[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO]

The State of Chemical Combination of Iodine^{131} Formed by Neutron Irradiation of Tellurium in Organic Liquids

BY F. J. KENESHEA, JR.,[1] AND MILTON KAHN

RECEIVED APRIL 11, 1952

An investigation has been made of the chemical forms assumed by I^{131} produced through beta decay of 25-minute Te^{131} in organic liquids. The Te^{131} was produced by irradiation of solutions of tellurium tetrachloride in the thermal column of a Los Alamos reactor. About 87% of the I^{131} activity produced in benzene was in a form extractable with aqueous solutions; the remaining 13% was in the form of organic-I^{131} compounds; 10% in a form chemically indistinguishable from iodobenzene and 3% as higher-boiling compounds. Addition of chlorobenzene, iodobenzene or carbon tetrachloride to benzene solutions of tellurium tetrachloride before irradiation caused an increase in the yield of organic-I^{131} compounds. The yield of radioactive iodobenzene increased to 40% in pure chlorobenzene and 30% in pure iodobenzene. A method for the production of radioactive iodobenzene of high specific activity has been developed.

Introduction

The chemical effects accompanying the production of radioactive atoms through beta decay have not been as extensively studied as those for thermal neutron capture since most beta emitters do not produce radioactive daughters and the detection of the product atom cannot be accomplished. Of those investigations which have been reported in the literature with regard to the chemical effects accompanying beta decay[2] none were concerned with chemical effects produced as a result of decay in organic liquids.

We wish to report a study of the chemical forms of 8.0-day I^{131} produced through beta decay of 25-minute Te^{131} in pure benzene and in solutions of carbon tetrachloride and chlorobenzene in benzene. It was thought that these experiments might suggest a practical method for the preparation of organic-I^{131} compounds of high specific activity which would be difficult to prepare by the usual methods of synthetic organic chemistry. Of particular interest was the formation of high-specific-activity radioactive iodobenzene. Experiments were also carried out with solutions of inactive iodobenzene in benzene in order to determine the effect of macro quantities of inactive iodobenzene on the yield of radioactive iodobenzene.

Experimental

Chemicals.—Tellurium tetrachloride was prepared by the direct chlorination of elemental tellurium according to the method of Suttle and Geckler[3] with the exception that the reaction was carried out at atmospheric pressure. The product was analyzed for tellurium by dissolving the solid in 6 *f* hydrochloric acid and oxidizing with potassium dichromate[4]; sodium diphenylamine sulfonate was used as an internal indicator[5] in the final titration.

Eimer and Amend C.P. benzene was treated with concentrated sulfuric acid and distilled.

Iodobenzene was prepared according to the procedure of Dains and Brewster.[6] The final product was practically colorless and had a b.p. of 179.0 to 180.0° at 646 mm. pressure.

Eastman Kodak Co. best-grade chlorobenzene was distilled once (b.p. 125.5–126.0° at 647 mm. pressure). Eastman Kodak best-grade carbon tetrachloride was distilled twice (b.p. 70.0° at 640 mm. pressure).

Analytical-grade reagents were used without further purification.

Radioactivity.—Solutions of tellurium tetrachloride were irradiated over a period of 10–15 hours. It was calculated from thermal neutron activation cross sections that approximately 98% of the I^{131} produced in these solutions during the irradiation resulted from the decay of 25-minute Te^{131}; the remainder (2%) was formed from 30-hour Te^{131} which decayed first to its lower isomeric state (25-minute). Ninety-five per cent. of the iodine activity detected formed during irradiation in the reactor.

The course of the I^{131} activity in the experiments was followed by detection of the γ-radiation. When necessary a correction was applied for the γ-radiation associated with the decay of the tellurium isotopes. This correction was estimated from an analysis of the total decay curve for the sample plotted for a period of 50 to 60 days.

Since the activities of the various samples were the same within 15% after correcting for differences in irradiation time and decay it is assumed that the gamma and neutron fluxes during the irradiations were approximately the same in all the experiments.

When solutions containing iodobenzene, chlorobenzene and carbon tetrachloride were irradiated, the active solutions were allowed to stand long enough to allow the 38-minute Cl^{38} and 25-minute I^{128} formed during the irradiation to decay to negligible values.

