[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Some Effects of Temperature, Phase and Nature of Chemical Species on Halogen Atom Reactions Initiated by Radiative Neutron Capture and by Isomeric Transition[1]

BY S. GOLDHABER, R. S. H. CHIANG AND J. E. WILLARD

The organic yield of bromine activated by either radiative neutron capture or isomeric transition in liquid CCl_3Br appears to increase slightly when the temperature is lowered from room temperature to the melting point (−5°), increases abruptly with change from the liquid to the solid phase at the melting point and increases slowly with cooling of the solid phase to −80°. The increase in the organic yield is qualitatively parallel to the increase in density of the medium. The distribution of the organic products of the (n,γ) reaction is about 45% CCl_3Br, 35% CCl_2Br_2, 20% higher boiling compounds at both 25° and −80°. Increases in the organic yield with decrease in temperature and/or change of phase occur for the (n,γ) reaction on bromine in CCl_2Br_2, in CBr_4 and in solutions of Br_2 in CCl_4; and for the (n,γ) reaction on chlorine in CCl_4 and in CCl_2Br_2. Low concentrations of bromine present in CCl_3Br during neutron irradiation decrease the organic yield of Br^{80} while low concentrations of α,β-dibromoethylene increase the yield. The organic yield of iodine activated by the (n,γ) reaction in dilute solutions of iodine in saturated hydrocarbons averages about 35% while that of dilute solutions of ethyl iodide in the same solvents is about 50%.

When a halogen atom captures a neutron to form an isotope of one higher mass it becomes radioactively tagged and at the same time emits one or more gamma rays which may impart to it a recoil energy up to several thousand kcal./mole. This energy causes the atom to split out of its parent compound and is dissipated in one or more collisions with other atoms. The "cooled" atom may then either[2] combine with one of the molecular fragments formed in these collisions or may exist as a thermal atom in the system until it undergoes thermal reaction with a molecule of the medium or sticks to the wall.

When a Br^{80} atom in its higher nuclear energy state Br^{80} (4.4 hr. half-life) undergoes isomeric transition to the lower state Br^{80} (18 min. half-life) the energy is lost in ejecting a K or L electron from the atom (internal conversion) thus leaving a positively charged bromine ion.[3] The positive charge may be increased by several units as the result of emission of Auger electrons instead of X-rays.[4] The conversion electrons from the isomeric transition do not impart sufficient recoil energy to the atom to be chemically significant[5] but the positive bromine ion splits out of its parent compound either because of the chemical instability resulting from loss of its binding electrons or because of coulombic repulsion following distribution of the charge over the whole molecule, or both. Eventually the bromine ion must be neutralized and in the course of this neutralization chemical processes may occur which lead to its entering stable combination with other molecules in the medium.[2a]

Studies of the reactions of the tagged atoms produced by the above processes offer promise of yielding information about energy transfer, charge transfer, "caging"[6] effects of liquid[7,2a,b,c] and solid solvents and relative activation energies for reactions of thermal atoms[2a,e,f] with different types of molecules.

The purpose of the present paper is to report new evidence obtained in an endeavor to answer the following questions: (1) Is the increase in organic combination of bromine activated by the neutron–gamma reaction in the propyl bromides at liquid air temperatures as compared to room temperature[8] a type of phenomenon which occurs for other halogens and other organic compounds? (2) Are such effects due to change in phase or change in temperature or both? (3) Does such an increase occur when activation is by isomeric transition? (4) Does an atom which has undergone isomeric transition in the liquid or solid phase have a greater probability of remaining in the parent cage and combining with its parent partner than of escaping? (5) Is it possible for the reaction resulting in formation of a stable compound from a hot atom to involve fragments from more than one molecule of the medium? (6) Do thermal reactions as well as hot atom reactions contribute to the organic yield of bromine which has undergone radiative neutron capture in CCl_3Br? (7) To what extent can high energy heavy atoms, such as iodine, enter organic combination in pure hydrocarbons where only a small fraction of the total energy can be lost per collision of the billiard ball type?

Experimental

Reagents.—Mallinckrodt "Low Sulfur" carbon tetrachloride; Michigan Chemical Co. bromotrichloromethane and dibromodichloromethane; Eastman Kodak Co. carbon tetrabromide; and Matheson Co. pentane, hexane, heptane, octane and ethyl iodide were used. The bromotrichloromethane and dibromodichloromethane were fractionally distilled through a 12″ Vigreux column to reduce the concentration of oxidation inhibitor present in the commercial material.

