preparation of *nor*-hyodesoxycholic acid. The alcohol was acetylated with acetic anhydride and pyridine at 100° for twenty hours. The solvents were evaporated *in vacuo* and the residue was taken up in ether. The ethereal solution was washed with dilute hydrochloric acid and sodium carbonate and was then evaporated to dryness. The residue was dehydrated for six hours by refluxing it with acetic acid. The solvent was evaporated *in vacuo*. The crude ethylenic compound was ozonized in chloroform solution at 0°. The ketones were separated by Girard's reagent and crystallized from ether–pentane. 3,6-Diacetoxy-*etio*-cholanyl methyl ketone melted at 100°.

Anal. Calcd. for $C_{25}H_{38}O_5$: C, 71.7; H, 9.2. Found: C, 72.0; H, 9.0.

Progesterone.—To 0.9 g. of 3,6-diacetoxy-*etio*-cholanyl methyl ketone in 200 cc. of methanol at 20° was added 42 cc. of methanolic potassium hydroxide containing 0.8 mole of base. The solution was allowed to stand at 20° for forty-eight hours. It was then exactly neutralized by addition of 1.7 cc. of 0.96 *N* sulfuric acid. The solvent was completely evaporated *in vacuo*, and the oily residue was oxidized in one hour at room temperature in 25 cc. of acetic acid with a solution of 5 cc. of 90% acetic acid containing 0.5 g. of chromic oxide. Water was added and the precipitated material was extracted with ether. The ethereal solution was washed with water, and then concentrated. This product was refluxed with 40 cc. of 2% methanolic potassium hydroxide for seventy-five minutes. Water was added and the organic material was extracted with ether. The ethereal solution was washed with water and was then evaporated to dryness. The solid remaining was covered with 5.0 g. of fused potassium bisulfate and was heated at 4 mm. at 130° for an hour and a half. The temperature was then raised to 180° for four hours. The ethereal solution of the distillate on evaporation left a pale, mobile oil, which, when crystallized from acetone–water, yielded greasy crystals. Recrystallization from ether–pentane produced small white crystals of m. p. 120°, which gave no depression in melting point with an authentic sample of progesterone.

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.2; H, 9.6. Found: C, 80.4; H, 9.6.

Summary

The Barbier–Wieland degradation applied to hyodesoxycholic acid produced 3,6-diacetoxy-*etio*-cholanyl methyl ketone. This compound was converted into progesterone by a method described for the conversion of 3,6-cholestanediol diacetate into cholestenone.

STATE COLLEGE, PENNA. RECEIVED NOVEMBER 7, 1939

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XXIV. The Addition of Hydrogen Iodide to Propene, 1-Bromopropene, Allyl Chloride, and Allyl Bromide

BY M. S. KHARASCH, JAMES A. NORTON,[1] AND FRANK R. MAYO

The work here reported was undertaken in extension of the previous studies of Kharasch and Hannum,[2] and for the purpose of discovering, if possible, the reasons for the discordance between the results of those studies and that of Ingold and Ramsden.[3]

The consensus among the earlier workers has been that isopropyl iodide is the sole product of the addition of hydrogen iodide to propene.[4] The cited work of Kharasch and Hannum confirms that opinion. Ingold and Ramsden, however, report addition products comprising as much as 25% of normal propyl iodide. The highest yields of the normal iodide were obtained in the absence of solvent and in the presence of the typically non-polar solvent propane. Relatively polar solvents, such as nitrobenzene, acetic acid, and water, were said to give rise to relatively smaller yields of the normal iodide. According to Ingold and Ramsden, the "solvent effect" varies with the "mean molecular fraction of hydrogen iodide in its mixture with the solvent (if any) during the course of the reaction." Unfortunately the "mean molecular fraction" is not precisely defined, nor are complete details of the experiments given. Their method consisted in breaking a sealed tube of propene within a sealed tube of hydrogen iodide (and solvent, if any) at a temperature of 18 ± 2°, which was maintained throughout the reaction.

