Dioxirane Chemistry. Part 23.[1] The Effect of Solvent on the Dimethyldioxirane Epoxidation Reaction

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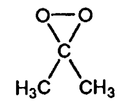
Second order rate coefficients for the epoxidation of *trans*-ethyl cinnamate (**3**) and cyclohexene (**4**) by dimethyldioxirane have been obtained in a number of binary solvents. These data were treated by the Kamlet–Taft multi-parameter solvent effect equation. These analyses indicate that solvents with hydrogen bond donor capacity (HBD) increase the rate of these reactions while solvents with hydrogen bond acceptor (HBA) capacity decrease the rate. Variable temperature rate determinations for the cyclohexene epoxidation permitted the calculation of E_a, log A, and transition state parameters for several solvent systems. These data also support the favourable effect of HBD solvents on the rate of epoxidation by dimethyldioxirane.

Dioxiranes have proved to be versatile and efficient oxygen atom transfer agents.[2] There is now a growing literature on the use of dioxiranes in organic synthesis. In some cases use of a dioxirane has led to the formation of oxygen transfer products, epoxides, for example, which were previously inaccessible or accessible only in poor yield.[2] The physical organic chemistry of dioxiranes has also received some attention by ourselves and others.[3] One aspect of this physical organic chemistry which has received relatively little attention is the influence of solvent on the oxygen transfer reactions. Perhaps the most comprehensive work to date is that of Baumstark and Vasquez[3a] who found that increasing the mole fraction of water in an acetone–water mixture led to an increased rate in the epoxidation of *p*-methoxystyrene by dimethyldioxirane (**1**). There are several other reports in the literature in which some effect of solvent on reactions of **1** has been reported. These include the reaction of **1** with quadricyclane,[4] polycyclic aromatic hydrocarbons,[5] and with pyranose glycals.[6] In addition Curci and co-workers have described the effect of solvent on the reaction of trifluoromethylmethyldioxirane (**2**) with adamantane and other hydrocarbons.[3c] In this work we describe a comprehensive study of the effect of a variety of solvents on the kinetics of two epoxidation reactions of **1**. The results have been correlated with a multi-parameter empirical equation.



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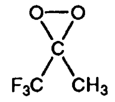

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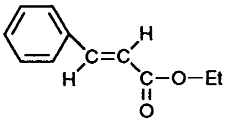

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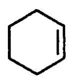

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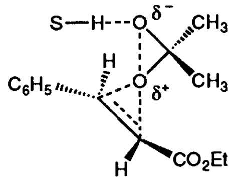

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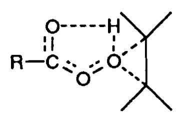

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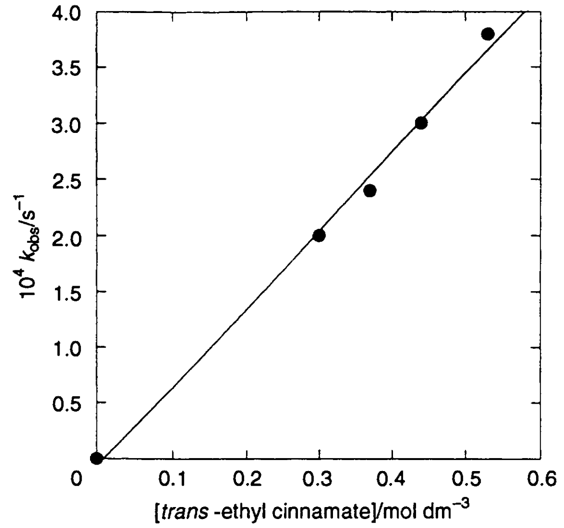

Fig. 1 Plot of k_{obs} *versus* *trans*-ethyl cinnamate concentration for the dimethyldioxirane epoxidation reaction in 1:1 ethyl acetate–acetone at 25 °C

