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THE BEHAVIOR OF ELEMENTS AT VERY LOW CONCENTRATIONS AND THE
KINETICS OF ISOTOPIC EXCHANGE REACTIONS. SOLVENT EFFECTS.

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by

Milton Kahn

MASTER

This report describes the progress made during the last ten months in the following studies:

- A. Chemical Behavior of Carrier-Free Antimony-125. *no*
- B. The Preparation of Dilute, Dry, Nonaqueous Solutions of Molecular Iodine Inoculated with Iodine-131.
- C. The Kinetics of Isotopic Exchange Reactions. Solvent Effects.
- D. Chemical Behavior of Carrier-Free Iodine-131. *no*

A. Chemical Behavior of Carrier-Free Antimony-125.

Enclosed is a reprint of a paper entitled "Some Observations on the Chemical Behavior of Carrier-Free Antimony-125," by K. H. Jones and Milton Kahn, reprinted from the Journal of Inorganic and Nuclear Chemistry, 27, 497 (1965).

B. The Preparation of Dilute, Dry, Nonaqueous Solutions of Molecular Iodine Inoculated with Iodine-131.

See enclosed report which includes results summarized in Progress Report

No. 6.

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C. The Kinetics of Isotopic Exchange Reactions. Solvent Effects.

See enclosed report.

D. Chemical Behavior of Carrier-Free Iodine-131.

A procedure for the preparation of aqueous solutions of carrier-free iodate-131 has been developed and some aspects of the chemical behavior of carrier-free iodate-131 were investigated. This work will be described by Mr. M. S. Reynolds in his doctoral dissertation which is in preparation.

B. The Preparation of Dilute, Dry, Nonaqueous Solutions of Molecular Iodine Inoculated with Iodine-131.

Introduction

Preliminary work in our laboratory indicated that in order to study satisfactorily a) the distribution of molecular iodine between organic liquids and aqueous solutions and b) the kinetics of isotopic exchange reactions between molecular iodine and organic iodides in nonaqueous solvents, 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. Several investigators^{1,2,3,4} have reported that under certain conditions carrier-free iodine-131 is almost quantitatively adsorbed from aqueous solutions by platinum. This report deals with the inoculation of dilute, dry, nonaqueous solutions of molecular iodine with iodine-131 via isotopic exchange with carrier-free iodine-131 adsorbed on a platinum surface.

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- 1) Toth, G., J. Inorg. & Nuclear Chem., 19, 186 (1961).
 - 2) Lin, Chien-chang, Chang, Chau-ting, and Yeh, Si Jung, J. Atomic Energy Soc. Japan, Vol. 5, No. 3, 187 (1963).
 - 3) Chang, Chau-ting and Lin-Chien-chang, Institute of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan, China. Reprint of the paper entitled "Preparation of Carrier-Free Iodine-131 by an Adsorption Method, Sorption of Iodine on Platinum." A/j-12, Proc. of the 5th Japan Conference on Radioisotopes, May 21, 1963, Tokyo.
 - 4) Osteryoung, R. A. and Anson, F. C., Anal. Chem., 36, 975 (1964).

Experimental

General Procedure. The procedure used to investigate various aspects of the preparation of dilute, dry, nonaqueous solutions of molecular iodine, inoculated with iodine-131, is summarized in Figure 1.

Five ml. of an aqueous reaction mixture followed by from 50 to 500 microliters of the iodine-131 stock solution of known specific activity were transferred to a reaction vessel. Pretreated platinum foil (#1) was then introduced into the solution which had been mixed and the whole stirred for a given time. Foil #1 was subsequently washed with three 1-ml. portions of water and then counted (count #1); count #2 represented the total activity present in the reaction mixture and the water washes subsequent to the removal of foil #1. The per cent activity adsorbed by the foil and the total per cent recovery were calculated from these data.

Initially, 15 mm. 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 r.p.m.. Subsequently, glass-stoppered 10-ml. Erlenmeyer flasks were used as reaction vessels. The reaction mixtures were stirred magnetically; the magnetic stirring bar consisted of a 0.5-cm.-long portion of an iron paper clip 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.

Except where noted in the Tables these adsorption studies were carried out in the presence of ordinary laboratory light.

The activated foil #1 was then placed in a reaction vessel and dried in an oven for two hours at 110°C. No detectable amount of activity was volatilized from the foil during the drying operation. Five ml. of a dry nonaqueous

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

solution of inactive molecular iodine was added to the reaction vessel containing foil #1 and the whole stirred for a predetermined time.

The dilute cyclohexane solutions of inactive molecular iodine were prepared by dilution of a 0.01 M stock solution of iodine in cyclohexane which had been stored in the presence of ordinary laboratory light for as long as 1 month. This isotopic exchange procedure was also used in connection with other nonaqueous solvents with the following exceptions; a) these inactive iodine solutions were freshly prepared and b) the exchange process in nitrobenzene was carried out in the dark.

The per cent exchange was calculated from the activity which remained on foil #1 (count #3) and the activity detected in the iodine solution (count #4).

For very dilute nonaqueous solutions of molecular iodine it is important to determine whether the initial concentration is decreased via adsorption on the platinum foil during the exchange process. Such information was obtained by immersing a platinum foil (foil #2) in the activated nonaqueous solution for a given time. The decrease in the iodine concentration was calculated from the activity on foil #2 and in the solution (see Fig. 2).

Pretreatment of the Platinum Foil. 0.0625 mm. foil was cut into 0.5 cm. by 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 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 sixteen hours at room temperature.

- 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.

Fig.-2. Procedure used to investigate the adsorption of active iodine on a clean platinum foil.

