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The Effects of Temperature and Various Solutes on the Radiolysis of CCl_4

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Some effects of temperature and of various solutes (Cl_2, Br_2, I_2, O_2 and C_2Cl_4) on the Co-60 gamma-ray induced decomposition of liquid CCl_4 have been investigated. Cl_2 and C_2Cl_6 were the only detectable products in pure, air-free, dry CCl_4. O_2 accelerated and C_2Cl_4 inhibited the decomposition. Scavenger studies indicated that an abundance of CCl_3-radicals were formed, most of which back reacted to form CCl_4 at measurable Cl_2 concentrations. No other radicals were detected. A rapid initial reaction with a temperature coefficient of about 3%/°C. was observed above room temperature. This reaction was strongly inhibited by Cl_2 to a terminal rate which was independent of temperature. A diffusion limited free-radical mechanism involving thermal CCl_3-radicals and excited CCl_3-radicals is proposed to rationalize the effects of temperature and Cl_2.

Introduction

It has been previously established that the gamma-radiolysis products of dry, air-free, liquid CCl_4 are chlorine and hexachloroethane produced in equal yields of about 0.7 to 0.8 molecules/100 ev. at room temperature.[3-5]

The object of this investigation has been to study the effects of temperature and various solutes (Cl_2, Br_2, I_2, O_2 and C_2Cl_4) at very small and moderately large dosages. Similar investigations have disclosed an acceleration at elevated temperatures of both the initial and terminal rates of bromine formation in the radiolysis of CCl_3Br and have demonstrated that Br_2 inhibits the decomposition above 20°.[6] These and other observations have been interpreted as evidence for diffusion controlled reactions involving possible excited intermediates. Thus, it was anticipated that the initial rate of Cl_2 formation in the radiolysis of CCl_4 might increase with increasing irradiation temperature with a similar apparent energy of activation (about 3 kcal./mole), and that Cl_2 would strongly inhibit the decomposition at low dosages. These expectations have been realized. Measurements of apparent free-radical yields have also been made, using a variety of halogens as scavengers, and the effects of oxygen and C_2Cl_4 (a common trace impurity in CCl_4) have been studied in an attempt to find an alternative explanation for the effects of temperature in the range 0 to 100°.

Experimental

"Baker Analysed" reagent grade CCl_4 was further purified by the following procedure: (1) irradiation of thoroughly outgassed CCl_4 to a dosage of about 10^{21} ev./g. in a 400-curie Co-60 gamma-ray source, (2) washing with dilute Na_2SO_3 solution followed by several washings with distilled water, (3) drying over $CaCl_2$, (4) distillation at atmospheric pressure through a 25 mm. i.d. × 1 meter column packed with lime glass beads under conditions providing 10 theoretical plates as determined by the method of McCabe and Thiele,[7] (5) storage of the middle third of the distillate over BaO in Pyrex bottles in the dark. Analyses for organic solutes were performed by gas–liquid partition chromatography in a 2-meter stainless steel column packed with DC-200 silicone oil on Celite and in a 150 foot, 0.01 in. i.d. stainless steel capillary column coated with polypropylene glycol, using alternately a hydrogen flame ionization detector and a thermal conductivity detector. "Baker Analysed" CCl_4 was found to contain traces of CS_2, $COCl_2$, CH_2Cl_2, $CHCl_3$ and C_2Cl_4 at about 0.01 mole-% each. The purification procedure removed all detectable impurities to concentrations less than about 1 p.p.m. No detectable traces of C_2Cl_6 were found in the middle third of the distillate following pre-irradiation. Tetrachloroethylene was prepared for use by distillation of Eastman White Label C_2Cl_4 to remove ethanol added as a stabilizer and was used immediately following distillation. Commercial tank Cl_2 and reagent grade Br_2 and I_2 were used without further purification except for passage of the Cl_2 through concentrated H_2SO_4 to remove moisture. Commercial tank O_2 was admitted to several samples after passage through a Drierite tower and a trap immersed in liquid nitrogen. Eastman White Label C_2Cl_6 was used without further purification in one experiment.

