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The Electrolytic Oxidation
of Carrier-Free Iodide-131

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University of California
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**The Electrolytic Oxidation
of Carrier-Free Iodide-131***

by

Darryl D. Jackson

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ABSTRACT

Solutions of carrier-free iodate- ^{131}I were prepared by electrolytic oxidation of iodide- ^{131}I in 0.01 M sodium bicarbonate solution at a graphite anode. The minimum anode potential necessary to carry out the oxidation was +0.79 volt vs. S.C.E.; above this the rate of the oxidation increased with increasing anode potential. The rate of the oxidation, in terms of the iodide fraction, was relatively independent of the total initial iodide concentration indicating that the reaction followed the first order rate law over the concentration range studied (carrier-free to 10^{-4} M iodide). Carrier-free iodate- ^{131}I solutions containing little extraneous material can be conveniently prepared in good yield using this method.

No evidence for the formation of periodate could be found when carrier-free iodide- ^{131}I in sodium bicarbonate or sodium carbonate solution was electrolyzed at anode potentials of up to +1.90 volts vs. S.C.E.

Several iodine species were produced when carrier-free iodide- ^{131}I in 0.01 M sulfuric acid solution was electrolyzed at a graphite anode. At anode potentials of +0.900 and +1.000 volt vs. S.C.E. a large fraction of the iodine was converted to species extracted by benzene but not back-extracted by aqueous iodide. At +1.500 volts vs. S.C.E. the activity was oxidized to iodate.

An all electronic potentiostat with good response time was designed and constructed from commercially available units. The potential of the controlled electrode could be varied over a range of ± 2 volts vs. the reference electrode and the regulation was better than ± 1 millivolt.

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Chapter 1

INTRODUCTION

1.1 General

The chemistry of materials at very low concentrations is becoming increasingly important. For elements such as astatine, radon, francium, actinium, promethium, and all the elements of atomic number greater than 96 which exist only as short-lived isotopes, our only knowledge of their chemical behavior is based upon their behavior at carrier-free concentrations. An accurate extrapolation from their observed behavior at carrier-free¹ concentrations to their predicted behavior at macro concentrations (which is desirable so that it can be compared with the known behavior at macro concentrations of related elements) depends upon a good knowledge of the general principles applicable to their chemical behavior at carrier-free concentrations (1).

The determination of fission product yields is important for a better understanding of the fission process. Determinations of this type require an understanding of the chemical behavior of the fission products at carrier-free concentrations.

The study of the chemistry of atoms, ions and molecules produced in nuclear reactions ("hot-atom" chemistry) obviously requires a knowledge of the chemistry of the materials at carrier-free concentrations.

Increasing use of radioactive materials in the medical field, both for diagnostic purposes and for treatment, requires that their chemistry

¹As used here the term "carrier-free" refers to an isotope to which no isotopic carrier has been deliberately added and in which no isotopic material can be detected by ordinary analytical methods.

be understood. Biological systems in general are known to be sensitive to extremely small quantities of materials. An investigation of this dependence would necessarily require an understanding of the chemistry of the materials at very low concentrations.

The chemistry of carrier-free iodine is of particular interest. Carrier-free iodide- ^{131}I is widely used for thyroid metabolism studies. Since the biological properties of the iodine depend upon its chemical form, it is necessary to have some understanding of the nature of the chemical behavior of tracer quantities of iodine in order to use it. One of the major problems encountered in the study of nuclear-reactor safety is the release of fission products into the environment. Radioiodine is the fission-product element that causes the greatest concern because of its volatility and its biological effects. In order to be able to effectively trap and contain the radioiodine released from a reactor, it is necessary to have some understanding of the chemical and physical behavior of iodine at carrier-free concentrations. A knowledge of the behavior of carrier-free iodine is also of interest in order that it might be compared with the behavior of astatine which is available only as carrier-free material.

In addition to the specific applications mentioned, the chemistry of materials at carrier-free concentrations is of general interest and studies of the behavior of materials at very low concentrations will contribute to the general chemical knowledge.

In most carrier-free materials the actual concentration of the substances is uncertain. Usually an analytical method of sufficient sensitivity to detect the small quantity of the tracer material is not

available; the material can be followed only by radioactivity measurements. The specific activity of the material can vary drastically because of inadvertent contamination of the carrier-free material with isotopic carrier. Therefore counting techniques cannot usually be employed to determine the concentration of the carrier-free material unless stable isotopes of the material are known not to exist. As a result of the uncertainty in the specific activity of carrier-free materials, the quantity measured is normally the fraction of the activity involved in the process.

Because of the very small quantity of the tracer material present in solutions of carrier-free materials, the loss of even a small amount of the tracer substance by reaction with impurities or adsorption on surfaces exposed to the solution may represent the loss of a large fraction of the total tracer material; in experiments with macro quantities the same total loss would represent a negligible fraction of the total material.

A greater fraction of the tracer material may exist in the form of an intermediate species at very low concentrations than would be present at macro concentrations. For example, an intermediate which is formed by a rate process in which the concentration of the reacting tracer material enters to a power less than one but which is consumed by a second order rate process, may have a much longer life at very low concentrations. This would result because the rate of formation of the intermediate would be increased at very low concentrations while the rate of consumption of the intermediate would decrease as the concentration was decreased yielding an increased fraction of the tracer material in the form of the

intermediate at tracer concentrations.

The equilibrium of a reaction may be affected by a change in concentration. If both species of the tracer material are soluble and both contain the same number of tracer atoms per molecule, the equilibrium will not be shifted with dilution. However, if both species in equilibrium do not contain the same number of tracer atoms per molecule the equilibrium will shift with dilution in a direction so as to decrease the quantity of the species containing the greater number of tracer atoms per molecule. All chemical equilibria, such as partition between solvents and oxidation-reduction potentials, are affected by dilution in the same manner so that at extremely low concentrations the chemical form of the major tracer species present may be different than that found at macro concentrations.

1.2 Previous Work

A detailed study of the chemistry of iodine at carrier-free concentrations was carried out by Kahn and Wahl (2). They identified five chemical species of iodine formed during the chemical oxidation of acid solutions of carrier-free iodide- ^{131}I based upon their solvent extraction and exchange behavior described as follows:

I_2 - "The behavior of the activity extracted into benzene from acid solution and back-extracted into water or aqueous potassium iodide is that expected for I_2 at low concentrations."

X - "The activity in this fraction is extracted from acid solution by benzene, is not back-extracted by water, or by aqueous solutions of potassium iodide, potassium iodate, ferrous sulfate, or sulfurous acid but is back-extracted by aqueous sodium hydroxide."

Y - "Same behavior as X except that it is not back-extracted by aqueous sodium hydroxide."

I^- - "The behavior of the activity not extracted from acid solution by benzene but extracted by a benzene solution of I_2 is that expected for iodide."

Z - "The behavior of the activity that is not extracted into benzene and does not exchange with I_2 is that expected for iodate. However, except under drastic oxidation conditions, little of the activity in this fraction is exchangeable with iodate ion."

Three of these iodine fractions (X, Y, and Z) do not correspond to any iodine species known to be stable at ordinary concentrations. They proposed that these unusual chemical fractions were the result of the reaction of a reactive form of iodine, formed during the oxidation, with trace impurities (organic and inorganic) in the solution or that fraction Z could be an inorganic ion or molecule containing iodine in an oxidation state intermediate between +1 and +5 which exists only at low concentration.

An additional study was made of the Z fraction by Eiland and Kahn (3). They reported that the Z fraction was made up of iodate plus at least two other iodine species. The predominant non-iodate component, R, was found to "react with hydriodic acid, sulfurous acid or sodium bicarbonate to yield water-soluble iodine species; no significant reaction was observed with iron (II). The reaction with sodium bicarbonate was irreversible, leading to iodine species rapidly exchangeable with molecular iodine at room temperature."

The R species was suggested to be an inorganic compound of iodine

or an organic compound formed by reaction between organic impurities in the solutions and some oxidized form of iodine.

Several investigators have reported discrepancies between the calculated and observed distribution of molecular iodine at low concentration between aqueous solutions and organic solvents. In the distribution of iodine between benzene and dilute sulfuric acid Kahn (4) found that the fraction of the iodine in the aqueous phase at low concentrations was greater than what would be expected considering the known iodine equilibria. Good and Edwards (5) observed a similar effect in a study of the distribution of iodine between carbon disulfide and aqueous solutions at various pH values. The experimental values of the distribution coefficient were much lower than calculated values at low iodine concentrations. Investigation of the distribution of iodine between carbon tetrachloride and aqueous solutions of various pH values by Wille and Good (6) showed the same phenomenon. There was a greater fraction of the iodine in the aqueous phase at low iodine concentrations than would be predicted from the known iodine equilibria.

Many workers (7-14) have observed the presence of unidentified iodine fractions in various commercial radioiodide solutions when the solutions were analyzed by paper chromatography. The properties of these iodine fractions do not correspond to any of the iodine species known to exist at macro concentrations. These unidentified iodine species were also found in aged solutions of carrier-free iodide-131 which had initially contained all of the activity in the form of iodide.

Eggleton and Atkins (15) using a gas chromatographic method identified methyl iodide as the principal iodine compound formed when

carrier-free iodine-131 was released into the atmosphere by oxidation of carrier-free iodide-131 or by heating irradiated uranium dioxide.

Several methods of preparing solutions of carrier-free iodate-131 employing chemical oxidizing agents to oxidize carrier-free iodide-131 have been described. Perkins and Kahn (16) described a procedure using nitric acid as the oxidizing agent. More recently Reynolds (17) described a method using chlorine dioxide which made it possible to prepare a solution of carrier-free iodate-131 essentially free of other materials.

All of these investigations of the chemical properties of carrier-free iodine have been conducted using chemical oxidizing and reducing agents. Electrolytic oxidation at a controlled anode potential offers an advantage in that it is not necessary to add large quantities of chemicals to the tracer solution as is the case when a chemical oxidizing agent is used. It also allows greater flexibility in the potential that can be employed. Since the value of the electrode potential can be precisely controlled and its magnitude can be varied over a large range, quantitative information as to the effect of various electrode potentials on the species existing in solution can be obtained. In some cases such information will allow determination of the potential of the oxidation-reduction couple of the species. A study of the electrolytic oxidation of carrier-free iodide-131 at controlled anode potentials would add to the general knowledge and understanding of the chemistry of carrier-free iodine and should contribute information which will aid in the identification of the various iodine species which exist in solution at very low concentrations.

1.3 Discussion of Various Iodine Couples

Several half-reactions involving iodine species in aqueous solution together with their standard electrode potentials at 25° as given by Latimer (18) are given below:

The value of the potential of a half-reaction can be calculated using the Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

where E is the potential of the couple in the solution, E° is the standard electrode potential, R is the gas constant, T is the absolute temperature, n is the number of faradays of electricity involved in the reaction as written, F is the value of the faraday and Q is the product of the activities of the resulting substances divided by the product of the activities of the reacting substances, each activity raised to that power whose exponent is the coefficient of the substance in the chemical equation as written.

For the reaction,

$$Q = \frac{[\text{I}_2]}{[\text{I}^-]^2},$$

where concentrations are substituted for activities. The potential of this couple will be dependent upon the total iodine concentration; as the total iodine concentration decreases the oxidation of iodide to molecular iodine becomes more difficult.

Conversely, the electrode potential for the other half-reactions will be independent of the total iodine concentration because each iodine containing molecule contains only one iodine atom. Therefore the values of the electrode potentials necessary to carry out an oxidation or reduction as shown in the half-reactions (2) through (7) should be the same at carrier-free concentrations as at macro concentrations.

1.4 Scope of the Investigation

The object of this investigation was to determine the disposition of the iodine activity following electrolytic oxidation of solutions of carrier-free iodide-131 at a controlled anode potential.

It was first necessary to design and construct (a) an instrument capable of controlling the electrode potential at the desired value and (b) an electrolysis cell suitable for carrying out the electrolyses. An instrument was constructed which was capable of maintaining either electrode to within less than ± 1 millivolt of the selected potential over a range of ± 2 volts versus the reference electrode. Several different types of electrolysis cell design were investigated in some

detail. A cell design using fritted-glass disks to separate the solutions was settled upon as offering the best compromise of the desired properties. With this cell it was possible to avoid mixing of the anolyte and catholyte and yet maintain good control of the electrode potential without introducing extraneous material into the iodine solution.

The electrolytic oxidation of iodide to iodate in sodium bicarbonate solution was studied as a function of the anode potential, the sodium bicarbonate concentration, and the iodine concentration. Except for a few experiments the only iodine species found in the sodium bicarbonate solutions were iodide and iodate. Electrolytic oxidation was demonstrated to be a good method for preparing carrier-free iodate solutions.

Electrolytic oxidation of carrier-free iodide in dilute sulfuric acid resulted in the formation of several different iodine species. At high anode potentials the principal product was iodate. At lower anode potentials a large fraction of the iodine activity was converted to a chemical form that did not correspond to any of the iodine species known to exist at macro concentrations. This material, which contained at least two components, was extracted by benzene but did not exchange with aqueous iodide.

Chapter 2

EXPERIMENTAL

2.1 Potentiostat

2.1.1 Requirements for Applied Potential. In order to carry out the electrolytic oxidation of carrier-free iodine-131 at a known anode potential, it was necessary to use an instrument which would automatically control the anode potential. Attempts to maintain the anode at a constant potential by manually controlling the voltage applied across the two working electrodes from the variable output of a D.C. power supply were unsuccessful. In manual operation a potentiometer was used to measure the anode potential against a reference calomel half-cell. It was not possible to maintain the anode at a constant potential in this manner because the rapid, short-term voltage swings of the anode could not be followed and there was much overshoot of the anode potential in both directions. In systems where a gross quantity of material is present, this type of control is often adequate because the electrode potential is stabilized by the reaction taking place at the electrode; however in this case there was no suitable electrode reaction to stabilize the electrode potential because of the extremely small quantity of iodine present. As a result, the electrode potential was easily perturbed and large fluctuations of the potential occurred. To avoid these variations a device was needed which could sense the change occurring in the electrode potential and quickly respond by adjusting the voltage across the working electrodes to keep the electrode potential constant with respect to a third, reference electrode.

Many instruments, called potentiostats, for maintaining one of a pair of electrodes at a constant potential with respect to a third or

reference electrode have been described (19-21). For this application the mechanical, servomechanism type of instrument was not suitable because of its inherently slow response. Rather an all electronic potentiostat with fast response was needed. Other desired features included the capability of maintaining up to 2 volts potential difference between the controlled electrode and the reference electrode and a minimum output of 25 volts and 250 milliamperes. Since none of the circuits that have been described satisfied the requirements completely, the decision was made to design and construct an instrument. A general discussion of the application of operational amplifiers in potentiostat circuits is given by Malmstadt, Enke and Toren (22), and Schwarz and Shain (23).

2.1.2 Description of Potentiostat. An instrument which was capable of maintaining the electrolysis electrode at a selected potential within the desired limits was constructed and is shown in simplified block form in Figure 2.1. In this simplified diagram the possibility of controlling only one polarity electrode (the anode) is shown; however in the actual instrument either electrode can be made the controlled electrode by appropriate switching. The instrument was assembled almost entirely from commercially available units. This approach offered many advantages. The initial construction was simplified as it consisted primarily of wiring a control panel and connecting together the various assemblies. Maintenance was also made much easier; in case of difficulty the unit at fault could be easily located and replaced and it was not necessary that the potentiostat be out of service while repairs were being made. Another advantage gained by this method of construction was that the potentiostat could be easily modified to meet different requirements by replacing the appropriate assembly with one having the desired specifications.

Figure 2.1 Potentiostat - Simplified Block Diagram

For example, the maximum output capability of the potentiostat could be increased by exchanging the output amplifier for one with a larger capacity.

In Figure 2.1, the Operational Amplifier is a Philbrick UPA-2 Chopper Stabilized Amplifier powered with a Philbrick R-100B Power Supply, the Current Amplifier is a Kepco Model ABC-40-0.5M Power Supply and the Adjustable Control Potential is a D.C., Zener-Reference-Voltage Power Supply. Briefly, the principle of operation is that the working electrode is set at some fixed potential above ground by means of the voltage divider across the Adjustable Control Potential; the reference electrode is maintained at ground potential by the Operational Amplifier acting through the feedback loop and adjusting the potential on the counter electrode. The difference in potential between the reference electrode and the working electrode (controlled electrode) is thus established at the desired value. Any change in the voltage of the reference electrode from ground potential is sensed as an error by the Operational Amplifier and the output of the amplifier, and thereby the potential of the counter electrode, varies to restore the reference electrode to ground potential. The Current Amplifier is simply the Kepco D.C. Power Supply functioning as a power amplifier. The input of the Philbrick UPA-2 Operational Amplifier is 1 megohm through a chopper to ground; the maximum error voltage across the operational amplifier is less than 0.1 millivolt (the low measuring limit of the voltmeter) which means the current drawn through the reference electrode is certainly less than 10^{-10} amperes (0.1 millivolt across 1 megohm) and is probably considerably less, so polarization of the reference electrode is avoided.

The complete circuit of the final instrument is shown in Figure 2.2; photographs of the instrument are shown in Figures 2.3 and 2.4. Two

NOTES:

1. UNLESS OTHERWISE SPECIFIED:

A. ALL RESISTORS 1/2 WATT.

B. RESISTANCE VALUES IN OHMS.

C. CAPACITANCE VALUES IN MICROFARADS.

D. ALL CRYSTAL DIODES IN2071.

E. S DENOTES SCREWDRIVER ADJUST.

F. * DENOTES MOST CLOCKWISE POSITION.

2. 0.1μF CAPACITOR ACROSS TRANSFORMER SECONDARIES TO SUPPRESS LINE VOLTAGE SWITCHING TRANSIENTS.

3. PS-4 ALSO MODIFIED BY OPENING CIRCUIT BETWEEN R24 AND R25.

4. THE CRYSTAL DIODE STRINGS PROTECT THE OUTPUT VOLTAGE METER.

5. CALIBRATE TO TWO VOLTS ACROSS POTENTIOMETER SPAN WITH METER LOAD.

Figure 2.2 Potentiostat Circuit

Figure 2.3 Photograph of Potentiostat - Front View

Figure 2.4 Photograph of Potentiostat - Rear View

control-potential power supplies were included in the instrument; switch S-3 (Control Potential Power Supply Selector) allows selection of either of these. One of the control-potential power supplies, PS-1 (a Los Alamos Power Supply P.S. 53), is a D.C., Zener-Reference-Voltage Supply, temperature stabilized, with very good long-term stability. The other power supply, PS-2, is a Kepco Model ABC-40-0.5M, the same as is used for the power amplifier, PS-3. This is a low impedance power supply. The control potential is set by means of a 10-turn potentiometer; the range of 0 to ± 2 volts is monitored on the Control Potential Meter.. Either the anode or cathode may be controlled as desired; switch S-4 (Reference Electrode Polarity Selector) selects the polarity of the reference electrode. The output of the operational amplifier can be used directly or a current amplifier inserted when desired with switch S-5 (Current Amplifier Selector). When the anode is the controlled electrode, PS-3, a Kepco Model ABC-40-0.5M Power Supply, is used as the current amplifier. When the cathode is being controlled, the current amplifier is PS-4, a Power Designs Model 500S Power Supply. Two separate floating power supplies are required to serve as the current amplifier (one for each polarity) because the working electrode must be connected directly to the control potential. Simply inverting the power supply polarity would not accomplish this.

