# Kinetics of Addition of Cyclopropyl Radicals to Olefins. II

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Abstract: The kinetics of addition of cyclopropyl radicals to vinyl halides and other haloethylenes was investigated in order to assess the relative importance of polar and steric effects. In the vinyl halides the activation energy increases from the fluoride to the iodide. Reactivity follows the same order because the preexponential Arrhenius factor increases faster than the activation energy. A comparison is made with the rates of addition of other radicals to these substrates. The data show a regular pattern with respect to the ionization potentials and polarizabilities of the olefins and also with the radius of the halogen atoms but not with respect to their polarity. It is suggested that the connection between ionization potentials and reactivity stems from additivity relations in the reaction parameters and it is shown that the activation energies are linear with the London dispersion forces. A critique of the additivity rules and their failure is elaborated.

A great deal of the work in the investigation of the quantitative aspects of the addition of radicals to unsaturated centers has been concerned with the discovery of the law which controls the factors contributing to the reciprocal reactivity relationships of the reactants in the addition mechanism as summarized by the equation

$$R\cdot + \; \diagdown C=C \diagup \longrightarrow R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$
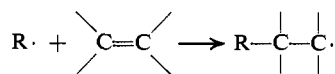
The theoretical collation of experimental data in terms of any particular model for the activated state is most meaningfully accomplished if the temperature dependence of the specific reaction rate is studied. In most previous work on radical addition reactions it has been assumed that the activated complex is a σ complex, and relative reactivity and selectivity have been discussed on the basis of rate data at a single temperature. This practice has contributed to the widely held opinion that changes in the specific rates of a given series of similar reactions are always controlled strictly by the energy term of the Arrhenius law,[1] and that the energies of the bonds involved in the reaction are expected to be the principal cause of the variation in reactivity.[2,3] Notable examples demonstrating the failure of these assumptions (and also examples of their applicability) may be found in the tabulation of Trotman-Dickenson and Milne[4] on hydrogen abstraction reactions, in the work of Hammond[5] on radical association reactions, and in the work of Whittle[6] and of Kobayashi, et al.,[7] on the addition of CF_3 and of C_6H_5 radicals to substituted benzenes. A critical analysis of these assumptions in terms of the available data has been given recently[8] where it was shown that the frequently observed disparity in the correlations of rate data with bond strengths and with electronic and steric[9-16] factors arises

from the inadequacy of the assumed model of the transition state, and from the neglect of the excess thermodynamic functions of the reactants (for reactions in solution) and transition states.

Szwarc,[16-18] who has investigated the addition of radicals to a large number of systems, has argued that the transition state in the reactions of both the aromatic and the aliphatic substrates is a σ complex, although he also pointed out that anomalies are likely to arise in theoretical correlations of the data based on this model when the charge density of the reaction site of the olefin is altered by the presence of substituents on the unsaturated carbon atoms.[19] Recent data confirm this conclusion. The rate-limiting step in the aromatic series is indeed the formation of a σ complex. This structure, however, is preceded by a π complex, which, in the case of the reactions of substituted aromatics, controls almost totally the variation in reactivity through its consequences upon the entropy of activation.[8,20] In the case of many aliphatic substrates the rate-limiting step is controlled by a π complex in which the unsaturated carbon atoms retain their trigonal symmetry. The evidence for this conclusion in the case of the hydrocarbon olefins has been presented in the previous paper of this series[21] where it was also shown that the rate data for the addition of cyclopropyl and trifluoromethyl radicals to these olefins suggested a linear relationship between steric and electronic factors during the activation process. The reactivity trends found in these systems and the implications suggested by the observed correla-

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(3) J. M. Tedder and J. C. Walton, *Progr. React. Kinet.*, 4, 37 (1967).

(4) See "Tables of Bimolecular Gas Reactions" in A. F. Trotman-Dickenson and G. S. Milne, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 9 (1967).

(5) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, 91, 986 (1969).

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(17) J. H. Binks, J. Gresser, and M. Szwarc, *J. Chem. Soc.*, 3944 (1960).

(18) M. Szwarc, and J. H. Binks, *Theor. Org. Chem., Pap. Kekule Symp.*, 1958, 262 (1959).

(19) M. Szwarc, *J. Phys. Chem.*, 61, 40 (1957).

