DOI: 10.1002/ejoc.200600427

Activation Parameters for the Epoxidation of Substituted *cis*/*trans* Pairs of 1,2-Dialkylalkenes by Dimethyldioxirane

Brian S. Crow,[a] W. Rucks Winkeljohn,[a] Angela Navarro-Eisenstein,[a]
Elba Michelena-Baez,[a] Paul J. Franklin,[a] Pedro C. Vasquez,[a] and Al Baumstark*[a]

Keywords: Epoxidation / Activation parameters / Kinetics / Dimethyldioxirane

---

The first activation parameter data for the reaction of dimethyldioxirane (**1**) with five *cis*/*trans* pairs of alkenes are reported. The epoxidation of *cis*-1,2-dialkylalkenes (**2*cis***: R^1 = Me, R^2 = *i*Pr; **3*cis***: R^1 = Me, R^2 = *t*Bu; **4*cis***: R^1 = R^2 = Et; **5*cis***: R^1 = Et, R^2 = *i*Pr; **6*cis***: R^1 = Et, R^2 = *t*Bu) and *trans*-1,2-dialkylalkenes (**2*trans***: R^1 = Me, R^2 = *i*Pr; **3*trans***: R^1 = Me, R^2 = *t*Bu; **4*trans***: R^1 = R^2 = Et; **5*trans***: R^1 = Et, R^2 = *i*Pr; **6*trans***: R^1 = Et, R^2 = *t*Bu) by **1** produced the corresponding epoxides, quantitatively and stereospecifically, as the sole observable products. Activation parameters of the epoxidation of the five pairs of alkenes, **2*cis*–6*cis*** and **2*trans*–6*trans***, by **1** were determined using the Arrhenius method. Enhanced selectivity for *cis*- vs. *trans*-alkene epoxidation was observed at lower temperatures. In general, the $\Delta G^{\ddagger}$ terms were larger and showed more variability for the reaction of **1** with *trans*-alkenes as compared to those for the corresponding *cis* isomers. The $\Delta H^{\ddagger}$ terms mirrored trends observed in $\Delta G^{\ddagger}$ because $\Delta S^{\ddagger}$ terms for all ten of the compounds were roughly identical. The $\Delta\Delta G^{\ddagger}$ values, a comparison of the *trans* to the *cis* isomer data, yielded positive values of 1.2 to 1.8 kcal/mol for the five sets of data and appeared to be dependent on relative steric interactions. The experimental activation parameter data, consistent with predictions from ab initio calculations based on a spiro transition-state model, showed that the lower reactivity of *trans*-alkenes is due to enthalpy factors.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Dioxiranes are important reagents for the derivatization of a wide variety of substrates.[1] Whether generated in situ[2] or isolated as a solution,[3] dioxiranes have been shown to be a powerful class of oxidizing agents. In particular, dimethyldioxirane (**1**) has been widely used due to the ease of preparation, efficiency of oxygen atom transfer and environmental factors. Oxidations by **1** continue to be a topic of great interest in part because of the high chemo-, regio- and stereoselectivity observed in these reactions. For example, there has been a recent report of the kinetic study of the *N*-oxidation of substituted pyridines with **1**;[4] however, the epoxidation of alkenes remains the most extensively studied process. Historically, kinetic studies at 23 °C have shown that the reaction of alkenes with **1** is sensitive to steric factors, with *cis*-alkenes having a greater relative reactivity as compared to that of the corresponding *trans* isomers[5] (see Figure 1).

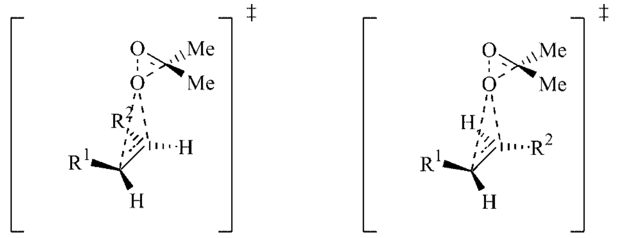


Figure 1. Representation of the spiro transition states for epoxidation of *cis*- and *trans*-alkenes by dimethyldioxirane (**1**).

