The Kinetics and Orientation of Free-Radical Addition to Olefins

John M. Tedder* and John C. Walton

Department of Chemistry, University of St. Andrews, St. Andrews, Scotland KY16 9ST

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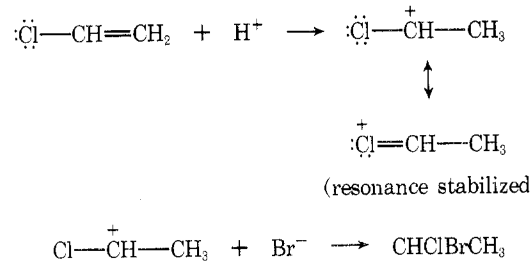
The Mechanism of Anti-Markownikoff Addition and the Mayo–Walling Hypothesis

The work of Kharasch and co-workers[1] and a review by Hey and Waters[2] simultaneously elucidated the "anti-Markownikoff" addition of hydrogen bromide to unsymmetrical olefins in the presence of ultraviolet light or peroxides, but it was left to Mayo and Walling in a brilliant review[3] to offer an explanation of the orientation of radical addition. In 1940, when their review was written, the electronic theory of organic chemistry was still in its infancy. The normal Markownikoff addition was explained in terms of "resonance stabilization" of the intermediate carbonium ion:

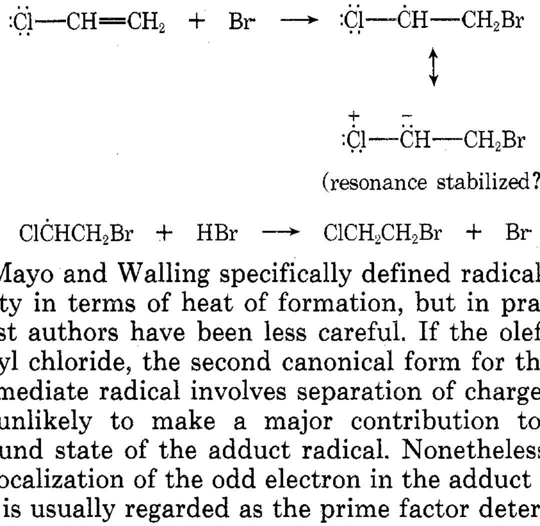


$$\mathrm{:\!\underset{\cdot\cdot}{\ddot{C}l}{-}CH{=}CH_2 + H^+ \longrightarrow :\!\underset{\cdot\cdot}{\ddot{C}l}{-}\overset{+}{C}H{-}CH_3}$$
$$\updownarrow$$
$$\mathrm{:\!\underset{\cdot\cdot}{\overset{+}{C}l}{=}CH{-}CH_3}$$

(resonance stabilized)

$$\mathrm{Cl{-}\overset{+}{C}H{-}CH_3 + Br^- \longrightarrow CHClBrCH_3}$$

Kharasch and co-workers and Hey and Waters had shown that anti-Markownikoff addition involved the initial addition of a bromine atom. Mayo and Walling's hypothesis was that the point of attack was determined primarily by the relative stabilities of the two possible bromoalkyl radicals formed.[3] By analogy with the explanation for ionic addition, most authors have attempted to assess this stability in terms of resonance theory:



$$\mathrm{:\!\underset{\cdot\cdot}{\ddot{C}l}{-}CH{=}CH_2 + Br \longrightarrow :\!\underset{\cdot\cdot}{\ddot{C}l}{-}\dot{C}H{-}CH_2Br}$$
$$\updownarrow$$
$$\mathrm{:\!\underset{\cdot\cdot}{\overset{+}{C}l}{-}\overset{-}{\ddot{C}}H{-}CH_2Br}$$

(resonance stabilized?)

$$\mathrm{Cl\dot{C}HCH_2Br + HBr \longrightarrow ClCH_2CH_2Br + Br}$$

Mayo and Walling specifically defined radical stability in terms of heat of formation, but in practice most authors have been less careful. If the olefin is vinyl chloride, the second canonical form for the intermediate radical involves separation of charge and is unlikely to make a major contribution to the ground state of the adduct radical. Nonetheless the delocalization of the odd electron in the adduct radical is usually regarded as the prime factor determining the orientation of radical addition.

The possible importance of polar effects was discussed by Waters[4] and by Barton,[5] and Price[6] was able to show that the normal concepts of polarity familiar to the organic chemist could be used to explain the relative reactivities of monomers in copolymerization studies. These conclusions were considered in a second important review by Mayo and Walling,[7] and later Walling[8] discussed the importance of polar and steric effects in determining the relative reactivities of radicals with olefins. However the studies of Haszeldine[9] seemed to show that those polar effects could not be used to explain the orientation of radical

John Tedder graduated from Magdalene College, Cambridge, in 1948, and completed his doctorate at Birmingham University in 1951. After postdoctoral work at Birmingham, Ohio State, and Edinburgh Universities, he was a lecturer at the University of Sheffield for 9 years. He was appointed Professor at Dundee in 1964, and moved to St. Andrews in 1969. Besides free radicals, he has research interests in ion–molecule reactions and in diazonium salts.

John Walton graduated from Sheffield University in 1963 and accompanied John Tedder to Dundee, where he obtained his Ph.D. in 1966. In 1969 he was appointed to a permanent lectureship at St. Andrews. His researches have been in the field of free-radical chemistry.

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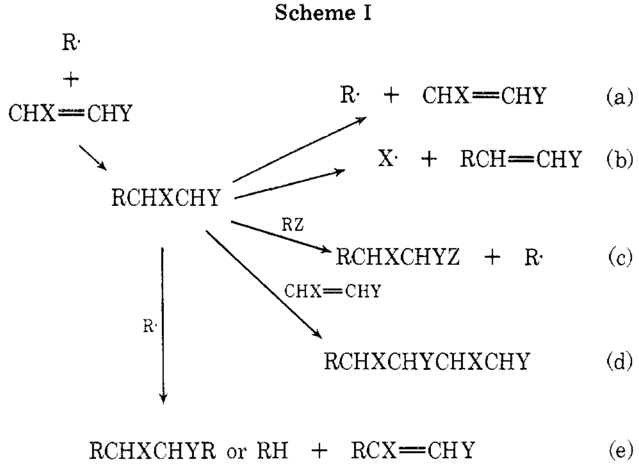
Scheme I



addition to unsymmetric olefins; that view has come to be generally accepted.

