

present method and those given by Mulliken is illusory, since ionization potential and electron affinity, though usually expressed in units of energy,

have an implied unit: per electron, because they represent the energy change which accompanies the removal or addition of one electron.

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The Influence of Phase, Temperature and Bromine Concentration on Bromine Production in the Decomposition of CCl_3Br by γ -Rays^{1a,b}

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The production of Br_2 by the radiolysis of CCl_3Br with Co^{60} γ -rays has been studied in the solid, liquid and gas phases and as a function of temperature and bromine concentration. In the solid state at -121° and below, the value of $G(\text{Br}_2)$ is 0.12 molecule produced/100 e.v., independent of temperature. From -78 to 98° $G(\text{Br}_2)$ increases with temperature to about 3.5 with an apparent activation energy of about 2 kcal./mole. Although this activation energy suggests a diffusion controlled process, there is no change in $G(\text{Br}_2)$ or its temperature dependence on crossing solid phase transitions at -35.5 and -13.5° or in going from the solid to the liquid state at the melting point -5.6° . Preliminary experiments indicate that there is no marked difference in yield in the gas phase as compared to the liquid phase at the boiling point. At bromine concentrations above about 0.01 M , $G(\text{Br}_2)$ is independent of bromine concentration at all temperatures in both the solid and the liquid. Below 0.01 M and at temperatures of 20° and above, however, $G(\text{Br}_2)$ decreases with increasing concentration. The bromine-sensitive reaction appears to have an activation energy of about 3 kcal./mole, slightly higher than the bromine insensitive reaction. The presence of oxygen raises $G(-\text{CCl}_3\text{Br})$ several-fold, the production of Cl_2 (a minor radiolysis product) being increased by a larger factor than Br_2 production.

Introduction

This paper reports investigations of the effects of phase, temperature and radical scavengers on the radiolysis of CCl_3Br , with particular reference to the yield of bromine in the liquid and solid phases. It is part of a more extensive investigation which has included² a comparison of the photochemical and radiation induced decomposition of CCl_3Br and the exchange of CCl_3Br with Br_2 in the gas and liquid phases. In the latter work² five organic products, CCl_4 , CCl_2Br_2 , CClBr_3 , C_2Cl_6 and $\text{C}_2\text{Cl}_5\text{Br}$, have been observed and their yields have been followed with the aid of gas chromatography.

These studies were designed to obtain information which would contribute to an understanding of the mechanisms of radiolysis of organic compounds. CCl_3Br was chosen because of its simplicity, because of the ease of following its decomposition by measurement of the bromine produced and because information was already available on its thermal³ and photochemical⁴ reactions and its reactions after activation by nuclear processes.⁵

Experimental

General Methods.—All irradiations of liquid and solid CCl_3Br were made on samples of about 5 ml. contained in

an annular vessel surrounding a 40 curie Co^{60} γ -ray source.⁶ Attached to the annular vessel at a distance sufficient to prevent troublesome darkening by irradiation was a cell made of square Pyrex tubing of 1 cm.² cross section. By pouring the liquid into this cell the optical absorbance of the liquid could be measured periodically with a spectrophotometer without opening the purified, air-free sample to the air.⁶ Thermostating media used in maintaining desired temperatures during irradiations included: liquid air, -190° ; liquid-solid butyl chloride, -121° ; Dry Ice-acetone, -78° ; liquid-solid anisole, -37° ; Dry Ice-acetone-aniline, -12° ; ice-water, 0° ; thermostated mineral oil-bath, temperatures above 20° .

Dosimetry.—Dosage rates were determined by measurement of the Fe^{+++} yield in air-saturated water solutions of ferrous ammonium sulfate, 0.8 N in H_2SO_4 , under irradiation conditions identical with those used for irradiation of CCl_3Br . It was assumed that the molar absorptivity index of Fe^{+++} is 2130 at 305 $m\mu$ and 25° and that 15.6 Fe^{+++} ions are formed per 100 e.v. absorbed.⁷ Energy absorption in CCl_3Br was determined from that in the dosimeter solution by use of the calculated ratio of the mass absorption coefficients of CCl_3Br and water for Co^{60} γ -rays. The value of this ratio is 1.12.