All samples were prepared by transfer on an all-glass high vacuum system of 5.0 cc. quantities of purified CCl_4 over BaO into Pyrex annular irradiation vessels with 1 cm. square Pyrex optical cells attached as described previously.[8] Irradiations were performed with a 100-curie Co-60 gamma-ray source of design essentially similar to one described previously.[8] Irradiations at room temperature and above were performed by enclosing sample and source capsule in a constant temperature hot air bath with control to ±2° at 100° and to ±1° or better at lower temperatures.

Analyses for free halogens were performed with a Beckman DU spectrophotometer at 25° ± 1°. Small corrections for slight coloration of the optical cells by gamma-rays were applied to all measured absorbances when significant (at dosages greater than about 10^{19} ev./g.). Molar absorptivities for Br_2, Cl_2, BrCl and I_2 in CCl_4 were carefully measured at wave lengths from 300 mμ to 600 mμ and were in excellent agreement with values measured by other workers.[9-12]

Dosage rates were measured with the Fricke dosimeter, using a value of 15.6 ev./Fe^{+++} [13] in air-saturated 0.8 *N* H_2SO_4–$FeSO_4$ solutions exposed to Co-60 gamma-rays at room temperature. All samples were irradiated at dosage rates in the range 3.3 to 5.4 × 10^{15} ev./g.-sec. as calculated directly from Fricke dosimeter measurements with corrections for the ratio of the electron densities of CCl_4 and 0.8 *N* H_2SO_4 (1.34).

G-values for the formation and disappearance of free halogens were calculated from measured slopes of plots of halogen concentration *vs.* dosage. Initial 100-ev. yields, $G(Cl_2)_0$ and $G(\text{-}X_2)_0$, were calculated from slopes at the origins of such plots. $G(Cl_2)_0$ values reported are probably accurate to ±10%. $G(\text{-}X_2)_0$ values for the initial rates of disappearance of Br_2 and I_2 are probably accurate to ±

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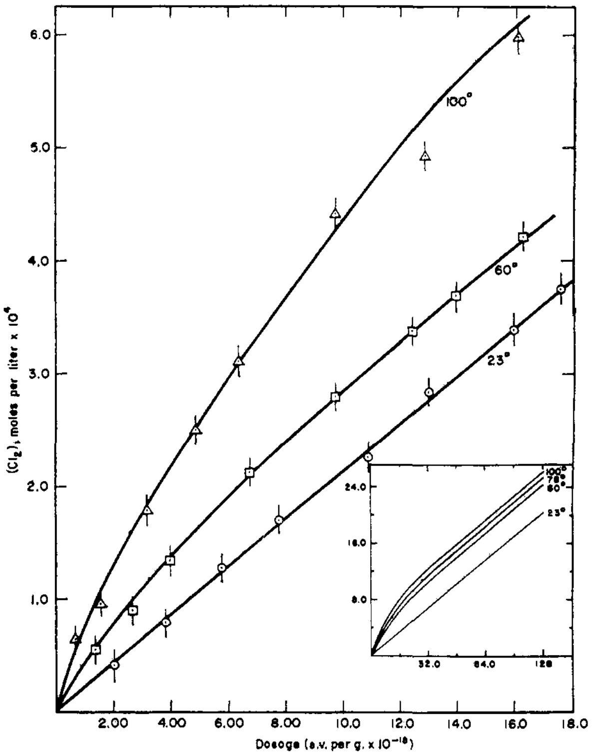

Fig. 1.—Cl_2 concentration as a function of dosage in initially pure, air-free, liquid CCl_4 at several temperatures.

10% or better. $G(Cl_2)$ values measured at high dosages are probably accurate within 5%. $G(C_2Cl_6)$ and $G(CCl_3Br)$ were calculated from GLC data using area fractions and sensitivities determined by careful calibrations with CCl_4 solutions of known concentrations bracketing the unknown concentrations and are probably accurate within ±3%.

