[CONTRIBUTION FROM RADIATION RESEARCH LABORATORIES, MELLON INSTITUTE PITTSBURGH, PA.]

The Photolysis of Carbon Tetrachloride in the Presence of Ethane and Ethylene¹

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The photolysis of carbon tetrachloride in the presence of ethane and ethylene has been investigated at various temperatures and at various ethane to ethylene ratios. The primary step in the photolysis of CCl₄ produces CCl_3 radicals and Cl atoms. Chlorine atoms react with ethylene to produce C_2H_4Cl radicals and with ethane to form HCl and C₂H₅ radicals. The recombination and disproportionation reactions 3, 5, 7, 8, 12, 14, 15 and 16 involving these radicals have been investigated. The data indicate: $k_5/k_3 \le 0.05$, $k_8/k_7 = 0.14 \pm 0.03$; k_{14}/k_{14} $k_{12} \simeq 0.22$; and $k_{16}/k_{15} = 0.22 \pm 0.03$. Data on the cross combinations of the various radicals are also reported.

Introduction

We have recently investigated the photolysis of carbon tetrachloride in the presence of ethylene.³ That investigation gave information regarding disproportionation and recombination reactions of CCl_3 and C₂H₄Cl radicals. We have now extended this investigation by studying the photolysis of carbon tetrachloride in the presence of ethane and ethylene. Trotman-Dickenson and co-workers⁴ report that only a small activation energy is required for the abstraction of a hydrogen atom from ethane by a chlorine atom. Thus we should produce ethyl radicals in the presence of C_2H_4Cl and CCl_3 radicals.

It should, therefore, be possible to obtain data regarding the various disproportionation and recombination reactions involving CCl₃, C₂H₄Cl and C₂H₅ radicals.

Until now, information on disproportionation and recombination reactions has been limited mainly to unsubstituted alkyl radicals. Information on the reactions of chlorinated alkyl radicals is, obviously, important for the understanding of the reaction mechanisms in the photolysis and radiolysis of chlorinecontaining compounds. We also hope that this information may contribute to a better understanding of disproportionation and recombination mechanisms in general.

Experimental

The experimental technique and equipment have been described elsewhere.³ A Hanovia type 73 A 10 medium pressure arc was used as the light source. The intensity of the arc was varied by inserting wire gauge screens between the light source and the reaction vessel. Constant temperature at 58° was maintained by an aluminum block furnace. Temperature control at 0° was obtained by placing the cell in an ice-water bath and transmitting the light through a 5-mm. layer of water into the cell.

The photolysis of carbon tetrachloride in the presence of ethylene and ethane produced the major reaction products: C_2H_5Cl , C_4H_{10} , CCl_3H , $(C_2H_4Cl)_2$, $C_2H_5Ccl_3$, $CH_2CiCH_2CCl_3$ and C_2Cl_8 . All the products mentioned above were determined quantitatively by gas chromatography. A 6-ft. column packed with 25% (by weight) of silicone grease on firebrick was used for the analysis. Trace amounts of vinyl chloride were also observed. Since we were not able to obtain pure samples of $C_2H_5CCl_3$ and of $CH_2ClCH_2CCl_3$ we could not measure the sensitivity of these compounds for quantitative determination by gas chromatography. We have attributed sensitivities to these compounds based on their molecular weights and their retention times on the gas chromatograph. This introduces the possibility of a the gas chromatograph. This introduces the possibility of a systematic error in reporting the amounts in which these compounds were formed. We do not believe that this error will exceed 10% of the values reported by us. To confirm the identification of the products, individual compounds were collected as they came off the gas chromatograph and excluded the ways reported by the sector of the gas chromatograph.

and analyzed by mass spectrometer.

Results and Discussion

The results of a series of experiments in which carbon tetrachloride was photolyzed in the presence of ethane and ethylene are reported in Table I. The ratio of ethylene to ethane was varied by a factor of 7. Less than 1% of the carbon tetrachloride initially present was decomposed during the photolysis.

