J. Am. Chem. Soc. **1998,** *120,* 9513−9516

MCPBA Epoxidation of Alkenes: Reinvestigation of Correlation between Rate and Ionization Potential

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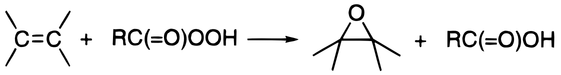
Received May 4, 1998

Abstract: A kinetic equation provides relative rate constants from product analysis under competition conditions. This has been applied to the epoxidation of a large number of alkenes with *m*-chloroperbenzoic acid in methylene chloride. The rate constants are well correlated with ionization potentials, but there are separate linear correlations for aliphatic and aromatic alkenes. However, the extent of electron transfer to the peracid is minimal. These results can be interpreted in terms of transition-state imbalance ("nonperfect synchronization"), frontier-orbital theory, and a transition state (**1**) that has little charge development at carbon.

Introduction

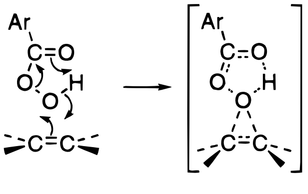
Peracids such as *m*-chloroperbenzoic acid (MCPBA) react directly with alkenes to afford the corresponding epoxide (eq 1). A large amount of data show that the reaction rate is



(1)

increased by electron-donating groups on the alkene and by electron-withdrawing groups on the peracids but that it is insensitive to the steric environment.[1] Since many epoxidation reactions have been observed in biological systems[2] and practical syntheses, including catalytic processes,[3] it is important to understand the epoxidation mechanism.

Although several mechanisms for the epoxidation of alkenes by peracids have been proposed, it is still not fully understood. No mechanism encompasses all the results, including the specific influence of solvent, the formation of rearranged byproducts, and the induced decomposition of peracids.[4] Bartlett's "butterfly" model (**1**) for the transition state has been widely accepted as accounting for the main features.[1,5] This mechanism involves a concerted attack on the alkene by the intramolecularly hydrogen-bonded peracid.[6] This mechanism is consistent with the observations that the reaction is stereospecific and occurs easily even in nonpolar solvents, indicating that free ions are not involved.[7]



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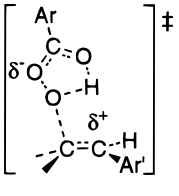

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Hanzlik and Shearer observed unequal secondary kinetic deuterium isotope effects at the two alkene carbons of *p*-phenylstyrene.[8] They proposed an asymmetric transition state with partial charge on one of the carbons (**2**). This structure, too, would be consistent with the previously reported kinetics, stereospecificity, and Hammett correlations. In support, several ab initio molecular orbital studies have suggested that asymmetric transition states are energetically more favorable than symmetric ones[9] but not by much.[10] In contrast, recent high-level DFT calculations on epoxidation of ethylene indicate synchronous or nearly synchronous formation of the two C−O bonds.[11] Moreover, the calculated kinetic isotope effects agree with the experimental ones, whereas those calculated for an asymmetric transition state do not. However, with substituted ethylenes, such as butadiene, the transition state becomes asymmetric.

Another measure of the symmetry of the transition state is the relationship between the second-order rate constant k_2 and

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S0002-7863(98)01531-5 CCC: $15.00

the ionization potential of the alkene. Shellhamer and Aue observed a linear relationship between log k_2 for epoxidation of some aliphatic alkenes (ethylene, propene, methylenecyclopropene, cyclopropene, cyclobutene, *trans*-2-butene, 2-methylpropene, cyclohexene, methylenecyclobutane, norbornene, cyclopentene, methylenecyclopentane, *trans*,*trans*-2,4-hexadiene, and 2-methyl-2-butene) by MCPBA and the ionization potentials of those alkenes.[12] This is consistent with a frontier-orbital interaction, between the LUMO of the peracid and the HOMO of the alkene, as dominant in modulating reactivity. Since the HOMO is delocalized over the alkene, the good correlation suggests that little localization of charge is involved in the transition state.

Yet recently, Shea and Kim have measured rates of MCPBA epoxidation of a series of cyclic alkenes, including bridgehead alkenes and *trans*-cycloalkenes.[13] For these strained alkenes there is a contribution to the rate acceleration from the relief of strain energy on passing from alkene toward epoxide. However, even with correction for the relief of strain, the overall correlation of log k_2 with ionization potential is poor. This is so because conjugated alkenes, which have higher HOMO energies than simple alkenes, are nevertheless less reactive. They concluded that the HOMO−LUMO interaction, which is a second-order perturbation, is not the dominant factor. More important is the first-order Coulombic interaction associated with the stabilization of partial positive charge in the transition state by an additional alkyl group or by conjugation.