Extensions to the resonance hypothesis were put forward notably by Haszeldine, who postulated that radical stability decreases as the number of hydrogen atoms attached to the carbon atom carrying the lone electron is increased,[9d] and by Cadogan, who estimated adduct radical stability in terms of hyperconjugation.[10]

Much work remains to be done before a complete understanding of the factors which control the rate and orientation of free-radical addition to olefins is reached, but we feel the work has reached a stage where an account of current research is justified. Although the work to be described shows the inadequacy of the original Mayo–Walling hypothesis when it is restricted to considering the stabilization of the odd electron, we emphasize that at the time the hypothesis was put forward this narrow interpretation was in complete accord with the facts then available. More importantly, the two reviews by Mayo and Walling provided the first understanding of directive effects in free-radical reactions.

Complete Reaction Mechanisms for Free-Radical Addition to Olefins

The work of Kharasch showed that not only bromine atoms but also a wide variety of other radicals could attack an olefin to give a new adduct radical.[11] However, the final stable product depends on the subsequent fate of the adduct radical, as indicated in Scheme I.

The addition step is usually exothermic so that reaction a is only important at high temperatures for alkyl radicals. However, with halogen atoms,[12] thiyl radicals,[13a] and organometallic radicals[13b] the reverse reaction is important even at room temperature; e.g.

$$SF_5\cdot + CHF{=}CF_2 \rightleftarrows SF_5CHF\dot{C}F_2{}^{13a}$$

$$(CH_3)_3Ge\cdot + CHF{=}CH_2 \rightleftarrows (CH_3)_3GeCH_2\dot{C}HF{}^{13b}$$

Loss of halogen from an adduct radical (b) can be a very facile process and render a study of orientation to polychloro or -bromo olefins almost impossible.[12,14]

$$CCl_3\cdot + CHCl{=}CHCl \rightarrow (CCl_3CHCl\dot{C}HCl) \rightarrow CCl_3CH{=}CHCl + Cl\cdot$$

Radical transfer leading to a chain reaction in which the initial radical is regenerated in the transfer process c is the ideal system for orientation studies.[11b]

$$CCl_3\cdot + CH_2{=}CH_2 \rightarrow CCl_3CH_2CH_2\cdot \xrightarrow{CCl_3Br} CCl_3CH_2CH_2Br + CCl_3\cdot$$

Addition of the adduct radical to a further molecule of olefin forming a telomer radical (d) is an important process. The so-called "transfer constant" ($C = k_{3r}/k_{2r}$) is highly relevant in copolymerization studies.

$$R(CF_2CF_2)_r\cdot + CF_2{=}CF_2 \xrightarrow{k_{2r}} R(CF_2CF_2)\cdot_{r+1}$$

$$R(CF_2CF_2)_r\cdot + RX \xrightarrow{k_{3r}} R(CF_2CF_2)_rX + R\cdot$$

In orientation studies these complications can be very important. If radical R· adds to both ends of an olefin $YCH{=}CH_2$, the transfer constants of the two adduct radicals $RYCH\dot{C}H_2$ and $RCH_2\dot{C}HY$ may be very different. An estimate of the relative rates of attack at each end of the olefin which was based solely on yields of the simple adducts $RYCHCH_2X$ and RCH_2CHXY could be seriously in error. In the gas-phase reactions of bromodifluoromethane and trifluoroiodomethane with tetrafluoroethylene, for example, telomers containing up to five alkene units were observed even at low pressures.[15]

Termination processes (e) which include both radical combination

$$R\cdot + RCHX\dot{C}HY \rightarrow RCHXCHYR$$

and disproportionation

$$R\cdot + RCHX\dot{C}HY \rightarrow RH + RCX{=}CHY$$

are of consequence when the chains are short. For example, in the reaction of CF_2Br_2 with trifluoroethylene, short chains were observed and the cross-combination reaction

$$CF_2Br\cdot + CF_2BrCHFCF_2\cdot \rightarrow CF_2BrCHFCF_2CF_2Br$$

accounted for a significant proportion of the adduct radicals even at low alkene concentrations. Cross-disproportionation reactions such as

$$CF_2Br\cdot + CF_2BrCH_2CF_2\cdot \rightarrow CHF_2Br + CF_2BrCH{=}CF_2$$

were important in the reactions of CF_2Br_2 with other fluoroalkenes; the disproportionation/combination rate constant ratios were large for these fluoroalkyl

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radicals.[16] Termination reactions can also be important if the chain-carrying properties of the two possible adduct radicals ($RCHX\dot{C}HY$ and $RCHY\dot{C}HX$) are very different (e.g., where the olefin is $CH_2{=}CF_2$).

Another problem can be the presence of more than one radical transfer process. For example, in their pioneering work Kharasch and co-workers studied the homolytic addition of bromodichloromethane to olefins ($RCH{=}CH_2$) using acetyl peroxide as initiator.[11d] The products were shown to include $RCHBrCH_2CHCl_2$, and it was assumed that dichloromethyl radicals were the chain carriers. Reinvestigation of the same reaction in the gas phase showed that bromodichloromethyl radicals were more important as chain carriers. This means that hydrogen abstraction from bromodichloromethane competes successfully with bromine abstraction.[17]

Previous Studies of the Orientation of Free-Radical Addition

The early qualitative work of Kharasch and his coworkers was critically compiled by Walling.[8] Haszeldine and his co-workers made extensive qualitative studies on the orientation of $CF_3\cdot$ radicals to fluoro olefins;[9] some of this work was reviewed by Cadogan and Hey[19] in 1954, and more recently Walling and Huyser[20] collated the reports of preparative reactions. Huang has also made extensive qualitative studies.[21] Some aspects of the limited quantitative data were reviewed in 1967 and 1974 by the present authors,[22,23] but the most important compilation is that of Kerr and Parsonage who collected and critically assessed all the kinetic data available up to 1971.[24]

Experimental Methods and Kinetic Analysis

In our studies, haloalkyl radicals were produced by photolysis of an excess of the appropriate haloalkyl iodide or bromide, in the presence of the olefins to be studied, at wavelengths at which the olefins do not absorb light. The wavelength of light absorbed by the starting bromide or iodide usually represents more than sufficient energy to break a carbon–bromine or carbon–iodine bond, so that the halogen atom is electronically excited. Moreover, the alkyl radical may be thermally excited, e.g.,

$$CH_3I + h\nu\ (254\ \text{nm}) \rightarrow CH_3\cdot^* + I(^2P_{1/2})$$[25]

