Addition of Methyl Radicals to Vinyl Chloride and Catalysis of Di-t-butyl Peroxide Decomposition by Chlorinated Compounds

By A. M. Hogg[1] and Paul Kebarle

Using di-t-butyl peroxide (DTBP) as a source of methyl radicals, the rate constant for the addition to ethylene was redetermined as $k_{4a}/k_3^{1/2} = 9 \times 10^{-8} e^{-7820/RT}$ cc.$^{1/2}$ molecules$^{-1/2}$ sec.$^{-1/2}$ (k_3 refers to the recombination of methyl radicals). Attempts to use DTBP for the addition of methyl to vinyl chloride showed that vinyl chloride catalyzes the decomposition of DTBP. Other chlorinated compounds showed similar catalytic properties. The effect is due to release of HCl by some unknown reaction dependent on the presence of methyl radicals. The catalytic reaction was found strongly dependent on the surface-to-volume ratio of the reaction vessel. Packing the reaction vessel for a ratio of 16 cm.$^{-1}$ achieved complete suppression. The methyl addition to vinyl chloride was studied under these conditions and the rate constant found to be $k_{4a}/k_3^{1/2} = 1.5 \times 10^{-6} e^{-9053/RT}$.

Introduction

The gas phase addition of alkyl radicals to unsaturated compounds has been studied by a number of investigators. The systems on which information is available involve mainly methyl or ethyl radical addition to the lower olefins and diolefins. A recent summary of this work is given by Kerr and Trotman-Dickenson.[2]

An extensive compilation of methyl radical addition data, in solutions, has been provided by Szwarc[2] and collaborators. This group has also studied influences of heteroatom substituents on the olefins. Thus, Szwarc and collaborators found that the introduction of a chlorine atom in α (but not terminal) position to the double bond increases the rate of methyl addition very considerably. For example the rate of methyl addition at 65° to chloroprene was found to be three times faster than that to butadiene and isoprene.[3a] Szwarc also found in some unpublished work[3b] that the methyl addition to vinyl chloride at 65° and isooctane as a solvent is 34 times faster than that to ethylene.

The present investigation of the gas-phase addition of methyl radicals to vinyl chloride was undertaken in order to examine whether the activating effect of the chlorine atom can be observed also in a gas phase system. Also, it is of interest to learn whether the rate increase is due to a larger frequency factor or a lower activation energy.

The kinetics of the vinyl chloride polymerization have been studied by several authors.[4,5] Burnett and Wright,[5] using photoinitiation and a rotating-sector technique, were able to determine the kinetic constants for the propagation reaction. The availability of rate data for the addition of methyl to vinyl chloride should allow a comparison to be made between the rate of addition of a small radical and the composite rate of the propagation reaction.

For the study of the methyl addition reaction, the method developed by Brinton[6,7] was selected. Brinton used the thermal decomposition of DTBP (di-t-butyl peroxide) as source of methyl radicals in determinations

of the addition to ethylene[6] and propylene.[7] It was soon found that this method did not work with vinyl chloride. The presence of vinyl chloride led to formation of HCl and an undesirable chain decomposition of the DTBP. The subsequent text describes the nature of this HCl-catalyzed reaction, gives a method for suppressing it, and finally deals with the methyl addition to vinyl chloride.

Experimental

Reaction System and Analysis.—A 375-cc. Pyrex vessel attached to a conventional vacuum system was used. The reaction vessel was in an aluminum block furnace whose temperature could be regulated by means of an electronic thermoregulator[8] to ±0.2°. Known concentrations of the reactants, generally DTBP and vinyl chloride, were premixed in a 2-l. bulb and then expanded into the heated reaction vessel. After the required contact time the reaction mixture was allowed to expand out of the furnace into a 2-l. vessel. The aliquot trapped in the 2-l. vessel, corresponding to the contents of a reaction vessel with an effective volume of 333 cc., was processed as follows. The condensables at liquid nitrogen temperature were trapped and separated by gas chromatography. The uncondensable portion (containing only methane) was collected and measured with a Toepler pump. Mass spectrometric determination of the composition of this fraction was done frequently for control purposes. The separation of the condensables was achieved with a 1.5-m. oxydipropionitrile column at 25°. Acetone, isobutylene oxide, t-butyl alcohol, and isobutyraldehyde were obtained as pure fractions. The ethane fraction containing ethylene, propylene, and propane was trapped and reseparated on a temperature-programmed alumina column. The DTBP fraction contained chlorobutane. It was trapped and reseparated on a tricresyl phosphate column.