The refractive index n^{25}_{D} of the fractionally distilled bromotrichloromethane was determined with the aid of an Abbe refractometer to be 1.5032, and that for dibromodichloromethane to be 1.5496, in agreement with values given in the literature.[9] Mixtures gave values which varied linearly between the values of the two pure components.

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(1) Presented, in major part, before the Division of Physical and Inorganic Chemistry at the April, 1950, Meeting of the American Chemical Society in Detroit.

(2) See for example and for other references: (a) E. G. Bohlmann and J. E. Willard, THIS JOURNAL, **64**, 1342 (1942); (b) W. F. Libby, *ibid.*, **69**, 2523 (1947); (c) J. M. Miller, J. W. Gryder, and R. W. Dodson, *J. Chem. Phys.*, **18**, 579 (1950); (d) R. R. Williams and W. H. Hamill, *ibid.*, **18**, 783 (1950); (e) J. M. Miller and R. W. Dodson, *ibid.*, **18**, 865 (1950); (f) W. H. Hamill, R. R. Williams and H. A. Schwarz, THIS JOURNAL, **72**, 2813 (1950).

(3) (a) W. H. Hamill and J. A. Young, *J. Chem. Phys.*, **17**, 215 (1949); (b) S. Wexler and T. H. Davies, *ibid.*, **18**, 376 (1950).

(4) E. P. Cooper, *Phys. Rev.*, **61**, 1 (1942).

(5) (a) J. E. Willard, THIS JOURNAL, **62**, 256 (1940); (b) G. T. Seaborg, G. Friedlander and J. W. Kennedy, *ibid.*, **62**, 1309 (1940).

(6) J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(7) J. E. Willard, THIS JOURNAL, **62**, 3161 (1940).

(8) (a) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949), (b) M. Fox and W. F. Libby, private communication.

(9) J. R. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **72**, 333 (1950).

The value −21° has been generally used as the melting point of bromotrichloromethane in tables of physical constants.[10] We have been unable to reproduce this value but have repeatedly observed the freezing point to be −5 ± 1°.[9]

All experiments were done in the presence of air and without rigid precautions to exclude moisture since hot atom reactions with compounds of this general type have previously been found to be insensitive to these variables.[5a] Exposure to the light of the laboratory or variations in the time of standing of the solutions did not affect the results under the conditions of these experiments.

Neutron Exposures and Radioactive Species Used.—Br^{80} (4.4 hr.) for use in the isomeric transition experiments was produced by irradiation of potassium bromide in the heavy water pile of the Argonne National Laboratory and also by irradiations with an Sb–Be photoneutron source[11] which produced about 6×10^6 neutrons/sec. Neutron bombardments in the studies of the (n,γ) reaction were made with the Sb–Be source, or with neutrons from an electrostatic generator or a 100 mg. Ra–Be source kindly made available by the Physics Department. For these experiments, samples of about 20 ml. of the liquid or solid to be bombarded were placed in a soft glass or quartz vessel adjacent to the source and surrounded by the thermostating medium (water, mineral oil, dry ice, butyl alcohol or liquid air).

The nuclear species on which measurements were made were Br^{80} (4.4 hr.) in equilibrium with its Br^{80} (18 min.) daughter, Br^{80} (18 min.), Cl^{38} (37 min.) and I^{128} (25 min.). When measurements were being made on the neutron–gamma reaction separated fractions for counting were always allowed to stand long enough for the Br^{80} (4.4 hr.)–Br^{80} (18 min.) equilibrium to be re-established before counts were taken. When significant, appropriate corrections were made for the presence of Br^{82} (35.5 hr.) and for decay of the other species present.

Counting Methods.—Counting was usually done with cylindrical glass Geiger tubes (Technical Associates type TA-Bl-J) having annular jackets which held 10 to 12 cc. of the solution to be counted. The wall thickness between the solution and the sensitive portion of the tube was about 30 mg./cm.^{2}.