A "hot" radical will be rather undiscriminating in its reactions with olefins. If the subsequent chain process is long, the unselectivity of the thermally excited alkyl radicals is unimportant; the "hot" radical ($R\cdot^*$) will add rapidly to the olefin (E) (reaction 2*), but all subsequent cycles of the chain will involve thermal radicals ($R\cdot$) (reaction 2). If the chains are short, reaction 2* is important, and photolysis of an alkyl iodide or bromide cannot be used for kinetic or orientation studies.

$$RX + h\nu \rightarrow R\cdot^* + X\cdot \tag{1}$$

$$R\cdot^* + E \rightarrow RE\cdot \tag{2*}$$

$$RE\cdot + RX \rightarrow REX + R\cdot \tag{3}$$

$$R\cdot + E \rightarrow RE\cdot \tag{2}$$

In order to avoid "hot" radicals, methyl has been prepared by photolysis of azomethane using the 365-nm mercury line,[26]

$$CH_3{-}N{=}N{-}CH_3 + h\nu\ (365\ \text{nm}) \xrightarrow{1} 2CH_3\cdot + N_2$$

or by the thermal decomposition di-*tert*-butyl peroxide.[27]

$$[(CH_3)_3CO]_2 \xrightarrow{>100\ ^\circ\text{C}} 2CH_3\cdot + 2(CH_3)_2CO$$

In each case a large excess of methyl iodide was present

$$CH_3\cdot + E \xrightarrow{2} CH_3E\cdot$$

$$CH_3E\cdot + CH_3I \underset{-3}{\overset{3}{\rightleftarrows}} CH_3EI + CH_3\cdot$$

This system is particularly prone to problems involving telomerization and radical–radical reactions. In some cases, parallel studies using both initiators could be used as a cross-check.

Qualitative studies on a number of radicals were made by placing the appropriate alkyl halide and olefin in a sealed tube and using di-*tert*-butyl peroxide as initiator.[28] Results from these experiments compare favorably with gas-phase studies when both methods are used on the same system.

The present work has at all times depended on product analysis. The complications to which the investigator must be alert in using this approach are emphasized above. The simplest kinetic studies were those involving direct competition. If E and E′ represent different olefins and if reaction 3 represents the only fate of the adduct radical, steady-state treatment leads to the simple expression

$$\frac{[RE'X]_f}{[REX]_f} = \frac{k_{2'}}{k_2}\frac{[E']_i}{[E]_i}$$

for small conversions (subscript f = final; i = initial).

If the study is concerned with the rates of addition to the two ends of an unsymmetric olefin, the product ratio is the *orientation ratio,* symbolized *Or,* and the concentration term disappears:

$$Or = k_{2'}/k_2 = [REX]_f/[XER]_f$$

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where REX and XER represent products of addition in opposite senses. Competitive studies either between two different olefins or between attack at the two ends of an unsymmetric olefin, when completed over a range of temperatures, enable ratios of Arrhenius *A* factors $[A_{2'}/A_2]$ and differences in activation energies $[E_{2'} - E_2]$ to be determined.

If the chains are long, but not too long, it is possible to relate the rate of the addition reaction to the combination rate of the attacking radicals (eq 4).

$$R\cdot + R\cdot \rightarrow R_2 \tag{4}$$

Steady-state treatment leads to the following expression for small conversions, provided reaction 4 is the only important chain termination process.[29]

$$\frac{[REX]_f}{[R_2]_f} = \frac{k_2[E]_i}{(\varphi I_a k_4)^{1/2}}$$

φI_a (φ being the quantum yield, I_a the absorbed light intensity, and the rate of reaction 1 φI_a) can be determined from the rate of formation of the dimer. Unfortunately it can be temperature dependent, so that an independent study of the photolysis of RX may be necessary.[30,31] This difficulty can be overcome by using an alternative rate expression (V_{REX} = rate of formation of REX; V_{R_2} = rate of formation of R_2).

$$V_{REX}/(V_{R_2})^{1/2} = k_2[E]_i/k_4^{1/2}$$

If the addition reaction is reversible, steady-state treatment leads to a somewhat more complex expression:[12]

$$\frac{[REX]_f}{[R_2]_f^{1/2}} = \frac{k_2[E]}{(k_4)^{1/2}} \times \frac{1}{1 + \dfrac{k_{-2}}{k_3[RX]_i}}$$

It is possible to separate the four rate constants into two ratios, $k_2/(k_4)^{1/2}$ and k_{-2}/k_3, by varying the concentration of RX.

Observed Orientation Ratios

We shall see later that consideration of orientation ratios without knowledge of the relative rates can be misleading. However, inasmuch as there are a great many orientation data unsupported by relative rates for different olefins, it seems appropriate to look at orientation ratios first. Table I (ref 16, 18, 26–28, 32–40) lists orientation ratios for the addition of a variety of radicals to vinyl fluoride, 1,1-difluoroethylene, and trifluoroethylene. All the radicals add preferentially to the CH_2 end of both vinyl fluoride and 1,1-difluoroethylene, although the orientation ratio varies very considerably from radical to radical. The orientation of addition to vinyl fluoride and 1,1-difluoroethylene is thus in accord with a hypothesis which is based on the extent of resonance (i.e., delocalization of the odd electron) in the initial adduct radical.