Counting Procedures.—The γ-radiation was detected with a thick-walled, copper, ethanol–argon-filled, Geiger–Müller tube. Solutions were counted in test-tubes which were calibrated by counting the same volume of an aqueous solution containing I^{131} activity in each tube; the liquid level was brought up to a standard height in each case with water. Thereafter, all samples were brought up to this standard height, water or benzene being used as the diluent. The samples were mixed with an air stream. The counting rates ranged from 50 c./m. to 3000 c./m. and in this range the response of the counter was linear. The effect of composition and density of the liquids on the counting rates was found empirically to be insignificant.

Beta counting of tellurium precipitates was done with a thin window Geiger–Müller tube. Coincidence corrections were not applied in the beta counting experiments since it was found that the samples in any one experiment all had about the same counting rate. To eliminate self-absorption corrections the same weight of tellurium (±2 mg.) was precipitated in each case.

Procedures Used in Characterizing the I^{131} Species.—The following general procedure was used to determine the chemical state of the I^{131} activity after its formation from Te^{131} in an organic solvent. Tellurium tetrachloride was dissolved in benzene or in mixtures of benzene with chlorobenzene, iodobenzene or carbon tetrachloride. Approximately 50 ml. of the solution containing about 0.02 g. of tellurium tetrachloride per milliliter was sealed in a quartz flask and irradiated with neutrons in the thermal column of a Los Alamos reactor. A 5- to 10-ml. sample of the active solution was sealed in a test-tube and decay of the total

---

[1] This paper is a portion of the dissertation presented by F. J. Keneshea, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1951.

[2] (a) R. A. Mortensen and P. A. Leighton, THIS JOURNAL, **56**, 2397 (1934); (b) T. H. Davies, *J. Phys. Colloid Chem.*, **52**, 595 (1948); (c) W. H. Burgus, T. H. Davies, R. R. Edwards, H. Gest, C. W. Stanley, R. R. Williams and C. D. Coryell, *J. chim. phys.*, **45**, 165 (1948); (d) W. H. Burgus and J. W. Kenndey, *J. Chem. Phys.*, **18**, 97 (1950) (on positron decay).

[3] J. F. Suttle and R. P. Geckler, *J. Chem. Ed.*, **23**, 135 (1946).

[4] V. Lenher and H. F. Wakefield, THIS JOURNAL, **45**, 1423 (1923).

[5] J. F. Suttle, R. Sanftner and H. Kruse, private communication.

[6] F. B. Dains and R. Q. Brewster, "Organic Syntheses," Coll. Vol. I, 2nd ed., edited by Gilman and Blatt, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 323.

gamma activity was followed. A portion of the active solution was extracted with 3 *f* sulfuric acid followed by washings with dilute solutions of sodium bisulfite, sodium hydroxide or sodium iodide. The initial washing with sulfuric acid in all instances removed all of the inactive tellurium from the organic solution as shown by an analysis of the aqueous phase. The aqueous phases were counted and the organic phase, after the extractions, was either counted or fractionally distilled after the addition of carrier iodobenzene; the activity in each fraction was then determined. In several instances the decay of the activity in the separated aqueous layers and the extracted organic phase was followed in order to determine how the tellurium activity was distributed.

Adsorption of I^{131} activity on the walls of the quartz irradiation vessel or on the walls of the glass extraction flasks was found to be negligible. Radioactive material balances (obtained by comparing the total I^{131} activity recovered with the I^{131} activity in the total decay sample) were for the most part better than 95%. The fraction of I^{131} activity present in any one phase was computed on the basis of the total I^{131} activity recovered.

It is believed that the error in the values reported for extraction and retention of I^{131} activity is no greater than 10%. The main sources of error were incurred in the statistical fluctuation in the counting rates (*ca.* ± 3%) and in the use of decay curves for the determination of I^{131} activity (*ca.* ±7%).

Results and Discussion

When irradiated solutions of tellurium tetrachloride in benzene were washed with 3 *f* sulfuric acid and either 0.1 *f* sodium iodide, 0.1 *f* sodium hydroxide or 0.05 *f* sodium bisulfite, 87% of the total I^{131} activity was extracted; the rest was retained by the organic phase; 10% in a form chemically indistinguishable from iodobenzene and 3% as higher-boiling iodine compounds as shown by distillation experiments.

