nonaqueous phase or the phase interface

Imp = reactive impurity originating in the nonaqueous phase,

I_{aq} = iodine species (probably either HIO or I^-) soluble in the aqueous phase,

I_{nonaq} = iodine species soluble in the nonaqueous phase, but not molecular iodine, and

Imp' = chemically changed form of the impurity and not containing iodine.

If it is postulated that the following conditions hold then it is possible to explain the observed discrepencies in the distribution of iodine between cyclohexane and aqueous solutions.

1. This reaction [1] proceeds to a measurable extent in the cyclohexane-iodine solutions, prior to preparation of the two-phase reaction mixture, due to the small amount of water present in the cyclohexanes (approximately 0.2 percent water in untreated Eastman Spectro Grade cyclohexane and approximately 0.01 percent water in Hinton Primary Standard grade cyclohexane).

Although the reaction is slow it reaches equilibrium within 24 hours. Decreasing the initial concentration of molecular iodine in cyclohexane and/or increasing the amount of water and reactive impurity (Imp) will cause a larger percentage of the molecular iodine, initially present in the cyclohexane, to be converted to I_{aq} and I_{nonaq}. Upon mixing this cyclohexane-iodine solution with an acidic aqueous solution with an acidic aqueous solution the I_{aq} will be extracted into the aqueous phase. Therefore, the initial (zero-time) distribution coefficient will decrease with decreasing iodine concentration and decreasing purity of the cyclohexane.

Hence, if condition No. 1 holds then reaction [1] is sufficient to explain the decrease in the initial (zero-time) distribution coefficient with decreasing iodine concentration and decreasing purity of the cyclohexane. Furthermore, if a second condition is postulated then reaction [1] can explain the observed decrease in the distribution coefficient with increasing duration of the mixing process and decreasing pH of the aqueous phase and the redistribution results.

2. Reaction [1] proceeds to the right when the cyclohexane-iodine solution is mixed with an acidic aqueous phase.

Reaction [1], however, is insufficient, by itself, to explain the presence, in each phase, of two different iodine-131 species which do not behave as iodine, iodide or hypoiodite. Therefore, it is necessary to postulate a second reaction which generates an iodine-131 species (not iodine, iodide, hypoiodite nor the I_{aq} or I_{nonaq} postulated in reaction [1]. The proposed reaction is

$$I_{nonaq} + Imp'' \longrightarrow I_{nonaq} - Imp'' \qquad [2]$$

where I_{nonaq} = the same species generated by reaction [1] and

Imp" = is an impurity, originating in the cyclohexane, which could be either the Imp or Imp' from reaction [1] or a different impurity altogether, also not containing iodine.

The I_{nonaq}-Imp" species behaves as an organic iodine compound (or complex) in that it does not extract into either aqueous sodium iodide or aqueous acidic sodium sulfite but rather extracts into aqueous sodium hydroxide.

B.IV.e. Suggestions for Further Work

The distribution coefficient for iodine between cyclohexane and aqueous solutions was observed to be dependent on the purity of the cyclohexane. It would be of interest to investigate further the distribution of iodine between cyclohexane and aqueous solutions with the emphasis placed on identifying the impurities in the cyclohexane which react with the iodine to cause the distribution coefficient to decrease with decreasing iodine concentration and increasing time of mixing.

BIBLIOGRAPHY

1. Allen, T. L. and R. M. Keefer, "The Formation of Hypoiodous Acid and Hydrated Iodine Cation by the Hydrolysis of Iodine," J. Amer. Chem. Soc., 77, 2957 (1955).

2. Bell, R. P. and E. Gelles, "The Halogen Cations in Aqueous Solution," J. Chem. Soc., 2734 (1951).

3. Bonner, W. A., "A Portable Semimicro Ozonizer," J. Chem. Educ., 30, 452 (1953).

4. Breiter, M. W., "Voltammetric Study of Halide Ion Adsorption on Platinum in Perchloric Acid Solutions," Electrochim. Acta 8, 925 (1963).

