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Effect of Density in the Region of the Critical Temperature on the Chemical Products of the $Br^{79}(n,\gamma)Br^{80}$ Reaction on Bromotrifluoromethane[1]

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The fraction of the bromine activated by the (n,γ) nuclear process in homogeneous mixtures of CF_3Br and one mole% Br_2 which becomes stabilized as CF_3Br, appears to increase linearly from about 1 to 12% with increase in density from 0.007 to 1.4 g./cc. There is no discontinuity in this yield at the critical temperature. In the absence of elemental bromine the yield is higher and less reproducible. The yield from solid CF_3Br at −183° is about 66%. Bromotrifluoromethane does not show detectable exchange of bromine with Br_2 when illuminated with a 1000-watt lamp for 1 hr. at 100°. The molar volumes of CF_3Br have been determined at a series of temperatures.

Introduction

When the halogen atom in an organic halide molecule undergoes radiative neutron capture the carbon–halogen bond is nearly always broken.[2–7] Thus, for example, less than 1% of the Br^{80m} (4.4 hr.) produced by the Br^{79} $(n, \gamma)Br^{80m}$ reaction on ethyl bromide gas at low pressure is retained in organic combination.[2] The rupture results from the recoil energy of several thousand kcal./mole which the halogen atom acquires as a result of emission of a high energy γ-ray or rays.[8] Since the recoil atoms in gaseous organic bromides do not in general react to re-enter organic combination they must attack the parent molecules to form HBr or Br_2 or must stick to the walls of the vessel.

When liquid instead of gaseous organic halides are irradiated with neutrons a considerable fraction of the recoil halogen atoms always becomes stabilized in organic combination. In most of the alkyl chlorides the fraction is 21%,[7] in ethyl bromide 32%,[9] in primary iodides 41%.[10] This "organic yield" is due to a re-entry into organic combination by the recoil atoms after they have spent their high energy in collisions with the medium. The various processes by which such reëntry may occur have been enumerated earlier.[9] Since they take place in the liquid phase and not in the gas phase it seems probable that they involve a combination of the radioactively-tagged recoil atom with a radical which it has formed in losing its recoil energy (or in losing the positive charge acquired as a result of internal conversion of some of the neutron capture energy). In the gas phase the tagged atom has a high probability of diffusing away from the radicals which it has formed, while in the liquid the probability of such escape is much decreased.

When solid alkyl halides are irradiated with neutrons organic yields which are much higher than observed in the liquid are obtained in some cases,[7,10–13] while in others there is little or no change[9,10] as a result of the phase change, even though a large density change occurs.

The observations cited raise important questions as to the detailed steps by which highly energetic atoms lose energy in condensed media. One of the complicating features in interpretation of the data is the fact that the density changes thus far used in attempts to correlate organic yield with density have been accompanied by either a phase change or a temperature change or both. The primary purpose of the present work has been to determine the organic yield from an alkyl halide as a function of density without crystallizing the system or making large changes in the temperature. In order to do this, experiments have been carried out above the critical temperature of the compound studied, and it has been of added interest to determine whether any discontinuity in organic yield occurs at the critical point. We have chosen bromotrifluoromethane as the compound for this study because its low critical temperature (67°) may be exceeded without thermal decomposition or thermal isotope exchange with inorganic bromine compounds, and because its critical pressure is sufficiently low (32.5 atm.) so that it can be contained in easily fabricated quartz tubes which are transparent to neutrons. Its boiling point at atmospheric pressure is −58°.

Properties of Bromotrifluoromethane

Absence of Thermal and Photochemical Exchange between CF_3Br and Br_2.—Pyrex tubes containing 7.5 cc. of gaseous bromotrifluoromethane and radioactively tagged bromine, at pressures in the range of 0.5 to 2 atm., were analyzed for radioactivity in organic form following heating and illumination. Less than 10^{-4} of equilibrium exchange was induced by heating for one hour at 100° while illuminating at the same time with a 1000-watt projection lamp at a distance of 15″.

Pressure–Volume–Temperature Properties.—The only published values of the density of liquid bromotrifluoromethane of which we are aware are 1.94 g./cc. at −54° and 1.78 g./cc. at −18°.[14] We have obtained additional data as follows. A sealed glass tube containing degassed liquid bromotrifluoromethane was slowly frozen, by gradually

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(1) Based in part on the Ph.D. thesis of W. E. Rice, University of Wisconsin, 1952.

