

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WISCONSIN]

## Reactions of Bromine with Carbon Tetrachloride and Tetrachloroethylene Following Neutron Capture and Isomeric Nuclear Transition

BY EDWARD G. BOHLMAN AND JOHN E. WILLARD

The *nuclear* processes of neutron capture<sup>1</sup> and isomeric transition<sup>2</sup> have been shown to be capable of initiating certain chemical reactions and considerable progress has been made toward understanding the mechanisms of these reactions. The purpose of this paper is to present further evidence on this subject.

The first part of the work has consisted of a comparison of the efficiency of neutron capture with the efficiency of isomeric transition in causing the reaction of bromine with carbon tetrachloride both in solution and in the gas phase.

The second series of experiments was designed to determine whether bromine atoms produced by neutron capture and by isomeric transition behave like photochemically produced bromine atoms after losing their excess energy or charge. The reaction of bromine with tetrachloroethylene has been used for this purpose.

Lastly,  $\text{CCl}_3\text{Br}$  and  $\text{CCl}_2\text{Br}_2$  have been used as carriers to determine the nature of the products of the reactions of bromine with carbon tetrachloride following isomeric transition and neutron capture, for the purpose of learning whether the reaction process breaks only a single bond of the carbon tetrachloride or is a miniature explosion.

### Experimental Procedure

**Neutron Source.**—Neutrons were obtained from the deuterium-beryllium reaction with the aid of an electrostatic generator of the type developed at Wisconsin<sup>3</sup> and operated for the production of artificial radioactivity by Dr. J. L. McKibben, Mr. Truman Kohnan and Mr. David Frisch under grants from the Wisconsin Alumni Research Foundation. A deuterium beam of about 1.8 mev. and 10 microamperes was used. Bottles of materials to be irradiated with neutrons were hung in the large vat of water which surrounded the target of the generator.

(1) (a) Szilard and Chalmers, *Nature*, **134**, 462 (1934); (b) Erbacher and Phillip, *Ber.*, **69B**, 893 (1936); (c) Paneth and Fay, *J. Chem. Soc.*, **384** (1936); (d) Glückauf and Fay, *ibid.*, 390 (1936); (e) Suess, *Z. physik. Chem.*, **B45**, 297 (1940); (f) Libby, *THIS JOURNAL*, **62**, 1930 (1940); (g) Libby, *Science*, **93**, 283 (1941).

(2) (a) Segre, Halford and Seaborg, *Phys. Rev.*, **55**, 321 (1939); (b) DeVault and Libby, *ibid.*, **55**, 322 (1939); (c) Willard, *THIS JOURNAL*, **62**, 256 (1940); (d) Willard, *ibid.*, **62**, 3161 (1940); (e) Suess, *Z. physik. Chem.*, **B45**, 312 (1940); (f) Fairbrother, *Nature*, **145**, 307 (1940); (g) Seaborg, Friedlander and Kennedy, *THIS JOURNAL*, **62**, 1309 (1940); (h) DeVault and Libby, *Phys. Rev.*, **58**, 688 (1940); (i) DeVault and Libby, *THIS JOURNAL*, **63**, 3210 (1941); (j) Cooper, *Phys. Rev.*, **61**, 1 (1942).

(3) Herb. Kerst and McKibben, *Phys. Rev.*, **51**, 75 (1937).

**Preparation of Radioactive Bromine.**—Radioactive bromine was prepared from ethylene dibromide by the Szilard-Chalmers<sup>1a</sup> neutron bombardment method. The aqueous extract, with sodium bromide added, was evaporated to dryness and fused to burn off contaminating non-volatile organic material, after which free bromine was formed by oxidation in the system previously described.<sup>2c</sup>

**Counting Radioactivity.**—Counts were made with a solution type glass Geiger-Müller counter tube (hydrogen filled) with an interpolating scale-of-64 counting circuit designed by Dr. J. L. McKibben.