Results and Discussion

We initially intended to study the influence of solvent on the kinetics of epoxidation by **1** by obtaining rate coefficients in a series of solvents. Since **1** is available only in acetone solution we planned to obtain the rate constants in the neat solvents by extrapolating the data obtained in a number of acetone–second solvent solutions. The data obtained were not suitable for such extrapolations, however. In most cases the rate constants varied in a more complex way with solvent composition. We then settled on obtaining data in 1:1 acetone–solvent X solutions. The kinetic data were obtained at 25 °C under pseudo first order conditions with **3** in excess (8–20 fold). The kinetics were followed by observing the decay in the absorption of **1** at 335 nm. Plots of ln $(A_t - A_\infty)$ *versus* time gave straight lines with excellent correlation coefficients ($R = 0.999$). The slopes of these lines give the k_{obs} values. Plots of these k_{obs} values *versus* concentration of **3** also gave excellent straight lines ($R > 0.99$) with slopes $= k_2$. An example of these plots is given in Fig. 1. A summary of the kinetic data is given in Table 1. It should be pointed out that the solvents chosen for this study were first screened for any conflicting first order processes, *e.g.*, autodecomposition of **1** in the solvent or second order processes, *e.g.*, reaction of **1** with the solvent. This was accomplished by beginning with a large group of solvents and then determining

k_1 values for the decomposition of **1**. The solvents chosen for the k_2 studies have k_1 values for **1** of *ca.* 10^{-6} s^{-1}. Given the values of k_2 obtained (Table 1) no interference from k_1 processes is expected.

A similar procedure was used to obtain second order rate coefficients for the epoxidation of cyclohexene (**4**) by **1**. In this case also, excellent correlation coefficients were obtained for the k_{obs} and k_2 plots (in most cases $R > 0.99$). A summary of the kinetic data obtained is given in Table 2. Next a study was made of the effect of solvent on the kinetics of epoxidation of **4** over the temperature range 10–30 °C. These data were used to construct Arrhenius plots for acetone and five acetone–solvent X mixtures. These plots gave excellent linear correlations ($R > 0.99$). Transition state theory parameters were then calculated from the Arrhenius values using the Eyring[7] equation. A summary of these data is given in Table 3.

Previous work has demonstrated that, like *m*-chloroperbenzoic acid (MCPBA), **1** is an electrophilic oxidant.[3] We have compared the kinetic results obtained for the epoxidation of **3** by **1** with those reported by Schwartz and Blumberg[8] for the epoxidation of *trans*-stilbene by MCPBA in order to learn more about the transition state involved in the reaction by **1**. In the case of MCPBA the generally accepted transition state is that proposed by Bartlett,[9] that is **5**. Solvents which can interrupt the intramolecular hydrogen-bond in **5** by forming intermolecular hydrogen-bonds with MCPBA will retard the rate. Such solvents include alcohols, dimethylformamide, and dioxane, for example. In comparing the two epoxidation processes, therefore, we have used only those solvents shown in Table 1 in which this type of intermolecular hydrogen-bonding cannot occur. A linear free energy plot between our data for the reaction between **1** and **3** and the data obtained by Schwartz and Blumberg for the MCPBA/*trans*-stilbene reaction shows a reasonably good correlation between the data ($R = 0.91$) with a slope of 0.82. We have also attempted a similar correlation between the data obtained for **3** and those reported by Curci, Edwards *et al.*[10] for the epoxidation of cyclohexene by perbenzoic acid (PBA). In this case a poorer correlation is obtained ($R = 0.84$) with a slope of 0.43. We conclude that these LFER studies indicate similarities in the transition states for the peracid epoxidations and that by **1**. The better correlation observed when the dioxirane data are compared with those for the *trans*-stilbene case than for the cyclohexene case is preumably due to the greater similarity between substrates *trans*-ethyl cinnamate and *trans*-stilbene than between *trans*-ethyl cinnamate and cyclohexene.

Table 1 Second order rate coefficients for the reaction of dimethyldioxirane with *trans*-ethyl cinnamate

Solvent[a]	10^4 k_2/mol^{-1} dm^3 s^{-1} [b]	Relative reactivity
Acetic acid	29.66 ± 0.12	3.42
Sulfolane	25.26 ± 0.26	2.92
Chloroform	16.30 ± 0.30	1.88
Methylene chloride	14.66 ± 0.57	1.69
1,2-Dichloroethane	12.55 ± 0.52	1.45
Chlorobenzene	19.00 ± 0.23	1.15
Benzene	9.41 ± 0.10	1.09
Acetone	8.66 ± 0.22	1.00
Methyl ethyl ketone	8.10 ± 0.14	0.935
Carbon tetrachloride	7.98 ± 0.02	0.921
Methyl acetate	7.74 ± 0.04	0.894
Ethyl acetate	6.81 ± 0.20	0.786

[a] The solvent is present in a 1:1 volume ratio with acetone. [b] $T = 25$ °C.

