

TABLE II
 VISCOSITY IN SURFACE POISES OF LONG CHAIN ALCOHOLS ON SUBSOLUTION WITH 0.01 N H^+

Alcohol	Viscosity at $P = 3$ dynes per cm.		Viscosity at $P = 20$ dynes per cm.		Transition press. dynes per cm.,
	Torsion pendulum	Canal 11	Torsion pendulum	Canal 11	
Tetradecyl	3×10^{-4}		1.1		6.2
Pentadecyl	2×10^{-3}	2.5×10^{-4}	1.3		8.2
Hexadecyl	6×10^{-3}	6.7×10^{-4}	0.85	3×10^{-2}	10.2
Heptadecyl	9×10^{-3}	8×10^{-4}	.60		11.8
Octadecyl	2×10^{-2}	1.7×10^{-3}	.17		12.9

width should be made. Observations on particles of talc flowing through the slit with the film indicated that the surface was to a sufficient approximation plane. A closer study might, however, demonstrate a small curvature which would change the actual slit width by an amount adequate to remove the discrepancy.

Summary

The viscosities of films of stearic acid and the normal alcohols containing 15 to 18 carbon atoms have been measured at 20–25°. All films were spread on 0.01 N sulfuric acid. Several types of canal viscosimeters were employed, and apparent viscosities determined with the different instruments varied considerably. The canal regarded as most satisfactory was made from glass plates with lightly paraffined edges. The top edges of the plates were at the surface level and the sides extended considerably below. The sides were

purposely hydrophilic. Canal widths ranged from 0.02 to 0.157 cm.

The viscosity calculated from the equation of Harkins and Kirkwood was found not to be exactly proportional to the cube of the canal width, but to be higher at the greater widths. The viscosity increases somewhat, and in a linear fashion, with the mean pressure on the films. The best values of the viscosity at a mean pressure of 3 dynes per cm., expressed in surface poises, are: stearic acid, 0.00009; pentadecyl alcohol, 0.00025; hexadecyl alcohol, 0.00067; heptadecyl alcohol, 0.00080; octadecyl alcohol, 0.00168.

The usefulness of the canal viscosimeter is severely limited by its incapacity for indicating changes in viscosity with small changes in film pressure. Since it does not give absolute viscosities, its principal usefulness may be in standardizing other surface viscosimeters.

CHICAGO, ILLINOIS

RECEIVED MAY 28, 1940

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

The Mechanism of Chemical Reactions Accompanying the Isomeric Radioactive Transition of Br^{80} †

By JOHN E. WILLARD

Artificially radioactive Br^{80} has two radioactive isomers. The one of these which has the higher nuclear energy changes into the other by the transition: Br^{80} (4.4 hr. half-life) \rightarrow Br^{80} (18 min. half-life) + a gamma ray or a conversion electron. It has been observed¹⁻⁶ that this transition is frequently accompanied by a chemical reaction of the Br^{80} (18 min.) atoms which it produces.

Before the energy of the conversion electrons

† Paper presented before the Division of Physical and Inorganic Chemistry at the April, 1940 meeting of the American Chemical Society.

- (1) Segrè, Halford and Seaborg, *Phys. Rev.*, **55**, 321 (1939).
- (2) DeVault and Libby, *ibid.*, **55**, 322 (1939).
- (3) LeRoux, Lu and Sugden, *Nature*, **143**, 518 (1939).
- (4) Willard, *THIS JOURNAL*, **62**, 256 (1940).
- (5) Fairbrother, *Nature*, **145**, 307 (1940).
- (6) Suess, *Z. physik. Chem.*, **B45**, 312 (1940).

had been measured⁷ this unusual reactivity was thought to be due to the recoil energy^{1,2,3} acquired by a bromine atom when it loses a gamma ray or a conversion electron, but has since been attributed to the highly reactive electronic state of the bromine ion which results from the loss of a conversion electron from the K or L shell of the atom.^{4,5,6,8}

The purpose of this paper is to present results which indicate that the reaction of the daughter activity of the Br^{80} transition with carbon tetrachloride is not due solely to the reactive nature of the bromine ion which has just undergone transi-

(7) Valley and McCreary, *Phys. Rev.*, **56**, 863 (1939).