Pretreatment B consisted of placing the foils in concentrated nitric acid for sixteen 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 sixteen 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 foils in a cyclohexane solution of inactive molecular iodine (usually 0.0001 M) for a specified time (usually sixteen hours) at room temperature in the presence of ordinary laboratory light.

Isotopic Exchange at 50°. The following procedure was used to study the rate of exchange, at 50°, of iodine atoms between iodine-131 adsorbed on a foil and molecular iodine dissolved in cyclohexane. A 50-ml. round-bottom flask with a 4-inch neck, ending in a 19-38 ground-glass joint served as the 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 ten minutes to allow the contents to attain thermal equilibrium. A dry active foil, bent in the shape of a U, was then added to the flask and the whole stirred with a small Pyrex-covered magnetic stirring bar at about 100 r.p.m.. 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 per cent recovery ranged from 100% to 102%, indicating little loss of solvent during the activation of the iodine solution.

The Effect of Light and Platinum on the Stability of Nonaqueous Iodine Solutions. Clearly, it is important to know whether the presence of platinum foil in the nonaqueous iodine solutions would catalyze the formation of organic iodine compounds with either the solvent itself or impurities in the solvent. We have arbitrarily assumed that any iodine activity not extracted by aqueous sulfite was a measure of the formation of these organic iodine compounds. The procedure outlined in Figure 3 was used to detect the presence of non-extractable compounds of iodine.

The effect of ordinary laboratory light on the formation of these non-extractable iodine compounds was investigated with a procedure identical to that shown in Figure 3 with two exceptions: a) the platinum foils were allowed to remain in the iodine solutions throughout the duration of the experiment, and b) one of these solutions, beginning with the activation step, was kept continuously in the dark.

Measurements of Radioactivity. The liquid samples were counted in a well-type scintillation detector to expected standard deviations of one per cent or less.

As indicated in Figure 1, it was necessary to count activity on the platinum foils as well as in solutions. Rather than dissolving the foils in aqua regia and diluting the solutions to the mark in a counting tube (a 15 by 125 mm. Pyrex test tube), 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 a platinum foil with the counting rate of the solution produced by dissolving the foil in aqua regia and diluting to the mark. This ratio was found to be 2.31 ± 0.01 . It is noteworthy that in the dissolution of an active foil in aqua regia, at room temperature, over four hours, at least 99% of the adsorbed iodine-131 was recovered.

Fig.-3. Procedure used to investigate the effects of light and platinum on the stability of nonaqueous iodine solutions.

Chemicals. Carrier-free iodide-131 was obtained from the Oak Ridge National Laboratory. Stock solutions of carrier-free iodide-131 were prepared by inoculation of freshly prepared 0.001 M sodium sulfite with the Oak Ridge activity.

Spectro Grade cyclohexane and methyl alcohol, obtained from Eastman Kodak, were used without further purification.

Baker Analyzed Reagent Grade nitrobenzene was distilled in the dark, under a nitrogen atmosphere, through a twenty-plate fractionating column, except where otherwise indicated.

Mallinckrodt perchloric acid was fumed at 165° for an hour in a platinum crucible, cooled, and immediately diluted with water. Prepurified Matheson nitrogen was passed through the perchloric acid during the heating and cooling process.

Distilled water was redistilled from alkaline permanganate in an all-Pyrex still.

Fisher Certified Reagent Grade iodine was resublimed under vacuum.

Mallinckrodt Reagent Grade sodium sulfite and benzene were used without further purification except where otherwise indicated in the case of the benzene.

Reagent Grade 30% hydrogen peroxide, obtained from Baker and Adamson, was used without further purification.

Spectro Grade carbon tetrachloride, obtained from Matheson, Coleman and Bell, was used without further purification.

Results and Discussion

Adsorption of Carrier-Free Iodine-131 from Aqueous Solutions by Platinum Foil.

The results of the studies of the adsorption of iodine-131 from dilute sodium sulfite and dilute sodium sulfite-perchloric acid solutions are summarized in Tables 1, 2, 3, 4, 5, and 6. In all instances the experiments were carried out in the presence of ordinary fluorescent light.

The results in Table 1 indicate that the per cent adsorption of iodine-131 increased with a decrease in sodium sulfite concentration and an increase in perchloric acid concentration. Also, the per cent adsorption increased with time and was generally greater than 90% over two hours from the acidic solutions. In these experiments the per cent recovery, based on activity initially present in the stock solutions of iodine-131, ranged from 98% to 100%. The most consistent results were achieved with a sulfite concentration of 10^{-5} molar and an acid concentration of 0.001 molar or greater.

The results in Table 2 show that aging the stock solution or reaction mixture had little effect upon the adsorption of iodine-131. The per cent activity adsorbed was significantly less than expected (see Table 1). In this connection it is noteworthy that different shipments of Oak Ridge activity were used for Tables 1 and 2.

The results in Table 3 show that the per cent adsorption of carrier-free iodine-131 by iodinated platinum foil was virtually the same as that found for platinum foil (see Table 2). The shipment of iodine-131 used here was the same as that used to obtain the results shown in Table 2. With subsequent shipments of iodine-131, the iodinated foils adsorbed about 93% of the activity. Generally, adsorption of activity significantly decreased, often to values as low as 50%, when the stock solutions were prepared from shipments kept 6 weeks or longer.

The data in Table 4 show that the per cent carrier-free activity adsorbed decreased with a decrease in the iodination time, but was independent of the concentration of the iodinating solution.

The results of experiments designed to study the per cent adsorption of carrier-free activity from acidic solutions containing hydrogen peroxide are summarized in Table 5. It is seen that although the presence of a moderate amount of hydrogen peroxide (0.02 M) caused the per cent adsorption to decrease, small quantities of hydrogen peroxide (0.002 M) had no significant effect.