Results and Discussion

A. Addition of Methyl Radicals to Ethylene.— For the purpose of familiarization with the technique used by Brinton[6] a set of experiments was made on the methyl addition to ethylene. It was attempted to reproduce as far as possible Brinton's results. The only difference in the present experiments was the use of gas-chromatographic techniques rather than Ward still distillation followed by mass spectrometric identification as was used by Brinton. A summary of this work is given in Fig. 1 where an Arrhenius plot of the data obtained is shown. The Arrhenius parameters obtained are $k_{4a}/k_3^{1/2} = 0.904 \times 10^{-7} e^{-7820/RT}$ (cc.$^{1/2}$ molecules$^{-1/2}$ sec.$^{-1/2}$) in fairly good agreement with Brinton's data, $k_{4a}/k_3^{1/2} = 3.3 \times 10^{-7} e^{-8860/RT}$. The k_{4a} refers to the rate constant for addition while k_3 is the methyl radical recombination rate constant.

(1) In partial fulfillment of the Ph.D. Thesis of A. M. Hogg, University of Alberta, 1964.

(2) "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, p. 119.

(3) (a) A. Radjbenbach and M. Szwarc, Proc. Roy. Soc. (London), A251, 394 (1959); (b) M. Szwarc, private communication.

(4) W. I. Bengough and R. G. W. Norrish, Proc. Roy. Soc. (London), A200, 301 (1950).

(5) G. M. Burnett and W. W. Wright, ibid., A221, 41 (1950).

(6) R. K. Brinton, J. Chem. Phys., 29, 781 (1958).

(7) M. Miyoshi and R. K. Brinton, ibid., 36, 3019 (1962).
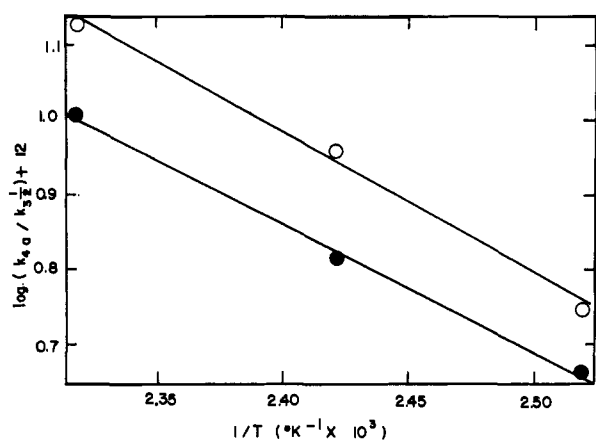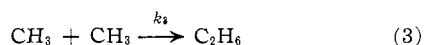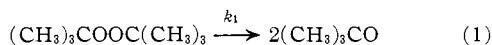
(8) Sargent Thermoniter.

Fig. 1.—Arrhenius plot for methyl addition to ethylene: k_{4a}, rate constant for methyl addition; k_3, rate constant for methyl recombination; O, Brinton[6]; ●, this study.

B. Catalysis of the DTBP Decomposition by Vinyl Chloride and Suppression of the Catalytic Action.—

When attempting to apply the DTBP method for the study of methyl addition to vinyl chloride it was found that the DTBP decomposition was greatly increased by the presence of vinyl chloride. It has been shown[9] that in the temperature range 120–170° DTBP decomposes smoothly by the following mechanism

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO \qquad (1)$$

$$(CH_3)_3CO \xrightarrow{k_2} CH_3COCH_3 + CH_3 \qquad (2)$$

$$CH_3 + CH_3 \xrightarrow{k_3} C_2H_6 \qquad (3)$$

Very little abstraction by (4) occurs as evidenced by a negligible yield of methane.

$$CH_3 + (CH_3)_3COOC(CH_3)_3 \longrightarrow$$
$$CH_4 + CH_2(CH_3)_2COOC(CH_3)_3 \quad (4)$$
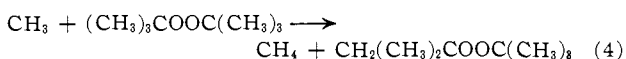
In the presence of a compound containing a double bond some of the methyl radicals disappear by addition. This leads to a fall-off in ethane formation, the rate of acetone formation remaining unaffected. The behavior in the presence of vinyl chloride is quite different. As shown in Fig. 2 the addition of vinyl chloride causes an increase in the rate of production of acetone, a very large increase in the rate of methane formation, and the appearance of a new product, isobutylene oxide. The following approximate equalities are also observed: $R_{CH_4} = R_{isobutylene\ oxide} = \Delta R_{CH_3COCH_3}$, where $\Delta R_{CH_3COCH_3}$ represents the increase in rate due to the presence of vinyl chloride. Obviously additional peroxide is being decomposed by the over-all reaction