The distribution of activity resulting from either isomeric transition or neutron bombardment was determined by extracting the organic reaction mixtures with aqueous sodium sulfite and sodium halide. In some cases elemental halogen was added to the organic liquid before extraction to serve as carrier. Care was taken to determine whether halogen which had been split out of organic combination by the Szilard–Chalmers reaction tended to stick to the walls of the bombardment vessel, and if so to recover it. All counting rates in solutions other than water were corrected for the density and atomic number of the medium by experimentally determined correction factors. For example, in one solution tube the counting rate of Br^{80} (18 min.) in carbon tetrachloride was 89% of that in water and the counting rate of Cl^{38} in carbon tetrachloride was 95% of that in water. These corrections were consistent with those estimated on the basis of a more general survey of such corrections.[12]

The fraction of halogen in the organic form after (n,γ) activation was determined by dividing the counting rate of the organic layer after extraction by the sum of the counting rates of the organic and inorganic layers. In order to determine the organic–inorganic distribution of the Br^{80} (18 min.) produced by the isomeric transition, the extracted phase containing the Br^{80} (4.4 hr.) parent was allowed to stand until the daughter had grown back to equilibrium. From the counting rate then observed the total equilibrium counting rate at the time of extraction was calculated. The counting rate of the phase containing the separated Br^{80} (18 min.) daughter, also corrected to the time of extraction, was divided by the total counting rate to determine the fractional separation produced by the transition. (The radiations from Br^{80} (4.4 hr.) give negligible contribution to the counting rate under the counting conditions used.)

Many of the results reported are the average of two or more determinations. These usually checked within a few per cent. Except for those experiments where dilute solutions of the bromine-containing compound were used the standard deviation of the actual counting measurements was less than 3%.

Preparation of CCl_3Br^{80} (4.4 hr.) and CBr_3Br^{80} (4.4 hr.).—Bromotrichloromethane labeled with Br^{80} (4.4 hr.) for isomeric transition studies was prepared by the photochemical exchange of $BrBr^{80}$ (4.4 hr.) with liquid bromotrichloromethane. Following illumination the free bromine was washed out, and the bromotrichloromethane was dried over phosphorus pentoxide and distilled before use. The elemental bromine was obtained by oxidizing KBr^{80}.

Carbon tetrabromide labeled with Br^{80} (4.4 hr.) was prepared by irradiating solid carbon tetrabromide with neutrons and subsequently purifying it by recrystallization from carbon tetrachloride.

Fractionation of Organic Products of (n,γ) Reaction.—In order to determine the fraction of the organically bound radiobromine from the neutron bombardment of CCl_3Br which was present as CCl_3Br, as CCl_2Br_2 and as higher boiling compounds 12 ml. of the bombarded CCl_3Br was distilled together with 12 ml. of CCl_2Br_2 through a 14″ Vigreux column in a nitrogen atmosphere. Successive 2-ml. fractions of the distillate were diluted with carbon tetrachloride and counted. The composition of each fraction was determined from its refractive index.

Density of CCl_3Br as a Function of Temperature.—A semiquantitative determination of the variation in density of bromotrichloromethane with temperature from 21 to −29° was made with a Pyrex dilatometer consisting of an 11-ml. bulb attached to 0.7 mm. i.d. capillary tubing (Table I). A known amount of bromotrichloromethane was placed in the instrument together with an immiscible calcium chloride solution with a melting point of −35° and known coefficient of expansion. The change in density of the bromotrichloromethane at temperatures both above and below its melting point were calculated from the observed changes in the height the meniscus of the calcium chloride solution. A value of 1.99 g./ml. at 25° has been reported.[13]

Table I

Density of Bromotrichloromethane as a Function of Temperature

Temp. °C.	25.0	21.0	18.0	10.5	1.0
Density, g./ml.	1.99805[a]	2.0370	2.0556	2.1015	2.1771
Temp. °C.	−4.0	−13.0	−16.0	−29.0	
Density, g./ml.	2.1922	2.3578	2.3709	2.3772	

[a] Accurate pycnometer value, values at other temperatures determined less accurately with the dilatometer.

Results and Discussion

Effects of Changes in Phase and Temperature on Distribution of Activity between Organic and Inorganic Forms.—Effects of changes in temperature and/or phase on the distribution of activity between organic and inorganic forms in seven hot atom reactions are shown in Table II and some of these data are plotted in Fig. 1.