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(21) A. P. Stefani, L. Y. Chuang, and H. E. Todd, *J. Amer. Chem. Soc.*, 92, 4168 (1970).

tions immediately raised the question of the effect of static polarity and of polarizability upon the reaction rate. In view of the conclusions reached by other workers in regard to the separability of steric and electronic factors,[22] the investigation of the effect of the size and electronegativity of substituents on the rate parameters is pursued further here. In the present article we report the results of measurements of the kinetics of addition of cyclopropyl radicals to halogenated ethylenes and of some other unsaturated substrates over the temperature range 45–90°.

Experimental Section

The experimental details of preparing the samples, the analytical technique, and the method of calculation of the rate parameters have already been described.[9,15,19,21] Cyclopropyl radicals were generated by the thermal decomposition of biscyclopropaneformyl peroxide. Experiments were carried out at five temperatures from 45 to 90° with peroxide concentrations of 10^{-2}–10^{-3} M in the absence and also in the presence of varying amounts of olefin. Reaction times with each olefin were varied so that olefin consumption was not more than 5%. Each experiment for a given rate constant was repeated about five times using different concentrations of olefin. Product analysis was performed by gas chromatography using a column packed with 15% didecyl phthalate on firebrick. Essentially 100% of the cyclopropyl radicals generated by the decomposition of the peroxide were accounted for; no isomerization to allyl radicals nor dimerization to bicyclopropane was detected. Rate constants were calculated by the material balance technique which was described previously.[21] Errors in the constants are within 2–3%. All substances employed in our experiments, except the peroxide, were acquired from commercial sources and prior to their use were purified to appropriate standards of purity using conventional techniques. Biscyclopropaneformyl peroxide was synthesized by the method described by Hart and Wyman.[23] Isooctane, which was used as a solvent in all experiments, was of spectrograde quality.

Results and Discussion

The rate data obtained in this investigation were calculated from the measurements of the partial pressure of cyclopropane and carbon dioxide employing the material balance technique. The quantities of interest are the ratios k_2/k_1 and their temperature dependence. In this ratio k_2 and k_1 represent, respectively, the rate constant of the addition reaction and the rate constant for hydrogen abstraction from the solvent as depicted by the competitive mechanism

$$R\cdot + HS \longrightarrow RH + S\cdot \qquad k_1$$
$$R\cdot + A \longrightarrow RA\cdot \qquad k_2$$
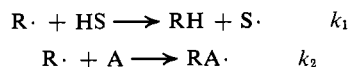
where HS is the solvent, A is the unsaturated substrate, and RH is the product of hydrogen abstraction (cyclopropane) from the solvent by the radical $R\cdot$ (cyclopropyl). The ratio k_2/k_1 is calculated from the Szwarc equation[9,13–21] where X_{HS} and X_A are the mole fractions

$$\frac{k_2}{k_1} = \frac{X_{HS}}{X_A}\frac{[RH]_b - [RH]_A}{[RH]_A}$$

of solvent and olefin, and $[RH]_b$ and $[RH]_A$ are, respectively, the partial pressures of cyclopropane formed in two separate but otherwise identical experiments, one with the olefin absent (b for blank) and the other with olefin present. The validity of the Szwarc equation and the conditions for its application have been discussed repeatedly in great detail;[9,13–21] its most rigorous ex-

perimental test is the constancy of the ratio (k_2/k_1) with varying concentrations of olefin at any given temperature. Since in all the experiments we used the same solvent, changes in the ratio k_2/k_1 for the various substrates at any given temperature are strictly due to the properties of the substrates.

The substrates examined in this study and their respective kinetic parameters are listed in Table I where, for

Table I. Relative Rate Constants for the Addition of Cyclopropyl Radicals to Ethylene Derivatives at 65° and Arrhenius Parameter

Substrate	k_2/k_1	$E_2 - E_1$	$\log(A_2/A_1)$
CH₂=CHF	16.1	−2.0	−0.08
CH₂=CHCl	40.6	−1.09	+0.9
CH₂=CHBr	80.1	−0.99	1.26
CH₂=CHI	253	−0.75	1.92
CHF=CHF	5.6		
CH₂=CF₂	11.2		
CHCl=CHCl-*trans*	1.8		
CHCl=CHCl-*cis*	6.5		
CH₂=CCl₂	399		
CHBr=CHBr	42.3		
CF₃CF=CFCF₃	114		
CH₃OCH=CH₂	50.0		
CH₂=CH₂[a]	23.4	−0.66	0.94
CH₃CH=CH₂[a]	10.4	0.14	1.1
trans-CH₃CH=CHCH₃[a]	5.8	0.98	1.4
cis-CH₃CH=CHCH₃[a]	6.1		
(CH₃)₂C=CH₂[a]	6.6		
(CH₃)₂C=CHCH₃[a]	3.1	1.7	1.6
(CH₃)₂C=C(CH₃)₂[a]	1.9	2.5	1.9

[a] Reference 21.

purposes of comparison, we also include some of the data which we reported in the previous paper. The Arrhenius parameters of the substances whose values of k_2/k_1 were investigated as a function of temperature are also given.