(2) S. Wexler and T. H. Davies, *J. Chem. Phys.*, **20**, 1688 (1952).

(3) W. F. Libby, *Science*, **93**, 283 (1941).

(4) H. Suess, *Z. physik. Chem.*, **B45**, 297 (1939).

(5) R. R. Williams, Jr., and W. H. Hamill, *J. Chem. Phys.*, **18**, 783 (1950).

(6) W. H. Hamill and J. A. Young, *ibid.*, **20**, 888 (1952).

(7) J. C. W. Chien and J. E. Willard, THIS JOURNAL, **75**, 6160 (1953).

(8) For further discussion and references see: J. E. Willard, "Ann. Rev. Nuclear Sci.," Vol. III, in press.

(9) S. Goldhaber and J. E. Willard, THIS JOURNAL, **74**, 318 (1952).

(10) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

(11) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949).

(12) M. S. Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

(13) S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951).

(14) Minnesota Mining and Manufacturing Co., private communication quoting *Fire Engineering*, 357 (May 1950).

TABLE I

VAPOR PRESSURES AND MOLAR VOLUMES OF LIQUID CF_3Br

A

T, °C.	34.9	63.8	64.2	64.2	65.0	65.9	65.9	66.4
P, atm.	19.6	31.1	31.3	31.3	31.7	32.1	32.1	32.3
Mol. vol., l.	0.103	0.143	0.142	0.142	0.320	0.292	0.304	0.303

B

T, °C.	63.9	62.1	60.2	57.7	53.9	51.6	48.6	39.3	30.0	20.7
P, atm.	31.1	30.3	29.4	28.7	26.8	25.8	24.6	21.0	17.8	14.6
Mol. vol., l.	0.143	0.138	0.131	0.127	0.120	0.118	0.113	0.106	0.095	0.0947
T, °C.	12.1	4.0	−1.5	−11.1	−20.7	−35.3	−50.8	−62.2	−74.9	
P, atm.	11.9	9.6	8.2	6.1	4.4	2.6	1.361	0.8126	0.4056	
Mol. vol., l.	0.0911	0.0877	0.0862	0.0831	0.0809	0.0768	0.0739	0.0715	0.0694	

lowering it into liquid oxygen. From the height of the solid, the dimensions of the tube and the mass of bromotrifluoromethane a density of 2.68 g./cc. for −183° was computed. In this and similar experiments described below the mass of CF_3Br was determined by weighing the sealed tube, then breaking it, allowing the contents to escape and weighing the fragments.

From the height of the liquid CF_3Br in a sealed tube just as the last bit of solid melted the density at the melting point (−166°) was estimated as 2.27 g./cc. At the temperatures of both of the above tests the mass of gas in the vapor phase was negligible.

In order to determine the density of the liquid at temperatures where the density of the vapor is significant two methods were used. One was to heat sealed tubes containing a liquid and gas phase to the temperature where the liquid had expanded to completely fill the tube. After this temperature had been observed the mass of CF_3Br and the volume of the tube were determined. The data so obtained together with the pressures are given in Table IA. The vapor pressures of CF_3Br from −117 to −55° are given by the equation[15]

$$\log_{10} P(\text{mm.}) = 16.0750 - 1250.75/T(°\text{K.}) - 3.1651 \log T$$

From a graph[16] extending from −50 to +30° and extrapolated to 67° the vapor pressures were obtained from −50 to +67°.[16] They are given by the equation

$$\log_{10} P_{\text{mm}} = -845/T + 6.877$$

The second method of determining the liquid densities was to measure the height (and hence the volume) of the liquid in a sealed tube at various temperatures. The mass was computed by subtracting the mass of the vapor from the total CF_3Br in the tube. The mass of the vapor was determined by using the vapor densities from a chart of corresponding states[17] employing the reported vapor pressures.[16] The molar volumes obtained by this method are given in Table IB.