Sample Preparation.— CCl_3Br from the Michigan Chemical Corporation, containing 0.1% glycidyl phenyl ether as a preservative, as well as other impurities, was purified by the following steps: vigorous mechanical stirring with successive portions of concentrated H_2SO_4 until no discoloration of the acid occurred on several hours of additional stirring; washing with Na_2CO_3 and water, drying with CaCl_2 and P_2O_5 ; illumination with a 1000 watt projection lamp at 6 inches for 10 hr. after making 0.01 M in Br_2 ; passage through a 30×1.5 cm. column of activated alumina; fractional distillation through a 12" Vigreux column; passage of the middle third of the distillate through a fresh activated alumina column. A similar procedure omitting the H_2SO_4 and alumina treatments gave a product which yielded radiolysis results indistinguishable from those on material prepared by the more extensive procedure. CCl_3Br from each method of purification had a boiling point of 103.5° at 745 mm., a freezing point of -5.6° , and a refractive index, n_D^{25} of 1.5032 ± 0.0002 . CCl_2Br_2 (Michigan Chemical Corp.), used as a carrier for small quantities of radioactive CCl_2Br_2 , was prepared for use by fractional distillation in a Vigreux column at 43° under 27 mm. pressure.

The irradiation vessels were prepared for filling by allowing them to stand filled with alcoholic KOH for an hour, following which they were rinsed, allowed to stand in boiling

(1) (a) Presented before the Division of Physical and Inorganic Chemistry at the April, 1955, meeting of the American Chemical Society in Cincinnati, Ohio. (b) This work is reported in greater detail in the Ph.D. thesis of Richard F. Firestone, University of Wisconsin, 1954.

(2) A. H. Young, Ph.D. thesis, University of Wisconsin (1958), available from University Microfilms, Ann Arbor, Michigan.

(3) (a) A. A. Miller and J. E. Willard, *J. Chem. Phys.*, **17**, 168 (1949); (b) N. Davidson and J. H. Sullivan, *ibid.*, **17**, 176 (1949); (c) E. Becker, Ph.D. thesis, University of Wisconsin, 1953.

(4) (a) E. Paterno, *Jahresb. Forts. Chem.*, **24**, 259 (1871); (b) W. Noddack, *Z. Elektrochem.*, **27**, 359 (1921); (c) H. Grusse, *ibid.*, **29**, 144 (1923); (d) H. G. Vesper and G. K. Rollefson, *J. Am. Chem. Soc.*, **56**, 1455 (1934); (e) W. Franke and H. J. Schumacher, *Z. physik. Chem.*, **B42**, 324 (1939); (f) W. U. Day, Ph.D. Thesis, University of Wisconsin, 1942.

(5) (a) S. Goldhaber, R. S. H. Chiang and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 2271 (1951); (b) S. Goldhaber and J. E. Willard, *ibid.*, **74**, 318 (1952).

(6) R. F. Firestone and J. E. Willard, *Rev. Sci. Instr.*, **24**, 904 (1953).

(7) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

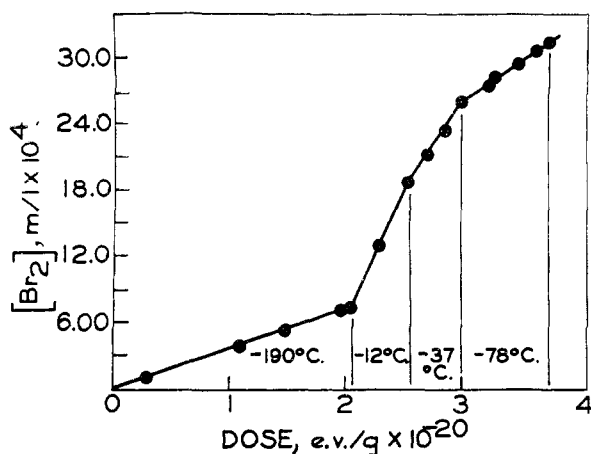


Fig. 1.—Bromine production during the radiolysis of a typical sample of solid CCl_3Br at successive temperatures of -190 , -12 , -37 and -78° .

distilled water for an hour and dried in an oven. They were then sealed to a vacuum system and thoroughly flamed. A measured amount of degassed CCl_3Br was transferred to the vessels by distillation through activated alumina or P_2O_5 *in vacuo* in the light of a red bulb. They were sealed from the vacuum line while the CCl_3Br was frozen with liquid air.

