ample, vapor phase photolysis of *trans*-methyl propenyl ketone yields the *cis* isomer.[5]

The formation of methyl isopropenyl ketone [$CH_3COC(CH_3)CH_2$] require migration of a methyl group and a hydrogen atom and probably occurs by a decomposition–recombination process.

Yields of methane and propylene (0.07 and 0.01) are low but $G(CH_4)$ is appreciably higher than $G(C_3H_6)$. Excited methyl propenyl ketone molecules probably decompose more readily by

$$CH_3COCH{=}CHCH_3 \longrightarrow CH_3\cdot + CH_3CH{=}CHCO\cdot$$

than

$$CH_3COCH{=}CHCH_3 \longrightarrow CH_3CO\cdot + CH_3CH{=}CH\cdot$$

because the crotonyl radical ($CH_3CH{=}CHCO\cdot$) is resonance stabilized. These radicals once formed do not decompose readily to give CO and $CH_3CH{=}CH\cdot$[14]

It is evident that unsaturated and cyclo substituted ketones are much more stable toward decomposition into radicals under radiolysis than saturated ketones and thus analogous with their photolytic behavior. The stability of unsaturated ketones may be put down in part to stability imparted by conjugation. However, non-conjugated ketones are also stable toward decomposition into radicals. Thus, Srinivasan[15] found that 5-hexene-2-one was remarkably stable toward photodecomposition and experiments in these laboratories confirm this observation.

By analogy one would expect methyl allyl ketone to be stable toward radiolysis. We have obtained radiolysis data on this compound which indicate that such is the case. However, we had reservations concerning the purity of our sample, and it was felt that the results did not warrant inclusion and discussion with the other data.

Acknowledgments.—Certain preliminary experiments in this investigation were conducted by Mr. J. Swinehart, whom we wish to thank. This research was supported in part by grants to J.N.P. from the Petroleum Research Fund of the American Chemical Society, Grant No. PRF 278-A, and the U. S. Public Health Service through Grant RG-7005. We are deeply indebted to these granting agencies and to Drs. D. P. Stevenson, Robert Brattain and John Otvos of the Shell Development Company at Emeryville, California, who made available their facilities, and to Dr. Charles Wagner and Mr. E. R. Bell, who directed the laboratory radiolyses and provided us with many stimulating discussions on radiation chemistry. J.N.P. also acknowledges with thanks his period as visiting scientist at the Shell Development Company, during which he initiated this research.

[14] A. D. Osborne and G. Skirrow, *J. Chem. Soc.*, 2750 (1960).

[15] R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960).

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

Photolysis of Phosgene in the Presence of Ethylene[1]

BY M. H. J. WIJNEN

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The photolysis of phosgene in the presence of ethylene has been carried out at various phosgene to ethylene ratios, and at different light intensities and temperatures. The results are quite different from those obtained by photochlorination of ethylene in the presence of molecular chlorine. The main reaction products were: carbon monoxide, 1-chlorobutane and 1,4-dichlorobutane. The formation of 1,4-dichlorobutane and 1-chlorobutane may be represented by the several reactions: $2C_2H_4Cl \longrightarrow (C_2H_4Cl)_2$ (4); $C_2H_4Cl + C_2H_4 \longrightarrow C_4H_8Cl$ (7); $C_4H_8Cl + R \longrightarrow C_4H_9Cl + R'H$ (9). An activation energy of about 7.5 kcal. is proposed for reaction 7. The carbon monoxide yield is directly proportional to the absorbed light intensity and may be used as an internal standard for the amount of chlorine atoms produced.

Introduction

The photochlorination of ethylene in the presence of molecular chlorine proceeds *via* the well-known chain process

$$Cl + C_2H_4 \longrightarrow C_2H_4Cl$$
$$C_2H_4Cl + Cl_2 \longrightarrow C_2H_4Cl_2 + Cl$$

The following information indicated that substitution of phosgene for molecular chlorine as the chlorine atom donor might prevent the occurrence of a chain reaction.

Schwab,[2] investigating the reactions of Cl atoms produced by the discharge tube method, observed that the addition of phosgene had very little effect on the chlorine atom concentration. Since consumption of Cl atoms would be expected by the sequence

$$Cl + COCl_2 \longrightarrow Cl_2 + COCl \qquad (A)$$
$$Cl + COCl \longrightarrow Cl_2 + CO \qquad (B)$$

he concluded that the activation energy of reaction A must be relatively high.