The observed reactivity differences between *cis*- and *trans*-alkenes led, in part, to our postulation that the electrophilic epoxidation of alkenes by **1** proceeds through an oxygen atom transfer process with a "spiro" transition state.[5] The synthesis of epoxides by reaction with asymmetric dioxiranes generated in situ in biphasic systems, of value for the preparation of chiral compounds, also has been shown to be mechanistically consistent with a spiro transition-state model.[6] Recent kinetic experiments on the epoxidation of geraniol and model olefins have further investigated medium effects on the reaction with dimethyldioxirane (**1**).[7] The relative reactivity of epoxidation of alkenes by **1** has been modeled using various theoretical methods, including ab initio calculations.[3c,8a–8c] Other than rate-constant data at one temperature, there is little experi-

---

[a] Department of Chemistry, Center for Biotechnology and Drug Design, Georgia State University,
Atlanta, Georgia 30303-3083, USA
Fax: +1-404-651-1416
E-mail: chealb@langate.gsu.edu

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

mental evidence to evaluate the factors determining relative reactivity of alkene epoxidation by dioxirane. In this study, we report the first set of experimental activation parameter data for the oxidation of five *cis*/*trans*-dialkylalkene pairs by dimethyldioxirane (**1**).

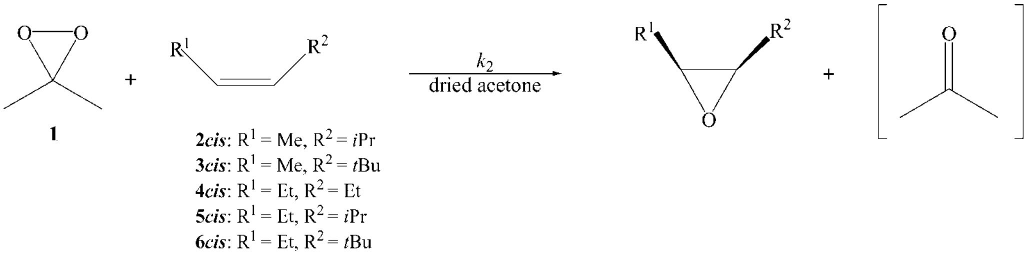
Results and Discussion

Solutions of dimethyldioxirane (**1**) in dried acetone were prepared from the reaction of "Oxone" with acetone. The reaction of **1** with five *cis*-1,2-dialkylalkenes [*cis*-4-methyl-2-pentene (**2*cis***), *cis*-4,4-dimethyl-2-pentene (**3*cis***), *cis*-3-hexene (**4*cis***), *cis*-2-methyl-3-hexene (**5*cis***), *cis*-2,2-dimethyl-3-hexene (**6*cis***)] and the five corresponding *trans*-1,2-dialkylalkenes [*trans*-4-methyl-2-pentene (**2*trans***), *trans*-4,4-dimethyl-2-pentene (**3*trans***), *trans*-3-hexene (**4*trans***), *trans*-2-methyl-3-hexene (**5*trans***), *trans*-2,2-dimethyl-3-hexene (**6*trans***)] was found to be stereospecific and produced the corresponding epoxides exclusively [reactions (1 and 2)], as expected.