Table 2 Second order rate coefficients for the reaction of dimethyldioxirane with cyclohexene

Solvent[a]	k_2/mol^{-1} dm^3 s^{-1} [b]	Relative reactivity
Acetic acid	3.48 ± 0.39	7.53
Methanol	2.26 ± 0.19	4.89
Chloroform	1.663 ± 0.025	3.60
$CDCl_3$	1.477 ± 0.026	3.20
Methylene chloride	1.03 ± 0.04	2.23
tert-Butanol	0.942 ± 0.010	2.04
1,2-Dichloroethane	0.920 ± 0.029	1.99
Chlorobenzene	0.641 ± 0.018	1.39
Benzene	0.488 ± 0.002	1.06
Carbon tetrachloride	0.478 ± 0.002	1.03
Acetone	0.462 ± 0.017	1.00
Methyl ethyl ketone	0.416 ± 0.007	0.90
Methyl acetate	0.387 ± 0.016	0.84
Ethyl acetate	0.349 ± 0.005	0.76

[a] The solvent is present in a 1:1 volume ratio with acetone. [b] $T = 25$ °C.

In order to better understand the origin of the increased epoxidation rates in some solvents we have treated our rate data with a variety of single parameter empirical solvent effect expressions. None of these attempts led to satisfactory correlations. We then turned to a multi-parameter solvent effect equation, in particular that proposed by Kamlet and Taft[11] and shown in eqn. (1). In this equation α is a measure of the

$$\log k_2 = \log k_0 + s(\pi^* + d\theta) + a\alpha + b\beta + h\delta \quad (1)$$

solvent hydrogen bond donor (HBD) capacity. It measures the ability of a solvent to donate a hydrogen bond to a solute molecule, for example. The α-scale was selected to extend from zero for non-HBD solvents, such as hexane, to *ca.* 1.0 for methanol. Beta is a measure of a solvent's hydrogen bond acceptor (HBA) capacity. This parameter measures a solvent's ability to accept a proton or to donate an electron pair when interacting with a solute. The scale extends from zero for hexane to 1.0 for hexamethylphosphoric acid triamide. The π^* parameter is an index of the solvent dipolarity/polarizability, that is, the capacity of the solvent to stabilize a charge or dipole *via* the solvent's dielectric effect. Use of π^* values is analogous to use of the dielectric constant and the refractive index as measures of polarization and polarizability interactions with solutes. Theta is a discontinuous polarizability correction term which equals 0.0 for non chlorine-substituted aliphatic solvents, 0.5 for polychlorine-substituted aliphatic solvents, and 1.0 for aromatic solvents. The solubility parameter, δ, is a measure of

Table 3 Transition state theory parameters for the reaction of dimethyldioxirane with cyclohexene[a]

Solvent	k_2/mol^{-1} dm^3 s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1}	$\Delta G^‡$/kJ mol^{-1}
Acetone	0.349 ± 0.03	30.81 ± 1.50	−148.63 ± 5.4	74.1 ± 1.55
Ethyl acetate	0.283 ± 0.008	24.91 ± 1.04	−170.39 ± 3.76	74.94 ± 0.58
CCl_4	0.369 ± 0.004	30.94 ± 0.12	−147.79 ± 4.61	74.1 ± 0.84
$CDCl_3$	1.361 ± 0.006	20.72 ± 1.33	−171.23 ± 5.02	70.75 ± 1.38
CH_3OH	2.120 ± 0.017	23.82 ± 1.42	−157.41 ± 5.44	69.91 ± 1.55
CH_3CO_2H	2.722 ± 0.007	31.98 ± 1.84	−127.69 ± 7.11	69.5 ± 1.92

[a] All error ranges are calculated from the standard deviations of the slope and intercept of the Arrhenius plots.

the work necessary to separate solvent molecules sufficiently so that a cavity is created to accommodate the solute.[12] Highly ordered, self-associated solvents exhibit relatively large δ values. k_2 is the rate constant for the process being studied and k_0 is the rate constant for that process in cyclohexane which is used as a standard. The regression coefficients s, a, and b in eqn. (1) measure the relative susceptibilities of the solvent-dependent solute property being studied, k_2 in the present case, to the indicated solvent parameters. Since the α, β, and π^* scales have been normalized the values of the regression coefficients are taken as measures of the relative importance of the associated solvent parameters.