Meters with appropriate range selection switches were included so that the output current and output voltage could be monitored. A timer, Standard Model SM-60, actuated by the Start-Stop switch, was incorporated to measure the electrolysis time. The timer was magnetically shielded by wrapping it in Co-Netic foil to attenuate the 60-cycle field that it generated.

2.1.3 Operation of Potentiostat. The temperature stabilized power supply, PS-1, was left on all the time; the operational amplifier and its power supply were allowed to warm up for several hours before using. No warm-up is necessary for the current amplifiers.

In use, a control-potential power supply is selected by S-3, usually PS-1 because of its somewhat better long-term stability, and the desired potential, as indicated on the Control Potential Meter, set with the appropriate Set Control Potential potentiometer. The desired polarity is set with switch S-4; it is set at the position labeled (-) for a controlled oxidation process. The Current Amplifier Selector, S-5, is set to the desired position; using only the operational amplifier, an output of 8 milliamperes at up to 100 volts is available. With the current booster in, the output capability is 500 milliamperes at 40 volts.

With the Start-Stop switch, S-6, in the Stop position, the output of the operational amplifier is connected to the input; under these conditions the Zero Set on the amplifier can be monitored at the terminals provided and balanced before starting a run. Terminals are also provided on the front panel for monitoring the Control Potential with an external instrument. The appropriate range is selected for the Voltmeter and Milliammeter. The Voltmeter monitors the voltage across the working electrodes and the Milliammeter the current through the counter electrode. Connections between the potentiostat and the electrodes were made with short lengths of insulated flexible wire; these could be connected either from the binding posts provided on the front panel or from a pin connector socket on the rear.

The capacitor, C-1, shown connected across the operational amplifier

input-output in Figure 2.2 is a stabilization capacitor which acts to compensate for phase shifts which take place in the entire system, including the electrolysis cell, thereby avoiding an unstable system. This was necessary to avoid oscillations which would otherwise occur. Various values of capacitors were connected across double banana plugs; the appropriate value for a particular cell and solution as determined by experimentation was plugged into a jack in the amplifier. The size capacitor used was the minimum value that would suppress any tendency for the system to go into oscillation.

Switching S-6 from the Stop and Zero position to the Start position started the timer and applied the necessary potential across the working (controlled) electrode and the counter electrode to cause the working electrode to attain a potential corresponding to the preset value with respect to the reference electrode.

An oscilloscope was considered a necessary part of the apparatus. By monitoring the output of the potentiostat with an oscilloscope any difficulties that arose could be observed and necessary corrective action taken. It was the oscilloscope that made it possible to be aware of the oscillation that occurred in the output when the capacitive effects of the external circuit were not correctly compensated; thus an oscilloscope must be used in order to determine the correct value stabilization capacitor. A Tektronix Model 560 Oscilloscope with Type 2B67 Time Base plug-in unit and Type 2A63 Differential Amplifier module was used. For monitoring the output of the potentiostat the sweep was usually set for 5 milliseconds per centimeter and the differential amplifier for D.C. at a sensitivity of 1 millivolt per centimeter.

2.1.4 Measurement of Electrode Potential. Preliminary measurements of the electrode potential were made with a Rubicon Potentiometer and a moving coil galvanometer as the null indicator. This system did not work well; when the setting on the potentiometer was even slightly off the balance point, closing the key on the potentiometer caused the galvanometer coil to swing rapidly to one side. It was virtually impossible to locate a null point on the potentiometer. The difficulty was probably caused by two effects. At any position of the potentiometer other than at the null point there was some loading of the potentiostat by the measuring circuit; any unbalance resulted in a movement of the galvanometer coil. The rotation of the galvanometer coil generated an E.M.F. which was fed into the control circuit of the potentiostat. The potentiostat saw this voltage as an error and attempted to correct for it resulting in an increasing unbalance and the wide excursion of the galvanometer coil. The direction of movement of the galvanometer coil depended not only upon the polarity of the error set on the potentiometer but also upon which key on the potentiometer was depressed. Substituting an electronic galvanometer (Kintel Model 204A) for the moving coil type eliminated this difficulty and made it possible to measure the electrode potential with the potentiometer set-up. But measuring the electrode potential in this manner was quite slow and inconvenient; also, the potential was known only at the time a measurement was taken. It was much more desirable to have a method which would constantly monitor the electrode potential so that any change that occurred would be noticed immediately. A system that required a minimum of operator time and attention was also desired. A digital voltmeter offered the desired characteristics. A Cimron Model 7200A Digital Voltmeter was used to

constantly monitor the electrode potential; this instrument has an input resistance of 10^{10} ohms at balance so it loaded the circuit very little. The digital voltmeter has an accuracy of ± 0.3 millivolt and a maximum balance time of 0.9 second.

2.1.5 Difficulties in Operation of Potentiostat. While the potentiostat was being checked out, large, random, transient pulses were occasionally observed on the oscilloscope; in addition at times a continuous noise pattern appeared. It was determined that this noise was coming in over the power line. A standard gun-transformer type of soldering iron was found to be a good noise generator; when the soldering gun was plugged into the power line at a point near to where the potentiostat was connected, the switching pulse that it generated could be seen on the oscilloscope which was connected across the output of the potentiostat. The soldering gun was used as a standard noise generator while attempting to eliminate the power-line noise pickup by the potentiostat. A Miller Radio Interference Filter, inserted between the potentiostat and the power line, reduced the magnitude of the noise pulses considerably. But best results were obtained using a Sola Constant Voltage Transformer, Model 20-13-150, and this transformer should be considered as part of the potentiostat. Not all constant voltage or isolation transformers which were tested reduced the noise level; on the contrary, some models of constant voltage transformers increased the magnitude of the pulses. In some locations the power line noise level might be sufficiently low that the transformer would not be necessary.

Line pulses are generated primarily as the result of a switching action; this can be either simple intermittent switching of some power

drawing device connected to the power line or switching electronically at line frequency as with a thyatron or silicon controlled rectifier control unit. These latter devices are most likely to cause serious difficulty. Silicon controlled rectifiers are coming into general use as power control devices; since these operate by instantaneous switching of the line voltage at line frequency, they generate voltage transients at line frequency which are carried over power lines and can feed into any instrument operating from the power line. Because of the nature of these voltage transients (very sharp rise and fall), they can and do make their way through the power supply and filtering of many instruments and show up as noise of some type in the instrument. One of the worst aspects of this problem is that the operator of the instrument might very well be unaware of the situation and have an error introduced without his knowledge. A Miller Radio Interference Filter was inserted between the scintillation counting system and the power line to eliminate the possibility of the line pulses affecting the count rate.

Another source of trouble was the pick-up of radio-frequency energy radiated by induction heating systems. Although the laboratory had double panel metal walls and was separated from the nearest induction heating system by several such walls, a considerable amount of radio-frequency energy was picked up by the system. No satisfactory method was found to keep this radio-frequency energy out of the potentiostat-electrolysis system; therefore no electrolysis experiments were carried out while the induction heating system was operating. The oscilloscope gave a visual indication of the presence of the radio-frequency energy whenever the induction heater was turned on.

The stabilization time of the potentiostat when switched on was usually less than one second and there was very little overshoot. The ripple voltage measured across the reference electrode and the controlled electrode as seen on the oscilloscope was typically well under one millivolt peak-to-peak; the voltage regulation was better than ± 1 millivolt. The only maintenance required was occasional replacement of tubes and the chopper in the operational amplifier.

2.2 Electrolysis Cell

2.2.1 Design Considerations for Electrolysis Cell. The design of a cell to be used for electrolysis experiments must necessarily be a compromise; the choice between different possibilities must take into account their effects on the results. It is necessary that the anolyte and catholyte be physically separated so that mixing of the two solutions cannot occur, but at the same time good electrical contact must be maintained between the two. One common method of accomplishing this is to use an agar plug saturated with a salt such as potassium chloride as the connecting link between the solutions; this will serve to avoid any mixing and yet the gel saturated with the salt will have a low electrical resistance. However, the desire to avoid as much as possible the contact of any unnecessary material with the carrier-free iodine-131 solution, particularly organic material, ruled out this approach. This same consideration also made the use of any connecting salt bridge undesirable.

In order to avoid the forementioned difficulties, a three-compartment cell was developed wherein the anode, cathode and reference compartments were separated. In order to investigate the electrode processes individually, it was necessary that the anolyte and catholyte be separated; this

made it possible to follow the changes that take place at each electrode (oxidation at the anode and reduction at the cathode). It was not necessary that the composition of the solutions in the different compartments be the same; in this study only the anolyte contained iodine-131. The material being reduced at the cathode was supplied by the solution and in the sodium bicarbonate solutions was probably hydrogen ion.

It would certainly have been better not to have had a separate reference solution compartment but rather to have placed the reference electrode in the solution as near as possible to the electrode whose potential was being measured. This would have minimized errors due to IR drop in the solution and maintained closer control on the electrode due to decreased capacitance and resistance between the two electrodes. But in this study, this measuring technique could not be used because of the need to avoid introducing any foreign materials into the solution being electrolyzed. Immersing the reference electrode directly in the solution would have allowed material from the reference electrode to contaminate the solution. The use of a salt bridge in a probe would have had the same disadvantage of introducing extraneous materials to the solution.

A Beckman Model 39270 Saturated Calomel Fiber Junction Reference Electrode was used in this study. This electrode was selected because it combined the desirable features of a low electrical resistance, reproducible potential, low volume flow rate of electrolyte solution, convenient size and ease of use. Although the rate of flow of the potassium chloride solution electrolyte from this electrode was quite low, any such material added to the solution being investigated would have been

very undesirable. Normally in a solution containing macro quantities of material, the extremely small amount of potassium chloride that would flow into the solution during an electrolysis would probably cause no difficulty. However, in the present investigation of solutions of carrier-free iodine-131 the quantity of chloride ion added to the solution during an electrolysis would be appreciable relative to the quantity of iodine present. This could well have caused variations in the observed electrolytic behavior of the carrier-free iodine-131 solution due to the presence of varying quantities of chloride ion. It would have been particularly bad to have added any chloride ion to the solution near the electrode, as would have been the case if the preferred arrangement of placing the reference electrode near the electrolysis electrode had been used. With these considerations in mind, it seemed wise to employ a cell with a separate reference solution compartment; this compartment contained solution of the same composition as the electrolysis solution with the exception of the iodine. With this type of cell, no extraneous material was added to the iodine solution being electrolyzed. The resistance between the reference electrode and the working electrode was moderately high in this cell but at the low currents used the effect on the measured potential was quite low. Because of the possibility of adsorption of iodine activity upon any surfaces which came into contact with the iodine solutions, strong reagents, such as concentrated nitric acid or chromic acid cleaning solution, were used to clean all such surfaces. If the reference electrode had been immersed in the iodine solutions, it would have been necessary to clean it with such a reagent which would probably have affected the potential of the reference electrode.

2.2.2 Properties of Various Types of Electrolysis Cells. In order to

investigate the effects of various design parameters of the electrolysis cell upon the electrical resistance and mass transfer between compartments, several models were constructed similar to that shown in Figure 2.5. The models were constructed entirely of glass and the main chambers were made of 35-millimeter-diameter by 6-centimeter-long Pyrex glass tubing with a flat bottom sealed on. The two compartments were joined with a length of capillary tubing. Several models were constructed as listed in Table 2.1; the only variables were the length and bore of the capillary tube connecting member. The object was to find a combination which would keep mixing of the solutions between compartments at a satisfactory low level and yet have a sufficiently low electrical resistance so that the desired electrode potentials could be attained. As the bore of the capillary tube was decreased and the length increased, mixing of the solutions between compartments decreased, but at the same time the electrical resistance between the two compartments increased.

Sodium bicarbonate solution, 0.01 M, was used to investigate the characteristics of the models since this solution was to be used for most of the electrolysis experiments. The approximate D.C. resistance between electrodes immersed in solution contained in the models was measured. Twenty-five milliliters of 0.01 M sodium bicarbonate solution was transferred by pipette to each compartment of a model. Two 1/8-inch-diameter spectroscopic graphite electrodes were mounted in a lucite holder 70 millimeters apart; when the holder was set on top of a model, the electrodes were immersed to a depth of 30 millimeters in the solution. The resistance between electrodes was measured using the ohmmeter section of a Triplet Model 310 Multimeter. The meter was connected across the electrodes and the resistance value noted immediately in order to keep

Figure 2.5 Preliminary Cell Model

Table 2.1 Electrical Resistance in Various Cell Models^a

Model	Capillary Tubing		D.C. Resistance, ohms
	Bore, mm	Length, mm	
I	1	40	500,000
II	1	20	230,000
III	2	40	150,000
IV	2	30	130,000
V	2	20	70,000
VI	2	15	60,000

^aThe resistance was measured with 0.01 M NaHCO₃ solution.

to a minimum the error introduced due to polarization by the small current flowing through the solution. The accuracy of a measurement made in this manner was adequate for the present purpose. The results are included in Table 2.1.

The amount of mixing that took place between compartments was determined for some of the models. Twenty-five milliliters of 0.01 M sodium bicarbonate solution was transferred by pipette to each side of model I; a small glass-covered stirring bar and a magnetic stirrer were used to stir the solution in one side of the model. Some iodide-131 activity was added to the stirred solution and 1-milliliter samples of each solution were removed by pipette at successive intervals. These samples were counted to determine the activity in each and thereby the degree of mixing of the two solutions that had taken place; after 1.5 hours 0.8% of the total activity had migrated to the side originally containing no activity. After 3.5 hours, the amount of iodide-131 in this chamber was up to 2.1% and after 6.5 hours 3.3%. Next, the movement of iodine-131 in this model was measured in the same manner except that this time a potential was maintained across electrodes immersed in the solutions in the two compartments. A 1/8-inch-diameter spectroscopic graphite electrode was placed into each compartment of the model and the potentiostat connected across the electrodes; a saturated calomel electrode (hereafter referred to as S.C.E.) was placed in the compartment containing the anode and it was also connected to the potentiostat. The solution in this compartment was stirred with a magnetic stirrer. Iodide-131 was added to the anolyte and the potentiostat turned on. The maximum anode potential which could be attained at full output of the potentiostat was +1.07 volts vs. S.C.E.; the potential across the working electrodes was 50 volts and the current

was less than 1 milliampere. This potential was maintained for 1.5 hours. One-milliliter samples were then removed from both compartments and their activity determined. With this potential across the electrodes, the transfer of activity was increased somewhat over that observed with no applied potential. With no potential across the electrodes, 0.8% of the activity migrated to the compartment initially containing no activity; with the applied potential, the amount was up to 1.4% which was still satisfactorily low. However, the resistance of this cell was too high; the maximum anode potential which could be attained was lower than desired and the control of the anode potential was poor.

Model III was set up in the same manner as just described for model I, the potentiostat connected and the solution electrolyzed. With 50 volts across the working electrodes the anode potential was +1.31 volts vs. S.C.E.; the current was approximately 0.4 milliampere.

In model IV at the maximum output of the potentiostat with the power booster in, the anode potential was +1.28 volts vs. S.C.E. The movement of iodine-131 in this model was determined both with and without an applied potential. With stirring but no applied potential, the solution in the one compartment, the originally inactive solution, contained 1.1% of the total activity after 5 hours; with 50 volts across the model (anode potential of +1.28 volts vs. S.C.E.) the catholyte contained 0.5% of the activity after 3 hours. With model V the anode potential was +1.50 volts vs. S.C.E. with 50 volts across the working electrodes and the current was 1 milliampere.

Mixing of the solutions between the two compartments was no particular problem in these models; even with the short lengths of

2-millimeter-bore capillary tubing there was little migration of the activity from one compartment to another. The major problem with this type of construction appeared to be the high resistance of the small column of liquid which resulted in poor control of the electrode potential.

Based upon the results obtained with the foregoing models, a three-compartment cell was constructed as illustrated in Figure 2.6. The three compartments are 6-centimeter lengths of 35-millimeter-diameter Pyrex tubing with a flat bottom sealed on. The connecting members are 2-millimeter-bore by 15-millimeter-long pieces of capillary tubing; the capillary tubing is joined to the walls with a minimum of enlargement of the bore. With 25 milliliters of 0.01 M sodium bicarbonate solution in each compartment, the D.C. resistance between adjacent compartments was approximately 60,000 ohms measured as previously described. Iodide-131 was added to the solution in the center compartment; after stirring the solution for 5 hours with a magnetic stirrer, 1-milliliter samples were taken of each solution and the activity in each determined. The center compartment contained 92.6% of the total activity with the remaining 7.4% divided between the other two compartments.

One major problem was encountered with this cell; namely, a "pumping" action which took place when samples were removed. Although the intermixing of solutions between compartments was normally low even with vigorous stirring, liquid would readily flow between compartments whenever there was a change in height of the liquid in one compartment over that of another. Such a situation always occurred when the solutions were sampled; insertion of the pipette into the liquid caused some change and then removal of a portion of the solution caused solution from the adjacent compartment(s) to flow into this chamber. As a result, each

Figure 2.6 Electrolysis Cell With Capillary Tube Connectors

time samples were taken from the cell, mixing of the solutions between compartments took place.

Because of the problems encountered in the cells with capillary tube connecting members (mixing of the solutions when samples were removed and the relatively high electrical resistance between compartments), the use of fritted-glass separators was investigated. A cell was constructed as shown in Figure 2.7. The compartments were made of 7-centimeter lengths of 3-centimeter-diameter Pyrex tubing with a flat bottom sealed on. The connecting legs contained a 10-millimeter-diameter fine-fritted-glass disk. The flow rate of liquid through the fritted-glass disks was quite low even with the maximum head of liquid that could be attained in the cell, so movement of solution between compartments as a result of removing samples was no problem with this type of cell. The resistance between graphite electrodes immersed in a 0.01 M sodium bicarbonate solution in this cell, using the measuring technique as previously described, was 16,000 ohms between adjacent compartments. This resistance is considerably less than the resistance of the solution contained in a cell employing a capillary tube as the joining member. The transfer of iodide-131 activity from the center compartment, vigorously stirred with a small glass-covered stirring bar, to each of the outer compartments (all containing 25 milliliters of 0.01 M sodium bicarbonate solution) was less than 0.1% in 4 hours. However, one bad feature of these cells was an electroosmosis effect when electrolyzing at high electrode potentials. When 0.01 M sodium bicarbonate solution was electrolyzed at a high potential (greater than about +1.00 volt vs. S.C.E.), there was a transfer of liquid from the anode compartment to the cathode compartment. As a consequence, there was a change in the concentration of both anolyte and catholyte during

Figure 2.7 Electrolysis Cell With Fritted-glass Connectors

the electrolysis. That this was a movement of water and not of the solution was shown by the observation that the specific activity of the anolyte increased. However, it was found that when 0.01 M sodium bicarbonate solution was electrolyzed at anode potentials of less than +1.00 volt vs. S.C.E. in a cell with fritted-glass disk separators, there was no change in the height of the liquid level in the compartments. Since the electrode potentials that would normally be used in this study would be less than +1.00 volt vs. S.C.E., this type of cell construction could be used. Some selection of the fritted-glass disks was necessary based upon the magnitude of the electroosmosis effect they produced. Several cells were constructed as shown in Figure 2.7. A solution of 0.01 M sodium bicarbonate was electrolyzed in each cell at an anode potential of +1.500 volts vs. S.C.E. for one hour. In most of the cells the quantity of liquid transferred from anode to cathode compartment was similar and increased the volume of the catholyte about 10%. However, in a few cells the electroosmosis effect was particularly large; these cells were not used.

