9 and 10 are obtained from Arrhenius plots of the olefin and ether yields, respectively. In isopropyl alcohol we obtained $E_9 = 40 \pm 10$ kcal/mol and $E_{10} = 41 \pm 2$ kcal/mol.

The activation energies of the four decomposition modes in the radiation-induced pyrolysis of isopropyl alcohol are similar to those of the corresponding modes in ethanol (Table IV).

The Radiolysis of Carbon Tetrachloride. Radical Yields and the Formation of Tetrachloroethylene as an Initial Product[1]

by Ned E. Bibler

Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, South Carolina 29801

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The radiolysis of liquid, air-free carbon tetrachloride containing a variety of solutes at 25° was investigated in detail. With Br_2 and HI as radical scavengers, the measured initial 100-eV yield of CCl_3 radicals was equal to 7.0 ± 0.2. The organic products resulting from spur reactions in these solutions were C_2Cl_4 and C_2Cl_6 ($G = 0.08$ and 0.47 molecule/100 eV, respectively). The total yield of scavengeable chlorine was 8.3 atoms/100 eV. With these two scavengers, evidence for the existence of intermediates other than Cl and CCl_3 was obtained. When I_2 was the scavenger, ICl was the most abundant product. The other major product, CCl_3I, was very susceptible to radical attack, and eventually all the initial iodine atoms appeared as ICl. In solutions containing ICl as a scavenger, $G(-ICl)$, $G(I_2)$, and $G(CCl_3I)$ were all equal to zero. With each of the above scavengers, tetrachloroethylene was an initial product; in the absence of scavengers, tetrachloroethylene presumably is removed by reaction with Cl or Cl_2. To explain C_2Cl_4 formation in the presence of ICl, an ICl_2 intermediate is proposed. Other scavengers suitable for Cl atoms included NH_3, C_2H_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$; CCl_3Br was not an efficient scavenger as suggested by the absence of C_2Cl_4 as a product. In solutions containing NH_3, a precipitate containing Cl^- ions was formed by the radiolysis. Also, in the presence of the chloromethanes, CH_2Cl_2 and $CHCl_3$, the radical yield in carbon tetrachloride was lowered considerably, apparently by an energy- or charge-transfer mechanism.

Introduction

Various authors have estimated[2-7] widely differing 100-eV yields of radicals in the ^{60}Co γ radiolysis of liquid air-free carbon tetrachloride with a variety of scavengers (Table I). These differences may be partly attributed to differences in the reactivity of the scavengers toward electronically excited or ionic precursors of the radicals and also the reactivity of the scavengers toward the radicals themselves.[8] However, there is no apparent reason for the differences obtained when the halogens Br_2 or I_2 are used as the scavengers. Both halogens have been shown to scavenge CCl_3 radicals in the radiolysis of chloroform;[9] both have ionization potentials lower than that for carbon tetrachloride;[10] and both can undergo exothermic reactions with CCl_3 radicals or Cl atoms. Accordingly, we have investigated the radiolysis of liquid carbon tetrachloride in detail using a variety of scavengers including Br_2, I_2, ICl, and HI. In the presence of these and other solutes (including NH_3, CH_2Cl_2, and C_2H_4) capable of reacting with Cl atoms, tetrachloroethylene was an initial product of the radiolysis. This compound is not produced in the radiolysis of pure carbon tetrachloride[2,3] or of carbon tetrachloride containing oxygen.[4]

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[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission. This work was sponsored by Division of Peaceful Nuclear Explosives.

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Table I: Values Estimated for $G(CCl_3)$ in the Radiolysis of Carbon Tetrachloride at ~23° with Various Scavengers

Scavenger	$G(CCl_3)$	Ref
Cl_2	<3.5	2
Br_2	>9.0	3
I_2	>12.0	3
$CHCl_3$	3-3.5	4
DPPH[a]	2.9	5
Ferrocene	>2.3	6
MMA[b]	19	7

[a] DPPH = Diphenylpicrylhydrazyl. [b] MMA = Methyl methacrylate.

Experimental Section

Carbon tetrachloride (Matheson Co.) was further purified by triple distillation in an inert atmosphere through a 1 m × 2 cm o.d. column filled with glass helices. In the final distillate no impurity was detected by gas chromatography (sensitivity $\sim 10^{-4}$ mol %). Iodine (research grade) was resublimed before use and research grade bromine was used without further purification. Hydrogen iodide was prepared by dehydrating a solution of hydriodic acid (Baker 47% aqueous HI solution) with P_2O_5 on a vacuum line.[11] Crystals of pure iodine monochloride were sublimed directly from research grade ICl at 25°. These crystals were freshly sublimed each time that solutions were prepared for radiolysis. All other solutes (NH_3, C_2H_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, C_2H_4, and CCl_3Br) were research grade materials and were further purified either by trap-to-trap distillation of the vapor or by distillation of the liquid.