Product Analyses.—Periodically during the course of irradiation the samples of CCl_3Br were brought to room temperature and analyzed by light transmission measurements with a Beckman DU spectrophotometer. Since Br_2 constituted about 98% of the total halogen yield in all degassed samples, it was possible to determine Br_2 by measurements at wave lengths greater than $400 \text{ m}\mu$ without interference from BrCl or Cl_2 . The small amounts of BrCl and Cl_2 were measured, in some samples, by a second measurement of absorption by Br_2 after causing exchange of all inorganic chlorine for bromine by the net photochemical reactions^{4d}: $\frac{1}{2} \text{Cl}_2 + \text{CCl}_3\text{Br} \xrightarrow{h\nu} \text{CCl}_4 + \frac{1}{2} \text{Br}_2$ and $\text{BrCl} + \text{CCl}_3\text{Br} \xrightarrow{h\nu} \text{CCl}_4 + \text{Br}_2$. Bromine sensitized photochemical decomposition of CCl_3Br to C_2Cl_6 and Br_2 was shown to be inhibited completely at bromine concentrations greater than 0.01 M under the conditions of illumination used (a 300 watt lamp at 15 cm. for 2.5 hr. at 25°).

When CCl_3Br was irradiated in the presence of oxygen, BrCl and Cl_2 were produced in yields similar to bromine. In such cases analysis was carried out by measuring light transmission at several wave lengths and solving the appropriate simultaneous equations of the form

$$\log(I_0/I_\lambda) = [\epsilon_{\text{Br}_2}[Br_2] + \epsilon_{\text{Cl}_2}[Cl_2] + \epsilon_{\text{BrCl}}[BrCl]] (1)^b$$

White crystals having properties of C_2Cl_6 were obtained from the evaporation of irradiated CCl_3Br . Stoichiometry requires that it be produced in equimolar amounts with Br_2 . Extensive attempts to isolate it quantitatively from CCl_3Br by fractional distillation were unsuccessful^{1b} because of limitations of this method, but it has since been studied in detail by gas chromatography.²

CCl_2Br_2 was identified as a product by irradiation of a sample of liquid CCl_3Br containing BrBr^{82} (36 hr.) and fractional distillation after addition of carrier CCl_2Br_2 .

Corrections to Br_2 Concentration Data.—The concentration of bromine at each temperature of irradiation was calculated from the concentration measured at room temperature by correcting for the change in density and for bromine present as vapor above the liquid samples at the higher temperatures (maximum correction 2.5%).

Results

Effect of Br_2 Concentration. (a) Solid Phase.—Figure 1 illustrates the linear dependence of bromine yield on dosage for typical gas-free solid CCl_3Br samples exposed to γ -rays. Bromine was undoubtedly formed homogeneously throughout the

solid during each irradiation period, but it is doubtful that it was distributed homogeneously during each irradiation, because it was necessary to liquefy the samples for analysis and re-freeze them prior to further irradiation. The fact that in the experiment of Fig. 1 and several similar experiments the rate of formation at each temperature was independent of the length of the irradiation period and also independent of the bromine present from previous periods, indicates that the solid phase decomposition is insensitive to Br_2 at all temperatures and concentrations investigated. Among the experiments carried out at a single temperature in the solid state with no deviation from a constant value of $G(\text{Br}_2)$, there were large variations in irradiation dose given between meltings (5×10^{19} to 3×10^{20} e.v./g.). It is also probable that in many cases where the sample to be irradiated was frozen rapidly at -190° the dissolved Br_2 from previous irradiations was rather uniformly distributed in the solid,⁸ while in other cases where it was frozen slowly at -12° or -37° it was not uniformly distributed. Values of $G(\text{Br}_2)$ for the five temperatures from -190° to -12° investigated for the solid state are included in Table I.