Reaction mixtures of organic material and elemental bromine were separated for counting by extracting with aqueous sodium hydroxide, sodium carbonate, sodium nitrite or potassium iodide. Pre-cooled 35% aqueous sodium hydroxide was used to extract solutions containing 50 mole per cent. or more of bromine. Repeated extractions showed that the organic radioactive bromine compounds being studied were not hydrolyzed by this treatment.

In all cases where the neutron capture reaction was being studied, the solutions which had been prepared for counting were allowed to stand long enough before counting so that any  $\text{Br}^{80}$  (18 min. half-life) activity which had reacted as a result of isomeric transition<sup>2c</sup> would decay.

The production of radioactive chlorine (37 min. half-life) from the chlorine in carbon tetrachloride or tetrachloroethylene by slow neutron capture necessitated allowing reaction mixtures to stand for several hours after neutron bombardment before making counts on bromine activity. It was found that the production of radioactive phosphorus (14.3 day half-life) from chlorine by fast neutrons could be avoided by placing the reaction mixtures at distances greater than six inches from the target, which was submerged in water.

**Gas Phase Reactions.**—Gas phase neutron capture reactions were carried out in a 12-liter flask mounted on a stand with lead feet which allowed it to be sunk in the vat of water surrounding the neutron source. The large volume flask was necessary in order to obtain enough of a low vapor pressure reactant in the gas phase to produce a measurable amount of activity. In preparation for use the flask was evacuated with a mercury vapor pump and the reactant or reactants were then vaporized into it. The reactants were frozen out after irradiation, and rapidly separated by the usual methods. Additional organic solvent was added to make a volume suitable for counting. The flask was painted black to preclude photochemical exchange reactions.

**Reagents.**—Mallinckrodt "Low Sulfur" carbon tetrachloride was used. Purification of this material by the chlorine and chlorine dioxide method did not alter the results obtained. Eastman Kodak Co. tetrachloroethylene was purified by illuminating with chlorine, washing with sodium hydroxide solution and with water and distilling.

Mallinckrodt bromine was used without further purification.

In experiments involving tetrachloroethylene the reaction mixtures were deoxygenized by bubbling oxygen-free nitrogen through them. In some cases this treatment was followed by freezing and evacuation.

$\text{CCl}_3\text{Br}$  and  $\text{CCl}_2\text{Br}_2$  were prepared photochemically by illuminating solutions of bromine in chloroform or  $\text{CH}_2\text{Cl}_2$ . The 500-watt Mazda lamps used produced sufficient heat to keep the solutions at the boiling point during illumination. After illumination the product was separated from the reaction mixture by distillation.  $\text{C}_2\text{Cl}_4\text{Br}_2$  was crystallized from mixtures of tetrachloroethylene and bromine after illumination.

### Results

#### Bromine-Carbon Tetrachloride Solutions.—

When bottles of bromine-carbon tetrachloride solutions were subjected to neutron bombardment it was always observed that part of the radioactive bromine which was formed by neutron capture reacted with the carbon tetrachloride to form an organic bromine compound which was insoluble in the aqueous extractants used. Curve A, Fig. 1, shows how the fraction of the total radioactive bromine formed which reacted in this way varied with the concentration. Most of the points plotted represent the average of six or more independent determinations. In many of the determinations two sets of counts were made, one as soon as the  $\text{Cl}^{38}$  (37 min.) had decayed and the other more than twenty-four hours later. Separate computations were then made of the fraction of  $\text{Br}^{80}$  (4.4 hr.) and of  $\text{Br}^{82}$  (36 hr.) which had entered organic combination. No consistent difference was observed so the counts were averaged in making Fig. 1 with the result that the majority of the points represent 10 or more independent counts. The average deviation from the average represented by these points was as much as 20 per cent. of the value of the point in a number of cases. It was shown that this was not due to counting error, to the particular extraction technique used or to variation in position of the reaction mixtures relative to the neutron source, but its cause was not discovered. Care was taken to wash the walls of the bottle in which bombardment occurred with the extraction solution.

