

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

## The Photolysis of Carbon Tetrachloride in the Presence of Ethane and Ethylene<sup>1</sup>

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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  $\text{CCl}_4$  produces  $\text{CCl}_3$  radicals and Cl atoms. Chlorine atoms react with ethylene to produce  $\text{C}_2\text{H}_4\text{Cl}$  radicals and with ethane to form HCl and  $\text{C}_2\text{H}_5$  radicals. The recombination and disproportionation reactions 3, 5, 7, 8, 12, 14, 15 and 16 involving these radicals have been investigated. The data indicate:  $k_5/k_3 \leq 0.05$ ,  $k_8/k_7 = 0.14 \pm 0.03$ ;  $k_{14}/k_{12} \approx 0.22$ ; 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.<sup>3</sup> That investigation gave information regarding disproportionation and recombination reactions of  $\text{CCl}_3$  and  $\text{C}_2\text{H}_4\text{Cl}$  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-workers<sup>4</sup> 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  $\text{C}_2\text{H}_4\text{Cl}$  and  $\text{CCl}_3$  radicals.

It should, therefore, be possible to obtain data regarding the various disproportionation and recombination reactions involving  $\text{CCl}_3$ ,  $\text{C}_2\text{H}_4\text{Cl}$  and  $\text{C}_2\text{H}_5$  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 chlorine-containing 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.<sup>3</sup> 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 gauze 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:  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{CCl}_3\text{H}$ ,  $(\text{C}_2\text{H}_4\text{Cl})_2$ ,  $\text{C}_2\text{H}_5\text{CCl}_3$ ,  $\text{CH}_2\text{ClCH}_2\text{CCl}_3$  and  $\text{C}_2\text{Cl}_6$ . 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  $\text{C}_2\text{H}_5\text{CCl}_3$  and of  $\text{CH}_2\text{ClCH}_2\text{CCl}_3$  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 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 analyzed by mass spectrometer.

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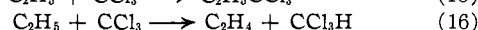
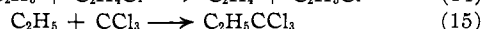
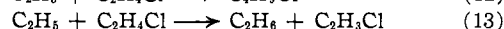
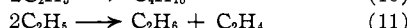
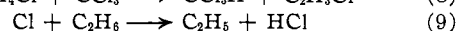
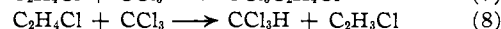
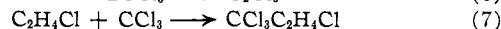
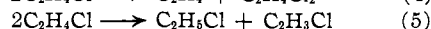
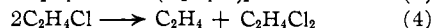
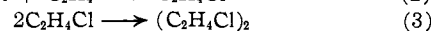
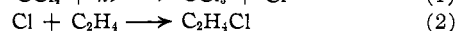
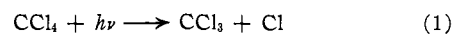
(3) B. C. Roquette and M. H. J. Wijnen, *J. Chem. Phys.*, **38**, 4 (1963).

(4) G. C. Fettes, J. H. Knox and A. F. Trotman-Dickenson, *Can. J. Chem.*, **38**, 1643 (1960).

### Results and Discussion

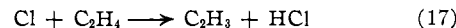
The results of a series of experiments in which carbon tetrachloride was photolyzed in the presence of ethane and ethylene are reported in Table I. The ratio of ethylene to ethane was varied by a factor of 7. Less than 1% of the carbon tetrachloride initially present was decomposed during the photolysis.

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



Reactions 1 to 8 describe the primary process and the resulting reactions if  $\text{CCl}_4$  is photolyzed in the presence of  $\text{C}_2\text{H}_4$ . These reactions have been discussed in detail previously.<sup>3</sup> The formation of butane and of 1,1,1-trichloropropane clearly suggests that ethyl radicals are produced if  $\text{CCl}_4$  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./mole<sup>4</sup> 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  $\text{C}_2\text{H}_4\text{Cl}$  and  $\text{CCl}_3$  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.



Although reaction 17 is analogous to reaction 9, several reasons may be advanced to exclude reaction 17. First, the C-H bond in  $\text{C}_2\text{H}_4$  is considerably stronger than the C-H bond in  $\text{C}_2\text{H}_6$ . Thus  $E_{17}$  will be considerably larger than  $E_9$ . Second, the addition of chlorine atoms to ethylene requires only a small<sup>5</sup> or no<sup>6</sup> activation energy. Thus reaction 17 is not expected to compete with reaction 2 except at high

(5) T. D. Stewart and B. Weidenbaum, *J. Am. Chem. Soc.*, **57**, 2036 (1935).