Table I
Orientation Ratios (α:β) for the Addition of Alkyl Radicals to Vinyl Fluoride, 1,1-Difluoroethylene, and Trifluoroethylene at 150 °C

Radical	α β $CH_2{=}CHF$	α β $CH_2{=}CF_2$	α β $CHF{=}CF_2$	Ref
CF_3	1:0.09	1:0.03	1:0.50	32
CHF_2	1:0.19	1:0.15	1:0.95	18
CH_2F	1:0.30	1:0.44	1:2.04	33
CH_3	1:0.20		1:2.10	26, 27
CCl_3	1:0.07	1:0.01	1:0.29	34
CH_2Cl	1:0.18	1:0.14	1:1.03	35
CBr_3	1:0.04		1:0.24	28
$CHBr_2$	1:0.06		1:0.31	28
CF_3	1:0.09	1:0.03	1:0.50	32
CF_2Br	1:0.09	1:0.03	1:0.47	16, 36
$CFBr_2$	1:0.08	1:0.02	1:0.37	37
CBr_3	1:0.06		1:0.31	28
CF_3	1:0.09	1:0.03	1:0.50	32
CF_3CF_2	1:0.05	1:0.01	1:0.29	40
$(CF_3)_2CF$	1:0.02	1:0.001	1:0.06	39, 40
CF_3CF_2	1:0.054	1:0.011	1:0.29	40
$CF_3(CF_2)_2$	1:0.050	1:0.009	1:0.25	38
$CF_3(CF_2)_3$	1:0.050	1:0.007	1:0.24	40
$CF_3(CF_2)_6$	1:0.049	1:0.007	1:0.23	40
$CF_3(CF_2)_7$	1:0.043	1:0.006	1:0.22	40

However, with trifluoroethylene the most halogenated radicals add preferentially to the CHF end of the molecule, while methyl and the monohalogeno radicals add preferentially to the CF_2 end. This observation shows that delocalization of the odd electron in the adduct radical either by resonance or by hyperconjugation is not the prime factor governing the orientation of addition to this olefin. Although there is no reversal of orientation, a similar trend is to be noted for the other two olefins: the proportion of attack at the more substituted end of the olefin decreases as the radical carries more halogen atoms. This effect is all the more striking if we remember that trifluoromethyl radicals are the most reactive (see below), and would therefore be expected to be the least selective of the fluoromethyl radicals. The series $CX_3\cdot$, $CX_2H\cdot$, $CXH_2\cdot$, $CH_3\cdot$, where X represents a halogen, delineates a range of decreasing electronegativity, and the orientation ratios suggest that polar forces play a significant role in determining the orientation of radical addition.

In the series $CF_3\cdot$, $CF_2Br\cdot$, $CFBr_2\cdot$, and $CBr_3\cdot$, the change in electronegativity is small. By analogy with the fluoromethyl series we would expect a small increase of the orientation ratio for trifluoroethylene along the series, but in fact they decrease. This result suggests that classical steric repulsion due to the bulk of bromine atoms is important. Stronger evidence for classical steric hindrance comes from the series $CF_3\cdot$, $CF_3CF_2\cdot$, and $(CF_3)_2CF\cdot$, which shows a large increase in orientation ratio along the series of radicals for all

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Table II
Orientation Ratios for the Addition of Trifluoromethyl Radicals (Liquid Phase) and Trichloromethyl Radicals (Gas Phase) to Chloroethylenes and Fluoropropenes

Olefin α—β	$CF_3\cdot^a$ $\alpha{:}\beta$	$CCl_3\cdot^b$ $\alpha{:}\beta$
$CHCl{=}CH_2$	$1{:}{>}50^{c,\,9b,\,41}$	$1{:}{>}50^{c,\,14}$
$CHCl{=}CF_2$	$1{:}11.5^{9g}$	$1{:}25^{14}$
$CHCl{=}CCl_2$		$1{:}0.03^{14}$
$CH_2{=}CHCH_3$	$1{:}0.12\ (1{:}0.08)^{42}$	$1{:}0.07^{43}$
$CH_2{=}CFCH_3$		$1{:}0.007^{43}$
$CH_2{=}CHCF_3$	$1{:}{<}0.01^{d,\,9a}$	$1{:}{<}0.01^{d,\,42}$
$CHF{=}CHCF_3$	$1{:}0.33^{44}$	
$CF_2{=}CHCH_3$	$1{:}{>}50^{c,\,9d}$	
$CF_2{=}CHCF_3$	$1{:}1.49^{9c}$	
$CF_2{=}CFCF_3$	$1{:}0.25^{9c}\ (1{:}0.27)^{42}$	$1{:}{<}0.1^{d,\,43}$

[a] Data of Haszeldine and coworkers,[9] except as otherwise noted. [b] Data from our laboratory. [c] Only the adduct from addition to the β end of the olefin was detected. [d] Only the adduct from addition to the α end of the olefin was detected.

three olefins. In contrast, the orientation ratios for the straight-chain radicals $C_nF_{2n+1}\cdot$ show almost negligible change from $n = 2$ to $n = 8$.

Haszeldine and his co-workers made extensive studies of the addition of trifluoromethyl radicals to olefins in sealed tubes in which the reaction occurs in both the liquid and the gas phases.[9] Where data are available from both homogeneous gas-phase experiments and from heterogeneous gas–liquid experiments, comparison shows excellent agreement. Table II lists orientation ratios reported by Haszeldine and co-workers for addition of trifluoromethyl radicals in the liquid phase (ref 9, 14, 41–43) and ours for addition of trichloromethyl radicals in the gas phase to chloroethylenes and fluoro-substituted propenes.

The preference for attack at the CH_2 end of vinyl chloride exhibited by both radicals can be accommodated by the "resonance-stabilization" hypothesis. However, this almost exclusive attack at the β position would require a single chlorine atom to be more effective in resonance stabilization than two fluorine atoms. The results could equally well be attributed to classical steric hindrance, the large chlorine atom being held to inhibit attack on the carbon atom to which it is attached. The preferential attack at the CH_2 end of propene would require resonance stabilization by hyperconjugation of the methyl group to be more effective than simple conjugation by a fluorine atom (cf. the *Or* data for vinyl fluoride in Table I).

These are further results which cannot be accommodated solely by the "resonance-stabilization" argument. The orientation of free-radical addition to unsymmetric olefins depends on the nature of the attacking radical. The earlier ideas of Price,[6] of Waters,[4] and of Mayo and Walling[7] are confirmed. Polar influences of a type familiar to the organic chemist are important in radical addition. They influence not only the rate but also the orientation of addition. There is also evidence that steric hindrance of a classical type may be involved.