It is necessary to know the extent of the loss of iodine from solution, via adsorption on the platinum foil, during the activation process; adsorption of small quantities of iodine could lead to a decreased and uncertain concentration of a dilute iodine solution. The results of experiments carried out to determine the decrease in iodine concentration during the activation process are given in Table 6. Additional experiments, not included in Table 6, were carried out to determine the amount of iodine adsorbed on a foil immersed in 10^{-4} M molecular iodine in cyclohexane, over relatively long periods; after sixteen hours this value was found to be $1 \times 10^{-9} \pm 10\%$ mole of iodine per cm^2 . Because increasing the time to seventy-two hours did not result in further adsorption, we concluded the foregoing value to represent the saturation value of the foil. This value is in good agreement with those found by other investigators^{1,2,3,4} and with the value calculated from atomic radii of platinum and iodine assuming a monolayer of iodine. From the data in Table 6 it is possible to calculate an expected loss of iodine during activation with non-iodinated foils. For example, a loss of approximately 6% of the iodine present in 5-ml. of a 10^{-6} molar iodine solution would be expected over a two hour activation period. However, by using active foils which had been iodinated for 16 hours or more in 10^{-4} molar iodine, to achieve saturation, the loss of iodine is virtually eliminated.

Table 1

Adsorption of Carrier-Free Iodine-131 by Platinum^a, from Aqueous Solutions, at Room Temperature, Over 0.5, 1 and 2 Hours.

Composition of Reaction Mixture ^{b,c}	Iodine-131 Adsorbed, % ^{d,e}		
	Over 0.5 hour	Over 1 hour	Over 2 hours
0.001 M Na_2SO_3	0.1, 1.0, 19	--	13, 3, 29
0.001 M Na_2SO_3 0.001 M HClO_4	8, 39, 71	--	61, 99, 99
0.001 M Na_2SO_3 0.1 M HClO_4	19, 77, 78	--	74, 99, 99
0.00001 M Na_2SO_3	7, 32, 65	--	45, 93, 78
0.00001 M Na_2SO_3 0.001 M HClO_4	54, 84, 89	--	89, 91, 96
0.00001 M Na_2SO_3 0.1 M HClO_4	60, 85, 91	--	92, 89, 92
0.00001 M Na_2SO_3 1.0 M HClO_4	--	94, 96	--

- a) The foils were subjected to pretreatment A.
- b) The Oak Ridge iodine-131 solution was, in all instances, less than 2 weeks old.
- c) The stock solution (see Figure 1) was, in all instances, less than 48 hours old.
- d) 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.
- e) A different activated foil was used for each value.

Table 2

The Effect of the Age of the Stock Solution and the Reaction Mixture^a
on the Adsorption of Carrier-Free Iodine-131 by Platinum^b.

Age of Stock Solution, hours	Age of Reaction Mixture, hours	Iodine-131 Adsorbed, % ^e
0 ^c	0	67, 66, 67, 64, 69
24 ^c	0	80, 55, 64
42 ^c	0	61, 85, 77
0 ^d	20.5	62, 58
0 ^d	30	68, 61

- a) The composition of the reaction mixture was: 0.001 M Na₂SO₃, 0.1 M HClO₄.
- b) The foils were subjected to pretreatment A. Adsorption took place at room temperature over 0.5 hour.
- c) The Oak Ridge solution, which represents a different shipment from that used in Table 1, was less than one week old. The stock solutions were aged in aluminum-capped counting tubes.
- d) The Oak Ridge solution was the same as in note c, but was two weeks old. The reaction mixtures were aged in 12-ml. glass-stoppered centrifuge tubes.
- e) These numbers represent maximum values because the foils were counted in the water-washed reaction vessels which may have contained adsorbed activity. Such adsorption, however, was previously found to be negligible (see Table 1, note d).

Table 3

Adsorption of Carrier-Free Iodine-131 by Iodinated Platinum
Foil^a at Room Temperature^b.

Time, hours	Adsorption, %
0.25	44
0.50	84, 92, 94
1.0	84

- a) The foils were subjected to pretreatment A, immersed in 0.0001 M iodine in cyclohexane for 16 hours, washed with cyclohexane and, subsequently, dried in the oven for 1 hour at 110°.
- b) The reaction mixture was 0.00001 M in Na_2SO_3 and 0.001 M in HClO_4 .

Table 4

Adsorption of Carrier-Free Iodine-131 by Platinum Foil which was Iodinated^a for Varying Times and at Various Iodine Concentrations^{b,c}.

Time of Iodination, hours	Iodine Concentration in Iodinating Solution, M	Adsorption, %
2	10^{-4}	52, 59 ^d
2	10^{-4}	57, 73 ^e
24	10^{-3}	90, 91 ^f
24	10^{-4}	91, 91 ^f
24	10^{-5}	92, 91 ^f

- a) The foils were subjected to pretreatment A, immersed in iodine in cyclohexane for the predetermined time, washed with cyclohexane and, subsequently, dried in the oven for 1 hour at 110°.
- b) The reaction mixture was 0.00001 M in Na_2SO_3 and 0.1 M in HClO_4 .
- c) The foils were activated for 1 hour at room temperature.
- d) The Oak Ridge solution was 60 days old.
- e) The Oak Ridge solution was 12 days old and a different shipment from that used for notes d and f.
- f) The Oak Ridge solution was 1 month old.