Product studies for the epoxidation of **2*cis*–6*cis*/2*trans*–6*trans*** were carried out with at least 1.1 equiv. of **1**. In all cases, the epoxides were obtained in essentially quantitative yields (≥ 98%). Epoxides generated from alkenes **3*cis*–6*cis*/3*trans*–6*trans*** have been previously reported as products of oxidation by **1**.[3b–3c,5,9] The data for epoxides from **2*cis*** and **2*trans*** have been published.[10–12] Physical and spectroscopic data for the ten epoxides [reactions (1) and (2)] are consistent with those of authentic samples and with the published data.[3b,9–12]

The kinetic study of the epoxidation of the ten alkenes by **1** was carried out employing UV methodology. As expected,[5] each reaction was found to be of the first order in both alkene and dioxirane, of the second order overall. The kinetic experiments, conducted under pseudo-first-order conditions, produced k_2 values that were within experimental error (±5%) regardless of the compound used in excess. The second-order rate constants for the reactions (1) and (2) were determined over approximately a 25–30 degree temperature range. The second-order rate constants at 23 °C for the epoxidation of alkenes **3*cis*–6*cis*** and **3*trans*–6*trans*** have been previously reported and are in agreement with the current data.[3b,3c,5,9,13] The rate constant data show that selectivity for the epoxidation of the *cis* vs. *trans* compounds increases at lower temperatures. For example, the reaction of **2*cis*** and **2*trans*** with **1** shows a k_{cis}/k_{trans} ratio of 9.4 at 15 °C which decreases to 7.1 at 40 °C. Earlier studies[3b] have investigated epoxidation selectivity by **1** as a function of steric interactions.[3b] The present results show that selectivity is quite sensitive to temperature changes as well. Clearly, to achieve maximum selectivity, epoxidation should be carried out at the lowest temperature possible. For each temperature, the k_2 values listed in Tables 1 and 2 are the average of at least three separate, kinetic experiments.

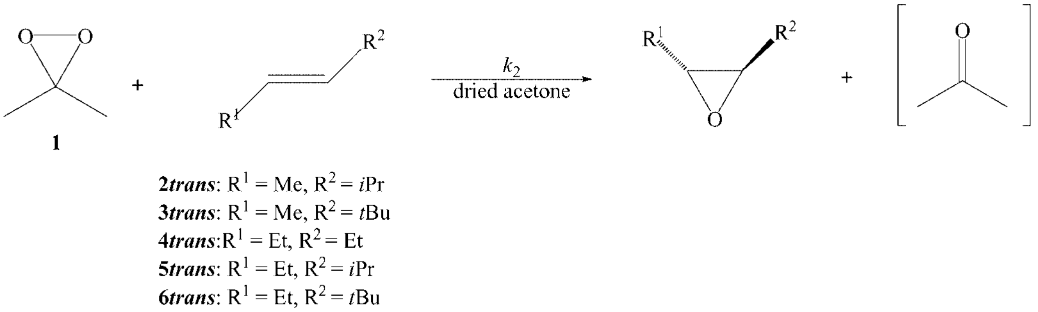
The activation parameters for each of the five pairs of *cis*/*trans*-alkenes were calculated from the data in Tables 1 and 2 by the Arrhenius method. Excellent correlations were obtained for all ten data sets. This is the first report of activation-parameter data for the reaction of **1** with *cis*/*trans* pairs of alkenes. Activation parameters have been previously reported for the epoxidation of several isolated alkenes by **1**.[14,15] Representative Arrhenius plots for alkene pairs **2** and **6** are shown in Figure 2 (r = 0.998 for **2*cis***, r = 0.998 for **2*trans***; r = 0.993 for **6*cis***, r = 0.996 for **6*trans***). The Arrhenius plots for the *cis*-alkenes are very closely grouped, indicative of essentially similar reactivity of all five *cis*-alkenes with dioxirane **1**, regardless of the R group. The Arrhenius plots for the *trans*-alkenes show a larger spread between the linear correlations, with those with the larger steric interactions showing lower reactivity towards **1**. The



1

2*cis*: R1 = Me, R2 = *i*Pr
3*cis*: R1 = Me, R2 = *t*Bu
4*cis*: R1 = Et, R2 = Et
5*cis*: R1 = Et, R2 = *i*Pr
6*cis*: R1 = Et, R2 = *t*Bu