Bodenstein, Brenschede and Schumacher[3] reviewed the work on reactions A and B in detail and concluded that $E_A = 23$ kcal.

Runge[4] studied the photochemical reactions of oxalyl chloride and of phosgene with hydrocarbons. Chlorine atoms reacted with hydrocarbons to form HCl and alkyl radicals. No reaction was observed between alkyl radicals and phosgene.

These data indicate clearly that in the photolysis of phosgene no regeneration of chlorine atoms occurs by secondary reactions. The resulting reaction mechanism should thus be quite different from photochlorination processes in the presence of molecular chlorine.

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[1] This work was supported in part by the U. S. Atomic Energy Commission.

[2] G. M. Schwab, *Z. physik. Chem.*, **A178**, 123 (1936).

[3] M. Bodenstein, W. Brenschede and H. J. Schumacher, *ibid.*, **B40**, 121 (1938).

[4] F. Runge, *Z. Elektrochem.*, **60**, 956 (1956).

Experimental

The apparatus has been described previously.[5] A Hanovia S-500 medium pressure arc was used as the light source. The light of the S-500 arc was filtered through Corning filter No. 9-54 (transmitting above 2200 Å.). The light intensity was varied by inserting wire gauze screens between the reaction cell and the arc.

The reaction products and excess phosgene and ethylene were cooled down to liquid nitrogen temperature. At this temperature the only volatile product observed was carbon monoxide, which was measured by gas chromatography. The excess ethylene was then pumped off at −165°. Subsequently, the remaining reaction products and the excess of phosgene were analyzed by gas chromatography. For this analysis a six-foot column containing 18% (by weight) of Reoplex 400 (Geigy Pharmaceuticals) on firebrick was used. This fraction contained two major reaction products: 1,4-dichlorobutane and 1-chlorobutane. Small to trace amounts of 1,2-dichloroethane and 1-chlorohexane were also observed. The last two products were formed in amounts too small to be measured accurately and are not reported in Table I. Hydrogen chloride was not detected as a reaction product.

TABLE I

PHOTOLYSIS OF PHOSGENE IN PRESENCE OF ETHYLENE

Run no.	Intensity rel., %	$COCl_2$	C_2H_4	CO	C_4H_9Cl	$(C_2H_4Cl)_2$
		Initial press., molec./cc. × 10^{-17}		Rate of formation of products, molec./(cc.) × sec. 10^{-12}		
		Temp. 28°				
1	3	12.6	28.2	1.15	0.12	0.14
2	3	12.7	36.1	1.28	0.21	0.19
3	100	14.0	11.7	29.80	n. obsd.	11.88
4	3	18.1	38.4	1.31	0.12	0.23
5	30	11.1	18.4	7.46	.23	2.66
20	100	14.9	28.2	27.40	.99	14.18
21	30	14.5	30.1	8.95	.65	4.75
22	30	14.3	25.5	9.23	.28	4.05
		Temp. 74.5°				
6	100	9.8	9.0	26.20	2.10	13.28
7	100	8.9	12.5	25.81	1.7	5.8
8	100	10.9	32.2	27.50	5.68	6.32
9	9	11.7	12.5	3.28	0.84	0.59
10	100	10.2	15.7	28.81	2.11	6.57
11	30	8.6	33.5	8.75	0.95	1.37
12	9	13.0	6.7	3.48	.45	0.80
13	9	11.6	24.2	3.48	.72	.47
14	3	11.9	12.2	1.29	6.41	.15
		Temp. 130°				
15	100	9.8	6.4	25.40	2.73	2.17
16	100	6.2	6.2	16.68	1.73	1.60
17	100	10.8	23.9	27.40	7.30	2.40
18	100	12.0	4.3	29.61	1.66	2.20
19	100	12.5	3.9	29.80	1.11	1.37

Results and Discussion

The photolysis of phosgene in the presence of ethylene was carried out at various phosgene to ethylene ratios and at different light intensities and temperatures. About 1% of the phosgene initially present was decomposed during the photolysis. The results are summarized in Table I.