Table 5

Adsorption of Carrier-Free Iodine-131 by Platinum Foil and Iodinated Platinum Foil from Solutions Containing Hydrogen Peroxide.^a

Hydrogen Peroxide Concentration, M	Adsorption, % ^b	
	I ^c	II ^c
0.002	92, 88	91, 64
0.02	55, 60	20, 36

- a) The reaction mixture was 0.00001 M in Na_2SO_4 , 0.1 M in HClO_4 , and contained hydrogen peroxide at the two given concentrations.
- b) The adsorption was carried out for 1 hour at room temperature.
- c) The experiment differed as follows:
- I. The foils were subjected to pretreatment A.
 - II. The foils were subjected to pretreatment A, immersed in iodine in cyclohexane (0.0001 M) for 24 hours, washed with cyclohexane and, subsequently, dried in the oven for 1 hour at 110°.

Table 6

Adsorption of Iodine-(127 and 131) on Platinum Foil^a During
Iodination^b at Room Temperature.

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

- a) The size of the platinum foil was $0.50 \times 1.50 \times 0.00625$ cm.; the area of each foil was 1.5 cm^2 .
- b) The iodination was carried out with 5 ml. of a cyclohexane solution of iodine made active by activating for two hours at room temperature with an active iodinated foil.
- c) The concentrations of iodine in the iodinating solutions were:
- I. 1×10^{-5} molar.
 - II. 1×10^{-6} molar.
 - III. 1×10^{-7} molar.

Loss of Iodine from Iodinated Foils to Various Organic 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 Figure 1 was followed with the exception that the active iodinated foil (#1) was added to 5 ml. of pure nonaqueous solvent. The results, summarized in Table 7, point up 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 concentration provided the initial iodine concentration was on the order of 10^{-4} molar or greater.

The Exchange Between Molecular Iodine in Cyclohexane and Iodine-131 Adsorbed on Platinum Foils. The data in Table 8 show that the percent exchange with non-iodinated active foils was essentially independent of time over the range from 0.25-2.5 hours. Aging of these foils decreased the per cent exchange significantly. For iodinated active foils the per cent exchange increased somewhat with time over the range from 0.25-2.0 hours. For any given reaction time the per cent exchange was greater for iodinated foils than for non-iodinated foils. In a subsequent experiment it was found that aging an active iodinated foil at room temperature over four hours decreased the exchange from the expected value of 45% to 30%.

A comparison of the data in Table 9 with those in Table 8 reveals that decreasing the iodine concentration from 10^{-4} M to 10^{-6} M decreased the per cent exchange for both iodinated and non-iodinated foils.

Inasmuch as the usual iodination time was 16-24 hours it was of interest to determine the effect of decreasing the iodination time on the per cent exchange. The data in Table 10 show that reducing this time to 2 hours had little effect on exchange, which was generally found to be 40-45% over 16-24 hours; the low values

Table 7

Iodine Removed from Active Iodinated Foils^a by
Various Organic Solvents.

Solvent	Iodine-131 Removed, %			
	Time, hours			
	1	2	19.1	20.5
Nitrobenzene ^b	45	50	66	--
Nitrobenzene	--	--	--	64
Benzene ^c	0.01	0.01	1.5	--
Benzene	--	--	--	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 0.0001 M iodine in cyclohexane, washed and then dried in an oven at 110° for 1 hour. They were then activated in 0.001 M sulfite and 0.1 M perchloric acid for 1 hour, washed and dried in the oven for 2 hours at 110°. The foils were then used immediately.
- b) This nitrobenzene was pretreated by allowing it to stand for 1 week with 0.001 moles of iodine per liter in it, then reducing the iodine with sulfite and distilling, under nitrogen and in the dark, through a 20 plate column.
- c) This benzene was Phillips research grade.

for the 10^{-4} M iodinating solutions, with 24 hour iodination time, shown in Table 10, are atypical. The data in Table 10 also show that the per cent 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 10^{-3} to 10^{-5} molar. Two experiments showed that measurable exchange occurred over 15 seconds with active foils which had been iodinated for 24 hours in 10^{-5} molar iodine.

The data in Table 11 show that the addition of hydrogen peroxide to the active aqueous reaction mixture did not alter the per cent exchange when non-iodinated foils were used; however, with iodinated foils the per cent exchange decreased (see Table 8).

Tables 12, 13 and 14 summarize the results of exchange experiments in cyclohexane, benzene, nitrobenzene, methanol and carbon tetrachloride. Tables 12 and 13 show that the per cent exchange between active non-iodinated foils and 0.01 molar iodine in nitrobenzene and benzene is virtually the same. Table 12 further shows that the per cent exchange increases with increasing iodine concentration and time. The results in Table 14 show that the per cent exchange between active iodinated foils and 10^{-4} molar iodine, in the aforementioned solvents, is essentially independent of the solvent.

Table 8

Exchange between Molecular Iodine in Cyclohexane (0.0001 M)
and Iodine-131 Adsorbed on Platinum^a, at Room Temperature.

Time, hours	Exchange, % ^b		
	I ^c	II ^c	III ^c
0.25	30	12	33
0.50	18, 19	4.7	32
1.0	25, 22	5.6	37
2.0	--	23	46
2.5	28	--	--

a) The foils were subjected to pretreatment A.

b) A different activated foil was used for each value.

c) The experiments differed as follows:

- I. The foils were activated (see Figure 1, foil #1) just prior to use.
- II. The foils were activated, dried in the oven at 110°, for 2 hours, 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 placed in 0.0001 M iodine in cyclohexane for 16 hours, at room temperature, in ordinary laboratory light. The foils were then activated and used immediately.

Table 9

Exchange between Molecular Iodine in Cyclohexane (10^{-6} M) and Iodine-131 Adsorbed on Platinum^a, at Room Temperature.