Linear Free Energy Relationships

The observation that familiar polar effects influence the orientation ratios for radical addition to olefins prompts the application of well-established free-energy relationships. The orientation data can be accommodated in a Hammett plot by assigning a polar constant, σ, to each radical.[45] This can be defined as the sum of the Hammett σ constants for the groups attached to the radical center. In practice, Taft σ^0 values have been used.[46]

Three good correlations (not shown) were observed between the logarithms of the orientation ratios and the σ values of the radicals for the data of Table I. This encouraged us to apply to our results the "patterns of reactivity" approach utilized by Bamford and Jenkins for interpreting polymer radical reactivities.[47] In the patterns treatment, which was developed from the earlier work of Price and Alfrey[6b] and of Mayo and Walling,[7] the specific velocity constant k_s for a radical reaction is given by

$$\log k_s = \log k_{3,\mathrm{T}} + \alpha\sigma + \beta$$

where $k_{3,\mathrm{T}}$ is the rate constant of the abstraction reaction of the radical with toluene, σ is the Hammett σ value of the radical, and α and β are constants for a given olefin. A simple extension of this equation gives an expression for the orientation ratio in reaction of a radical with an unsymmetrical alkene. The rate constant for addition of the radical to one end of the alkene k_2 is given by:

$$\log k_2 = \log k_{3,\mathrm{T}} + \alpha\sigma + \beta$$

and that for addition to the other end of the alkene by:

$$\log k_2' = \log k_{3,\mathrm{T}} + \alpha'\sigma + \beta'$$

where α, β and α', β' now characterize the respective ends of the alkene. Hence:

$$\log Or = \log k_2'/k_2 = \sigma(\alpha' - \alpha) + \beta' - \beta$$

In the present work the values of $\alpha' - \alpha$ and $\beta' - \beta$ have been determined for vinyl fluoride, 1,1-difluoroethylene, and trifluoroethylene from the gradients and intercepts of the plots of log *Or* against σ. Calculated orientation ratios are plotted against the experimental orientation ratios in Figure 1. The resulting correlation is a reasonable straight line with a correlation coefficient of 0.98, and compares well with the line of unit slope (shown dotted in Figure 1).

The success of this modified "patterns of reactivity" treatment shows that the orientation of free-radical addition to unsymmetrical olefins is governed to a major extent by familiar polar forces which are given quantitative expression in the Hammett equation. The correlations indicate that both the polarity of the olefin and the polar character of the radical are important. These conclusions are consistent with the pictures of relative reactivity that Mayo and Walling developed from copolymerization data.[7]

Unfortunately, Taft steric substituent constants E_s

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(41) R. N. Haszeldine, D. W. Keen, and A. E. Tipping, *J. Chem. Soc. C*, 414 (1970).

(42) J. M. Tedder and J. C. Walton, unpublished work.

(43) J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, **65**, 2103 (1969).

(44) R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. C*, 1750 (1970).

(45) L. P. Hammett, "Physical Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1970.

(46) R. W. Taft, *J. Phys. Chem.*, **64**, 1808 (1960).

(47) C. H. Bamford and A. D. Jenkins, *Trans. Faraday Soc.*, **59**, 530 (1963); A. D. Jenkins, *Adv. Free-Radical Chem.*, **2**, 139 (1967).

Table III
Relative Rates of Addition of Radicals to Specific Sites in Fluoroethylenes[a]

Alkene[b]	$CF_3\cdot$[32]	$CHF_2\cdot$[18]	$CH_2F\cdot$[33]	$CH_3\cdot$[27]	CF_2-$Br\cdot$[16,36]	$CF_2I\cdot$[18]	$CFBr_2\cdot$[37]	$CCl_3\cdot$[34]	$C_3F_7\cdot$[38]	$CH_2Cl\cdot$[c,35]	$CBr_3\cdot$[c,28]
$^*CH_2{=}CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$^*CH_2{=}CHF$	0.48	0.32	0.28	0.57	0.39	0.38	0.29	0.56	0.32	0.40	0.27
$^*CH_2{=}CF_2$	0.15	0.10			0.14	0.11	0.14	0.25	0.07	0.10	0.19
$^*CHF{=}CH_2$	0.056	0.06		0.11	0.037	0.08	0.027	0.06	0.03	0.06	0.01
$^*CHF{=}CF_2$	0.031	0.15		1.00	0.079	0.10	0.10	0.22	0.04	0.18	0.05
$^*CF_2{=}CH_2$	0.006	0.016		0.02	0.004	0.02	0.003	0.004	0.001	0.014	
$^*CF_2{=}CHF$	0.016	0.14		1.90	0.046	0.06	0.040	0.07	0.01	0.18	0.012
$^*CF_2{=}CF_2$	0.12	1.10	3.4	9.51	0.13	0.79	0.23	0.89	0.18	0.60	0.15

[a] Measurements from gas-phase reactions at 164 °C unless otherwise stated. [b] The asterisk indicates site of addition.
[c] Relative rates from sealed-tube experiments at 150 °C.

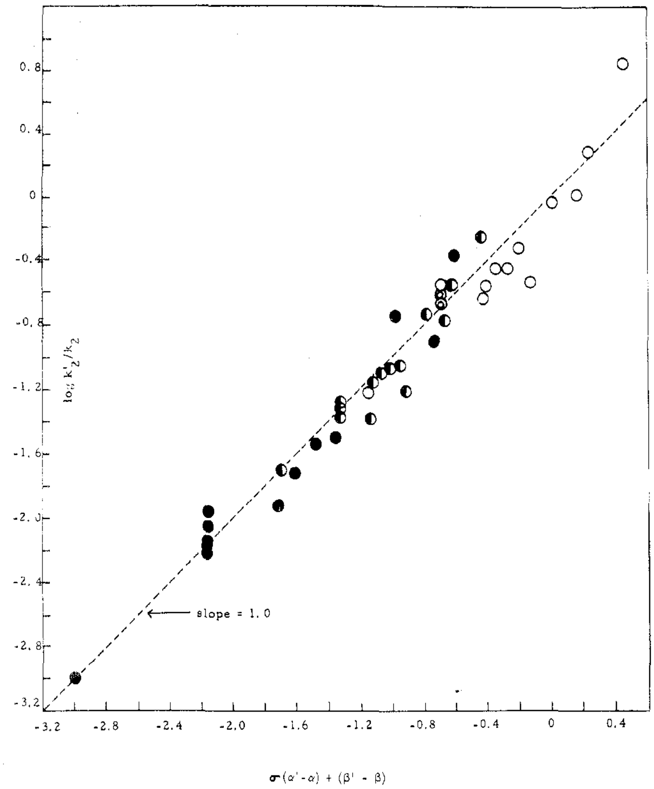

Figure 1. Correlation of orientation ratio with Hammett value for the radical (cf. patterns of reactivity treatment in text). Dotted line has unit slope. Open circles, trifluoroethylene; half-filled circles, vinyl fluoride; filled circles, 1,1-difluoroethylene.

are available for only a few radicals,[48] but for these few log *Or* correlates well with E_S. The diameters of the radicals D_C were calculated from the covalent atomic radii, and significant correlations were found between radical diameters so calculated and log *Or* for each set of results.[28] The correlation coefficients were 0.95 for vinyl fluoride and 1,1-difluoroethylene, and 0.94 for trifluoroethylene. So, besides polar effects, radical orientation is also to some extent governed by classical steric hindrance. Again a semiquantitative treatment gives good correlation with experiment.