Primary Process.—The primary step in the photolysis of phosgene is generally[3,6–8] accepted to be

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

Bodenstein and co-workers[3] obtained 5.7 kcal., Burns and Dainton[9] 6.3 kcal. as the activation energy for the thermal decomposition of the COCl radical. This indicates that COCl radicals will decompose readily into carbon monoxide and chlorine atoms. Our data confirm this observation. If the COCl radical were stable, it would undoubtedly take part in some of the following reactions at high radical concentrations and low temperatures.

$$2COCl \longrightarrow (COCl)_2 \qquad (a)$$

$$COCl + Cl \longrightarrow CO + Cl_2 \qquad (b)$$

$$COCl + Cl \longrightarrow COCl_2 \qquad (c)$$

$$COCl + C_2H_4Cl \longrightarrow CH_2ClCH_2COCl \qquad (d)$$

It seems quite possible that in our case reactions b and c might be of minor importance since Cl atoms are taken up rapidly by ethylene. The absence of oxalyl chloride and β-chloropropionyl chloride as reaction products confirms that the COCl radical does not survive long enough to take part in radical–radical reactions. The absence of β-chloropropionyl chloride is particularly convincing, since the C_2H_4Cl radical is present in relatively large concentrations, as shown by the formation of 1,4-dichlorobutane. Our results at 74.5 and at 130° indicate that the CO yield is directly proportional to light intensity and to initial phosgene pressure. This confirms that all COCl radicals decompose into carbon monoxide and chlorine atoms. Unfortunately, a direct comparison of our data at 28° with those at higher temperatures is not possible since the absorbed light intensity at 28° is not proportional to the phosgene pressure, due to somewhat high phosgene pressures employed in this series. A few experiments on the CO yield at lower initial pressures (not reported in Table I) indicate that the CO yield does not vary by more than 10% over the temperature region 28 to 130°.

Reaction Mechanism.—At low temperatures, the photochlorination of ethylene in the presence of molecular chlorine proceeds *via* the chain reaction

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

$$C_2H_4Cl + Cl_2 \longrightarrow C_2H_4Cl_2 + Cl \qquad (B)$$

The only important reaction product is thus 1,2-dichloroethane.

As pointed out in the Introduction, information in the literature indicates that substitution of phosgene for molecular chlorine may prevent the regeneration of chlorine atoms by type B reactions. This is indeed observed, since only small to trace amounts of $C_2H_4Cl_2$ could be detected. Kharasch,[10] discussing the addition of free radicals to simple olefins, suggested that the prevention of type B reactions might lead to initiation of poly-

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[5] K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *J. Am. Chem. Soc.*, **74**, 714 (1952).

[6] M. Bodenstein, *Z. physik. Chem.*, **B3**, 459 (1926).

[7] F. Almasy and Th. Wagner-Jauregg, *Naturwissenschaften*, **19**, 270 (1931).

[8] (a) G. K. Rollefson and co-workers, *J. Am. Chem. Soc.*, **55**, 142, 4025, 4036 (1933); **56**, 1089 (1934); (b) M. S. Kharasch and H. C. Brown, *ibid.*, **62**, 454 (1940).

[9] W. G. Burns and F. S. Dainton, *Trans. Faraday Soc.*, **48**, 39 (1952).

[10] M. S. Kharasch, "Le Mecanisme de l'Oxydation," Rapports et Discussions, Huitieme Conseil de Chimie, Bruxelles, 1950, p. 77, reprinted by W. A. Waters in "Vistas in Free-Radical Chemistry," Pergamon Press, New York, N. Y., 1959, p. 96.

merization chains. If this suggestion is applied to our data, the formation of 1,4-dichlorobutane and 1-chlorobutane may be given by the reaction sequence

$$2C_2H_4Cl \longrightarrow (C_2H_4Cl)_2 \qquad (4)$$

$$C_2H_4Cl + C_2H_4 \longrightarrow C_4H_8Cl \qquad (7)$$

$$C_4H_8Cl + (C_2H_4)_xCl \longrightarrow C_4H_9Cl + CH_2{=}CH(C_2H_4)_{x-1}Cl \qquad (9)$$

In reaction 9 the $(C_2H_4)_xCl$ radical may be C_2H_4Cl or a radical formed by addition of one or more C_2H_4 molecules to the C_2H_4Cl radical. This reaction sequence explains why the formation of 1,4-dichlorobutane is favored by high light intensities and low ethylene pressures. Decreased light intensities and increased ethylene pressures favor addition reaction 7 and thus increased production of 1-chlorobutane. Since reaction 7 undoubtedly requires an activation energy, these reactions also are consistent with the fact that C_4H_9Cl production increases at the expense of $C_4H_8Cl_2$ formation with increasing temperatures.