2.3 Electrodes

Both the anode and the cathode were 3-inch-lengths of 1/8-inch-diameter spectroscopic graphite electrodes (National Carbon Company, Special Spectroscopic Electrodes, Graphite AGKSP). The spectroscopic graphite rod was selected as an electrode material because it offered a good combination of properties. It was very pure, was easily available and offered a reproducible shape and surface. The graphite seemed to function well as an inert electrode under the conditions used in this study. The graphite was used as received and new electrodes were used for each experiment.

There was some sorption of the iodine-131 activity by the graphite electrode; the amount of activity sorbed was determined. Twenty-five milliliters of 0.01 M sodium bicarbonate solution was inoculated with iodide-131 and a 1-milliliter sample removed immediately. Three graphite electrodes were immersed in the solution and it was stirred with a magnetic stirrer; no electrical connections were made to the electrodes. After one hour a 1-milliliter sample of the solution was taken and one electrode was removed, rinsed, put into a counting tube and covered with chromic acid cleaning solution. This procedure was repeated after five hours with a second electrode and after seven hours with the third electrode; each time a 1-milliliter sample of the solution was removed. The solution was removed from the cell, the cell was rinsed with sodium bicarbonate solution and the walls of the cell were treated with chromic acid cleaning solution to remove any adsorbed iodine-131. All of the samples were counted. The 1-milliliter sample of the initial solution had an activity of 5,174 c/m, the one-hour sample 4,884 c/m (94.4%), the five-hour sample 4,710 c/m (91.0%) and the seven-hour sample 4,641 c/m (89.7%). Recovery was 110,142 c/m from the solution, 915 c/m from the cell walls and 20,336 c/m from the electrodes for a total of 131,393 c/m which represents 101.6% recovery of the initial 129,345 c/m. Each electrode picked up 2% of the total activity in the first hour and each added another 2% in the next six hours. In an electrolysis the single electrode in the solution would sorb about 4% of the iodide-131 in seven hours. This small amount of uptake of the iodide-131 by the electrode was not considered to be a problem.

2.4 Determination of Radioactivity

2.4.1 Scintillation Counter. The iodine-131 activity was measured by gamma counting of solutions using a scintillation detector; a Harshaw Type 75F8, Integral Line Assembly Scintillation Detector was employed. This detector has a 1.75-inch-diameter by 2-inch-thick thallium activated sodium iodide crystal directly attached to a photomultiplier tube; the crystal is a well-type with a 0.75-inch-diameter by 1.5-inch-deep hole. A John Fluke Model 404M Power Supply furnished the high voltage for the photomultiplier tube. A Nuclear Data Model ND-130A 512 Channel Pulse Height Analyzer was used for counting. The limits on the analyzer were set so that only the gamma pulses falling in the region from 120 kev to 765 kev were counted. By eliminating those pulses with energy less than 120 kev, the measured activity was less subject to error caused by variations in the density of the solution or in the wall thickness of the cells.

Since the analyzer had a live timer, there should have been no coincidence error; however the coincidence error of the counting system was checked. A Standard Model SM-60 Timer, graduated to 0.01 minute, was connected to the analyzer in such a manner that the timer was running whenever the analyzer was measuring the activity of a sample. This made it possible to get both live time and calendar time for an analysis. Samples of various activities were counted and a plot made of expected activity versus measured activity, Figure 2.8. As can be seen, using live time the points fell in a straight line passing through the origin indicating no coincidence error. The plot for calendar time gave a curve which deviated from the predicted straight line at higher activities due to coincidence losses.

Figure 2.8 Counting Rate, Live Time and Calendar Time

2.4.2 Counting Tubes. Pyrex test tubes, 16 by 150 millimeter, were used as counting tubes. Tubes were selected on the basis of their external diameter; only those tubes with an external diameter falling in the interval from 0.632 to 0.644 inch were used. The tubes that fell within this size range were then further checked by counting a standard amount of iodine-131 activity in each one. Any tube in which the measured activity varied more than 1% from the average was discarded.

A permanent reference mark was made on a graduated cylinder; when a test tube was placed in the graduated cylinder and filled with liquid up to the reference mark scribed on the graduated cylinder, the tube contained approximately 11 milliliters of liquid. This was a convenient quantity because it easily allowed samples of up to 10 milliliters to be added to the tube for counting without going over the established reference height. Before a sample was counted the counting tube was set in the graduated cylinder and liquid (normally water or benzene) added to bring the solution height up to the reference mark. The solution was mixed by stirring briefly on a Vortex Mixer (Scientific Industries Vortex Test Tube Mixer, Model K-500).

Some 15-milliliter conical Pyrex centrifuge tubes, which would be used in the fractional precipitation method of analysis, were also checked by counting a standard quantity of iodine-131 activity; any tube in which the measured activity varied more than 1% from the average value was discarded.

The activity in a graphite electrode was determined by dropping the electrode into a counting tube and counting it in the scintillation detector. A geometry correction factor to be used when counting the

activity in this manner was determined by comparing the activity measured in this manner with the value found by removing all of the activity from the graphite electrode with chromic acid cleaning solution and determining the activity in this solution in the usual manner.

2.5 Analytical Methods

2.5.1 Solvent Extraction. An extraction procedure similar to that employed by Kahn and Wahl (2) was used to characterize the nature of the iodine species present in solution. The aqueous solutions were extracted with benzene in a 12-milliliter, Standard Taper No. 13 glass-stoppered, conical, Pyrex centrifuge tube. In order to effect a better seal, each stopper was fitted to a matching tube by lapping it with No. 600 Carborundum powder. Water was used as a lubricant on the stopper to prevent either liquid phase from creeping into the joint.

The tube containing the two phases was shaken by hand for four minutes and then centrifuged for five minutes with a clinical centrifuge to separate the phases. A Pumpette pipette control device, in conjunction with a micro transfer pipette, was used to separate the phases. The micro transfer pipette was made by drawing out a piece of 7-milliliter glass tubing to form a capillary tip. Pressure was gradually applied to the pipette while passing the tip through the benzene layer and into the aqueous phase. This slow ejection of air kept any benzene from getting into the pipette. The aqueous layer was then drawn into the pipette, the pipette removed and the liquid transferred to another centrifuge tube. The tube containing the benzene was centrifuged an additional five minutes and the remaining small amount of aqueous material removed in the same manner. This time a small amount of the benzene phase was also drawn

into the capillary tip in order to ensure that all of the aqueous solution was removed; after withdrawing the pipette from the liquid the benzene in the capillary section could easily be seen and ejected from the pipette without losing any of the aqueous fraction. Complete separation of the phases in this manner gave more consistent results and was faster than the method of removing only a portion of each phase by pipette.

The extraction procedure used is outlined in Figure 2.9. One-half milliliter of aqueous solution containing the iodine-131 to be analyzed was extracted with 5 milliliters of benzene and the phases separated as described. The aqueous phase was then extracted with 5 milliliters of a solution of 0.005 M iodine in benzene and these phases separated. The original benzene solution was back-extracted with 0.5 milliliter of 0.01 M aqueous potassium iodide. The activity in each of these four fractions, designated A, B, C, and D, was measured as described in Section 2.4; this gives information on these four fractions as follows:

A - extracted by benzene but not back-extracted by
0.01 M aqueous potassium iodide.

B - extracted by benzene and back-extracted by
0.01 M aqueous potassium iodide.

C - not extracted by benzene but extracted by
0.005 M iodine in benzene.

D - not extracted by benzene or by 0.005 M iodine in benzene.

Some general statements can be made about the possible composition of these fractions.

The iodine activity in fraction A does not correspond to any iodine

Figure 2.9 Solvent Extraction Procedure

species known to exist at macro concentrations.

Fraction B should contain most of any I_2 present in the solution. The 10 to 1 ratio of benzene to aqueous phase would favor extraction of most of the I_2 by the benzene phase. The I_2 would be back-extracted by the aqueous potassium iodide solution because of the rapid rate of exchange between I^- and I_2 and the large concentration difference of total iodine between the aqueous and benzene phases.

Fraction C would contain any I^- and any IO^- . Neither I^- nor IO^- would be extracted by benzene but would be extracted by the benzene solution of I_2 because of the rapid exchange between I_2 and I^- or IO^- and the high ratio of the concentration of total iodine in the benzene phase to that in the aqueous phase.

Fraction D would contain any IO_3^- . Iodate would not be extracted by benzene or by a solution of I_2 in benzene as the rate of exchange between IO_3^- and I_2 is slow. Any IO_4^- should also be found in D for the same reasons.

This method of analysis is very useful for obtaining general information about the distribution of the various iodine species in solution but it does not give a definitive value for any one material because species that may be found in the various fractions are not limited to those described above.

2.5.2 Fractional Precipitation. A method of analysis specific for carrier-free iodate- 131 was needed. It has been reported that in the chemical oxidation of carrier-free iodide- 131 solutions, fraction D, as isolated in the extraction process (which corresponds to Kahn's fraction Z), contains varying amounts of at least one other iodine species in addition to iodate (2,3).

The iodate content of the solutions was determined by a fractional precipitation method as described by Kahn and Wahl (2). One milliliter of 0.10 M potassium iodate was added to a portion of the solution to be analyzed in a 15-milliliter conical Pyrex centrifuge tube. One-half milliliter of 0.04 M silver nitrate was added to precipitate a fraction of the iodate as silver iodate. After mixing briefly on a Vortex Mixer, the tube was centrifuged for five minutes in a clinical centrifuge. A transfer pipette, made by drawing out a length of 7-milliliter glass tubing to form a capillary tip, was used to transfer the supernatant liquid to another centrifuge tube. The tube containing the precipitate was centrifuged again and the remainder of the liquid removed and combined with the first portion. Another 0.5 milliliter of the silver nitrate solution was added to the liquid and the supernatant liquid separated from the silver iodate precipitate as before; this process was repeated a total of five times to give five precipitates and a supernatant liquid. Two milliliters of 3M ammonium hydroxide was added to each of the precipitates and they were mixed on the Vortex Mixer until the silver iodate had dissolved; water was added to each to bring the solution level up to a standard reference mark and the solutions were counted. The fraction of the total iodate precipitated in each case was next determined by an iodometric method of analysis employing thiosulfate. The solution was acidified by adding 5 milliliters of 4M sulfuric acid, an excess of solid potassium iodide (0.2 gram) was added and the liberated iodine was titrated with 0.015 M sodium thiosulfate using starch as an indicator. From this information the specific activity (in this case defined as the fraction of total activity divided by the fraction of total iodate) of each fraction was calculated. The iodate-¹³¹I content

of the original iodine sample could then be determined. Any iodate-131 present would act the same as the carrier iodate; if all of the activity present were in the form of iodate, the specific activity of each fraction would be the same and equal to one. Non-iodate forms of activity present would either tend to be carried by the silver iodate precipitate or not carried. If non-iodate activity which is not carried by the silver iodate precipitate were present, the specific activity of all the fractions would be the same and less than one. The activity of the final supernatant liquid would be large because it would contain all of the non-iodate activity. If non-iodate activity which is carried by the precipitate were present the specific activity of the first fractions would be large but would drop to a constant value less than one in the later precipitates as all of the non-iodate material was removed. Mixtures containing all three types of iodine activity would give a combination of these two situations (the specific activity of the first precipitates and of the final supernatant liquid would both be large) but in any case the minimum specific activity found would represent the iodate-131 content. In this procedure it is necessary to assume that the non-iodate species will not exchange with iodate since a non-iodate species which exchanges rapidly with iodate would be determined as iodate.

It should be noted that the value obtained by the fractional precipitation method of analysis represents the maximum percent of iodate and that this method of analysis is best suited for samples rich in iodate. A consideration of the following extreme situations will illustrate this fact.

In a sample containing primarily non-iodate activity, the activity

will either be carried by the iodate precipitate, making the early precipitates rich in activity, or not carried, concentrating the activity in the liquid. When the non-iodate activity is carried by the silver iodate precipitate, most of the activity will come down with the first precipitate with less remaining in solution after each precipitation. This will result in some activity in each precipitate from this non-iodate material which is carried, although the amount will decrease with each succeeding precipitation. The quantity of non-iodate activity found in the precipitate will drop rapidly and will be down to a low value after the first few precipitations. This activity adds to that due to iodate-131 in the precipitate. When the fraction of iodate-131 is large, the contribution of the non-iodate activity will be insignificant but when the iodate-131 is a small fraction of the total activity, the contribution of the non-iodate activity can be appreciable. In any case, the effect will be to cause the value for iodate to be too large.

The value for iodate will also tend to be large when the non-iodate activity is not carried by the silver iodate precipitate due to the supernatant liquid which is not removed from the precipitate. Some of the supernatant liquid always remains with the precipitate. When the sample consists primarily of iodate activity, the composition of the liquid is approximately the same as the composition of the precipitate and the small amount of entrapped liquid contributes little. However, if there is an appreciable quantity of activity which is not carried by the silver iodate precipitate, this activity will remain in the liquid. The supernatant liquid which is not removed from the precipitate will contribute non-iodate activity to the precipitate resulting in a large value for the iodate fraction.

Typical results for a fractional precipitation method of analysis of a solution rich in iodate are given in Table 2.2. The percent iodate was taken as the minimum number obtained for the ratio of Fraction Activity to Fraction Iodate, 97% iodate in this example. Typical results for a fractional precipitation method of analysis of a solution low in iodate are shown in Table 2.3; the iodate fraction was taken as 7.8%. From the large quantity of activity found in the first silver iodate precipitate as shown in Table 2.3, it can be seen that the iodide-131 was in some manner carried by the precipitate (this activity in this solution was 93% iodide as characterized by extraction analysis).

2.5.3 Chromatography. Analysis by either the extraction or fractional precipitation method requires much operator time and attention and thus limits the number of determinations that can be made during an electrolysis. Also, the amount of information obtained is limited. With the fractional precipitation method a quantitative value is obtained only for the iodate content although general information is available concerning other species present. From observation as to what degree the activity is carried on the silver iodate precipitate, some general comments can be made as to its character. The extraction method of analysis is limited to dividing the activity into four groups without any specific information as to the make-up of the activity in the group.

Many workers have employed paper chromatography to characterize carrier-free iodine-131 activity (7-14). The general advantages of using paper chromatography to effect separations are well known (24,25). It allows a large number of separations to be carried out rapidly with little operator attention. Also, the technique is not necessarily limited to making only predetermined separations but can show up unexpected species.

Table 2.2 Determination of Iodate in a Sample Rich in Iodate
by the Fractional Precipitation Method

Activity, c/m ^a	Fraction Activity ^b	Iodate, ml ^c	Fraction Iodate ^d	F.A./F.I. ^e
28,132	0.2240	8.62	0.220	1.02
26,778	0.2132	8.30	0.212	1.01
25,176	0.2005	8.06	0.206	0.973
23,798	0.1895	7.67	0.196	0.967
19,326	0.1539	6.15	0.157	0.980
2,379	0.0189	0.32	0.0082	2.3

^aThe first five values represent the activity found in the successive unwashed precipitates and the sixth is the activity remaining in the supernatant liquid.

^bThe fraction of the total activity in the analytical sample.

^cCarrier iodate as represented by the quantity of standard thiosulfate (approximately 0.015 M) required to titrate the iodine liberated when the carrier iodate reacts with excess acid iodide.

^dThe fraction of the total carrier iodate in the analytical sample.

^eThe ratio of the Fraction Activity to Fraction Iodate.

Table 2.3 Determination of Iodate in a Sample Low in Iodate
by the Fractional Precipitation Method

<u>Activity, c/m^a</u>	<u>Fraction Activity^b</u>	<u>Iodate, ml^c</u>	<u>Fraction Iodate^d</u>	<u>F.A./F.I.^e</u>
96,087	0.6525	8.52	0.221	2.95
6,900	0.04686	8.43	0.219	0.214
2,377	0.01615	7.97	0.207	0.0780
2,725	0.01851	7.73	0.201	0.0921
9,418	0.06396	5.71	0.148	0.432
29,743	0.2020	0.14	0.0036	56.

^aThe first five values represent the activity found in the successive unwashed precipitates and the sixth is the activity remaining in the supernatant liquid.

^bThe fraction of the total activity in the analytical sample.

^cCarrier iodate as represented by the quantity of standard thiosulfate (approximately 0.015 M) required to titrate the iodine liberated when the carrier iodate reacts with excess acid iodide.

^dThe fraction of the total carrier iodate in the analytical sample.

^eThe ratio of the Fraction Activity to Fraction Iodate.

Some separations were carried out using a 4-centimeter by 25-centimeter strip of Whatman No. 1 Chromatography Paper and an eluant of n-butanol saturated with 3M ammonium hydroxide. A 1-liter graduated cylinder with the lip cut off was used as the chromatography chamber. About 1 lambda of the untreated, undiluted Oak Ridge solution of iodine-131 activity was spotted 2.5 centimeters from one end of the paper, the paper was air-dried and the spot was eluted using an ascending technique with the n-butanol - ammonium hydroxide solution. After the liquid had traveled about 17 centimeters along the paper, requiring about five hours, the paper was removed from the chamber, the position of the liquid front was marked and the paper was air-dried. The distribution of the activity along the paper was determined by autoradiography using Polaroid 4 x 5 inch Sheet Film Type 57. The chromatography paper strip was taped in place on the film pack, the pack sandwiched between two pieces of 3/8-inch-thick phenolic sheet and this assembly clamped together with C clamps to maintain intimate contact between the pieces. The film was exposed for 16 hours. Before separating the paper strip from the film pack, the positions of the liquid front and of the origin were marked by making an impression on the film through the mask with a ball-point pen. The paper strip was separated from the film pack and the picture was processed using a standard Polaroid 4 x 5 processing device. The activity appeared as a light region against a black background. The use of Polaroid film made a darkroom unnecessary and provided a positive picture of the distribution of the activity within a minute after completing the exposure. A spot on the paper containing 2,500 disintegrations per minute of iodine-131 gave an easily discernible spot on the film with overnight exposure. After locating the position of the activity in this manner, the paper was cut

into pieces such that the regions containing activity were separated and each section was counted. Each piece of paper was rolled longitudinally and dropped into a counting tube which was then placed into the well of the scintillation crystal. In this geometry the paper was contained entirely within the well of the crystal.