Organic combination of the activity from both the (n, γ) and isomeric transition reactions of the bromine in bromotrichloromethane and also from the (n, γ) reaction of chlorine in carbon tetrachloride seems to increase slightly with decreasing temperature from room temperature to the freezing point, increases abruptly as a result of the change from liquid to solid at the freezing point, and increases with further cooling of the solid phase to −80° but shows little or no further increase below −80° (Fig. 1). A similar increase occurs for the (n, γ) reaction on both chlorine and bromine in dibromodichloromethane as a result of decrease in temperature or change in phase or both (Table II).

These data may be rationalized qualitatively in terms of a mechanism which assumes that atoms

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[10] "International Critical Tables," Vol. 1, 1926, p. 176.

[11] U. S. Atomic Energy Commission Isotopes Catalogue No. 3, page 29.

[12] R. S. H. Chiang and J. E. Willard, *Science*, **112**, 81 (1950).

[13] N. Davidson and J. H. Sullivan, *J. Chem. Phys.*, **17**, 179 (1949).

TABLE II

A. ORGANIC YIELD OF (n,γ) HALOGEN IN THE LIQUID AND SOLID PHASES OF CCl_3Br, CCl_2Br_2, CBr_4 AND CCl_4

	CCl_3Br	CCl_2Br_2		CBr_4	CCl_4	$CCl_4 + Br_2$[a]
F.p., °C.	−5	22		90	−23	−23
Element measured	Br	Cl[b]	Br	Br	Cl	Br
Organic yield in liquid state, %	40 (25°)				43 (30°)	
	44 (−3°)	51 (50°)	40 (32°)	*ca.* 88 (100°)	44 (0°)	27 (25°)
Organic yield in solid state, %	58 (−6°)			93 (85°)	51 (−37°)	
	75 (−80°)	81 (−80°)	75 (0°)	93 (25°)	75 (−80°)	*ca.* 50 (−190°)
	72 (−190°)					

B. ORGANIC YIELD OF ISOMERIC TRANSITION BROMINE IN CCl_3Br

Temperature, °C.	25	0	−8	−80	−190
Organic yield, %	54	63	70	86	87

[a] 1 mole % Br_2 in CCl_4. [b] Values for the retention of Cl in CCl_2Br_2 are minimum values due to the Br^{80} gamma rays which penetrated the 900 mg./cm.^{2} counter wall which was used to cut out Br^{80} beta particles while allowing some of the 5 Mev. beta particles of Cl^{38} to count.

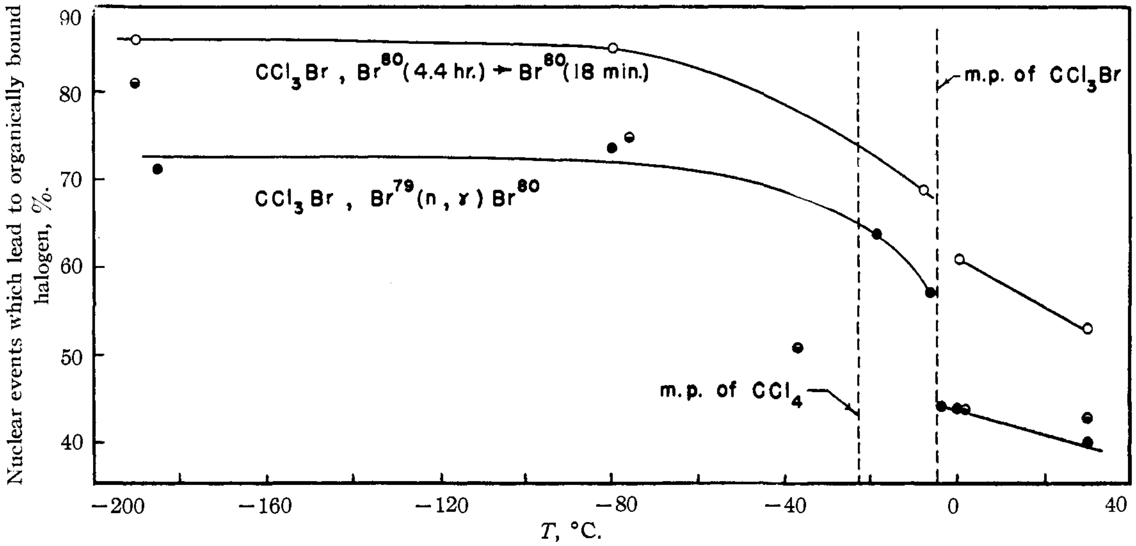

Fig. 1.—Effect of phase and temperature on the organic yield of reactions of halogens initiated by radiative neutron capture and by isomeric transition: ○, I. T. reaction of the bromine in CCl_3Br; ●, (n,γ) reaction of the bromine in CCl_3Br; ◒, (n,γ) reaction of the chlorine in CCl_4.