It is, however, obvious that if we accept reactions 4, 7 and 9, we will have to consider other possible recombination and disproportionation reactions of the radicals involved in these reactions. The mechanism of (1) to (11) is therefore proposed to explain the important features of the photolysis of phosgene in the presence of ethylene.

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

$$COCl \longrightarrow CO + Cl \qquad (2)$$

$$Cl + C_2H_4 \longrightarrow C_2H_4Cl \qquad (3)$$

$$2C_2H_4Cl \longrightarrow (C_2H_4Cl)_2 \qquad (4)$$

$$2C_2H_4Cl \longrightarrow C_2H_5Cl + C_2H_3Cl \qquad (5)$$

$$2C_2H_4Cl \longrightarrow C_2H_4Cl_2 + C_2H_4 \qquad (6)$$

$$C_2H_4Cl + C_2H_4 \longrightarrow C_4H_8Cl \qquad (7)$$

$$C_4H_8Cl + (C_2H_4)_xCl \longrightarrow C_4H_8(C_2H_4)_xCl_2 \qquad (8)$$

$$C_4H_8Cl + (C_2H_4)_xCl \longrightarrow C_4H_9Cl + CH_2{=}CH(C_2H_4)_{x-1}Cl \qquad (9)$$

$$C_4H_8Cl + (C_2H_4)_xCl \longrightarrow \text{other dispr. products} \qquad (10)$$

$$C_4H_8Cl + C_2H_4 \longrightarrow C_6H_{12}Cl \qquad (11)$$

Reactions 1 and 2 have been discussed earlier. Reaction 3 is well established from photochlorination studies in the presence of molecular chlorine. Stewart and Weidenbaum[11] suggested $E_3 < 1.4$ kcal. Schmitz, Schumacher and Jager[12] conclude $E_3 \simeq 0$ kcal. We have not included in the reaction mechanism the substitution reaction $Cl + C_2H_4 \rightarrow HCl + C_2H_3$ since HCl was not observed as a reaction product. This is in agreement with data of Rust and Vaughan.[13] These authors studied the high temperature thermal chlorination of ethylene in a flow system. They observed that even at 235° the addition was the only important reaction and that the substitution reaction became important only at higher temperatures. Reactions 4, 7 and 9 have been shown to explain the formation of 1,4-dichlorobutane and 1-chlorobutane. Accepting reaction 4, we will have to consider reactions 5 and 6. Unfortunately our experimental technique did not allow analysis for C_2H_5Cl and C_2H_3Cl. No information is therefore available on reaction 5. The amount of $C_2H_4Cl_2$ produced was extremely small in all experiments. Even accepting that all $C_2H_4Cl_2$ originates from reaction 6, k_6/k_4 would not exceed 0.2. There seems little doubt that under certain conditions considerable amounts of 1,6-dichlorohexane and higher dichloro compounds are formed according to reaction 8. The boiling points of these compounds are, however, too high to allow their determination by gas chromatography. Accepting that two chlorine atoms are produced per molecule of CO, material balance calculations show that even under the most favorable conditions, only 60 to 70% of the chlorine was recovered. This chlorine deficiency, as well as the increase in the deficiency with increasing ethylene pressures and/or decreasing intensities, may well be explained by reactions 8 and 11, which become important under these conditions.