(8) Seaborg, Friedlander and Kennedy, *THIS JOURNAL*, **62**, 1309 (1940).

tion but is dependent also upon the concentration of carbon tetrachloride in its vicinity. This conclusion is based on experiments which show that in the *gas phase* very little reaction occurs between carbon tetrachloride and bromine which is undergoing transition.

The results of other experiments dealing with the bromine-carbon tetrachloride reaction and with other reactions activated by the Br^{80} transition will also be presented; the present evidence as to the magnitude of the internal conversion coefficient of the transition will be reviewed; and a classification of reactions activated by the transition will be made.

Experimental Procedure

The experimental methods used in the work to be discussed here were similar to those outlined earlier⁴ save that rigid purification of carbon tetrachloride and exclusion of oxygen from reaction systems were sometimes omitted when these procedures had been shown not to affect the results obtained. Activities were determined with a Geiger-Müller counter tube with an annular jacket for holding solutions. Gaseous ethylene bromide and gaseous mixtures of bromine and carbon tetrachloride were prepared for counting by dissolving them in carbon tetrachloride. Half of the solution so obtained was immediately extracted with aqueous potassium iodide or sodium nitrite. Counts were made as desired on the extracted carbon tetrachloride, the extraction solution and the unextracted solution. In these experiments with gaseous mixtures correction was made for reaction occurring while the reactants were in the liquid phase during the three or four minute extraction process.

The pressure of gaseous reactants was determined with a Daniels diaphragm or was estimated from a knowledge of the weight of reactant used and the volume of the reaction vessel.

Solutions of radioactive cinnamic acid dibromide were prepared by illuminating radioactive bromine in a degassed solution of cinnamic acid in carbon tetrachloride until the bromine color had disappeared. After standing for two hours these solutions were distilled and the activity of the carbon tetrachloride distillate was compared with the activity of the solution before distillation, by means of the Geiger-Müller counter. Correction was made for decay occurring during distillation.

Preparation of Radioactive Bromine.—Ethylene dibromide was used in place of ethyl bromide in the preparation of radioactive bromine, by the Szilard Chalmers neutron bombardment method, since it gives a greater yield. When the dibromide was used it was found that the aqueous sodium bromide extract was apt to be contaminated with non-volatile organic material. This difficulty was avoided by precipitating, filtering and washing the bromide as silver bromide and then releasing it as hydrogen bromide by treatment with hydrogen sulfide in aqueous suspension. The excess hydrogen sulfide was boiled off and the hydrogen bromide solution, after neutralization

with sodium hydroxide, was evaporated to dryness for use in the bromine preparation system previously described.⁴

Results

Gas Phase Bromine-Carbon Tetrachloride.

When gaseous mixtures of radioactive Br^{80} and carbon tetrachloride were allowed to stand less than 2% of the Br^{80} (18 min. half-life) which was formed reacted with the carbon tetrachloride. These results (Table I) are in contrast to those obtained in the liquid and solid phases where 30% and 12%, respectively, of the Br^{80} transitions were found to result in reaction.

TABLE I

P_{CCl_4} , mm.	P_{Br_2} , mm.	T , °C.	Total count	% of transitions resulting in reaction
585	150	95	500	0
700	100	180	682	1.3
700	150	180	3860	1.2
700	90	95	1794	1.2
350	90	95	2750	2.0
350	90	95	2360	0.9
350	90	95	2965	1.3

The data given in Table I are for gaseous mixtures of radioactive bromine and carbon tetrachloride which were allowed to stand for at least ninety minutes (five 18-min. half-lives) before extracting and counting. The column labelled "Total count" gives the total count per min. in half of the reaction mixture, after correction for the Br^{82} 34-hour activity. It includes both the free bromine and that which had reacted with the carbon tetrachloride. Since the number of radiations from Br^{80} (4.4 hr.) which affect the counter is negligible the "Total count" is proportional to the concentration of Br^{80} (18 min.).

The last column gives the percentage of the "Total count" which was found in the second half of the reaction mixture after extraction of the free bromine. This activity decayed with an 18-min. half-life and represents the fraction of the Br^{80} transitions which led to reaction with the carbon tetrachloride in the gas phase. These values were obtained after correction for the Br^{80} (18 min.) which reacted with liquid carbon tetrachloride during the two or three minute extraction process.

No significant difference was observed between experiments in which the reaction flask was kept in the dark and those in which it was exposed to the diffuse light of the room or illuminated with a 60-watt lamp.