Samples were prepared for irradiation by passing the carbon tetrachloride solution through a 5-Å molecular sieve attached to a buret[12] connected directly to a vacuum line. Aliquots (3 ml) of this solution were then passed from the buret to the vacuum line and degassed by several freeze-pump-thaw cycles. The entire aliquot was then distilled into the irradiation vessel (15-mm o.d. tube) and further degassed and sealed from the line while the sample was frozen with liquid nitrogen.

When the solutes to be dissolved in the carbon tetrachloride were solids or liquids at room temperature, they were added to the solution before it was passed through the sieve. The only suitable drying agent for solutions containing ICl was "Drierite" (Registered trademark of W. A. Hammond Drierite Co.) because other drying agents reacted with ICl to produce I_2 and presumably Cl^-. When the solutes to be dissolved were gases at room temperature, measured amounts were added to samples of carbon tetrachloride after it was distilled into the irradiation cells. In these cells the void space above the liquid was approximately 10-20% of the volume of the liquid, and all the gas was assumed to be dissolved in the sample.

The samples were irradiated at 25 ± 1° with a ^{60}Co Gammacell 220 (Atomic Energy of Canada Ltd.). The dose rate in carbon tetrachloride, determined by multiplying the appropriate electron density ratio by the dose rate in the Fricke dosimeter, was 1.77×10^{16} eV/(g) (sec).

Free halogens in the samples after irradiation were analyzed with a Beckman DU spectrophotometer. Molar absorptivities for Cl_2, BrCl, Br_2, I_2, and ICl were determined and were in good agreement with published values.[13] Chlorine was also determined by breaking open the irradiation cell containing the sample while the cell was immersed in an 0.1 *M* solution of KI. The liberated I_2 was titrated with 0.01 *N* $Na_2S_2O_3$ to a starch end point.

Organic products were determined with an F & M Model 400 gas chromatograph with a flame ionization detection system. For $CHCl_3$ and CCl_3Br a 12-ft long, $^1/_4$-in. column (20% Silicone 200) was operated isothermally at 90°. For CCl_2Br_2, C_2Cl_4, and C_2Cl_6 a 50-ft long, $^1/_8$-in. column (2% SE-30) was used isothermally at 100°. The columns were calibrated each time samples were analyzed. All the solutes used to prepare standard solutions of radiolytic products except CCl_2Br_2 were research grade and were further purified. Dichlorodibromomethane was prepared by photolyzing a mixture of $CHCl_2Br$ and Br_2. The final product was purified using an F & M Model 776 preparative gas chromatograph.

In the irradiated solutions of carbon tetrachloride containing iodine in addition to ICl, a product suspected to be CCl_3I was formed. Pure CCl_3I could not be synthesized because of its limited thermal stability, but its presence in the irradiated solutions was proven as follows. The production of an organic iodide was indicated because: (1) radioactivity was retained by carbon tetrachloride after irradiation in the presence of $^{131}I_2$ and washing with an aqueous sulfite solution to remove unreacted I_2, and (2) after standing ~16 hr these extracted solutions became pink. The organic iodide was shown to be CCl_3I because its retention time on the gas chromatograph was slightly less than that for $C_2H_2Cl_4$, which boils only four degrees higher than CCl_3I. Also, the height of the peak assigned to CCl_3I at any dose, *d*, was directly proportional to the quantity $2[I_2]_0 - 2[I_2]_d - [ICl]_d$ where $[I_2]_0$ is the initial concentration of iodine and $[I_2]_d$ and $[ICl]_d$ are the concentrations of these species at the dose *d*.