All disproportionation reactions between C_4H_8Cl and $(C_2H_4)_xCl$ radicals, except for 9, are summarized in reaction 10. One of these reactions might be the formation of 1,4-dichlorobutane according to

$$C_4H_8Cl + (C_2H_4)_xCl \longrightarrow (C_2H_4Cl)_2 + (C_2H_4)_x \qquad (12)$$

It is obvious that reaction 12 cannot be solely responsible for the production of 1,4-dichlorobutane since in that case 1,4-dichlorobutane and 1-chlorobutane would vary in a similar way rather than at the expense of each other with varying experimental conditions. For kinetic reasons, our experiments, reported in Table I, were carried out in such a way that measurable quantities of 1,4-dichlorobutane and 1-chlorobutane were formed. Some experiments, not reported in Table I, were carried out at low intensities and at high $C_2H_4/COCl_2$ ratios. As expected from the proposed reaction mechanism, relatively large quantities of C_4H_9Cl were formed but no $(C_2H_4Cl)_2$ could be detected. This proves that reaction 12, if it occurs at all, plays only a very minor role. This is also in agreement with observations on the disproportionation and recombination reactions of two C_2H_4Cl radicals, where we noted that $k_6/k_4 < 0.2$.

The foregoing discussion has shown that the results may be explained qualitatively by the proposed mechanism. It is interesting to attempt a quantitative study of the data. According to reaction 9, the rate of 1-chlorobutane is given by

$$R_{C_4H_9Cl} = k_9[C_4H_8Cl][(C_4H_8)_xCl] \qquad (I)$$

Stationary state derivations yield

$$[(C_2H_{4x}Cl] = I^{1/2}/(k_d + k_r)^{1/2} = R_{CO}{}^{1/2}/(k_d + k_r)^{1/2} \qquad (II)$$

and

$$[C_4H_8Cl] = \frac{k_7R_{(C_2H_4Cl)_2}{}^{1/2}[C_2H_4]_0}{k_4{}^{1/2}k_{11}[C_2H_4]_0 + k_4{}^{1/2}(k_d + k_r)^{1/2}R_{CO}{}^{1/2}} \qquad (III)$$

Substituting in equation I the values obtained in equations II and III for $[(C_2H_4)_xCl]$ and $[C_4H_8Cl]$, we obtain

$$\frac{R_{CO}{}^{1/2}}{[C_2H_4]_0} + \frac{k_{11}}{(k_d + k_r)^{1/2}} = \frac{k_7k_9R_{(C_2H_4Cl)_2}{}^{1/2}R_{CO}{}^{1/2}}{k_4{}^{1/2}(k_d + k_r)R_{C_4H_9Cl}} \qquad (IV)$$

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

[12] H. Schmitz, H. J. Schumacher and A. Jager, *Z. physik. Chem.*, **B51**, 281 (1952).

[13] F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **5**, 472 (1940); **7**, 491 (1942).

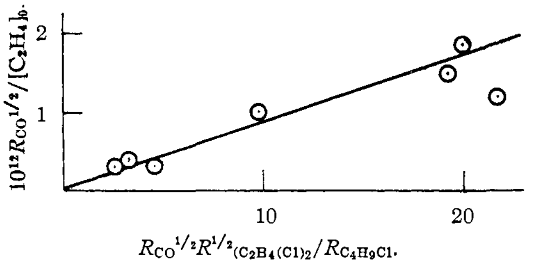

Fig. 1.—Plot of $R_{CO}{}^{1/2}/[C_2H_4]_0$ *versus* $R_{(C_2H_4Cl)_2}{}^{1/2}R_{CO}{}^{1/2}/R_{C_4H_9Cl}$ at 28°.

In the expressions above, k_d and k_r denote the rate constants for chain termination reactions by disproportionation and by recombination, respectively. $[C_2H_4]_0$ is the initial pressure of ethylene. To derive equation IV several assumptions have been made. First, termination reactions involving chlorine atoms may be neglected. It may be pointed out that it is customary in polymer chemistry to neglect termination reactions involving radicals formed from the catalyst. Although the chain length is short in our system, we have not observed evidence invalidating this assumption. Secondly, we have assumed that k_9 is independent of the size of the $(C_2H_4)_xCl$ radical. Some justification for this may be obtained from the following consideration. Ausloos and Steacie[14] and recently Kraus and Calvert[15] have indicated that the dominant factor determining the role of disproportionation reactions may well be the number of abstractable hydrogens which can be removed from the radical to form a stable olefin product. The number of hydrogen atoms available for disproportionation in the $(C_2H_4)_xCl$ radical is independent of the size of the radical.