The following reaction mechanism is suggested to explain the formation and distribution of the reaction products

$CCl_4 + h\nu \longrightarrow CCl_3 + Cl$	(1)
$Cl + C_2H_4 \longrightarrow C_2H_4Cl$	(2)
$2C_2H_4Cl \longrightarrow (C_2H_4Cl)_2$	(3)
$2C_{2}H_{4}Cl \longrightarrow C_{2}H_{4} + C_{2}H_{4}Cl_{2}$	(4)
$2C_{2}H_{4}Cl \longrightarrow C_{2}H_{5}Cl + C_{2}H_{3}Cl$	(5)
$2CCl_3 \longrightarrow C_2Cl_6$	(6)
$C_2H_4Cl + CCl_3 \longrightarrow CCl_3C_2H_4Cl$	(7)
$C_2H_4Cl + CCl_3 \longrightarrow CCl_3H + C_2H_3Cl$	(8)
$Cl + C_2H_6 \longrightarrow C_2H_5 + HCl$	(9)
$2C_2H_5 \longrightarrow C_4H_{10}$	(10)
$2C_2H_5 \longrightarrow C_2H_6 + C_2H_4$	(11)
$C_2H_5 + C_2H_4Cl \longrightarrow C_4H_9Cl$	(12)
$C_2H_5 + C_2H_4C1 \longrightarrow C_2H_6 + C_2H_3C1$	(13)
$C_2H_5 + C_2H_4C1 \longrightarrow C_2H_4 + C_2H_5C1$	(14)
$C_2H_5 + CCl_3 \longrightarrow C_2H_5CCl_3$	(15)
$C_2H_5 + CCl_3 \longrightarrow C_2H_4 + CCl_3H$	(16)

Reactions 1 to 8 describe the primary process and the resulting reactions if CCl4 is photolyzed in the presence of C_2H_4 . These reactions have been discussed in de-tail previously.³ The formation of butane and of 1,1,1-trichloropropane clearly suggests that ethyl radicals are produced if $CC1_4$ is photolyzed in the presence of ethylene and ethane. The formation of ethyl radicals is explained by reaction 9. Reaction 9 has an activation energy of about 1 kcal./mole⁴ and is thus quite probable even at the relatively low temperatures of this investigation. Reactions 10 to 16 represent possible recombination and disproportionation reactions of ethyl radicals with each other and with C_2H_4Cl and CCl₃ radicals.

We have not observed any evidence in this and in our previous study to suggest that reaction 17 is of any importance under the experimental conditions of this investigation.

$$Cl + C_2H_4 \longrightarrow C_2H_3 + HCl$$
(17)

Although reaction 17 is analogous to reaction 9, several reasons may be advanced to exclude reaction 17. First, the C-H bond in C₂H₄ is considerably stronger than the C-H bond in C_2H_6 . Thus E_{17} will be considerably larger than E_9 . Second, the addition of chlorine atoms to ethylene requires only a small⁵ or no⁶ activation energy. Thus reaction 17 is not expected to compete with reaction 2 except at high

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⁽⁶⁾ H. Smitz, H. J. Schumacher and A. Jager, Z. physik. Chem., B51, 281 (1952).

TABLE I

PHOTOLVELS OF	CARRON TETRACHIORIDI	TH THE DREEN	DE OF FTUANE	ND FTUVI ENE
1 1101011313 01	CARBON I EIRACHEORIDI	S IN THE I RESENV	LE OF LINANE A	ND DINILENE