Results and Discussion

Carbon Tetrachloride Containing the Halogens Br_2, I_2, or ICl. In air-free carbon tetrachloride with Br_2

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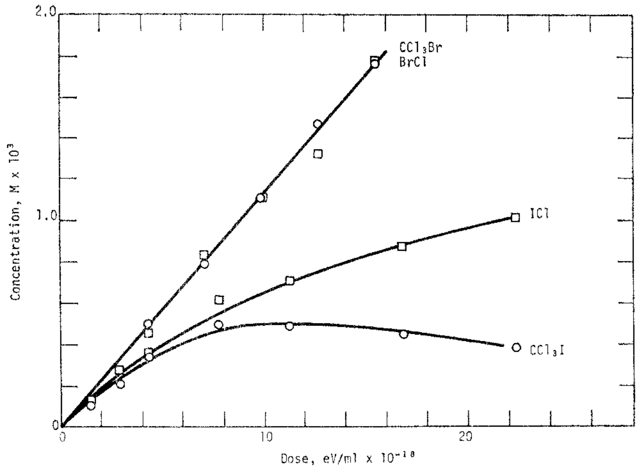

Figure 1. Dose dependence of the major radiolysis products of CCl_4 containing Br_2 or I_2: O, CCl_3X; □, XCl.

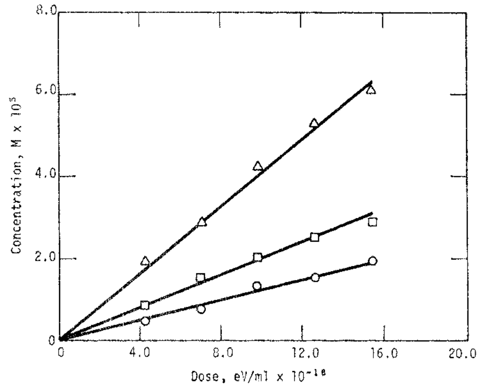

Figure 2. Dose dependence of the minor radiolysis products of CCl_4 containing 0.027 M Br_2: Δ, $C_2Cl_6/2$; □, CCl_2Br_2; O, C_2Cl_4.

as scavenger, the radiolysis products and their 100-eV yields were: CCl_3Br, 7.1; BrCl, 7; C_2Cl_6, 0.48; C_2Cl_4, 0.07; and CCl_2Br_2, 0.12. The dose dependence of the concentrations of the major products is shown in Figure 1 and that of the minor products in Figure 2. Also shown in Figure 1 is the dose dependence of the major products in the radiolysis of carbon tetrachloride containing I_2. Clearly, in this system the 100-e Vyields of CCl_3I and ICl are dose dependent, with $G(CCl_3I)$ becoming negative at large doses. At very large doses ($>10^{20}$ eV/ml), the only iodine-containing product in these solutions was ICl. This is similar to results from the radiolysis of air-saturated solutions of I_2 in carbon tetrachloride where ICl is the only iodine-containing product at all doses.[14] In the degassed CCl_4–I_2 system, as in the system containing Br_2, the concentrations of the minor products, C_2Cl_6 and C_2Cl_4, were linear with dose. Their 100-eV yields were 0.45 and 0.073, respectively, in a 2×10^{-3} M solution of I_2. In the radiolysis of carbon tetrachloride containing 10^{-2} M ICl, the only products were C_2Cl_6 ($G = 0.54$) and C_2Cl_4 ($G = 0.12$). The compounds CCl_3I and I_2 were not detected and $G(-\text{ICl})$ was equal to zero.

The major radiolytic products in solutions containing Br_2 or I_2 indicate that CCl_3 radicals and Cl atoms are the most significant neutral intermediates formed by ionic or neutral dissociation processes and charge neutralization reactions. When Br_2 was present, both $G(CCl_3Br)$ and $G(BrCl)$ were approximately equal to the 100-eV yield for the disappearance of Br_2, suggesting the following mechanism as seen in eq 1–3.

$$Cl + Br_2 \longrightarrow BrCl + Br \qquad (1)$$

$$CCl_3 + Br_2 \longrightarrow CCl_3Br + Br \qquad (2)$$

$$2Br \longrightarrow Br_2 \qquad (3)$$

Reactions similar to eq 1–3 can be written for the mechanism in the system with I_2 as a scavenger.

Reactions consistent with the slow decrease of CCl_3I at large doses are shown in eq 4 and 5.

$$Cl + CCl_3I \longrightarrow ICl + CCl_3 \qquad (4)$$

$$CCl_3 + ICl \longrightarrow CCl_4 + I \qquad (5)$$

As the dose increases, the concentration of I_2 decreases, and an increasing fraction of the Cl atoms reacts with CCl_3I as in reaction 4. Also, as the concentration of ICl increases, more of the CCl_3 radicals react with ICl as in reaction 5 and are converted back to CCl_4. Reaction 4 is proposed instead of an alternative reaction in which Cl_2 and CCl_2I are products because the energy of the C–I bond is about 30 kcal/mol lower than that for a C–Cl bond,[15] while the bond strength of Cl_2 is only approximately 7 kcal/mol greater than that for ICl.[15] The exclusive occurrence of reaction 5 over an alternative reaction in which CCl_3I and Cl are products is established by the absence of CCl_3I in the radiolysis of carbon tetrachloride containing ICl as a scavenger. Based on standard heats of formation,[16] the alternative reaction is slightly endothermic (neglecting solvation energies), while reaction 5 is exothermic.

