

## Relative Rates of Addition of Cyclopropyl Radicals to Olefins. I

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**Abstract:** The relative rates of addition of cyclopropyl radicals to a series of olefins were measured in order to obtain information in regard to the electronic and steric demands of these radicals. A monotonic decrease in reactivity is observed as the number of alkyl groups about the double bond increases. The relationship of the rate data with the ionization potentials of the olefins and the effect of electronegative substituents upon the rates suggest that cyclopropyl radicals are decidedly nucleophilic. A compensation effect is noted in the trends of the energies and entropies of activation. The analysis of the variations of the activation parameters with substrate structure implies a proportionality between electronic and steric effects in the transition state. The magnitude of the observed secondary deuterium effect and the correlation of the data with bond localization energies are discussed in terms of the mechanism of the reaction and the structure of the transition state.

The addition of methyl radicals to unsaturated compounds has been studied in great detail by Szwarc and coworkers,<sup>1-5</sup> who showed that these radicals are very slightly nucleophilic. Subsequently these studies were extended to the addition reactions of trifluoromethyl radicals,<sup>6-13</sup> and on the basis of comparisons of their reaction rates with those of other radicals it was proposed that trifluoromethyl radicals are strongly electrophilic species. In the sequel, however, more work revealed that in comparisons of this sort anomalies are always observed, for the very structural elements which portend a given generalization under a set of conditions do not seem to conform to the same rules under another set of conditions which, from a theoretical standpoint, is quite similar to the first.<sup>14</sup> Indeed such anomalies are discernible in most work dealing explicitly with polar and other factors which allegedly are responsible for the observed trends in radical reactivity.<sup>8,14-20</sup> The concepts of nucleophilic and electrophilic reactivity in radical systems have been discussed at great length in the literature, and although a large amount of perceptive work has been reported in this regard,<sup>18,20-27</sup> the fundamental

relationships between molecular structure and what is usually taken to be electrophilic or nucleophilic behavior have eluded all attempts for a general systematic synthesis.

Most of the radicals whose chemical properties have been examined from the standpoint of such electrical behavior are of the type which, on the basis of the usual criteria, are recognized as electrophilic reagents. Radicals which are manifestly more nucleophilic than methyl or ethyl have not been described in analogous reaction systems in order that comparisons in reactivity be made possible. In this communication we report our results of a study of the addition of cyclopropyl radicals to a series of simple olefins and present evidence suggesting that these radicals exhibit electrical properties which are of opposite character to those of trifluoromethyl and other electrophilic radicals and that they may be decidedly more nucleophilic than the trifluoromethyl radicals are electrophilic. This property of cyclopropyl radicals was anticipated on the basis of published spectroscopic data,<sup>28</sup> dipole moment data,<sup>29</sup> and from solvolytic data<sup>30</sup> of cyclopropane derivatives, and particularly from the high value of the quenching cross section of cyclopropane for cadmium resonance radiation.<sup>31</sup>

## Experimental Section

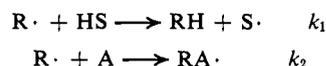
Cyclopropyl radicals were generated thermally from bicyclopropaneformyl peroxide, which was synthesized by the method of Hart and Wyman.<sup>32,33</sup> Experiments were carried out in isooctane

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- (31) E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, **19**, 329 (1951).
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- (33) The kinetics and mechanism of decomposition of this peroxide in the gas phase and in a variety of solvents will be discussed in a subsequent communication, where it will be shown that 100% of the radicals produced in the decomposition, as well as their fate, can be accounted for.

solution with peroxide concentrations of  $10^{-2}$  to  $10^{-3}$  M in the absence and also in the presence of varying amounts of unsaturated substrates. Reaction times with each olefin were varied so that olefin consumption was not more than about 5%. The partial pressures of cyclopropane and carbon dioxide were determined by gas chromatography using a column packed with 15% decyl phthalate on firebrick. The experimental details of preparing the samples, of the analytical procedure on the vacuum system, and of the calibration and standardization of the apparatus have been described in detail repeatedly in earlier communications.<sup>6-10</sup> 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.