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow$$
$$CH_4 + \overset{O}{\overset{\diagup\diagdown}{CH_2-C(CH_3)_2}} + CH_3COCH_3$$
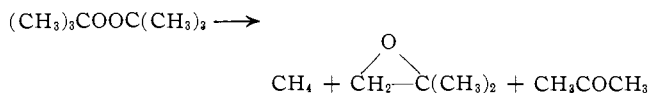
A clue to the cause of this phenomenon was obtained from the work of Cvetanović, Raal, and Steacie.[10–12] These authors, when studying the hydrogen abstraction

(9) (a) N. A. Milas and D. M. Sturgenor, J. Am. Chem. Soc., 68, 205 (1946); (b) P. George and A. D. Walsh, Trans. Faraday Soc., 42, 54 (1946); (c) J. H. Raley, F. F. Rust, and W. E. Vaughan, J. Am. Chem. Soc., 70, 88 (1948).

(10) F. A. Raal and E. W. R. Steacie, J. Chem. Phys., 20, 578 (1952).

(11) R. J. Cvetanović and E. W. R. Steacie, Can. J. Chem., 31, 158 (1953).

(12) R. J. Cvetanović, F. A. Raal, and E. W. R. Steacie, ibid., 31, 171 (1953).

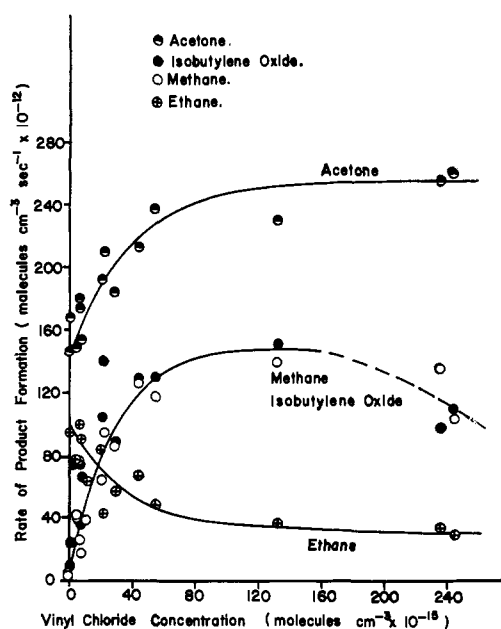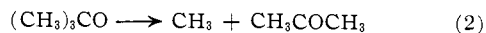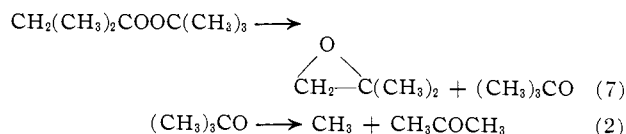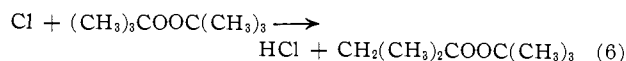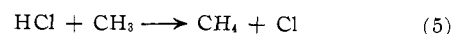Fig. 2.—Effect of addition of vinyl chloride on decomposition of DTBP at 158.5°.

by methyl radicals from the chloromethanes, had noticed that small amounts of HCl are released during the reaction and that methyl radicals abstract hydrogen from HCl at a very rapid rate.[11] The Cl atoms regenerate HCl by hydrogen abstraction from the substrate molecules. In the DTBP system this should lead to the following reactions.

$$HCl + CH_3 \longrightarrow CH_4 + Cl \qquad (5)$$

$$Cl + (CH_3)_3COOC(CH_3)_3 \longrightarrow$$
$$HCl + CH_2(CH_3)_2COOC(CH_3)_3 \quad (6)$$

$$CH_2(CH_3)_2COOC(CH_3)_3 \longrightarrow$$
$$\overset{O}{\overset{\diagup\diagdown}{CH_2-C(CH_3)_2}} + (CH_3)_3CO \quad (7)$$

$$(CH_3)_3CO \longrightarrow CH_3 + CH_3COCH_3 \qquad (2)$$

This reaction chain results in the over-all reaction given previously. The reaction mechanism 1–6 is essentially the same as that proposed by Raley, Rust, and Vaughan[13] in their study of the effect of HCl addition on the peroxide decomposition.