Time, hours	Exchange, % ^b	
	I ^c	II ^c
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) A different activated foil was used for each value.
- c) The experiments differed as follows:
- I. The foils were activated (see Figure 1, foil #1) just prior to use.
 - II. The inactive foils were iodinated in 0.0001 M iodine in cyclohexane for 16 hours, at room temperature, in ordinary laboratory light. The foils were then activated and used immediately.

Table 10

Exchange between Molecular Iodine in Cyclohexane (0.0001 M) and Iodine-131 Adsorbed on Platinum Foil^a, which was Iodinated over Two Different Intervals, and at Various Iodine Concentrations, at Room Temperature.

Time of Iodination, hours,	Time of Exchange	Exchange, % ^{b,c}		
		I	II	III
2	2 hours	--	40, 41	--
2	2 hours ^d	--	39, 46	--
24	15 sec.	--	--	7, 26
24	2 hours	26, 14	10, 24	24, 26

- a) The foils were subjected to pretreatment A, immersed in iodine in cyclohexane for the allotted time, washed with cyclohexane and, subsequently, dried in the oven for 1 hour at 110°.
- b) A different foil was used for each value.
- c) The experiments differed as follows:
- I. The concentration of the iodinating solution was 0.001 M in molecular iodine.
 - II. The concentration of the iodinating solution was 0.0001 M in molecular iodine.
 - III. The concentration of the iodinating solution was 10^{-5} M in molecular iodine.
- d) 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 11

Exchange between Molecular Iodine in Cyclohexane (0.0001 M) and Iodine-131 Adsorbed^a, from Solutions Containing Hydrogen Peroxide on Platinum Foil.

Hydrogen Peroxide, M	Exchange, % ^b	
	I ^c	II ^c
0.002	21	20
	26	29
0.02	31	39
	21	29

- a) The reaction mixture was 0.00001 M in Na_2SO_4 , 0.1 M in HClO_4 , and contained hydrogen peroxide at the two given concentrations.
- b) The exchange was carried out for 2 hours at room temperature. (See Table 5 for the associated adsorption data.)
- c) The experiments differed as follows:
- I. The foils were subjected to pretreatment A.
 - II. The foils were subjected to pretreatment A, immersed in iodine in cyclohexane (0.0001 M) for 24 hours, washed with cyclohexane and, subsequently, dried in the oven for 1 hour at 110°.

Table 12

Exchange between Molecular Iodine in Nitrobenzene and Iodine-131 Adsorbed on Platinum^a, at Room Temperature, in the Absence of Light.

Time, hours	Exchange, % ^{b,c}			
	$2 \times 10^{-5} \text{ M I}_2$	$2 \times 10^{-4} \text{ M I}_2$	$2 \times 10^{-3} \text{ M I}_2$	$1 \times 10^{-2} \text{ M I}_2$
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) 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.
- c) The foils were activated (see Figure 1, foil #1) just prior to use.

Table 13

Exchange between Molecular Iodine in Benzene (0.01 M) and Iodine-131

Adsorbed on Platinum, at Room Temperature.

Time, hours	Exchange, % ^{b,c}
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) After a specified time the foil was removed, counted, and then returned to the reaction vessel, etc..
- c) The foil was activated (see Figure 1, foil #1) just prior to use.

Table 14

Exchange between Molecular Iodine in Organic Solvents (0.0001 M) and Iodine-131 Adsorbed on Iodinated Platinum Foil^a, at Room Temperature, Over Two Hours.

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

- a) The platinum was subjected to pretreatment A, immersed in iodine in cyclohexane (0.0001 M) for 24 hours, washed with cyclohexane, and subsequently, dried in the oven for 1 hour at 110°.
- b) A different foil was used for each value.

The Effect of Light and Platinum on the Stability of Nonaqueous Iodine

Solutions. It was thought possible that platinum foil, in the presence or absence of light, could catalyze the formation of organic iodine compounds with either the solvent itself or impurities in the solvent during the activation of the nonaqueous iodine solutions. Although the data in Tables 15 and 16 show that a small fraction of the activity in the nonaqueous solutions was non-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.

The Exchange Between Molecular Iodine in Cyclohexane and Iodine-131 Adsorbed on Platinum Foils, at 50°C. The dependence of the per cent exchange, at 50°C, on reaction time and pretreatment of the foils, is summarized in Figures 4, 5, 6, and 7. The rate of exchange generally decreased significantly after about 2 hours. Because of the wide variations in the plots of data obtained from identical experiments (see Figures 4, 5, and 7), the relative effectiveness of any one of the pretreatments cannot be assessed.

Table 15

The Effect of Platinum on the Stability of Molecular Iodine Solutions in Cyclohexane in the Presence of Ordinary Laboratory Light.

Time, hours	Iodine concentration, M	Activity not extracted by Na ₂ SO ₃ , % ^b	
		Pt present ^c	Pt absent
0	10 ⁻³	1.0	2.6
2	10 ⁻³	1.5	2.2
6.75	10 ⁻³	2.2	3.0
0	10 ⁻⁵	9.6	6.8
3	10 ⁻⁵	2.3	2.5
16.5	10 ⁻⁵	3.9	6.5

- a) The foil was subjected to pretreatment A, immersed in iodine in cyclohexane (0.0001 M) for 24 hours, washed with cyclohexane and, subsequently, dried in the oven for 1 hour at 110°. The foil was then activated (see Figure 1, foil #1) for 2 hours at room temperature.
- b) A different foil was used for each value.
- c) The foil was the same foil that was used to activate the solution.

Table 16

The Effect of Light on the Stability of Molecular Iodine Solutions in
Cyclohexane in the Presence of Platinum^a.