The method of analysis of the experimental data is that of Szwarc,<sup>4</sup> which has been used in the study of methyl,<sup>1-5,9,34</sup> ethyl,<sup>35</sup> propyl,<sup>36</sup> and trifluoromethyl radicals,<sup>6-8,10</sup> all of which had been generated from the corresponding diacyl peroxides and/or from azo compounds. All these studies, as in the present case, involved competitive systems, and the mechanism assumed in the treatment of the data is the following



where HS is the solvent, A is the unsaturated substrate, RA· is the adduct radical, and RH is the product of hydrogen abstraction from the solvent by the radical R·. Applying the material balance condition to the kinetic analysis of this mechanism yields

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

where  $X_{HS}$  and  $X_A$  are the mole fractions of solvent and olefin, and the subscripts b and A denote, respectively, the absence (b for blank) and presence of olefin in otherwise identical experiments. The validity of this equation and the conditions for its application have been discussed repeatedly in great detail.<sup>1-11</sup> It is sufficient here to point out that its most rigorous experimental test is the constancy of the ratio ( $k_2/k_1$ ) with varying concentrations of olefin at any given temperature, within a range of temperatures in which it may be assured that the stationary concentration of radicals is very small.

## Results and Discussion

The substrates investigated in this study may be divided into two classes, namely symmetrical and unsymmetrical olefins. These together with the values of the relative rates ( $k_2/k_1$ ) are listed in Table I. Each

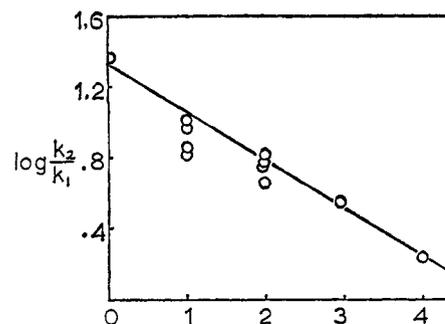
**Table I.** Relative Rate Constants and Arrhenius Parameters for the Addition of Cyclopropyl Radicals to Olefins

Olefin	Mean $k_2/k_1$ at 65°	$E_2 - E_1$ , kcal/mol	Log $(A_2/A_1)$	$k_D/k_H$
1. Ethylene	23.4	-0.66	0.94	
2. Propylene	10.4	+0.14	1.1	
3. <i>cis</i> -2-Butene	6.1			
4. <i>trans</i> -2-Butene	5.7	+0.98	1.4	
5. Isobutylene	6.6			
6. Trimethylethylene	3.6	+1.7	1.6	
7. Tetramethylethylene	1.7	+2.5	1.9	
8. 1-Butene	9.6			
9. 1-Pentene	7.1			
10. 1-Hexene	6.6			
11. 2-Octene	4.2			
12. CD <sub>2</sub> =CD <sub>2</sub>	26.1			1.11
13. CH <sub>3</sub> CH=CD <sub>2</sub>	11.3			1.09
14. CD <sub>3</sub> CD=CD <sub>2</sub>	11.2			1.08
15. Vinyl chloride	40.6			
16. Diethyl fumarate	630			
17. Diethyl maleate	240			

(34) M. Feld, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, **84**, 4451 (1962).

(35) J. Smid, A. Rembaum, and M. Szwarc, *ibid.*, **78**, 3315 (1956).

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**Figure 1.** The effect of alkyl substitution on the relative rate constants for cyclopropyl radical addition to olefins. Plot of  $\log(k_2/k_1)$  vs. the number of substituents at the double bond. Line is drawn through methylated ethylenes in order to emphasize the constant factor contributed by each methyl group.

olefin was investigated over a range of concentrations, and a representative sample of experimental data is given in Table II for ethylene to illustrate the repro-

**Table II.** Experimental Data for the Measurement of the Relative Rate of Addition of Cyclopropyl Radicals to Ethylene at 65° in Isooctane Solution

Mol % ethylene	(C <sub>3</sub> H <sub>8</sub> /CO <sub>2</sub> ) <sub>formed</sub>	(C <sub>3</sub> H <sub>8</sub> /CO <sub>2</sub> ) <sub>lost</sub>	( $k_2/k_1$ )
1.60	0.386	0.138	21.9
1.95	0.354	0.171	24.2
2.59	0.318	0.206	24.4
3.31	0.298	0.226	22.9
4.45	0.254	0.270	23.8

ducibility of the method and the independence of the rate ratio ( $k_2/k_1$ ) upon the substrate concentration.