E-at	p ., b	n h	т b			D.	D		0	D	D	k7/	k15/	k2/
Expt.	$P_{C_2H_4}$	$P_{C_2H_6}$	PCCI4	$R_{C_4H_{10}}$	$K_{C_2H_5C1}$	KCHCl3	KC4H9Cl	KC2H5CCI3	$R(C_2H_4Cl)_2$	R _{CCl3} C ₂ H ₄ Cl	$R_{C_2C_{1_6}}$	R61/2R31/2	R6 ^{1/2} R10 ^{1/2}	Rş
							l'emperat	ure, 0°						
1	14.5	7.5	33.5	1.84	• •	5.98	5.41	10.20	3.99	19.33	16.09	2.42	1.87	
2	9.0	21.0	31.0	8.13		6.80	5.41	20.07	0.92	8.64	14.64	2.46	1.84	
3	23.0	16.0	34.5	2.40	1.19	5.89	5.95	12.54	3.68	17.44	16.23	2.26	2.00	0.85
4	10.5	4.5	29.0	3.61	1.41	5.30	7.03	12.93	3.44	17.44	13.06	2.60	1.87	. 46
5	15.0	5.5	33.5	1.81	1.20	5.89	5.92	10.03	4.91	24 , 00	17.41	2.61	1.79	. 68
6*	10.5	7.5	18.0	3.01		4.71	4.19	12.04	1,47	10.16	11.87	2.44	2.01	
7	12.0	11.0	21.0	3.01		5.30	4.19	12.04	1.47	11.16	13.06	2.55	1.93	
8	15.5	7.5	22.0	1.18		3.48	3.38	7.87	2.41	14.17	12.46		2.04	
9	11.0	21.5	20.5	6.62		4.71	5.09	16.55	0.98	8.47	11.87	2.50	1.86	
10	25.0	11.0	22.0	0.60		3.42	2.86	5.06	3.41	15.73	12.17	2.43	1.87	
11	4.5	15.0	20.0	7.83		4.71	5.32	18.56	0.90	8.00	13.06	2.33	1.83	
12*	11.0	57.0	20.0	7.16	0.98	4.68	4.82	16.91	0.81	7.30	11.01	2.45	1.90	2.43
						Т	`emperati	ure, 30°						
13	6.54	42.0	46.5	3.39		2.58	1.85	7.62	0.25	2.57	4.45	2.44	1.96	
14	40.0	14.5	41.0	0.73	0.68	1.44	2.63	3.20	2.39	7.37	3.67	2.47	1.96	0.67
15	36.0	36.0	44.5	1.39	.38	1.84	1.83	4.37	0.61	2.97	3.46	2.48	1.99	. 62
16	34.0	5.0	31.5	0.29	.34	1,44	1.62	1.97	2.27	6.96	3.48	2.45	1.97	.41
17	18.0	5.0	31.5	.65		1.44	2.08	2.81	1.68	5.93	3.28	2.52	1.94	
18	11.6	4.5	33.0	. 88		1.72	1.95	3.69	1.08	4,66	3.28	2.48	2.17	
19	16.0	4.5	30.0	. 88		1.46	1.87	3.45	0.99	4.86	3.58	2.58	1.94	
20	24.0	5.6	32.0	.90		1.46	2.72	3.71	2.04	6.71	3.48	2.52	2.03	
21	18.6	28.5	31.0	2.06		1.76	1.60	5.54	0.31	2.68	3.86	2.46	1.98	
22*	20.0	38.0	31.0	1.76		1.72	2.39	5.14	. 81	3.62	2.70	2.42	2.36	
23*	20.0	54.0	30.0	1.76		1.58	2.39	5.14	. 81	3.84	3.09	2.43	2.20	
						Т	`emperati	ure, 58°						
24	11.0	10.5	29.0	1.91	0.28	1.59	1.38	4.65	0.25	2.20	3.28	2.44	1.86	0.38
25	11.0	17.0	29.5	2.06	. 24	1.45	1.14	4.90	. 16	1.83	3.48	2.47	1.86	0.48
26	10.8	33.0	32.0	2.64	. 39	2.05	1.94	5.92	. 36	2.81	3.67	2.44	1.90	1.19
27	19.0	5.5	29.5	0.88	. 29	1.15	1.32	2.95	. 84	3.35	2.70	2.91	1.90	0.28
28	19.6	11.5	26.5	1.17	. 34	1.43	1.51	3.92	. 49	2.80	2.90	2.35	2.13	. 59
29*	20.5	20.0	31.5	1.76	.38	1.38	1.60	4.41	. 36	2.29	2.70	2.34	2.02	. 46