Concentration Effect in Liquid Phase.—Determinations of the fraction of Br^{80} transitions

leading to reaction of free bromine with carbon tetrachloride in *solutions* varying in concentration from a bromine mole fraction of 0.001 to 0.9 have shown the following relationship, in which N_{CCl_4} and N_{Br_2} represent the mole fractions of the respective components.

$$\text{Fraction of transitions which lead to reaction} = \frac{0.34 N_{\text{CCl}_4}}{1 + N_{\text{Br}_2}}$$

Other Reactions.—Two experiments with dilute solutions of radioactive cinnamic acid dibromide in carbon tetrachloride show that about 50% of the Br^{80} transitions result in the formation of an organic compound of the Br^{80} (18 min.) daughter activity which can be distilled off from the cinnamic acid dibromide with the carbon tetrachloride. This indicates that the daughter activity has split out of one compound and entered into a new one as a result of the transition.

Other experiments show the existence of a transition-activated decomposition of gaseous ethylene dibromide and of liquid ethyl bromide, and of a transition-activated substitution of bromine in mineral oil.

Discussion of Results

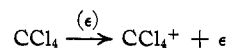
It has been suggested that the reaction of the daughter activity of the Br^{80} transition with liquid and solid carbon tetrachloride is due to the reactivity of the Br^{80} (18 min.) ion formed by the emission of a conversion electron.⁴ This ion may be either Br_2^+ or its dissociation product Br^+ . According to a corollary hypothesis the *decomposition* reactions which have been observed to accompany nuclear isomeric transitions are due to the fact that the loss of a conversion electron from one atom in a molecule leaves the resultant molecular ion in an unstable repulsive state.^{5,6,8}

An hypothesis which assumes a reaction in a single step between the bromine transition product and a normal carbon tetrachloride molecule to form the final organic bromine compound will not satisfactorily account for the fact that bromine which is undergoing transition does not react with carbon tetrachloride in the gas phase nearly as readily as it does in the condensed phases. The facts would be in agreement with such an hypothesis only if the freshly formed daughter activity possessed the ability to react with carbon tetrachloride at the instant of formation but lost this ability in a time interval which was longer than the time between collisions with carbon tetra-

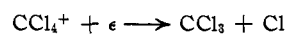
chloride in the liquid but shorter than the time between collisions in the gas.

However, the facts can be explained without such an assumption. The emission of a conversion electron in the formation of a Br^{80} (18 min.) ion leads to a number of processes which produce free radicals in the vicinity of the ion or of the atom which is formed when the ion gains an electron. The chance that one of these radicals will react with the Br^{80} (18 min.) atom from which the conversion electron was lost is large in dilute solutions of bromine in carbon tetrachloride. In the gas however the chance that the fragments will diffuse away from the vicinity of the transition before colliding with the particular bromine atom that has just undergone transition is large. They will eventually form stable molecules by combination with one another or with non-radioactive bromine molecules (less than 1×10^{-12} of the bromine molecules are radioactive). The Br^{80} (18 min.) atom will eventually become part of a halogen molecule (photochemical experiments show that the probability that a normal bromine atom will react with carbon tetrachloride is small).

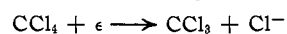
Free radicals may be formed by a variety of processes following the emission of a conversion electron. The conversion electron may ionize carbon tetrachloride molecules in the neighborhood of its path



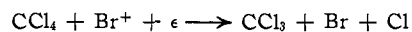
and these ions may then be neutralized with accompanying dissociation



Other possible radical forming reactions include



which is thought to be responsible for the increase in the breakdown potential of gases in the presence of small amounts of carbon tetrachloride, and



in which the energy of neutralization of the bromine ion is removed by the carbon tetrachloride and results in the dissociation of the latter.

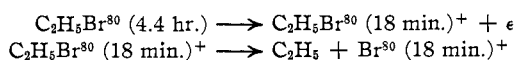
It seems probable that the free radicals formed by the last mentioned process account for the reaction of carbon tetrachloride with Br^{80} (18 min.). These radicals are formed in close proximity to the Br^{80} (18 min.) atoms whereas calculations show that, on the average, the nearest radical formed as the result of the direct action of the conversion electron in liquid or solid carbon tetrachloride is

about 100 Å. from the bromine atom which emitted the electron. The probability that the kinetic energy received by the radical from the neutralization process will carry it away from the vicinity of the Br^{80} (18 min.) atom before reaction occurs is much greater in the gas phase than it is in the liquid, where the reaction partners are held in a common envelope of solvent molecules.