The most striking feature of the present data is the reactivity trend of the vinyl halides which is also manifested by the 1,2-dihaloethylenes. Evidently the effect of the various halogens upon the reactivity of the double bond falls in the order I > Br > Cl > F which is opposite to that normally anticipated on the basis of either the steric properties of these substituents or from considerations in regard to polar effects.[24,25] This behavior is also encountered in the addition reactions of methyl and trifluoromethyl radicals to the vinyl halides as may be seen from the data in Table II and thus we must conclude once again[21] that steric and electronic factors cannot be dealt with separately. The parallel behavior of the reactivity pattern of the CF₃, CH₃, and c-C₃H₅ radicals with the haloethylenes is to be contrasted with the pattern found in the reactions of these radicals and also in the reactions of NF₂ radicals and oxygen atoms with the hydrocarbon olefins because in the latter case there is an inverse proportionality in the steric and the electronic factors between the two types of radicals, the CH₃ and c-C₃H₅ radicals on the one hand, and the NF₂, CF₃, and oxygen atoms on the other. The energy of activation for the addition of cyclopropyl radicals to the hydrocarbon olefins increases monotonically with the number of alkyl groups

(22) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.
(23) H. Hart and D. P. Wyman, *J. Amer. Chem. Soc.*, **81**, 4891 (1959).

(24) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).
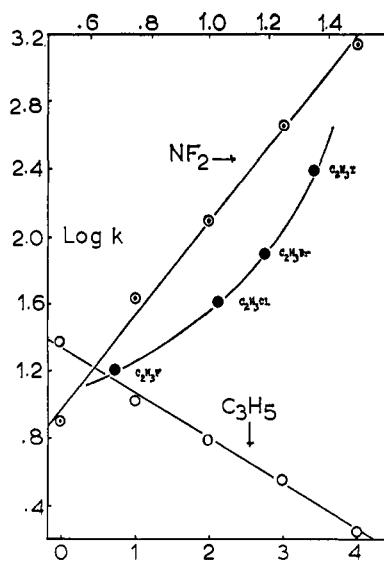(25) M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, **86**, 242 (1964).

Figure 1. Correlation of reactivity with the size of the halogen atoms and the number of methyl groups at the double bond: ⊙, NF₂ with methylated ethylenes; O, C₃H₅ with methylated ethylenes; ●, C₃H₅ with vinyl halides. Data for radii of halogens from J. A. A. Ketelaar, "Chemical Constitution," Elsevier, New York, N. Y., 1958.

Figure 2. Ionization potentials of olefins *vs.* log (k_2/k_1) for the addition of various radicals: O, c-C₃H₅ with methylated ethylenes; ⊙, CF₃ with vinyl halides; ●, c-C₃H₅ with vinyl halides; ⊝, CH₃ with vinyl halides. Ionization potential data from R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc., Ser. A*, **258**, 459 (1960).

at the double bond and decreases with increasing ionization potential of the olefin. The opposite of this is true[21] for trifluoromethyl[26] and for difluoroamino[27] radicals as well as for oxygen atoms.[28] The slope of the linear relationship between the activation energy (or ln *k*) and the ionization potential of the olefins is posi-

Table II. Comparison of the Addition Reactions of Some Radicals to Ethylene Derivatives at 65° Referred to Ethylene

Substrate	c-C₃H₅	CH₃[a]	CF₃[a]	CCl₃[b]	NF₂[c]
CH₂=CH₂	1.00	1.00	1.00	1.00	1.00
CH₂=CHF	0.69	0.53	0.16	0.68	
CH₂=CHCl	1.7	5.7	0.61		3.2
CH₂=CHBr	3.4	7.6	0.79		3.2
CH₂=CF₂	0.48	0.65	0.088	0.16	
CHF=CF₂		1.5	0.02	0.066	
CF₂=CF₂		10.1	0.15	0.43	
CH₂=CCl₂	17.1	26.7	1.13		
cis-CHCl=CHCl	0.28		0.014		
trans-CHCl=CHCl	0.077		0.028		