With the n-butanol - 3M ammonium hydroxide solvent, iodide had an R_f value of 0.28 (R_f = distance traveled by spot/distance traveled by liquid front). In most of the runs of untreated, undiluted Oak Ridge activity, the only spot observed was that due to iodide; however in one case a spot with R_f = 0.40 containing 10% of the activity was observed. Although the only region of localized activity was that due to iodide, this spot usually contained only about 80% of the activity. The remaining 20% of the activity was spread more or less uniformly along the paper. These figures are based upon the recovered activity; in every case approximately 5% of the original activity could not be accounted for. A similar loss of activity was reported by Anghileri (26). Inasmuch as this activity was not found on the paper or in the solvent, it must have vaporized during the chromatographic process. This system gives good separation of iodide from iodate and periodate. However, the separation of iodate and periodate was poor; the R_f for each of these species was approximately 0.

Because most of the previous studies on the chemical oxidation of carrier-free iodine-131 had employed the fractional precipitation or solvent extraction method of analysis, it was felt that it would be desirable to employ these methods of analysis in this study in order to facilitate the comparison of results obtained by chemical oxidation with

those obtained by electrolytic oxidation. However, in the investigation of the production of periodate, a method of determining periodate and iodate in the presence of one another was needed. A precipitation method similar to that used for determining iodate could have been used by adding carrier periodate and precipitating silver periodate but it was desirable to have a method which would allow determination of both iodate and periodate. Separation of the iodate and periodate by adding carrier quantities of each, precipitating the iodate as the barium salt at pH 3 followed by precipitating the periodate as the bismuth salt as described by Burgus and Davies (27) was not satisfactory. The precipitation of the iodate was slow and incomplete under these conditions.

Separation of iodide, iodate and periodate by paper chromatography has been reported using a mixture of equal volumes of acetone and 3M ammonium hydroxide as the elutant (28). One lambda quantities of 0.01 M solutions of iodide, iodate and periodate were spotted across separate strips of Whatman No. 1 Chromatography Paper. After drying, the papers were eluted using an ascending technique with an acetone - 3M ammonium hydroxide mixture; the liquid traveled about 16 centimeters in 2 hours. The papers were removed from the chamber and the position of the liquid front marked; the papers were air-dried and the position of the iodine compounds determined. The iodide was located by applying a stripe of ferric nitrate - starch solution down the length of the paper with a capillary tube. The iodide was oxidized to iodine which gave a blue color in the presence of the starch. The positions of the iodate and periodate were located by painting stripes of acidified potassium iodide solution the length of the papers. Both iodate and periodate gave a characteristic brown iodine color upon reacting with the acidified potassium iodide.

For iodide only one spot was found at $R_f = 0.97$ and for iodate only one spot was seen at $R_f = 0.78$. In the case of periodate two iodine containing regions were always observed. The major portion of the material was at $R_f = 0$ and the second spot (which varied in intensity) was at $R_f = 0.78$, corresponding to the value for iodate. This was probably the result of some iodate present in the periodate and perhaps some reduction of periodate on the paper. This procedure was used to analyze solutions of carrier-free iodine-131 for iodide, iodate and periodate as described below.

A portion of the solution to be analyzed was spotted on a strip of paper, air-dried and eluted using an ascending technique with the acetone - ammonium hydroxide mixture. The iodine species were separated by cutting the paper at the appropriate positions, namely at $R_f = 0.05$, 0.65 and 0.84. The amount of each species present was then determined by counting the pieces of paper. As a check on the separations, indicator solutions containing 0.01 M potassium iodide, 0.01 M potassium iodate and 0.01 M potassium periodate were spotted near the edge of the paper in line with the spot of the solution being analyzed. When the strip was eluted, the corresponding iodine species in the two spots traveled along the paper in the same manner. Locating the iodine species from the indicator solution as previously described (ferric nitrate - starch solution for iodide and acidified potassium iodide solution for iodate and periodate) served to verify the separations.

Analysis of a sample of the untreated, undiluted Oak Ridge iodide-131 solution gave 0.6% of the activity in the region of R_f less than 0.05 (position of any periodate), 0.8% between R_f of 0.05 and 0.65, 3% between

R_f of 0.65 and 0.84 (position of any iodate) and 95.6% of the activity in the area above $R_f = 0.84$ (position of the iodide). These figures are based upon the recovered activity; approximately 5% of the total initial activity spotted on the paper was not recovered.

2.6 General

2.6.1 Reagents and Materials. Mallinkrodt Analytical Reagent, Thiophene-free Benzene was distilled through a Pyrex Vigreux distilling column; the middle half of the distillate was collected and this fraction was used for all the extraction work. Ordinary laboratory distilled water was redistilled from alkaline permanganate solution. The other chemicals were reagent grade and were used without further purification.

The carrier-free iodine-131 was obtained as an iodide solution of fission produced iodine-131 in basic sodium sulfite solution from Oak Ridge National Laboratory. At first the iodine-131 was purified before use by distillation following the method described by Kahn, Freedman, and Shultz (29). In the course of the work, it was noticed that the analysis of the starting material for an electrolysis showed wide variations in the distribution of the iodine activity. Analysis of the distillate by the extraction method gave values for the iodide content ranging from 76% to 93%, whereas samples of the as-received material analyzed in the same manner typically gave values of 96 to 98% with a low value of 94% iodide observed. Apparently storage in the basic sulfite solution maintained the iodine in the reduced form. The primary reason for the distillation step was to attempt to attain a starting material of consistent composition. Since this goal was not being accomplished, it was decided to eliminate this step and use the activity as received.

A fresh supply of iodine-131 was received every one to two months.

2.6.2 Cleaning Procedures. All glassware except the cells was cleaned with chromic acid cleaning solution. The cells were cleaned with concentrated nitric acid. Nitric acid rather than cleaning solution was used to clean the cells because of the feeling that it was less likely to leave traces of materials on the cells, particularly in the fritted-glass disks. Even though a vacuum was used to pull rinse water through the fritted-glass disks, they could not be rinsed as well as the other surfaces. After cleaning with concentrated nitric acid and rinsing with large quantities of water, the cells were dried in an oven at 110°C overnight to drive off any reduction products of the nitric acid which were not removed by the rinse water.

2.6.3 Electrolysis Procedure. Except where otherwise indicated, the following procedure was used in carrying out all of the electrolysis experiments. The electrolyses were performed at room temperature (relatively constant at 22°C) and in the presence of normal laboratory illumination. Twenty-five milliliters of 0.01 M sodium bicarbonate solution was transferred by pipette to each of the three compartments of the electrolysis cell. A 5-millimeter-diameter by 18-millimeter-long glass-covered stirring bar was added to the center compartment and the cell was clamped in position with the center compartment resting on a magnetic stirrer. The electrode holder was a piece of 1/4-inch-thick lucite plastic with three holes in a row on 45-millimeter centers. The diameter of two of the holes was such that the graphite electrodes fit into them snugly; the electrodes were forced into these holes and held in place by friction. The hole for the calomel reference electrode, a

Beckman No. 39270, Fiber Type, was oversize so that the electrode dropped down to and was supported by the electrode side arm. Three-inch lengths of spectroscopic graphite electrode material were pressed into the holes in the support leaving 6 centimeters of the electrodes protruding from the bottom of the holder.

The iodide-131 was transferred to the center compartment with a small glass stirring rod. The end of the rod was touched to the iodide-131 solution and then used to stir the solution in the cell. Immediately, samples were taken of the solution, usually a 0.5-milliliter sample for analysis and a 250-lambda sample for counting, to establish the initial composition and quantity of iodine-131 present, respectively. The electrode assembly was set in place on the cell and the electrical connections made. The potentiostat was connected to all three electrodes; the digital voltmeter and oscilloscope were connected across the reference electrode and the anode. The potentiostat (which had been adjusted to give the desired anode potential) was switched on thereby applying the required potential across the electrodes and starting the timer. The anode potential was monitored with the digital voltmeter and any necessary adjustment of the potential made with the "Set Control Potential" control on the potentiostat. The oscilloscope indicated any difficulties that arose either external to or in the equipment. At intervals samples were taken of the anolyte. The samples were removed without disrupting the electrolysis and were analyzed immediately. At the conclusion of an electrolysis, samples were taken of the anolyte, catholyte and reference solution.

Chapter 3

RESULTS AND DISCUSSION

3.1 Electrolysis of Iodine-131 in Basic Solution

3.1.1 Early Electrolysis Experiments. The first experiments were carried out to determine if carrier-free iodate-131 could be formed by electrolysis of carrier-free iodide-131 solutions and to determine the best electrolysis cell design. The results of these first electrolysis experiments are presented in this section. Two types of electrolysis cells were used in these early experiments; one employed fine-fritted-glass disks to separate the compartments and the other used short lengths of capillary tubing to connect the compartments. Neither of the electrolysis cells used in these first experiments represents exactly the final cell design but the results obtained with them are given in this section for the information that they contain.

Three electrolysis experiments were performed in a cell where fine-fritted-glass disks were used to separate the compartments (see Figure 3.1). Twenty milliliters of solution was electrolyzed in this cell at an anode potential of +1.986 volts vs. S.C.E. The electrolyses were carried out as previously described (see Section 2.6.3) and the samples were analyzed by the solvent extraction method (see Section 2.5.1). The results are shown in Table 3.1. During the electrolyses there was considerable transfer of liquid from the anode to the cathode compartment by electroosmosis. Both compartments originally contained 20 milliliters of solution; at 4 hours the anode compartment contained about 13 milliliters and the cathode compartment approximately 26 milliliters of solution. That this was primarily a transfer of solvent and not of the entire

Figure 3.1 Electrolysis Cell With Fritted-glass Connectors

Table 3.1 Electrolysis of Carrier-free Iodide-131
in 0.01 M NaHCO₃ Solution at an Anode
Potential of +1.986 volts vs. S.C.E.^a

Time, hr.	Distribution of Activity, % ^b			
	A	B	C	D
0	0.5	0.1	95	4.4
4	0.1	0	0.4	100
0	0.8	1.9	92	5.0
2	1.7	2.1	1.8	94
4	0.4	0.5	1.1	98
0	0.2	0.8	94	5.1
0.25	1.7	1.3	27	70
1	1.4	0.5	2.1	96

^aThe potential across the working electrodes at the beginning of an electrolysis was 30 volts and it dropped to 10 volts at 4 hours.

^bThe percent distribution is based upon the total activity in the analytical sample; the samples were analyzed by the solvent extraction procedure.

solution was apparent from the observation that the specific activity of the anolyte increased and that little activity was found in the catholyte.

To determine what portion of Fraction D was iodate, other solutions were electrolyzed in an identical manner and the electrolysis product analyzed by the fractional precipitation method which is specific for iodate. The starting materials were of the same general composition as those shown in Table 3.1, (A = 0.7%, B = 0.8%, C = 94.8% and D = 3.7%). The results of three different electrolyses are given in Table 3.2. Fraction D appeared to be virtually all iodate. Because of the electro-osmosis effect encountered in this cell at this anode potential, no attempt was made to establish the total recovery of iodine-131 activity.

The transfer of solvent from anolyte to catholyte was an undesirable effect. For production of carrier-free iodate-131 this might be no problem (it could even be an advantage at times in that it concentrates the activity) but in an investigation of the electrolytic oxidation of carrier-free iodide-131, this change in composition of the solution was an undesirable complication. To circumvent this problem, a change was made to a cell which used a capillary tube to connect the compartments as in Figure 3.2. Several electrolyses were carried out in this cell; no electroosmosis effect was observed. Two samples were taken for analysis each time except for the initial solution. One sample was analyzed by the solvent extraction method and the other by fractional precipitation.

The results of the electrolyses in the cell with the capillary tube connecting member are given in Table 3.3. By comparing the results for the percent iodate obtained by the fractional precipitation procedure with

Table 3.2 Electrolysis of Carrier-free Iodide-131
in 0.01 M NaHCO₃ Solution at an Anode
Potential of +1.986 volts vs. S.C.E.^a

<u>Time, hr.</u>	<u>Iodate, %^b</u>
1.25	92
1	85
2.25	97

^aThe potential across the working electrodes at the beginning of an electrolysis was 30 volts and it dropped to 10 volts at 4 hours.

^bThe percent iodate is based upon the total activity in the analytical sample as determined by the fractional precipitation method of analysis.

Figure 3.2 Electrolysis Cell With Capillary Tube Connectors

Table 3.3 Electrolysis of Carrier-free Iodide-131
in 0.01 M NaHCO₃ Solution in Cell
With Capillary Tube Connectors

Anode Potential, volts vs. S.C.E.	Time, hr.	Analysis				Precipitation, % IO_3^- ^c
		Extraction, Distribution of Activity, % ^b				
		A	B	C	D	
0.500	0	0.2	0.6	98	1.3	----
	2	0.8	0.6	95	3.4	5.4
	4	1.7	0.9	93	4.5	7.8
1.000	0	0.2	0.5	98	1.7	----
	2	0.2	0.7	8.0	91	93
1.000	0	1.0	0.6	96	2.7	----
	2	0.9	0.4	12	87	86
1.340	0	0.4	0.6	97	2.1	----
	2	0.4	0.7	0.7	98	98
1.340	0	0.9	0.8	96	2.2	----
	2 ^a	1.0	0.6	5.2	93	87
1.350	2	0.8	0.9	0.8	98	97

^aThe electrolysis was interrupted several times for short periods.

^bThe percent distribution is based upon the total activity in the analytical sample; the samples were analyzed by the solvent extraction procedure.

^cThe percent iodate is based upon the total activity in the analytical sample as determined by the fractional precipitation method of analysis.

the results found by the solvent extraction method of analysis, it can be seen that the material found in Fraction D is all iodate. Additional information concerning these electrolysis experiments is given in Table 3.4. As shown in Table 3.4, there was greater movement of iodine-131 activity from the anode compartment to the cathode compartment when electrolyzing at an anode potential of +0.500 volt vs. S.C.E. than when electrolyzing at the higher anode potentials of +1.000 and +1.340 volts vs. S.C.E.

The two major disadvantages of the cell with capillary tube connecting members were the mixing of the solutions between adjacent compartments, particularly when samples were removed, and the relatively high electrical resistance between adjacent compartments (see Section 2.2.2). These difficulties were of sufficient magnitude to make the use of this cell design undesirable for the present investigation.

The only problem encountered with the cell employing fine-fritted-glass disks to separate the compartments was an electroosmosis effect. However, it was found that when 0.01 M sodium bicarbonate solution was electrolyzed at an anode potential of less than +1.000 volt vs. S.C.E. in a cell using fine-fritted-glass disks to separate the compartments, no change in the height of the liquid in the compartments could be observed. Since it was also found that anode potentials of greater than +1.000 volt vs. S.C.E. would not normally be necessary in this investigation, the cell employing fine-fritted-glass disks to separate the compartments could be used. Several electrolysis cells of this type were constructed and these were used for the remainder of this investigation.

Table 3.4. Additional Information on the Electrolysis Experiments Summarized in Table 3.3^a

Anode Potential, volts vs. S.C.E.	Potential Across Working Electrodes, volts ^b		Current, milliamperes ^c	Activity Distribution, % ^d		
	Initial	Steady		Anolyte	Catholyte	Reference
0.500	3	0.7	< 0.01	72	20	8
1.000	14	3	0.04	93	3	4
1.340	49	34	0.5	97	0.4	3

^aThe values listed are the average of the values observed at each anode potential.

^bThe initial value is that seen when the electrolysis was first started; within 10 to 30 minutes it dropped to the steady value and remained at that point.

^cThis is the value observed during most of the electrolysis; a higher current was observed for the first 10 to 30 minutes.

^dDistribution of the activity after electrolyzing for 2 hours; total recovery was 98 to 101%.

3.1.2 Production of Carrier-free Iodate-131 as a Function of the Anode Potential. Carrier-free iodide-131 in 0.01 M sodium bicarbonate solution was electrolyzed in the cell employing fritted-glass separators (illustrated in Figure 2.7). The results of these electrolysis experiments are summarized in Table 3.5 and the production of iodate is illustrated in Figure 3.3. These results show that the percent of activity converted to iodate depends upon the anode potential and the time of electrolysis; for example, at an anode potential of +1.000 volt vs. S.C.E. greater than 90% of the iodine-131 activity is converted to iodate in 2 hours but at an anode potential of +0.700 volt vs. S.C.E. there is no increase in the percent iodate over that observed with no applied potential. No activity was found in the reference compartment solutions and never more than 0.1% of the total in the catholyte after an electrolysis. In the electrolyses at +1.00 volt vs. S.C.E., the activity in the anolyte remained constant; in the solutions electrolyzed at lower potentials the activity in the anolyte decreased during the electrolysis. Commonly the anolyte would contain about 90% of the initial activity after electrolyzing for 6 hours.

It was of interest to determine what happened to the activity which was lost from the anolyte during an electrolysis. This activity was not found in the reference compartment solution or the catholyte; it could have been lost by volatilization, by adsorption on the cell walls or to the graphite anode. Experiments were performed to determine the distribution of the iodine activity following electrolysis. A typical experiment is described below. An electrolysis was carried out as usual in 0.01 M sodium bicarbonate solution. The iodide-131 was added to the anolyte, the solution stirred for about 30 seconds and a 1-milliliter sample of

Table 3.5 Production of Carrier-free Iodate-131 by Electrolysis
of Carrier-free Iodide-131 in 0.01 M NaHCO₃ Solution

Electrode Potential, volts vs. S.C.E.	Time, hr.	Potential Across Working Electrodes, volts ^a	Current, milliamperes	Iodate, % ^b
-- ^c	0	0	0	9.9 ^d
	4	0	0	9.0
	6	0	0	10
	24	0	0	16
--	0	0	0	3.0
	2	0	0	6.2
	5	0	0	15
	28	0	0	13
0.700	0	1.5	0.04	1.6
	2	0.9	< 0.01	9.0
	4	0.9	< 0.01	10
	6	0.9	< 0.01	16
0.700	1	0.9	--	2.8
	2	0.9	--	3.2
	4	0.9	--	4.2
0.800	0	2.4	0.12	4.3
	2	1.1	0.01	18
	4	1.1	0.01	16
	6	1.1	0.01	24
0.800	2	1.1	0.01	12
	4	1.1	0.01	20
	9.2	1.0	--	31
0.850	0	2.0	0.10	5.2
	2	1.2	0.01	28
	4	1.2	0.01	36
	6	1.2	0.01	47

Table 3.5 (Continued)

Electrode Potential, volts vs. S.C.E.	Time, hr.	Potential Across Working Electrodes, volts ^a	Current, milliamperes	Iodate, % ^b
0.900	0	2.5	0.14	3.0
	2	1.3	0.01	54
	4	1.3	0.01	66
	6	1.3	0.01	78
0.900	0	3.5	0.24	0
	1	1.3	0.02	39
	5	1.3	0.01	73
	8	1.3	0.01	81
1.000	0	4	0.31	1.7
	1	2	0.02	76
	2	2	0.01	94
1.000	3	2.5	0.01	93
1.000	1	2.5	0.02	76
	2	2.2	0.01	90
	4	2.0	0.01	94
1.200 ^e	0	7.0	0.54	1.3
	1	4.2	0.24	92
	6	4.0	0.22	92

^aThis value was observed during most of the electrolysis; at the beginning of an electrolysis the potential was larger.