In order to prove that the catalytic effect in the present system was due to HCl the following tests were made: The condensable products and excess reactant were frozen with liquid nitrogen in a sampling trap containing a small amount of silver nitrate solution. On warming, white precipitates soluble in ammonia and reprecipitated by nitric acid were formed. Blank experiments in which the pyrolysis step was omitted showed no silver chloride precipitates. In a separate test the sampling trap contained 2 cc. of water. The pH of the reacted mixture was 3.3 while the blank experiment of the unreacted mixture gave a pH of only 4.5. Converting the pH 3.3 to HCl concentration (effective volume of reaction vessel, 333 cc.) one obtains for the HCl concentration 1.8×10^{15} molecules/cc. The following estimate shows that this is of the order of magnitude to be expected. The concentration of HCl should be dependent on the relationship $R_{CH_4}/R_{C_2H_6}^{1/2} = (k_5/k_3^{1/2})(HCl)$. The experiment in question was done

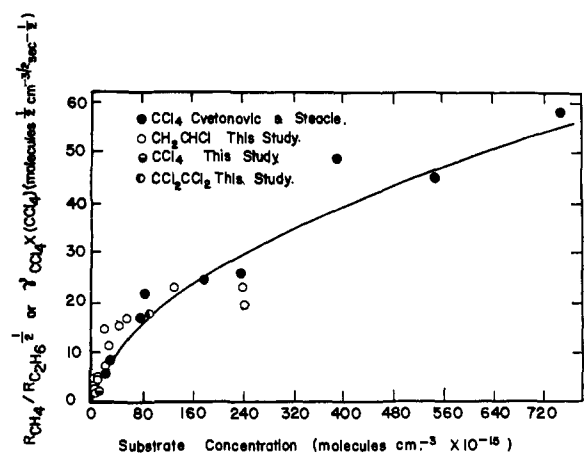(13) J. H. Raley, F. F. Rust, and W. E. Vaughan, J. Am. Chem. Soc., 70, 2767 (1948).

Fig. 3.—$R_{CH_4}/R_{C_2H_6}{}^{1/2}$ vs. substrate concentration in various CH_3-RCl reactions: temperature 158.5°; peroxide concentration 200 × 10¹⁵ molecules/cc.; contact time, 5 min.

at 159° and 260 × 10¹⁵ molecules/cc. of vinyl chloride and 200 × 10¹⁵ molecules/cc. of DTBP. From Fig. 3 we can read off $R_{CH_4}/R_{C_2H_6}{}^{1/2} = 30 \times 10^6$. From Cvetanović and Steacie's work[11] one obtained $k_5/k_3{}^{1/2} = 4.5 \times 10^{-9}$ at 159°. Combining these data one calculates an HCl concentration of 6.5 × 10¹⁵ molecules/cc., in agreement with the pH obtained value considering the approximate nature of the calculation.

The origin of HCl (or the kinetically equivalent Cl atoms or molecular chlorine) presents an interesting problem. As mentioned previously, Steacie and co-workers[12] observed its formation in the photolysis of acetone in the presence of chloromethanes. The present observation shows that it occurs also during pyrolysis so that one can eliminate all processes considered by the above authors which require the presence of light. In order to see whether the phenomenon is quite general, experiments were made using carbon tetrachloride and tetrachloroethylene. In both cases an effect ismilar to that with vinyl chloride was observed. The catalytic effect of the compounds can be examined by plotting $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ vs. the concentration of the added chlorine-containing compound. This is done in Fig. 3. The plot contains also the results obtained by Steacie and co-workers[14] with carbon 'tetrachloride. Remembering that $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ should be proportional to the average concentration of HCl we see that the effect of the various chlorine-containing compounds RCl is quite similar.