Types of Reactions.—On the basis of the evidence now available reactions accompanying the isomeric transition of Br^{80} , which lead to the separation of the daughter from the parent activity, may be classified tentatively according to three types as follows.

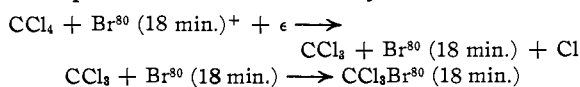
(1) Decomposition reactions which occur because a bromine-containing molecule is left in a repulsive (unstable) ionic state as the result of the loss of a conversion electron by the bromine atom in the molecule. This may lead to the decomposition of the molecular ion into a radical and a Br^{80} (18 min.) ion. Included among the published examples of this type of reaction are the decompositions of bromate ion,² ethylene dibromide³ and other organic bromides.⁵ The loss of Br^{80} (18 min.) by *t*-butyl bromide in water-alcohol solution¹ is probably also a result of this type of reaction.

The type may be illustrated by the case of ethyl bromide



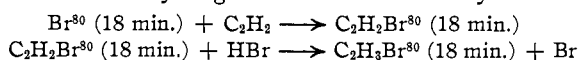
(2) Addition reactions in which a Br^{80} (18 min.) ion formed in a reaction of type (1) acquires an electron and then combines with a free radical. This free radical may be formed from a neighboring molecule by the energy released in the process of neutralization of the bromine ion. Reactions of type (2) will have a much greater probability of occurrence in solution than in the gas phase. The reaction of liquid and solid carbon tetrachloride with elemental radioactive bromine and the reaction of carbon tetrachloride with bromine incorporated in the cinnamic acid dibromide molecule are examples of this type of mechanism.

Steps such as those below may be involved.



(3) Reactions in which a Br^{80} (18 min.) ion formed in a reaction of type (1) acquires an electron and then reacts with a normal molecule rather than with a radical as in type (2). This type of reaction is similar to reactions resulting from the

photochemical production of bromine atoms. It occurs in the gas phase as well as in solution. It is illustrated by the reaction of Br^{80} (18 min.) from radioactive hydrogen bromide with acetylene.⁶



Conversion Coefficient.—In a previous paper⁴ it was pointed out that, if the isomeric transition of bromine was capable of producing chemical reaction only in the case of those transitions where a conversion electron was emitted, there was an inconsistency between Siday's⁹ value of about 0.3 for the conversion coefficient and experimental values as high as 0.9³ for the fraction of the transitions producing reaction. The conversion coefficient must be at least as large as the largest value observed for the fraction of transitions resulting in reaction. Lower observed values for this fraction may result from secondary chemical effects.

Experiments conducted in this Laboratory show: (1) agreement with the value of 0.9 of LeRoux, Lu and Sugden for the fraction of transitions leading to decomposition of ethylene bromide containing aniline; (2) a reaction efficiency of much more than 0.3 for a number of other reactions activated by the bromine transition, including the decomposition of liquid ethyl bromide, the reaction of bromine with mineral oil and the reaction of the bromine of cinnamic acid dibromide with carbon tetrachloride in carbon tetrachloride solution.

No satisfactory explanation for the chemical reaction which accompanies the isomeric transition of bromine is available which does not require the emission of a conversion electron by the atom undergoing transition as a prerequisite to reaction. Since as high as 0.9 of the transitions have been observed to lead to reaction Siday's value of 0.3 for the conversion coefficient must be much too low. Valley has recently been cited¹⁰ as having obtained a value of 0.75. The chemical evidence indicates that the true value must be 0.9 or higher.

The author wishes to express his appreciation to Mr. William Van Horne for the use of the counting apparatus used in this work, to Dr. Joseph O. Hirschfelder for helpful discussions and to the Wisconsin Alumni Research Foundation for the use of the radium-beryllium source.

Summary

1. It has been shown that in the gas phase the isomeric radioactive transition Br^{80} (4.4 hr.) \rightarrow

(9) Siday, *Nature*, **143**, 681 (1939).

(10) Liberatore and Wiig, *J. Chem. Phys.*, **8**, 165 (1940).