The concentration of ICl at large doses in the carbon tetrachloride–iodine system increases, regardless of the identity of the products formed by the attack of Cl atoms on ICl. If Cl_2 results from the Cl atom attack, it will react spontaneously with the I_2 to form ICl.[17] If ICl results from the Cl atom attack, the resulting Cl atom will eventually appear as ICl either by recombination with an I atom or by forming Cl_2 that would subsequently react with I_2. These reactions explain the fact that $G(-\text{ICl})$ is equal to zero in the solutions containing ICl as a scavenger and also account for the failure to observe the formation of I_2 in these solutions.

Of the three radical scavengers (Br_2, I_2, and ICl), only in solutions with Br_2 can the initial 100-eV yield

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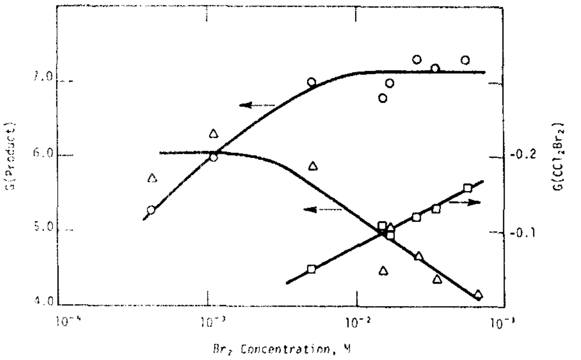

Figure 3. Dependence of the 100-eV yields of CCl_3Br, C_2Cl_6, and CCl_2Br_2 on the concentration of Br_2: ○, $G(CCl_3Br)$; △, $G(C_2Cl_6) \times 10$; □, $G(CCl_2Br_2)$.

of radicals be determined. When I_2 is the scavenger, the yields of the products of the scavenging reactions are dose dependent; when ICl is the scavenger, the products of the scavenger reactions cannot be measured. In the system containing Br_2, the initial 100-eV yield of CCl_3 radicals can be measured accurately because CCl_3Br is formed. The yield of Cl atoms cannot be measured as accurately since they form BrCl; small concentrations of this compound cannot be accurately measured in 50–100 times excess Br_2 because of the overlapping absorption spectra of the two compounds. However, in most of the experiments G(BrCl) is usually within 15% of $G(CCl_3Br)$. Values for $G(CCl_3Br)$ were dependent upon the initial concentration of Br_2 as shown in Figure 3. In solutions with >0.005 M Br_2, $G(CCl_3Br)$ is constant at 7.1 ± 0.2 molecules/100 eV. This is equal to the 100-eV yield of CCl_3 radicals and agrees well with 7.0 radicals/100 eV calculated for this quantity from the data of Schulte.[2,18] In his experiments Cl_2 containing ^{36}Cl was used as a scavenger. The radiation-induced formation of CCl_4 containing ^{36}Cl was then measured.

The formation of C_2Cl_6 in the presence of Br_2, I_2, or ICl is evidence for the occurrence of spur reactions. Whether CCl_3 radicals are the precursors is not certain. As shown in Figure 3, Br_2 can compete for these precursors, suggesting that they may be CCl_3 radicals. However, the data in Figure 3 are not conclusive because the expected increase in $G(CCl_3Br)$ as Br_2 competes with the spur reactions is within the limits of the experimental uncertainty in determining $G(CCl_3Br)$.

The formation of CCl_2Br_2 in the system containing Br_2 indicates that intermediates other than CCl_3 radicals or Cl atoms are being scavenged. These intermediates may be CCl_2 radicals, and the CCl_2Br_2 molecules result from successive bromination. If I_2 or ICl is the scavenger, the expected product is CCl_2I_2 or CCl_4. CCl_2I_2 may not be detected because of its low thermal stability rather than its lack of formation. As shown in Figure 3, the value for $G(CCl_2Br_2)$ increases as the concentration of Br_2 increases. This indicates that the scavenging process is incomplete and that the initial 100-eV yield of these intermediates is >0.16. Evidence implying the existence of CCl_2 radicals has also been obtained in the radiolysis of liquid chloroform.[9] When chloroform containing 0.045 M Br_2 was irradiated, CCl_2Br_2 was formed with a 100-eV yield of 0.4. Precursors of CCl_2 may be ions or excited CCl_4 molecules.