Results and Discussion

The gamma-ray induced decomposition of pure, dry, air-free CCl_4 has been studied at irradiation temperatures from 0° to 100°. Cl_2 and C_2Cl_6 were the only products observed. Numerous attempts were made to detect other possible products at dosages up to 10^{21} ev./g. At 23° the 100-ev. yields of C_2Cl_6 and Cl_2(0.76 and 0.72) were equal within experimental error at a dosage of 5.8 × 10^{19} ev./g. It was also observed, as reported in Table I, that the initial rate of formation of Cl_2, $G(Cl_2)_0$, increased with increasing temperature between 23° and 100° with a temperature coefficient of about 3%/°C. Inhibition of the initial fast process was rapid and was complete at Cl_2 concentrations greater than about 0.001 *M*, illustrated in Fig. 1. The rate of Cl_2 formation following the early inhibition period was the same (0.74 ± 0.06 molec./100 ev.) at all temperatures from 0° to 100° independent of dosage up to 10^{21} ev./g. and of Cl_2 concentration up to 0.01 *M*.

Table I

Irradn. temp. (°C.)	$G(Cl_2)_0$	$G(C_2Cl_6)$	G-$(-Cl_2)_0$	G-$(-Br_2)_0$	G-$(-I_2)_0$
0	0.7	...	..	..	..
20	0.65[a]	...	..	..	..
23	0.72; 0.8[b]	0.76; 0.8[b]	3.5[b]	..	..
Room temp.	0.8[c]	0.9[c]	..	..	..
28	0.80	...	..	4.5	6.1
60	1.5	...	..	..	..
78	1.8	...	..	5.5	..
100	2.4	...	..	..	..

[a] *Cf.* ref. 5. [b] *Cf.* ref. 3. [c] *Cf.* ref. 4.

Table I also reports initial rates of disappearance of Br_2 and I_2 in CCl_4–Br_2 and CCl_4–I_2 solutions at 28° and a $G(-Br_2)_0$ value measured at 78°. Schulte's *G*-value for the gamma-ray induced exchange of Cl_2 and CCl_4[3] is included for comparison. In agreement with Schulte's observations with radiochlorine,[3] $G(-Br_2)_0$ and $G(-I_2)_0$ were observed to be independent of initial halogen concentrations greater than about 0.001 *M*. CCl_3Br was the only brominated product detected in irradiated CCl_4–Br_2 solutions. Measurements with the gas chromatograph demonstrated that GLC peaks of CCl_2Br_2, $CClBr_3$ and $C_2Cl_4Br_2$ would have been resolved under conditions used for analysis of these solutions. Cl_2 and C_2Cl_6 were again detected as major products in irradiated CCl_4–Br_2 solutions. Chlorine, appearing as BrCl, was formed at a more rapid initial rate [G(BrCl) = 11] in the presence of Br_2, but $G(Cl_2)$ returned to its normal value at dosages sufficiently large to effect total conversion of Br_2 initially present into CCl_3Br. The initial rate of BrCl formation was equal to $2G(-Br_2)_0 + 2G(Cl_2)_0$ at room temperature.

Johnston, Chen and Wong's observation[14] that CCl_4, but not Cl_2, is a product of the radiolysis of solid C_2Cl_6 prompted a brief investigation of the bromine scavenger products formed in an air-free, 1 *M* solution of Br_2 in CCl_4 saturated with C_2Cl_6-(28 wt. %) at room temperature. CCl_3Br was the only brominated product clearly identified and produced in appreciable yield at a dosage of about 10^{20} ev./g. Formation of partially brominated 2-carbon products in barely detectable yields was indicated by several uncharacterized peaks on the tail of the C_2Cl_6 GLC peak. C_2Cl_4 was formed in a yield comparable to that of CCl_3Br. Neither were present in the starting materials. The observed formation of C_2Cl_4 and CCl_4 and the absence of Cl_2 and CCl_2Br_2 suggest that an important mode of decomposition of C_2Cl_6 may be $2C_2Cl_6 = C_2Cl_4 + 2CCl_4$. Other observations reported below indicate that C_2Cl_4 formed in the radiolysis of C_2Cl_6 could account for the reported observation that large quantities of C_2Cl_6 inhibit formation of Cl_2 in irradiated mixtures of C_2Cl_6 and CCl_4.[14]