Equation IV is plotted in Figs. 1, 2 and 3 for the temperatures 28, 74.5 and 130°. In spite of some scatter, the data show clearly a general agreement with equation IV and thus with the proposed reaction mechanism. Equation IV indicates that a negative intercept at the abscissa should be observed in Figs. 1, 2 and 3. With the possible exception of Fig. 3, no negative intercept is visible, indicating that $k_{11}/(k_d + k_r)^{1/2}$ is small in regard to the units in which the abscissa is expressed. From the slope of the lines in Figs. 1, 2 and 3, we obtain $k_7k_9/[k_4{}^{1/2}(k_d + k_r)] \simeq 0.85 \times 10^{-13}$ at 28°, 6.2×10^{-13} at 74.5° and 25.0×10^{-13} at 130°, the units being given in molecules$^{1/2}$/(sec.$^{1/2}$. cc$^{1/2}$). Accepting disproportionation and recombination reactions to have a zero activation energy, a value of about 7.5 kcal. may be calculated as the activation energy for reaction 7.

$$C_2H_4Cl + C_2H_4 \longrightarrow C_4H_8Cl \qquad (7)$$

No other data are available on E_7. It might have been interesting to compare E_7 with the activation energy of reaction 13.

$$C_2H_5 + C_2H_4 \longrightarrow C_4H_9 \qquad (13)$$

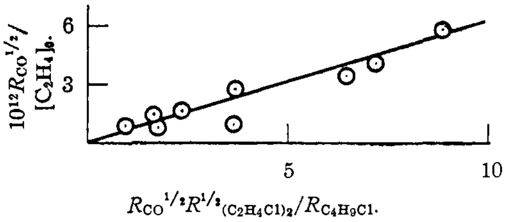

Fig. 2.—Plot of $R_{CO}{}^{1/2}/[C_2H_4]_0$ *versus* $R_{(C_2H_4Cl)_2}{}^{1/2}R_{CO}{}^{1/2}/R_{C_4H_9Cl}$ at 74.5°.

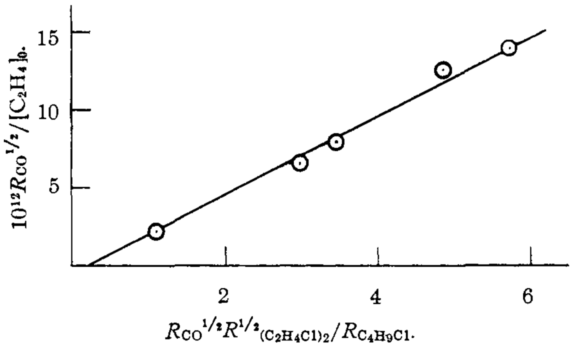

Fig. 3.—Plot of $R_{CO}{}^{1/2}/[C_2H_4]_0$ *versus* $R_{(C_2H_4Cl)_2}{}^{1/2}R_{CO}{}^{1/2}/R_{C_4H_9Cl}$ at 130°.

Unfortunately, E_{13} is not well established as may be seen from the following data: $E_{13} = 5.5$,[16] 7.0 ± 0.2,[17] 5.5[18] and 8.6 to 9.6[19] kcal. At the present time, therefore, it seems unwarranted to attempt a discussion of possible differences in reactivity between the C_2H_5 and the C_2H_4Cl radical.

It should be pointed out that in deriving equation IV we have not considered possible hydrogen abstraction reactions by the $(C_2H_4)_xCl$ radical such as

$$C_2H_4Cl + C_2H_4 \longrightarrow C_2H_5Cl + C_2H_3 \qquad (14)$$

and

$$C_4H_8Cl + C_2H_4 \longrightarrow C_4H_9Cl + C_2H_3 \qquad (15)$$

The occurrence of such reactions to any appreciable extent would invalidate equation IV and the activation energy obtained for reaction 7. Considering, however, the high values recently reported for the activation energies of hydrogen abstraction reactions by ethyl radicals,[20] it seems unlikely that reactions 14 and 15 may play an important role at the relatively low temperatures of our investigation.

Acknowledgment.—The author wishes to express his sincere thanks to Mr. J. A. Guercione for carrying out part of the experiments described in this paper.

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