^bThe percent iodate is based upon the total activity in the analytical sample as determined by the fractional precipitation method of analysis.

^cIn the two runs listed with 0 volts across the working electrodes, no electrical connections were made to the electrodes; otherwise everything was carried out as usual.

^dA relatively old stock (almost 3 months) of carrier-free iodide-131 was used for this run which probably accounts for the high value for Fraction Iodate at 0 time; normally activity this old was not used.

^eThis was the only case in which an electroosmosis effect was observed; the anolyte lost about 10% in volume and the catholyte volume increased a corresponding amount.

Figure 3.3 Production of Carrier-free Iodate-131 by Electrolysis of Carrier-free Iodide-131 in 0.01 M NaHCO_3 Solution

the anolyte removed for counting. The electrodes were immersed into the solution and the potentiostat connected. The potentiostat was switched on and the solution was electrolyzed for 6.5 hours at an anode potential of +0.800 volt vs. S.C.E. and another 1-milliliter sample of the anolyte removed. The solution in each compartment of the cell was transferred by pipette to a volumetric flask. Each compartment was rinsed with a 5-milliliter portion of 0.01 M sodium bicarbonate solution three times and the rinsings added to each flask. The solutions in the flasks were diluted to volume and a sample of each counted to determine the iodine-131 activity. Chromic acid cleaning solution was added to each compartment of the electrolysis cell to remove any activity that might have been adsorbed on the cell walls; after several hours the cleaning solutions were transferred to counting tubes and the activity in each determined. The graphite anode was rinsed with 0.01 M sodium bicarbonate solution, dropped into a counting tube and counted (see Section 2.4.2).

The 1-milliliter sample of the original solution had an activity of 34,029 c/m; the sample taken after electrolyzing for 6.5 hours had an activity of 30,273 c/m for a loss from solution of 11.0%. The total activity initially present was 850,728 c/m; the following amounts were recovered:

797,227 c/m or	93.7%	in the anolyte
1,915 c/m or	0.2%	from the walls of the cell
<u>73,301 c/m or</u>	<u>8.6%</u>	<u>in the graphite anode</u>
872,443 c/m or	102.5%	total recovery.

No activity was found in the reference solution or catholyte. The results of many such experiments suggest that the activity which was lost from the anolyte when electrolyzing at potentials of +0.900 volt or less vs.

S.C.E. was lost to the graphite anode; as previously mentioned there was no loss of activity from the anolyte when electrolyzing at an anode potential of +1.000 volt vs. S.C.E.

The pH of the 0.01 M sodium bicarbonate solutions before electrolysis was 8.95 as determined with a Beckman Model G pH Meter. The pH of the anolyte increased slightly during an electrolysis; typically the pH of the anolyte at the conclusion of an electrolysis was 9.0 to 9.1.

As can be seen from both Table 3.5 and Figure 3.3, at an anode potential of +0.700 volt vs. S.C.E. there was no electrolytic oxidation to iodate. The numbers found for percent iodate at this potential are intermingled with those found with no applied potential. At an anode potential of +0.800 volt vs. S.C.E., there was a small but definite production of iodate; as the anode potential was further increased, the rate of production of iodate increased.

In order to determine the minimum anode potential necessary to produce iodate under these conditions, a plot was made of the fraction of the activity as iodate versus anode potential at various constant times. The iodate fraction at any time was corrected for the small amount of iodate produced when there was no applied potential using the information in Figure 3.3. Extrapolation of the curves to zero percent iodate should give the minimum anode potential necessary to form iodate in the solution. Such a plot is shown in Figure 3.4 for 2, 4 and 6 hours. Straight lines drawn through the points and extrapolated to zero percent iodate intercept the X-axis at +0.79 volt vs. S.C.E. giving this as the minimum anode potential necessary to oxidize carrier-free iodide- 131 I to carrier-free iodate- 131 I in 0.01 M sodium bicarbonate solution using graphite electrodes.

Figure 3.4 Iodate Fraction vs. Anode Potential

In order to show that the oxidation of iodide to iodate was an electrolytic oxidation rather than a chemical oxidation by some material formed during the electrolysis, the following experiment was performed. A solution of 0.01 M sodium bicarbonate was electrolyzed for 1.5 hours at an anode potential of +1.00 volt vs. S.C.E. The electrolysis was carried out as usual except that no iodine was present during the electrolysis. At the conclusion of the electrolysis, the leads to the electrodes were disconnected and immediately some carrier-free iodide-131 was added to the anolyte. The stirring of the anolyte was continued and samples were removed at 5 minutes and 1 hour; analysis of these samples gave an iodate content of 2.5% at 5 minutes and 2.5% at 1 hour. These results suggest that the oxidation of the carrier-free iodide-131 to carrier-free iodate-131 is an electrolytic oxidation rather than a chemical oxidation by some material formed in the solution during the electrolysis.

3.1.3 Effect of Total Iodide Concentration on Production of Iodate.

Other workers in the field have observed that iodine at very low concentrations behaves differently than when it is present in gross amounts (2-6). To determine if this phenomenon was observable in the electrolytic oxidation of iodide, a study was made of the electrolytic production of iodate from iodide as a function of total initial iodide concentration. These electrolyses were carried out in 0.01 M sodium bicarbonate solution; with the exception of the iodine concentration, all of the conditions were the same as those previously described. The appropriate amount of freshly prepared potassium iodide solution was added to the sodium bicarbonate solution in the anode compartment to give a solution having the desired iodide concentration; this solution was then inoculated with the iodide-131 in the usual manner. The results of this study are given in Table 3.6.

Table 3.6 Effect of Total Initial Iodide Concentration on the Electrolytic Oxidation of Iodide to Iodate in 0.01 M NaHCO₃ Solution

Initial Iodide Concentration, Molarity	Anode Potential, volts vs. S.C.E.	Time, hr.	Iodate, % ^a
10 ⁻⁴	0.900	0	0
		1	26
		4	73
		6	89
	0.900	0	0.5
		1	40
		4	80
		6	92
	1.000	0	0.8
		4	95
	1.000	0	0.7
		4	92
	1.000	0	0.3
		4	95
10 ⁻⁵	0.900	0	0.6
		3	70
	0.900	0	0.7
		3	81
10 ⁻⁷	0.900	0	2.4
		3	65
	0.900	0	1.4
		3	59
	1.000	0	2.8
		3	85
C.F. ^b	0.900	0	3
		1	39
		4	67
		6	78
C.F.	1.000	4	94

^aThe percent iodate is based upon the total activity in the analytical sample as determined by the fractional precipitation method of analysis.

^bResults with carrier-free material are included for comparison.

Figure 3.5 shows some results obtained at an anode potential of +0.900 volt vs. S.C.E. over a total iodine concentration range of carrier-free 10^{-4} M. The fraction of iodate found at any time is seen to be essentially independent of the total initial iodide concentration at a constant anode potential over the concentration range investigated (carrier-free to 10^{-4} M). No activity was found in the reference solution or catholyte following an electrolysis. There was a small loss of activity from the anode compartment in the 10^{-4} M iodide solutions during the electrolysis. This loss usually amounted to about 5% of the total initial activity after electrolyzing for 4 hours. In a check of total recovery after electrolyzing a 10^{-4} M iodide solution at +1.000 volt vs. S.C.E. for 4 hours, 88% of the initial activity was found in the anolyte, 7% in the anode and no activity was recovered from the walls of the cell, the catholyte or the reference solution giving a total recovery of 95%.

The observation that the fraction of iodide reacted is independent of the total initial iodide concentration over the concentration range of carrier-free to 10^{-4} M suggests that over this concentration range the iodide concentration enters the rate law to the first power. If the iodide concentration entered the rate law to a power greater than one, the rate of the reaction would decrease as the iodide concentration decreased. If the iodide concentration entered the rate expression to a power less than one (as might be the case if it existed in solution as a dimer and its concentration entered the rate law to a fractional power) the rate of reaction, expressed in terms of the fraction reacted, would increase as the iodide concentration decreased because at the lower concentration a larger fraction of the material would dissociate into the reactive species. In general, the rate of reaction of a tracer quantity

Figure 3.5 Effect of Total Initial Iodide Concentration on the Electrolytic Oxidation of Iodide to Iodate in 0.01 M NaHCO₃ Solution at an Anode Potential of +0.900 volt vs. S.C.E.

of material, expressed in terms of the fraction of the tracer reacted or unreacted, will depend upon the initial concentration of the tracer in a manner which is a function of the order to which the tracer enters the rate law. If it is assumed that the other reactants are present in large excess so that their concentrations do not change during the reaction and that the products of the reaction do not take part in the reaction, the rate of the reaction is given by

$$-\frac{dA}{dt} = kA^n$$

where A is the concentration of the material at time t, n is the apparent order of the reaction and k is the rate constant. (The value of k will vary if the experimental conditions under which the reaction is carried out are changed, but for the same conditions it is a constant.)

Then

$$-\frac{dA}{A^n} = k dt$$

and for n not equal to 1, integration yields

$$-\frac{A^{1-n}}{1-n} = kt + C.$$

At t = 0, A = A₀, so

$$\frac{A^{1-n}}{n-1} = kt + \frac{A_0^{1-n}}{n-1}$$

or

$$A^{1-n} = (n-1)kt + A_0^{1-n}. \quad (1)$$

For n = 0, from equation (1), A = -kt + A₀. The fraction remaining

at any time, $\frac{A}{A_0}$, is given by

$$\frac{A}{A_0} = -\frac{kt}{A_0} + 1.$$

The manner in which the fraction remaining will vary with the initial concentration is given by

$$\left. \frac{\partial \frac{A}{A_0}}{\partial A_0} \right)_t = \frac{kt}{A_0^2}.$$

Since $\left. \frac{\partial \frac{A}{A_0}}{\partial A_0} \right)_t$ is positive for any value of t and A_0 , the fraction

of the material remaining at any time, t , increases as the initial concentration increases or the rate of the reaction, expressed in terms of the fraction of the material reacted, decreases as the initial concentration increases for $n = 0$.

For $n = \frac{1}{2}$, from equation (1), $A^{\frac{1}{2}} = -\frac{1}{2} kt + A_0^{\frac{1}{2}}$.

The fraction remaining at any time, $\frac{A}{A_0}$, is given by

$$\frac{A}{A_0} = \frac{(-\frac{1}{2} kt + A_0^{\frac{1}{2}})^2}{A_0}$$

thus

$$\left. \frac{\partial \frac{A}{A_0}}{\partial A_0} \right)_t = \frac{A_0^{\frac{1}{2}}(-\frac{1}{2} kt + A_0^{\frac{1}{2}}) - (-\frac{1}{2} kt + A_0^{\frac{1}{2}})^2}{A_0^2}.$$

Simplifying and making the substitution

$$kt = 2 A_0^{\frac{1}{2}} - 2 A^{\frac{1}{2}} \text{ gives}$$

$$\begin{aligned} \left. \frac{\partial \frac{A}{A_0}}{\partial A_0} \right)_t &= \frac{A_0^{\frac{1}{2}} A^{\frac{1}{2}} - A}{A_0^2} \\ &= \frac{1}{A_0} \left[\left(\frac{A}{A_0} \right)^{\frac{1}{2}} - \frac{A}{A_0} \right]. \end{aligned}$$

Because $\frac{A}{A_0}$ is less than one and the value of the square root of a number less than one is greater than the number, the expression on the right is positive for any value of A_0 and t (the expression

$$\left. \frac{\partial \frac{A}{A_0}}{\partial A_0} \right)_t \text{ is always positive). Thus, the fraction}$$

remaining, $\frac{A}{A_0}$, at any time, t , will always increase as the initial concentration, A_0 , increases; therefore the rate of the reaction, expressed in terms of the fraction reacted, will decrease as the initial concentration increases for $n = \frac{1}{2}$.

For $n = 2$, from equation (1), the expression becomes

$$\frac{1}{A} = kt + \frac{1}{A_0}$$

or

$$\frac{A}{A_0} = \frac{1}{A_0 kt + 1}$$

then

$$\left. \frac{\partial \frac{A}{A_0}}{\partial A_0} \right)_t = \frac{-kt}{(A_0 kt + 1)^2}.$$

Since this quantity is always negative for any value of A_0 and t , as the initial concentration, A_0 , increases the fraction remaining, $\frac{A}{A_0}$, decreases. Therefore, for $n = 2$, the rate of the reaction, expressed in

terms of the fraction reacted, increases as the initial concentration, A_0 , increases.

$$\text{For } n = 1, \quad -\frac{dA}{A} = kt$$

and integrating

$$\ln \frac{A}{A_0} = -kt$$

$$\frac{A}{A_0} = e^{-kt}$$

$$\left(\frac{\partial \frac{A}{A_0}}{\partial A_0} \right)_t = 0.$$

In the case of $n = 1$, the fraction remaining and therefore the rate of the reaction expressed in terms of the fraction reacted, is independent of the initial concentration.

When the solutions were analyzed by the extraction method it was found that essentially all the activity was present as iodate or a species which behaved in the extraction like iodide (not extracted by benzene but extracted by 0.01 M iodine in benzene), so all non-iodate activity was assumed to be iodide. A plot of the logarithm of the fraction of iodide remaining versus time at a constant anode potential gives reasonably good agreement with the straight line predicted for a reaction which follows the first order rate law, Figure 3.6.

$$\log \left(\frac{a-x}{a} \right) = -\frac{k}{2.303} t.$$

The slope of the line is $-\frac{k}{2.303}$. The value of k will depend upon the stirring rate, the electrode area and the electrode potential among other things. The dependence of the value of k upon the anode potential is

Figure 3.6 Log (Iodide Fraction) vs. Time

illustrated by the different slopes for the plots at different anode potentials keeping everything else constant.

3.1.4 Electrolysis in 10^{-4} M Sodium Bicarbonate Solution. For some uses, such as in the medical field, it is desirable to have the iodine in a solution containing as little other materials as possible. Considering this, it would be of interest to see what effect decreasing the concentration of the sodium bicarbonate solution would have upon the electrolytic oxidation of carrier-free iodide-131 to iodate. Twenty-five milliliters of 10^{-4} M sodium bicarbonate solution was added to each compartment of the cell; carrier-free iodide-131 was added to the center compartment. The solution was electrolyzed for 4 hours at an anode potential of +1.00 volt vs. S.C.E. The potential across the working electrodes was very unsteady; the current was less than 0.01 milliampere. There was considerable transfer of liquid from the anode compartment to the cathode compartment due to electroosmosis during the electrolysis. No electroosmosis is observed when 0.01 M sodium bicarbonate solutions are electrolyzed at an anode potential of +1.00 volt vs. S.C.E. After the electrolysis the solutions were removed from each of the three compartments by pipette and transferred to volumetric flasks. Each compartment was rinsed two times with 10^{-4} M sodium bicarbonate solution and the rinsing added to the solutions. Chromic acid cleaning solution was used to remove any activity which might have been adsorbed on the walls of the cell. The activities of the anode and cathode were also determined. Total recovery was 100.7% of the initial activity. The iodine was distributed as follows: 80.4% in the anolyte, 0.4% in the catholyte, 0.7% from the walls of the cell and 19.2% in the anode. No activity was found in the reference solution and less than 0.01% in the cathode. The pH of

the original anolyte was 7.35; at the conclusion it was 7.30. The results for the percent iodate formed in two such electrolyses in 10^{-4} M sodium bicarbonate solution are given in Table 3.7; the values for the other quantities were essentially the same in the two electrolyses. The fraction of the activity converted to iodate is much less when the electrolysis is carried out in 10^{-4} M sodium bicarbonate solution than when it is done in 0.01 M sodium bicarbonate solution. In 0.01 M sodium bicarbonate solution at an anode potential of +1.000 volt vs. S.C.E., greater than 90% of the activity was converted to iodate in 2 hours; at the same anode potential in 10^{-4} M sodium bicarbonate solution less than 50% of the activity was converted to iodate at 4 hours.

3.1.5 Distribution of Iodine Activity. In most of the work discussed up to this point the solution was analyzed by the fractional precipitation method, which is specific for iodate, in order to follow the change of iodate in the solution during the electrolysis. Had a different method of analysis been used which did not give a definitive value for a species, interpretation of the results would have been more difficult. For example, if the extraction procedure had been used to analyze the solutions, the amount of activity found in D would represent the activity due to iodate plus that due to any other species which extracted in the same manner. Thus, the extraction method of analysis would set an upper limit on the amount of iodate but would not give a definite value for it. It is known that in the chemical oxidation of solutions of carrier-free iodide- 131 I, an iodine species is often formed which behaves like iodate in this extraction procedure but which does not exchange with iodate (2,3).

After the rate of formation of iodate under controlled conditions at

Table 3.7 Electrolysis of Carrier-free Iodide-131
in 10^{-4} M NaHCO_3 Solution

<u>Anode Potential,</u> <u>volts vs. S.C.E.</u>	<u>Time, hr.</u>	<u>Iodate, %^a</u>
1.00	0	1.2
	4	37
1.00	0	1.4
	4	49

^aThe percent iodate is based upon the total activity in the analytical sample as determined by the fractional precipitation method of analysis.

various anode potentials had been established, it was of interest to determine the other chemical species of iodine that might be formed during electrolysis. It seemed likely that other chemical forms of iodine, intermediate in oxidation state between iodide and iodate, might be found in the solution, particularly when electrolyzing at intermediate anode potentials (+0.800 to +0.900 volt vs. S.C.E.) where the rate of formation of iodate is relatively slow. Therefore electrolyses were carried out in a manner identical to that used in the investigation of iodate formation and the solutions were analyzed by the solvent extraction procedure as previously described (see Section 2.5.1). The results of two such electrolyses at an anode potential of +0.850 volt vs. S.C.E. are given in Table 3.8 and Figures 3.7 and 3.8. Additional information concerning these electrolyses is given in Table 3.9.

The activity found in fraction D could be iodate or other materials which extract in the same manner in the extraction procedure used, but comparison of the results found for fraction D with the values found for iodate by the fractional precipitation method indicates that fraction D is primarily iodate. Thus, in the electrolytic oxidation of solutions of carrier-free iodide-131 in 0.01 M sodium bicarbonate at an anode potential of +0.850 volt vs. S.C.E., fraction D contains only iodate. The D fraction here corresponds to the Z fraction of Eiland and Kahn (3). They found that chemical oxidation of carrier-free solutions of iodide-131 with nitric acid and acid solutions of chromium (IV) and cerium (IV) resulted in a Z fraction which contained iodate and at least one other species of iodine in varying amounts.

Fraction A represents activity which was extracted by benzene but not

Table 3.8 Characterization of Iodine-131 Activity
Present in 0.01 M NaHCO₃ Solution Follow-
ing Electrolysis at +0.850 volt vs. S.C.E.