Discussion

The Addition of Hydrogen Iodide to Propene.—A series of experiments performed in accordance with our usual technique (i. e., with exclusion of air, moisture, and light), and with hydrogen iodide–propene ratios varying from 0.36/

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(1) University Fellow, 1938–1939. This paper is an abstract of a thesis submitted by James A. Norton in partial fulfilment of the requirements for the Ph.D. degree, the University of Chicago, 1939.

(2) Kharasch and Hannum, THIS JOURNAL, **56**, 712, 1782 (1934).

(3) Ingold and Ramsden, *J. Chem. Soc.*, 2746 (1931).

(4) For references see ref. 2; *cf.* also Emschwiller, *Ann. chim.*, (10) **17**, 500 (1932).

1.0 to 3.51/1.0 (the majority at approximately 1/1), at temperatures from −80° to room temperature (the majority at 0°), and with reaction times varying from one to twenty-one hours, yielded only isopropyl iodide as the addition product. To obtain 90% or more of addition product under the conditions indicated, about three hours were required at 0° or one hour at room temperature.

In order to make sure of the stability of normal propyl iodide under these experimental conditions at room temperature, about one-third mole of normal iodide per mole of propene was added in one experiment, and about one mole in another. In both cases the normal iodide added was unchanged, and the addition product was exclusively the secondary iodide.

The homogeneity of the reaction at 0° was tested by an experiment in which 0.5 g. of powdered Pyrex glass was present during the reaction of 5 g. of propene with an equimolecular quantity of hydrogen iodide. The direction of addition was not altered, and there was no appreciable change of rate.

The admission of air to reactions otherwise similarly conducted at 0° and at 10° did not materially affect the rate of addition, and did not alter the product (100% secondary iodide). Moisture in the ratio of 0.05 mole of water to one mole of propene had no marked catalytic effect, and did not alter the direction of addition.

Since the results of these experiments gave no clue to the discrepancy in the observations of Ingold and Ramsden and of this Laboratory, an attempt was made to reproduce some of their experiments as closely as the available description would permit. Three experiments were carried out in the absence of a solvent, using 1.01 to 1.11 moles of hydrogen iodide. One of these reaction tubes contained air; the other two did not. A fourth otherwise similar reaction mixture contained 0.78 mole of propane as solvent and no air. All of these experiments gave more than 90% yield of addition products which were exclusively isopropyl iodide. Other experiments in which propane, pentane, acetic acid, and nitrobenzene[5] were employed in similar proportions as solvents, but in which the reactants were not mixed by the Ingold procedure, also gave isopropyl iodide as the exclusive addition product.

In several experiments there was a small amount of high-boiling residue, in accord with the previous observation of Michael and Leighton.[6] However, the index of refraction was lower than that of isopropyl iodide, indicating that the normal iodide could not have been present in significant amount. The quantity of high-boiling material available was too small for conclusive identification, but it is suspected to be a hexyl iodide.

Catalysis of Hydrogen Iodide Addition to Propene.—It was previously reported by Kharasch and Hannum[2] that peroxides accelerate the addition of hydrogen iodide to olefins without affecting the direction of addition. In the present study it was found that with our usual technique equimolecular quantities of hydrogen iodide and propene react completely at 0° in about two hours. Under similar conditions, in the presence of 0.005 mole of ascaridole, the addition is complete in less than one minute at −80°. Since ascaridole must react with hydrogen iodide to liberate iodine (as is further indicated by the color of ascaridole reaction solutions), a similar experiment was conducted in the presence of 0.005 mole of iodine (without ascaridole). Again the addition was complete in less than a minute at −80°. (At higher temperatures peroxide- or iodine-catalyzed reactions proceed with almost explosive violence.) It seems likely, therefore, that peroxide catalysis of hydrogen iodide additions is essentially iodine catalysis.