Attempts to suppress the vinyl chloride catalyzed decomposition of DTBP were made with the twofold burpose of further examining the nature of this reaction and, if a suppression could be achieved, of studying the methyl addition to vinyl chloride. Cvetanović, Raal, and Steacie,[12] using ammonia to remove the HCl, were able to suppress the methane formation at room temperature but not at 160° since the ammonium chloride is largely dissociated at this temperature. In the present work triethylamine was tried since its chloride should be more stable at elevated temperatures. A suppression by only a factor of two could be achieved at 160° when using the amine in concentrations similar to that of the vinyl chloride. Packing the reaction vessel with Raschig rings proved to be a far more con-

(14) Steacie's data used for the plot are corrected to take into account the H abstraction by methyl radicals from acetone. They correspond to $\gamma_{CCl_4}(CCl_4)$ of ref. 12.
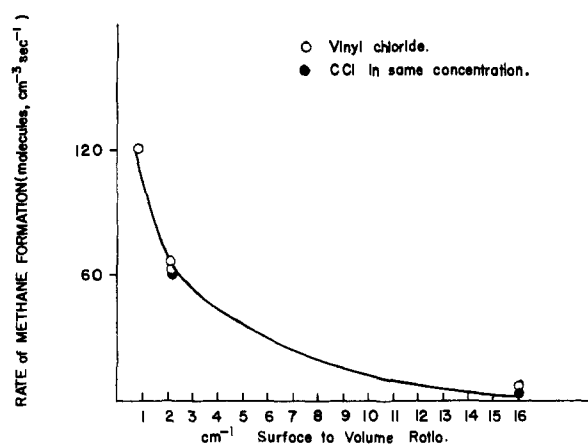

Fig. 4.—Effect of surface to volume ratio of reaction vessel on vinyl chloride catalyzed decomposition of DTBP: DTBP 200 × 10¹⁵ molecules/cc.; vinyl chloride 200 × 10¹⁵ molecules/cc.; temperature, 158.5°; contact time, 5 min.; volume of reaction vessel, 350 cc.

venient and efficient way of suppressing the reaction. The effect of the increased surface to volume ratio is shown in Fig. 4. The ratio was varied by packing vessels with glass rings of different diameter and keeping the volume approximately constant. The rate of methane formation per cc. was used as a convenient measure of the catalytic effect. The surface to volume ratio of the unpacked vessel was 0.8 cm.⁻¹. It can be seen that the catalysis is strongly dependent on the surface ratio exactly in this range. Complete suppression is achieved for a ratio of 16 cm.⁻¹ where the methane is equal to that formed when pure DTBP is decomposed. Glass rings from lime glass, Pyrex, and fused silica seemed equally effective when the surface ratio was 16 cm.⁻¹. The surface must be helping remove Cl or HCl from the cycle 5–7. Attempts to determine whether the effect of the surface was due to surface recombination of Cl atoms with some other species like methyl or to sorption of the HCl by the glass proved inconclusive. Thus, it could be shown[15] that the sorption on a Pyrex packing with a surface to volume ratio of 16 cm.⁻¹ is capable of reducing the HCl concentration by a factor of about five. However the reduction of HCl concentration indicated from Fig. 4 is more than 20-fold. Thus, no explanation on the nature of the suppressing effect of the surface can be given at this time.

An attempt was made to determine the nature of the chlorine-releasing reaction responsible for the HCl formation. Since HCl is formed in pyrolysis or photolysis whenever methyl radicals and chlorine-containing compounds are present, a reaction considered likely is

$$CH_3 + RCl \longrightarrow Cl + \text{products} \qquad (8)$$

In the case of vinyl chloride this should lead to the formation of propylene. Utilizing fully deuterated vinyl chloride at concentration and reaction conditions similar to those used in the pH determination, the presence of 4 × 10¹⁵ molecules/cc. of propylene-d_3 could be established. The separation was done by gas chromatography and the deuterium content determined with the mass spectrometer at low ionizing voltage. The deuterated propylene is thus about twice

(15) These experiments are described in the Ph.D. Thesis of A. M. Hogg, University of Alberta, 1964.
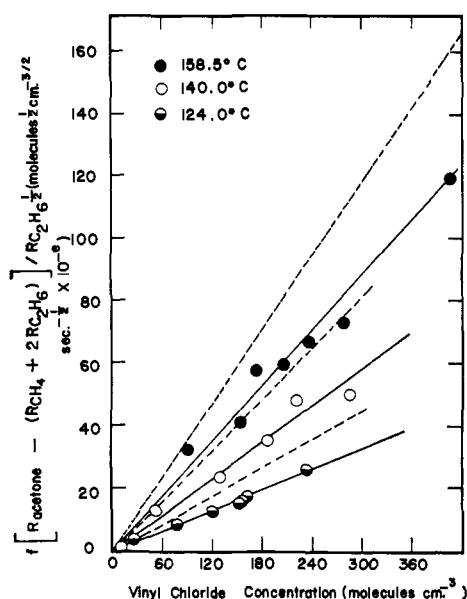
Fig. 5.—Rate constant plot for methyl addition to vinyl chloride: ———, $f = 0.5$; — — — —, f as calculated.