Time, hr.	Distribution of Activity, % ^a			
	A	B	C	D
0	0.2	0.6	96	3.6
2	9.8	1.2	70	19
4	10	0.8	60	29
6	11	1.0	47	41
24	3.4	0.6	21	75
0	0.1	1.4	96	2.3
2	9.2	0.7	68	22
4	9.3	1.0	58	32
6	7.5	0.8	51	41
24	1.0	0.3	22	77

^aThe percent distribution is based upon the total activity in the analytical sample as determined by the solvent extraction method of analysis.

Figure 3.7 Electrolysis at +0.850 volt vs. S.C.E. in 0.01 M NaHCO_3 Solution

Figure 3.8 Electrolysis at +0.850 volt vs. S.C.E. in 0.01 M NaHCO_3 Solution

Table 3.9 Additional Information on Electrolysis Experiments Summarized in Table 3.8

<u>Time, hr.</u>	<u>Potential Across Working Electrodes, volts^a</u>	<u>Current, milliamperes^b</u>	<u>Activity Remaining in Anolyte, %^c</u>
2	1.4	0.02	91
4	1.3	0.01	87
6	1.2	0.01	85
24	1.1	< 0.01	81
2	1.2	0.01	92
4	1.2	0.01	87
6	1.1	< 0.01	86
24	1.1	< 0.01	81

^aThe initial potential was much higher but it dropped rapidly in the first 10 to 30 minutes.

^bThe current was also much higher in the first 10 to 30 minutes of the electrolysis.

^cThis is the percent activity in the anolyte based upon a sample of the anolyte taken immediately after adding the iodide activity.

back-extracted with aqueous iodide (did not exchange rapidly with iodide). About 10% of the activity was in fraction A after electrolysis for 2 to 4 hours (see Figure 3.7); continued electrolysis resulted in a decrease of the quantity of this species (see Figure 3.8). Electrolyzing for 24 hours converted most of the material in solution that was extracted into fraction A to a form that was extracted into fraction D. Fraction C continuously decreased during the electrolysis.

At the end of the electrolyses no activity was found in the reference compartment solution and less than 0.4% of the total initial activity was found in the catholyte. In each case the anode contained 18% of the initial activity after electrolyzing for 24 hours. The total recovery was 99% for each of the electrolyses.

Electrolyses were carried out at various anode potentials in order to determine the effect of the anode potential on the production of the species found in fraction A. The results are given in Table 3.10. The very small quantity of activity found in fraction A in every case was unexpected. This was particularly true of the electrolysis at +0.850 volt vs. S.C.E. which was a repeat of previous electrolyses at that potential which had yielded about 10% of the activity in A (see Table 3.8). Identical conditions were used for the electrolyses. The earlier electrolysis at +0.850 volt vs. S.C.E. had been duplicated at the time with good agreement between the two runs. The only difference between the present electrolyses and the previous ones was the shipment of iodide-131 activity used. In both cases the iodide-131 was fission-produced, processed material from Oak Ridge National Laboratory and was used as received. No effect on the results had been observed in any of the other electrolyses

Table 3.10 Characterization of Iodine-131 Activity Present
in 0.01 M NaHCO₃ Solution Following Electrolysis

Anode Potential, volts vs. S.C.E.	Time, hr.	Distribution of Activity, % ^a				Activity Remaining in Anolyte, % ^b
		A	B	C	D	
0.800	0	0.2	0.4	97	2.9	100
	2	1.4	0.4	87	11	87
	4	2.5	0.5	80	17	83
	6	3.2	0.5	75	21	80
	24	2.9	0.4	53	44	74
0.850	0	0.1	0.3	97	2.8	100
	0.25	0.6	0.5	93	5.6	96
	0.5	1.0	0.6	89	9.1	94
	1	0.9	0.4	85	14	92
	4	2.0	0.4	60	37	86
0.900	0	0.1	0.4	97	2.7	100
	1	3.3	0.7	59	37	98
	2	2.5	0.5	43	54	98
	4	3.1	0.4	22	75	93
	6	2.2	0.3	13	85	91

^aThe percent distribution is based upon the total activity in the analytical sample as determined by the solvent extraction method of analysis.

^bBased upon a sample taken immediately after adding the iodide activity.

as a result of using different shipments of iodide-131 activity.

However, since this was the only known difference between the electrolyses reported in Tables 3.8 and 3.10, the variation of the quantity of material found in fraction A may be attributed to this difference. No activity was found in the reference compartment solution or the catholyte at the end of an electrolysis. In every case the graphite anode contained the activity lost from the anolyte. Total recovery of the iodine activity ranged from 96 to 101%.

To check the possibility that the shipment of iodide-131 was causing the variation in the quantity of material found in fraction A, a new shipment of iodide-131 was obtained from Oak Ridge National Laboratory and used for additional electrolyses. Except for the change in the iodide-131 activity, the conditions used for these electrolyses were identical to those previously used. The results are shown in Table 3.11; the production of fraction A is shown in Figure 3.9. An appreciable quantity of activity was found in fraction A when the iodide-131 from this shipment of activity was electrolyzed at an anode potential of +0.800 or +0.850 volt vs. S.C.E.

At the conclusion of an electrolysis no activity was found in the reference compartment solution, the catholyte, the walls of the cell or the cathode. In every case the activity found in the anode accounted for most of the activity lost from the anolyte. Total recovery of the initial activity was 98 to 100%.

Since the only change made in the three sets of electrolyses shown in Tables 3.8, 3.10 and 3.11 was in the shipment of iodide-131 activity used to inoculate the sodium bicarbonate solution, the variation in the

Table 3.11 Characterization of Iodine-131 Activity Present
in 0.01 M NaHCO₃ Solution Following Electrolysis

Anode Potential, volts vs. S.C.E.	Time, hr.	Distribution of Activity, % ^a				Activity Remaining in Anolyte, % ^b
		A	B	C	D	
0.800	0	0.5	0.8	96	2.7	100
	1	5.3	0.9	88	6.3	92
	4	7.9	0.8	76	15	83
0.850	0	1.5	0.9	95	2.9	100
	1	3.7	0.8	87	8.6	95
	4	6.4	0.6	68	25	88
0.850	0	0.8	1.0	96	2.1	100
	1	4.0	1.0	82	13	93
	4	8.8	0.9	56	35	88
	6	7.1	0.7	47	46	86
0.950	0	0.5	1.1	96	2.2	100
	1	4.2	0.9	42	53	98
	4	2.6	0.3	8.4	89	95
	6	1.3	0.8	2.9	95	94

^aThe percent distribution is based upon the total activity in the analytical sample as determined by the solvent extraction method of analysis.

^bBased upon a sample taken immediately after adding the iodide activity.

Figure 3.9 Production of Fraction A in 0.01 M NaHCO_3 Solution

quantity of activity found in fraction A after electrolyzing must be due to the iodide-131 used. The activity used should have been identical but apparently it was not. The analyses at zero time (the sample for this analysis was removed within a minute or two after adding the activity to the sodium bicarbonate solution) for the various solutions show no significant variation for the different shipments of activity. No other evidence of any differences among shipments of iodide-131 activity as received from Oak Ridge National Laboratory had been observed during previous electrolyses. But certainly the formation of the material found in fraction A was a function of the shipment of iodide activity used. The formation of fraction A does not depend upon the age of the iodide-131 activity used. A shipment of Oak Ridge iodide-131 activity which did not form any of fraction A upon electrolysis when first received did not do so when the activity was two months old. Also, a shipment of iodide-131 activity which did yield some fraction A upon electrolysis when first received gave approximately the same fraction as A when the activity was two months old. From the results presented in Table 3.11, it does not seem that production of fraction A depends to any great extent upon the anode potential used in the electrolysis. At intermediate anode potentials (+0.800 to +0.850 volt vs. S.C.E.) the fraction of the activity found in A appears to be independent of the potential. At an anode potential of +0.950 volt vs. S.C.E. less activity was found in A. This was probably due to the relatively rapid oxidation of the material to iodate. At each potential there is competition between the two processes (the oxidation to the species found in A and oxidation to iodate). The higher anode potential favors the production of iodate over that of the species in A because the rate of production of iodate increases directly

as the anode potential increases while the production of the species in A is relatively independent of the anode potential.

From the results in Tables 3.8 and 3.11 and Figures 3.8 and 3.9, it can be seen that the material in A was formed relatively rapidly, reached a maximum amount after electrolyzing for about 4 hours, and decreased in quantity with continued electrolysis.

No explanation can be offered for the variation in the fraction of the iodine-131 activity found in fraction A following electrolysis. The same sodium bicarbonate stock solution was used for the electrolysis experiments so an impurity in this solution should have affected all the experiments in the same manner. The same line of reasoning eliminates the electrolysis cell, the method of cleaning the cell and the graphite electrodes as the source of the different results since these items were also constant for all the electrolysis experiments. And, as stated above, the age of the iodide-131 activity (measured from the date of receipt) did not affect the results. The only variable that was observed to cause the effect was the shipment of iodide-131 activity used in the electrolysis.

From the results that have been reported for the chemical oxidation of iodide solutions (2,3), it would not be expected that activity would be found in fraction A when solutions containing iodide in concentration greater than 10^{-5} M total iodine are electrolyzed. To check this point a solution 10^{-4} M in iodide and 0.01 M in sodium bicarbonate was electrolyzed at an anode potential of +0.850 volt vs. S.C.E. The solution was prepared by adding 250 μ l of freshly prepared 0.01 M potassium iodide solution to 25 milliliters of 0.01 M sodium bicarbonate solution. The

solution was then inoculated with iodide-131 activity from the same shipment as used for the electrolysis experiments summarized in Table 3.11; this activity yielded an appreciable quantity of material in fraction A when electrolyzed at carrier-free concentrations. A sample of the solution was removed for analysis immediately after adding the iodide-131 and the solution was electrolyzed in the usual manner. The results of this electrolysis are shown in Table 3.12. As was expected, no appreciable quantity of activity was found in fraction A. At the conclusion of the electrolysis no activity was found in the reference compartment solution, the catholyte, the cathode or the cell walls. The anolyte contained 63% of the initial activity and the anode 4% for a total recovery of 67%. The remaining activity was apparently lost by volatilization during the electrolysis. A loss of activity during electrolysis of solutions 10^{-4} M in iodide had previously been noticed (see Section 3.1.3).

3.1.6 Attempts to Prepare Carrier-free Periodate-131. At the high anode potentials it was quite possible that some periodate was produced. Experiments were performed to locate any periodate present in the solutions. The paper chromatography method of analysis was used employing Whatman No. 1 Chromatography Paper and equal volumes of acetone and 3M ammonium hydroxide as the elutant. This allowed detection of any periodate and also gave an analysis for iodate (see Section 2.5.3). The electrolyses were carried out in the usual manner; the results are given in Table 3.13. No periodate was found in any of the solutions. For the electrolysis at +1.000 volt vs. S.C.E., 1/2-milliliter samples were taken and analyzed for iodate by the fractional precipitation method. This method of analysis gave 1.0% iodate for the starting solution and 94.3% iodate at 4 hours which was in good agreement with the chromatographic analyses.

Table 3.12 Characterization of Iodine-131 Activity Present
in 0.01 M NaHCO₃ Solution Initially 10⁻⁴ M in
Iodide Following Electrolysis at an Anode
Potential of +0.850 volt vs. S.C.E.

Time, hr.	Distribution of Activity, % ^a			
	A	B	C	D
0	0.0	0.2	99	0.5
4	0.7	29	9.2	61

^aThe percent distribution is based upon the total activity
in the analytical sample as determined by the solvent
extraction method of analysis.

Table 3.13 Electrolysis of Carrier-free Iodide-131
in Basic Solution at High Anode Potentials

Anode Potential, volts vs. S.C.E.	Time, hrs.	Analysis, % ^a			
		I	II	III	IV
1.00	0	8	4	4	84
	4	4	4	89	4
1.00	0	7	5	8	81
	0 (IO ₄ ⁻) ^b	7	3	14	77
	1	6	1	65	29
	2	3	1	80	15
	4 (IO ₄ ⁻) ^b	1	2	88	9
	6	0	1	94	5
	6 (IO ₄ ⁻) ^b	0	1	94	5
1.50	0	8	4	5	83
	2	1	3	85	11
	4	1	3	90	7
	6	1	3	92	4
1.90	0	4	3	2	92
	0 (I ⁻) ^c	1	2	1	96
	2 (IO ₄ ⁻) ^b	3	5	83	9
	4 (IO ₄ ⁻) ^b	3	5	88	4
1.90	0	3	2	3	92
	1	1	2	80	17
	1.5	2	2	85	11
1.22 ^d	0	1	1	1	98
	1	1	4	87	9
	3	1	3	92	5

Table 3.13 (Continued)

^aThese percentages are based upon the activity recovered. Analysis was by paper chromatography method (see Section 2.5.3); any periodate would be found in I along with other possible species, iodate would be found in III and iodide would be found in IV.

^bOn entries labeled in this manner, a periodate solution was spotted on the paper at the origin and air dried before adding the sample.

^cAn iodide solution was spotted on the paper and air dried before adding the sample.

^dThis electrolysis was in 0.1 M sodium carbonate solution; all the others were in 0.01 M sodium bicarbonate solution.

As shown in Table 3.13, in some cases a solution of periodate or iodide was added to the paper prior to adding the sample under analysis. This was done to avoid erroneous results which could have occurred as the result of a reaction between the tracer quantity of iodine in the sample and material in or on the paper. It was possible that the chromatography paper might have contained a small quantity of some material that would have reacted with the iodine, particularly the periodate. It was hoped that by adding a carrier quantity of periodate to the paper any such material would be consumed; when the tracer quantity of iodine in the sample was then added, it would not be affected by any such reaction. When the spot was eluted, the composition of the iodine-131 sample was protected by the presence of the gross quantity of carrier iodine. A similar result could have been obtained by adding the iodine-131 sample to a solution containing a carrier quantity of periodate and spotting this solution on the paper. There are several disadvantages to this approach. First, it would have diluted the activity of the sample which would have been very undesirable. Also, it would have required additional handling and transferring of the sample with the possibility of contamination increased with each operation. Applying the carrier periodate to the paper before adding the iodine-131 sample offered the same protection to the sample and yet avoided any reduction of the quantity of activity on the paper.

The analyses obtained with and without the protective carrier periodate were in good agreement which would indicate that the composition of the sample was not altered by the method of analysis.

No periodate was found in any of the solutions. Electrolysis in

0.01 M sodium bicarbonate solution at anode potentials up to +1.90 volts vs. S.C.E. did not result in the formation of any detectable amount of periodate. Nor did electrolysis at +1.22 volts vs. S.C.E. in 0.1 M sodium carbonate solution produce any periodate. There was considerable transfer of liquid from the anode compartment to the cathode compartment during the electrolyses at +1.50 and +1.90 volts vs. S.C.E. A typical material balance of the activity following the electrolysis at +1.50 volts vs. S.C.E. gave the following:

Recovered from Anolyte	87.5%
Catholyte	1.6
Reference Solution	0
Cell Walls	0.7
Anode	13.0
Cathode	0
Total Recovery	102.8%

In 0.10 M sodium carbonate solution +1.22 volts vs. S.C.E. was the highest anode potential that could be maintained with good control. At this potential the current was 200 milliamperes and the voltage across the working electrodes was 10 volts. Raising the Set Control Potential on the potentiostat above this point increased the anode potential slowly but the current through the cell increased rapidly. The maximum anode potential that could be attained was +1.30 volts vs. S.C.E.; at this anode potential the current was 500 milliamperes and the voltage across the working electrodes was 20 volts.

3.2 Electrolysis of Iodine-131 in Acidic Solution

Solutions of carrier-free iodide-131 in 0.01 M sulfuric acid were

electrolyzed in a manner identical to that previously described for basic solution. The results of some electrolyses in 0.01 M sulfuric acid solution at various anode potentials are shown in Table 3.14. The information given for the initial solution represents the data obtained for a sample removed within a minute or two after adding the iodide-131 to the sulfuric acid solution. The samples of the anolyte were removed without interrupting the electrolysis and analyzed immediately. The information given for zero anode potential represents a run where everything was set up in the usual manner including graphite electrodes immersed in the solutions but no connections were made to the electrodes. Electrolysis in 0.01 M sulfuric acid converted much of the activity in solution to a species that was found in fraction A; electrolysis at an anode potential of +1.000 volt vs. S.C.E. for 6 hours converted 50 to 60% of the activity in solution to a form that was extracted in fraction A. Continued electrolysis at this potential for an additional 18 hours did not change the fraction of activity in A.

The first electrolyses in acid solution were carried out using iodide-131 activity from the same shipment that had been used for the electrolyses in basic solution reported in Table 3.11. (Electrolysis of solutions of carrier-free iodide-131 from this shipment of activity in 0.01 M sodium bicarbonate solution yielded approximately 8% of the activity in fraction A after electrolyzing for 4 hours.) To make certain that the formation of the species found in A was not due only to the particular shipment of iodide-131 used, duplicate electrolyses were performed using a different shipment of iodide-131. There was good agreement between the two sets of electrolyses.

Table 3.14 Electrolysis of Carrier-free Iodide-131 in 0.01 M H₂SO₄ Solution

Anode Potential, volts vs. S.C.E.	Time, hr.	Distribution of Activity, % ^a				Activity Remaining in Anolyte, % ^b
		A	B	C	D	
0	0	0.9	11	86	2.2	100
	2	6.9	17	74	2.1	88
	6	23	17	53	7.2	57
	24	36	10	38	16	47
0 ^c	0	2.5	12	83	2.8	100
	2	22	16	61	1.7	100
	6	29	21	45	5.2	76
	24	31	13	47	9.9	46
0.900	0	4.0	12	83	1.0	100
	2	31	14	42	13	64
	4	38	11	33	18	58
	6	45	9.4	26	20	56
0.900	0	2.2	16	80	1.8	100
	2	27	18	43	12	66
	4	31	14	37	18	62
	6	37	12	30	21	60
1.000	0	2.2	6.8	90	1.2	100
	2	29	12	43	13	75
	4	40	16	21	23	68
	6	46	14	14	25	66
1.000 ^c	0	7.0	14	77	2.9	100
	2	44	15	29	12	74
	6	62	8.3	11	19	67
	24	60	9.2	8.5	23	60
1.000 ^c	0	3.4	13	79	4.1	100
	6	50	10	13	26	68

Table 3.14 (Continued)

Anode Potential, volts vs. S.C.E.	Time, hr.	Distribution of Activity, % ^a				Activity Remaining in Anolyte, % ^b
		A	B	C	D	
1.500	0	7.0	17	73	2.8	100
	2	19	5.2	7.6	68	84
	6	5.9	4.2	7.6	82	82
1.500 ^c	0	7.9	15	73	3.6	100
	2	30	8.1	11	51	97
	4	13	6.1	11	70	96
	6	7.8	8.2	13	71	94

^aThe percent distribution is based upon the total activity in the analytical sample as determined by the solvent extraction method of analysis.

^bBased upon a sample taken immediately after adding the iodide-131 activity.

^cIodide activity from one shipment from Oak Ridge National Laboratory was used for these electrolyses; a different shipment was used for the others.