A possible mechanism of iodine catalysis is found in the observation of Malbot[7] that hydrogen iodide reacts with propene iodide to give iodine and isopropyl iodide

$$C_3H_6 + I_2 \longrightarrow CH_3CHICH_2I$$
$$CH_3CHICH_2I + HI \longrightarrow CH_3CHICH_3 + I_2$$

Mercuric iodide also proved to be an effective catalyst. In experiments similar to those just described, in the presence of about 0.015 mole of mercuric iodide (per mole of olefin), the reaction of equimolecular quantities of propene and hydrogen iodide was complete in less than ten minutes at 0°. An addition reaction carried out in a tube in which a mercury mirror had previously been deposited was complete in about one-half hour.

Antioxidants do not appear to inhibit or otherwise affect the reaction. Thus, the presence of 0.005 mole of diphenylamine was without effect.

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(5) Some reduction of the nitrobenzene with precipitation of crystalline hydroiodide was observed; *cf.* Baumhauer, *Ann., Supp.*, **7**, 208 (1870).

(6) Michael and Leighton, *J. prakt. Chem.*, [2], **60**, 445 (1899).

(7) Malbot, *Ann. chim.*, [6] **19**, 345 (1890).

In the presence of ethyl mercaptan (0.27 mole), however, there was thioether formation, with consequent reduction in yield (59%, as compared with the usual 95–98%). In all cases investigated the sole addition product was isopropyl iodide.

Two additional experiments show that hydrogen iodide can prevent the peroxide-catalyzed addition of hydrogen bromide. Ascaridole promotes the "abnormal" addition of hydrogen bromide to propene. In the presence of ascaridole (0.4 mole %) and (11 mole %) of hydrogen iodide, 1.02 moles of hydrogen bromide added to propene to give only the "normal" addition product (isopropyl bromide). In a similar experiment conducted for a month at room temperature, vinyl chloride and hydrogen bromide gave a 38% yield of the "normal" addition product, together with unchanged reactants; no ethylene chlorobromide was formed. The logical inference is that either peroxides are immediately and completely destroyed in the presence of hydrogen iodide or that hydrogen iodide inhibits the abnormal addition of hydrogen bromide.

Addition of Hydrogen Iodide to Allyl Bromide.—The addition of hydrogen iodide to allyl bromide yielded 1-bromo-2-iodopropane as the sole addition product but this reaction was accompanied by an oxidation–reduction reaction which yielded iodine and addition products of propene. The latter consisted of isopropyl bromide and iodide and contained no normal propyl halides. To reduce the reduction reaction to a minimum, only a small excess (1–10%) of hydrogen iodide and temperatures of 0° and below were usually employed. Air, moisture, and light were generally excluded. Observations of volume changes of reaction mixtures indicated that in reaction at 0° there is an induction period of about one hour during which little or no adddition takes place but iodine is slowly liberated. As iodine accumulates, addition becomes more rapid and reaches completion in two to four hours, with a yield of 70–90% of addition product and weights of recovered allyl and isopropyl halides ranging up to 30% of the initial allyl bromide used. Both addition and reduction take place more slowly at −33°, and at −80° no reaction was observed during twenty-one hours.

That iodine catalyzes the addition reaction at 0° is shown by the fact that addition of 0.5 to 1 mole % of iodine eliminated the induction period, and caused the reaction to take place in a few minutes. At −33°, addition was also accelerated by iodine but a day was required for complete reaction. No reduction was observed under these conditions and yields as high as 96% are readily obtained. At −80°, addition took place at the rate of 30–35% a day in the presence of iodine. The iodine catalysis may be due to the easy reduction of the unknown 1-bromo-2,3-diiodopropane by hydrogen iodide.

These experiments and the fact that the addition product, 1-bromo-2-iodopropane, is fairly stable toward hydrogen iodide at 0°, suggest that it is allyl iodide, formed by halogen exchange between allyl bromide and hydrogen iodide, or its hydrogen iodide addition product, which is reduced to isopropyl iodide by hydrogen iodide.[7,8] The effect of 6 mole per cent. of water in shortening the induction period at 0° is ascribed to facilitation of the halogen interchange necessary for formation of iodine.