Fig. 6.—Arrhenius plot of methyl addition to vinyl chloride: ———, $f = 0.5$; — — —, f as calculated.
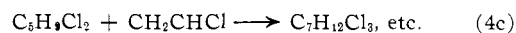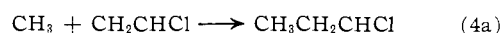
the amount of HCl estimated from the pH determination. It is not possible to decide whether this amount of deuterated propylene is enough to account for all the HCl released, since there is no information on the reactions which might be removing HCl from the cycle. However the finding shows at least that (8) cannot be excluded as a source of chlorine.

An investigation of the gas phase HCl-catalyzed decomposition of DTBP, by Benson and co-workers,[16] examined the reaction at much higher (one to two orders of magnitude) HCl concentrations. While the reaction products are quite similar, Benson finds that the induced decomposition of the DTBP is independent of the HCl concentration. The present results (Fig. 2 and 3) show that the induced decomposition and the CH_4/C_2H_6 ratio is dependent on the amount of chlorine-containing compound and thus presumably on the HCl concentration. This difference in behavior is not unexpected considering the very much higher HCl concentration used by Benson.
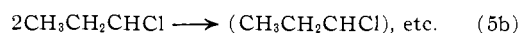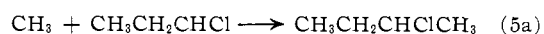
C. Methyl Radical Addition to Vinyl Chloride.— In the previous section it was shown that packing the reactor with Raschig rings suppressed the undesired HCl-catalyzed decomposition of DTBP in the presence of vinyl chloride. Using the packed reactor, experiments were undertaken to determine the rate of methyl radical addition to vinyl chloride.

In the presence of vinyl chloride the following polymerization reactions may be expected to occur.

$$CH_3 + CH_2CHCl \longrightarrow CH_3CH_2CHCl \qquad (4a)$$

$$CH_3CH_2CHCl + CH_2CHCl \longrightarrow C_5H_9Cl_2 \qquad (4b)$$

$$C_5H_9Cl_2 + CH_2CHCl \longrightarrow C_7H_{12}Cl_3, \text{ etc.} \qquad (4c)$$

Chain termination should proceed by the recombination reactions.

$$CH_3 + CH_3CH_2CHCl \longrightarrow CH_3CH_2CHClCH_3 \qquad (5a)$$

$$2CH_3CH_2CHCl \longrightarrow (CH_3CH_2CHCl), \text{ etc.} \qquad (5b)$$

If R_{4a} is to be determined through product analysis two principal methods can be used. The first one is based

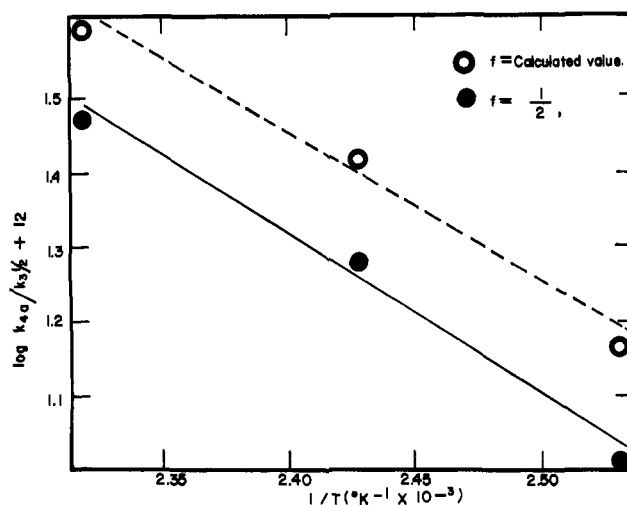(16) M. Flowers, L. Batt, and W. Benson, *J. Chem. Phys.*, **37**, 2662 (1962).