Experimental Methods

Bromotrifluoromethane from a tank obtained from the New Products Division of the Minnesota Mining and Manufacturing Co. was passed through a tube containing P_2O_5 on glass wool into a vacuum system where it was frozen out in a quartz sample tube and degassed by a series of cycles of freezing, evacuating and thawing. The height of liquid CF_3Br in the tube of known bore was measured just as the last bit of solid melted (density *ca.* 2.27), and from the amount of CF_3Br found in this manner there was calculated the volume of bromine needed to prepare a one mole % solution. This amount of bromine was micropipetted and frozen in the bottom of a glass tube fitted with a ground glass joint which could be attached to a branch of the vacuum system containing the CF_3Br. The bromine was degassed and distilled into the CF_3Br to serve as "scavenger"[9,10] during the neutron irradiation. The irradiation tube was then sealed off from the system. These quartz tubes which were 6 mm. inside diameter with a wall thickness of 2 mm. proved very dependable in holding pressure as high as 35 atm. but failed in two instances out of several attempts to hold a pressure of 70 atm.

Neutron irradiations were carried out with an antimony-beryllium photoneutron source (5×10^6 neutrons/sec.) in an oil-bath controlled to within half a degree of the nominal temperature. For irradiations below room temperature, sample and source were placed in a dewar flask containing the cooling medium (Dry Ice–acetone or liquid air). Irradiations were also made of gaseous CF_3Br at 30° and one atmosphere in the thermal column of the CP3′ pile at the Argonne National Laboratory.

After irradiation, the neutron-bombarded sample tube was cooled in liquid air and the top cut off. In those cases where bromine had not been added for scavenger purposes prior to irradiation, a microliter or two of carrier bromine was added to the tube at this point. With the contents still frozen, the open end was inserted into a larger glass tube opening into a vacuum system and cemented into place with beeswax–rosin. After degassing, the system was shut off from the vacuum pump, and the sample allowed to warm up and partially vaporize. The vapors passed from the sample tube through a train of freshly reduced copper wire, which removed the elemental bromine, and into the remainder of the system which contained a manometer and the annular jacket of a cylindrical thin-walled glass Geiger tube. When the pressure rose to one atmosphere the stopcock to the counting tube jacket was closed and the remainder of the CF_3Br–Br_2 sample was passed through the copper into a liquid air trap.

Concentrated ammonium hydroxide was used to wash the inorganic radioactive bromine compounds from the copper and from all glass, quartz and wax surfaces which came into contact with the sample before the latter had passed through the copper. Rigorous tests with other reagents showed that the ammonium hydroxide gave complete removal of the activity.

Each of the ammoniacal solutions obtained in the analysis of the samples was diluted to 25 ml., and counted in the annular jacket of a solution-type Geiger tube. At least two hours was allowed to elapse after the distillation through copper before counting in order to ensure that Br^{80m} (4.4 hr.) and its daughter Br^{80} (18 min.) would be essentially in equilibrium.

After a similar wait of two hours, the CF_3Br gas was counted by means of the Geiger tube into which it was condensed after passage through the copper extraction train. Five 30-minute counts were usually made and the back-

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[15] A. A. Banks, H. J. Emeleus, R. N. Hazeldine and V. Kerrigan, *J. Chem. Soc.*, 2188 (1948).

[16] Furnished by courtesy of the Minnesota Mining and Manufacturing Co.

[17] O. A. Hougen and K. M. Watson, "Chemical Process Principles," John Wiley and Sons, Inc, New York, N. Y., 1947.

ground with the clean empty tube was determined for a similar length of time. The standard deviation of the organic yield due to the statistical error of counting was usually less than 5% of the value of the yield, the counting rate of the sample being at least 20 c./min. and that of the background 20 c./min.

The Br^{80} (18 min.) atoms which were born by isomeric transition from CF_3Br^{80m} (4.4 hr.) during the two-hour standing period in the annulus of the Geiger tube prior to counting stuck to the walls of the tube in proportions varying from 0 to 100% in the different runs. This was demonstrated by observing the counting rate of the tube after withdrawing the CF_3Br and flushing several times with air. Since the observed counting rate is essentially all due to the beta particles from Br^{80} (18 min.) and since the average counting "geometry" is different for atoms distributed over the walls of the annulus than for atoms in the gas a correction was made for this effect on the basis of the calculated counting geometry and the fraction of the activity observed on the walls. In no case was this correction enough to alter the calculated value of the organic yield by more than 7% of its value without the correction. The counting rates were also corrected for decay and for the experimentally determined difference in counting efficiencies in the gas and solution counters. This included allowance for the small amount of Br^{82} (36 hr.) present and the fact that the ratio of its counting efficiencies in the two counters is different from that of Br^{80}. It was assumed that the organic yield of Br^{82} is the same as that of Br^{80}.