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

TABLE I  
 PHOTOLYSIS OF CARBON TETRACHLORIDE IN THE PRESENCE OF ETHANE AND ETHYLENE<sup>a</sup>

Expt.	$P_{C_2H_4}^b$	$P_{C_2H_6}^b$	$P_{CCl_4}^b$	$R_{C_4H_{10}}^a$	$R_{C_2H_5Cl}$	$R_{CHCl_3}$	$R_{C_4H_9Cl}$	$R_{C_2H_5CCl_3}$	$R_{(C_2H_4Cl)_2}$	$R_{CCl_3C_2H_4Cl}$	$R_{C_2Cl_6}$	$k_7/k_6^{1/2}k_3^{1/2}$	$k_{15}/k_8^{1/2}k_{10}^{1/2}$	$k_2/k_9$
Temperature, 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
Temperature, 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	
Temperature, 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

<sup>a</sup> 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%. <sup>b</sup> Pressures in mm. at temperature of investigation.  $R$  = rate of product formed in molecules/(sec. cc.)  $\times 10^{-12}$ .

temperatures as indeed observed by Rust and Vaughan.<sup>7</sup>

Accepting the reaction mechanism we may derive the following equations for the cross combinations of the various radicals produced during the photolysis

$$R_{CCl_3C_2H_4Cl}/R^{1/2}C_2Cl_6R^{1/2}(C_2H_4Cl)_2 = k_7/k_6^{1/2}k_3^{1/2} \quad (I)$$

$$R_{C_2H_5CCl_3}/R^{1/2}C_2Cl_6R^{1/2}C_4H_{10} = k_{15}/k_8^{1/2}k_{10}^{1/2} \quad (II)$$

$$R_{C_4H_9Cl}/R^{1/2}C_4H_{10}R^{1/2}(C_2H_4Cl)_2 = k_{12}/k_{10}^{1/2}k_3^{1/2} \quad (III)$$

The data obtained for  $R_{CCl_3C_2H_4Cl}/R^{1/2}C_2Cl_6R^{1/2}(C_2H_4Cl)_2$  and  $R_{C_2H_5CCl_3}/R^{1/2}C_2Cl_6R^{1/2}C_4H_{10}$  are given in Table I and indicate  $k_7/(k_6^{1/2}k_3^{1/2}) = 2.5 \pm 0.15$  and  $k_{15}/(k_8^{1/2}k_{10}^{1/2}) = 2.0 \pm 0.15$ . An identical value for  $k_7/(k_6^{1/2}k_3^{1/2})$  has been obtained by us previously.<sup>3</sup> No other data are available in the literature for the ratio  $k_{15}/(k_8^{1/2}k_{10}^{1/2})$ . In deriving eq. I and II we have accepted that 1,4-dichlorobutane is formed by recombination of two  $C_2H_4Cl$  radicals and that  $C_4H_{10}$  is formed by recombination of two ethyl radicals. It is obvious that in that case we must also accept recombination of  $C_2H_5$  and  $C_2H_4Cl$  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  $CCl_4$  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  $R_{C_4H_9Cl}$  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. Schindler<sup>8</sup> 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.

$$\frac{R_{CCl_3H}}{R_{C_2H_5CCl_3}} = \frac{k_{16}}{k_{15}} + \frac{k_8}{k_8^{1/2}k_3^{1/2}} \frac{R^{1/2}C_2Cl_6R^{1/2}(C_2H_4Cl)_2}{R_{C_2H_5CCl_3}} \quad (IV)$$

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  $E_8 - (1/2E_6 + 1/2E_3)$  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  $k_8/k_8^{1/2}k_3^{1/2} = 0.36 \pm 0.04$ . Recently, Gregory and Wijnen<sup>9</sup> 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  $k_8/k_8^{1/2}k_3^{1/2}$  and  $k_7/k_6^{1/2}k_3^{1/2}$  (eq. I) we calculate  $k_8/k_7 = 0.14 \pm 0.03$ . This value is in good agreement with previous data yielding  $k_8/k_7 = 0.11 \pm 0.02$ .<sup>3</sup>

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.

