to occur in Sn1 reactions of *t*-butyl chloride and α-phenylethyl bromide, the two substances for which carbon isotope effects on Sn1 substitution have been measured. In *t*-butyl chloride, hyperconjugative interaction between the forming positive charge and adjacent methyl groups will strengthen the nonreacting C–C bonds, whereas in α-phenylethyl bromide, hyperconjugation of the positive center with the single methyl group will be aided by ordinary conjugation with the phenyl substituent. The fact that the C–C stretching force constant of the trimethylcarbonium ion is 35% stronger than the corresponding force constant in alkanes[27] indicates that hyperconjugative bond strengthening is appreciable. Ordinary conjugation, however, should have a stronger influence on bond strength than hyperconjugation, and this may be the reason why the isotope effect for *t*-butyl chloride is greater than that for α-phenylethyl bromide even when the former is reduced to a carbon-12 : carbon-13 ratio.

It can be concluded, therefore, that carbon isotope effects in these carbonium ion-producing reactions are low because conjugation strengthens the nonreacting bonds to the isotopically substituted atom. It is tempting to generalize these results by saying that all carbon isotope effects on Sn1 substitution will be low, but such a generalization may prove to be correct only because Sn1 substitution is commonly observed in systems where conjugative stabilization of the forming positive charge makes this kind of reaction possible. Should a system be examined in which Sn1 substitution is forced in the absence of conjugative assistance, a large isotope effect may be found, and this may in fact be the reason why the solvolysis of methyl iodide in the presence of silver ion (possibly an Sn1 reaction) shows a carbon-14 isotope effect of nearly 9%.[9a]

The Photolysis of Phosgene–Ethylene Mixtures[1]

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Contribution from the Aerospace Corporation, El Segundo, California. Received September 19, 1964

Chlorine atoms were produced by the photolysis of $COCl_2$ with 2537-Å. radiation at 23°. The atoms were quantitatively scavenged by C_2H_4, and the reactions of the resulting radicals were studied. The significant variable in the system is $(C_2H_4)/I_a^{1/2}$, which was varied by a factor of 10^4. Only two radicals, C_2H_4Cl and C_4H_8Cl, are important. At high $(C_2H_4)/I_a^{1/2}$, the products of the less important $C_6H_{12}Cl$ radical can also be detected. The photochemical products found were CO, 1-C_6H_{12}, C_2H_5Cl, 1-C_4H_9Cl, 1-$C_6H_{13}Cl$, $1,2$-$C_2H_4Cl_2$, $1,3$-$C_4H_8Cl_2$, $1,4$-$C_4H_8Cl_2$, and $1,6$-$C_6H_{12}Cl_2$. Also, another C_6 hydrocarbon, a C_4H_7Cl compound, and two $C_6H_{11}Cl$ compounds were detected. Not detected, but surely present, were C_2H_3Cl and C_4 hydrocarbons. From the generalized propagation–termination mechanism and the behavior of the products with changes in $(C_2H_4)/I_a^{1/2}$, the classes of radical–radical reactions that lead to each product could be established without a detailed knowledge of the particular radical–radical reactions. This classification is listed in Table III. The detailed mechanism was deduced; in order to explain the results, it was necessary to introduce, as the principal reaction of two C_4H_8Cl radicals, the unusual reaction $2C_4H_8Cl \rightarrow C_4H_7Cl + C_2H_5Cl + C_2H_4$. Many ratios of rate constants were determined; they are collected in Table IV. When the free-electron ends of two radicals approach each other, either H-atom transfer or combination can occur. The ratio of the rates of the two processes is about 0.4 irrespective of the radicals. On the other hand, Cl-atom transfer occurs from a different orientation. The evidence indicates that the ratio of Cl-atom transfer to H-atom transfer is markedly altered as the chain length of the radicals is enhanced with the heavier of the two dichlorides being preferentially produced. The ratio of the rate constant for propagation to the square root of that for termination is about $1/100$th as large for the C_4H_8Cl radical as for the C_2H_4Cl radical.

Introduction

A number of studies of chlorine-atom addition to olefinic compounds have been done in recent years. The two groups of experimenters associated with Dainton and with Goldfinger have predominated the field. Their work has been concerned mainly with the initial chlorination mechanism and rates, and the reactions of the initially formed radicals with molecular chlorine. Their results and conclusions are summarized in the excellent review by Cvetanović.[2]

Wijnen[3,4] has studied the reactions of the chlorinated radicals by using the elegant technique of generating chlorine atoms by the photodecomposition of phosgene. The photolysis yields quantitatively two chlorine atoms for each carbon monoxide molecule. No complicating side reactions occur. The COCl intermediate is too unstable at room temperature and

(2) R. J. Cvetanović, *Advan. Photochem.*, 1, 115 (1963).
(3) M. H. J. Wijnen, *J. Am. Chem. Soc.*, 83, 3014 (1961).
(4) M. H. J. Wijnen, *J. Chem. Phys.*, 36, 1672 (1962).

above[3-6] to be detected. Chlorine atoms,[7] alkyl radicals,[8] and chloroalkyl radicals[3,4] do not attack phosgene; thus, the carbon monoxide produced acts as an internal actinometer for measurement of the absorbed intensity.

In ref. 3, phosgene was photolyzed in the presence of ethylene, and CO, 1-C_4H_9Cl, and 1,4-$C_4H_8Cl_2$ were found as major products. The ratio of C_2H_4 addition to the square root of termination for chloroethyl radicals was determined, and an activation energy for addition of 7.5 kcal./mole was reported.

A large number of other products should be produced too. Consequently, we have re-examined this problem to search for these other products and, thus, to examine all of the radical reactions.

Experimental

Matheson high purity ethylene and phosgene were used as reactants. Before use, the ethylene was degassed twice at −196°. A gas chromatographic analysis showed that the only impurity in the ethylene was 54 p.p.m. of ethane. The phosgene was degassed twice at −160° before use. It was difficult to assess the purity of the phosgene because if chromatographic analysis was attempted, hydrolysis occurred. Hydrolysis can occur readily, and thus, HCl and CO_2 might be present as impurities. Any CO_2 would be removed, of course, by the degassing procedure, but the HCl would not. To test for the extent of hydrolysis, the effluent gas during the degassing procedure was collected and analyzed. No carbon dioxide was found, thus indicating that the starting material was quite pure.

Mixtures were prepared by first filling the quartz reaction cell with the lower-pressure gas and carefully reading the pressure on previously calibrated Wallace and Tiernan absolute pressure indicators. By using four such gauges for different pressure regions, the pressure could be determined accurately to better than 0.5%. Subsequently, the higher-pressure reactant was expanded into the reaction cell by opening slightly the stopcock to the reaction vessel, and the total pressure was measured on the Wallace and Tiernan gauges. The back diffusion of the lower-pressure gas was negligible, as determined in previous experiments. The materials of the vacuum line are Pyrex, quartz, and various metals associated with the pressure indicators and National Research Corp. alphatron gauge; these metals are principally copper, brass, and Kovar. All the stopcocks are Teflon with Vyton O rings. The ethylene is nonreactive with any of these materials. Apparently, the phosgene is also. No evidence was found for product formation when the phosgene was stored alone in the vacuum system.

The reaction mixture was exposed to radiation from a Hanovia, flat, spiral, low-pressure, mercury lamp which emitted mainly at 2537 Å. The radiation passed through a Corning 9-54 glass before entering the reaction vessel to remove any radiation below 2200 Å. and thus prevent the ethylene from absorbing. To avoid sensitized reactions, mercury had been carefully excluded from the vacuum system. If reduced intensities were desired, then the radiation also passed through one or more Corning 9-30 glasses which transmit 42% of the radiation at 2537 Å.

The exposure was always terminated before less than 20% of either reactant was consumed, and usually at much smaller conversions. All runs were at 23°. The absorption coefficient of phosgene had been measured previously on a Cary Mode 115 spectrometer and found to be 0.91 ± 0.01 × 10^{-3} reciprocal mm. for a 1-cm. path length where the log of the transmittance is to base 10. This corresponds to about 50% absorption in the 10-cm.-long reaction cell at 30 mm. pressure of phosgene. Thus, at these pressures and below, even if no diffusion had occurred, the average intensity would have been within 33% of the intensity anywhere in the reaction volume. Since subsequent analysis will show that the significant variable goes as the square root of intensity, the average results must be within 18% of any localized result. The actual error in the average results will be considerably smaller than this, because of both diffusion and the averaging process.