Previous to this study tetrachloroethylene has not been reported as a product in the radiolysis of liquid carbon tetrachloride. Recently, Marcotte and Hanrahan[19] have reported that this product is formed in the gamma radiolysis of mixtures of CCl_4 and CF_4 vapor at 920 mm and 85°. In the radiolysis of liquid carbon tetrachloride, C_2Cl_4 is not a product in solutions containing Cl_2,[2] O_2,[3] or in pure CCl_4.[2,3] These results have been confirmed in this laboratory. However, C_2Cl_4 is an initial product when Br_2 is present as a scavenger (Figure 2). C_2Cl_4 is also an initial product in solutions containing I_2 or ICl. In each of the solutions where C_2Cl_4 is not formed, Cl_2 is a major product.[2,3] Also in these solutions, the Cl atoms probably have much longer lifetimes than in the presence of Br_2 or I_2. Both Cl_2 and Cl atoms may easily react with and saturate any C_2Cl_4 that is formed. If a scavenger in carbon tetrachloride converts Cl atoms (or Cl_2) to a less reactive species, the C_2Cl_4 may be protected. This is possible when Br_2 or I_2 is present.

In the solutions with ICl, Cl probably reacts with ICl to abstract an I atom. Because this abstraction of I does not remove Cl atoms as an abundant intermediate, this reaction is not compatible with the appearance of C_2Cl_4 as a product. It is proposed that Cl atoms add to ICl to form ICl_2. This intermediate would then react with an I atom to produce two molecules of ICl. Possible support for the transient existence of ICl_2 is that in the pulse radiolysis of carbon tetrachloride evidence has been obtained for the formation of Cl atom–solute complexes when electron donating solutes are present.[20]

Carbon Tetrachloride Containing Hydrogen Iodide. Hydrogen iodide was investigated as a solute to provide additional confirmation of initial radical yields obtained in the CCl_4–Br_2 system. When solutions of carbon tetrachloride containing 0.01 M HI were irradiated, the products and their 100-eV yields were: $CHCl_3$, 7.4; I_2, 8.9; C_2Cl_6, 0.52; C_2Cl_4, 0.12; and C_2HCl_5, 0.07. Each of these 100-eV yields is independent of dose up to 1.36×10^{19} eV/ml, the largest dose used. Gas chromatographic analysis of these irradiated solutions indicated that CCl_3I was not a product. From the absorption

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[18] In his original calculations a factor of 2 was omitted and the 100-eV yield of CCl_3 radicals reported as 3.5.

[19] R. E. Marcotte and R. J. Hanrahan, Abstracts of the Southeastern Regional Meeting of the American Chemical Society, Dec 4–7, 1968, Tallahassee, Fla., p 46.

[20] R. E. Bühler and M. Ebert, *Nature*, **214**, 1220 (1967); R. Cooper and J. K. Thomas, *Advan. Chem. Ser.*, **82**, 351 (1968).

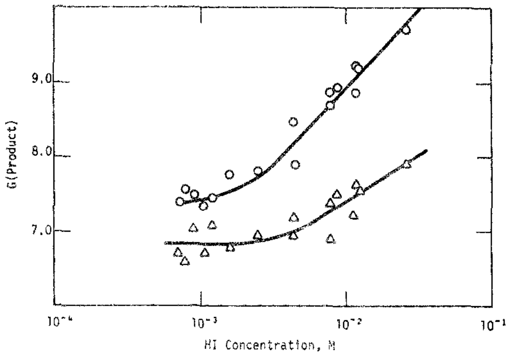

Figure 4. Dependence of the 100-eV yields of I_2 and $CHCl_3$ on the concentration of HI: O, $G(I_2)$; Δ, $G(CHCl_3)$.

spectrum of solutions irradiated to the largest dose, the 100-eV yield of ICl was estimated to be less than 7% of $G(I_2)$ or ~0.5 molecule/100 eV.