on tracing of the fate of the radical product by the methyl addition reaction 4a through analysis of the products containing this radical. For this method to be analytically possible it is necessary to suppress further polymerization (4b, 4c, etc.) by terminating the chains as in reaction 5a and b. This was the method used by Brinton with ethylene and its success depends on using high enough methyl radical concentrations. It had been hoped that it could be applied also to the vinyl chloride system. It was soon found that for similar concentration conditions the chain could not be terminated after the initial addition. By carefully measuring the amount of vinyl chloride used up in typical runs, it could be established that 1.5 molecules of vinyl chloride were used up per methyl radical. This leads to bichlorooctane as an expected average reaction product. Since the analytical difficulties in the quantitative detection of such high molecular height products are very great and the methyl radical concentration could not be increased sufficiently, the second method for determining the rate of addition had to be used. This method is based on a material balance of the methyl radicals. In the absence of vinyl chloride $R_{CH_4} + 2R_{C_2H_6} = R_{CH_3COCH_3}$ (see Table I). The rate of methyl radicals disappearing through addition and termination when vinyl chloride is present (R_A) is given by $R_A = R_{CH_3COCH_3} - R_{CH_4} - 2R_{C_2H_6}$. Of course, $R_A = R_{4a}$ only if termination always involves the recombination of two "polymer" radicals. If termination is produced always by one "polymer" and one methyl radical, $0.5R_A = R_{4a}$. The actual factor, f, before R_A would vary from 0.5 to 1 from run to run depending on the concentration of vinyl chloride and methyl radicals. Assuming $R_{4a} = 0.5R_A$ one can obtain $k_{4a}/k_3^{1/2}$ from the slope of the plots in Fig. 5. An Arrhenius plot of the rate constant ratio (Fig. 6) gives the rate constant parameters $k_{4a}/k_3^{1/2} = 2.5 \times 10^{-6}e^{-9730/RT}$ cc.$^{1/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$. Before discussing this result a corrective procedure should be mentioned which takes into account the variation of f under the changing experimental conditions. Details of the method are given in the Appendix. It suffices to say here that the procedure takes into account variation of the vinyl chloride and methyl radical concentration and is based on a comparison with the ethyl-

ene system where the information is much more complete.

The computed values of f are given in Table I. The new Arrhenius parameters are $k_{4a}/k_3^{1/2} = 1.5 \times 10^{-6} \cdot e^{-9053/RT}$ cc.$^{1/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$. Using Gomer and Kistiakowsky's[17] value $k_3 = 7.1 \times 10^{-11}$ cc. molecule^{-1} sec.$^{-1}$ and $E_3 = 0$, we obtain $k_{4a} = 2.1 \times 10^{-11} \cdot e^{-9730/RT}$ from the uncorrected and $k_{4a} = 1.3 \times 10^{-11} \cdot e^{-9503/RT}$ from the corrected results.

Comparing the individual rate constants with these for ethylene (see section A and ref. 6), one finds that, in the temperature range 120–160°, the addition of methyl to vinyl chloride is roughly three times faster. Thus the chlorine substituent has a considerable activating effect. Szwarc has found that in solution at 65° chloroprene adds methyl radicals 3.5 faster than butadiene and isoprene[2] and 2-chlorobenzoquinone adds methyl radicals 1.5 times faster than benzoquinone.[18] It was mentioned in the Introduction that Szwarc in some unpublished work[3] found that the methyl affinity of vinyl chloride is about 30 times higher than that of ethylene at 65°. The present gas-phase results extrapolated to 65° will give only a factor of about 3.5. The discrepancy is hard to understand.

It is of interest to know whether the activating effect of the chlorine atom is exerted through the frequency factor or the activation energy. Unfortunately, the present results are not sufficiently accurate to allow a safe decision on this point. Thus an error of 5% in the rate constants for the two extreme temperatures brings about a 1-kcal. error in the activation energy.

Appendix

Evaluation of the Methyl Addition to Vinyl Chloride.[19]—It was mentioned in section C that the experimental results allow only a determination of the rate of total methyl loss, R_A, and that the true methyl addition, $R_{4a} = fR_A$, where $0.5 \leqslant f \leqslant 1$ depending on how many methyl radicals are used up in the reaction sequence leading to a stable product. The evaluation of f is based on a comparison with the ethylene addition results obtained in section A and by Brinton.[6]

Considering first the addition to ethylene we define

$$U = k_9(P)(M)/2k_{10}(P)^2 \qquad (I)$$

where (P) is the concentration of all radicals produced by addition, i.e., propyl together with the higher polymer radicals; (M) is the methyl radical concentration; and k_9 and k_{10} are the respective recombination constants which include also disproportionation. Thus U is the ratio of methyl addition reactions requiring ultimately two methyl radicals to methyl addition requiring only one methyl.