Because of our interest in hemin-catalyzed epoxidations,[14] we wanted to use substituent effects in the most widely studied MCPBA epoxidations as a standard for comparison. Therefore we have reinvestigated MCPBA epoxidation for a series of alkenes across a wide range of ionization potentials. Although many rate constants have been published, it is not easy to make comparisons among them because they were determined under different conditions, especially of temperature or solvent. Herein we report the development of a kinetic method to determine relative rate constants for the reactions of a number of alkenes with MCPBA. This method is applicable over a range of ca. 10^3-fold in reactivity. Unexpectedly we find good correlations of log k_2 vs the ionization potential of the alkene, in contrast to the results of Shea and Kim.

Experimental Section

Instrumentation. UV−visible absorption spectra and kinetic measurements were obtained on a Kontron 810 spectrophotometer interfaced to a Celerity computer.

Materials. *m*-Chloroperbenzoic acid was purified as previously described.[15] 1-Octene (C&B Manufacturing Co., 97%) and norbornene (Aldrich) were distilled before use. Benzonorbornadiene, 6*b*,8*a*-dihydrocyclobut[*a*]acenaphthylene, vinylcyclopropane, and a mixture of *syn*- and *anti*-7-vinyl-bicyclo[4.1.0]-heptanes were all obtained from previous studies.[16] Other alkenes were of the highest grade available (Aldrich) and were used as received. The solvent was methylene chloride (Fisher Spectrograde).

Kinetic Measurements. All of the kinetic studies were carried out at room temperature. A solution of 2.20×10^{-3} M MCPBA and 7.3×10^{-6} M β-carotene in CH_2Cl_2 was made up quickly at room temperature. The disappearance of β-carotene was followed by a decrease in absorbance at 460 nm ($\epsilon = 1.5 \times 10^5$). The pseudo-first-order rate constant was divided by the concentration of MCPBA to afford a second-order rate constant of 1.5 ± 0.2 M^{-1} s^{-1}.

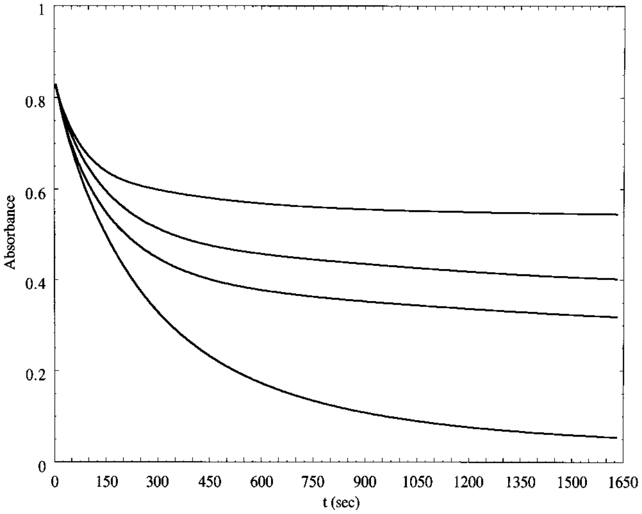

Figure 1. Time dependence of 460-nm absorbance during competitive epoxidations by 2.20×10^{-3} M MCPBA of 7.30×10^{-6} M β-carotene and 1-octene (0, 2.63×10^{-2}, 4.39×10^{-2}, 8.78×10^{-2} M from bottom to top).

The relative rates of epoxidation of alkenes were determined by competition with β-carotene as a reference alkene, whose disappearance could be monitored at 460 nm. In all cases, at least three different concentrations of the substrate alkene were used to determine the relative rates. In such experiments, sufficient 0.1 M MCPBA solution was added to a solution of 7.3×10^{-6} M β-carotene and at least 2.2×10^{-2} M of a second alkene, all in methylene chloride, to bring the oxidant concentration to 2.20×10^{-3} M in a total volume of 0.5 mL. A higher concentration of less reactive alkenes was used for more effective competition with the carotene. The rate of decrease of the β-carotene absorbance at 460 nm was then followed. Plots of absorbance vs time of a solution of β-carotene and MCPBA in the presence of increasing amounts of 1-octene are shown in Figure 1. It is clear that 1-octene reduces the extent of β-carotene epoxidation.