For formation of the major products the following mechanism is proposed.

$$CCl_3 + HI \longrightarrow CHCl_3 + I \qquad (6)$$

$$Cl + HI \longrightarrow HCl + I \qquad (7)$$

$$2I \longrightarrow I_2 \qquad (8)$$

Although the yield of HCl was not measured, its formation can be inferred because $G(I_2)$ is greater than $G(ICl)$. From this mechanism, it follows that $G(CHCl_3)$ should equal $G(I_2)$. However, as shown in Figure 4, $G(I_2)$ is always greater than $G(CHCl_3)$ at all concentrations of the scavenger. Part of this difference can be attributed to the spur reactions forming C_2Cl_4 and C_2Cl_6. For each molecule of C_2Cl_6 or C_2Cl_4 formed, either two or four Cl atoms remain to react either as Cl_2 molecules or as Cl atoms with HI to increase the yield of I_2. Consequently, $G(I_2)$ should equal $G(CHCl_3) + G(C_2Cl_6) + 2G(C_2Cl_4)$ and thus be 0.8 unit larger than $G(CHCl_3)$. As shown in Figure 4, this is the case at HI concentrations lower than ~0.002 *M*. The increases in $G(CHCl_3)$ and $G(I_2)$ at higher concentrations of HI probably result from energy or charge transfer mechanisms. Similar effects have been observed in the radiolysis of hydrocarbons containing HI. The yields of alkyl iodides[21] and also iodine[22] increase with increasing scavenger concentration. As shown in Figure 4, $G(CHCl_3)$ and $G(I_2)$ become constant below approximately 1.5 m*M* HI. These data indicate that the initial 100-eV yield of CCl_3 radicals is 6.8 ± 0.2 radicals/100 eV. This is within the experimental error of values determined with Br_2. From mass balance considerations, the lower limit of the initial yield of Cl atoms is 6.8 since it is not certain whether Cl or Cl_2 results from the spur reactions.

Values for $G(C_2Cl_6)$ and $G(C_2Cl_4)$ are close to those observed when the halogens were used as scavengers. In the solutions with HI, the small yield of C_2HCl_5 may result from the scavenging of C_2Cl_5 radicals. These radicals may result from the dissociation of excited C_2Cl_6 molecules formed by recombination of CCl_3 radicals or from the addition of a small portion (<1%) of the Cl atoms to C_2Cl_4. In carbon tetrachloride containing Br_2 or I_2, C_2Cl_5Br, and C_2Cl_5I were not detected. These products were either not formed or were not detected because of the poorer sensitivity for their analysis than for that of C_2HCl_5.

No evidence for any CCl_2 species was obtained when HI was the scavenger. The products CH_2Cl_2 and $CHCl_2I$ were not detected at concentrations of HI sufficiently large (0.06 *M*) to ensure scavenging of at least a portion of the precursors of the CCl_2Br_2 in the other system (see Figure 3). This suggests that the CCl_2Br_2 does not result from successive bromination of CCl_2 because the expected product in the presence of HI is CH_2Cl_2. If the precursors of CCl_2Br_2 are CCl_2^+ ions, these might preferentially abstract I atoms from HI leading eventually to CCl_2I_2, which cannot be analyzed.

Carbon Tetrachloride Containing Other Solutes. Solutions of carbon tetrachloride containing other solutes were irradiated primarily to determine the effect of these solutes on the formation of C_2Cl_4. The results are summarized in Table II. Tetrachloroethylene was a product in all the solutions except those containing CCl_3Br. All the solutes are presumably capable of reacting with Cl atoms to produce free radicals that do not react with C_2Cl_4. However, it has been shown[23]

Table II: Products in the Radiolysis of Carbon Tetrachloride Containing Various Solutes (~0.02 *M*) at 25°

Solute	Products[a]
NH_3	C_2Cl_4 0.10); C_2Cl_6 (2.8); Cl^{-}[b]
C_2H_4	C_2Cl_4 (0.10); C_2Cl_6 (4.3); $CCl_3CH_2CH_2Cl$; CCl_3CHCH_2
$CHCl_3$	C_2Cl_4 (0.09); C_2Cl_6 (2.7)
CH_2Cl_2	C_2Cl_4 (0.10); $CHCl_3$ (2.0); $C_2H_2Cl_4$ (0.4); C_2HCl_5 (1.7); C_2Cl_6 (2.6)
CH_3Cl	C_2Cl_4 (0.13); CH_2Cl_2 (5.5); $CHCl_3$ (0.1); C_2Cl_6 (2.8)[c]
CCl_3Br	C_2Cl_6 (0.75);[d] Cl_2 (0.47);[e] BrCl (0.24);[e] Br_2 (0.04)[e]

[a] 100-eV yields are given in parentheses, where determined. [b] This species was in the form of an insoluble salt in the irradiated solution. [c] Other products were present but not identified. [d] This yield was nonlinear with dose (see Figure 5). [e] Determined at doses >2.7 × 10^{19} eV/ml.

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(21) C. E. McCauley and R. H. Schuler, *J. Amer. Chem. Soc.*, **79**, 4008 (1957); R. W. Fessenden and R. H. Schuler, *ibid.*, **79**, 273 (1957).