If phosgene pressures above about 30 mm. were used, then exposure was done with matched lamps at each end of the cell to ensure that the maximum difference in intensities throughout the reaction volume never exceeded a factor of two. The matched lamps were also used for some runs with 30 mm. of phosgene to increase the incident intensity.

After irradiation, the product mixture was expanded into the vacuum line through traps cooled to −196°. At this temperature, only carbon monoxide is volatile; its pressure was measured with the alphatron gauge. Thus, the amount of carbon monoxide produced could be determined by using the appropriate ratios of volumes.

The carbon monoxide was pumped away, and the ethylene fraction was separated at −160° and collected. After collection, the amount of unused ethylene was measured by reading the pressure in a known volume. The ethylene was refrozen into the product mixture, and the procedure was repeated twice to ensure the accuracy of the ethylene value. The ethylene fraction was then either discarded or, for some runs, analyzed on the gas chromatograph.

The phosgene fraction, which included C_4 hydrocarbons and monochloro C_2 compounds, was removed at −97° and collected for gas chromatographic analysis. Finally, the residual high-boiling material was collected for chromatographic analysis.

Two chromatographs were used. The first was a temperature-programmed Beckman GC-2A with a 16-ft. silica gel column. It was used to analyze the ethylene and phosgene fractions. The second was an F and M Model 720, also temperature-programmed, with a 10-ft. long, 0.25-in. o.d. column containing 15% Carbowax 20 M on 60–80 mesh Diatoport P. It was used for analysis of the high-boiling fraction.

The products were identified by comparing their retention times with those of known standards. All hydrocarbons, saturated monochloro compounds, and dichlorides were unambiguously identified in this way. The absence of a number of compounds was also established. Standards for the monochloro ole-

(5) M. Bodenstein, W. Brenschede, and H. J. Schumacher, Z. physik. Chem. (Leipzig), B40, 121 (1938).
(6) W. G. Burns and F. S. Dainton, Trans. Faraday Soc., 48, 39 (1952).
(7) G. M. Schwab, Z. physik. Chem. (Leipzig), A178, 123 (1936).
(8) F. Runge, Z. Elektrochem., 60, 956 (1956).

fins could not be obtained. However, there is little doubt concerning their identification because they have retention times similar to the corresponding saturated compounds. Absolute calibrations were obtained by using known amounts of the standards. The standards were made by collecting a known pressure of the vapor contained in the reaction volume, by using a known volume of the liquid, or by both methods. If the liquid was used, it was necessary to measure its specific gravity in a separate experiment. For each chromatograph, the calibration factors were within a factor of two or three for all compounds. Regular trends prevailed within any class of compound and from class to class. Thus, for the monochloro olefins, for which standards could not be found, it was apparent that their calibration factors would be almost identical with the corresponding saturated chlorides. These values were used and are undoubtedly accurate to within about 10%.

Results

Table I lists the quantum yield of CO formation, $\Phi(CO)$, for various incident intensities I_0, ethylene pres-

Table I. CO Yield

(C$_2$H$_4$), mm.	(COCl$_2$), mm.	Φ(CO)
$I_0 = 0.0030$ (one lamp + 1.3% filter)		
654	32.2	1.15
646	32.7	1.00[a]
158.2	32.4	1.15
148.6	31.3	1.02
68.6	32.4	1.07
$I_0 = 0.017$ (one lamp + 7.4% filter)		
667	32.7	0.86
666	28.6	0.94
611	29.2	0.97
156.5	28.2	1.03
18.84	29.6	1.04
$I_0 = 0.097$ (one lamp + 42% filter)		
668	32.8	0.93
660	30.7	1.12
143.0	30.7	0.94
57.4	31.8	0.86
18.34	28.4	0.98
$I_0 = 0.440$ (lamps at both ends of cell)		
610	31.5	0.92
624	61.7	1.00[a]
588	103.1	~0.49
543	98.7	~1.09
597	107.1	~1.16
146.5	30.1	1.03
59.4	33.1	0.96
19.24	34.2	1.03
7.42	75.2	0.84
0.0	11.30	1.03
0.0	15.78	0.84
0.0	22.28	0.96
0.0	32.1	~0.94
0.0	44.4	~1.04
0.0	60.9	~1.09

[a] Relative intensity chosen to make this value of Φ(CO) = 1.00.

sures, and phosgene pressures. The absolute intensities of the lamps were not known. Thus, for the results in Table I, the emission from the lamps was assumed constant for the various runs. The absolute incident intensities were determined by arbitrarily assuming that $\Phi(CO)$ was unity for one of the runs when one lamp

was used and for one of the runs when both lamps (one at each window) were used. With this assumption, both lamps produced the same incident intensity at the cell windows. The absolute absorbed intensities could then be computed using the absorption coefficient of phosgene at 2537 Å.

The absorbed intensity was varied by a factor of about 370, the ethylene pressure varied from 0 to 668 mm., and the phosgene pressure varied from 11.3 to 107.1 mm. This corresponds to the whole range of variables employed in our studies. Yet, $\Phi(CO)$ remained unity to within about 15% for all runs but one. Furthermore, the results reported in Table I are for various per cent decompositions up to 20%. Mr. Dana Marsh of this laboratory has followed the pressure buildup with exposure time for pure phosgene at pressures from 5 to 20 mm. He has found the increase in pressure to be linear with exposure time for short exposures.

The results clearly indicate, in conformance with the earlier work, that the carbon monoxide production is proportional to the absorbed intensity, that the COCl radical is not important, and that RCl radicals do not attack COCl$_2$. For all the subsequent analysis, the absorbed intensity I_a will be equated with the rate of carbon monoxide production.

In addition to CO, many other products are found. Those unambiguously identified are C$_2$H$_2$, CO$_2$, 1-C$_6$H$_{12}$, C$_2$H$_5$Cl, 1-C$_4$H$_9$Cl, 1-C$_6$H$_{13}$Cl, 1,2-C$_2$H$_4$Cl$_2$, 1,3-C$_4$H$_8$Cl$_2$, 1,4-C$_4$H$_8$Cl$_2$, and 1,6-C$_6$H$_{12}$Cl$_2$. Other compounds were found which could be classified because of their retention times. These are a C$_6$ hydrocarbon, which we label α-C$_6$H$_{12}$; a C$_4$ monochloride, C$_4$H$_7$Cl; and two C$_6$ monochlorides, which we call β-C$_6$H$_{11}$Cl and γ-C$_6$H$_{11}$Cl. At very high $(C_2H_4)/I_a^{1/2}$, trace amounts of a monochloro C$_8$ compound could also be detected. Compounds definitely established as absent or too small to detect are C$_2$H$_6$, cyclohexane, 2-C$_4$H$_9$Cl, 1,1-C$_2$H$_4$Cl$_2$, 2,3-C$_4$H$_8$Cl$_2$, and 1,8-C$_8$H$_{16}$-Cl$_2$. The C$_4$ hydrocarbons should be produced, but their retention times are similar to that of phosgene, and, thus, analyses could not be effected.

The chromatographic retention times of 1,2-C$_2$H$_4$Cl$_2$ and 1-C$_6$H$_{13}$Cl were similar. Therefore, when one of these compounds was present in considerably larger amounts than the other, the larger peak obscured the smaller, and analysis of the less prevalent compound was prevented.

No evidence was found for C$_2$H$_3$Cl. Under some conditions, it must have been a major product. The only explanation consistent with the chromatograms, the carbon–hydrogen mass balance, and the carbon monoxide–chlorine mass balance is either that C$_2$H$_3$Cl has a retention time identical with C$_2$H$_5$Cl, or that somehow before or during analysis the C$_2$H$_3$Cl was quantitatively converted to C$_2$H$_5$Cl. In either case, the C$_2$H$_5$Cl analysis would have corresponded to the sum of C$_2$H$_5$Cl and C$_2$H$_3$Cl. The results are reported that way in Table II, and all subsequent arguments are based on that assumption.