For comparison purposes the data previously obtained for the reaction of bromine with carbon tetrachloride following *isomeric transition*<sup>2c</sup> are plotted in Curve B, Fig. 1. Except for the point representing the lowest bromine concentration which is the average  $(34 \pm 3.5)$  of six determinations and which has recently been confirmed

$(32.4 \pm 1)^{2d}$  the other points represent single determinations.

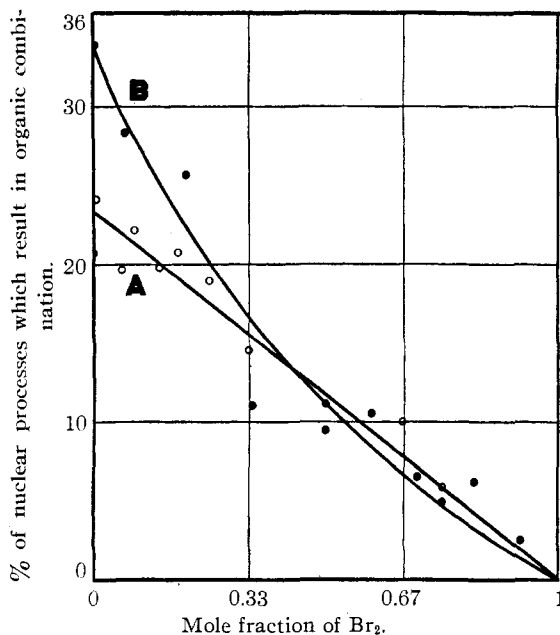


Fig. 1.—Reaction of bromine with carbon tetrachloride: Curve A, reaction initiated by neutron capture; Curve B, reaction initiated by isomeric transition.

#### Gas Phase Bromine-Carbon Tetrachloride.—

Three experiments were made on the *neutron irradiation* of gaseous mixtures of bromine and carbon tetrachloride containing 60 mm. pressure of each reactant. They showed an average of 1.9% of the radioactive bromine in organic combination. Within experimental error this is no reaction at all and is a result similar to that observed when radioactive bromine undergoing *isomeric transition* was placed with carbon tetrachloride in the gas phase.<sup>2d</sup>

#### Bromine-Tetrachloroethylene Reactions.—

Figure 1 shows that not more than 35% of the bromine atoms which are activated as a result of neutron capture or isomeric transition react to form bromo-organic compounds with carbon tetrachloride; yet it has been shown that 85 to 100% of these atoms are sufficiently activated for a number of other reactions<sup>1,2</sup> such as the rupture of ethyl bromide. In order to determine whether the atoms which do not enter organic combination behave like photochemically produced atoms the reactions of bromine with tetrachloroethylene<sup>4</sup> following neutron capture and following isomeric transition have been measured, with the results shown in Table I. Each value is the average of

(4) Willard and Daniels, *THIS JOURNAL*, **57**, 2240 (1935).

two or more determinations. Values taken from Fig. 1 for the bromine-carbon tetrachloride reaction are included in the table.

TABLE I

PERCENTAGE OF BROMINE WHICH ENTERS ORGANIC COMBINATION FOLLOWING NUCLEAR ACTIVATION

Concentrations: solns. for  $n, \gamma$  reacns., 0.7 mole %  $\text{Br}_2$ ; solns. for I.T. reacns. 0.1 mole %  $\text{Br}_2$ ; gas phase  $\text{Br}_2\text{-C}_2\text{Cl}_4$   $n, \gamma$  reacn. 15 mm.  $\text{C}_2\text{Cl}_4$  to 30 mm.  $\text{Br}_2$ ; gas phase  $\text{Br}_2\text{-C}_2\text{Cl}_4$  I.T. reacn. about 3 mm.  $\text{Br}_2$  to 3 mm.  $\text{C}_2\text{Cl}_4$ ; gas phase  $\text{Br}_2\text{-CCl}_4$ ,  $n, \gamma$  reacn. 60 mm.  $\text{CCl}_4$  to 60 mm.  $\text{Br}_2$ ; gas phase  $\text{Br}_2\text{-CCl}_4$  I.T. reacn. 700 mm.  $\text{CCl}_4$ -100 mm.  $\text{Br}_2$ .<sup>2d</sup>