The formation of fraction A at various anode potentials is shown in Figure 3.10. After several hours about 25% of the activity was converted to a form extracted in fraction A even when no electrical connections were made to the electrodes; however, this was appreciably less than the fraction found in A when the solution was electrolyzed at an anode potential of +0.900 or +1.000 volt vs. S.C.E. for the same length of time.

When the acid solutions were electrolyzed at an anode potential of +1.500 volts vs. S.C.E., little activity was found in A after 6 hours. Rather, most of the activity was found in fraction D after electrolyzing for a few hours. The lack of activity in fraction A when electrolyzing at this high anode potential was probably due to rapid oxidation to iodate. The fraction of activity in A was relatively large after electrolyzing for 2 hours (19 to 30%) but dropped thereafter and was down to 6 to 8% after electrolyzing for 6 hours.

Figure 3.11 illustrates the formation of fraction D at the different anode potentials. As shown, the fraction of the activity in D always increased with increasing anode potential and time.

The manner in which the fraction of the various species changed during the electrolyses is shown in Figures 3.12, 3.13, 3.14 and 3.15 for no applied potential, +0.900, +1.000, and +1.500 volts vs. S.C.E., respectively. The fraction of the activity found in B was relatively constant. In the initial solution (a sample taken before starting the electrolysis) fraction B usually contained 11 to 16% of the activity and, with the exception of the electrolyses at +1.500 volts vs. S.C.E., the value changed little during an electrolysis. During the electrolyses at +1.500 volts vs. S.C.E. the fraction of activity found in B dropped to

Figure 3.10 Production of Fraction A by Electrolysis of Carrier-free Iodide-131 in 0.01 M H_2SO_4 Solution

Figure 3.11 Production of Fraction D by Electrolysis of Carrier-free Iodide-131 in 0.01 M H_2SO_4 Solution

Figure 3.12 Change in Distribution of Iodine-131 Activity in 0.01 M H_2SO_4 Solution With no Applied Potential

Figure 3.13 Change in Distribution of Iodine-131 Activity in 0.01 M H_2SO_4 Solution as a Result of Electrolysis at +0.900 volt vs. S.C.E.

Figure 3.14 Change in Distribution of Iodine-131 Activity in 0.01 M H_2SO_4 Solution as a Result of Electrolysis at +1.000 volt vs. S.C.E.

Figure 3.15 Change in Distribution of Iodine-131 Activity in 0.01 M H_2SO_4 Solution as a Result of Electrolysis at +1.500 volts vs. S.C.E.

4 to 8%. The fraction of activity found in D increased continuously and the fraction of the activity found in C decreased continuously in every case.

As shown in Table 3.14, activity was continuously lost from the anolyte; the loss amounted to over 40% in some cases. At anode potentials of +0.900 and +1.000 volt vs. S.C.E. the loss was relatively large after electrolyzing for 2 hours and continued thereafter but at a considerably reduced rate. At +1.500 volts vs. S.C.E. the total loss of activity from the anolyte was much less (6 to 18%) but here also most of the loss took place within the first 2 hours. In the experiments where no electrical connections were made to the electrodes, the loss of activity from solution was small during the first 2 hours but increased considerably during the next several hours.

Additional information concerning the electrolyses in 0.01 M sulfuric acid solution is given in Table 3.15. The activity recovered at the conclusion of the electrolysis is given. In no case was any activity found in the reference compartment solution, the catholyte or the cathode. Never more than a few tenths of a percent of the total activity was recovered from the cell walls when the empty cell was treated with chromic acid cleaning solution. Except for the runs where no electrical connections were made to the electrodes, all of the activity lost from the anolyte was found in the graphite anode. Total recovery of the initial activity in the electrolysis experiments was 98 to 103%. In the runs with no applied potential, approximately 10% of the initial activity could not be accounted for at the end of the run. This activity was probably lost by volatilization.

In the electrolyses in 0.01 M sodium bicarbonate solution the potential across the working electrodes and the current generally dropped

Table 3.15 Additional Information on Electrolysis Experiments Summarized in Table 3.14

Anode Potential, volts vs. S.C.E.	Potential Across Working Electrodes, volts ^b		Current, milliamperes ^c		Recovered Activity, %	
	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>	<u>Anolyte</u>	<u>Anode</u>
0					47	42
0					46	40
0.900	1.1	0.96	0.02	0.01	56	44
0.900	1.2	1.0	0.02	0.01	60	40
1.000	1.3	1.1	0.02	0.01	66	33
1.000	1.3	1.1	0.02	0.01	60	38
1.000	1.3	1.1	0.02	0.01	68	35
1.500	5.0	6.3	1.0	1.9	82	20
1.500	4.6	6.2	0.78	2.0	94	5

^aListed in the same order as in Table 3.14.

^bThe potential across the working electrodes changed continuously during the electrolyses; the values given are those observed during the first few minutes and at the conclusion of the electrolysis. The value at any time during an electrolysis was between these two limits.

^cThe current changed continuously during the electrolyses; the values given are those observed during the first few minutes and at the conclusion of the electrolysis. The value at any time during an electrolysis was between these two limits.

rapidly during the first few minutes of the electrolysis and reached a steady value after about 30 minutes. There was normally little, if any, further decrease in these items. However, when electrolyzing in 0.01 M sulfuric acid, at anode potentials of +0.900 and +1.000 volt vs. S.C.E. there was an initial rapid drop in the current and the potential across the working electrodes during the first few minutes of the electrolysis and both continued to decrease very slowly for the remainder of the electrolysis. At an anode potential of +1.500 volts vs. S.C.E. the current and the potential across the working electrodes decreased slightly for the first 30 minutes and then both increased slowly for the remainder of the electrolysis.

Experiments were conducted to determine the stability of fraction A species in 0.01 M sulfuric acid. Solutions of carrier-free iodide-131 in 0.01 M sulfuric acid were electrolyzed at an anode potential of +1.000 volt vs. S.C.E. for several hours to prepare a solution rich in A. Following the electrolysis, samples of the solutions were removed and analyzed immediately by the solvent extraction procedure (see Section 2.5.1). The remaining portions of the solutions were covered and allowed to stand for 1 to 2 days at room temperature exposed to normal laboratory illumination. Additional samples were then taken and analyzed. The results are given in Table 3.16 not only for fraction A but also for fractions B, C and D. There was no change in the distribution of the activity among any of the fractions after standing for 2 days as determined by the solvent extraction method of analysis (see Section 2.5.1). Nor was there any loss of activity from the solutions; that is, the solutions contained the same concentration of activity after standing for 2 days as they had when the electrolysis was stopped.

Table 3.16 Change in Distribution of Iodine-131 Activity in 0.01 M H₂SO₄ Solution Upon Standing Following Electrolysis at +1.000 volt vs. S.C.E.

Time, hr. ^a	Distribution of Activity, % ^b			
	A	B	C	D
0	60	9.2	8.5	23
28	60	9.4	8.9	22
0	50	10	13	26
44	49	11	13	27

^aTime given is that after stopping the electrolysis.

^bThe percent distribution is based upon the total activity in the analytical sample as determined by the solvent extraction method of analysis.

When the acid solutions were electrolyzed at an anode potential of +0.900 or +1.000 volt vs. S.C.E., a large fraction of the activity was converted to a species that was found in fraction A. However, when the solutions were electrolyzed at an anode potential of +1.500 volts vs. S.C.E., little activity was found in A; rather, most of the activity was rapidly converted to species found in fraction D. This observation suggested the possibility of a stepwise oxidation of iodide to iodate; that is, oxidation of iodide to fraction A at a low anode potential followed by oxidation of fraction A to iodate at a higher anode potential. A solution containing iodide- 131 I in 0.01 M sulfuric acid was electrolyzed at an anode potential of +1.000 volt vs. S.C.E. for several hours to prepare a solution rich in the species that was found in fraction A. A sample of the solution was removed for analysis, fresh graphite electrodes were inserted into the solution, and the electrolysis was resumed at an anode potential of +1.500 volts vs. S.C.E. The results of these electrolyses are shown in Table 3.17.

Electrolyzing at a high anode potential did convert the iodine activity from a species that was found in fraction A to a species that was found in fraction D. There was very little activity lost from the anolyte during the electrolysis at the higher anode potential. No activity was recovered from the reference compartment solution, the catholyte, the cathode, or the walls of the cell. The anode contained less than 2% of the total activity at the end of the electrolysis.

Although the iodine species found in fraction A was formed by electrolytic oxidation of an iodide solution, it does not necessarily follow that it must have an oxidation number greater than iodide. For example,

Table 3.17 Change in Distribution of Iodine-131 Activity in 0.01 M H_2SO_4 Solution as a Result of Electrolysis of a Solution Rich in Fraction A at +1.500 volts vs. S.C.E.^a

Time, hr. ^b	Distribution of Activity, % ^c			
	A	B	C	D
0	60	9.4	8.9	22
2	27	6.1	7.2	60
0	49	11	13	27
2	29	7.5	9.2	55

^a Solution prepared by electrolyzing a solution 0.01 M in sulfuric acid containing iodide-131 at an anode potential of +1.000 volt vs. S.C.E.

^b Time electrolyzed at +1.500 volts vs. S.C.E.

^c The percent distribution is based upon the total activity in the analytical sample as determined by the solvent extraction method of analysis.

the iodide could be oxidized to a higher oxidation state electrolytically and this species could then react with impurities in the solution to form the species found in fraction A.

To further characterize the chemical species in fraction A, additional extraction procedures were employed. A benzene solution of fraction A was prepared by electrolyzing an acid solution of iodide-131 at an anode potential of +1.000 volt vs. S.C.E. for 6 hours and subjecting a portion of this solution to the standard extraction procedure (extracting the aqueous sample with benzene and then back-extracting the benzene phase with an aqueous iodide solution). Five milliliters of this benzene phase (fraction A) was extracted with one-half milliliter of 0.1 M sodium hydroxide solution; 34.2% of the activity was left in the benzene and 65.8% was removed by the aqueous sodium hydroxide. After separating the phases the sodium hydroxide solution was acidified with sulfuric acid and extracted with 5 milliliters of benzene. The benzene extract contained only 2.0% of the total activity. The remainder of the activity, 63.8% of the initial, was left in the aqueous phase.

Another 5-milliliter portion of fraction A in benzene was extracted with one-half milliliter of 0.1 M sodium hydroxide solution as before. This time 33.8% of the activity was left in the benzene phase and 66.2% was removed by the sodium hydroxide solution. The sodium hydroxide phase was acidified with sulfuric acid and extracted with 5 milliliters of 0.01 M iodine in benzene. Virtually all of the activity, 66.1% of the total initial, was removed from the aqueous phase by the iodine-benzene phase.

The material in fraction A as prepared in this manner (electrolysis of carrier-free iodide-131 in 0.01 M sulfuric acid solution at an anode

potential of +1.000 volt vs. S.C.E.) contained at least two components. All of the material contained in fraction A was extracted from aqueous acid solution by benzene but was not back-extracted from the benzene by aqueous iodide solution (did not exchange with nor was reduced by iodide). One of the components in fraction A was not extracted from the benzene by 0.1 M sodium hydroxide solution. When the aqueous sodium hydroxide phase containing the material extracted from the benzene phase was acidified and back-extracted with benzene, very little activity was removed. However, when another portion of the aqueous sodium hydroxide phase was acidified and extracted with a solution of iodine in benzene, all of the activity was removed from the aqueous phase. These two components correspond to the X and Y species found by Kahn and Wahl (2) when they chemically oxidized acid solutions of carrier-free iodide. The Y species was extracted from the acid aqueous sample by benzene and was not back-extracted from the benzene by 0.1 M potassium iodide or 0.1 M sodium hydroxide solution. The X species was extracted from the acid aqueous sample by benzene, was not back-extracted from the benzene by 0.1 M potassium iodide, but was extracted by 0.1 M sodium hydroxide. The X species was not back-extracted from the acidified aqueous phase by benzene but was removed by iodine in benzene indicating that X decomposed irreversibly in 0.1 M sodium hydroxide and the decomposition product was not extracted by benzene but exchanged rapidly with iodine.

Chapter 4

SUMMARY AND DISCUSSION

4.1 General

A study was made of the electrolytic oxidation of carrier-free iodide-131 in acidic and basic solutions at various controlled anode potentials. In basic solution the iodide was oxidized directly to iodate; no species other than iodide and iodate were detected in the solutions. There was no evidence for the formation of periodate in the electrolyzed basic solutions. In acidic solution under certain electrolysis conditions as much as 50 to 60% of the activity in solution could be converted to iodine species other than iodide or iodate. These species could be oxidized to iodate by electrolyzing at a higher anode potential.

4.2 Experimental Techniques

4.2.1 Circuitry. An instrument suitable for carrying out the controlled electrolytic oxidation or reduction of carrier-free iodine-131 solutions was designed and constructed. The instrument, called a potentiostat, was capable of maintaining an electrode at a potential of ± 2 volts versus a reference electrode. The output capability of the potentiostat was 500 milliamperes at up to 40 volts or 8 milliamperes at up to 100 volts across the working electrodes. The response time of the all electronic instrument was very fast; the potential of the controlled electrode was maintained to better than ± 1 millivolt of the set value. The potentiostat was assembled almost entirely from commercially available units.

4.2.2 Electrolysis Cell. Many electrolysis cell designs were investigated. It was necessary that the anolyte and catholyte be kept separated so that no iodine species was exposed to the cathode. Also, it was desirable to

provide a separate compartment for the reference electrode in order to avoid introducing extraneous material into the solution and to avoid contamination of the reference electrode by the iodine-131 activity. The cell design used for most of the work was a three-compartment glass cell with the compartments connected near the bottom by a glass tube containing a fine-fritted-glass disk. The fritted-glass disk prevented mixing of the solutions between compartments yet resulted in a relatively low electrical resistance between compartments. The only difficulty encountered with this design was an electroosmosis effect at high potentials wherein the water moved from the anode to the cathode compartment. However, with the composition of solutions used during this investigation, electroosmosis was not observed when maintaining the anode at a potential of +1.000 volt or less vs. S.C.E.

4.2.3 Analytical Methods. The three methods used to characterize the nature of the iodine species in solution were fractional precipitation, solvent extraction and paper chromatography. Each had special features which made it particularly suitable for certain phases of the investigation. The fractional precipitation method of analysis is specific for iodate which made it the best choice of analysis for the bulk of the work where the primary interest was in the fraction of iodate produced. The solvent extraction procedure divides the iodine species into four basic groups as a function of their extractibility by benzene and isotopic exchange with iodide or iodine and this method of analysis was used primarily to determine iodine species other than iodide or iodate in the solution. The paper chromatography procedure was devised to determine periodate specifically; this procedure was also used for analysis of iodide, iodate and as yet unidentified iodine species. Good agreement among the three methods of

analysis was noted when they were used to analyze samples from the same solutions.

4.2.4 Autoradiography. An autoradiographic technique using Polaroid film was developed for locating the iodine activity on the paper chromatographs. The use of Polaroid film simplified the procedure considerably in that no darkroom was necessary for preparing the film before exposure or processing the film after exposure. Using a standard Polaroid processing device to develop the film, a finished positive print could be obtained within a minute after exposure.

4.3 Electrolysis in Basic Solution

4.3.1 Production of Iodate. Determination by the solvent extraction procedure of the distribution of the iodine activity in 0.01 M sodium bicarbonate solution shortly after adding the activity to the solution usually gave values of about 96% iodide, 3% iodate and 1% benzene-extractible species. Back-extraction of the iodine-benzene phase containing the extracted iodide- 131 I activity with 0.01 M sodium bicarbonate solution did not remove any of the activity indicating that the 3% iodate is actually a component of the initial solution rather than a hydrolysis product of the iodine in the basic solution (although the iodate fraction may be formed when the activity is added to the sodium bicarbonate solution). Analysis of similar solutions by the fractional precipitation method supported this observation by also giving a value of about 3% for the iodate content. Analyses of the initial solutions were quite consistent as to the distribution of activity.

Carrier-free iodide- 131 I in 0.01 M sodium bicarbonate solution was oxidized to iodate when the solution was electrolyzed at a graphite anode

at a potential of +0.800 volt or greater vs. S.C.E. When solutions of carrier-free iodide-131 in 0.01 M sodium bicarbonate containing a graphite electrode (but with no electrical connection to the electrode) were prepared and allowed to stand at room temperature, a small amount of iodate formed in the solutions. The fraction of the activity converted to iodate was about 10% of the total activity after the solution had been standing for 6 hours and it had not increased further after 24 hours. Since no attempt was made to exclude oxygen from the solutions, the oxidation of this small fraction of the iodide to iodate was probably due to atmospheric oxygen. Electrolysis at an anode potential of +0.700 volt vs. S.C.E. gave no increase in the fraction of the activity present as iodate at any time over that small amount observed when there was no applied potential. Electrolysis at an anode potential of +0.800 volt vs. S.C.E. gave a small but definitely increased fraction of the activity as iodate at any time over that observed in the blank experiments. Increasing the anode potential increased the rate of production of iodate. At an anode potential of +1.000 volt vs. S.C.E., 95% of the activity in solution was converted to iodate after electrolyzing for 2 hours. A plot of the fraction of activity in solution as iodate versus electrolysis time for various constant anode potentials between +0.700 and +1.000 volt vs. S.C.E. generated a family of curves, illustrating the dependence of the fraction of iodate upon the anode potential and the electrolysis time. Good agreement was obtained in duplicate experiments. The results observed for this type of experiment were found to be independent of the shipment of Oak Ridge iodide-131 activity used.

At higher anode potentials the conversion to iodate was virtually complete after electrolyzing for a few hours. Electrolysis at an anode

potential of +1.350 volts vs. S.C.E. for 2 hours oxidized 98% of the activity to iodate. As a method of preparing carrier-free iodate solutions employment of a high anode potential could be very advantageous as it allows good conversion to iodate in a relatively short time. However, such high anode potentials had a side effect which limited their usefulness in the study of the electrolytic oxidation. In the electrolysis cell used for most of the experiments (which used a fritted-glass disk to separate the compartments) an electroosmosis effect was observed when the anode potential was much greater than +1.00 volt vs. S.C.E. Liquid was transferred from the anode compartment to the cathode compartment causing a continuous change in the concentration of the solutions during the electrolysis. The specific activity of the anolyte increased during the electrolysis.

The process was shown to be an actual electrolytic oxidation of the iodide rather than oxidation by some material formed in the solution during the electrolysis. A sodium bicarbonate solution was electrolyzed for several hours, the electrolysis was discontinued, and immediately some carrier-free iodide-131 was added to the solution. There was no oxidation of the iodide to iodate demonstrating that no appreciable concentration of any material was formed in the solution which was capable of oxidizing the iodide. Also, in the usual electrolysis there was no additional oxidation of the iodide after the electrolysis was stopped. Oxidation of the iodide took place only if it were present in the solution during the electrolysis.

The carrier-free iodate prepared by the anodic oxidation of carrier-free iodide in sodium bicarbonate solution was stable. The distribution of the iodine activity in solutions composed primarily of carrier-free

iodate prepared electrolytically did not change upon allowing the solutions to stand for 2 days at room temperature.