TABLE I
 $G(\text{Br}_2)$ AS A FUNCTION OF TEMPERATURE

T, °C.	$G(\text{Br}_2)$, molecules/100 e.v.—	
	Terminal (Br_2 independent)	At 10^{-3} mole/l. (Br_2)
-190	0.12	
-121	.12	
-78	.20	
-37	.44	
-12	.65	
0	.70	0.70
20	.94	1.5
63	1.3	2.5
80	1.5	2.9
98	1.7	3.4

(b) **Liquid Phase.**— $G(\text{Br}_2)$ for liquid CCl_3Br at 0° was 0.70, independent of bromine concentration at all concentrations tested (from 0.17×10^{-3} to 7.4×10^{-3} mole/l).

At the higher temperatures investigated (20° , 63° , 80° , 98°) a different behavior was observed, *i.e.* $G(\text{Br}_2)$ decreased with increasing bromine concentration in the concentration range from 0 to about $1 \times 10^{-2} \text{ M}$ as shown in Fig. 2. At higher concentrations $G(\text{Br}_2)$ was independent of bromine concentration, as at the lower temperatures. Thus at 20° $G(\text{Br}_2)$ was 0.93 at 0.010 M and 0.95 at 0.035 M . At each temperature the points on a plot of bromine concentration *vs.* dose fell on a smooth curve, usually with a deviation of less than 1%. The magnitude of the decrease in rate with increase in bromine concentration is indicated by the G -values at a bromine concentration at 10^{-3} mole/l. as compared to the "terminal" G -values shown in Table I. Bromine was shown to be the only product acting as an inhibitor by an experiment with initially added $7 \times 10^{-3} \text{ M}$ Br_2 for which a plot of $G(\text{Br}_2)$ *vs.* bromine concentration was identical with that for experiments in which all the bromine was produced by irradiation.

(8) M. J. Milman, *J. Am. Chem. Soc.*, **79**, 558 (1957).

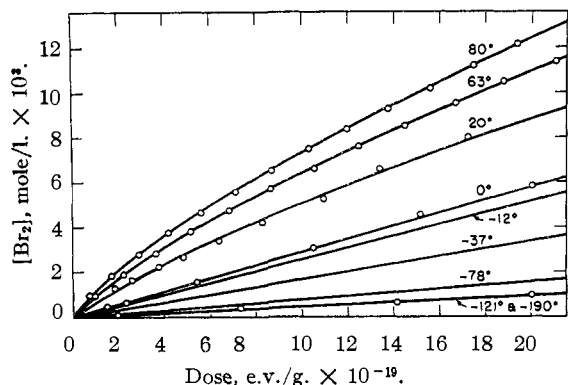


Fig. 2.—Production of Br_2 as a function of γ -ray dose in the radiolysis of CCl_3Br , showing the dependence of the initial rate on Br_2 concentration at 20° and above, as contrasted to the linear production at 0° and below. Lines for -12 , -37 and -78° are derived from the slopes of sections of curves of the type of Fig. 1.

Effect of Temperature.— $G(\text{Br}_2)$ was observed to be insensitive to temperature between -190° and -121° and to increase with temperature above -121° . The activation energy for that process which produces Br_2 at rates independent of bromine concentration is about 1.6 kcal./mole (Fig. 3). To estimate the activation energy of the bromine-sensitive process which occurs at 20° and above, $G(\text{Br}_2, \text{terminal})$ at each temperature was subtracted from values for $G(\text{Br}_2, \text{total})$.

This gave the necessary data for making Arrhenius plots of $\log G(\text{Br}_2, \text{bromine sensitive})$ against $\log 1/T$ for each of several bromine concentrations. These plots gave an apparent activation energy of 3.0 kcal./mole for the bromine-sensitive process.