[a] Data from A. P. Stefani and M. Szwarc, Proceedings of the 2nd International Symposium on Fluorine Chemistry, Estes Park, Colo., July 17–20, 1962, pp 304–324. [b] Calculated from data given in ref 3. [c] Calculated from the data of A. J. Dijkestra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 864 (1967).

tive for c-C₃H₅ and negative for CF₃ and NF₂ radicals and O atoms. The slope of the activation energy (or ln *k*) *vs.* the number of substituents plot is negative for c-C₃H₅, and positive for the other three radicals. These relationships for the vinyl halides are depicted in Figures 1 and 2 which include also the plots for CH₃, CF₃, and NF₂ radicals. It is noteworthy that reactivity in the vinyl halides and in the polyhaloethylenes has no obvious simple dependence on the dipole moment of the olefin regardless of which radical is added to the double

(26) A. P. Stefani, L. Herk, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 4732 (1961).

(27) A. J. Dijkstra, J. A. Kerr, and A. F. Trotman Dickenson, *J. Chem. Soc.*, 105 (1967).
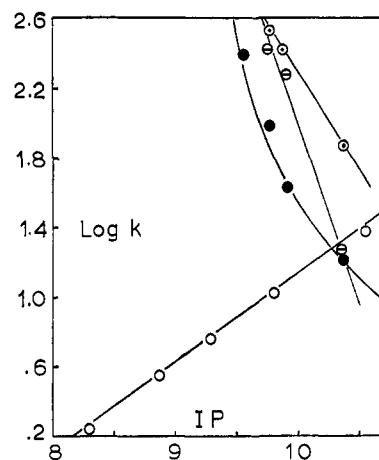
(28) R. J. Cvetanovic, *Advan. Photochem.*, 1, 115 (1963).

bond (see Table II), although it may be argued that there is little reason to expect such dependence on the ground-state properties of the reactants. The source of the manifestation of electrophilic or nucleophilic characteristics is obviously buried in the interplay between the attraction and repulsion potential fields as well as extent of involvement of the primary valence (and resonance) field during the activation process. Steric and electronic contributions to the activation process are certainly not independent functions of structure in these addition reactions. In fact, the data suggest very strongly that these factors are proportional to each other;[21] this situation quite likely arises because the variation in the structure of the substrates involves directly the reaction center. It is perhaps significant that when the substituent is separated from the double bond by one or more methylene groups there is a regular variation in reactivity with the polarity of the substituent from the point of view of the Hammett–Taft relations, as shown recently by Martin.[25] Martin's data, however, are difficult to interpret from a fundamental standpoint because, as in most Hammett-type studies, reactivity is examined at a single temperature, and the consequences of the thermodynamic excess functions of the solution process upon the activation parameters are not evaluated. This point is particularly critical since the dependence of the variation as well as the magnitude of the excess functions on structure is quite frequently comparable to the variation (and sometimes comparable even to the magnitude) of the activation parameters of the pertinent rate process. Our results suffer from the same limitation, but, in our case, the severity of the limitation is small because of two reasons: (a) our solvent is invariable, and mainly (b) our reaction systems are essentially regular solutions.[29,30] For such solutions the influence of the solvent upon rates and/or equilibria is quite small. Its origin resides in the cross relations between the cohesive energy densities and volume changes of the solute–solvent system.[30] Indeed for such solutions the ratio (k_1/k_g) of the rate con-

(29) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962.

(30) A. P. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968).

stant in solution (k_1) to that in the gas phase (k_g) is very nearly constant[31] in a given solvent. This suggests that the perturbation of the rate process by the solvent is approximately the same for the various reactions investigated.