The Relative Rates of Addition of Free Radicals to Olefins

The relative rates of addition of a whole range of alkyl radicals to ethylene and to fluoroethylenes are listed in Table III. The table shows an important feature of radical addition which was not apparent from the orientation data. For all the radicals studied, addition to the CH_2 end of vinyl fluoride is slightly slower than addition to one end of ethylene. Radicals add preferentially to the unsubstituted end, not because attack at this end is favored by resonance stabilization of the resulting adduct radical, but because the substituent fluorine atom inhibits addition to the CHF end.

In addition to ethylene and to the substituted ends of vinyl fluoride and 1,1-difluoroethylene, the unpaired electron of the adduct radical is sited on a carbon atom bonded to two hydrogen atoms ($RCH_2\dot{C}H_2$; $RCHF\dot{C}H_2$ and $RCF_2\dot{C}H_2$). Opportunities for resonance stabilization (as distinct from hyperconjugation) are similar in the three cases, and yet there is a decrease in relative reactivity of about two orders of magnitude for most radicals. In these examples a fluorine atom attached to an olefinic carbon atom primarily affects radical attack at the carbon atom to which it is attached and only has a secondary effect on attack at the other olefinic carbon atom. This observation is also true for propene where attack at C-2 is much retarded, although attack at C-1 is slightly accelerated for some radicals.

It is not surprising that a substituent should have a greater effect on the reactivity of the carbon to which it is bonded than on a more remote atom. Nevertheless, substituents do affect the rates of attack at the other end of the double bond, and in some cases this effect can be substantial. (Compare the relative rates of addition to the CF_2 end of tetrafluoroethylene, trifluoroethylene, and 1,1-difluoroethylene). In discussing the orientation data, we found the "resonance-stabilization" hypothesis unable to explain the differences between different radicals; in some cases it incorrectly predicted the orientation. We now find that when it does predict the orientation correctly it often implies a relative rate of attack which is contrary to experiment.

Table III also shows that as the total number of fluorine substituents increases the overall rate of addition (i.e., the sum of the rates of addition at the two ends) passes through a minimum at difluoroethylene; see Figure 2. It is also noteworthy that the electrophilic radicals, such as the trihalomethyl radicals, add faster to ethylene than to tetrafluoroethylene, but

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[48] R. W. Taft, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 633.

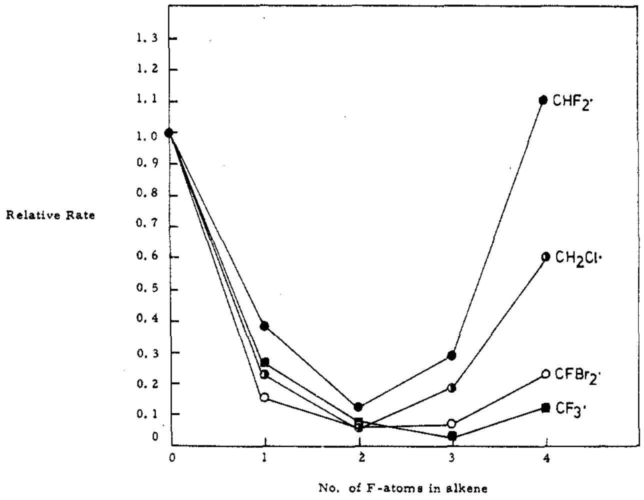

Figure 2. Plot of the overall rate of addition of radicals against number of fluorine atoms in the olefins (rate to ethylene taken as unity).

Table IV
The Rates and Arrhenius Parameters for the Addition of Alkyl Radicals and Halogenoalkyl Radicals to Ethylene[24]

Radical	log A	E	$k^{164\ °C}$
$CH_3\cdot$	8.5	7.7	4.7×10^4
$C_2H_5\cdot$	8.2	7.3	3.5×10^4
$CH_2F\cdot$	7.6	4.3	2.6×10^5
$CCl_3\cdot$	7.8	6.3	4.5×10^4
$CF_2Br\cdot$	8.0	3.1	4.4×10^6
$CF_3\cdot$	8.3	2.0	5.4×10^7

Table V
The Relative Activation Parameters for Addition of $CH_3\cdot$,[24,27] $CH_2F\cdot$,[33] $CHF_2\cdot$,[18] and $CF_3\cdot$[32] to Ethylene and Tetrafluoroethylene[a]

Radical	$\log \frac{A_{CF_2=CF_2}}{A_{CH_2=CH_2}}$	$E_{CF_2=CF_2} - E_{CH_2=CH_2}$	$\frac{k_{CF_2=CF_2}}{k_{CH_2=CH_2}}$ (164 °C)
$CH_3\cdot$	0.34	−2.5	6.0
$CH_2F\cdot$	0.76	−1.3	3.4
$CHF_2\cdot$	0.83	−0.2	1.1
$CF_3\cdot$	0.87	+1.7	0.1

[a] E in kcal mol^{-1}.

methyl radicals and some others add faster to tetrafluoroethylene.

Activation Parameters for Radical Addition to Olefins

Table IV lists rate constants and Arrhenius parameters for the addition of alkyl and haloalkyl radicals to ethylene. Although the rate constants vary by more than three orders of magnitude, the preexponential factors vary by less than a power of ten; in other words the marked difference in reactivity of the various radicals is almost entirely attributable to changes in activation energy. Kerr has pointed out that it is possible to set a lower limit for the A factor for addition by considering the A factor for the reverse reaction.[24]

The difficulty in measuring absolute rates has limited the number of radicals for which activation parameters are available. However, if we are primarily concerned with orientation and relative rates for one radical with different olefins, then ratios of A factors and differences in activation energies can be determined comparatively easily. Table V lists the relative Arrhenius parameters for the addition of $CH_3\cdot$,[24,27] $CH_2F\cdot$,[33] $CF_2H\cdot$,[18] and $CF_3\cdot$[32] to ethylene and tetrafluoroethylene. The steep increase in the activation energy difference (from −2.5 to +1.7) puts a quantitative measure on the polar effects discussed earlier.