Time, hours	Iodine concentration, M	Activity not extracted by Na ₂ SO ₃ , % ^{b,c}	
		Light present	Light absent ^d
1.0	10 ⁻³	0.80	0.14
3	10 ⁻³	1.3	0.33
1	10 ⁻⁵	0.87	0.54
3	10 ⁻⁵	1.1	0.62

- a) The foil was subjected to pretreatment A, immersed in iodine in cyclohexane (0.0001 M) for 24 hours, washed with cyclohexane and, subsequently, dried in the oven for 1 hour at 110°. The foil was then activated (see Figure 1, foil #1) for 2 hours at room temperature.
- b) A different foil was used for each value.
- c) The foil was the same foil that was used to activate the solution.
- d) Light was excluded by wrapping the reaction vessel in aluminum foil.

Fig. 4. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment A) and 0.0001 M molecular iodine in cyclohexane; at 50°C.

Fig. 5. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment B) and 0.0001 M molecular iodine in cyclohexane, at 50°C.

Fig. 6. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment C) and 0.0001 M molecular iodine in cyclohexane, at 50°C.

Fig. 7. Exchange between carrier-free iodine-131 adsorbed on foil (pretreatment D) and 0.0001 M molecular iodine in cyclohexane, at 50°C.

Summary

On the basis of the results reported here, it would appear that the most suitable procedure for the inoculation of a dilute ($\geq 10^{-4}$ M), dry, nonaqueous solution of molecular iodine with iodine-131 is as follows: a) iodinate a platinum foil, which has been subjected to pretreatment A, for 16 to 24 hours; b) immerse the iodinated platinum foil in an acidic solution of carrier-free iodine-131 and stir for 0.5 to 2 hours at room temperature; c) wash the activated foil with water and dry in an oven for 1 to 2 hours at 110°C; d) immerse the dried active foil in a nonaqueous solution of molecular iodine and stir for 1 to 2 hours at room temperature.

Each nonaqueous solvent used and each batch of the particular solvent should be tested with regard to the following items: a) the extent to which the pure solvent removes iodine from an iodinated foil and conversely, the extent to which a non-iodinated foil removes iodine from a nonaqueous solution of a known iodine concentration, and, b) the fraction of activity in the final active solution which is not extracted by both aqueous sodium sulfite and aqueous potassium iodide.

Item (a) increases in importance as the concentration of the desired iodine solutions decreases because these losses may change the initial concentration of an iodine solution significantly during the activation procedure. This altering of the iodine concentration may be obviated by: 1) reducing the activation time for the iodine solutions from 1 to 2 hours to, on the order of, one minute, and/or, 2) reducing the size of the platinum foil. In the event that these changes in the procedure are ineffective then it becomes necessary to activate more concentrated solutions which can subsequently be diluted to the desired concentration.

Generally, using Oak Ridge iodine-131 shipments less than 30 days old, overall activity yields were about 40%.

Although activation of iodine solutions at 50° results in slightly higher activity yields this small advantage may be offset by the troublesome possibilities of volatilization of iodine and/or solvent and reactions between the solvent and the molecular iodine.

C. The Kinetics of Isotopic Exchange Reactions. Solvent Effects.

Preliminary studies¹ of the isotopic exchange of iodine atoms between tetra-

(1) See Progress Report No. 6, Contract No. AT(11-1)-733-12

tetramethylammonium iodide and methyl iodide, in nitrobenzene, indicated that this reaction proceeds at a rate slow enough at 24.9° to allow the eventual determination of the temperature dependence of the specific reaction rate. Plots of log (1-fraction exchange) versus time, however, were found to be concave upward after about two half-lives, particularly for reaction mixtures where the tetramethylammonium iodide concentration was as low as 10^{-7} molar. This departure from linearity may be explained by postulating the slow oxidation of iodide to molecular iodine which, in turn, exchanges relatively slowly with methyl iodide. Therefore, in order to better interpret these and future data, it was decided to study the exchange of iodine atoms between molecular iodine and methyl iodide in nitrobenzene.

The numerous exchange experiments carried out here were characterized by the non-reproducibility of the results. The exchange reaction was catalyzed by unidentified impurities in the nitrobenzene and, furthermore, was found to depend on the age of stock solutions of iodine in nitrobenzene and on the age of reaction mixtures; the reaction was not affected by the aging of solutions of methyl iodide in nitrobenzene. Such unusual and unpredictable behavior has also been observed by other workers^{2,3,4,5} in their studies of exchange reactions between alkyl

(2) Behrens, H. and Maddock, A.G., J. Chem. Phys., 22, 1139 (1954); Radioisotope Conference, 2nd, Oxford, 1954, Proceedings, Vol. 2, pp. 33-40.

(3) Daxbee, L.R. and Harris, G.M., J. Phys. Chem., 61, 111 (1957).

(4) Cohen, E.D. and Trumbore, C., J. Am. Chem. Soc., 87, 954 (1965).

(5) Noyes, R., J. Am. Chem. Soc., 70, 2614 (1948); *ibid.*, 83, 1547 (1961).

iodides and molecular iodine. The detailed nature of these observations remains to be explained.

Recent work in our laboratory has revealed that plots of $\log$ (1-fraction exchange) versus time for the methyl iodide - tetrabutylammonium iodide exchange reaction are, indeed, linear provided account is taken of the small degree of hydrolysis of methyl iodide during the separation procedure. Consequently, for the present, we have abandoned further studies of the methyl iodide - iodine exchange reaction and have resumed an investigation of the methyl iodide - tetrabutylammonium iodide exchange reaction in nitrobenzene.