(1)

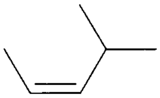
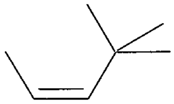
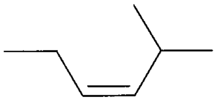
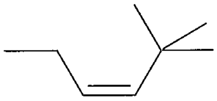


1

2*trans*: R1 = Me, R2 = *i*Pr
3*trans*: R1 = Me, R2 = *t*Bu
4*trans*: R1 = Et, R2 = Et
5*trans*: R1 = Et, R2 = *i*Pr
6*trans*: R1 = Et, R2 = *t*Bu

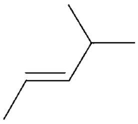
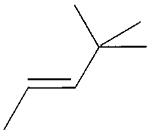
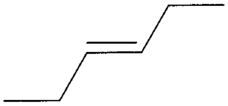
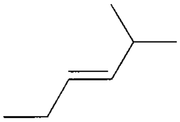
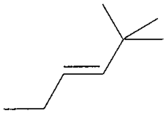
(2)

Table 1. Second-order rate constants for the epoxidation of *cis*-alkenes, **2*cis*–6*cis***, by **1** in dried acetone.

Compound	Alkene structure	Temperature [°C][a]	k_2 [$M^{-1}s^{-1}$][b]
2*cis*		15.1	0.281 ± 0.008
		20.0	0.35 ± 0.01
		23.0	0.43 ± 0.01
		30.0	0.55 ± 0.02
		35.3	0.69 ± 0.03
		40.2	0.85 ± 0.03
3*cis*		14.8	0.184 ± 0.002
		19.9	0.232 ± 0.003
		22.8	0.261 ± 0.002
		30.0	0.36 ± 0.03
		35.2	0.41 ± 0.02
		40.2	0.61 ± 0.02
4*cis*		11.0	0.210 ± 0.003
		16.0	0.303 ± 0.007
		17.0	0.325 ± 0.006
		23.0	0.47 ± 0.03[c]
		29.5	0.57 ± 0.02
		35.0	0.63 ± 0.02
		39.0	0.78 ± 0.04
		40.0	0.85 ± 0.05
5*cis*		15.0	0.224 ± 0.008
		18.0	0.257 ± 0.005
		23.1	0.322 ± 0.009
		28.2	0.40 ± 0.01
		36.8	0.62 ± 0.02
		43.1	0.84 ± 0.04
6*cis*		16.0	0.202 ± 0.004
		17.0	0.209 ± 0.006
		23.0	0.263 ± 0.009[d]
		30.0	0.33 ± 0.01
		44.0	0.65 ± 0.02
		45.0	0.69 ± 0.02
		48.0	0.77 ± 0.02
		50.0	0.92 ± 0.04

[a] ±0.3 °C. [b] Errors are standard deviation of three experiments. [c] Ref.[5] [d] Ref.[3c]

Table 2. Second-order rate constants for the epoxidation of *trans*-alkenes, **2*trans*–6*trans***, by **1** in dried acetone.