Results

Organic Yield in the Presence of Scavenger.—Eight determinations were made of the organic yield of the (n, γ) reaction on bromotrifluoromethane containing 0.5 or 1 mole % added bromine as "scavenger"[9,10] to prevent organic combination by "thermal" processes. These covered a density range from 0.0068 g./cc. (1 atm. pressure) to 1.398 g./cc. and a temperature range of 30 to 71°, four of the irradiations being done above the critical temperature of the bromotrifluoromethane. The results are given in Table II and plotted as the solid circles of Fig. 1. They are consistent with the conclusion that there is a linear increase in organic yield as a function of density over the range covered and that there is no discontinuity in yield at the critical temperature.

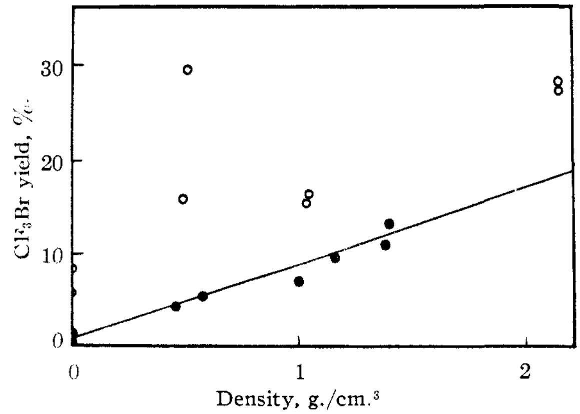

Fig. 1.—Yield of CF_3Br^{80} from the $Br^{79}(n,\gamma)Br^{80}$ process in CF_3Br. Solid circles are for experiments with Br_2 scavenger present during irradiation. Open circles are for experiments with little or no scavenger. Detailed conditions are given in Tables II and III.

TABLE II

ORGANIC YIELD OF (n, γ) PROCESS ON BROMINE OF CF_3Br AS A FUNCTION OF DENSITY IN THE PRESENCE OF Br_2

Mole % Br_2	Density, g./cc.	T, °C.	Org. yield, %[a]
0.5	0.00680	*ca.* 30	0.3
0.5	.00680	*ca.* 30	1.2
1.0	.467	70[b]	4.2
1.0	.579	71[b]	5.3
1.0	1.001	70[b]	7.0
1.0	1.159	71[b]	9.9
1.0	1.391	44	11.2
1.0	1.398	44	13.3

[a] Fraction of (n, γ) events for which the radioactive bromine atom is chemically stabilized as CF_3Br. [b] Above critical temperature.

TABLE III

ORGANIC YIELD OF (n, γ) PROCESS ON BROMINE OF CF_3 Br AS A FUNCTION OF DENSITY IN THE ABSENCE OF Br_2

Density, g./cc.	T, °C.	Org. yield, %
0.00680	*ca.* 30	5.8
.00680	*ca.* 30	8.5
.4916	76[a]	15.8
.5104	71[a]	29.8
1.041	71[a]	15.6
1.048	71[a]	16.6
2.145	−75	27.7[b]
2.145	−75	28.8[b]
2.145	−75	35
2.68	−183	64.1

[a] Above critical temperature. [b] Contained approximately 0.3 mole % dissolved Br_2.

The organic yields reported in Tables II and III and Fig. 1 represent the fraction of the $Br^{79}(n, \gamma)Br^{80m}$ and $Br^{81}(n, \gamma)Br^{82}$ events which led to the product atom being bound as CF_3Br. Less volatile molecules such as CF_2Br_2, if formed, would have tended to remain behind in the liquid phase during the partial vaporization of the irradiated sample which was used to fill the Geiger tube annulus with gas for counting.