(22) For a summary of these results see R. A. Holroyd in "Aspects of Hydrocarbon Radiolysis," T. Gaumann and J. Hoigne, Ed., Academic Press, London, 1968, p 5.

(23) A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, **91**, 4626 (1969).

that organic radicals produced by the radiolysis of various hydrocarbons can react with C_2Cl_4 added initially to the solutions. In the present study, the radicals do not react with C_2Cl_4. Similar results were found[24] when C_2Cl_4 appeared as a product of the radiolytically induced chain reactions in cyclohexane containing mM concentrations of C_2Cl_6. In this study[24] C_2Cl_4 resulted from the dissociation of C_2Cl_5 radicals formed by the abstraction of Cl atoms from C_2Cl_6 by c-C_6H_{11}. A similar mode of formation of C_2Cl_4 in the radiolysis of carbon tetrachloride is possible if C_2Cl_5 radicals result from the dissociation of a portion of the excited C_2Cl_6 molecules formed by the recombination of CCl_3 radicals. However, this possibility is eliminated by the observation that in those systems where $G(C_2Cl_6)$ has increased (Table II) over its value in presence of the halogens, $G(C_2Cl_4)$ has not increased significantly.

In the irradiated solutions containing NH_3, a precipitate that contained Cl^- ions was formed. Davis and Hanrahan,[25] by irradiating carbon tetrachloride that contained 0.2 M NH_3, have demonstrated that this solid is predominantly NH_4Cl. In their study, they determined that the 100-eV yields for NH_4Cl and C_2Cl_6 were 25 and 2.1, respectively, but they apparently failed to detect C_2Cl_4. Their value for $G(C_2Cl_6)$ is lower than that determined in the present study, but this may be caused by more CCl_3 radicals being scavenged by NH_3 in their experiments since higher scavenger concentrations were used. Assuming the absence of a chain mechanism, an estimate of the yield of the scavengeable organic radicals in their experiments can be calculated by summing the yields of the carbon atoms in all the products and subtracting from this sum the yield of C_2Cl_6 molecules formed by spur reactions. This latter yield is 0.5 molecule/100-eV, and the calculated organic radical yield is 9 radicals/100-eV. This value is somewhat higher than that determined in this study using Br_2 or HI. Part of the larger yield may result from the interaction of the NH_3 at such high concentrations with the ionic processes in the carbon tetrachloride. This effect has been observed in chloroform[26] where the presence of NH_3 at concentrations greater than 0.03 M increases the yield of radicals.

In the presence of ethylene, C_2Cl_4 was a product, and evidence was obtained for both the addition of Cl atoms to C_2H_4 and the loss of H atoms from C_2H_4 leading to the formation of $CCl_3CH_2CH_2Cl$ or CCl_3CHCH_2.

When the chloromethanes were used to react with the Cl atoms, CCl_3, $CHCl_2$, and CH_2Cl radicals were formed from $CHCl_3$, CH_2Cl, and CH_3Cl, respectively (Table II). In the presence of any of these three solutes, Cl_2 was not a product. This agrees with other results[4] on the radiolysis of carbon tetrachloride that indicate that $CHCl_3$ inhibits the formation of Cl_2. In the present study, most of the experiments with chloromethanes were with CH_2Cl_2 and the results of these are summarized in Table III. The following mechanism is consistent with the results.

$$Cl + CH_2Cl_2 \longrightarrow HCl + CHCl_2 \tag{9}$$

$$CHCl_2 + CCl_4 \longrightarrow CHCl_3 + CCl_3 \tag{10}$$

$$2CHCl_2 \longrightarrow C_2H_2Cl_4 \tag{11}$$

$$CHCl_2 + CCl_3 \longrightarrow C_2HCl_5 \tag{12}$$

$$2CCl_3 \longrightarrow C_2Cl_6 \tag{13}$$

Table III: Products in the Radiolysis of Carbon Tetrachloride Containing CH_2Cl_2

CH_2Cl_2, M	100-eV yield				
	$CHCl_3$	C_2Cl_4	$C_2H_2Cl_4$	C_2HCl_5	C_2Cl_6
0.001	1.9	0.09	0.15	1.2	2.6
0.007	2.0	0.10	0.41	1.6	2.6
0.057	2.0	0.11	0.40	1.7	2.6
0.12	2.0	0.10	0.38	1.8	2.5