Compound	Alkene structure	Temperature [°C][a]	k_2 [$M^{-1}s^{-1}$][b]
2*trans*		15.1	0.0300 ± 0.0006
		20.0	0.0375 ± 0.0007
		23.0	0.0488 ± 0.0015
		30.0	0.0713 ± 0.0021
		35.3	0.0900 ± 0.0036
		40.2	0.1200 ± 0.0042
3*trans*		15.0	0.0127 ± 0.0005
		20.0	0.0169 ± 0.0009
		23.0	0.0182 ± 0.0007
		30.0	0.0309 ± 0.0009
		35.0	0.0357 ± 0.0014
		41.1	0.0480 ± 0.0019
		45.8	0.0704 ± 0.0028
4*trans*		10.0	0.0320 ± 0.0006
		15.0	0.0420 ± 0.0008
		23.0	0.0570 ± 0.0037[c]
		24.0	0.0640 ± 0.0022
		30.0	0.0770 ± 0.0021
		31.0	0.0832 ± 0.0025
		35.0	0.1260 ± 0.0042
		40.6	0.1441 ± 0.0038
		46.0	0.1610 ± 0.0046
5*trans*		15.0	0.0169 ± 0.0005
		18.0	0.0175 ± 0.0005
		20.1	0.0288 ± 0.0008
		23.0	0.0295 ± 0.0012
		30.5	0.0431 ± 0.0013
		35.0	0.0515 ± 0.0029
		45.8	0.0730 ± 0.0035
6*trans*		11.0	0.0051 ± 0.0002
		23.0	0.0119 ± 0.0006[d]
		35.0	0.0241 ± 0.0005
		45.0	0.0352 ± 0.0011
		50.0	0.0439 ± 0.0013

[a] ±0.3 °C. [b] Errors are standard deviation of three experiments. [c] Ref.[5] [d] Ref.[3c]

findings are consistent with previous studies, at 23 °C, which showed that the k_2 values for epoxidation of *cis*-alkenes by **1** are essentially independent of the relative substituent size while those for *trans*-alkenes are highly dependent on the relative alkyl substituent size.[5] The calculated activation-parameter data for epoxidation of the five pairs of *cis*/*trans*-alkenes are summarized in Table 3.

Interestingly, the $\Delta G^{\ddagger}$ values for the *cis*-alkene epoxidation in this study are all roughly of the same magnitude (within ±0.2 kcal/mol) with an average value of 18.6 kcal/mol, indicative of essentially little or no sensitivity to alkyl group variation and the resulting steric interactions. In contrast, the $\Delta G^{\ddagger}$ values for the *trans*-alkenes are of greater magnitude than those for the *cis*-alkenes. The variability of the $\Delta G^{\ddagger}$ values for the *trans*-alkenes, ranging from 19.6 to 20.5 kcal/mol, appear to correlate directly with increasing steric interactions (vide infra). Normally, interpretation of activation-parameter data is focused on the $\Delta G^{\ddagger}$ values due to the inherent problem of compensating errors between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms. However, the $\Delta S^{\ddagger}$ values determined in this study are essentially constant across both series with the magnitude of the difference generally close to the error (±0.8 eu). Thus, the $\Delta H^{\ddagger}$ terms in the present study should be less prone to systematic error. A comparison of the $\Delta H^{\ddagger}$ terms shows essentially the same trends as observed in comparison of the $\Delta G^{\ddagger}$ value, which verifies the consistency of the data. The inherent reactivity difference between the *trans*- and *cis*-alkenes toward **1** can be readily evaluated by examination of a $\Delta\Delta G^{\ddagger}$ term (obtained by subtracting the $\Delta G^{\ddagger}$ value for the *cis*-alkene from that for the corresponding *trans* isomer). All five $\Delta\Delta G^{\ddagger}$ terms are consistent with one another, yielding positive values of 1.2 ± 0.3 to 1.8 ± 0.4 kcal/mol. This clearly shows that the *cis*-alkenes are more reactive toward **1** than the corresponding *trans* isomers. In addition, it appears that the increasing relative alkyl size correlates with the increase in the magnitude of the $\Delta\Delta G^{\ddagger}$ values.