The trends in the data in Table I show that the rate of addition decreases as the number of alkyl groups about the double bond increases, and on the basis of this observation it is tempting to invoke arguments for a generalization in regard to the nature and magnitude of the effect of crowding at the reaction site. Indeed, for all practical purposes, the free energy change in the activation process is a linear function of the degree of methyl substitution at the double bond, as illustrated in Figure 1, where the straight line has been drawn through the methylated ethylenes in order to emphasize the constant factor contributed to the trend by each methyl group. From the known behavior of activation parameters of radical additions to homologous series of olefins, similar trends, with negative slopes, are anticipated in the corresponding reaction rates of such series as the chloroethylenes and the bromoethylenes. However, conclusions of this sort are undoubtedly overstatements, and in the absence of more detailed experimental results can lead one astray.<sup>37,38</sup> Thus olefins such as 2,2-disubstituted-1-alkenes are not always the most reactive in radical additions<sup>39</sup> (see Table I), and nucleophilic-electrophilic relationships in such reactions need not always have anything to do with the orientation of addition.<sup>37</sup> In fact the trends in

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(38) J. I. G. Cadogan and D. H. Hey, *Quart. Rev. Chem. Soc.*, **8**, 308 (1954).

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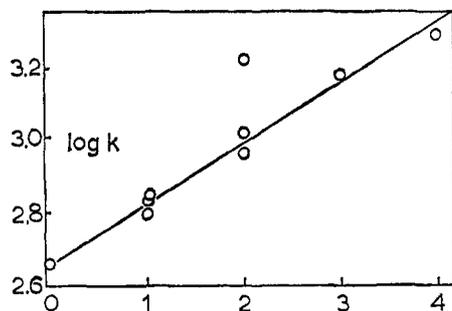


Figure 2. The effect of alkyl substitution on the relative rates of addition of  $\text{CF}_3$  radicals to olefins. Plot of  $\log(k_2/k_1)$  vs. the number of substituents at the double bond.

the rates of addition of trifluoromethyl radicals (Figure 2), of oxygen atoms,<sup>40</sup> and of difluoroamino radicals<sup>39</sup> to ethylene and its methylated derivatives follow a pattern in the opposite direction to that which we report here; *i.e.*, the slopes of  $\log k$  vs. the number of substituents at the double bond are lines with positive slopes. To be sure, these inverse relations connote mechanistic implications, and they simply suggest that factors other than steric come into play in the activation process.

One of the simplest criteria for deciding whether a given radical is electrophilic or nucleophilic is the investigation of the trends in the rate constants of a series of reactions relative to the trends in the ionization potentials of the substrates with which the radicals react.<sup>6,8,18,40</sup> Another method is the examination of a particular series of substrates in terms of the Hammett-Taft  $\sigma$ - $\rho$  relations.<sup>21</sup> For the addition of methyl and trifluoromethyl radicals and of oxygen atoms to olefins it happens that the plot of the logarithms of the rate constants against the ionization potentials of the olefins are fairly good straight lines, and thus linear free energy relations exist between the reactions of these radicals with common series of substrates. Evidently, these relations encompass the reactions of divalent carbon species,<sup>41</sup> as well as the reactions of difluoroamino radicals,<sup>39</sup> and of peracetic acid with olefins.<sup>40</sup> These correlations may then serve as a guide in assigning relative electrophilic or nucleophilic characteristics to the radicals. Figure 3 illustrates the response of  $\log(k_2/k_1)$  for cyclopropyl radicals to the ionization potentials of the olefins we studied. The plots for trifluoromethyl and difluoroamino radicals are also given in the figure for comparison purposes.<sup>42</sup> The conclusions to be drawn from this correlation are obvious. On the basis of classical arguments in regard to the double bond as an electron sink and the change in its electron density with alkyl substitution, the concomitant increase in reactivity from tetramethyl ethylene through ethylene and vinyl chloride and the esters of fumaric and maleic acids (see Table I), we may say that the cyclopropyl radical is definitely

(40) R. J. Cvetanović, *J. Chem. Phys.*, **30**, 19 (1959).

(41) T. S. Skell and Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956).