^{*a*} Open spaces indicate that under the given conditions this compound was formed in too small amounts to allow its determination; experiment numbers marked * were carried out at 9% intensity, all others at 100%. ^{*b*} Pressures in mm. at temperature of investigation. $R = \text{rate of product formed in molecules/(sec. cc.)} \times 10^{-12}$.

temperatures as indeed observed by Rust and Vaughan.⁷ Accepting the reaction mechanism we may derive the following equations for the cross combinations of the various radicals produced during the photolysis

$$\begin{split} R_{\rm CC1_3C_2H_4C1}/R^{1/2}{}_{\rm C_2C1_6}R^{1/2}{}_{\rm (C_2H_4C1)_2} &= k_7/k_6{}^{1/2}k_3{}^{1/2} \qquad ({\rm I}) \\ R_{\rm C_{2H_6CC1_3}}/R^{1/2}{}_{\rm C_2C1_6}R^{1/2}{}_{\rm C_4H_{10}} &= k_{15}/k_6{}^{1/2}k_{10}{}^{1/2} \qquad ({\rm II}) \\ R_{\rm C_{4H_9C1}}/R^{1/2}{}_{\rm C_{4H_{10}}}R^{1/2}{}_{\rm (C_{2H_4C1_2})} &= k_{12}/k_{10}{}^{1/2}k_3{}^{1/2} \qquad ({\rm III}) \end{split}$$

The data obtained for $R_{\rm CCl_3C_2H_4Cl}/R^{1/2}C_2Cl_6R^{1/2}(C_2H_4Cl)_2$ and $R_{C_{2}H_{5}CCl_{5}}/R^{1/2}c_{4}Cl_{6}R^{1/2}c_{4H_{10}}$ are given in Table I and indicate $k_{7}/(k_{6}^{1/2}k_{3}^{1/2}) = 2.5 \pm 0.15$ and $k_{15}/(k_{6}^{1/2}k_{10}^{1/2})$ $= 2.0 \pm 0.15$. An identical value for $k_{1}/(k_{6}^{1/2}k_{3}^{1/2})$ has been obtained by us previously.³ No other data are available in the literature for the ratio $k_{15}/(k_6^{1/2}k_{10}^{1/2})$. In deriving eq. I and II we have accepted that 1,4dichlorobutane is formed by recombination of two C₂H₄Cl radicals and that C₄H₁₀ is formed by recombination of two ethyl radicals. It is obvious that in that case we must also accept recombination of C2H5 and C₂H₄Cl radicals to form 1-chlorobutane. Unfortunately, we have not been able to measure the amounts of 1-chlorobutane formed since the retention time of this compound coincided with the appearance of the excess undecomposed CCl₄ on the gas chromatograph. For reasons to be discussed later it was important to us to obtain an estimate of the amounts of 1-chlorobutane formed. We have calculated therefore the amounts of 1-chlorobutane formed according to eq. III from the amounts of C_4H_{10} and $(C_2H_4Cl)_2$ observed assuming $k_{12}/(k_{10}^{1/2}k_3^{1/2})$ to be equal to 2.0. (7) F. F. Rust and W. E. Vaughan, J. Org. Chem., 5, 472 (1940); 7, 491 (1942).

Thus the data given in Table I for $R_{C_4H_5Cl}$ are not experimentally observed values but calculated values subject to a systematic error if $k_{12}/(k_{10}^{1/2}k_3^{1/2})$ deviates from 2.0. Schindler⁸ obtained $k_{12}/k_{10}^{1/2}k_3^{1/2} = 1.92$ from a study of the radiolysis of C_2H_5Cl in the gas phase.