It is important to emphasize here the fact that the connection between reactivity and ionization potential which intuitively leads to considerations in regard to electrophilic or nucleophilic properties must not always be used indiscriminantly. Whatever the connection is between the free energy of activation and the ionization potential of the substrates in a reaction with a given radical, it cannot be the sole factor that controls the variation in reactivity. This situation is analogous to the connection between reactivity and substituent constants in the Hammett relations which frequently break down when, for example, the effect of the solvent on reactivity varies in a manner which is not linear with the variation in the substituent constants.[32]

We suggest that the particular relationships between the ionization potential and reactivity described or referred to here and in the previous paper[21] stem from the contribution of the London dispersion potential to the activation energy and from the proportionality of this contribution to other potentials which may tend to decrease or increase the barrier to reaction. This may be shown quite simply if we assume that the activation energy E_a may be formulated in terms of a linear combination of the conceivably significant intermolecular potentials (eq 1). Here E_o is the intrinsic energy of activation for the interaction of a radical with a hypothetical bare double bond, E_r is a repulsion term which includes steric effects, the third term is a temperature dependent polarization term arising from multipolar interactions, and the fourth term is the London dispersion potential. For the reaction systems under consideration calculation shows that the magnitude of the third term is always within the range of 5–10% of the magnitude of the dispersion term, and for a qualitative discussion we may initially neglect it. Now since the data suggest a proportionality between steric and electronic factors we might set E_r and E_1 proportional to each other and thus write explicitly

$$E_a = E_o + E_r + E_p + E_1 \quad (1)$$

$$E_a \simeq E_o - b\frac{\alpha_R \alpha_S}{r^6} I_S/(1 + I_S/I_R) \quad (2)$$

The subscripts R and S refer to the radical and the substrate, respectively, α is the polarizability, I is the ionization potential, and b is a constant. The ratio I_S/I_R is usually close to unity, and for a given radical the polarizability α_R is a constant. Thus E_a is given by

$$E_a \simeq E_o - c\frac{I_S \alpha_S}{r^6} \quad (3)$$

where r is the distance between the radical and the substrate in the transition state. The formation of the transition state may now be viewed in one of two ways. (1) The radical interacts with the hypothetical bare double bond at a constant distance r_o and with energy E_o. Substituents are then fed in, which change the
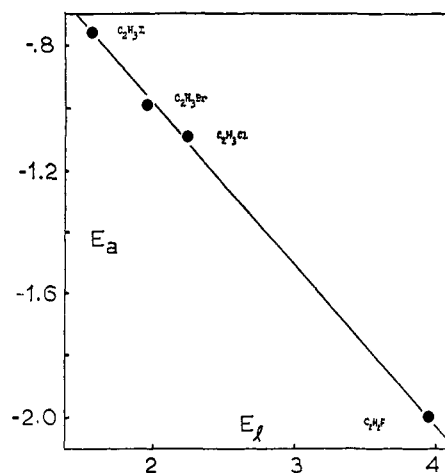

Figure 3. Plot of the experimental activation energy $E_a = E_2 - E_1$ vs. the London dispersion energy for the addition of cyclopropyl radicals to the vinyl halides. Data for polarizabilities and atomic radii from J. A. A. Ketelaar "Chemical Constitution," Elsevier, New York, N. Y., 1958.

activation energy through their steric and electronic effects. (2) The radical interacts with the double bond at a variable distance ($r_o + \delta r$) whose value depends on the nature of the substituent. The first model requires a linear dependence of the experimental activation energy on the product of the ionization potential and the polarizability of the substrates with a positive or negative slope consistent with the type of proportionality pertaining to the relationship between steric and electronic factors. Indeed the experimental data conform to this condition, and since $\log A$ is proportional to E_a, the plot of $\log (k_2/k_1)$ vs. $I_S \alpha_S$ is also linear. Due to the additive properties of the polarizability, the product $I_S \alpha_S$ has the form $I_S(\alpha_1 + mx)$ in which α_1 is the polarizability of the first member of the set of substrates under consideration (i.e., ethylene or vinyl fluoride), m is an integer including zero, and x is the polarizability increment for each member of the set. Examination of the numerical values of the quantities $I_S \alpha_1$ and mxI_S for the substrates of interest here reveals that the two quantities are very nearly proportional to each other, with deviations from proportionality being greater for the halogen compounds. We can thus understand the connection between the rate parameters and the ionization potential. For the second model we may employ eq 2 or 4 in which the dispersion energy is expressed in terms of the effective number n of electrons.[33-35]

$$E_1 = -\frac{3}{4}\frac{eh}{\pi m^{1/2}}\frac{\alpha_R \alpha_S}{(\alpha/n)_R^{1/2} + (\alpha/n)_S^{1/2}}\frac{1}{r^6}$$

$$(4)$$

$$E_a \simeq E_o - \frac{B\alpha_S}{(\alpha/n)_R^{1/2} + (\alpha/n)_S^{1/2}}\frac{1}{r^6}$$