It is easy to show that

$$f = (U + 1)/(2U + 1) \qquad (II)$$

Thus, knowledge of U allows determination of f. We proceed further as follows. The steady-state condition on (P) gives

(17) R. Gomer and G. B. Kistiakowsky, J. Chem. Phys., **19**, 85 (1951).
(18) A. Rembaum and M. Szwarc, J. Am. Chem. Soc., **77**, 4468 (1955).
(19) The calculations are presented in greater detail in A. M. Hogg, Ph.D. Thesis, University of Alberta, 1964.

$$k_{4a}(M)(E) - k_9(M)(P) - 2k_{10}(P)^2 = 0 \qquad (III)$$

where (E) is the ethylene concentration.

Solving for (P) and substituting in (I) one obtains

$$B = \left[\left(\frac{1}{U} + 1 \right)^2 - 1 \right] \frac{R_{C_2H_6}^{1/2}}{(E)} \qquad (IV)$$

$$B = 8k_{10}k_3^{1/2}k_{4a}/k_9^2 \qquad (V)$$

Reaction conditions in the ethylene system are such that (P) is almost entirely made up of propyl radicals. Thus, $U = R_{butane}/2.26R_{hexane}$ where the 2.26 also takes care of the disproportionation.[6] The B's are evaluated using the known rates of formation of ethane, butane, and hexane. These calculated B's are found (approximately) constant at a given temperature as required by (V).

Equations IV and V can be rewritten for the vinyl chloride system. Now k_{4a} is the rate constant for addition to vinyl chloride and (E) is replaced by (V) where V stands for vinyl chloride.

Assuming that the k_{10}/k_9^2 ratio is the same for both systems we have $B_V/B_E = k_{4aV}/k_{4aE}$. From this ratio one obtains B_V by substituting as a first approximation k_{4aV} obtained from $R_{4a} = 0.5R_A$. The B_V is then used in eq. V to determine U_V for different concentrations of vinyl chloride. The U_V substituted in II gives f_V, a function of the vinyl chloride concentration. The f_V values are given in Table I. While the corrective pro-

TABLE I

Temp., °C	$C_2H_3Cl^a$	DT-BP^a	$R_{CH_4}{}^b$	$R_{C_2H_6}{}^b$	$R_{acetone}{}^b$	$R_A{}^c$	f_V
122	0	192	2.42	14.0	38.2		
122	0	189	3.32	16.2	36.1		
122	0	214	3.20	19.6	41.4		
122	27.5	206	2.59	14.0	38.0	6.26	0.55
122	78.9	213	2.02	9.23	36.1	16.2	0.63
122	121	229	2.54	7.42	38.4	24.4	0.67
122	163	187	3.12	4.42	34.5	34.0	0.72
122	158	187	1.83	4.11	30.6	32.0	0.72
122	154	193	2.02	4.99	33.0	29.8	0.71
122	235	217	1.94	3.54	39.5	51.3	0.76
139.5	0	173	24.3	96.5	211		
139.5	0	143	13.3	97.5	206		
139.5	12.7	197	12.3	92.0	204	2.63	0.52
139.5	54.7	200	13.8	65.6	211	25.8	0.58
139.5	134	230	13.3	55.9	236	47.0	0.65
139.5	188	222	16.6	41.2	240	69.5	0.68
139.5	222	236	14.2	36.6	256	95.9	0.71
139.5	285	219	12.0	31.9	254	99.8	0.73
158.5	0	195	74.3	652	1620		
158.5	0	182	68.2	753	1560		
158.5	0	186	69.7	717	1550		
158.5	92.2	195	107	533	1640	64.4	0.58
158.5	156	200	110	514	1730	82.3	0.62
158.5	174	188	122	438	1760	115	0.63
158.5	206	189	92	376	1480	119	0.65
158.5	236	170	141	314	1520	134	0.67
158.5	278	204	142	363	1760	146	0.68
158.5	380	163	87	426	2490	237	0.70

^{a} Molecules cm.$^{-3} \times 10^{-15}$. ^{b} Molecules cm.$^{-3}$ sec.$^{-3} \times 10^{-11}$. ^{c} Molecules$^{1/2}$ cm.$^{-3/2}$ sec.$^{-1/2} \times 10^5$.

cedure does not change the rate constants or activation energy significantly it illustrates that it is permissible in the present system to identify R_A with R_{4a}.