In the radiolysis of CCl_3Br[6] the presence of O_2 at an initial partial pressure of 400 mm. (about 0.006 *M*) was observed to increase the initial rate of free halogen formation approximately threefold at 25°. Samples of CCl_4 containing dry O_2 at an initial partial pressure of about 300 mm. at 25° were irradiated at 28° and 95°. $G(Cl_2)_0$ in the presence of O_2 was 3.0 at 28° and 11 at 95°. Radiolysis products detected were $COCl_2$, C_2Cl_6 and Cl_2. The final rate of formation of Cl_2 was the same at both temperatures and was equal to the final rate in samples irradiated in the absence of O_2. These observations demonstrate that samples containing large quantities of O_2, like carefully outgassed samples irradiated at elevated temperatures, ex-

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hibit an initial rapid rate of Cl_2 formation which steadily approaches a constant value at large dosages. It is also apparent that traces of O_2 cannot have been responsible for the initial rapid rates of Cl_2 formation in outgassed samples irradiated at temperatures above 28°.

The possibility that traces of C_2Cl_4, a persistent trace impurity and possible radiolysis product, might have inhibited the formation of Cl_2 and that this might in some manner have produced the observed curvature in the higher temperature curves of Fig. 1 prompted investigation of the effects of C_2Cl_4 on the initial rates at higher irradiation temperatures. A 0.0098 M solution of C_2Cl_4 in CCl_4 exhibited an initial $G(Cl_2)$ of 0.25 at 99° and assumed a normal terminal value of 0.75 after further irradiation. The C_2Cl_4 was completely converted to C_2Cl_6; C_2Cl_6 and Cl_2 were the only detectable radiolysis products. Thus, if C_2Cl_4 were formed in the radiolysis of pure CCl_4, it could be expected to scavenge Cl-atoms at a steadily increasing rate until a steady state concentration of C_2Cl_4 was reached, analogous to the postulated role of olefins in the radiolysis of aliphatic hydrocarbons.[15] If, however, this effect is to serve as an explanation for the rapid inhibition of the initial rate of Cl_2 formation observed only at elevated temperatures, one must account for the absence of C_2Cl_4 as an abundant product at room temperature and for the absence of $C_2Cl_4Br_2$ in irradiated CCl_4–Br_2 solutions. An argument which might appear to overcome this objection is that C_2Cl_4 is formed only at higher temperatures, thus accounting for the initial rapid rate of formation of Cl_2 and for inhibition as the C_2Cl_4 concentration approaches a steady-state concentration sufficiently low to escape detection ($10^{-5}M$ or less). Stoichiometry requires, however, that $G(C_2Cl_4)_0 = (1/2)\cdot\Delta G(Cl_2)$, where $G(C_2Cl_4)_0$ is the initial (maximum) net rate of C_2Cl_4 formation and $\Delta G(Cl_2)$ is the observed increase in the initial rate above that at room temperature (*i.e.*, $G(Cl_2)_0 - G(Cl_2)_{\text{terminal}}$). Thus, if this hypothesis were tenable, the terminal rate at higher temperatures would have to be greater than the rate at room temperature by at least $(1/2)\Delta G(Cl_2)$, where in fact the terminal rates have been observed to be independent of temperature. It is clear that an alternative explanation for the positive temperature coefficient of $G(Cl_2)$ must be found and that C_2Cl_4 is not responsible for inhibition of the temperature sensitive process.