Phase	Activation	With $\text{C}_2\text{Cl}_4$	With $\text{CCl}_4$
Soln.	$n, \gamma$	37	24
Gas	$n, \gamma$	0	1.9
Soln.	I.T.	85	34
Gas	I.T.	19	1.1

Observations of the reaction following neutron capture in tetrachloroethylene solutions more concentrated in bromine than shown in Table I showed that the organic bound activity falls off with increasing bromine concentration in this case much as in the case of the reactions with carbon tetrachloride shown in Fig. 1.

The results in Table I are to be regarded as only semi-quantitative. They are subject to the undetermined source of error mentioned above in connection with the carbon tetrachloride reactions, and possibly also to error due to the effects of small amounts of oxygen on reactions of bromine with tetrachloroethylene.<sup>4</sup> They are, however, sufficiently accurate to indicate (1) that there is little or no reaction of bromine with tetrachloroethylene in the gas phase following neutron capture, (2) that an appreciable gas phase reaction occurs as the result of isomeric transition, (3) that the probability of a bromine atom forming a bromo-organic compound by reaction with liquid tetrachloroethylene following isomeric transition is much greater than the probability of its reaction with carbon tetrachloride, (4) that the probability of a bromine atom forming a bromo-organic compound by reaction with liquid tetrachloroethylene as a result of isomeric transition is much greater than the probability that it will do so as a result of neutron capture.

**Product Determination.**—In order to determine whether the reactions of bromine with carbon tetrachloride activated by neutron capture and by isomeric transition form solely  $\text{CCl}_3\text{Br}$ , or produce also more highly brominated compounds, carriers were used. For example, in one case a solution of bromine in carbon tetrachloride was

bombarded with neutrons, the free bromine was extracted with aqueous sodium hydroxide, the organic layer was dried with phosphorus pentoxide, 20 cc. of  $\text{CCl}_3\text{Br}$  was added, the solution was fractionally distilled in an atmosphere of nitrogen, fractions of about 3 cc. each were collected, and the radioactivity of each was measured. The activity in the residue was also counted and then  $\text{CBr}_2\text{Cl}_2$  was added and a further fractional distillation carried out. In the distillation of each carrier it was assumed that the middle fraction contained a representative amount of the activity present in that form. After multiplying the count per cc. of this fraction by the total volume of the carrier added it was possible to calculate distributions of the type recorded in Table II. Solutions containing about  $10^{-3}$  mole per liter of bromine were used for the isomeric transition reactions recorded here, and about 50 mole per cent. of bromine for the neutron capture reactions. It is to be expected that in solutions of different concentrations the relative amounts of different types of products would be different.

TABLE II  
NATURE OF PRODUCTS

Carrier	Neutron capture	Isomeric transition
$\text{CCl}_3\text{Br}$	55%	70%
$\text{CBr}_2\text{Cl}_2$	20	
Residue of higher boiling compounds	25	{ 30

One experiment in which  $\text{C}_2\text{Cl}_4\text{Br}_2$  was used as carrier showed that less than 2% (possibly none) of the isomeric transition product was this substance.

The results indicate that an appreciable portion of both the neutron capture and isomeric transition reactions leads to products which are higher boiling than  $\text{CCl}_3\text{Br}$ .

### Discussion

**Bromine-Carbon Tetrachloride.**—It is apparent from Fig. 1 that a bromine atom which is recoiling from the emission of a gamma ray emitted as the result of neutron capture has about the same probability of reacting with liquid carbon tetrachloride as a bromine atom which has just undergone isomeric transition. (The probability is somewhat lower and possibly shows a different dependence on bromine concentration than the probability of the isomeric transition reaction.) Practically no reaction occurs in the gas phase for either type of activation. These facts are in ac-

cord with the theory that both types of reaction occur as the result of an interaction between the activated radioactive bromine atom and a carbon tetrachloride molecule to form a reactive organic fragment which has a certain probability of reacting with the radioactive bromine atom which formed it.