Table VI lists Arrhenius parameters for addition of the halomethyl radicals in the gas phase to diverse olefins, all relative to ethylene. The majority of the A factor ratios are close to one and although, as we shall see below, some variation is to be expected, the few ratios greater than 10 (or less than 0.1) probably arise from sets of experiments in which an erroneously high A factor is compensated by an overestimated activation energy. The activation energy differences show similar trends for each radical. The different values for each end of the unsymmetric olefins establish that the activated complex for alkyl radical addition to olefins is of a "σ complex" type and not, as some authors have suggested, a "π complex".

Probably the most consistent set of results is that for trifluoromethyl radicals. The fundamental vibration frequencies of the trifluoromethyl radical have been observed in the infrared, and the radical's entropy has been established with reasonable certainty. The fundamental vibrations and entropies of ethylene, vinyl fluoride, trifluoroethylene, and tetrafluoroethylene have also been determined. With this experimental information at hand, as well as the vibration frequencies of a number of fluoropropanes, we considered two possible models for the activated complex. One was based on the structure and vibrational frequencies of the adduct radical $CF_3E\cdot$ (a tight transition state), and the other on the structures and vibrational frequencies of the appropriate ethylene and the trifluoromethyl radical with minimum mutual interaction (a loose transition state).[32]

The "tight transition state" model predicts A_2 factors between 10 and 100 lower than the experimental values, while the "loose" model gives values of about the right magnitude. However the "tight" transition state predicts a *relative order* of the A_2 factors nearer to experiment. The main reason for this is the loosening of the alkene double bond in the "tight" model which converts the double bond twisting vibration into an internal rotation. It would seem that, although the transition state is "loose", there must be appreciable bonding between the radical and the olefin with concomitant loosening of the double bond and loss of planarity in the alkene. This would be consistent with the observations of Safarik and Strausz concerning the secondary deuterium isotope effect in the addition of trifluoromethyl radicals to ethylene.[51]

The results for most of the radicals in Table VI are insufficiently accurate to detect the small variations in the A_2 factors predicted by transition-state theory. An important feature of the calculations is that the predicted variation in A factors is small and never greater than a factor of 12.5, whereas rates of addition at 164 °C vary by nearly three orders of magnitude for most radicals (see Table IV). This wide vari-

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(49) J. A. Kerr and M. J. Parsonage, *Int. J. Chem. Kinet.*, **4**, 245 (1972).

(50) H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Int. J. Chem. Kinet.*, **4**, 249 (1972).

(51) I. Safarik and O. P. Strausz, *J. Phys. Chem.*, **76**, 3613 (1972).

Table VI
Relative Arrhenius Parameters for Radical Addition to Olefins

	$^bCH_2$=CHF		$^bCH_2$=CF_2		^{b}CHF=CH_2		^{b}CHF=CF_2		$^bCF_2$=CH_2		$^bCF_2$=CHF		$^bCF_2$=CF_2		$^bCH_2$=$CHCH_3$		$^bCF_2$=$CFCF_3$	
	log *A*	*E*	log *A*	*E*	log *A*	*E*	log *A*	*E*	log *A*	*E*	log *A*	*E*	log *A*	*E*	log *A*	*E*	log *A*	*E*
CF_3[32]	−0.1	+0.5	−0.2	+1.2	−0.3	+1.9	−0.6	+1.9	−0.6	+3.2	−0.5	+2.7	−0.1	+1.7				
CF_2Br[16,36]	−0.2	+0.4	+0.0	+1.8	−0.6	+1.6	−1.0*	+0.2	−0.1	+4.4	−0.3	+2.0	+1.1	+3.9				
$CFBr_2$[37]	−0.4	+0.3	−0.5	+0.8	−0.4	+2.3	+1.2*	+4.3	+1.5*	+8.1	+1.4*	+5.6*	−0.5	+0.2				
CF_2I[18]	−0.1	+0.6	−0.1	+1.7	−0.5	+1.2	−0.7	+0.6	−0.2	+3.0	−0.3	+1.8	+0.4	+1.0				
C_3F_7[38]	−0.1	+0.8	+0.7	+2.7	+0.1	+3.2	+0.2	+3.1	+1.1*	+8.2	+0.2	+4.1	+1.6	+4.7				
CCl_3[29,34]	−0.2	+0.1	+0.1	+1.4	−0.2	+2.1	+0.8	+2.9	+0.1	+5.1	+0.8	+3.9	+1.4	+2.9	+1.3	+0.2	+1.0	+3.0
CH_3[24,26,27]	0.2	+0.4			−0.7	+0.3	−0.1	−0.7	−0.4	+2.2	−1.5	−4.1	−0.1	−1.8	−0.8	−0.8		
$CHF_2\cdot$[18]	0.0	+0.3											−0.1	−0.2				
$CH_2F\cdot$[33]													−0.1	−1.3				
$(CF_3)_2CF$[39]	+0.1	+0.8	0.0	+1.2	−0.3	+3.6	−0.4	+2.8	−0.6	+6.1	−0.7	+4.2						

[a] Log *A* (l. mol^{-1} s^{-1}) = log A_x − log $A_{CH_2=CH_2}$; *E* (kcal mol^{-1}) = E_x − $E_{CH_2=CH_2}$. [b] Indicates site of addition.

Table VII
The Activation Energies for the Addition of Trichloromethyl and Trifluoromethyl Radicals to Fluoro Olefins Compared with Hückel Parameters[a]

Atom μ asterisked	Free valence, F_μ	Charge density, q_μ	Localization energy, L_μ	Activation energy,[32] $CF_3\cdot$	Activation energy,[34] $CCl_3\cdot$
*CH_2=CH_2	0.73	1.00	2.00	2.0	6.3
*CH_2=CHF	0.77	1.13	1.96	2.5	6.4
*CH_2=CF_2	0.81	1.25	1.95	3.2	7.7
*CHF=CH_2	0.51	0.93	2.23	3.9	8.4
*CHF=CF_2	0.62	1.17	2.11	3.9	9.2
*CF_2=CH_2	0.29	0.87	2.46	5.2	11.4
*CF_2=CHF	0.35	0.98	2.36	4.7	10.2
*CF_2=CF_2	0.42	1.09	2.29	3.7	9.2

[a] The Hückel parameters used were α_C = 2.590, α_F = 5.315, β_{CC} = 1.000, β_{FC} = 0.908. The localization energies are in units of β_{CC} and the activation energies are in kcal mol^{-1}.

ation in rate is, as Table VI shows, principally due to changes in the activation energy.