In all of the experiments at 30° and above recorded in Tables II and III the reaction tubes contained only a single phase at the temperature of irradiation. The variation in temperature was dictated by experimental expediency. This resulted from the fact that it was necessary to irradiate the 0.0068 g./cc. tubes in the Argonne pile (where use of elevated temperature was inconvenient) in order to obtain sufficient activity, and from the fact that the quartz tubing available for use with the samples of 1.39 g./cc. was prone to fracture under the pressure attained at 70°. Since the chemical processes being observed result from the high energy of the recoil atoms they may be expected to have zero activation energy. Likewise, effects of temperature on the nature of the molecular aggregates in the medium are probably small for the 40° temperature range used, compared to effects due to the changes in density.

Organic Yield in the Absence of Scavenger.—By contrast with the experiments of Table II, in which 0.5 or 1 mole % of elemental bromine was present, experiments with no added bromine showed high and variable results as indicated by the data of Table III. This is probably because recoil bromine atoms which are cooled to thermal energy without entering stable combination are free to diffuse in the system until they encounter something with which they can react with low activation energy. This may be an impurity, a radical or the walls. Variations from tube to tube and irradiation to irradiation in the availability of these reaction paths can account for the variable organic yield in the absence of added bromine. In the presence of bromine the exchange reaction $Br^* + Br_2 \rightarrow BrBr^* + Br$ competes effectively with all reactions of the recoil atom except those which occur by "high energy processes," *i.e.*, before the atom has had a chance to diffuse in the system as a thermal atom. It has previously been shown that in the case of ethyl bromide[9] and the alkyl iodides[10] 1 mole % of free halogen is enough to compete effectively with thermal processes leading to organic combination of recoil atoms. Experiments on the organic yield of the $I^{127}(n, \gamma)I^{128}$ reaction on gaseous ethyl iodide at 80 mm. pressure have shown it to be variable and relatively high in the absence of scavenger but about 1% in the presence of scavenger,[18] as in the case of bromotrifluoromethane at a density of 0.0068 g./cc. (760 mm.).

The data of Table III indicate an organic yield of about 28% for liquid bromotrifluoromethane at −75° where the density is 2.145 g./cc. Bromine equivalent to 1 mole % was added to the reaction tubes used in these experiments but the solubility at this temperature was so low that some of it crystallized out leaving a roughly estimated concentration of 0.3 mole % in the liquid. It is impossible to say whether the fact that the organic yield at this temperature lies above the straight yield *vs.* density line of Fig. 1 is due to the low scavenger concentration or the fact that there is a true upward curvature of the line due to the effect of greater density and/or molecular aggregation on the high energy processes.

The data of Table III for solid CF_3Br at −183° show a much higher organic yield than the liquid phase samples. This increase is qualitatively similar to that shown by a number of other compounds[10-13] but in contrast to still others.[9,10] The differences in the effects of crystallization on the organic yields of different compounds have not yet been explained.

Discussion

The fact that the organic yield of CF_3Br^* from the (n, γ) reaction on CF_3Br at a density of 0.0068 g./cc. and containing one mole % of Br_2 scavenger is only about 1% indicates that a bimolecular inversion step of the type $Br^* + CF_3Br \rightarrow CF_3Br^* + Br$ occurs with low probability if it occurs at all. The fact that the organic yield increases as the density of the medium increases may mean that this inversion type reaction between a bromine atom with kinetic energy or positive charge becomes more favored in the presence of other molecules. It seems more probable that as the density of the medium increases a greater fraction of the energy of the recoil atom is used to produce radicals because each molecule which it hits in the condensed phase is constrained by a wall of other molecules and cannot be knocked out of the way. As the density increases this effect, together with the decrease in diffusion coefficients of the radicals presumably leads to a rapid increase in their local concentration in the immediate vicinity of the tagged atom. If the tagged atom encounters a CF_3 radical in this situation it will combine with it and thus appear in the organic yield. Possible mechanisms of such reactions have been discussed in more detail elsewhere.[8-10,19-21]

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MADISON, WISCONSIN

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[18] J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

[19] W. F. Libby, THIS JOURNAL, **69**, 2523 (1947).

[20] J. M. Miller, J. W. Gryder and R. W. Dodson, *J. Chem. Phys.*, **18**, 579 (1950).

[21] P. C. Capron and Y. Oshima, *ibid.*, **20**, 1403 (1952).