Over the concentration range from carrier-free to 10^{-4} M iodide the rate of the anodic oxidation of iodide to iodate, expressed as the fraction of the activity oxidized, was independent of the total iodide concentration indicating that the iodide concentration entered the rate law to the first power. Also, a plot of the logarithm of the fraction of iodide remaining versus time at a constant anode potential gave a straight line as would be expected for a reaction which followed the first order rate law.

The reversible oxidation potential of the iodide-iodate couple was calculated for the experimental conditions used in order to compare the experimentally determined anode potential found necessary to carry out the electrolytic oxidation of iodide to iodate with the theoretical value of the reversible potential of the couple. For the half-reaction

Latimer (18) gives $E^\circ = -0.26$ volt vs. hydrogen electrode or $E^\circ = -0.02$ volt vs. S.C.E. Using the Nerst equation

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

the potential for the half-reaction under the conditions of the experiment can be calculated. Because both of the oxidation states contain one iodine atom per molecule, the value of Q depends on the ratio of the activities of the iodine species and not on the absolute values. The electrode potential of this couple should thus be the same at tracer concentrations as it is for macro quantities of iodine. In 0.01 M sodium bicarbonate solution with a pH of 9 the hydroxyl ion concentration is

10^{-5} molar, so at a temperature of 22° the electrode potential of the half-reaction is given by

$$E = -0.02 - \frac{0.0586}{6} \log \frac{[\text{IO}_3^-]}{[\text{I}^-] 10^{-30}}$$

$$E = -0.31 - 0.00977 \log \frac{[\text{IO}_3^-]}{[\text{I}^-]} .$$

Some calculated values for the potential of the half-reaction for a few representative values of the iodide-iodate ratio are given in Table 4.1. These calculated electrode potentials are the reversible potentials for the half-reaction and give a measure of the minimum anode potential necessary to carry out the oxidation of iodide to iodate in this solution. The minimum anode potential found necessary to oxidize iodide to iodate in 0.01 M sodium bicarbonate solution, +0.79 volt vs. S.C.E., is much greater than the reversible potential of the couple for any reasonable ratio of iodate to iodide. For example, in a solution containing 1% iodate, or a ratio of iodate to iodide of 0.010, from Table 4.1, the calculated oxidation potential of the couple is -0.29 volt vs. S.C.E. This means that an anode potential greater than +0.29 volt vs. S.C.E. would be required to carry out the oxidation.

When a solution 10^{-4} M in sodium bicarbonate containing carrier-free iodide-131 was electrolyzed at an anode potential of +1.000 volt vs. S.C.E. there was a considerable transfer of liquid from the anode compartment to the cathode compartment due to electroosmosis. The increase in the electroosmosis effect in the more dilute solution was due to the increased resistance of the solution; a much higher potential across the working electrodes was necessary to maintain the same anode potential. It was

Table 4.1 Calculated Electrode Potentials for the Iodide-Iodate Couple in 0.01 M NaHCO_3 Solution

<u>IO_3^- to I^- Ratio</u>	<u>Electrode Potential, volts vs. S.C.E.</u>
0.010	-0.29
0.011	-0.30
0.333	-0.31
1	-0.31
3	-0.32
9	-0.32
99	-0.33

difficult to maintain a steady anode potential in this dilute solution probably due to the lack of sufficient material in the solution to establish a stable couple at the electrode. In two experiments electrolysis for 4 hours at this potential converted 37% and 49%, respectively, of the activity to iodate. The variation in these results, which was greater than usually encountered, was probably due to the various circumstances arising from the dilute solution such as the instability of the anode potential and the electroosmosis phenomenon.

The effect of the solution pH on the potential of the half-reaction can be seen from the following:

At 22°

$$E = -0.02 - 0.00977 \log \frac{[\text{IO}_3^-]}{[\text{I}^-]} + 0.00977 \log [\text{OH}^-]^6$$

$$E = -0.02 - 0.00977 \log \frac{[\text{IO}_3^-]}{[\text{I}^-]} + 0.0586 \log [\text{OH}^-].$$

For every factor of 10 increase in the hydroxyl ion concentration the electrode potential of the half-reaction will increase by +0.0586 volt. Thus, in changing from a 0.01 M sodium bicarbonate solution with a hydroxyl ion concentration of 10^{-5} M to a 10^{-4} M sodium bicarbonate solution with a hydroxyl ion concentration of $10^{-6.6}$ M, the oxidation potential of the half-reaction will become more negative by 0.094 volt. This means that at the same anode potential, the driving force for the oxidation is 0.094 volt less in the 10^{-4} M sodium bicarbonate solution than in the 0.01 M sodium bicarbonate solution, which could account for the slower rate of oxidation observed in the more dilute solution.

4.3.2 Production of Periodate. Attempts to prepare periodate were unsuccessful. Solutions of carrier-free iodide-131 in 0.01 M sodium bicarbonate were electrolyzed at anode potentials of up to +1.900 volts vs. S.C.E. for several hours and no periodate was found in any of the solutions. Nor did electrolysis at +1.22 volts vs. S.C.E. in a more basic 0.10 M sodium carbonate solution produce any detectable amount of periodate. Latimer (18) gives $E^\circ = -0.5$ volt vs. S.C.E. for the half-reaction

Calculation of the potential of the half-reaction at a pH of 9 and a temperature of 22°, making the assumption that the ratio of the activities of the iodate and periodate is one (50% iodate and 50% iodide), gives

$$E = -0.5 - \frac{0.0586}{2} \log \frac{[\text{H}_3\text{IO}_6^{3-}]}{[\text{IO}_3^-] 10^{-15}}$$

or a value of -0.9 volt vs. S.C.E. for the iodate-periodate couple at a pH of 9. The anode potential of +1.900 volts vs. S.C.E. used in the electrolysis is sufficiently higher than the potential of the couple that some oxidation to periodate would be expected. But either no periodate was formed during the electrolysis or any that formed reacted with some material in the solution and was reduced so that no appreciable concentration accumulated in the solution.

4.3.3 Anomalous Iodine Species. The oxidation of iodide to iodate probably takes place stepwise since there is a net loss of 6 electrons in the change in oxidation number from -1 to 5. The production of an iodine species having an oxidation number between iodide and iodate would be most likely at lower anode potentials where the conversion to iodate

is slow. Solutions were electrolyzed at low anode potentials (+0.800 to +0.900 volt vs. S.C.E.) and analyzed by the solvent extraction procedure in order to detect iodine species other than iodate. However, anodic oxidation at these potentials in 0.01 M sodium bicarbonate solution did not produce any significant fraction of any iodine species other than iodate. In some experiments electrolysis at anode potentials which ranged from +0.800 to +0.900 volt vs. S.C.E. for a few hours converted about 10% of the total iodine activity to a form other than iodide or iodate as determined by the solvent extraction procedure. This iodine species was extracted by benzene but was not back-extracted by aqueous iodide solution (did not exchange with iodide).

Continued electrolysis converted this species to iodate. The rate of the conversion depended upon the anode potential; for example, at +0.800 volt vs. S.C.E. about 16 hours were required for the conversion but at +1.000 volt vs. S.C.E. the species was converted to iodate in 2 hours. When carrier iodide was added to the bicarbonate solution containing the iodide- ^{131}I activity before electrolysis to make the solution 10^{-4} M in iodide, none of the anomalous species was found.

The formation of this species depended for unknown reasons upon the shipment of Oak Ridge iodide- ^{131}I activity used. A shipment of activity which would give this species upon electrolysis would do so consistently; in other shipments the species was never formed. Nor was it dependent upon the age of the activity. Electrolysis of a sample of activity two months old gave the same fraction of the iodine activity in this form as had a sample of this shipment when it was first received. The distribution of the iodine activity in 0.01 M sodium bicarbonate solution prior to

electrolysis was the same for all the shipments as determined by the solvent extraction and fractional precipitation procedures.

4.4 Electrolysis in Acidic Solution

4.4.1 Production of Iodate. Several iodine species were formed, as determined by the solvent extraction method of analysis, when solutions of carrier-free iodide-131 in 0.01 M sulfuric acid were electrolyzed. The rate of formation of iodate increased very little when the anode potential was raised from +0.900 to +1.000 volt vs. S.C.E. and in both cases was rather slow. After electrolyzing for 4 hours at +0.900 volt vs. S.C.E. the solution contained only 18% iodate and the iodate fraction increased to 20% at 6 hours. At +1.000 volt vs. S.C.E. the iodate fraction was 22% at 4 hours and 24% after electrolyzing for 6 hours. In one experiment the electrolysis at an anode potential of +1.000 volt vs. S.C.E. was continued for 24 hours; there was virtually no additional increase in the iodate fraction over that found at 6 hours. Raising the anode potential to +1.500 volts vs. S.C.E. increased the rate of production of iodate considerably. After electrolyzing for 2 hours at this potential about 60% of the activity was converted to iodate and the iodate fraction increased to 75% at 6 hours.

Iodate formed to some extent in the acid solution when there was no applied potential (no electrical connections made to the electrodes) but the fraction was small amounting to only 6% iodate after 6 hours and 10 to 15% after 24 hours.

For the half-reaction

At a pH of 2 and a temperature of 22°, the potential of the half-reaction is given by

$$E = -0.73 - 0.00977 \log \frac{[\text{IO}_3^-]}{[\text{I}^-]} .$$

Thus, in a solution containing 1% iodate and 99% iodide, $E = -0.71$ volt vs. S.C.E.; with 10% iodate and 90% iodide, $E = -0.72$ volt vs. S.C.E. and with 50% iodate and 50% iodide, $E = -0.73$ volt vs. S.C.E. The observation of some formation of iodate at an anode potential of +0.900 volt vs. S.C.E. in these solutions is in agreement with the calculated values.

4.4.2 Anomalous Species. Electrolysis in 0.01 M sulfuric acid converted a large fraction of the activity to a form that was found in fraction A when analyzed by the solvent extraction procedure (fraction A contains activity that is extracted by benzene and not back-extracted by aqueous iodide). At an anode potential of +0.900 volt vs. S.C.E. 30% of the activity was in this form after electrolyzing for 2 hours and this increased to about 41% at 6 hours. At +1.000 volt vs. S.C.E. there was a small increase in the fraction of the activity in A at any time over that seen at +0.900 volt vs. S.C.E.; after electrolyzing for 6 hours the fraction of the activity in A ranged from 50 to 60%. Continuation of the electrolysis for 24 hours at +1.000 volt vs. S.C.E. did not change the fraction of the activity in A. At an anode potential of +1.500 volts vs. S.C.E. the fraction of the activity found in A was much less. Thus, electrolysis for 2 hours at this potential converted only 20 to 30% of the activity to A; continued electrolysis decreased the fraction of this species and it was down to about 6% after 6 hours. A moderate fraction of

the activity was converted to the species found in fraction A even with no applied potential but the fraction was always much less than what was found after electrolyzing for the same length of time at +0.900 or +1.000 volt vs. S.C.E. When a 0.01 M sulfuric acid solution containing carrier-free iodide- 131 activity was allowed to stand for 6 hours with no applied potential, approximately 22 to 29% of the activity was converted to fraction A.

The iodine species in fraction A could be converted to iodate by electrolytic oxidation. Solutions rich in this species were prepared by anodic oxidation at +1.000 volt vs. S.C.E. of carrier-free iodide in 0.01 M sulfuric acid. The activity was then converted to iodate by increasing the anode potential to +1.500 volts vs. S.C.E. and continuing the electrolysis for a few hours. When the species in fraction A was formed in sodium bicarbonate solution, it could be converted to iodate by continued electrolysis at the lower anode potential or, more quickly, by increasing the anode potential. In the acid solution, however, continued electrolysis at the lower anode potential did not oxidize the material; it was oxidized to iodate only when the anode potential was increased.

Although the iodine species found in fraction A was produced by electrolytic oxidation of iodide, it does not necessarily have an oxidation number greater than iodide. For example, the iodide could be oxidized to a higher oxidation state electrolytically and this species could then react with a reducing agent present in the system to form the species found in fraction A. However, it must have an oxidation number less than iodate since it can be electrolytically oxidized to iodate. The species is stable upon standing; no change was observed in the composition

of a solution rich in the species after standing for two days at room temperature.

Additional studies of fraction A revealed that it consisted of at least two components. One of the components was extracted from the benzene by 0.10 M sodium hydroxide and the other was not. The material in the sodium hydroxide solution decomposed to a species that was not extracted by benzene but exchanged rapidly with iodine.

From the results of the extraction and isotopic exchange experiments, none of the species in fraction A is I^- , I_2 , HIO or IO_3^- . One or more of the species could be an organic compound formed in the aqueous solution during the electrolytic oxidation of the iodide but if so it must be an organic compound that can be electrolytically oxidized in solution to give iodate. It is also possible that one or more of the species could be an organic compound formed during the extraction with benzene. They could also be complex inorganic compounds. The material which was extracted by benzene and removed from the benzene by sodium hydroxide solution could possibly be a weak oxygen acid but it must be one that does not undergo isotopic exchange with iodide or iodine and is not reduced by iodide.

4.5 General Observations on the Electrolytic Oxidation of Iodide in Both Acidic and Basic Solutions

4.5.1 Material Balance of Iodine Activity. During the electrolysis of acidic reaction mixtures of carrier-free iodide-131, there was always a large loss of activity from the solution amounting to as much as 40% of the initial activity. Most of the loss took place during the first two hours of the electrolysis but there was some additional loss after that. The loss was greatest at the lower anode potentials; thus, at +1.500

volts vs. S.C.E. there was very little loss of activity from the solution. At all of the anode potentials investigated essentially all of the activity lost from solution was found on the graphite anode. No activity was recovered from the catholyte, cathode, reference solution or cell walls; nor was there any detectable loss by volatilization. When acidic, carrier-free iodide- 131 I solutions were electrolyzed at a low anode potential to prepare solutions rich in fraction A, there was a large loss of activity to the graphite anode during the first few hours of the electrolysis; however when this solution, rich in fraction A, was electrolyzed at a high anode potential, there was very little additional loss of activity.

When solutions of carrier-free iodide- 131 I activity in 0.01 M sodium bicarbonate were electrolyzed, the amount of activity lost from the solutions was usually about 15% and the rate of loss was relatively constant; as was the case with the acidic solutions, all of the activity lost from solution was found on the graphite anode. It was also true in the basic solutions, as was observed in the acidic solutions, that the loss of activity was less at high anode potentials; at an anode potential of +1.000 volt vs. S.C.E. there was virtually no loss of activity from the solutions.

When solutions 0.01 M in sodium bicarbonate containing carrier iodide, 10^{-4} M, were electrolyzed at an anode potential of +1.000 volt vs. S.C.E., about 5% of the activity was lost by volatilization.

When a graphite anode which had been used in the alkaline electrolysis experiments was soaked in chromic acid cleaning solution for several hours, about 90% of the activity was removed from the graphite. However, the same treatment given to the graphite anodes which had been used in

the acidic electrolysis experiments removed only about 30 to 50% of the activity. Concentrated ammonium hydroxide removed 60 to 70% of the activity from the graphite anodes which had been used in the acidic electrolysis experiments.

4.5.2 Initial Composition of Starting Mixtures. Distribution of the iodine activity in the solutions immediately after adding the carrier-free iodide- ^{131}I was very different for the acidic and basic solutions. In the sodium bicarbonate solutions usually less than 1% of the activity was extracted by benzene (fractions A and B), about 96% exchanged with iodine (fraction C) and about 3% was not extracted by benzene or by iodine in benzene (fraction D). When some of the same carrier-free iodide- ^{131}I was added to 0.01 M sulfuric acid solution and analyzed immediately, the distribution was usually about 4% in fraction A, 13% in B, 80% in C, and 3% in D.

There was much greater variation between duplicate experiments in acidic solution than in basic solution. In basic solution the results were generally reproducible. In acidic solution the distribution of the activity among the various species was much less reproducible both for the starting mixture (the solution immediately after adding the activity) and for various points during the electrolysis.

4.5.3 Preparation of Carrier-free Iodate- ^{131}I . Anodic oxidation is a good method for preparing carrier-free iodate- ^{131}I in basic solution. One of the major advantages that it offers over chemical oxidation is that little extraneous material need be present in the solution. Certainly for many uses the presence of macro quantities of other materials (particularly a strong oxidizing agent and its by-products)

would be a disadvantage. Electrolytic oxidation works quite well in 0.01 M sodium bicarbonate solution; virtually 100% of the activity can be oxidized to iodate in a few hours. In 10^{-4} M sodium bicarbonate solution the rate of oxidation was slower but a good fraction of the activity was converted to iodate after a few hours of electrolysis. The presence of as little additional material as possible in the solution would be particularly advantageous when the activity is to be used in the medical field which is one of the major uses of carrier-free iodine activity. There was little loss of activity from the solution during the electrolysis and the loss that did occur was to the graphite electrode. There was no loss of activity to the atmosphere so the protective measures that must be taken to insure the safety of the personnel carrying out the oxidation are relatively simple.

Chapter 5

SUGGESTIONS FOR FURTHER WORK

5.1 Basic Solution

The effect of different electrode materials on the electrolytic oxidation of carrier-free iodide-131 in alkaline solution would certainly be of interest. An electrode material such as pyrolytic carbon might offer the advantage of reacting less with the material in solution. Other electrode materials would probably have a different overvoltage for the oxidation which might reduce the potential necessary to carry out the oxidation.

A study of the effect of alkalinity on the oxidation should also be carried out.

Investigation of the electrolytic reduction of carrier-free iodate-131 at various controlled cathode potentials would be of great interest. The iodine species formed by reduction of carrier-free iodate should be determined. Also, the effect of added carrier iodate, electrode material and alkalinity on the reduction would be of interest. Any loss of activity from solution during the electrolytic reduction should be investigated.

5.2 Acidic Solution

Additional work on the electrolytic oxidation of carrier-free iodide-131 in acidic solution should be carried out. The formation of carrier-free iodate-131 in these solutions as a function of the cathode potential should be further investigated; also, further work should be done on the formation of fraction A by electrolytic oxidation of carrier-free iodide. The effect of electrode material, acidity and added carrier

iodide on the oxidation in acidic solution should be determined. Additional information as to the nature of the iodine species lost to the graphite anode during the electrolysis would be very interesting.

The electrolytic reduction of carrier-free iodate-131 at various controlled cathode potentials in acidic solution should also be carried out. The same items would be of interest here as were stated for the reduction in basic solution; that is, the iodine species formed during the reduction and the effect of added carrier iodate, electrode material and acidity.

Some electrolyses using acids other than sulfuric acid might also yield interesting results.

5.3 General

Application of various techniques to further characterize the nature of the iodine species in fraction A could be undertaken since the material can now be prepared easily in good quantity. Among the approaches which might be fruitful are paper or thin-layer chromatography, paper electrophoresis and perhaps gas chromatography in addition to further extraction experiments.

Additional work on the use of paper or thin-layer chromatography to characterize the iodine species in solution might make this technique more useful as a dependable, rapid method of analysis.

Electrolytic oxidation or reduction at a controlled electrode potential could also be used to investigate the chemical properties of other carrier-free materials. It would be very interesting to compare the results for astatine with those obtained for iodine.

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