The fact that products of higher boiling point than  $\text{CCl}_3\text{Br}$  are found indicates that the process of forming the organic radical is in some cases at least a miniature explosion rather than the removal of a single chlorine atom from a carbon tetrachloride molecule. The fragments produced must finally form stable molecules containing more than one bromine atom or more than one carbon atom.

In the case of the isomeric transition it is quite certain that the ability of the bromine to rupture the carbon tetrachloride arises from the charge of the bromine atom,<sup>2c,2i,2j</sup> while in the case of neutron capture this ability is probably due to the recoil energy of the bromine atom<sup>1f</sup> ( $\sim 4000$  kcal./mole) which is far more than enough to allow it to break a carbon chlorine bond, by a billiard ball mechanism.

**Bromine-Tetrachloroethylene.**—For every bromine atom which enters organic combination with carbon tetrachloride following isomeric transition or neutron capture there are two or three which do not. What becomes of them? Suess<sup>1e</sup> has shown that bromine atoms which have split out of hydrogen bromide following isomeric transition add to acetylene as photochemically produced atoms would.

We have chosen tetrachloroethylene as the compound most similar to carbon tetrachloride which would add bromine photochemically and have allowed bromine to react with it as a result of isomeric transition and of neutron capture in the dark.

Because of the presence of the tetrachloroethylene double bond those bromine atoms which are activated by neutron capture or isomeric transition but which become normal bromine atoms before entering organic combination might still be expected to react, just as photochemically produced atoms would. This should lead to a larger fraction of the captures or transitions resulting in the formation of organic bound radiobromine in tetrachloroethylene than in carbon tetrachloride. However, such an increase might also result from the formation of organic bound radiobromine in

tetrachloroethylene by a free radical mechanism similar to that of the carbon tetrachloride reaction but more efficient due to the different nature of tetrachloroethylene.

Table I shows that for the case of the isomeric transition the predicted increase occurs; the amount of reaction with tetrachloroethylene is much greater than with carbon tetrachloride. The fact that a reaction occurs in the gas phase with tetrachloroethylene suggests that the increased reaction is due to the reaction of normal atoms with the double bond, instead of an increased efficiency of the type of free radical mechanism which is believed to account for the reaction with carbon tetrachloride. A free radical combination would not be expected to occur in the gas,<sup>2d</sup> but a gas phase photochemical bromination of tetrachloroethylene occurs at room temperature,<sup>5</sup> indicating that bromine atoms can add to the double bond in the gas. In any case it is to be expected that the possibility for radioactive bromine atoms to exchange with non-radioactive bromine molecules will prevent some of the activity from appearing in organic combination. This exchange may account for the difference between the percentages of organic bound bromine in the solution and gas phase isomeric transition reactions with tetrachloroethylene. The ratio of bromine to tetrachloroethylene molecules in the gas was about 1 to 1, and in solution only 1 to 1000.

There remains the question as to why, as shown in Table I, isomeric transition is much more effective than neutron capture in causing reaction of bromine with tetrachloroethylene. One hypothesis will be suggested.

This assumes that a bromine atom with high recoil energy may collide with a chlorine atom of a tetrachloroethylene molecule with the formation of a bromine chloride molecule which has enough kinetic energy to escape from the trichloroethylene radical formed. If bromine chloride, like bromine<sup>4</sup> and chlorine,<sup>6</sup> does not readily react with tetrachloroethylene in the dark, radioactive bromine would thus be prevented from entering organic combination. The bromine atom resulting from isomeric transition is activated by virtue of its charge rather than its kinetic energy and would not be expected to take part in a process such as that outlined. If it did not combine with a free radical formed in the process of its

(5) Snell, Senior Thesis, University of Wisconsin, 1940.