The data in Table 1 were treated with the Kamlet–Taft equation using a multi regression analysis of log k_2 *versus* α, β, and π^* values for the different solvents. Since the kinetic data were obtained in 50/50 binary solvents the correlations were tried using solvent parameters which were the sums of those for the two solvents involved in each case as well as using the solvent parameters for the pure second solvent. In fact these two analyses gave nearly identical results. When the parameters for the pure solvents are used the regression analysis gives the following result for the reaction of **1** with **3** [eqn. (2)].

$$\log k_2 = -3.834 + 0.0839\,(\pi^* + 0.0418\theta) + 0.425\alpha - 0.246\beta + 0.0851\delta \quad (2)$$

The regression analysis also gave the correlation coefficient R (=0.970), the standard deviation s (=0.033) and the F value (=25.56). Using the F value analysis given by Shorter[13] and statistical tables[14] the significance level for the results shown in eqn. (2) is found to be above 99%.

The regression coefficients in eqn. (2) indicate that solvent HBD capacity is the most important for the epoxidation process. Furthermore the negative coefficient for the HBA property suggests that this property may even retard the rate. Further evidence for the relative importance of the solvent properties included in eqn. (2) was obtained by successively deleting each of the properties and then rerunning the regression analyses and determining the effect of the deletion on the correlation coefficient. By comparing the correlation coefficients obtained in these analyses it was determined that the solvent property relative contribution sequence is $\alpha > \beta > \delta > \pi^*$. This analysis clearly points to the solvent HBD capacity as being the dominant one for the reaction studied. The positive sign of the coefficient of α indicates that increasing solvent HBD capacity will increase the reaction rate. Next the rate data in Table 1 were correlated separately with the single solvent parameter α. This correlation gave a linear plot with a reasonably good correlation coefficient (R = 0.93).

These results suggest a transition state **6**, for the epoxidation of *trans*-ethyl cinnamate by **1**. This transition state is based on the spiro model suggested by Baumstark.[3a] This model has also received support from *ab initio* calculations.[15] Since **1** is known to epoxidize in an electrophilic manner one of the oxygens in **1** will acquire some positive character as oxygen transfer begins. The remaining oxygen will consequently become more negative in character. Solvents with good HBD capacity can stabilize this negative character as shown in **6**. Conversely, solvents with HBA capacity will destabilize such a transition state and slow the reaction rate.

When the rate data for the epoxidation of cyclohexene by **1** in binary solvents (Table 2) are similarly treated with the Kamlet–Taft equation the regression analysis gives eqn. (3).

$$\log k_2 = -0.647 + 0.210\,(\pi^* + 0.228\theta) + 0.737\alpha - 0.336\beta + 0.030\delta \quad (3)$$

This analysis also gave the correlation coefficient R (=0.96), the standard deviation s (=0.08), and the F value (=33.92). The F value indicates that the significance level for eqn. (3) is >99.9%. Again the process of successively deleting single solvent parameters, rerunning regression analyses, and determining the effect on the correlation coefficient was followed. These analyses give the relative contribution sequence of $\alpha > \beta > \delta = \pi^*$. The results for the cyclohexene case suggest a transition state analogous to that shown in **6**. A comparison of eqns. (2) and (3) shows that the coefficients of α, β and π^* are larger for cyclohexene than for ethyl cinnamate. These results suggest that the cyclohexene epoxidation reaction is more sensitive to solvent properties than is that for ethyl cinnamate. This difference is presumably due to the presence of the electron-withdrawing group in the cinnamate reaction making it less sensitive to an electrophilic attack.

The rate data for the cyclohexene case were also treated separately with the single solvent parameter α. In this correlation only those solvents in Table 2 with HBD capacity were used. It should be noted that the epoxidation rates for cyclohexene are sufficiently faster (*ca.* 1 *vs.* 10^{-3}) than those for the cinnamate that alcohols could be included in the group of cosolvents without concern about competing processes. When all of the solvents are included then the plot of k_2 *versus* α values gave a straight line with R = 0.83. However, if the solvents are treated as belonging to two subgroups, *i.e.*, either weak or strong HBD solvents, then excellent correlations are obtained. The plot for the weak HBD solvents (methyl ethyl ketone, methylene chloride, and chloroform) was linear with R = 0.999, while the plot for the strong HBD solvents (*tert*-butanol, methanol, and acetic acid) was also linear with R = 0.987.

Included in the solvents used for the cyclohexane epoxidations were both normal and deuteriochloroform. The rate constants obtained allow one to calculate a solvent isotope effect [eqn. (4)]. The lower rate in the deuteriated solvent is

$$\frac{k_2(\mathrm{CHCl_3})}{k_2(\mathrm{CDCl_3})} = 1.13 \quad (4)$$

presumably due to the reduced polarizability of deuterium and the resultant lower HBD capacity.