The simplest parameters which can be compared with the experimental activation energies are those derived from Hückel theory. The parameters we shall consider are the π-electron charge density at atom μ ($q_\mu = 2\Sigma_{r\text{occ}}C_r{}^2{}_\mu$), Coulson's free valence index ($F_\mu = n_{\max} - n_\mu$, where n_μ is the sum of the mobile bond orders emitting from atom μ and $n_{\max}$ is the maximum possible value, usually taken at $3^{1/2}$), and localization energy L_μ (i.e., the total loss in π-electron energy in localizing an electron on atom μ).[34] Table VII lists the parameters and compares them with the activation energies for the addition of trichloromethyl and trifluoromethyl radicals.

In Table VII there is little correlation with the free valence index, and likewise the correlation with charge density is poor. However a reasonable but by no means perfect correlation can be found between the experimental activation energies and the localization energies for both radicals. Better correlation with localization energy is to be expected since it represents an attempt to model the transition state, unlike F_μ and q_μ, which simply refer to the ground state of the alkene. In order to allow for the manifest polar character of the reaction we tried including a term, δQ_μ, which represents the calculated net atom charge.

$$E_{\text{obsd}} = A(L_\mu + B\delta Q_\mu)$$

When B is put equal to 0.5 for the addition of trichloromethyl and trifluoromethyl radicals the correlation is a marked improvement on plots involving simple localization energies. Similar plots can be obtained for $C_3F_7\cdot$ and $CF_2Br\cdot$ radicals; the correlation is less good, but this may be due to poor experimental points. However this type of expression can never account for the reversal in orientation observed for the less electrophilic radicals. Even if the constant B changes sign, the proposed expression will still not give a good correlation with methyl radicals.

In terms of frontier electron theory we can distinguish between the electrophilic radicals in which a charge-transfer structure involving a loss of electron from the olefin may be considered to contribute:

$$CF_3\cdot\ {>}C{=}C{<} \leftrightarrow CF_3{:}^-\ {>}C^+{-}\dot{C}{<}$$

and the nucleophilic radicals for which any charge-transfer state would involve the transfer from the radical to the olefin:

$$\mathrm{CH_3}\cdot\ {>}\mathrm{C}{=}\mathrm{C}{<} \leftrightarrow \mathrm{CH_3}^+\ {>}\ddot{\mathrm{C}}{-}\dot{\mathrm{C}}{<}$$

The important feature of this picture is that it involves both the radical and the olefin. Charge-transfer structures were postulated as intermediates in radical copolymerization by Mayo, Walling, and coworkers in 1948[52] to explain relative reactivity, but their significance in determining orientation of addition was not appreciated. The charge-transfer structure is most likely between hydrocarbon olefins and the electrophilic radicals, or between the fluorinated olefins and the nucleophilic radicals. In the charge-transfer structures the lone electron is in the π orbital (the HOMO) for the electrophilic model and in the π^* orbital (the LUMO) for the nucleophilic model, so that reversal of orientation is to be expected. If the uncertain orientation data for methyl radicals are correct, the electron affinity of trifluoroethylene must be sufficiently great to promote the charge transfer whereas with 1,1-difluoroethylene it is not.

More sophisticated molecular orbital calculations are difficult because of the number of electrons involved and the open-shell configurations. Clark and Scanlan[53] have investigated the potential-energy surfaces for several radical additions, using INDO SCF–MO calculations, and obtained independent evidence for the model suggested above.

Conclusions

Our studies of the kinetics and orientation of free-radical addition to olefins show that the almost universally accepted resonance theory of reactivity in these reactions is frequently inconsistent with experiment. The results do not offer a simple qualitative picture to replace the resonance theory, but instead show that the rate and orientation of free-radical addition depend on the complex interplay of polar, steric, and bond-strength terms. Similar conclusions were originally drawn from copolymerization studies,[7] but they were subsequently neglected in favor of the simpler resonance picture.

If an experimentalist requires a simple qualitative theory, he should seek to estimate the strength of the new bond formed during the initial addition step rather than the delocalization of the unpaired electron.[34] The important feature of such an approach is that the characteristics of the radical as well as those of the olefin are brought into consideration.

The polar influences which we have found to be important can be expressed in terms of the electronegativity difference between the radical and the attacked site in the olefin. Similarly the classical steric effects we have observed have a bearing on the strength of the new bond. Experimental measurement of the strength of the new bond in the adduct radical is possible if the Arrhenius parameters for both the forward and backward reaction are known. Efforts are now being made to study the kinetics of the backward reaction.

Mechanistic organic chemistry is rapidly moving out of the realm of qualitative resonance pictures into that of approximate molecular orbital calculations. It will be some time before all-electron calculations can be completed for the addition of trichloromethyl radicals to trifluoroethylene and complete potential energy surfaces become available, but SCF programs are already available for the simpler radicals, and the present results look promising. Some chemists will undoubtedly be disappointed that a simple pictorial theory has to be abandoned to be replaced either by a complex picture involving interplay of a number of factors or alternatively by quantum mechanical calculations completed by the computer. However, there is no reason to suppose that nature can be correctly understood in terms of simple pictures. The deeper we wish to understand, the more sophisticated the theories we have to employ. It would be fatal to retain a qualitative theory known to be wrong simply because it fits in with our other qualitative ideas. Rather we should look again at some of our other resonance-based theories to see if they are really as soundly based as we like to think.

The authors thank Professor W. A. Waters for important suggestions; they also thank Professors T. S. Stevens and P. L. Pauson and Drs. D. Nonhebel, D. T. Clark, and A. R. Butler who also made valuable comments. Above all, they acknowledge the industry and enthusiasm for their research colleagues who made so much of the work described possible.

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(52) C. Walling, E. R. Briggs, K. B. Walfstirn, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

(53) D. T. Clark, personal communication.

Additions and Corrections

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Page 189. The second column of Table V should be headed $A_{\mathrm{CF_2{=}CH_2}}/A_{\mathrm{CH_2{=}CH_2}}$ rather than the logarithm of this quotient.