For example, alkenes studied with the least steric size (**2*trans***, **2*cis*** and **4*trans***, **4*cis***) have a $\Delta\Delta G^{\ddagger}$ value of 1.2–1.3 kcal/mol. Furthermore, pairs **3*trans*/3*cis*** and **5*trans*/5*cis*** have a $\Delta\Delta G^{\ddagger}$ value of 1.6–1.4 kcal/mol, while the most hindered pair **6*trans*/6*cis*** has the highest net steric bulk and exhibits a $\Delta\Delta G^{\ddagger}$ value of 1.8 kcal/mol. However, the magnitude of the maximum difference (0.6 kcal/mol) is less than the error. Because the $\Delta G^{\ddagger}$ values for the *cis*-alkenes are essentially identical, the observed apparent increase in magnitude of the $\Delta\Delta G^{\ddagger}$ values appears to be due to the changes in $\Delta G^{\ddagger}$ values for the epoxidation of the *trans*-alkenes. Clearly, the $\Delta G^{\ddagger}$ values of the *trans*-alkenes are consistently 1 kcal/mol or more larger than those for the corresponding *cis* isomers. Since the $\Delta S^{\ddagger}$ values for all ten of the alkenes are essentially identical, the increase in $\Delta G^{\ddagger}$ for the *trans* compounds is solely due to enthalpy factors.

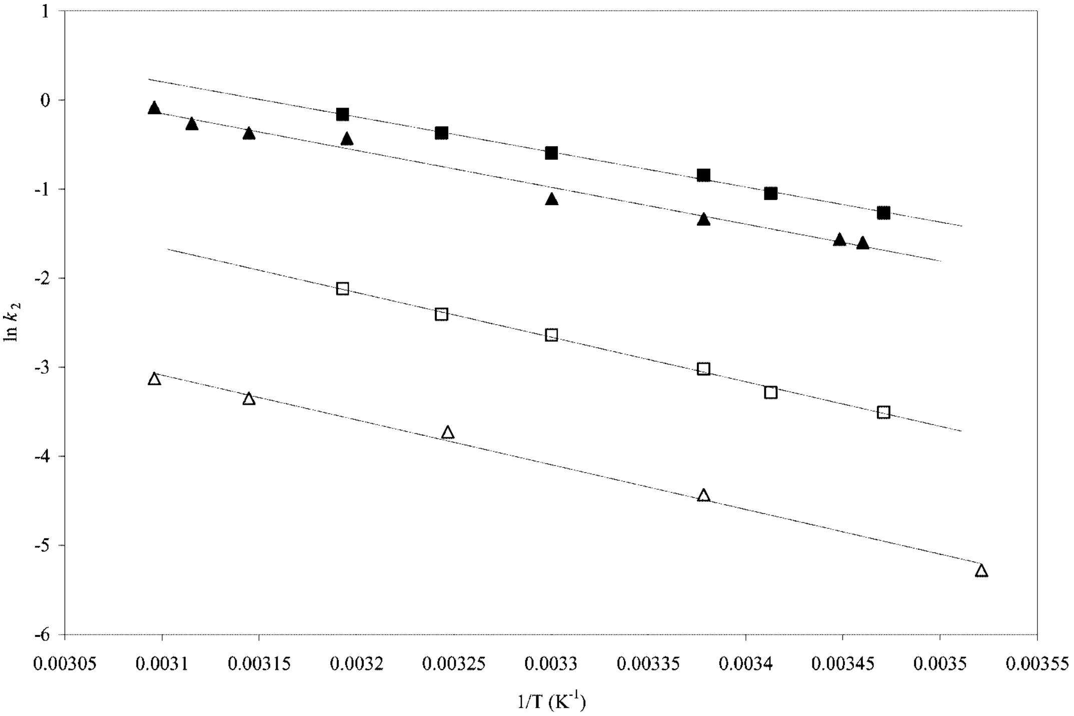


Figure 2. Arrhenius plots for the epoxidation of *cis*-4-methyl-2-pentene (**2*cis***, ■)/*trans*-4-methyl-2-pentene (**2*trans***, □) and *cis*-2,2-dimethyl-3-hexene (**6*cis***, ▲)/*trans*-2,2-dimethyl-3-hexene (**6*trans***, Δ) by **1** in dried acetone.

Table 3. Activation parameters[a] for the epoxidation of **2*cis*/2*trans*–6*cis*/6*trans*** by **1** in acetone.