According to the reaction mechanism, chloroform is produced by reactions 8 and 16 only. The following equation may be derived under this condition.

$$\frac{R_{\rm CCl_3H}}{R_{\rm C_2H_5CCl_3}} = \frac{k_{16}}{k_{15}} + \frac{k_8}{k_6^{1/2}k_3^{1/2}} \frac{R^{1/2}c_2c_{16}R^{1/2}c_2H_4Cl_3}{R_{\rm C_2H_5CCl_3}} \quad (IV)$$

Equation IV is plotted in Fig. 1. In spite of some scatter, the data show clearly a general agreement with eq. IV and thus with the proposed reaction mechanism. Figure 1 also shows that there is no noticeable temperature effect indicating that $E_{16} - E_{15}$ and $E_8 - (1/2\dot{E}_6 + 1/2E_3)$ are zero or close to zero. This is in agreement with general observations regarding activation energy differences between recombination and disproportionation reactions. From Fig. 1 we obtain $k_{16}/k_{15} = 0.22 \pm 0.03$ and $k_8/k_6^{1/2}k_3^{1/2} = 0.36 \pm 0.04$. Recently, Gregory and Wijnen⁹ studied the photolysis of mixtures of diethyl ketone and carbon tetrachloride. They obtained $k_{16}/k_{15} = 0.24 \pm 0.04$ in excellent agreement with the value obtained in this investigation. From $k_8/k_6^{1/2}k_3^{1/2}$ and $k_7/k_6^{1/2}k_3^{1/2}$ (eq. I) we calculate $k_8/k_7 =$ 0.14 ± 0.03 . This value is in good agreement with previous data yielding $k_8/k_7 = 0.11 \pm 0.02.^3$ Equation V is derived from the reaction mechanism

(8) R. N. Schindler, to be published.

(9) J. E. Gregory and M. H. J. Wijnen, to be published.

and relates $R_{C_2H_3Cl}$ to $R_{(C_2H_4Cl)_2}$ and $R^{1/2}_{C_4H_{10}}$

$$\frac{R_{C_2H_5C_1}}{R_{(C_2H_4Cl)_2}} = \frac{k_5}{k_3} + \frac{k_{14}}{k_3^{1/2}k_{10}^{1/2}} \frac{R^{1/2}C_{4H_{10}}}{R^{1/2}(C_{2H_4Cl)_2}}$$
(V)

Equation V is plotted in Fig. 2 for the data obtained at 0, 30 and 58°. Again no temperature effect is visible. From Fig. 2 we obtain $k_2/k_3 \leq 0.05$ and $k_{14}/k_3^{1/2}k_{10}^{1/2} = 0.42 \pm 0.03$. Previous estimates indicated $k_5/k_3 \leq 0.1.^3$ No data are available in the literature for $k_{14}/k_3^{1/2}k_{10}^{1/2}$. Accepting $k_{12}/k_3^{1/2}k_{10}^{1/2} = 1.92^8$ we calculate $k_{12}/k_{14} = 0.22$.

It is interesting to compare the various ratios of rate constants for disproportionation over recombination (D/R) obtained in this investigation

$$C_{2}H_{5} + CCl_{3} \longrightarrow CCl_{3}H + C_{2}H_{4} \qquad D/R = 0.22$$

$$C_{2}H_{4}Cl + CCl_{3} \longrightarrow CCl_{3}C_{2}H_{5} \qquad D/R = 0.12$$

$$C_{2}H_{4}Cl + CCl_{3} \longrightarrow Ccl_{3}C_{2}H_{4}Cl \qquad D/R = 0.12$$

$$C_{2}H_{5} + C_{2}H_{4}Cl \longrightarrow C_{2}H_{5}Cl + C_{2}H_{4} \qquad D/R = 0.22$$

$$C_{2}H_{5} + C_{2}H_{4}Cl \longrightarrow C_{3}H_{5}Cl + C_{2}H_{4} \qquad D/R = 0.22$$

$$C_{2}H_{4}Cl + C_{2}H_{4}Cl \longrightarrow C_{3}H_{5}Cl + C_{2}H_{3}Cl \qquad D/R < 0.05$$

The ratio of disproportionation over recombination for two ethyl radicals is 0.14 ± 0.02 .¹⁰⁻¹² The results clearly indicate that the substitution of one or more ethyl radicals by chlorinated alkyl radicals has a considerable effect on the ratio of disproportionation over recombination. The number of hydrogen atoms available for disproportionation seems to have little or no relation to the observed ratios.