(42) (a) For reasons which will become apparent presently no symmetry factor has been applied to the rate constants of the symmetrical olefins in Figures 1 and 2, *i.e.*, the values of  $(k_1/k_2)$  for these substances were not taken to be one-half of the measured magnitude; (b) for a complete analysis in such comparisons between different radicals the electron affinities of the radicals must also be considered. These quantities, however, will only affect the intercept of the curves and not their slope.

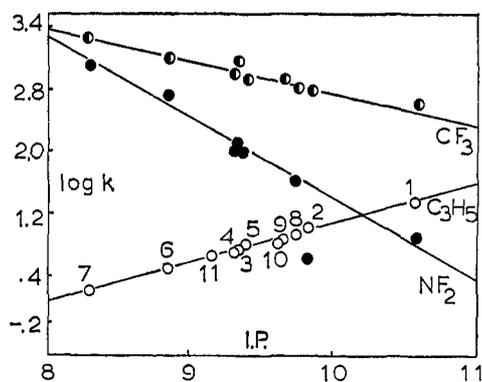


Figure 3. Ionization potential vs.  $\log k$  of olefins:  $\circ$ ,  $\text{C}_3\text{H}_5$ ;  $\bullet$ ,  $\text{NF}_2$ ;  $\odot$ ,  $\text{CF}_3$ . Data for  $\text{CF}_3$ , (except that for no. 5, which is a new datum from our laboratory) are from ref 6. Ionization potential data are from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

nucleophilic relative to  $\text{CF}_3$  and  $\text{NF}_2$ , assuming that the influence of steric factors is recognized.

The relative importance of steric effects in the activation process is not completely clear at the present time, although one might attempt a partial assessment of these from the values of the activation energies as has been indicated by Trotman-Dickenson<sup>39</sup> for difluoroamino radicals. Preliminary values of activation parameters for some of our reactions are given in Table I, from which it may be seen that for each methyl group added to the double bond there is an increase of about 0.8 kcal in the activation energy. It is noteworthy that the corresponding changes in the activation energy per methyl group for  $\text{NF}_2$  and  $\text{CF}_3$  radicals is also constant, but it is negative for both species. For the former its value is  $-1.8$  kcal, whereas for the latter it is approximately  $-0.4$  kcal. These energetic comparisons together with the foregoing considerations of the electrical properties of the corresponding radicals make it quite clear that steric and electronic effects cannot be dealt with separately. However, the interplay between these factors in the activation process is brought forth by the cross relations, suggested by Figures 1-3, between the ionization potentials and the degree of substitution of the olefins. These cross relations reveal that there is a proportionality between steric and electronic factors, an observation which led us to anticipate a correlated variation in the magnitudes of the Arrhenius activation parameters.

An insight into the finer details of the mechanism of addition may be obtained from an analysis of our data from the point of view of the transition state theory and the molecular orbital theory. There are two limiting structures which one may assume for the transition state of the addition reaction, a  $\sigma$  complex and a  $\pi$  complex. In the  $\sigma$  complex a well-defined primary valence bond between the radical and the substrate is developed and the structure of the complex is essentially that of the product radical. In the molecular orbital theory of chemical reactivity this activation process is related to the localization of an electron on the carbon atom of the substrate which undergoes rehybridization during the reaction. Structural rearrangements occurring in the activation process of a set of similar reactions, each of which proceeds through a  $\sigma$  complex (Figure 4), are due to this re-

**Table III.** Comparison of the Activation Parameters for the Reactions of  $C_3H_5$ ,  $CF_3$ ,  $NF_2$ , and O Atoms with Olefins

Olefin	$C_3H_5$		$CF_3^a$		$NF_2^b$		O atoms <sup>c</sup>	
	Log $A_2/A_1$	$E_2 - E_1$	Log $A_2/A_1$	$E_2 - E_1$	Log $A$	$E$	$A/A_{ep}$	$E - E_{tme}$
1. Ethylene	0.94	-0.66	0.38	-2.35	10.6	15.5	1.01	2.6
2. Propylene	1.1	+0.14	0.18	-2.76	10.2	13.7		
3. <i>cis</i> -2-Butene					9.5	11.9		
4. <i>trans</i> -2-Butene	1.4	+0.98			9.5	11.9		
5. Isobutylene			0.16	-3.52	9.8	11.8	0.67	
6. Trimethylethylene	1.6	1.7			9.0	10.1	1.18	0.11
7. Tetramethylethylene	1.9	2.5	-0.52	-3.9	8.3	8.3	1.25	0.0
8. 1-Butene					10.1	13.6	0.74	1.4