The amounts of all products, except C$_2$H$_2$ and CO$_2$, increased with exposure. The C$_2$H$_2$ and CO$_2$ pressures were always about 0.02 and 0.25 mm., respectively, when about 30 mm. of COCl$_2$ was used. One run was done in which 114.3 mm. of C$_2$H$_4$ and 28.6 mm. of

Table II. Photolysis of C_2H_4–$COCl_2$ Mixtures at 23°

$(C_2H_4)/I_a^{1/2}$, mm. min.	13.7	40.4	90.5	90.5	129	245	205	302	321	611	573	620	689	897	992	884
$(C_2H_4),^a$ mm.	7.42	19.24	17.64	18.34	59.4	19.5	18.84	57.4	146.5	109.3	108.4	113.1	143	71.6	74.2	597
(CO), mm.	0.58	1.14	1.52	1.70	3.16	0.76	1.52	3.04	6.3	0.48	1.61	4.0	5.1	0.76	0.76	~2.3
Time, min.	2.00	5.00	40.00	40.00	15.00	120.00	180.00	75.00	30.00	15.00	45.00	120.00	120.00	120.00	120.00	5.00
I_a, mm. of CO/min.	0.29	0.23	0.0380	0.042	0.21	0.0063	0.0085	0.040	0.21	0.032	0.036	0.033	0.043	0.0063	0.0063	~0.46
$(COCl_2),^a$ mm.	75.2	34.2	32.8	28.4	33.1	30.3	29.6	31.8	30.1	33.2	29.2	29.2	30.7	32.2	32.5	107.1
$-\Delta(C_2H_4)$, mm.	1.23	2.21	...	3.46	6.8	...	3.11	6.9	11.2	...	...	...	10.9	...	...	...
$\Phi(\alpha\text{-}C_6H_{12})$	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$\Phi(1\text{-}C_6H_{12})$	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$\Phi(C_2H_5Cl) + \Phi(C_2H_3Cl)$	0.50	0.46	0.32	0.26	0.35	0.84	0.29	0.24	0.20	1.50	0.56	0.25	0.19	1.06	0.93	...
$\Phi(C_4H_7Cl)$	...	0.0045	0.0052	0.0087	0.012	0.034	0.017	0.031	0.028	0.058	0.076	0.053	0.049	0.100	0.090	...
$\Phi(1\text{-}C_4H_9Cl)$	...	~0.003	0.0024	0.0060	0.0019	...	0.0067	0.0050	0.0042	...	0.0035	0.0068	0.0074	~0.003	...	...
$\Phi(\beta\text{-}C_6H_{11}Cl)$	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$\Phi(\gamma\text{-}C_6H_{11}Cl)$	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$\Phi(1\text{-}C_6H_{13}Cl)$	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$\Phi(1,2\text{-}C_2H_4Cl_2)$	0.057	0.060	0.072	0.082	0.074	0.094	0.096	0.088	0.074	0.058	0.054	0.076	0.076	0.074	0.088	0.055
$\Phi(1,3\text{-}C_4H_8Cl_2)$	0.0116	0.0091	0.0079	0.0073	0.0100	0.0156	0.0073	0.0048	0.0022	...	0.0025	0.0025	0.0025	0.0057	0.0061	...
$\Phi(1,4\text{-}C_4H_8Cl_2)$	0.79	0.71	0.59	0.63	0.69	0.64	0.58	0.70	0.73	0.85	0.59	0.62	0.58	0.60	0.61	0.64
$\Phi(1,6\text{-}C_6H_{12}Cl_2)$	...	0.021	0.019	0.025	0.030	0.026	0.035	0.065	0.080	0.055	0.081	0.087	0.16	0.102	0.136	...
$\frac{1}{2}\Phi(\Sigma Cl)$	1.12	1.03	0.93	0.88	0.99	1.21	0.87	1.00	1.00	1.74	1.05	0.94	0.94	1.36	1.35	...
$\Phi(\Sigma C_2)^b$	2.16	2.06	1.70	1.75	1.97	2.42	1.75	2.07	2.12	2.58	2.28	2.04	2.18	2.96	2.97	...
$-\Delta(C_2H_4)/(CO)$	2.12	1.94	...	2.04	2.15	...	2.04	2.3	1.8	...	...	...	2.1	...	...	...

Table II (*Continued*)

$(C_2H_4)/I_a^{1/2}$, mm. min.	845	1112	1387	1390	1703	1735	3160	2940	3860	4240	3880	7750	7750	6930	15,900	16,500
$(C_2H_4),^a$ mm.	543	624	610	588	68.6	156.5	668	660	158.2	160.4	148.6	667	666	611	654	646
(CO), mm.	~8.3	9.5	1.93	~11.6	1.65	3.9	1.33	4.6	0.60	0.51	2.6	0.88	0.88	5.6	0.61	3.3
Time, min.	20.00	30.00	10.00	60.00	1020.00	480.00	30.00	90.00	360.00	360.00	1800.00	120.00	120.00	720.00	360.00	2160.00
I_a, mm. of CO/min.	~0.42	0.32	0.19	~0.19	0.0016	0.0081	0.044	0.051	0.0017	0.0014	0.0015	0.0074	0.0074	0.0078	0.0017	0.0015
$(COCl_2),^a$ mm.	98.7	61.7	31.5	103.1	32.4	28.2	32.8	30.7	32.4	33.9	31.3	32.7	28.6	29.2	32.2	32.7
$-\Delta(C_2H_4)$, mm.	...	27	11	37	4.3	9.1	9	19	2.5	2.6	7.3	...	11	28	11	25
$\Phi(\alpha\text{-}C_6H_{12})$	...	...	...	...	...	...	...	...	...	...	0.0068	...	...	...	0.024	0.0050
$\Phi(1\text{-}C_6H_{12})$	...	...	...	...	...	...	...	...	...	...	0.011	0.0096	0.0080	...	0.017	0.025
$\Phi(C_2H_5Cl) + \Phi(C_2H_3Cl)$	...	0.087	0.34	...	0.42	...	0.19	0.12	0.70	1.30	0.28	0.45	0.40	...	0.59	0.20
$\Phi(C_4H_7Cl)$	...	0.068	0.23	...	0.103	0.092	0.29	0.102	0.40	0.49	0.145	0.66	0.48	0.18	0.83	0.19
$\Phi(1\text{-}C_4H_9Cl)$	...	0.013	0.010	...	0.012	0.014	0.014	0.016	0.013	0.014	0.021	0.032	0.017	0.031	0.019	0.023
$\Phi(\beta\text{-}C_6H_{11}Cl)$	...	...	...	...	...	...	0.0020	0.0014	...	...	0.0046	0.0089	0.0078	...	0.020	0.027
$\Phi(\gamma\text{-}C_6H_{11}Cl)$	...	...	...	...	...	...	0.0040	0.0053	...	0.0051	0.0035	0.016	0.011	...	0.029	0.016
$\Phi(1\text{-}C_6H_{13}Cl)$	...	...	...	...	...	...	0.026	...	0.015	...	0.043	0.089	0.079	0.045	0.105	0.056
$\Phi(1,2\text{-}C_2H_4Cl_2)$	0.051	0.048	0.058	0.040	0.092	0.081	0.034	0.030	0.057	0.087	...	0.023	...	...	...	...
$\Phi(1,3\text{-}C_4H_8Cl_2)$	...	0.0006	...	...	0.0010	...	...	0.0009	...	0.0064	...	...	...	...	...	...
$\Phi(1,4\text{-}C_4H_8Cl_2)$	0.64	0.52	0.52	0.43	0.38	0.38	0.30	0.27	0.27	0.34	0.26	0.22	0.15	0.16	0.103	0.078
$\Phi(1,6\text{-}C_6H_{12}Cl_2)$	...	0.059	0.17	...	0.18	0.19	0.20	0.19	0.16	0.195	0.24	0.17	0.080	...	0.087	0.060
$\frac{1}{2}\Phi(\Sigma Cl)$	...	0.71	1.04	...	0.92	...	0.80	0.61	1.05	1.53	0.76	1.00	0.73	...	0.99	0.39
$\Phi(\Sigma C_2)^b$	...	1.57	2.60	...	2.22	...	2.33	1.71	2.61	3.88	2.24	3.37	2.34	...	3.43	1.41
$-\Delta(C_2H_4)/(CO)$	...	2.8	5.7	3.2	2.6	2.3	6.8	4.1	4.2	5.1	2.8	...	12	5.0	18	7.6

ᵃ Average value during run.   ᵇ Including calculated value of C_4H_8.