Experimental

Chemicals. - Allied Chemical Reagent Grade iodine was sublimed under vacuum.

Baker's Analyzed Reagent Grade benzene was distilled under Matheson "pre-purified" nitrogen; only the middle fraction was retained.

Eastman Kodak methyl iodide was distilled from silver foils under "pre-purified" nitrogen in the dark; only the middle fraction was retained.

Baker's Reagent Grade sodium bisulfite was used without further purification.

Distilled water was redistilled from alkaline permanganate in an all-Pyrex still.

Carrier-free iodine-131, obtained from Oak Ridge, was stored as a stock solution in 0.0005 M sodium sulfite.

Baker's Reagent Grade aluminum oxide was used without further purification.

Baker's Analyzed Reagent Grade nitrobenzene was fractionally distilled from alumina, under vacuum, in the dark, through a 20-plate Oldershaw column. The distillation system had been previously evacuated and flushed with "prepurified" nitrogen several times and subsequently maintained under vacuum; only the middle fraction was retained.

Preparation of Reactant Solutions. - Methyl iodide solutions were prepared by dilution of known volumes of methyl iodide to the mark with nitrobenzene.

Iodine solutions were prepared by dissolving weighed amounts of iodine in nitrobenzene and subsequently diluting to the mark with nitrobenzene.

Nitrobenzene solutions of iodine were inoculated with iodine-131 via isotopic exchange with iodine-131 adsorbed on a platinum foil. This procedure is described elsewhere⁶.

(6) See accompanying Progress Report, Part B.

Procedure for Exchange Reaction Experiments. - The reactant solutions and reaction vessel (25-ml. glass-stoppered volumetric flask) were brought to the reaction temperature ($24.90 \pm 0.01^\circ$) in a constant-temperature water-bath over 30 minutes. Five ml. of each reactant solution was then pipetted into the reaction vessel and mixed well. The reaction vessel was wrapped with aluminum foil to exclude light. All transfer and sampling processes were conducted in the dark. At appropriate times, 1 ml. of the reaction mixture was transferred to a glass-stoppered 15-ml. centrifuge tube which contained 3 ml. of benzene and 4 ml. of 0.1 M sodium bisulfite and the whole shaken vigorously for 2 minutes. The resulting two-phase system (with methyl iodide in the organic layer and iodine reduced to iodide in the aqueous phase) was centrifuged and separated. In general, the organic phase was washed with another 4-ml. portion of 0.1 M sodium bisulfite; this wash was added to the first aqueous extract. In this separation procedure less than 0.1% of the molecular iodine was retained in the organic phase and less than 1.5% of the methyl iodide was extracted into the aqueous phase.

For most of the reaction mixtures, the reaction was followed over a period long enough so that about 60% exchange had taken place. In some instances, as much as 10% zero-time exchange was observed. Also, in some experiments plots of $\log$ (I-fraction exchange) versus time were linear only over a range from 10% to 60% exchange and then departed from linearity in a manner consistent with an increase in the rate of reaction. In each instance, however, the half-time for exchange was obtained from the linear portion of the plot of $\log$ (I-fraction exchange) versus time.

Measurement of Radioactivity. - The liquid samples were counted with a well-type scintillation detector to expected standard deviations of 1% or less. It was experimentally determined that there was no need to correct counting rates for the difference in densities between benzene samples and aqueous samples.

Results and Discussion

Reaction between Unidentified Impurities in Distilled Nitrobenzene and Molecular Iodine. - Early in the course of studying the exchange reaction between molecular iodine and methyl iodide in nitrobenzene it was found that unidentified impurities in the nitrobenzene reacted with iodine to yield iodo-species which were not extractable with 0.1 M sodium bisulfite. Furthermore, it was found that these unknown iodine compounds were high-boiling and remained in the still-pot on vacuum distillation of nitrobenzene which had been treated with molecular iodine inoculated with iodine-131.

The results of experiments designed to study the growth of these iodo-impurities in nitrobenzene solutions of various molecular iodine concentrations are summarized in Table 1. These results suggest that the concentration of the iodo-impurities in the 10^{-2} M iodine solution reached a saturation value in a few days. By assuming that iodine combined with impurities in the ratio of 1:1, it is estimated that the concentration of the impurities in nitrobenzene was about 2×10^{-4} molar.

Inasmuch as these iodo-impurities remained in the still pot on vacuum distillation of iodinated nitrobenzene (see above), it was of interest to determine whether nitrobenzene could be further purified by exposure to iodine with subsequent distillation. The following purification procedure was adopted. Distilled nitrobenzene, containing molecular iodine at a concentration of 10 grams per liter, was stored at room temperature in the dark. After a given time had elapsed, the nitrobenzene solution was washed with 1 M sodium bisulfite and, subsequently, with several portions of water. This wet nitrobenzene was then dried over alumina in the dark for 24 hours and then distilled under vacuum.

The data in Table 2 show that nitrobenzene can, indeed, be further purified by pretreatment with molecular iodine. Furthermore, the degree of purity increased with an increase in the iodination time. Also, from these data, it is estimated that the concentrations of the impurities in nitrobenzene A and nitrobenzene B were 5×10^{-6} M and 3.7×10^{-6} M, respectively.

Effect of Impurities on the Reaction Rate. - Experiments were carried out to determine whether the impurities in distilled nitrobenzene would affect the rate of the exchange reaction. By using iodine-pretreated nitrobenzene as the solvent it was possible to increase the concentration level of these impurities with the addition of known quantities of non-pretreated distilled nitrobenzene. The results, summarized in Table 3, show that these impurities had a pronounced catalytic effect on the exchange reaction.