The application of this equation to the data for the vinyl halides is shown in Figure 3 in which the distance r is set equal to ($r_o + \delta r$), with δr varying according to the radii of the halogen atoms. A similar relationship has also been discussed for the variation in the rate parameters of the metathetical reactions of methyl and trifluoromethyl radicals.[8] The important consequence

(31) P. S. Dixon and M. Szwarc, Trans. Faraday Soc., 59, 112 (1963).
(32) C. D. Ritchie and E. S. Lewis, J. Amer. Chem. Soc., 84, 591 (1962).

(33) K. S. Pitzer, ibid., 78, 4565 (1956).
(34) J. C. Slater and J. G. Kirkwood, Phys. Rev., 37, 682 (1931).
(35) C. Mavroyannis and M. J. Stephens, Mol. Phys., 5, 629 (1962).

of the foregoing analysis is not so much the fact that the rate data for the abstraction and addition reactions of various radicals conform to eq 3 and 4; more significant are the implications which are brought forth by this analysis. The interrelationships that exist between the various structural and electronic parameters of the reactants, e.g., proportionalities, are the very source of the difficulties encountered when one attempts to identify in an unambiguous manner the factors contributing to reactivity and discuss these from the point of view of fundamental principles. The problem is obviously much more complicated when external parameters, such as solvent effects, are introduced, for the variation of these parameters may mask completely the variation in the intrinsic parameters which one wishes to relate to the phenomenological properties of reactivity and selectivity. These interrelations which give rise to the additivity rules represent a serious drawback in the conclusions deduced from rate data based on correlations involving log–log plots or linear free energy relations because frequently one cannot be certain of whether, for example, the particular parameter with which the rate data are correlated is an intrinsic property of the reaction itself or whether it is a consequence of the external conditions constraining the reaction system. This point is clearly illustrated by the properties of many reactions in solution,[32,36] by the variability of the effect of the halogens on the optical and electrical properties of molecules and on their reactivities,[37–39] and by the disparity in the correlations of reactivity with ionization potentials and steric factors. The molecular interpretation of such correlations cannot be the same for two similar reaction series for which the preexponential factors are constant for one series and variable for the other, or for the cases where the preexponential factor varies linearly or randomly with the energy factor. The breakdown of the additivity relations which, for a given reagent undergoing two similar reactions, places

the logarithms of the rate constants on two different lines is evidently caused by the occurrence of different proportionality relations between the experimental and the molecular parameters[40] (see, for example, Figures 1 and 2).

The decrease in reactivity in the 1,2-dihaloethylenes relative to the corresponding vinyl halides and the (occasional) large increase in reactivity in the 1,1-disubstituted analogs might suggest a σ model for the transition state. However, the bromine compounds are more reactive than the chlorine compounds, and perhaps the iodine analogs are even more reactive in the systems of interest here. Furthermore, the 1,1-disubstituted derivatives are not always more reactive than the monosubstituted ones, and, in the case of the fluorinated ethylenes, reactivity, although it follows a regular pattern, does not display the same characteristics as those found in the other halogenated ethylenes. These findings, together with the inference of the proportionality between steric and electronic factors that is suggested by the cross relations of Figures 2 and 3 as well as by the linearity between the activation energies and the preexponential factors, imply to us π-complex properties for the transition state. A π complex was also proposed for the reactions of methylated ethylenes with c-C_3H_5, CF_3, and NF_2 radicals,[21,27] and with oxygen atoms[28] in order that the interpretation of their rate parameters be consistent with their molecular properties considered from several points of view.[21] The two models, σ and π complexes, are extremes, however, and we suspect that they are not mutually exclusive; the former requires a considerable change in orbital symmetry in the substrate and the formation of a well-defined σ bond, whereas the latter involves the perturbation of the double bond and of the vibrational and rotational modes of motion of the substituents of both carbon atoms in the double bond.

(36) E. F. Caldin, *J. Chem. Soc.*, 3345 (1959).
(37) D. T. Clark, J. N. Murrell, and J. M. Tedder, *ibid.*, 1250 (1963).
(38) J. R. Hoyland and L. Goodman, *J. Phys. Chem.*, 64, 1816 (1960).
(39) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc., Ser. A*, 258, 459 (1960).
(40) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.