Finally, we have attempted to measure the activation energy difference between reactions 2 and 9

$$Cl + C_2H_4 \longrightarrow C_2H_4Cl$$
 (2)

$$C_1 + C_2 H_6 \longrightarrow C_2 H_5 + HCl \tag{9}$$

According to these reactions $R_{C_2H_4Cl}/R_{C_2H_6}[C_2H_6]/[C_2H_4] = k_2/k_9$. In the above equation $R_{C_2H_4Cl}$ denotes the rate of production of C_2H_4Cl radicals, $R_{C_2H_6}$ the rate of production of ethyl radicals. Approximate values for $R_{C_2H_4Cl}$ and $R_{C_2H_6}$ may be calculated from $R_{C_2H_4Cl} = 2R_{(C_2H_4Cl)_2} + R_{C_4H_5Cl} + R_{C_2H_4Cl} + R_{C_2H_4Cl} + 0.12R_{CC_1A_2C_1A_2C_1}$ (to account for C_2H_3Cl pro-

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Fig. 2.—Plot of $R_{C_{2}H_{5}Cl}/R_{(C_{2}H_{4}Cl)_{2}}$ vs. $R^{\frac{1}{2}C_{4}H_{10}}/R^{\frac{1}{2}}(C_{2}H_{4}Cl)_{2}$ at 0° (•), 30° (\odot) and 58° (\triangle).

duced by reaction 8) and $R_{C_2H_8} = 2R_{C_4H_{10}} + 0.28$ - $R_{C_4H_{10}}$ (to account for C_2H_6 and C_2H_4 production by reaction 11) + $R_{C_4H_9C1}$ + $0.22R_{C_4H_9C1}$ (= $R_{C_2H_4}$ produced by reaction 14) + $R_{C_2H_5CC_{18}} + 0.22R_{C_2H_5CC_{18}}$ (= $R_{C_2H_4}$ produced by reaction 16). Data thus obtained for k_2/k_9 are given in Table I for all runs where we were able to measure C_2H_5C1 production. It is obvious that this method was not expected to give and does not give accurate values for k_2/k_9 . In spite of the scatter, the data, nevertheless, indicate that k_2/k_9 does not vary considerably between 0 and 58°. This indicates that E_9 is approximately equal to E_2 . If we accept $E_2 = 0$ kcal.,⁶ our data thus substantiate the relatively low value of $E_9 = 1$ kcal. reported by Trotman-Dickenson and co-workers.⁴

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Effect of Gases on the Conductivity of Organic Solids. I. The Anthracene–Iodine Interaction¹

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Although gases are generally thought to affect the surface conductivity of organic crystals alone, evidence is presented that the bulk dark conductivity of anthracene is increased in a sensitive, specific and reversible manner upon exposure to iodine.

Introduction

In several investigations of the effect of gases on the dark and photoconductivity of organic crystals,² it has

(1) Supported by the U. S. Army Chemical Center under Subcontract SCE-17250-60 with Melpar, Inc.

generally been accepted that these phenomena are restricted to the surface. Thus in a sandwich cell provided with a guard ring, Waddington and Schneider^{2g} report no effect of oxygen on the photocurrent of anthracene, whereas in a surface cell a pronounced increase is observed.

These same types of surface effects on the conductivity have been observed for a large number of dye films exposed to gases.³ A particularly unusual example is the claim of the sensitivity of photoconduction in a

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