<sup>a</sup> Gas-phase values from ref 15.  $A_2$  and  $E_2$  refer to the addition reaction and  $A_1$  and  $E_1$  to the abstraction reaction from 2,3-dimethylbutane. <sup>b</sup> Values of  $A$  and  $E$  for gas-phase reactions taken from ref 39. <sup>c</sup> Gas-phase values from ref 18.  $A$  and  $E$  refer to the addition reaction and  $A_{ep}$  and  $E_{tme}$  to cyclopentene and tetramethylethylene.

hybridization and are quite likely to be similar for all members of the set; thus relative changes in rates will be controlled by the activation energy since changes in the entropy term will be insignificant. The activation

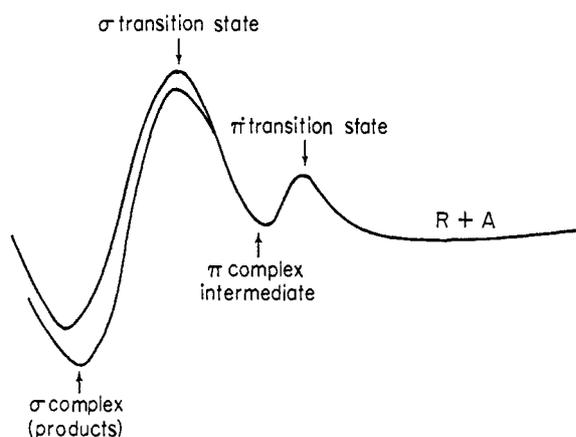


Figure 4.

energies for this set of reactions will be expected to correlate with atom localization energies.<sup>43-45</sup> Examples of reactions whose properties conform to these principles are the additions of methyl,<sup>3</sup> trifluoromethyl,<sup>7</sup> and cyclopropyl<sup>46</sup> radicals to unsubstituted alternant aromatic hydrocarbons.

Reactions which are constrained to proceed through a  $\pi$  transition state (Figure 5) will manifest rather different properties. In a  $\pi$  complex the binding arises from the mutual perturbation of the dispersion fields of the reactants<sup>14,47</sup> and perhaps also from contact charge transfer forces as described by Orgel and Mulliken.<sup>48</sup> No rehybridization is assumed in this complex. The molecular orbital theory describes the formation of the  $\pi$  complex by means of a  $\pi$ -bond localization process<sup>43-45</sup> and suggests that the activation energy will correlate with the bond localization energies

(43) R. D. Brown, *Quart. Rev. Chem. Soc.*, **6**, 63 (1952); *J. Chem. Soc.*, 3129 (1951).

(44) C. A. Coulson in "The Chemistry of Alkenes," S. Patai, Ed., Wiley, New York, N. Y., 1964, Chapter 1; *Research*, **4**, 307 (1951).

(45) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(46) Unpublished data from our laboratories.

(47) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1964.

(48) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, **79**, 4839 (1957).

and also with the average (not maximum) free valencies of the unsaturated centers, provided that the change in the entropy of activation in the reaction series is constant or it is proportional to the activation energy. But the entropy changes in a reaction series of this type cannot be expected to remain constant, since the vibrational degrees of freedom in the vicinity of the double bond in the  $\pi$  complex are highly perturbed and the corresponding partition functions in the preexponential term of the transition state theory equation do not cancel out. The data collected in Table III show