5. Brewer, L., T. R. Simonson and L. K. J. Tong, "A Vapor Phase Equilibrator for Activity Coefficient Determinations," J. Phys. Chem., 65, 420 (1961).

6. Chang, Chau-ting and Chien-Chang Lin, "Preparation of Carrier-free Iodine-131 with Adsorption Method. (II) Sorption of Iodine on Platinum Metal Surface," A1j-12, Proc. of the 5th Japan Conference on Radioisotopes, May 21, 1963, Tokyo.

7. Chia, Y. T., "Chemistry of +1 Iodine in Alkaline Solution," UCRL 8311 (1958).

8. Davies, M. and E. Gwynne, "The Iodine-Iodide Interaction," J. Amer. Chem. Soc., 74, 2748 (1952).

9. Eggleton, A. E. J., "A Theoretical Examination of Iodine-Water Partition Coefficients," A. E. R. E. R 4887 (1967).

10. Eiland, H. M., Thesis submitted for degree of Doctor of Philosophy, University of New Mexico, Albuquerque, N. M. (1957).

11. Good, M. L. and R. R. Edwards, "A Tracer Study of the Distribution of Iodine Between Carbon Disulfide and Aqueous Solutions," J. Inorg. Nucl. Chem., 2, 196 (1956).

12. Kahn, M., Thesis submitted for degree of Doctor of Philosophy, Washington University, St. Louis, Mo. (1950).

13. Kahn, M., A. J. Freedman, R. D. Feltham and N. L. Lark, "Counting Techniques for Chlorine-36," Nucleonics, 13, 58 (1955).

14. Katzin, L. I., "Note on the Absorption Spectrum of Iodine in Oxygenated Solvents and the Dissociation of Iodine in Water," J. Phys. Chem., 21, 490 (1953).

15. Kennedy, J. W., "The Hydrolysis of Iodine and a Reaction with 'Propanol'," BNL-30(T-14), 1949.

16. Lin, Chien-chang, Thesis submitted for degree of Doctor of Philosophy, University of New Mexico, Albuquerque, N. M. (1968).

17. Lin, Chien-change, Chau-ting Chang and Si Jung Yeh, "Preparation of Carrier-free I-131 with Adsorption Method," J. Atomic Energy Soc. Japan, 5, No. 3 187 (1963).

18. Lundberg, W. O., C. S. Vestling and J. E. Ahlberg, "The Electrode Potential of the Iodine-Iodate Electrode at 25°C," J. Amer. Chem. Soc., 59, 264 (1937).

19. Osteryoung, R. A. and F. C. Anson, "Behavior of the Iodine-Iodine Couple at Platinum Electrodes," Anal. Chem., 36, 975 (1964).

20. Reid, C. and R. S. Mulliken, "Molecular Compounds and Their Spectra. IV. The Pyridine-Iodine System," J. Amer. Chem. Soc., 76, 3869 (1954).

21. Reynolds, M. S., Thesis submitted for degree of Doctor of Philosophy, University of New Mexico, Albuquerque, N. M. (1966).

22. Schwabe, K., "Untersuchung Über Die Anionenadsorption Mit Hilfe Markierter Ionen," Electrochim. Acta 6, 223 (1962).

23. Schwabe, K. and W. Schwenke, "Untersuchungen Über Anionenadsorption An Metalloberflächen In Abhängigkeit Vom Potential," Electrochim. Acta 9, 1003 (1964).

24. Tóth, G., "Production of Carrier-free I-131 from Telluric Acid by an Adsorption Method," J. Inorg. and Nucl. Chem., 19, 186 (1961).

25. Wille, R. G. and M. L. Good, "The Distribution of Iodine Between Carbon Tetrachloride and Water and a Proposed Mechanism for Dilute, Aqueous Iodine Reactions," J. Amer. Chem. Soc., 79, 1040 (1957).

26. Wolfenden, J. H., "Reduction of Aqueous Iodine by Trace Impurities," Anal. Chem., 29, 1098 (1957).