COCl$_2$ were allowed to stand 16 hr. with no exposure. The C$_2$H$_2$ and CO$_2$ were still found to be present at the above-mentioned pressures. No evidence was found for other products. Careful checks revealed that CO and C$_2$H$_5$Cl were definitely absent. Apparently, some impurity in the COCl$_2$ rapidly reacts with C$_2$H$_4$, thus accounting for the CO$_2$ and C$_2$H$_2$.

The results of the experiments are listed in Table II. The C$_2$H$_4$ pressure was varied by a factor of 90 and I_a by a factor of 170. Experiments were also done for various percentage decompositions. In addition to the CO production, the C$_2$H$_4$ consumption, and the quantum yields of the pertinent products, three other entries are also included. These are one-half the quantum yield of the sum of the chlorine atoms in the products, $(^1/_2)\Phi(\Sigma Cl)$; and the quantum yield of ethylene units in the products, $\Phi(\Sigma C_2)$; and the quantum yield of monomer consumption, $-\Delta(C_2H_4)/(CO)$. In computing $\Phi(\Sigma C_2)$, the estimated butene production was included. The butenes produced were about one-half the amount of 1,6-C$_6$H$_{12}$Cl$_2$ as the subsequent detailed analysis will demonstrate.

In Table II are the results of several sets of runs in which only the exposure time was varied. With the notable exception of $\Phi(C_2H_5Cl) + \Phi(C_2H_3Cl)$, the product quantum yields were nearly constant with exposure time, at least for short exposures. With extended exposures, the yields fell. This effect was most pronounced with C$_4$H$_7$Cl and was undoubtedly due to the subsequent reactions of the products to form higher molecular weight compounds. The value $\Phi(C_2H_5Cl) + \Phi(C_2H_3Cl)$ was large at small exposures and dropped regularly as exposure increased. The quantity $(^1/_2) \cdot \Phi(\Sigma Cl)$ is a measure of the CO to Cl mass balance and should be unity. In a large number of the runs, it was. However, for very small exposures it exceeded unity, and for long exposures it fell below unity. The falloff reflects the fact that the products further react to form unreclaimed heavier compounds at extended conversions. The values in excess of unity are difficult to understand. Apparently, some chlorinated impurity in the COCl$_2$(HCl?) readily yields C$_2$H$_5$Cl when exposed to 2537-Å. radiation in the presence of C$_2$H$_4$. This effect was most pronounced at low conversions, but was obscured at larger conversions as the impurity was exhausted.

Figures 1 and 2 are log-log plots of the product quantum yields vs. $(C_2H_4)/I_a^{1/2}$ for the runs with $(^1/_2) \cdot \Phi(\Sigma Cl)$ within 15% of unity. The variations of the quantum yields are complex. The two dichlorobutanes had constant yields at low $(C_2H_4)/I_a^{1/2}$ but diminished at larger values of $(C_2H_4)/I_a^{1/2}$. The diminution of 1,3-C$_4$H$_8$Cl$_2$ preceded that of 1,4-C$_4$H$_8$Cl$_2$. The C$_2$-H$_5$Cl + C$_2$H$_3$Cl yields were constant at low $(C_2H_4)/I_a^{1/2}$, then fell off, passed through a minimum, and rose again as $(C_2H_4)/I_a^{1/2}$ was enhanced. The $\Phi(1,2$-C$_2$H$_4$Cl$_2)$ was fairly constant for most values of $(C_2H_4)/I_a^{1/2}$, but was reduced at the highest values. The compounds 1-C$_4$H$_9$Cl, C$_4$H$_7$Cl, and 1,6-C$_6$H$_{12}$Cl$_2$ rose rapidly for values of $(C_2H_4)/I_a^{1/2}$ below 1000 (mm. min.)$^{1/2}$. Above this value, $\Phi(C_4H_7Cl)$ continued to increase but $\Phi(1$-C$_4$H$_9$Cl) and $\Phi(1,6$-C$_6$H$_{12}$Cl$_2)$ tended to level off. The C$_6$ hydrocarbons and monochlorides were not detected below $(C_2H_4)/I_a^{1/2}$ of about 10^3 (mm. min.)$^{1/2}$,
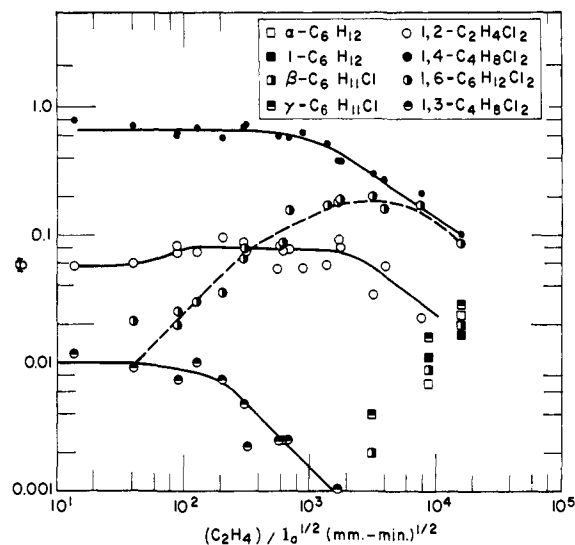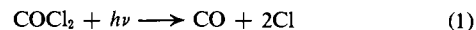

Figure 1. Product quantum yields vs. $(C_2H_4)/I_a^{1/2}$.

but the quantum yields, though small, rose rapidly for larger values of $(C_2H_4)/I_a^{1/2}$.

The quantities $\Phi(\Sigma C_2)$ and $-\Delta(C_2H_4)/(CO)$ should be identical for runs with good CO–Cl mass balances. At low ethylene pressures, both quantities had values close to two. However, at higher C$_2$H$_4$ pressures [or more precisely $(C_2H_4)I_a^{1/2}$], both quantities rose, but the rise in $-\Delta(C_2H_4)/(CO)$ was faster. The excessive enhancement of $-\Delta(C_2H_4)/(CO)$ is an artifact caused by the difficulty in obtaining accurate measurements for $-\Delta(C_2H_4)$ at small conversions at high pressures. As the per cent decomposition was enhanced, more accuracy was obtained. However, the excessive enhancement then became real because the products had reacted further with C$_2$H$_4$ to give unreclaimed heavier compounds. Thus, $\Phi(\Sigma C_2)$ was reduced, but $-\Delta$(C$_2$H$_4$)/(CO) was enlarged. Figure 3 is a semilog plot of $\Phi(\Sigma C_2)$ and $-\Delta(C_2H_4)/(CO)$ vs. $(C_2H_4)/I_a^{1/2}$. For $\Phi(\Sigma C_2)$ only those values were plotted that correspond to runs with $(^1/_2)\Phi(\Sigma Cl)$ within 15% of unity. However, for $-\Delta(C_2H_4)/(CO)$, the runs corresponding to the largest per cent decomposition for any set of conditions were utilized to enhance the accuracy. Of course, these points should lie above those for $\Phi(\Sigma C_2)$, as indeed they do.