with kinetic energy from the (n, γ) process have a considerable chance of being reduced to energies in the thermal range by a collision which knocks a halogen atom out of an organic molecule and out of the surrounding solvent cage leaving the impinging atom in the cage with the remaining free radical. If the cage is sufficiently effective the cooled hot atom will produce a stable compound with the radical, the excess energy being taken up by the molecules in the cage wall. If this is the true picture it means, as has been suggested,[8] that the various cages are not completely effective at room temperature for all energies of atoms and radicals to be caged but become more so as the temperature is lowered. Such an increase in caging effect might result from a decrease in free space between the molecules (an increase in density), from a change in molecular aggregation, or from a combination of these. Bromotrichloromethane undergoes significant density changes over the range of temperature where the changes in retention recorded in Fig. 1 occur (Table I) and the density may, therefore, be an important factor in determining the efficiency of the cage.

The fact that isomeric transition of CCl_3Br^{80} in bromotrichloromethane produces a higher organic yield in the solid state than the liquid suggests the hypothesis that there is a considerable probability that the Br^{80} (18 min.) atom can combine with the radical with which it was associated before transition, and that this probability is favored by the stronger cages of the solid system. This hypothesis is also favored by other observations which are currently being extended in our laboratory.

The very high organic yield of (n, γ) bromine in both solid and liquid carbon tetrabromide (Table I) is quite probably associated with the chemical reactivity of this compound and its ease of exchange with bromine.[14]

Effect of Changes in Phase and Temperature on the Nature of the Organic Products of the (n,γ) Reaction.—In light of the discovery[8] that the chemical form of the organic bromine resulting from the (n, γ) reaction in the propyl bromides may be affected by change in temperature and/or phase, it was of interest to determine whether a similar effect occurs in the relatively simple com-

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(14) (a) J. H. Hodges and A. S. Miceli, *J. Chem. Phys.*, **9**, 725 (1941); (b) L. B. Seely, Jr., and J. E. Willard, THIS JOURNAL, **69**, 2061 (1947).

pound bromotrichloromethane where all of the substituent atoms on the carbon are of more nearly equal weight than in the case of the propyl bromides. The data of Table III indicate that the relative amounts of different organic products formed from the (n, γ) bromine of bromotrichloromethane at −80° are about the same as at 25° although the organic yield is much higher.

TABLE III

EFFECT OF CHANGE OF PHASE AND TEMPERATURE OF CCl_3Br ON THE FRACTION OF (n,γ) BROMINE WHICH FORMS MONOBROMO, DIBROMO AND HIGHER BOILING SUBSTITUTION PRODUCTS

Chemical form	(n,γ) bromine, %	
	25°	−80°
CCl_3Br	18	32
CCl_2Br_2	13	28
Higher boiling	8	15

It is not possible on the basis of the data thus far available to picture with certainty the molecular events which lead to such a distribution of products although plausible rationalizations are possible. In this connection it is interesting to note that the energy lost by a hot bromine atom in a billiard ball collision with a chlorine atom is always 0.86 as much as the energy which would be lost in a similar collision at the same angle with a bromine atom.

The fact that a significant fraction of the retained activity (Table III) is present as a higher boiling compound than CCl_2Br_2 (therefore, containing either at least three bromine atoms or two carbon atoms) indicates that *many of the processes must be more complicated* than the simple billiard ball type. The hot atom must be able to break bonds in two or more adjacent bromotrichloromethane molecules at one time or the molecule which it forms by replacement of a chlorine atom must be activated in such a way that it can exchange a chlorine atom for a bromine atom of an adjacent molecule. The former possibility seems more probable than the latter. It seems not improbable that in some cases there may be a "brush heap" of fragments consisting of several halogen atoms and two or more radicals in close proximity.