Mechanism.—The most abundant ions in the mass spectrum of CCl_4 are CCl_3^+(54%), CCl_2^+(13%), CCl^+(15%), Cl^+(14%) and Cl^-(4%).[16,17] The emission spectrum of CCl_4 vapor between 1900 and 2700 Å., excited by electrical discharge[18] and by ultraviolet light,[19] indicates the probable presence of excited states of CCl_2, CCl, Cl_2 and Cl-atoms. Thus, a wide variety of precursors of the simple radiolysis products of CCl_4 is possible. The presence of CCl_3-radicals seems to be clearly indicated by the observed formation of CCl_3Br in the Br_2 scavenger experiments. The absence of other scavenger products and of C_2Cl_4 indicates a virtual absence of other free-radicals and would appear to rule out the presence of CCl_2 and CCl-radicals. Scavenger yields reported in Table I set a probable lower limit of about 12 radicals/100 ev. to the thermal CCl_3-radical yield. A possible upper limit of about 20 has been established with DPPH and styrene scavengers.[20,21] An abundance of CCl_3-radicals can be expected as dissociation products of CCl_4 following excitation without ionization, as possible products of electron attachment processes,[17] and possibly as products of ion-molecule and neutralization reactions of ionic species. The temperature independent yield of Cl_2 and C_2Cl_6 may be attributed to track reactions, to reactions of short-lived excited species, and possibly to ion-molecule processes. The relatively low $G(Cl_2)$ values reported for the photolysis of liquid CCl_4 (approx. 0.1)[22] and for the alpha-radiolysis of CCl_4 vapor (0.6)[23] and the reported marked increase in $G(Cl_2)$ with increasing LET in the liquid phase (0.7 for Co-60 gamma-rays; 1.6 for radon alpha-particles)[23] suggest that track effects are of special importance in liquid CCl_4.

The net chemical changes can be summed up in Reactions I and II

I. $2CCl_4 \rightsquigarrow C_2Cl_6 + Cl_2$ (ion-molecule and "hot" reactions)

II. $CCl_4 \rightsquigarrow CCl_3\cdot$ (or $CCl_3{}^*$) + $Cl\cdot$ (or $Cl\cdot{}^*$)

Reaction II may then lead to the reactions

$$CCl_3\cdot \xrightarrow{Cl\cdot} CCl_4 \text{ (Primary recombination)} \tag{1a}$$

$$CCl_3\cdot \xrightarrow{CCl_3\cdot} C_2Cl_6 \text{ (Track reaction)} \tag{1b}$$

$$CCl_3\cdot \xrightarrow{Cl_2} CCl_4 + Cl\cdot \tag{1c}$$

$$CCl_3^*\cdot \xrightarrow{Cl\cdot} CCl_4 \tag{2a}$$

$$CCl_3^*\cdot \xrightarrow{CCl_3\cdot} C_2Cl_6 \tag{2b}$$

$$CCl_3^*\cdot \xrightarrow{Cl_2} CCl_4 + Cl \tag{2c}$$

$$CCl_3^*\cdot \xrightarrow{CCl_4} CCl_3 + CCl_4^* \tag{2d}$$

$$Cl^*\cdot + CCl_4 \longrightarrow Cl_2 + CCl_3\cdot \tag{3}$$

$$2\,Cl\cdot \xrightarrow{M} Cl_2 \tag{4}$$

The scavenger yields measured with bromine and iodine indicate that a large fraction of the radicals back react *via* reactions (1c) and (2c) in initially pure CCl_4 at measurable chlorine concentrations. The small observed increase in $G(-Br_2)_0$ at 78° suggests that the higher temperature promotes escape of radicals from the track spurs at the expense of primary recombination, rather than an increased rate of radical formation *via* thermal Cl-atom attack on the solvent. It would appear, at