Br⁸⁰ (18 min.) results in much less reaction of the daughter activity with carbon tetrachloride than it does in the liquid and solid. These observations lead to the conclusion that the reaction in the condensed phases is due to the reaction of Br⁸⁰ (18 min.) atoms with free radicals which are produced as by-products of the transition process.

2. It is suggested that chemical reactions

which lead to the separation of the daughter activity from the parent activity of the Br⁸⁰ transition may be classified under three types.

3. Chemical evidence indicates that at least 90% of the Br⁸⁰ (4.4 hr.) \rightarrow Br⁸⁰ (18 min.) transitions occur with the emission of a conversion electron rather than a gamma ray.

MADISON, WIS.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Determination of Crystal Densities by the Temperature of Flotation Method. Density and Lattice Constant of Lithium Fluoride

BY CLYDE A. HUTCHISON* AND HERRICK L. JOHNSTON

Submergence in liquids of different density has been employed by mineralogists for many years as a routine method of distinguishing qualitatively between minerals of different specific gravity. The method was made quantitative by Retgers,¹ by the procedure of determining the densities of two close compositions of a binary mixture of organic liquids, in one of which the specimen would rise while in the other it would sink. Retger's method has been employed more recently as one of the relatively accurate methods of crystal density measurement² but has the disadvantage of relative difficulty in securing fine adjustment for close bracketing.

Lewis and MacDonald³ used the temperature change of liquid density in conjunction with crystal "flotations," in a semi-quantitative way, as a densimetric method of determining relative atomic weights. This method is essentially the "free submerged float" method⁴ employed extensively for the isotopic analysis of water. We have found it possible to develop this as a precision method of densimetric analysis which, for lithium fluoride, is capable of giving relative densities to within an error limit of about $\pm 5 \times 10^{-6}$ g./ml. and of giving absolute densities to within an error about 10 times larger. The latter could be somewhat improved upon.

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(1) Retgers, *Z. physik. Chem.*, **3**, 289 (1899).

(2) Spangenberg, *Z. Krist.*, **57**, 497 (1922); Wulf and Heigl, *Z. physik. Chem.*, **A153**, 187 (1931); Kohler, *Z. Physik*, **78**, 375 (1932).

(3) G. N. Lewis and R. T. Macdonald, *THIS JOURNAL*, **58**, 2519 (1936).

(4) G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.*, **1**, 341 (1933).

Experimental

Procedure.—The details of the procedure, and techniques employed, that apply to the relative as well as to the absolute density determinations will be described elsewhere⁵ and will not be elaborated here, except to outline the general steps.

1. Crystals of high purity, physically uniform, were prepared by an adaptation of the method of Kyropoulos⁶ and were carefully annealed. Fragmentation along sharp fault lines occurred at a step prior to the annealing. Clear fragments were produced. Fragments that revealed no blemishes under a magnifying glass were chosen for the flotations.

2. A stable flotation liquid of the proper density, and constancy of density toward evaporation, was prepared by vacuum distillation of bromoform into a mixture of *n*-hexanol and *n*-pentanol. The composition of the final satisfactory mixture was: 115.7 g. of bromoform with 170 drops of hexanol (68 drops equal 1 ml.) and 149 drops of pentanol. This liquid was calibrated against water by hydrostatic weighings to obtain values of its density and of its density-temperature coefficient. Individual densities were reproducible to within about ± 0.00005 g./ml., and 17 points in two series of runs⁵ over a 3° temperature range gave a good straight line with a slope of $-2.49 (\pm 0.01) \times 10^{-3}$ g./ml./degree.

3. Crystal fragments of lithium fluoride prepared from high purity lithium carbonate of supposedly normal isotope composition, were floated submerged in the bromoform mixture. Flotations were carried out in a glass-stoppered tube of about 15 mm. diameter, which was immersed in a small water-bath with transparent windows in the sides. The temperature of the water-bath was controlled manually to within $\pm 0.001^\circ$ and narrow limits of temperature were established that distinguished between the rise and the fall of the crystals. A telescope with crosshair was used in making observations and it was possible to fix the flotation temperature of an individual crystal to within $\pm 0.002^\circ$. Ordinarily it is possible to obtain

(5) H. L. Johnston and C. A. Hutchison, *ibid.*, **8**, Nov. issue (1940).

(6) Kyropoulos, *Z. anorg. Chem.*, **154**, 308 (1926).