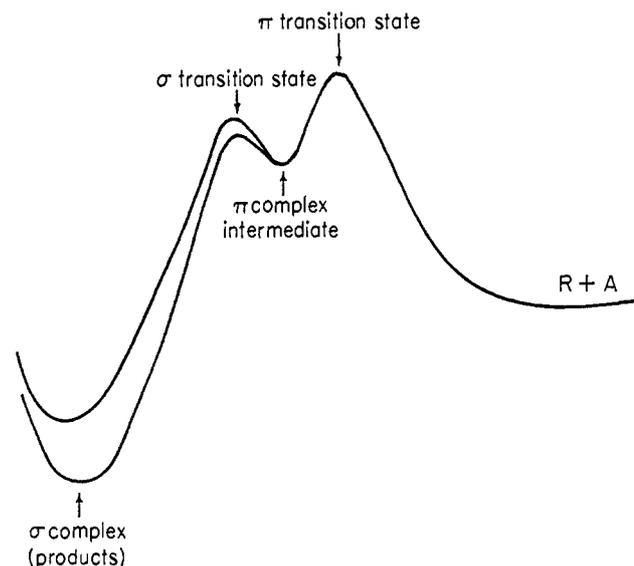


Figure 5.

clearly that radical addition to ethylenes is accompanied by a monotonic variation in both activation parameters in accord with the foregoing analysis. Figure 6 illustrates the correlated variation in these factors and Figures 7 and 8 represent the expected correlation of the data with the MO theory indices. Incidentally, the correlation in Figure 6 (and its implications) is exactly analogous to that observed in the investigation of virtual  $\pi$  complexes.<sup>49</sup> It is significant that our data do not correlate with atom localization energies or with maximum free valencies. Consequently, we take the observed correlations to mean that in the transition state the olefin retains its planar symmetry and that

(49) L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

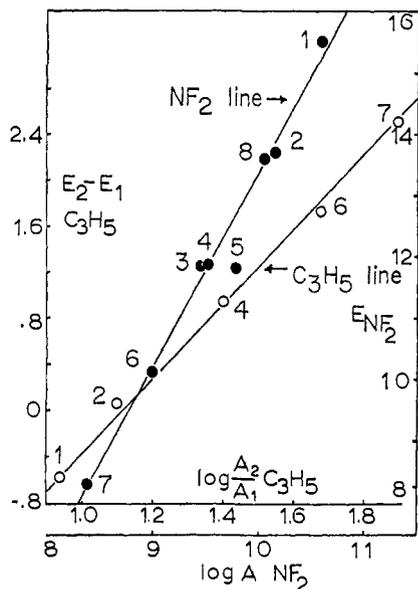


Figure 6. Variations in  $\log(A_2/A_1)$  and  $\log A$  with  $(E_2 - E_1)$  and  $E$  for cyclopropyl and difluoroamino radicals:  $\circ$ ,  $C_3H_5$ ;  $\bullet$ ,  $NF_2$ . Rate data for  $NF_2$  radicals are from ref 39. Numbers of points correspond to numbers in Table I.

rehybridization of the carbon atom on which the new bond is made in the product begins only after the  $\pi$  transition state moves away from its equilibrium position through the  $\pi$  complex intermediate (Figure 5). It is easy to see that if we estimate the activation parameters of radical additions to unsymmetrical olefins by means of the temperature variation of product ratios (Figure 5) and then proceed to dissect these to evaluate the absolute values of the parameters for each product,<sup>16</sup> the values thus obtained will be representative of the  $\sigma$  transition states and not necessarily of the primary activation process (Figure 5). Under these circumstances the correlation of the activation energy for each product will be with atom localization energies and with the strengths of the newly formed bonds,<sup>16</sup> but not with the average free valencies and bond localization energies, even though the activation process follows the path depicted by Figure 5.

The distinction between a  $\pi$  and a  $\sigma$  transition state and the consequent implications in connection with these, as discussed above, have been overlooked quite frequently in the literature, and this gave rise to a great deal of confusion and pointless argument in regard to correlations of radical reaction rates with quantities derived from molecular orbital theory considerations. A lucid discussion regarding these quantities and illustrations of their application to a variety of reactions with implied models of  $\pi$  or  $\sigma$  transition states have been given by Brown<sup>43</sup> and more colorfully recently by Dewar.<sup>45</sup>

Additional evidence regarding the nature of the transition states in the addition reactions of cyclopropyl radicals is provided by the secondary isotope effect in connection with Streitwieser's suggestion<sup>50,51</sup>

(50) A. Streitwieser and R. C. Fahey, *Chem. Ind. (London)*, 1417 (1959).