Discussion

The generalized reaction that explains the propagation and termination is

$$COCl_2 + h\nu \longrightarrow CO + 2Cl \qquad (1)$$

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

$$C_2H_4 + C_2H_4Cl \longrightarrow C_4H_8Cl \qquad (3a)$$

$$C_2H_4 + C_4H_8Cl \longrightarrow C_6H_{12}Cl \qquad (3b)$$

$$2C_2H_4Cl \longrightarrow P_4 \qquad (4)$$

$$2C_4H_8Cl \longrightarrow P_5 \qquad (5)$$

$$C_2H_4Cl + C_4H_8Cl \longrightarrow P_6 \qquad (6)$$

where P$_4$, P$_5$, and P$_6$ represent products of reactions 4, 5, and 6, respectively. Additional reactions involving the C$_6$H$_{12}$Cl radical should be included to account for the C$_6$ hydrocarbons and monochlorides. However, since these latter products are unimportant under our
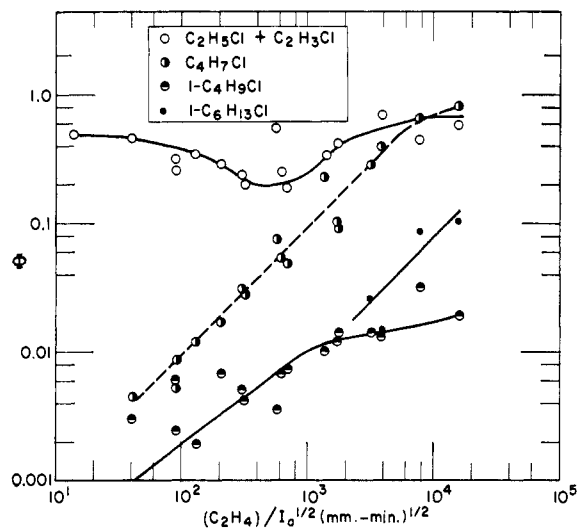
Figure 2. Product quantum yields vs. $(C_2H_4)/I_a^{1/2}$.

Figure 3. Monomer consumption vs. $(C_2H_4)/I_a^{1/2}$.

conditions, the reactions involving $C_6H_{12}Cl$ radicals can be neglected, as can reaction 3b, without seriously altering the conclusions.

The class of reactions in which a radical reacts with chlorine atoms also can be neglected, as the chlorine atoms are effectively scavenged by ethylene. If scavenging were not complete, then $\Phi(\Sigma C_2)$ would fall below 2. The results in Table II and Figure 3 show that within the experimental scatter, $\Phi(\Sigma C_2) \geq 2$ for the whole range of variables.

The absence of ethane as a product effectually eliminates the possibility of ethyl radicals. By analogy, the likelihood of other alkyl radicals is small.

Consequently, reactions 1–6 should explain the results, and the only two important radicals should be C_2H_4Cl and C_4H_8Cl. The expressions for the radical concentrations are

$(C_2H_4Cl) =$

$$\frac{2I_a}{k_{3a}(C_2H_4) + 2k_4(C_2H_4Cl) + k_6(C_4H_8Cl)} \quad (7)$$

$$(C_4H_8Cl) = \frac{k_{3a}(C_2H_4)(C_2H_4Cl)}{2k_5(C_4H_8Cl) + k_6(C_2H_4Cl)} \quad (8)$$

Equations 7 and 8 have simplified solutions for three regions of interest: i.e., first, when $(C_2H_4Cl) \gg (C_4H_8Cl)$; second, when $2k_5(C_4H_8Cl) \approx k_6(C_2H_4Cl)$; and third, when $(C_2H_4Cl) \ll (C_4H_8Cl)$.

Under conditions for which $(C_2H_4Cl) \gg (C_4H_8Cl)$, then

$$(C_2H_4Cl) \approx (I_a/k_4)^{1/2} \quad (7a)$$

$$(C_4H_8Cl) \approx k_{3a}(C_2H_4)/k_6 \quad (8a)$$

and

$$\Phi(P_4) \approx 1 \quad (9a)$$

$$\Phi(P_5) \approx k_5k_{3a}{}^2(C_2H_4)^2/k_6I_a \quad (10a)$$

$$\Phi(P_6) \approx k_{3a}(C_2H_4)/(k_4I_a)^{1/2} \quad (11a)$$

Under conditions for which $2k_5(C_4H_8Cl) \approx k_6(C_2H_4Cl)$, then

$$(C_2H_4Cl) \approx 2I_a/k_{3a}(C_2H_4)(^3/_2 + 2k_4k_5/k_6{}^2) \quad (7b)$$

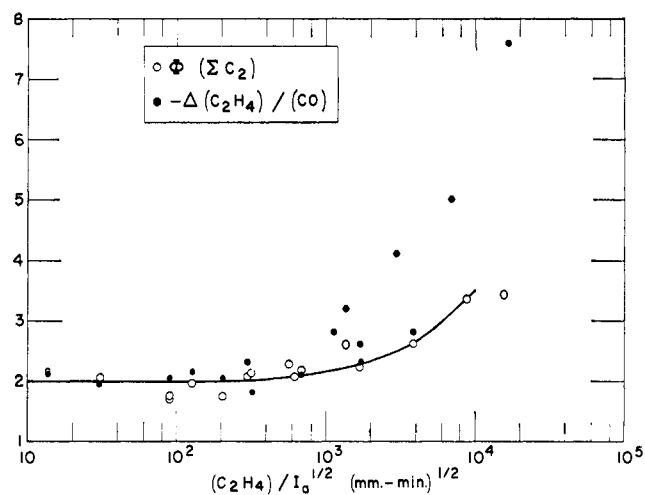$$(C_4H_8Cl) \approx k_{3a}(C_2H_4)/2k_6 \quad (8b)$$

and

$$\Phi(P_4) \approx 4k_4I_a/k_{3a}{}^2(C_2H_4)^2(^3/_2 + 2k_4k_5/k_6{}^2)^2 \quad (9b)$$

$$\Phi(P_5) \approx k_5k_{3a}{}^2(C_2H_4)^2/4k_6{}^2I_a \quad (10b)$$

$$\Phi(P_6) = (^3/_2 + 2k_4k_5/k_6{}^2)^{-1} \quad (11b)$$

Under conditions for which $(C_2H_4Cl) \ll (C_4H_8Cl)$, then

$$(C_2H_4Cl) \approx 2I_a/k_{3a}(C_2H_4) \quad (7c)$$

$$(C_4H_8Cl) \approx (I_a/k_5)^{1/2} \quad (8c)$$

and

$$\Phi(P_4) \approx 4k_4I_a/k_{3a}{}^2(C_2H_4)^2 \quad (9c)$$

$$\Phi(P_5) \approx 1 \quad (10c)$$

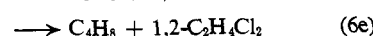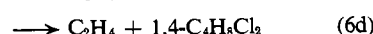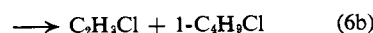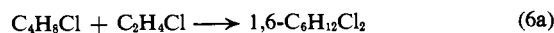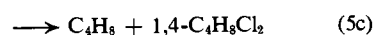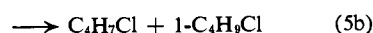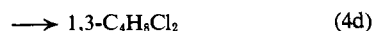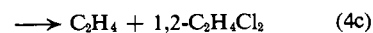$$\Phi(P_6) \approx 2k_6I_a^{1/2}/k_5^{1/2}k_{3a}(C_2H_4) \quad (11c)$$

Regardless of the conditions, the product quantum yields are functions only of the quantity $(C_2H_4)/I_a^{1/2}$, which is the fundamental variable of the system. The quantum yields are plotted vs. this function in Figures 1 and 2. Region a applies for values of $(C_2H_4) I_a^{1/2}$ below about 300 $(mm. min.)^{1/2}$; region b applies in the range of $(C_2H_4)/I_a^{1/2}$ from 10^3 to 10^4; and region c is for values of $(C_2H_4)/I_a^{1/2}$ greater than 10^4.

The classification of the appropriate products is given in Table III. It can be seen that $1,3$-$C_4H_8Cl_2$ is a P_4 product, and $1,6$-$C_6H_{12}Cl_2$ is a P_6 product, at least for $(C_2H_4)/I_a^{1/2} < 10^4$ $(mm. min.)^{1/2}$. However, the other products change classification and thus must be produced by more than one class of reactions. The double entries indicate behavior intermediate to the two classes so that both classes of reactions must participate.