Data Analysis. The relative rates of reaction of an alkene and a reference diene can be obtained from either the differential or the integrated forms of the equations describing the plots in Figure 1. The integrated form was used, adapted as follows from the competitive epoxidation by an iodosylbenzene as catalyzed by a hemin:[17]

If S and R are substrate and reference alkenes, reacting with oxidant O with second-order rate constants k_S and k_R, respectively, and if the absorbance of R (β-carotene) is monitored, then

$$-\frac{d[S]}{dt} = k_S[S][O] \tag{2}$$

and correspondingly for d[R]/d*t*, so that

$$\frac{d[S]}{[S]} = \frac{k_S}{k_R}\frac{d[R]}{R} \tag{3}$$

Integrating from 0 to *t* gives

$$\ln\frac{[S]}{S_0} = \frac{k_S}{k_R}\ln\frac{[R]}{R_0} \tag{4}$$

From the stoichiometry

$$O_0 - [O] = R_0 - [R] + S_0 - [S] \tag{5}$$

or

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$$\frac{[\mathrm{S}]}{\mathrm{S}_0} = 1 - \frac{(\mathrm{O}_0 - [\mathrm{O}]) - (\mathrm{R}_0 - [\mathrm{R}])}{\mathrm{S}_0} \qquad (6)$$

We neglect the complication due to diepoxidation of β-carotene, since this contribution is expected to be small, owing to the reduction in conjugation and to the electron-withdrawing character of an epoxy group.[18] If $\mathrm{S}_0 \gg \mathrm{O}_0$ or R_0, the logarithm on the left in eq 4 can be approximated, leading to

$$\frac{k_\mathrm{S}}{k_\mathrm{R}} \ln \frac{[\mathrm{R}]}{\mathrm{R}_0} = \ln \frac{[\mathrm{S}]}{\mathrm{S}_0} \approx - \frac{(\mathrm{O}_0 - [\mathrm{O}]) - (\mathrm{R}_0 - [\mathrm{R}])}{\mathrm{S}_0} \qquad (7)$$

and to

$$\frac{k_\mathrm{S}}{k_\mathrm{R}} \approx - \frac{(\mathrm{O}_0 - [\mathrm{O}]) - (\mathrm{R}_0 - [\mathrm{R}])}{\mathrm{S}_0 \ln(\mathrm{R}_0/\mathrm{R}_\infty)} \qquad (8)$$

At infinite time, [O] approaches 0, so

$$\frac{k_\mathrm{S}}{k_\mathrm{R}} = \frac{\mathrm{O}_0 - (\mathrm{R}_0 - \mathrm{R}_\infty)}{\mathrm{S}_0 \ln(\mathrm{R}_0/\mathrm{R}_\infty)} \qquad (9)$$

Therefore the rate ratio $k_\mathrm{S}/k_\mathrm{R}$ can be obtained from the stoichiometry of the samples and from the initial and final concentrations of the reference alkene R, measured by absorption spectrophotometry. Thus, eq 9 can give the bimolecular rate constant for each of the substrate alkenes, relative to that for β-carotene. The concentration of the alkene was adjusted so as to aim for $\mathrm{R}_\infty \approx \mathrm{R}_0/2$, which maximizes accuracy.

Table 1 shows that the results obtained by this method are in good accord with those previously published, which validates our analytical method. The largest discrepancy is for 1-octene, but our rate agrees well with that of the similar vinylcyclohexane.

Results

The relative rates for epoxidation by MCPBA of a number of alkenes, along with published ionization potentials, are listed in Table 2. These rate constants k_rel are all relative to the rate constant for epoxidation of β-carotene. Rate constants for dienes have been corrected for statistics.

A plot of log k_rel vs gas-phase ionization potential I_P is shown in Figure 2. It is readily seen that the alkenes fall into two groups, aromatic and simple aliphatic alkenes. The polyene β-carotene does not fit on either line.

Discussion

Relative rates of epoxidation can be determined from the extent to which they reduce the extent of epoxidation of β-carotene. This method permits measurement under conditions guaranteed to be identical, including temperature and medium.

Table 1. Comparison of Rates or Selectivities in MCPBA Epoxidation with Literature Values

k_2, $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ or k_rel	this work	literature	ref
cyclohexene	0.0375	0.0225	1
trans-stilbene	0.0056	0.0036	19
norbornene/cyclohexene	2.8	2.8	16
1-octene/styrene	1.5	0.71[a]	20
vinylcyclohexane/styrene	1.2	1.1	20
methylenecyclohexane/styrene	21	33	20

[a] 1-Decene, assumed to be equivalent to 1-octene.