Effect of Aging of Reactant Iodine Solutions on the Reaction Rate. - Under a given set of conditions, as shown in Table 4, the half-time for the exchange reaction decreased with increased age of the reactant iodine solutions. This aging effect was not detected in similar experiments where the nitrobenzene used had been pretreated with iodine for at least one week. From the foregoing results it is clear

that this aging effect is dependent on the concentration of the impurities in nitrobenzene. However, attempts to correlate half-times with the amounts of non-extractable activity were unsuccessful.

Effect of Aging of Reactant Methyl Iodide Solutions on the Reaction Rate. -

For a given set of conditions the half-time for the exchange reaction was found to be independent of the age of the reactant methyl iodide solution.

Effect of Aging of Reactant Mixtures on the Reaction Rate. - An inactive reaction mixture was prepared from fresh reactant solutions of methyl iodide and iodine in nitrobenzene which had been pretreated with iodine for at least one week. At appropriate times a portion of the reaction mixture was inoculated with iodine-131 and the half-time for exchange determined. The results, summarized in Table 5, show that the half-time of the reaction decreased with the increase in age of the reactant mixture.

On the basis of the foregoing discussions, it was not expected that the aging of the methyl iodide or the iodine in the reaction mixture would have any effect on the rate of exchange. It is believed, therefore, that the observed aging effect may be attributed to a reaction between iodine and methyl iodide or some impurity in methyl iodide to yield a species that catalyzed the reaction.

Table 1

Growth of Iodo-Impurities in Nitrobenzene Solutions of Molecular Iodine.

Time, Hrs.	Iodo-impurities in various iodine solutions, % ^a				
	1×10^{-2} M	4.3×10^{-3} M	0.8×10^{-3} M	1×10^{-4} M	0.8×10^{-5} M
1	1.8	2.5	2.9	3.6	2.5
20	1.9	4.3	8.7	11.1	5.5
40	1.9	4.5	10.7	12.7	8.7
60	1.9	4.9	13	12.8	9.2

a. Percentage of total activity non-extractable with aqueous sodium bisulfite.

Table 2

Growth of Iodo-Impurities in Iodine-Pretreated Nitrobenzene.

Time, hrs.	Iodo-impurities in various iodine solutions, % ^a			
	In nitrobenzene A ^b		In nitrobenzene B ^c	
	4.65×10^{-3} M	3.97×10^{-4} M	9.85×10^{-3} M	4.50×10^{-5} M
8	--	--	0.03	--
24	0.11	0.61	--	0.75
40	--	--	0.037	--
48	--	--	--	0.93
65	--	--	0.037	--
72	--	0.80	--	0.96
96	--	--	--	1.03
120	--	1.22	--	--

a. Percentage of total activity non-extractable with aqueous sodium bisulfite.

b. Nitrobenzene pretreated with iodine over 1 day.

c. Nitrobenzene pretreated with iodine over 2 days.

Table 3

Effect of Impurities on the Half-Time for the Exchange Reaction between
Methyl Iodide and Iodine in Iodine-Pretreated Nitrobenzene^a,
at 24.9°, in the Dark.

Impure nitro- benzene, % ^b	$[\text{CH}_3\text{I}]^c$ M	$[\text{I}_2],$ $\text{M} \times 10^5$	Age of I_2 solution, hours ^d	Non-ext. activity, at $t = 0$, % ^e	$t_{1/2}$, hours
0	0.9633	2.482	24	0.75	3.83
2	0.9633	2.482	24	6.5	1.33
5	0.9633	2.482	24	8.6	0.52
10	0.9633	2.482	24	12.5	0.042

- a. Nitrobenzene pretreated with iodine over 2 days.
- b. Per cent, by volume, of distilled but untreated nitrobenzene.
- c. Freshly prepared solutions.
- d. Age of iodine solution prior to use.
- e. Percentage of total activity non-extractable with aqueous sodium bisulfite.

Table 4

Effect of Aging of Reactant Iodine Solutions on the Half-Time
for the Exchange Reaction between Methyl Iodide and Iodine
in Iodine-Pretreated Nitrobenzene, at 24.9°, in the Dark.

Nitro- benzene	$[\text{CH}_3\text{I}]^a$ M	$[\text{I}_2]$, $\text{M} \times 10^5$	Age of I_2 solution, hours ^b	Non-ext. activity at $t = 0$, % ^c	$t_{1/2}$, hours
A ^d	0.9633	2.302	15	0.88	3.17
A	0.9633	2.302	96	1.8	0.63
A	0.9633	18.59	15	0.72	65
A	0.9633	18.59	96	1.9	45
B	0.9633	2.482	24	0.75	3.83
B ^e	0.9633	2.482	48	0.93	2.83
B	0.9633	2.482	72	0.97	1.92
B	0.9633	2.482	96	1.03	1.47
B	0.9633	19.86	24	0.61	63
B	0.9633	19.86	72	0.80	58
B	0.9633	19.86	96	1.21	55

a. Freshly prepared solutions.

b. Age of iodine solution prior to use.

c. Percentage of total activity non-extractable with aqueous sodium bisulfite.

d. Nitrobenzene pretreated with iodine over 1 day.

e. Nitrobenzene pretreated with iodine over 2 days.

Table 5

Effect of the Age of a Reaction Mixture^a on the Half-Time for the Exchange Reaction between Methyl Iodide and Iodine in Nitrobenzene^b, at 24.9°, in the Dark.

Age of reaction mixture, hours	$t_{1/2}$, hours
2	155
24	80
48	65
72	53
96	50

- a. Composition of reaction mixture: 0.916 M methyl iodide, 4.562 M iodine.
- b. Nitrobenzene was pretreated with iodine for 2 weeks.

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