Table III. Classification of Products

Product	Region a	Region b	Region c
$C_2H_3Cl + C_2H_5Cl$	P_4	P_5, P_6	P_5
C_4H_7Cl	P_6	P_5	P_5
1-C_4H_9Cl	P_4, P_8	P_8	P_5
$1,2$-$C_2H_4Cl_2$	P_4	P_8	. .
$1,3$-$C_4H_8Cl_2$	P_4	P_4	. .
$1,4$-$C_4H_8Cl_2$	P_4	P_4, P_6	P_5, P_6
$1,6$-$C_6H_{12}Cl_2$	P_8	P_6	P_5, P_6

The detailed mechanism that fits the products to the appropriate classifications is, in addition to reactions 1, 2, and 3a

$$2C_2H_4Cl \longrightarrow 1,4\text{-}C_4H_8Cl_2 \qquad (4a)$$

$$\longrightarrow C_2H_3Cl + C_2H_5Cl \qquad (4b)$$

$$\longrightarrow C_2H_4 + 1,2\text{-}C_2H_4Cl_2 \qquad (4c)$$

$$\longrightarrow 1,3\text{-}C_4H_8Cl_2 \qquad (4d)$$

$$2C_4H_8Cl \longrightarrow 1,8\text{-}C_8H_{16}Cl_2 \qquad (5a)$$

$$\longrightarrow C_4H_7Cl + 1\text{-}C_4H_9Cl \qquad (5b)$$

$$\longrightarrow C_4H_8 + 1,4\text{-}C_4H_8Cl_2 \qquad (5c)$$

$$C_4H_8Cl + C_2H_4Cl \longrightarrow 1,6\text{-}C_6H_{12}Cl_2 \qquad (6a)$$

$$\longrightarrow C_2H_3Cl + 1\text{-}C_4H_9Cl \qquad (6b)$$

$$\longrightarrow C_2H_5Cl + C_4H_7Cl \qquad (6c)$$

$$\longrightarrow C_2H_4 + 1,4\text{-}C_4H_8Cl_2 \qquad (6d)$$

$$\longrightarrow C_4H_8 + 1,2\text{-}C_2H_4Cl_2 \qquad (6e)$$

This mechanism satisfies the observations listed in Table III except in three particulars. The first is that 1-C_4H_9Cl is not produced by any of reactions 4. It is difficult to see how it could be produced in such a manner. Most likely the observation is an artifact caused by the large experimental error associated with the measurement of the small quantum yields of 1-C_4H_9Cl. The second inadequacy of the mechanism is that it does not account for the partial P_5 behavior exhibited by 1,6-$C_6H_{12}Cl_2$ at the highest values of $(C_2H_4)/I_a^{1/2}$. However, the observation can be explained by introducing reactions of $C_6H_{12}Cl$ radicals which are becoming important in this region. The subsequent analysis will, in fact, show that 1,6-$C_6H_{12}Cl_2$ is produced from these radicals to a measurable extent under these conditions. Finally, the mechanism fails to explain the P_5 behavior of the monochloro C_2 compounds. Furthermore, the mechanism predicts that

$$\frac{\Phi(C_4H_7Cl) - \Phi(1\text{-}C_4H_9Cl)}{\Phi(1,6\text{-}C_6H_{12}Cl_2)} = \frac{k_{6c} - k_{6b}}{k_{6a}}$$

Thus, the left-hand side of the expression should be constant over the whole range of variables. This quantity is plotted in Figure 4, and it rises from 0.3 to 8.5 as $(C_2H_4)/I_a^{1/2}$ increases from 50 to 15,000 (mm. min.)$^{1/2}$. It is clear that additional class-5 reactions are needed to account for the excess monochloro C_2 compounds and the C_4H_7Cl. A reaction that does just this is

$$2C_4H_8Cl \longrightarrow C_4H_7Cl + C_2H_5Cl + C_2H_4 \qquad (5d)$$

The analogous reaction

$$C_4H_8Cl + C_2H_4Cl \longrightarrow C_2H_3Cl + C_2H_5Cl + C_2H_4 \qquad (6f)$$

is also included for generality.

The rates of product formation, $R(x)$, are related to the rates of reaction, $R(y)$, by

$$R(C_4H_8) = R(5c) + R(6e)$$

$$R(C_2H_3Cl) = R(4b) + R(6b) + R(6f)$$

$$R(C_2H_5Cl) = R(4b) + R(5d) + R(6c) + R(6f)$$

$$R(C_4H_7Cl) = R(5b) + R(5d) + R(6c)$$

$$R(1\text{-}C_4H_9Cl) = R(5b) + R(6b)$$

$$R(1,2\text{-}C_2H_4Cl_2) = R(4c) + R(6e) \qquad (12)$$

$$R(1,3\text{-}C_4H_8Cl_2) = R(4d)$$

$$R(1,4\text{-}C_4H_8Cl_2) = R(4a) + R(5c) + R(6d)$$

$$R(1,6\text{-}C_6H_{12}Cl_2) = R(6a)$$

$$R(1,8\text{-}C_8H_{16}Cl_2) = R(5a)$$

$$R(3a) = 2\sum_{i=a}^{d} R(5i) + \sum_{i=a}^{f} R(6i)$$

Equations 12 can be manipulated to yield many rate constant ratios. For example, at low values of $(C_2H_4)/I_a^{1/2}$, the C_4H_8Cl radical is much less important than the C_2H_4Cl radical and the following expressions should hold.

$$k_{4a}/k_{4d} = \Phi(1,4\text{-}C_4H_8Cl_2)/\Phi(1,3\text{-}C_4H_8Cl_2) \qquad (13a)$$

$$k_{4b}/k_{4d} = (^1/_2)[\Phi(C_2H_3Cl) + \Phi(C_2H_5Cl)]/\Phi(1,3\text{-}C_4H_8Cl_2) \qquad (13b)$$

$$k_{4c}/k_{4d} = \Phi(1,2\text{-}C_2H_4Cl_2)/\Phi(1,3\text{-}C_4H_8Cl_2) \qquad (13c)$$

$$k_{6b}/k_{6a} = \Phi(1\text{-}C_4H_9Cl)/\Phi(1,6\text{-}C_6H_{12}Cl_2) \qquad (13d)$$

$$k_{6c}/k_{6a} = \Phi(C_4H_7Cl)/\Phi(1,6\text{-}C_6H_{12}Cl_2) \qquad (13e)$$

The quantities on the right-hand side of eq. 13 are plotted in Figures 4–6. All of the quantities are essentially constant at low $(C_2H_4)/I_a^{1/2}$ but then rise at higher values of $(C_2H_4)/I_a^{1/2}$ as additional reactions become important. The rise occurs at different points for the different expressions, depending on the importance of the complicating reactions. The low $(C_2H_4)/I_a^{1/2}$ limiting values give the appropriate rate constants, which are listed in Table IV.

In a similar fashion, at high values of $(C_2H_4)/I_a^{1/2}$, the C_4H_8Cl radical is more important than the C_2H_4Cl radical, and other expressions should be valid.

$$k_{5a}/k_{5b} = \Phi(1,8\text{-}C_8H_{16}Cl_2)/\Phi(1\text{-}C_4H_9Cl) \qquad (14a)$$

$$k_{5b}/k_{5c} = \Phi(1\text{-}C_4H_9Cl)/\Phi(1,4\text{-}C_4H_8Cl_2) \qquad (14b)$$

$$k_{5d}/k_{5b} = [\Phi(C_2H_3Cl) + \Phi(C_2H_5Cl)]/\Phi(1\text{-}C_4H_9Cl) \qquad (14c)$$

No 1,8-$C_8H_{16}Cl_2$ was found as a product, even though it would have been detected had it been produced. Consequently, reaction 5a must be unimportant. The right-hand side of (14b) is plotted in Figure 6. It rises continually with $(C_2H_4)/I_a^{1/2}$ and does not become level. Thus, insufficient 1,4-$C_4H_8Cl_2$ is produced by reaction 5c to have a noticeable effect, and that reaction must also be unimportant. The right-hand side of eq. 14c, plotted in Figure 5, does become quite constant at 37 for values of $(C_2H_4)/I_a^{1/2}$ greater than 400 (mm. min.)$^{1/2}$. Thus $k_{5d}/k_{5b} = 37$, and it is included in Table IV.