The absolute rate data obtained for the epoxidation of cyclohexene by **1** as well as the derived transition state parameters (Table 3) indicate that these reactions involve large negative entropy factors. The activation free energy values (Table 3) for the stronger HBD solvents (acetic acid, methanol, and chloroform) are *ca.* 4.18 kJ lower than those for the weaker or non-HBD solvents (acetone, ethyl acetate, and CCl_4). These results are consistent with a rate promoting effect of the HBD solvents as seen earlier in the application of the Kamlet–Taft equation. The large entropy effects observed in these reactions are consistent with the expected constraints required by spiro transition state, **6**, first suggested by Baumstark.[3a]

The results obtained here may also provide an explanation for the earlier results of Baumstark and Vasquez[3d] cited above. These workers observed an increase in the rate of epoxidation of *p*-methoxystyrene by **1** as the mole fraction of water in an acetone–H_2O solution was increased. We believe that this rate increase may be due to the HBD capacity of the water, a possibility considered at the time by the authors.

Summary

Treatment of the rate data obtained in the epoxidation of *trans*-ethyl cinnamate and cyclohexene by dimethyldioxirane with the Kamlet–Taft multi-parameter solvent effect equation

Table 4

Solvent	Grade	Supplier	Drying agent/Comment
CH_2Cl_2	HPLC	Fisher Scientific	P_2O_5
$CHCl_3$	HPLC	Fisher Scientific	P_2O_5
CCl_4	Certified	Fisher Scientific	P_2O_5
Butan-2-one	Certified	Eastman Kodak	P_2O_5
1,4-Dioxane	Certified	Fisher Scientific	Na
Benzene	Purified	Fisher Scientific	Na
Chlorobenzene	Certified	Fisher Scientific	P_2O_5
Methyl acetate	Certified	Fisher Scientific	4 Å mol. sieve
Ethyl acetate	Certified	Fisher Scientific	4 Å mol. sieve
Sulfolane	Certified	Aldrich	Vacuum distil.
Pentane	Certified	Aldrich	Na
Tetrahydrofuran	Gold label	Aldrich	Stored under N_2
Methanol	HPLC	Aldrich	None
tert-Butyl alcohol	Certified	Fisher Scientific	Na
Dimethylformamide	Gold label	Aldrich	Stored under N_2
1,2-Dichloroethane	Certified	Fisher Scientific	P_2O_5
Diethyl ether	Certified	Fisher Scientific	CaH_2
Methyl *tert*-butyl ketone	Practical	Eastman Kodak	P_2O_5
Acetic acid	Reagent (glacial)	Fisher Scientific	K_2CO_3

demonstrates that hydrogen bond donor solvents promote these reactions. This conclusion may be useful in selecting reaction solvent systems designed to promote reaction site selectivity or stereoselectivity. The observed solvent effects are not large, for example, a 10:1 variation for cyclohexene (Table 2). However, we anticipate that this effect could very well be used in synthetic strategies particularly when the influence is exerted intramolecularly.

Experimental

Instrumentation.—UV–VIS spectra were obtained on either: (1) a UV–VIS spectrophotometer equipped with a temperature control system (0–80 °C) and a kinetic calculation program, kinetic storage program, and a multi-scan program; (2) a UV–VIS spectrophotometer equipped with a UV–VIS 6-cell positioner and temperature control at 25, 30 and 37 °C; or (3) a UV–VIS spectrophotometer equipped with a constant temperature circulator. Temperature control was from 10–80 °C. Gas chromatography was performed on a gas chromatograph interfaced with a chromatopic or other integrator. NMR spectra were recorded using a 300 MHz spectrometer.

Materials.—Solvents. All solvents were refluxed 12–48 h with a drying agent followed by distillation. Solvent grades, names of suppliers, and drying agents used are given in Table 4.