(51) A. Streitwieser, R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

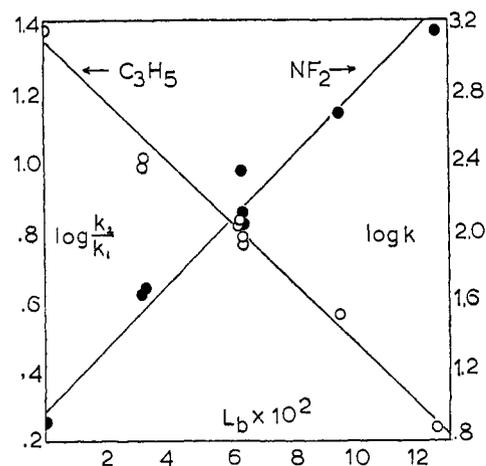


Figure 7. Correlation of  $\log(k_2/k_1)$  for cyclopropyl radicals and  $\log k$  for difluoroamino radicals with bond localization energy. Data for bond localization energies are from S. Sato and R. J. Cvetanović, *J. Amer. Chem. Soc.*, **81**, 3223 (1959). Rate data for  $NF_2$  radicals are from ref 39.

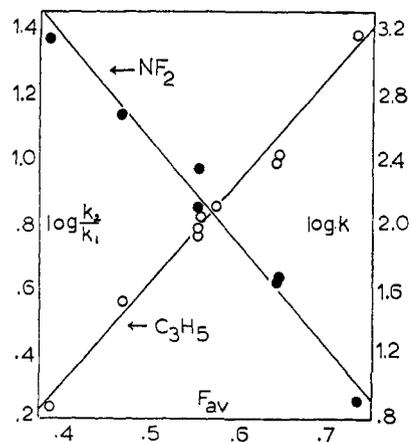


Figure 8. Correlation of  $\log(k_2/k_1)$  for cyclopropyl radicals and  $\log k$  for difluoroamino radicals with average free valence:  $\circ$ ,  $C_3H_5$ ;  $\bullet$ ,  $NF_2$ . Data for free valencies are from Sato and Cvetanović (see legend of Figure 7). Rate data for  $NF_2$  radicals are from ref 39.

that the soft out-of-plane bending vibration of an olefin C-H bond becomes a harder bending vibration when it is rehybridized to a tetrahedral state. The calculated value of  $(k_D/k_H)$  for a reaction proceeding through a  $\sigma$  transition state, in which the point of attack is at a terminal methylene group,<sup>34</sup> is about 1.82. The experimental values  $(k_D/k_H)$  for the addition of cyclopropyl radicals to ethylene and propylene and to their deuterated analogues is about 1.1 (Table I), which is about the same value as that reported in an earlier communication for methyl and trifluoromethyl radicals.<sup>34</sup> Assuming that the theoretical prediction is valid, the observed isotope effect means that the perturbation of the double bond by the radical in the transition state is quite different from that involved during the formation of an incipient  $\sigma$  bond in which primary valence forces come into play. This again means that the transition state is not a  $\sigma$  complex. A

$\pi$  transition state was proposed by Cvetanović<sup>18</sup> in his studies of the addition of oxygen atoms to olefins, and recently Trotman-Dickenson<sup>19</sup> discussed the same idea in terms of steric and energetic considerations.

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## A Cationic Chain Reaction in the Radiolysis of Ethanol Vapor

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**Abstract:** During the radiolysis of ethanol vapor at 350° and higher temperatures, diethyl ether is formed by a cationic chain reaction. At 380°,  $G(\text{Et}_2\text{O})$  decreased from 62 at an ethanol pressure of 85 Torr to 2.6 at 1630 Torr. The overall activation energy of the chain mechanism was  $43 \pm 4$  kcal/mol, independent of ethanol pressure within experimental error. The values of the rate constants of one or both of the reactions  $(\text{EtOH})_m\text{H}^+ \rightarrow \text{Et}_2\text{O} \cdot \text{H}^+ \cdot (\text{OH}_2)(\text{EtOH})_{m-2}$  ( $4_m$ ) and  $\text{Et}_2\text{O} \cdot \text{H}^+ \cdot (\text{OH}_2)(\text{EtOH})_{m-2} + 2\text{EtOH} \rightarrow \text{Et}_2\text{O} + \text{H}_2\text{O} + (\text{EtOH})_m\text{H}^+$  ( $5_m$ ) decreased with increasing  $m$  for  $m \geq 2$ . The rate of ether formation is reduced by the presence of ammonia, a proton scavenger. The vapor-phase reaction  $\text{CH}_2\text{O} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{CHO}$  occurs at 200–380° by a thermal mechanism that is not appreciably sensitized by radiation. The rate of the reaction is unaffected by the presence of propylene, a free radical scavenger.