At intermediate and low values of $(C_2H_4)/I_a^{1/2}$ additional expressions can be derived. These are

$$\frac{k_{6d}}{k_{6a}} = \frac{\Phi(1,4\text{-}C_4H_8Cl_2) - (k_{4a}/k_{4d})\Phi(1,3\text{-}C_4H_8Cl_2)}{\Phi(1,6\text{-}C_6H_{12}Cl_2)} \qquad (15a)$$

$$\frac{k_{6f}}{k_{6a}} = \frac{(^1/_2)\Phi(C_2H_3Cl) + (^1/_2)\Phi(C_2H_5Cl) - (k_{4b}/k_{4d})\Phi(1,3\text{-}C_4H_8Cl_2)}{\Phi(1,6\text{-}C_6H_{12}Cl_2)} \qquad (15b)$$

$$\frac{k_{3a}}{k_{4d}^{1/2}} = \frac{[I_a^{1/2}/(C_2H_4)]\left(\sum_{i=a}^{f} k_{6i}/k_{6a}\right)\Phi(1,6\text{-}C_6H_{12}Cl_2)}{[\Phi(1,3\text{-}C_4H_8Cl_2)]^{1/2}} \qquad (15c)$$

Table IV. Rate Constant Ratios

Ratio	Value	Units	Source
k_{4a}/k_{4d}	66	None	Eq. 13a, Figure 5
k_{4b}/k_{4d}	24	None	Eq. 13b, Figure 5
k_{4c}/k_{4d}	5.8	None	Eq. 13c, Figure 5
k_{5a}/k_{5b}	...	None	Eq. 14a
k_{5b}/k_{5c}	...	None	Eq. 14b, Figure 6
k_{5d}/k_{5b}	37	None	Eq. 14c, Figure 5
k_{6b}/k_{6a}	0.07	None	Eq. 13d, Figure 6
k_{6c}/k_{6a}	0.40	None	Eq. 13e, Figure 4
k_{6d}/k_{6a}	4.0	None	Eq. 15a, Figure 4
k_{6e}/k_{6a}	0.5	None	Eq. 16a, Figure 4
k_{6f}/k_{6a}	...	None	Eq. 15b, Figure 4
$k_{6a}/[k_{4d}^{1/2}(k_{5b}+k_{5d})^{1/2}]$	17	None	Eq. 16b, Figure 4
$k_8/k_4^{1/2}k_5^{1/2}$	10.3	None	...
$k_{3a}/k_{4d}^{1/2}$	0.017	(mm. min.)$^{-1/2}$	Eq. 15c, Figure 6
$k_{3a}/k_4^{1/2}$	1.7×10^{-8}	(mm. min.)$^{-1/2}$	...
$k_{3a}/k_7^{1/2}$	1.6×10^{-4}	(mm. min.)$^{-1/2}$	Eq. 17, Figure 5
$k_{3b}/k_5^{1/2}$	$\sim 2 \times 10^{-5}$	(mm. min.)$^{-1/2}$	Eq. 19, 20
k_{4b}/k_{4a}	0.36	None	...
$(k_{6b}+k_{6c})/k_{6a}$	0.47	None	...
k_{4c}/k_{4b}	0.24	None	...
$(k_{6d}+k_{6e})/(k_{6b}+k_{6c})$	9.6	None	...

The right-hand sides of expressions 15a and 15b are plotted in Figure 4 using the previously determined values of k_{4a}/k_{4d} and k_{4b}/k_{4d}. The right-hand side
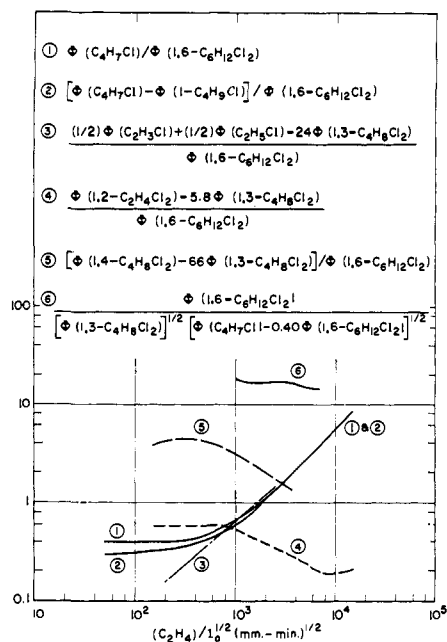

Figure 4. Appropriate functional relations vs. $(C_2H_4)/I_a^{1/2}$.

of (15a) is reasonably constant for $(C_2H_4)/I_a^{1/2}$ from 150 to 1000, yielding a value of k_{6d}/k_{6a} of 4.0. The right-hand side of (15b) rises steadily with $(C_2H_4)/I_a^{1/2}$, indicating that reaction 6f is always less important in producing monochloro C_2 compounds than alternate reactions. Thus, there is no evidence to support reaction 6f. The right-hand side of (15c) is plotted in Figure 6 using the previously computed values of the k_{6i}/k_{6a} and the value of k_{6e}/k_{6a}, which will be subsequently found. The constancy of this expression is quite good and yields a value for $k_{3a}/k_{4d}^{1/2}$ of 0.017 (mm. min.)$^{-1/2}$.

By judiciously combining rate constants ratios, the value of $k_{3a}/k_4^{1/2}$ is found to be 0.0017 (mm.

min.)$^{-1/2}$, where $k_4 = \sum_{i=a}^{d} k_{4i}$. This value is tabulated in Table IV. Wijnen[3] has reported a value of k_{3a}-

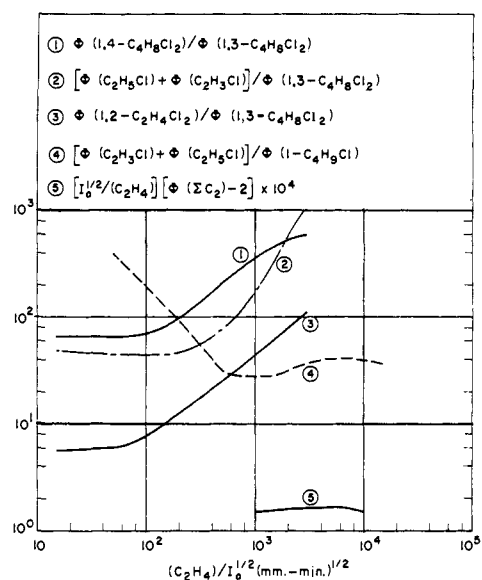Figure 5. Appropriate functional relations vs. $(C_2H_4)/I_a^{1/2}$.

$(k_{5b}+k_{6b})/k_4^{1/2}(k_5+k_6)$ of about 1.2×10^{-4} (mm. min.)$^{-1/2}$ at 28°, where $k_5 = \sum_i k_{5i}$ and $k_6 = \sum_i k_{6i}$. Under Wijnen's operating conditions, the class of reactions 6 dominate those of class 5, and his value is approximately equal to $k_{3a}k_{6b}/k_4^{1/2}k_6$. From our results this ratio is estimated to be 1.2×10^{-4} (mm. min.)$^{-1/2}$ at 23° in fortuitously good agreement.

There are two additional expressions that should hold under all conditions.

$$\frac{k_{6e}}{k_{6a}} = \frac{\Phi(1,2\text{-}C_2H_4Cl_2) - (k_{4c}/k_{4d})\Phi(1,3\text{-}C_4H_8Cl_2)}{\Phi(1,6\text{-}C_6H_{12}Cl_2)}$$

(16a)

$$\frac{k_{6a}}{k_{4d}^{1/2}(k_{5b}+k_{5d})^{1/2}} =$$

$$\frac{\Phi(1,6\text{-}C_6H_{12}Cl_2)}{[\Phi(1,3\text{-}C_4H_8Cl_2)]^{1/2}[\Phi(C_4H_7Cl) - (k_{6c}/k_{6a})\Phi(1,6\text{-}C_6H_{12}Cl_2)]^{1/2}} \quad (16b)$$

The right-hand sides of (16a) and (16b) are plotted in Figure 4 using the previously found values of k_{4c}/k_{4d} and k_{6c}/k_{6a}. The first expression is quite constant for values of $(C_2H_4)/I_a^{1/2}$ less than 10^3 (mm. min.)$^{1/2}$ but drops by about a factor of three as $(C_2H_4)/I_a^{1/2}$ rises to 10^4 (mm. min.)$^{1/2}$. At the very high values of $(C_2H_4)/I_a^{1/2}$, as pointed out earlier, 1,6-$C_6H_{12}Cl_2$ is produced by additional steps to those included in our mechanism. This excess 1,6-$C_6H_{12}Cl_2$ undoubtedly is produced by chlorine-atom transfer to $C_6H_{12}Cl$ radicals and accounts for the decline of the right-hand side of (16a). Additional evidence for the excess 1,6-$C_6H_{12}Cl_2$ formation is the fact that $\Phi(1,4\text{-}C_4H_8Cl_2)/\Phi(1,6\text{-}C_6H_{12}Cl_2)$ falls considerably below the ratio k_{6d}/k_{6a}. A comparison of the C_6 products indicates that chlorine-atom transfer to the $C_6H_{12}Cl$ radical is one of the predominant reactions of this radical.