All of the Cl atoms are reacting with CH_2Cl_2 because an increase in scavenger concentration did not increase the yield of $CHCl_2$ radicals. Reaction 10 is reasonable because it is exothermic based on gas phase heats of formation. From the low yield of $CHCl_3$ when CH_3Cl was the solute, the $CHCl_3$ in the system containing CH_2Cl_2 is not a result of CCl_3 radicals attacking CH_2Cl_2. This reaction is probably close to 4 kcal endothermic based on heats of formation.[27] From the above mechanism, the sum $2G(C_2H_2Cl_4) + G(C_2HCl_5) + G(CHCl_3)$ should equal $2G(C_2Cl_6) + G(C_2HCl_5) - G(CHCl_3)$. The average values of these quantities using the data in Table III are 4.5 and 4.8, respectively. These are equal within experimental error, lending support to the proposed mechanism. This number can be equated to the yield of Cl atoms in this system and is close to the value for G(HCl) (5.1 molecules/100 eV) determined by Johnston and coworkers[4] in the radiolysis of carbon tetrachloride containing 0.016 M $CHCl_3$. These values are considerably lower than the 100-eV yield of Cl atoms determined with Br_2 or HI scavengers. These data suggest that both CH_2Cl_2 and $CHCl_3$ are in some manner inhibiting the formation of radicals in irradiated carbon tetrachloride. This process is fairly efficient because the inhibition is complete at 7×10^{-3} M CH_2Cl_2. Presumably these solutes interact with the intermediates in the radiolysis of carbon tetrachloride by an energy- or charge-transfer mechanism.

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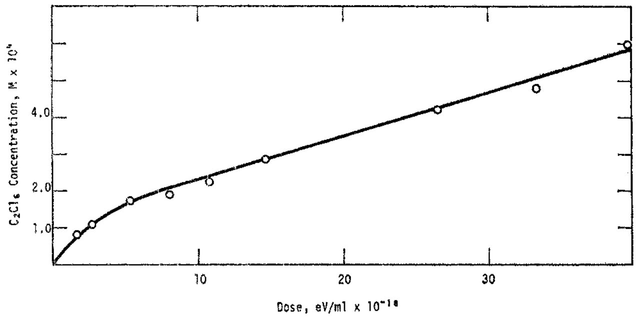

Figure 5. Dose dependence of C_2Cl_6 in the radiolysis of CCl_4 containing CCl_3Br (~0.02 *M*).

Failure to detect C_2Cl_4 as a product when CCl_3Br is a solute is consistent with the appearance of Cl_2 as the most abundant free halogen. As mentioned earlier, in all other systems reported when Cl_2 is a product, C_2Cl_4 is not. This suggests that CCl_3Br does not scavenge Cl atoms efficiently and these atoms either recombine or react with C_2Cl_4. The nonlinearity (at low doses) of the dose dependence of the yield of C_2Cl_6 (Figure 5) is similar to that observed for Cl_2 in the radiolysis of pure carbon tetrachloride at temperatures of 60° and above.[3,28] Also, from the slope of the linear portion of Figure 5, $G(C_2Cl_6)$ is 0.75, a value equal to $G(Cl_2)$ and $G(C_2Cl_6)$ determined in pure carbon tetrachloride.[2,3] This system is similar to pure carbon tetrachloride[3] except that a fraction (21%) of the free halogen is bromine. It is suggested that the nonlinearity of Figure 5 at low doses results from the dose necessary for the free halogen concentration to become large enough to scavenge CCl_3 radicals and cause a decrease in the rate of production of C_2Cl_6.

Conclusions

The initial 100-eV yield of CCl_3 radicals in the radiolysis of carbon tetrachloride measured by Br_2 or HI is 7.0 ± 0.2. In the experiments with HI, $7.0 < G(Cl) < 8.3$. In addition to a spur yield of C_2Cl_6, C_2Cl_4 is also an initial radiolytic product ($G = 0.07 - 0.10$ molecule/100 eV). In pure CCl_4 or in solutions containing solutes that do not remove Cl atoms or Cl_2, these intermediates react with C_2Cl_4 and remove it as a product. When CH_2Cl_2 or $CHCl_3$ are solutes, the values of $G(CCl_3)$ and $G(Cl)$ are lowered considerably by an interaction that does not involve the scavenging of Cl atoms.

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(28) Experiments in this laboratory have established that the yield of C_2Cl_6 is also nonlinear with dose in the radiolysis of pure carbon tetrachloride at 25°. Preliminary results indicate that the extent of nonlinearity is dependent on the void space above the sample. As the void space increases, the dose necessary to reach the linear portion of the curve increases.