In a recent communication we reported the discovery of a gas-phase cationic chain reaction that converted ethanol to ether and water during radiolysis at 350°. The present article includes experimental details and new results about this system.

It has also been found that the reaction of formaldehyde with ethanol to form methanol and acetaldehyde<sup>2</sup> occurs by a thermal mechanism that is not appreciably sensitized by radiation.

### Experimental Section

**Materials.** Absolute ethanol (2 l.) from Rossville Gold Shield was refluxed for approximately 4 hr in an atmosphere of nitrogen, after the addition of 3 g of 2,4-dinitrophenylhydrazine and 2 ml of concentrated sulfuric acid. The solution was then distilled on a Nester-Faust spinning band column. The middle fraction of the distillate was retained for use and was stored under vacuum in a Pyrex reservoir.

Paraformaldehyde (trioxymethylene) from Fischer Scientific Co. was used without further purification.

**Sample Handling.** The 300-ml cylindrical irradiation cells were cleaned with permanganic and nitric acids, followed by many rinsings with doubly distilled water. They were then baked overnight at about 500° in air and finally for 2 hr at 500° while being evacuated.

The desired amount of ethanol was measured as a liquid in a calibrated tube in a vacuum line, then distilled into the cell.

The ethanol-formaldehyde samples were prepared as follows. Paraformaldehyde was weighed into a breakseal tube and was thoroughly degassed, using liquid nitrogen as coolant. The tube was sealed off and then sealed to the sample preparation manifold of the vacuum apparatus. A known amount of ethanol was distilled into the irradiation cell. The paraformaldehyde tube and the tubing connecting it to the irradiation cell were heated with electrical tape. The seal was then broken. Paraformaldehyde on heating formed formaldehyde vapor, which then condensed into the irradiation cell.

The filled and sealed irradiation cells were placed in an electric furnace, heated to the desired temperature, and irradiated in a

Gammacell-220 (Atomic Energy of Canada Ltd.). The temperature was maintained constant to within 3°. The heating and cooling times were kept constant at each temperature. The entire cycle required about 1 hr at all temperatures.

The dose rate was  $8.6 \times 10^{19}$  eV/(g hr), measured with ethylene and assuming  $G(\text{H}_2) = 1.31 \pm 0.03$ .<sup>3,4</sup> Sufficient ethylene was placed in the cell so that the electron density of ethylene in the dosimeter was approximately the same as that of ethanol in the samples. The dose rate in ethanol was corrected for the difference between the stopping powers of ethanol and ethylene. All radiolysis samples were given a dose of  $4.3 \times 10^{19}$  eV/g.

The radiolysis products were analyzed by gas chromatography using two 4-mm i.d. columns (a) 7 ft, Polypak-1, 40–80 mesh; (b) 13 ft, the first 9 ft packed with 25% 1,2,3-tris-2-cyanoethoxypropane on Chromosorb P, and the next 4 ft packed with 10% Carbowax-4000 on Chromosorb W, acid-washed, 60–80 mesh. The gas chromatograph was an F and M Model 5750 equipped with a flame ionization detector. Calibration factors were determined with solutions of authentic products at known concentrations.

### Results

(A)  $2\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}$ . Although water was observed to be a radiolysis product, its yield was not measured accurately.

1. **Effect of Ethanol Pressure on the Ether Yield at 380°.** The pressure was varied over the range 85–1630 Torr, which corresponded to ethanol densities from 0.096 to 1.85 g/l. The diethyl ether yield decreased from 62 to 2.6 as the pressure was increased (Figure 1).

The possibility of ether formation by normal pyrolysis or by a catalytic reaction on the vessel wall was checked by putting two ethanol samples through the same heating cycle as was used for the irradiated samples, but without irradiation. An ethanol pressure of 85 Torr was used because the ether yield in the irradiated samples was highest at the lowest pressure. No ether was detected after the heating cycle, which means

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