The right-hand side of (16b) remains about 17 for the limited range of $(C_2H_4)/I_a^{1/2}$, i.e., 1000 to 7000 (mm. min.)$^{1/2}$, where computation could be effected. From this value and the other rate constants, $k_6/k_4^{1/2}k_5^{1/2}$ was found to be about 10. If all the radical–radical reactions occurred at the same rate (e.g., every collision), the ratio would have been 2. The fact that the ratio exceeds 2 indicates that the absolute reaction rates differ, a result that is not too surprising.

An alternative approximate route to compute the ratio of propagation constant, k_{3a}, to the square root of the average termination constant, k_r, is to consider the consumption of monomer. This leads to the expression

$$k_{3a}/k_r^{1/2} = [I_a^{1/2}/(C_2H_4)][\Phi(\Sigma C_2) - 2] \quad (17)$$

where k_r is defined as

$$k_r = \frac{k_4(C_2H_4Cl)^2 + k_5(C_4H_8Cl)^2 + k_6(C_2H_4Cl)(C_4H_8Cl)}{(C_2H_4Cl)^2} \quad (18)$$

Equation 17 assumes that no monomer is regenerated by the termination reactions, which in fact is not true; thus (17) can only give a lower limit for $k_{3a}/k_r^{1/2}$. The right-hand side of (17) is plotted in Figure 5. Surprisingly, over the range of $(C_2H_4)/I_a^{1/2}$ from 10^3 to 10^4 (mm. min.)$^{1/2}$, the function is quite constant at about 1.6×10^{-4} (mm. min.)$^{-1/2}$. Since $k_r > k_4$, the function must be smaller than $k_{3a}/k_4^{1/2}$, as indeed it is.

When the free-electron ends of any two radicals combine, either hydrogen-atom transfer or combination can occur. It is difficult to see why the length of the radicals should influence the relative likelihood of the reactions. Thus, the ratio of H-atom transfer to combination should be nearly constant for all radical combinations. This ratio is given by $k_{4b}/k_{4a} = 0.36$ for two C_2H_4Cl radicals, which is quite similar to the corresponding ratio $(k_{6b} + k_{6c})/k_{6a} = 0.47$ for a C_4H_8Cl and a C_2H_4Cl encounter. On the other hand, chlorine-atom transfer transpires when the active end of one radical approaches the chlorine end of the second radical. Here the chain length could make a significant difference as to which end is more likely to be at-
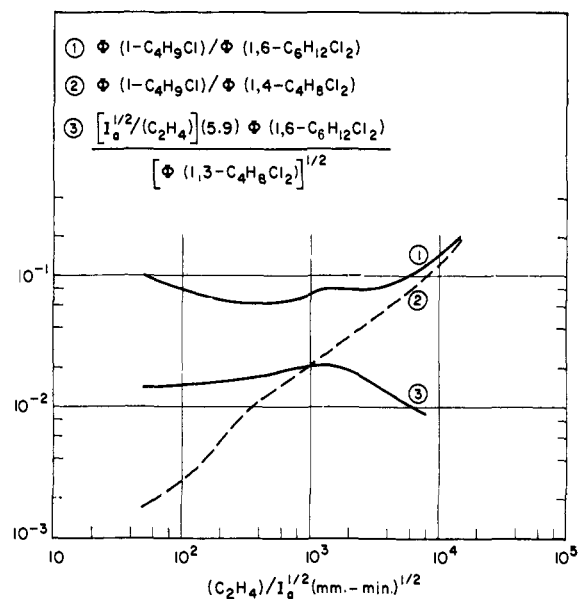

① Φ (1-C_4H_9Cl)/Φ (1,6-$C_6H_{12}Cl_2$)

② Φ (1-C_4H_9Cl)/Φ (1,4-$C_4H_8Cl_2$)

③ $\dfrac{[I_a^{1/2}/(C_2H_4)](5.9)\ \Phi\ (1,6\text{-}C_6H_{12}Cl_2)}{[\Phi\ (1,3\text{-}C_4H_8Cl_2)]^{1/2}}$

Figure 6. Appropriate functional relations vs. $(C_2H_4)/I_a^{1/2}$.

tacked. Thus, the ratio of chlorine-atom transfer to hydrogen-atom transfer for two C_2H_4Cl radicals $k_{4c}/k_{4b} = 0.24$, is about $1/40$th as large as that for the corresponding ratio, $(k_{6d} + k_{6e})/(k_{6b} + k_{6c}) = 9.6$, for a C_4H_8Cl-C_2H_4Cl encounter. With the $C_6H_{12}Cl$ radical, the evidence also suggests large amounts of chlorine-atom transfer with the products favoring the longer dichloride as in the C_2H_4Cl-C_4H_8Cl case. Unfortunately, the unusual reaction 5d obscures the situation for collisions of two C_4H_8Cl radicals. Nevertheless, a trend to relative enhancement of Cl-atom transfer with the heavier dichloride being favored seems to be indicated as the radicals increase in length.

A crude estimate can be made for $k_{3b}/k_5^{1/2}$. The mechanism yields the expression

$$\frac{k_{3b}}{k_5^{1/2}} = \frac{I_a^{1/2}}{(C_2H_4)}\left[\frac{\Phi(3b)}{\Phi(5)}\right]^{1/2} \quad (19)$$

At the highest values of $(C_2H_4)/I_a^{1/2}$, the C_2H_4Cl radical is not very important, and a significant proportion of the 1,6-$C_6H_{12}Cl_2$ comes from reactions of the $C_6H_{12}Cl$ radical. Approximate expressions for $\Phi(3b)$ and $\Phi(5)$ are

$$\Phi(3b) \approx \Phi(\alpha\text{-}C_6H_{12}) + \Phi(1\text{-}C_6H_{12}) + \Phi(\beta\text{-}C_6H_{11}Cl) +$$
$$\Phi(\gamma\text{-}C_6H_{11}Cl) + \Phi(1\text{-}C_6H_{13}Cl) + \Phi(1,6\text{-}C_6H_{12}Cl_2) \quad (20a)$$

$$\Phi(5) \approx \Phi(1,4\text{-}C_4H_8Cl_2) + (1/2)\Phi(C_4H_7Cl) +$$
$$(1/2)\Phi(1C_4H_9Cl) + (1/2)\Phi(C_2H_5Cl) \quad (20b)$$

Substituting the experimental values gives $k_{3b}/k_5^{1/2} \approx 2 \times 10^{-5}$ (mm. min.)$^{-1/2}$, which is $1/100$th as large as the corresponding ratio $k_{3a}/k_4^{1/2}$ for C_2H_4Cl radicals.

The rate constant data are summarized in Table IV. In some cases, the ratios of rate constants are more reliable than in other cases. The first three entries as well as the values for k_{6c}/k_{6a}, $k_{6a}/[k_{4d}^{1/2}(k_{5b} + k_{5d})^{1/2}]$, and $k_6/k_4^{1/2}k_5^{1/2}$ should be good to $\pm 20\%$, whereas the values for k_{5d}/k_{5b}, k_{6b}/k_{6a}, k_{6d}/k_{6a}, k_{6e}/k_{6a}, and $k_{3a}/k_{4d}^{1/2}$ probably have an uncertainty of $\pm 50\%$.