Ascaridole had about the same effect as iodine in eliminating the induction period and accelerating the addition. The best result at 0° was obtained with the smallest proportion of peroxide, 0.7 mole per cent., when the yield of addition product was 93% within one hour. Equally good results were obtained with a sample of allyl bromide which gave a strong peroxide test. Use of larger amounts of ascaridole resulted in tar formation and reduction, probably because of rapid reaction and overheating.

Attempts to obtain an addition product from allyl bromide other than 1-bromo-2-iodopropane were made. Thus, additions were carried out in the presence of 0.7 mole per cent. of diphenylamine at 0°, and by adding hydrogen iodide and ascaridole very slowly at room temperature (and in the presence of air) to allyl bromide mixed with 1.68 moles of pentane.

The Addition of Hydrogen Iodide to Allyl Chloride.—The addition of hydrogen iodide to allyl chloride differs from the addition to allyl bromide chiefly because of the slower halogen exchange to give allyl iodide. Since the iodine formed by the interaction of this product with hydrogen iodide is the controlling factor in the rate of addition, the reaction is slow compared to that with allyl bromide. The addition of hydrogen iodide to allyl chloride gave exclusively 1-chloro-2-iodopropane in yields of 90–100%. Fur-

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(8) Simpson, *Ann.*, **129**, 127 (1864).

thermore, since this dihalide is more stable to hydrogen iodide than that formed from allyl bromide, the extent of formation and reduction of the allyl halide by hydrogen iodide could be determined conveniently by titration of the iodine formed. All the reactions with allyl chloride were carried out at 0°, using a 10 to 20% excess of hydrogen iodide.

In the absence of air, peroxides, iodine, moisture, and light, the induction period was about twelve hours. The reaction proceeded to completion in the next twenty-four hours, and 0.3 to 0.4% of iodine was formed. Six mole per cent. of water decreased the induction period so that reaction was complete in six to twelve hours, and increased the iodine formed to nearly 3%.

One-half mole per cent. of iodine eliminated the induction period so that reaction was complete in six hours or less. One mole per cent. of mercuric iodide appeared to shorten the induction period without markedly affecting the rate of the subsequent addition reaction. The addition of 19–27 mole per cent. of reduced iron[9] to one addition reaction carried out at room temperature and to another at −33° was without effect on the direction of addition.

Addition of Hydrogen Iodide to 1-Bromopropene.—Previous work in this Laboratory[10] has shown that the addition of hydrogen chloride and hydrogen bromide to 1-bromopropene gives rise to mixtures of 1,1- and 1,2-dihalides. It was concluded that such mixtures represent the "normal" addition products and that the directing influences of the bromine atom and methyl group on the ethylene bond are nearly balanced. Although this work indicated that ferric chloride catalyzes the "normal" additions of both acids without influencing the direction of addition, the necessity for the use of this catalyst in both additions (to attain practical addition rates), and the extreme sensitivity to peroxides of the hydrogen bromide addition, suggested the desirability of confirming earlier conclusions by the addition of hydrogen iodide. The latter reagent should add sufficiently rapidly without a catalyst, and the direction of addition to unsaturated compounds is not affected by peroxides.

Three experiments were carried out with hydrogen iodide and a mixture of the *cis* and *trans* isomers of 1-bromopropene, at 0°, in the absence of air, moisture, and light, and using about 1.15 moles of hydrogen iodide per mole of 1-bromopropene. In one experiment, 17.6 g. of 1-bromopropene giving a strong peroxide test was used. At the end of two days, a 76% yield of addition product was obtained along with unchanged bromopropene. The product was shown to contain 36% of 1-bromo-1-iodopropane and 64% of 1-bromo-2-iodopropane, in excellent agreement with the proportion of 1,1-dihalide found[10] in hydrogen chloride (35, 36%) and hydrogen bromide (33, 33, 41%) additions. The other two experiments (10 g. peroxide-free 1-bromopropene) gave 21 and 24% 1,1-dihalide. The rates of all of these reactions were about the same, and iodine (1.4 mole %) apparently had little effect on the rate of the reaction. In no experiment was there evidence of much reduction.