Reagents. trans-Ethyl cinnamate (Eastman Kodak) was distilled *in vacuo* (4.5 mmHg, 130–130.5 °C fraction) and the purity (> 99%) verified by GLC and NMR data. Cyclohexene (Aldrich Chem. So.) was distilled (b.p. 83 °C) and the purity (> 99%) verified by GLC and NMR. Oxone, 2-$KHSO_5$·KH-SO_4·K_2SO_4 (DuPont), was obtained from Aldrich Chem. Co. and used as such. Thioanisole (99% purity) and cyclohexene oxide (98% purity) were obtained from Aldrich and used as such.

trans-*Ethyl cinnamate epoxide. trans*-Ethyl cinnamate (0.46 g, 2.6 mmol) in acetone (5 cm^3) was added to a freshly prepared solution[16] of **1** (0.05 mol dm^{-3}; 1.0 mmol) in a 50 cm^3 round bottom flask. The solution was stirred (magnetic stirrer) at room temp. for 30 min. At this point additional **1** was added (10 cm^3, 0.5 mmol). After 10 h a GLC analysis indicated that 40% conversion had been achieved. The solvent was removed by rotary evaporation and the epoxide isolated by column chromatography (silica gel). This gave epoxide of 90% purity. The procedure was repeated to give 0.1 g (20% yield) of epoxide with 97% purity; $\delta(CDCl_3)$ 1.32 (t, 3 H, J 7 Hz), 3.50 (d, 1 H, J 2 Hz), 4.09 (d, 1 H, J 2 Hz), 4.29 (m, 2 H) and 7.28–7.37 (m, 5 H).

Determination of the Kinetics of the Epoxidation of trans-*Ethyl Cinnamate by* **1** *in* 1:1 *Binary Solvent Systems at* 25 °C.—A freshly prepared[16] solution of **1** was dried with Na_2SO_4 and 4 Å molecular sieves. The concentration of **1** was determined by UV absorption and a previously constructed working curve correlating UV absorption with chemically determined concentrations. The suitable equivalents of *trans*-ethyl cinnamate, **3**, were weighed into a 1 cm^3 UV cell. The second solvent (1.0 cm^3) was transferred to the cell using a 1 cm^3 volumetric pipette. The concentrations of **1** and **3** were corrected for the volume of *trans*-ethyl cinnamate (d = 1.049 at 25 °C). UV cells containing the solutions of **1** and **3** were kept in the cell compartment of the UV spectrophotometer in order to permit temperature equilibrium. A 1 cm^3 aliquot of the solution of **1** was transferred to the cell containing the solution of **3** using a 1 cm^3 volumetric pipette. The combined solution was shaken vigorously by hand and kinetic data recording begun immediately. The absorption of the solution at 335 nm was monitored *versus* time for 15 min. The reaction solution was kept at room temp. for one or two days in order to record final absorption (A_∞). This procedure was repeated at several concentrations of **3**. Plots of $-\ln(A_t - A_\infty)$ gave straight lines with slopes = k_{obs}. Plots of k_{obs} *versus* concentration of **3** gave straight lines with slope = k_2. Table 1 summarizes the results of these experiments. In five of the solvents used the reaction solutions were worked up and shown to contain only the epoxide of **2**. In the case of acetic acid solvent it was found that initially produced epoxide was converted to other products after 70 min time. Under these circumstances the formation of secondary products did not interfere with the kinetic determinations. In separate experiments it was also shown that, within experimental error, the same k_2 values are obtained from solutions of **3** with either argon or oxygen pretreatment.

Determination of the Kinetics of Epoxidation of Cyclohexene, **4**, *by* **1** *in* 1:1 *Binary Solvents at* 25 °C.—The experimental procedure was the same as used in the *trans*-ethyl cinnamate reactions with the following modifications: (1) the solution of **1** was diluted to $\frac{1}{5}$–$\frac{1}{12}$ of its original concentration; (2) the total volume of the reaction solution was 3 cm^3; (3) the absorption data were recorded within 1 min at 6 s intervals; (4) the final absorption (A_∞) was obtained when the absorption of the reaction solution was constant; (5) the calculation for the concentrations of **4** and **1** were corrected for the volume of **4** ($d = 0.811$). The k_2 values for the epoxidation of **4** by **1** in several solvent systems are shown in Table 2. The reaction solutions for acetone and three of the binary solvents were worked up and shown to contain only cyclohexene epoxide. In acetic acid solvent the reaction gave a second product within 30 min and two others after 4 h. These same products are produced when authentic epoxide is treated with acetic acid. Since these products arise after epoxide production there is no interference with the kinetic determinations.

Absolute Rate Study for the Reaction of **1** *with* **4**.—The experimental procedure used was the same as that described above for **4** except that data were collected over the temperature range 10–30 °C. Second order rate constants were determined in acetone and in five binary solvents. Arrhenius plots were constructed and E_a and log A values determined. Using these data and the Eyring expression[7] transition state parameters were calculated for the reactions. The results of these calculations are given in Table 3.

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