Distinction between Hot Atom and Thermal Processes of (n,γ) Bromine in CCl_3Br.—The organic yield of the (n, γ) reaction on the bromine in pure liquid bromotrichloromethane at room temperature is about 40% (Table II). Current work in our laboratory indicates that this yield is decreased by the presence of molecular bromine and increased by α,β-dibromoethylene[2f] even when the concentrations of these reagents are too low to make them significant as targets for the *hot* atoms. The results suggest that perhaps 20% or more of the atoms from the (n, γ) reaction enter stable combination by thermal rather than hot atom processes.

One mechanism by which tracer concentrations of thermal bromine atoms might enter organic combination with bromotrichloromethane would be a reaction of the type $CCl_3Br + Br^* \rightarrow CCl_3 + Br^*Br$ followed, with a certain probability, by reaction of the radical with the molecule before the two escape from the cage ($CCl_3 + Br^*Br \rightarrow CCl_3Br^* + Br$). Such a process, as written, may lead to a permanent stabilization of the tagged atom in organic combination whereas if the bromine molecule escapes from the vicinity of the radical the tagged atom is stabilized in inorganic form. The activation energy for the reaction $Br + CCl_3Br \rightarrow CCl_3 + Br_2$ is about 9 kcal./mole.[15] It is probable that reaction of bromine atoms by an inversion type of mechanism ($Br^* + CCl_3Br \rightarrow CCl_3Br^* + Br$) is relatively unimportant,[15a,c] if it occurs at all. The exchange reaction $Br^* + Br_2 \rightarrow BrBr^* + Br$ probably has an activation energy of about 4 kcal./mole or less, by analogy with the similar reaction of iodine,[16] and, therefore, would be expected to fix all thermal tagged atoms in the form of elemental bromine before they react with bromotrichloromethane. The organic yield would be expected to be higher when α,β-dibromoethylene is added than when it is not because the olefin can react with thermal atoms which would otherwise have entered inorganic combination as well as with those which would have entered organic combination.

Another mechanism which may account for part or all of the distribution of thermalized atoms between the organic and inorganic forms is reaction with organic and inorganic radicals produced in the medium by the hot atoms and other radiations. Small amounts of added bromine would reduce the concentration of such organic radicals and also compete with them for reaction with the active bromine atom, while added dibromoethylene would compete with the inorganic radicals (atoms) for the active atom.

Preliminary Results on Reaction of (n,γ) Iodine with Hydrocarbons.—It has been reported[17,8] that 31 to 38% of the halogen activated by the (n, γ) process in dilute solutions of elemental iodine or bromine in pentane appears as the amyl halide. Current work in our laboratory has shown similar gross organic yields for the (n, γ) reaction on iodine dissolved in several hydrocarbons and still higher yields (*ca.* 50%) for dilute (<0.3 mole %) ethyl iodide in hydrocarbons. These results are of particular interest in the elucidation of hot atom processes because it may be estimated that an iodine atom can transfer only about 3% of its energy to a hydrogen atom in a head-on collision. Therefore, if it strikes the hydrogen atom with sufficient energy to break the carbon–hydrogen bond it must retain about 3000 kcal./mole of energy after the collision and would, therefore, be expected to escape from the cage containing the residual radical in every instance. Thermal reaction of iodine atoms with carbon–hydrogen bonds at room temperature appears to be precluded by activation energy considerations. It seems probable, therefore, that the organically bound iodine observed must be due to the combination of the I^{128} with reactive organic fragments formed by

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(15) (a) N. Davidson and J. H. Sullivan, *J. Chem. Phys.*, **17**, 176 (1949); (b) A. A. Miller and J. E. Willard, *ibid.*, **17**, 168 (1949); (c) A. A. Miller, Ph.D. thesis, University of Wisconsin, 1949.

(16) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

(17) A. F. Reid, *Phys. Rev.*, **69**, 530 (1946).

collisions of the hot iodine atoms with molecules as a whole[8] or with radicals produced by the neutrons, beta rays and gamma rays in the system. It is to be expected that a variety of fragments would be formed by such a process and that by careful fractionation experiments the organically bound iodine might be found to be in several different compounds rather than as a single organic iodide.

Although the elemental iodine solutions used in our tests were in all cases at a concentration below the solubilities reported in the literature,[18] a slowly forming iodine-like deposit was observed on the walls of the bombardment tube in a majority of the cases. If, as this might indicate, the iodine actually is present as much larger aggregates than I_2, it would be expected that there would be a high probability that the hot atoms from the (n, γ) process would lose their energy to atoms in the parent aggregate before escaping into the hydrocarbon medium. This may possibly account for the lower organic yield when iodine is used as the solute than when ethyl iodide is used. A perhaps more probable explanation is that elemental iodine both reduces the concentration of organic radicals in the system and exchanges with thermalized hot atoms to fix them in inorganic combination.