Effect of Phase.—Absence of any effect of the solid-liquid transition upon the decomposition processes is indicated by the absence of a discontinuity in the Arrhenius plot of Fig. 3 at the melting point (-5.6°). A change in the structure of solid CCl_3Br , evidenced in this work^{1b} by temperature plateaus at -35.5° on warming and cooling curves, also had no apparent effect upon the radiolysis in the solid. This change in structure and one at -13.5° have also been observed in CCl_3Br by other workers.⁹ It is similar to a solid state transition in CCl_4 at -48° and to others in other carbon tetrahalides.¹⁰

In several exploratory experiments $G(\text{Br}_2)$ for the radiolysis of CCl_3Br vapor at pressures in the range of 500 mm. at 109° was found to be essentially the same as in the liquid, for irradiations in which 0.2 mole % Br_2 was formed, indicating that this change of phase causes no marked effect. This observation has been confirmed by recent more extensive studies in the gas phase.²

Effect of Oxygen.—In the radiolysis of degassed CCl_3Br only one chlorine atom, as Cl_2 or BrCl , is formed per 50 bromine atoms as Br_2 . In the presence of 0.0006 mole fraction of dissolved O_2 , however, the G for total inorganic chlorine produc-

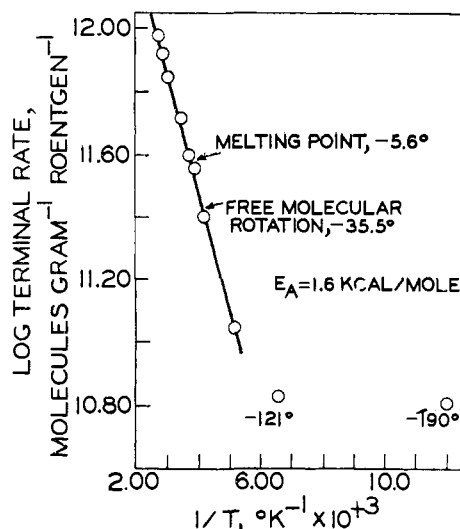


Fig. 3.—Temperature dependence of the bromine-insensitive rates of bromine production.

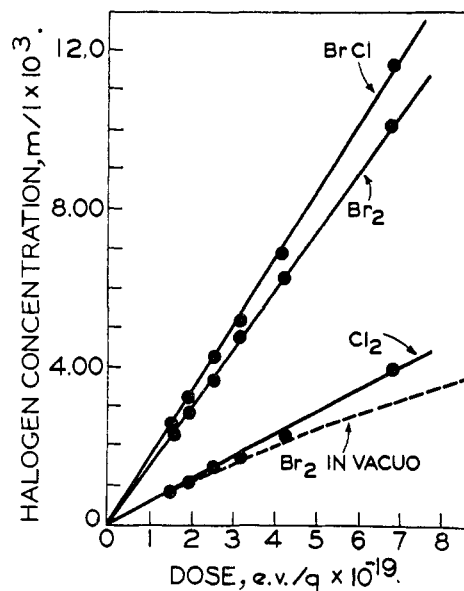


Fig. 4.—Production of Br_2 , Cl_2 and BrCl during the radiolysis of liquid CCl_3Br at 20° in the presence of 460 mm. of O_2 .

tion becomes nearly equal to that of bromine production while the $G(\text{Br}_2)$ is more than double that in the absence of O_2 (Fig. 4). It is probable that these increases result from a combination of elementary steps. By scavenging CCl_3 radicals which would otherwise revert to CCl_3Br by reaction with Br_2 , or react with Cl_2 or BrCl to form CCl_4 , the O_2 increases the halogen yield. The CCl_3O_2 species formed undoubtedly undergoes further complex reactions which lead to additional halogen formation.