Table 2. Relative Rates for Epoxidation of Alkenes and Literature Ionization Potentials

alkene	log $k_{2\mathrm{rel}}$	I_P, eV	ref
β-carotene	0.0	6.73	21
benzonorbornadiene	−1.21		
1,4-diphenylbutadiene	−2.09[a]	7.55	22
trans-stilbene	−2.41	8.00	23
cis-stilbene	−2.36	8.20	23
trans-2-*cis*-4-hexadiene	−0.98[a]	8.25	24
1,3-cyclohexadiene	−0.66[a]	8.25	25
styrene	−2.57	8.47	25
2,6-dimethylstyrene	−3.05	8.57	25
7-vinylbicyclo[4.1.0]heptane	−1.51	8.75	16
norbornene	−1.17	8.81	26
1,4-cyclohexadiene	−1.82[a]	8.82	25
vinylcyclopropane	−1.83	8.90	16
methylenecyclohexane	−1.24	8.97	26
cyclohexene	−1.60	9.00	25
allyltrimethylsilane	−1.65	9.02	26
cis-2-pentene	−1.24	9.04	27
6*b*,8*a*-dihydrocyclobut[*a*]acenaphthylene	−2.57	9.41	16
vinylcyclohexane	−2.47	9.50	16
1-octene	−2.39	9.52	25
vinyltrimethylsilane	−3.00	9.85	16

[a] Corrected for statistics.

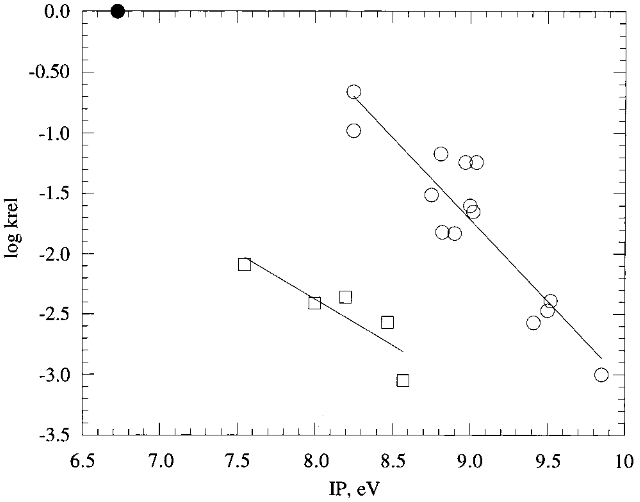

Figure 2. Plot of log k_rel for MCPBA epoxidation of alkenes vs ionization potential. Lines are separate least-squares fits for aliphatic (○) and aromatic (□) alkenes, relative to β-carotene (●).

The slopes of log k vs I_P for aromatic and aliphatic alkenes in Figure 2 are -0.76 ± 0.24 and $-1.36 \pm 0.17\ \mathrm{eV}^{-1}$, respectively. The magnitude of the slope for the aromatics would be even lower, with less error, if 2,6-dimethylstyrene were excluded. This alkene might be retarded by steric hindrance, although significant retardation has been seen only in extreme cases.[29]

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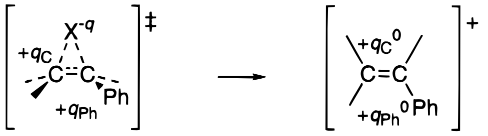
Each of these correlations indicates that the epoxidation rate increases as the alkene becomes more electron-rich. This is certainly reasonable for a reaction with a reagent containing electronegative oxygens. The uniformly low slopes of the two correlation lines in Figure 2 suggest that the transition states of simple aliphatic and aromatic alkenes in MCPBA epoxidation are rather similar. Moreover, these correlations imply that the epoxidation of alkenes with peracids is related to electron density, such that the partially charged transition-state structure (**2**) cannot be rejected. Nor can the frontier-orbital interaction be neglected.

Since a lowering of activation energy by 1 eV, or 23 kcal/mol, corresponds to a rate acceleration of 1.6×10^{17}-fold at 20 °C, the observed slopes of log k vs I_P represent only 4% and 8% electron transfer at the transition state, for aromatic and aliphatic alkenes, respectively. Even though the reagent has electronegative oxygens, there is little transfer of electron density from carbon to those oxygens. Instead, the slopes are so low that it might appear that electron transfer is hardly involved. Indeed, Shea and Kim's observation that the correlation is poor led them to conclude that frontier-orbital interactions are not dominant.[13] In particular, they noted that 2,4-hexadiene and 1,4-diphenylbutadiene, which differ significantly in ionization potential, nevertheless have nearly the same rate of epoxidation. However, Figure 2 indicates that these lie on two different correlations.