(6) Leermakers and Dickinson, *THIS JOURNAL*, **54**, 4648 (1932).

neutralization it might then be expected to be free to add to the double bond.

**Franck and Rabinowitsch Hypothesis.**—Franck and Rabinowitsch<sup>7</sup> have discussed factors which might be expected to cause lower quantum yields in solution than in the gas phase in the case of photochemical reactions in which the primary process in the gas involves the production of atoms or radicals.

The reactions of bromine atoms following neutron capture and following isomeric transition appear to offer a definite experimental example of the effect of solvent in favoring the combination of atoms and radicals which are formed in the same solvent envelope. If the mechanism which is pictured is correct, these bromine atoms split carbon tetrachloride molecules into radicals and atoms and then may react with the radicals formed. The atoms resulting from either neutron capture or isomeric transition are *tagged* with radioactivity so it is possible to determine whether the *particular* atom which forms a radical reacts with it. The fact that little or no reaction between these atoms and the carbon tetrachloride occurs in the gas phase in contrast to the liquid seems to indicate the ability of an envelope of carbon tetrachloride molecules to bring about the combination of carbon tetrachloride fragments and bromine atoms by decreasing the probability of their diffusing away from each other, and by removing their

(7) Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934). See also: Rollefson and Burton, "Photochemistry," Prentice-Hall, New York, N. Y., 1939; Leighton and Noyes, "The Photochemistry of Gases," Reinhold Publishing Co., New York, N. Y., 1941; Atwood and Rollefson, *J. Chem. Phys.*, **9**, 506 (1941).

energy of combination before such diffusion occurs.

We wish to express our appreciation for support given by the Wisconsin Alumni Research Foundation to the work described in this paper.

### Summary

1. It has been shown that the nuclear  $n, \gamma$  process whereby radioactive bromine is produced is capable of causing reaction of the bromine with carbon tetrachloride in solution but that little or no reaction occurs in the gas phase.

2. An appreciable fraction of the organic bound radiobromine resulting from both the isomeric transition and neutron capture reactions of bromine with carbon tetrachloride is in compounds of higher boiling point than  $\text{CCl}_3\text{Br}$ . This indicates that the mechanism of reaction involves a disruption of the carbon tetrachloride molecule more serious than the removal of a single chlorine atom.

3. Bromine will react with liquid tetrachloroethylene following neutron capture with a probability of about 37% and following isomeric transition with a probability of about 85%. It will react in the gas phase following isomeric transition but not following neutron capture. The different probabilities of reaction following the two types of activation are discussed.

4. The difference between the probability of reaction in solution and in the gas phase, observed in this work, is evidence in support of the Franck and Rabinowitsch "cage" hypothesis.

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## Energy States of Solids: Evidence from Thermal Data for the Existence of Low Electronic Energy Levels in Europium Ion. The Heat Capacity of Europium Sulfate Octahydrate from 60 to 300°K.

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The investigations of Spedding and co-workers<sup>1</sup> have established the existence of low-lying electronic energy levels in a number of rare-earth salts. Certain of these levels result from the splitting of a degenerate ground state of the rare-earth ion by the crystalline field; others are excited electronic levels whose energy is comparable with  $kT$ , and which may or may not be split by

(1) Spedding, Nutting and Hamlin, *J. Chem. Phys.*, **5**, 191 (1937), and previous articles.

the field. The number and spacing of the energy levels have been investigated theoretically<sup>2</sup> and fair agreement with the observed spectroscopic and magnetic susceptibility data has been obtained. The calculations almost invariably involve the simplifying assumption of an electrical field of cubic symmetry.

(2) Cf. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford, 1932; Penney and Schlapp, *Phys. Rev.*, **41**, 194 (1932); Penney and Kynch, *Proc. Roy. Soc. (London)*, **A170**, 112 (1939); Spedding, *J. Chem. Phys.*, **5**, 316 (1937).