The yields of radioactive iodobenzene formed when benzene–chlorobenzene and benzene–iodobenzene solutions containing tellurium tetrachloride were irradiated are plotted in Fig. 1. These solutions were washed with 3 *f* sulfuric acid and 1 *f* sodium hydroxide before being distilled. The yield of higher-boiling iodine compounds varied from 18% to 49% in the chlorobenzene–benzene solutions and from 0% to 9% in the iodobenzene–benzene solutions, there being no apparent dependence in either instance on the concentration of the phenyl halide.

The results of the experiments with benzene and benzene–chlorobenzene solutions of tellurium tetrachloride suggest a practical method for the synthesis of radioactive iodobenzene of high specific activity.

Two experiments were carried out with solutions of tellurium tetrachloride in mixtures of benzene and carbon tetrachloride. At carbon tetrachloride mole fractions of 0.10 and 0.25 approximately equal amounts of iodobenzene and higher-boiling compounds were formed; in each case 30% of the total iodine activity was retained in the organic phase.

Three formal sulfuric acid followed by 1 *f* sodium hydroxide removed all of the tellurium activity from the irradiated benzene and benzene–iodobenzene solutions whereas some tellurium activity was retained by the benzene–chlorobenzene and benzene–carbon tetrachloride mixtures in a form higher boiling than iodobenzene; the tellurium activity retained ranged from 18–72% and did not vary in a regular manner with the concentration of chlorobenzene. The benzene–carbon tetrachloride solutions of carbon tetrachloride mole fractions 0.10 and 0.25 retained 30% and 5%, respectively, of the tellurium activity. Since in all instances the inactive tellurium was removed quantitatively the foregoing results suggest a method for the enrichment of tellurium activity.

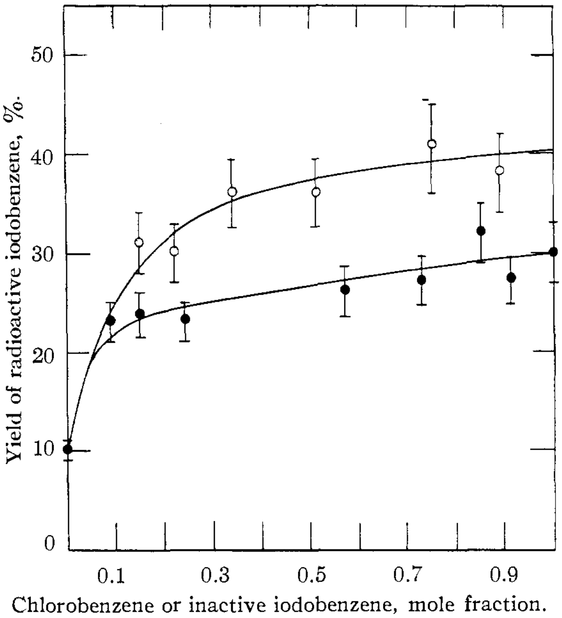

Fig. 1.—The yield of radioactive iodobenzene formed during irradiation of benzene–chlorobenzene (○) and benzene–iodobenzene (●) solutions containing tellurium tetrachloride.

It was of interest to determine whether the tellurium activity formed in pure benzene exchanged with tellurium tetrachloride. This possibility was investigated by fractionally crystallizing the tellurium tetrachloride from an active solution through slow evaporation at room temperature and comparing the tellurium specific activity (beta activity) found in successive fractions with the total tellurium specific activity in solution. Two experiments were carried out; one, 44 hours after the end of irradiation, and the other, 50 days after the end of irradiation. In both instances the results indicated complete exchange. Measurements of the activity in these experiments were made several weeks after the tellurium counting samples were prepared so that the activities observed were due solely to the 32-day and 90-day tellurium isotopes. Assuming that the 25-minute Te^{131} activity would behave as did the long-lived tellurium activities it is possible that the short-lived tellurium was present as tellurium tetrachloride before its decay into I^{131}. If this is true, then the rate of exchange must be fairly rapid, since the mean life of this short-lived tellurium is only 36 minutes.

Acknowledgment.—The authors wish to express their appreciation to Dr. R. W. Spence and Mr. James Sattizahn of the Los Alamos Scientific Laboratory for irradiation of the solutions of tellurium tetrachloride.

ALBUQUERQUE, NEW MEXICO