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first glance, that $G(Cl_2)$ should, as observed, increase with increasing temperature at very low chlorine concentrations as a direct result of a decreasing efficiency for primary recombination. At "high" chlorine concentrations, however, reactions 1c and 2c could be expected to exactly cancel the gain obtained at the expense of reactions 1a and 2a. The lowest temperature at which an increasing rate of expansion of the track can promote an increase in $G(Cl_2)$ and the lowest chlorine concentration at which the net gain in the initial rate of Cl_2 formation is cancelled out would appear to depend upon: (1) the relative rates of diffusion of Cl-atoms and CCl_3-radicals, (2) the relative reactivities of the radicals toward Cl_2 and other possible reactants and (3) the distribution, shape and population of the spurs at zero time. For the case of Co-60 gamma-rays the tracks consist of a series of widely separated discrete groups of more or less spherical spurs containing more than one radical-pair on the average.[24] A majority of spurs are formed by secondary electrons of less than about 30 ev. and will be very closely spaced.[25] Thus, overlapping of spurs within a closely spaced group or of groups of spurs would appear to favor Cl_2 and C_2Cl_6 formation, if there is a significant difference in the diffusion rates of unlike radicals. An expected increasing rate of overlap caused by increasing temperature, then, should favor reactions 1b, 2b and 4 at the expense of reactions 1a and 2a, since Cl-atoms probably diffuse faster than CCl_3-radicals in CCl_4. However, this effect will be observable at measurable Cl_2 concentrations only if the average distance between spurs is small and/or the rate constants for reactions 1c and 2c are relatively small. The rate constant of reaction 1c will, however, increase with increasing temperature more rapidly than the rate of spur overlap, assuming an activation energy of about 3 kcal. for radical diffusion in CCl_4[26] and about 8 kcal./mole for E_{1c}.[27] Thus, it appears that a positive temperature coefficient for $G(Cl_2)$ would not be observable, if only thermal radicals are scavenged by Cl_2, because reaction 1c is clearly important even at room temperature at measurable Cl_2 concentrations ($>10^{-5}$ M). It is suggested, therefore, that the observed positive temperature coefficient of $G(Cl_2)$ may be attributed to the occurrence of a diffusion-limited reaction of an excited species which requires no energy of activation for reaction with Cl_2. The apparent energy of activation obtained from the slope of a plot of log-$[G(Cl_2) - 0.7]$ *vs.* $1/T$ is about 4 ± 2 kcal./mole, a value within experimental uncertainty of the activation energy for self-diffusion of CCl_4.[26] A suggestion that the responsible species is a trichloromethyl radical is supported by the observation that temperature-sensitive initial reactions which are rapidly inhibited by free halogen products occur in CCl_4 and in CCl_3Br[6] but do not occur in liquid CCl_2Br_2, as demonstrated in this Laboratory by L. L. Schwartz in a series of experiments at temperatures ranging from 0 to 140°. The behavior of CCl_2Br_2 is otherwise essentially identical to that of CCl_3Br. It has been assumed in a previous paper[6] that excited radicals in CCl_3Br must retain sufficient energy of excitation to react with the solvent following 10^4 to 10^5 encounters in order to exhibit a sensitivity to halogen concentration in very dilute solutions. It now appears that this assumption is not necessary, if radical combination reaction 2b predominates for excited radicals which manage to escape primary recombination. The diffusing excited radical need not be sufficiently excited to react with the solvent at any time but need retain only a relatively low level of vibrational excitation (>8 kcal.) during the time required for completion of radical combination reactions between neighboring spurs ($>\sim 10^{-8}$ sec. but $<\sim 10^{-4}$ sec. for the case of spherical spurs in liquid water exposed to 1 Mev. gamma-rays).[28] Observation that inhibition of the temperature sensitive reaction is complete beyond a Cl_2 mole-fraction of 10^{-4} also indicates a lower limit for the lifetime of the hypothetical excited radicals of the order of 10^{-8} to 10^{-9} seconds, assuming that they react with Cl_2 on every encounter and a collision time of the order of 10^{-13} sec.

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