To resolve this discrepancy, it is necessary to understand why there are two separate correlations in Figure 2. The divergence is such that aromatic alkenes undergo epoxidation more slowly than aliphatic ones of comparable ionization potential. The need to consider these two classes separately has long been recognized.[30] In contrast, there is no such divergence in oxidation by the oxene ($\mathrm{Hm}^{+}{=}\mathrm{O}$) formed from an iron(III) porphyrin, and the good correlation with ionization potential was taken as evidence for an electron-transfer mechanism.[17]

We propose that the difference between aromatic and aliphatic alkenes is a consequence of transition-state imbalance ("non-perfect synchronization").[31] Even though electron density is transferred from alkene to peracid, the delocalization of positive charge to the phenyl lags behind. To the extent that epoxidation rates correlate with ionization potentials, the radical cation **3**, with a full positive charge, is a model for the product of the reaction. Some of that charge, $+q_{\mathrm{Ph}}^{0}$, is delocalized into the phenyl, and some, $+q_{\mathrm{C}}^{0}$, remains at the double bond. In the transition state (**4**), only a fraction $+q$ of the full charge is developed on the alkene. Some of that positive charge, $+q_{\mathrm{Ph}}$, is delocalized into the phenyl, and some, $+q_{\mathrm{C}}$ ($= q - q_{\mathrm{Ph}}$) remains at the double bond. According to Kresge's model,[32] q_{Ph} is proportional to q^2, rather than simply to q. This leads to $q_{\mathrm{Ph}}/q < q_{\mathrm{Ph}}^{0}$, meaning that the extent to which charge is delocalized into the phenyl ring is lower in **4** than in **3**. Consequently, the phenyl does not provide as much stabilization to the transition state as might be expected on the basis of its effect on ionization potential. In contrast, stabilization by alkyl substitution, which does not operate via delocalization (at least not to as great an extent), is not subject to a lag. Thus, aliphatic alkenes are epoxidized faster than aromatic ones of comparable ionization potential, and the rates of the former class are more sensitive to ionization potential, as measured by the slope of Figure 2.



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Alternatively, this difference can be interpreted in terms of frontier molecular orbital theory.[33] One measure of the energy of interaction between the alkene and an electrophilic reactant is given by eq 10,

$$E \propto c_{\mathrm{C}}^{2}/\Delta\epsilon \tag{10}$$

where c_{C} is the coefficient of an alkene carbon in the highest occupied MO (for utmost simplicity) and $\Delta\epsilon$ is the energy gap between that MO and the lowest unoccupied MO of the electrophile. It is this latter that represents the dependence on ionization potential. In simple Hückel theory, the HOMO coefficient at C_{α} is 0.707 in ethylene, larger than the 0.595 for styrene. Therefore, even at constant $\Delta\epsilon$, the interaction with an aliphatic alkene is stronger, and also more sensitive to the ionization potential.

This analysis suggests that polyenes, which also stabilize the transition state by delocalization, should lie on a line separate from aromatic and aliphatic alkenes. Certainly β-carotene does. However, the two examples in Figure 2 lie close enough to the line for aliphatic alkenes that it is not possible to verify this further.

These data do not permit us to distinguish directly between symmetric (**1**) and asymmetric (**2**) transition states. However, a substantial positive charge at one of the carbons, as in **2**, is not consistent with the very low slopes in Figure 2. The absence of charge development suggests a transition state resembling **1**, consistent with results of calculations on ethylene itself.[10,11]

For substituted ethylenes, there is no requirement for symmetry, and a decidedly asymmetric transition state was calculated for epoxidation of butadiene.[11] Yet it must be recognized that the positive charge in **2** is so low that the asymmetry cannot be accompanied by any substantial delocalization into an aromatic substituent, even though that delocalization ought to enhance the asymmetry. Moreover, the slope for aromatic alkenes is even lower than for aliphatic ones, owing to the lag in delocalization that we propose. This lag is further evidence against appreciable charge asymmetry in the transition state.

Conclusions

A kinetic equation has been developed to accomplish relative rate measurements under common competition conditions. This has permitted the measurement of rate constants for the reactions of *m*-chloroperbenzoic acid with a large number of alkenes. The rate constants vary over 3 orders of magnitude.

The rate constants are well correlated with ionization potentials, suggesting that the frontier-orbital interaction is important. However, the extent of electron transfer to the peracid is minimal. Separate correlations are obtained for aliphatic and aromatic alkenes. These results can be interpreted in terms of transition-state imbalance (nonperfect synchronization), frontier-orbital theory, and a transition state (**1**) that has little charge development at either carbon.

Acknowledgment. We are grateful to the National Institutes of Health (T.G.T., Grant HL 13581) and the National Science Foundation (T.G.T., Grant CHE 87-21364) for financial support.

JA981531E

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