Conclusions

It has been established in this paper that only one product results from the addition of hydrogen iodide to propene, allyl bromide, and allyl chloride. A similar conclusion was drawn by Kharasch and Hannum[2] from their work on propene, 1-butene, neopentylethylene, vinyl chloride, and allyl bromide. In view of the extent of the work, these data provide strong evidence that the direction of addition of hydrogen iodide to olefins cannot be reversed. The present paper elucidates the accelerating effect of peroxides on this addition. It shows that peroxides are immediately destroyed by hydrogen iodide with the liberation of iodine, and that the latter catalyzes the normal addition reaction. It is noteworthy that the direction of addition of hydrogen iodide, hydrogen chloride, and the normal addition of hydrogen bromide to unsaturated compounds of several types, including 1-bromopropene which yields a mixture, is the same, within the experimental error, for all three halogen acids.

Experimental

Materials and Reagents.—Propene and propane of higher than 99% purity were obtained from commercial sources. The pentane was a commercial *n*-pentane–isopentane mixture. Allyl bromide[11] and allyl chloride[12] were prepared from allyl alcohol and the concentrated halogen halides in the presence of 1–2% of the corresponding cuprous halides. Before use they were agitated with

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(9) Urushibara and Takabayashi, *Bull. Chem. Soc. Japan*, **11**, 692, 754 (1936); **12**, 51 (1937). They report that iron, among other metals, causes an abnormal addition of hydrogen bromide to allyl bromide.

(10) Kharasch, Engelmann, and Mayo, *J. Org. Chem.*, **2**, 288 (1937); Kharasch, Kleiger, and Mayo, *ibid.*, **4**, 428 (1939).

(11) Kharasch and Mayo, THIS JOURNAL **55**, 2468 (1933).

(12) Dewael, *Bull. soc. chim. Belg.*, **39**, 40 (1930).

acidulated ferrous sulfate solution to destroy peroxides, dried rapidly over phosphorus pentoxide, and distilled. 1-Bromopropene was prepared by treatment of propylene bromide with alcoholic sodium ethoxide.[10] The crude product was washed with dilute sulfuric acid to remove unsaturated ethers. which were inseparable by fractionation.

Hydrogen iodide was prepared by the convenient method of Houben, Boedler and Fischer.[13] The gas was collected in a large trap containing some phosphorus pentoxide and a mercury mirror (prepared by heating a drop of mercury in the empty trap). The trap was cooled by dry ice–acetone. After collection, the gas was distilled in the absence of air into the storage vessel, which was a large 30-mm. glass tube mirrored with mercury and equipped with ground joint and stopcock. The usual high-vacuum technique was employed for this purpose; air was not permitted to come in contact with the hydrogen iodide. The storage vessel was kept in dry-ice–acetone when not in use.

Experimental Procedure.—The usual apparatus employed in most of the propene addition experiments, as well as in the allyl bromide. and 1-bromopropene additions, consisted of a series of tubes attached to a vacuum line. In most cases the olefin and volatile solvent (if any) were weighed into a tube containing a little phosphorus pentoxide, which was then sealed to the vacuum line for degassing and eventual distillation of the contents into the reaction tube. When nitrobenzene and acetic acid were used as solvents. the solvent and the propylene were dried and degassed in separate tubes. When water, iodine, diphenylamine, ascaridole or other relatively non-volatile addenda were used, these were weighed into the tube that was eventually to become the reaction tube, which was then sealed to the line. Hydrogen iodide was distilled from a storage reservoir through a ground-glass joint into a tube already attached to the vacuum line. Rough estimation of quantity was made by volume calibration of one tube; exact amounts used were determined by weighings of the storage reservoir. Transfer of reactants to the reaction tube was effected by high-vacuum distillation with appropriate manipulation of stopcocks and cooling baths. Except in the experiments expressly designed to investigate the effect of air upon the addition, the reaction tube was sealed off without access of air, and was maintained at the desired temperature throughout the reaction period.

