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-

(1) G. von Hevesy and M. Biltz, *Z. physik. Chem.*, **B8**, 271 (1929).

fully washed, then shaken with water for several hours and its activity tested. It was found to have acquired an activity corresponding to an exchange with the solution of about 150 atomic layers of the metal (assuming the actual surface of the metal is the same as the measured surface).

(b) The experiment was repeated using sheets of gold and platinum instead of silver. These were also found to have acquired an activity representing the transference of about 100 atomic layers from the solution. The activity was apparently not due to simple contamination with ions as it was not appreciably reduced by further washing with water for forty-eight hours.

(c) In this experiment the solution was shaken with a different type of surface. The surface was a silver mirror deposited on the inside of a glass flask by evaporation of silver in a vacuum from a heated tungsten strip. After evaporation of the mirror the flask was filled with nitrogen and the solution introduced. The flask was then evacuated again and shaken so that the solution was in contact with the mirror for one hour. After careful washing the solution was found to have an activity corresponding to the transference of about twenty atomic layers.

B. Active Surface Shaken with Inactive Solution.— The radioactive silver was obtained by electrolysis of the active nitrate solution. The surface was prepared by evaporation of a few milligrams of the silver in vacuum as in (c) above. Before evaporation the silver was carefully washed to free it from silver ions. After deposition of the mirror the flask was filled with nitrogen and the mirror washed several times with distilled water. The mirror was then shaken for one hour with distilled water (under vacuum), this water then discarded, a fresh quantity introduced and the shaking repeated. In this way the mirror was freed from all radioactive contamination as shown by testing the second water washing by adding silver ions (as carrier), precipitating the silver as bromide and testing the bromide with a Geiger counter. The mirror was now shaken for two hours with a solution of silver nitrate (containing 1 g. of silver nitrate in 20 cc. of water). On precipitating the silver as bromide it was found to contain an activity corresponding to the exchange of ten atomic layers.

To investigate whether the nitrate ion had any influence on the exchange, the mirror was now shaken for one hour with a solution of sodium nitrate (0.5 g. sodium nitrate in 20 cc. of water). Following the usual procedure of adding silver ion as carrier and then precipitating the silver as bromide and testing its activity, it was found that no activity had been taken up by the solution.

On washing the mirror again with silver nitrate solution for one hour and measuring the activity taken up by the silver solution, an unexpected result was found. The activity was now very high corresponding to the transference of about 150 atomic layers from the mirror. On washing the mirror with water and then shaking with silver nitrate solution again for two hours it was found that the activity in the solution was now that of only ten layers again. To verify the effect of treatment of the mirror with sodium nitrate solution, the experiment was repeated and again an exchange of about 100 atomic layers was found.

The results are summarized in Table I.

TABLE I

Soln.	Time of shaking, hours	Activity (atomic layers)
Water	2	Not measd.
Water	1	Less than 1
Water	1	Not measd.
$AgNO_3$	2	10
$NaNO_3$	1	0
$AgNO_3$	1	150
$AgNO_3$	2	10
$NaNO_3$	1	Not measd.
$AgNO_3$	1	100

Discussion

The experiments with silver in a solution of silver nitrate show that there is an actual exchange of atoms between the metal and the solution. The exchange appears to involve from ten to a hundred atomic layers and, as one can completely neglect the diffusion over these distances in the metal, the only reasonable mechanism seems to be that of local electrolysis caused by the existence of irregularities on the surface of the metal. However this hypothesis does not account for the activity obtained by the gold and platinum sheets from the silver solution unless the surfaces of the metals contained considerable impurities, which seems unlikely. It is very difficult to explain why treatment of the silver surface with sodium nitrate should increase the activity obtained by the silver surface solution from the mirror. The phenomenon is perhaps due to some kind of activation of points on the surface of the silver by sodium ions but no reason can be seen why this should take place. It seems that further experiments will be needed before the mechanism of these effects can be explained.

It is a pleasure to record the advice and coöperation in these experiments of Dr. G. T. Seaborg and also of Dr. S. Ruben, who very kindly made all the Geiger counter measurements. I am especially indebted to Professor E. O. Lawrence for enabling me to use the cyclotron to obtain the radioactive substances.

Summary

Experiments using radioactive silver have shown that exchange takes place between a solution of silver ions and a surface of metallic silver. In two hours an exchange of silver corresponding to ten atomic layers was found. The exchange was increased by a factor of ten if the surface was pretreated with sodium nitrate solution.

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 2, 1939