Discussion

Three separate processes each of which appears to contribute to Br_2 formation in air-free liquid CCl_3Br are distinguishable by differences in their sensitivity to temperature and to inhibition by Br_2 . One of these is the sole process responsible

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(10) J. C. McCullough and H. E. Phipps, *ibid.*, **50**, 2213 (1928); H. L. Johnston and E. A. Long, *ibid.*, **56**, 31 (1934).

for decomposition below about -121° . It is insensitive to both temperature and bromine concentration. Increasing the irradiation temperature above -78° in the solid causes a second process to contribute simultaneously with and apparently independently of the lower temperature process. The second process exhibits an apparent activation energy of about 2 kcal./mole but is insensitive to bromine concentration. Between 0 and 20° in the liquid phase a third process appears to set in with an activation energy of about 3 kcal./mole and a marked sensitivity to bromine concentration. This process is almost completely inhibited by free bromine at concentrations greater than 0.01 *M*. The absence of phase or structural effects in the condensed phases suggests that the sites of all effective reactions below about 20° are the small regions of high local reactive intermediate concentration associated with spurs produced by the secondary electrons along the tracks of high energy electrons. This suggestion is supported by the insensitivity to Br_2 of the two processes which contribute between -190 and 0° . Conversely, reactive intermediates responsible for the Br_2 -sensitive process must be able to escape their birth sites and react with Br_2 . The insensitivity to temperature of that process which contributes to decomposition below -121° indicates that the responsible reactive species (radicals, excited molecules or ions) are able to react infallibly with neighboring CCl_3Br molecules, or with other reactive species formed in adjacent positions, without necessity for escape from the parent cage. The only fates possible for other intermediates below -121° must be collisional de-excitation for excited species and recombination with the parent partner for free-radical species (*e.g.*, $\text{CCl}_3 + \text{Br} \rightarrow \text{CCl}_3\text{Br}$). As the temperature rises, an increasingly larger fraction of labile intermediates (*e.g.*, free radicals) escape recombination with the parent partner and react to form carbon-carbon bonds. There are two types of reactions by which CCl_3 radicals can contribute to the formation of carbon-carbon bonds (and thus to the observed yield of Br_2): a thermal step, $\text{CCl}_3 + \text{CCl}_3 \rightarrow \text{C}_2\text{Cl}_6$, and an excited radical step, as for example, $\text{CCl}_3^* + \text{CCl}_3\text{Br} \rightarrow \text{C}_2\text{Cl}_6 + \text{Br}$.

There seems to be no way in which the $\text{CCl}_3 +$

$\text{CCl}_3 \rightarrow \text{C}_2\text{Cl}_6$ reaction can explain the onset of the bromine-sensitive process between 0 and 20° . To do so it would have to have a higher activation energy than the $\text{CCl}_3 + \text{Br}_2$ reaction with which it must compete. Also, estimates based on plausible assumptions for the rate of production of CCl_3 radicals and the relative rate constants for their reactions with Br_2 and with other CCl_3 radicals suggest that combination of radicals formed in different tracks is negligible compared to the reaction with Br_2 at all Br_2 concentrations in the range observed in this work. On the other hand, it is improbable that Br_2 concentrations in the bromine-sensitive range of Fig. 2 can compete effectively with radical-radical reactions within the spurs of the electron tracks. Thus it appears that the species responsible for the Br_2 -sensitive process must be an excited species which, on the average, retains its excitation through many collisions with CCl_3Br before reacting with it and which is capable of deactivation by Br_2 . Since inhibition by Br_2 was observed at mole fractions as low as 10^{-5} , some molecules of the reactive species must survive some 10^5 encounters with CCl_3Br before reaction. This is several orders of magnitude longer than the usual lifetime of excited electronic states relative to collisional deexcitation but may be possible for vibrationally excited species. There is evidence that such species may survive 10^6 to 10^{11} collisions before de-excitation in gases exposed to ultrasonic excitation.¹¹ The activation energy for the self diffusion of CCl_4 at constant pressure (3.3 kcal./mole)¹² is consistent with interpretation of the temperature dependence for the Br_2 sensitive process being the temperature dependence for the escape of the excited labile intermediate (*e.g.*, CCl_3^*) from the parent "cage," that is, from recombination with its parent partner.

Acknowledgments.—This work was supported in part by the Atomic Energy Commission under contract AT(11-1)-32 and in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation.

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