In about one-fourth of the propene, and in all of the allyl chloride experiments, hydrogen iodide and olefin were stored in the absence of air, in containers attached to the vacuum line. Hydrogen iodide and propylene were measured as gases, allyl chloride as a liquid, in calibrated bulbs, from which they were condensed in an empty tube before distillation into the reaction tubes. This procedure removed small amounts of non-condensable gases, mercury (from manometers), and mercuric iodide (from the hydrogen iodide storage vessel). High-boiling materials were placed in the bomb tube directly, as before.

About 0.1 mole of unsaturated compound usually was employed. The techniques described ordinarily gave colorless reaction mixtures, but a faint iodine color appeared in a few hours in propylene experiments, faster in others.

In attempts to reproduce the experiments of Ingold and Ramsden, the following procedure was employed. Propene was condensed in a small bomb tube in the absence of air, using high vacuum technique. The end of this tube was drawn out to a long capillary, and sealed, and the tube was slipped into a larger bomb tube. The open end of the large bomb tube was drawn down (meanwhile the other end, containing the propene bomb tube, occasionally was cooled in liquid nitrogen), and was sealed onto the vacuum line. Then, after evacuation. hydrogen iodide (and solvent, if used) were distilled into the large bomb tube and the whole was sealed from the line. The bomb was allowed to warm to room temperature, and by suitable manipulation the long capillary was shattered and the contents mixed. Evacuation was omitted in one experiment.

Analysis of Reaction Products.—In most of the propene experiments the bomb contents (after completion of the reaction) were washed with aqueous sodium sulfite and aqueous potassium carbonate to remove iodine and hydrogen iodide, dried over potassium carbonate, and distilled through a Podbielniak column. A single fraction of boiling point corresponding to the "normal" addition product (isopropyl iodide) was obtained in each case. These products were later combined and refractionated. The index of refraction of the principal fraction was that of isopropyl iodide ($n^{20}\text{D}$ 1.4988). The relatively small forerun and residue had lower indices of refraction, excluding the possibility of the presence of appreciable amounts of normal iodide ($n^{20}\text{D}$ 1.5052). In the propene experiments involving the presence of added normal iodide, and in several others, the bomb contents were distilled at 10 mm. into a trap cooled by dry-ice–acetone. The distillate was then analyzed by index of refraction, the index being a linear function of the composition of iso–normal propyl iodide mixtures.

In some of the propene and all of the allyl bromide experiments the first procedure was modified in that the distillate was cut into several fractions of which the indices of refraction were determined separately. The addition product of allyl bromide was distilled at 20 mm. pressure. The 1-bromo-2-iodopropane was found to boil at 66.8° at this pressure and to have the refractive index $n^{20}\text{D}$ 1.5916.

In the allyl chloride experiments free iodine was first titrated with standard thiosulfate solution, and the product was then dried and fractionated at 40 mm. pressure. The 1-chloro-2-iodopropane boiled at 66.2° at 50 mm., $n^{20}\text{D}$ 1.5472.

Reduction Products of Allyl Bromide.—The low-boiling materials from a number of allyl bromide experiments were combined and fractionated through a Podbielniak column. They comprised about 40% allyl bromide and a like amount of iospropyl iodide together with about 10% isopropyl bromide. The last was identified by halogen analysis and preparation of isopropyl 3,5-dinitrobenzoate.

1-Bromo-1-iodopropane.—The various fractions from the 1-bromopropene experiments were combined and fractionated to obtain a sample of 1-bromo-1-iodopropane. The amount of available material was too small to permit isolation of a pure sample, but the index of refraction was estimated from those of several fractions: $n^{20}\text{D}$ 1.5826;

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[13] Houben. Boedler, and Fischer. *Ber.*. **69B**, 1773 (1936).

b. p. 61.3° at 20 mm. Fractions having indices both above and below the estimated value were obtained, and it is believed that the error in the index of refraction is less than ±0.0010.