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[18] (a) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, **42**, 2180 (1920); (b) W. Jaok, *Rocz. Chem.*, **6**, 501 (1926); (c) G. R. Negishi, L. H. Donnally and J. H. Hildebrand, THIS JOURNAL, **55**, 4793 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

Reactions of 2,4-Dinitrobenzeneselenenyl Bromide with Alcohols and Amines[1]

BY WENDELL S. COOK AND ROBERT A. DONIA[2]

2,4-Dinitrobenzeneselenenyl bromide was condensed with a series of alcohols in the presence of silver acetate to form alkyl 2,4-dinitrobenzeneselenenates. The aromatic amines, aniline, *p*-bromoaniline and *p*-toluidine reacted with the bromide giving N-aryl 2,4-dinitrobenzeneselenenamides whereas 1- and 2-naphthylamine formed aminonaphthyl 2,4-dinitrophenyl selenides.

The recent interest in sulfenic acid derivatives, particularly the reactions of nitrobenzenesulfenyl halides,[3] and the enhanced stability of selenenic acids and derivatives over that of the corresponding sulfenic acid type suggested the present study of 2,4-dinitrobenzeneselenenyl (hereafter abbreviated as DNBSe) bromide.

The principal investigators of selenenic acids have been Behaghel and co-workers[4] who isolated 2-nitrobenzene, 2,4-dinitrobenzene-, and 1-anthraquinoneselenenic acids; they also used corresponding selenenyl halides in the synthesis of selenenyl acetates, cyanides, selenenamides and diaryl selenides. Recently, Foss[5] prepared selenothio compounds by reaction of 2-nitrobenzeneselenenyl bromide with potassium salts of several thio acids and Rheinboldt and Giesbrecht[6] studied the preparation and properties of aromatic selenenyl selenocyanates. We have found that 2,4-DNBSe bromide reacts readily with alcohols to produce alkyl 2,4-dinitrobenzeneselenenates; likewise, aniline, *p*-bromoaniline and *p*-toluidine condense with the bromide, giving the corresponding N-aryl selenenamides. However, 1- and 2-naphthylamines form diaryl selenides instead of selenenamides.

Reaction of 2,4-DNBSe Bromide with Alcohols.—Selenenic acids are amphoteric and esterification with either an acid [reaction (a)] or an alcohol (b) is anticipated; for example

$$C_6H_5SeOH + CH_3COOH \longrightarrow C_6H_5SeOOCCH_3 \text{ (benzeneselenenyl acetate)} \quad \text{(a)}$$

$$C_6H_5SeOH + CH_3OH \longrightarrow C_6H_5SeOCH_3 \text{ (methyl benzeneselenenate)} \quad \text{(b)}$$

Behaghel and Müller[4d] reported the formation of aryl selenenyl acetates as shown in (c) and (d)

$$ArSeBr + CH_3COOAg \xrightarrow{CH_3OH} ArSeOOCCH_3 + AgBr \quad \text{(c)}$$

(Ar = 2-nitrophenyl, 4-nitrophenyl and 2,4-dinitrophenyl)

$$1\text{-}C_{14}H_7O_2Se(OH) \text{ (or Br)} + CH_3COOAg \xrightarrow{CH_3COOH} 1\text{-}C_{14}H_7O_2SeOOCH_3 + AgBr \quad \text{(d)}$$

($1\text{-}C_{14}H_7O_2$ = 1-anthraquinonyl)

Selenenate esters (b) could not be prepared according to these investigators for they observed that treatment of 2-nitrobenzeneselenenyl bromide with sodium ethylate produced a mixture of the diselenide, selenenic acid and perhaps some selenophenol. Furthermore, in the sulfenic acid series, direct esterification with an alcohol has been successful only with 1-anthraquinonesulfenic acid or chloride.[7]

In repeating the work of Behaghel and Müller[4d] on reaction (c) using 2,4-DNBSe bromide, we

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[1] From the thesis of W. S. Cook in partial fulfillment of the requirements for the M.S. degree, December, 1948.

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