Structure of 1-Chloro-2-iodopropane.—The structure of the addition product of hydrogen iodide and allyl chloride was established by the action of zinc and hot alcohol on the addition product. An 87% yield of propylene (identified by its addition of hydrogen iodide to give nearly the theoretical yield of isopropyl iodide) was obtained. Had the product been a 1,3-dihalide, cyclopropane (which yields *n*-propyl iodide upon treatment with hydrogen iodide) would have been produced. A 1,1-dihalide would have given 3-hexene. It was then shown that the 1,2-dihalide was 1-chloro-2-iodopropane by adding to it an equimolecular proportion of warm alcoholic sodium ethoxide. The product was a mixture of propene with the *cis* and *trans* isomers of 1-chloropropene.[10] The latter were identified by boiling point and index of refraction.

Summary

1. In a thorough investigation of the addition of hydrogen iodide to propene, allyl bromide and allyl chloride only one (the "normal") addition product was obtained in each case.
2. The addition of hydrogen iodide to 1-bromopropene yields a mixture of approximately one-third 1,1- and two-thirds 1,2-dihalides.
3. It is shown that iodine is a catalyst for the addition of hydrogen iodide, and that peroxides accelerate this addition because they liberate iodine from hydrogen iodide.
4. 1-Chloro-2-iodopropane and 1-bromo-1-iodopropane have been prepared in the pure and nearly pure states, respectively.

CHICAGO, ILLINOIS RECEIVED SEPTEMBER 2, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

An Investigation of the Exchange between a Metal and Ions in Solution by Using Radioactive Indicators

BY B. V. ROLLIN

In experiments using the naturally radioactive isotope of lead, Hevesy and Biltz[1] have shown the existence of an exchange of atoms between the surface of a sheet of metallic lead and a solution of a plumbous salt in contact with it. In one hour, under the conditions of their experiment, they found that the quantity of lead which had exchanged with the solution corresponded to a depth of about a thousand atomic layers of the metal. The study of this type of exchange is interesting because it is important in understanding the mechanism of corrosion processes and so it was considered worth while to continue the investigation with other metals using, as indicators, artificially radioactive isotopes produced by bombardment in the cyclotron.

A. Inactive Metal Shaken with Active Solution

(1) **Zinc.**—For a preliminary experiment radioactive zinc was prepared by deuteron bombardment of zinc followed by chemical separation. The zinc was used in the form of the chloride in a solution of about 300 mg. of chloride in 30 cc. of water acidified to a *p*H of about 5. The total activity of the solution was about 10 microcuries. The metal, in the form of a powder, was first shaken for one hour with a concentrated solution of inactive zinc chloride, then filtered and washed, and about 1 g. of the powder then shaken with the active solution for one hour. The solution was filtered off and the powder very carefully washed. On testing the powder with an electroscope it was found to be quite appreciably radioactive. No quantitative results could be deduced from this experiment because the metallic zinc was slowly attacked by the solution during the period of shaking.

(2) **Silver.**—Silver was chosen because (in the absence of oxygen) it is only dissolved to a negligible extent by water and because it forms stable ions in solution which are not reduced to a lower valence state by contact with the metal. It would, for example, have been impossible to study the exchange between copper and cupric ions because the results would be obscured by the exchange brought about by the reaction

$$Cu^{++} + Cu \rightleftarrows 2Cu^{+}$$

Preparation of the Radioactive Silver.—The isotope used was Ag^{106} having an eight-day half-life and was obtained by bombarding palladium with 8 Mev. deuterons. The palladium was digested with fuming nitric acid and 9 *N* perchloric acid and 100 mg. of silver added as carrier. The silver was precipitated as chloride, washed and dissolved in excess of ammonium hydroxide, then precipitated with ammonium sulfide, filtered and the precipitate dissolved in hot nitric acid. The solution was evaporated to dryness and the silver nitrate residue dissolved in 30 cc. of water. The total (β-ray) activity of the solution was 10 microcuries.

(a) A sheet of silver of area 20 sq. cm. was polished with crocus cloth, washed with nitric acid and water, shaken with inactive silver nitrate solution for two hours and then shaken with the active silver nitrate solution for twenty-four hours. At the end of this time it was care-

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(1) G. von Hevesy and M. Biltz, *Z. physik. Chem.*, B3, 271 (1929).