Alkene	k_2 [M^{-1} s^{-1}][a]	$\Delta H^\ddagger$ [kcal/mol][b]	$\Delta S^\ddagger$ [eu][b]	$\Delta G^\ddagger$ [kcal/mol][b]	$\Delta\Delta G^\ddagger$ [kcal/mol][c]
2*cis*	0.43 ± 0.01	7.28 ± 0.15	–37.7 ± 0.3	18.45 ± 0.16	1.3 ± 0.3
2*trans*	0.0488 ± 0.0015	9.42 ± 0.25	–34.8 ± 0.4	19.73 ± 0.17	
3*cis*	0.261 ± 0.002	7.37 ± 0.48	–38.3 ± 0.4	18.70 ± 0.21	1.6 ± 0.4
3*trans*	0.0182 ± 0.0007	9.27 ± 0.49	–37.2 ± 0.4	20.28 ± 0.17	
4*cis*	0.46 ± 0.01	7.14 ± 0.54	–37.9 ± 0.3	18.38 ± 0.17	1.2 ± 0.3
4*trans*	0.0570 ± 0.0017	8.25 ± 0.68	–38.3 ± 0.4	19.61 ± 0.17	
5*cis*	0.322 ± 0.009	7.92 ± 0.20	–36.0 ± 0.4	18.60 ± 0.17	1.5 ± 0.4
5*trans*	0.0295 ± 0.0012	9.92 ± 0.21	–34.3 ± 0.4	20.08 ± 0.18	
6*cis*	0.263 ± 0.005	7.51 ± 0.35	–37.8 ± 0.4	18.71 ± 0.17	1.8 ± 0.4
6*trans*	0.0119 ± 0.0004	9.47 ± 0.46	–37.3 ± 0.4	20.52 ± 0.21	

[a] 23 °C. [b] Errors listed at 60% confidence limits. [c] $\Delta G^\ddagger$(*trans*) – $\Delta G^\ddagger$(*cis*).

Epoxidation of alkenes by **1** have been extensively modeled using several different computational approaches. Several ab initio studies successfully modeled the epoxidation of ethylene by dioxirane.[8] In general, this approach has strongly supported[8a] a one-step reaction with a "spiro" transition state.[5] High-level calculations on the epoxidation of *cis*/*trans*-2-butene by dimethyldioxirane have been carried out by Jorgensen and Houk.[8b] This extensive study predicted that the epoxidation for *cis*-2-butene by dioxirane would be more reactive than that for the *trans* isomer by 1.7 kcal/mol with essentially equal entropy of activation values for epoxidation for the *cis* and *trans* isomers based on the "spiro transition state" model.[8b] Subsequent calculations[8c] also predicted $\Delta\Delta G^\ddagger$ values and that the activation entropies would be very similar for epoxidations of *cis*- and *trans*-alkenes by dioxirane.[16] Less time-consuming semiemperical (AM1) calculations have been performed, independently, on the epoxidation of a series of *cis*- and a series of *trans*-alkenes with dimethyldioxirane.[3c,9] As expected, the "spiro" model was again found to be the only acceptable transition state geometry. Using this semiemperical approach, relative transition state energies were calculated for the epoxidation of a series of configurationally similar alkenes which allowed for relative rates to be estimated. Interestingly, the resulting calculated relative rates of epoxidation were in good agreement with relative rates based on the actual k_2 values for each series.[3c,9] Since the AM1 modeling approach does not take entropy into account, the excellent correlation would be consistent with the entropy of activation values being essentially constant for *cis*- or *trans*-alkene series.

In the current study, the entropy of activation values were found to be essentially identical for the epoxidation of all ten alkenes (average is equal to –37.0 with an average deviation of 1.1 eu). The entropy of activation terms, in this study, are in excellent agreement with the reported value for the oxidation of cyclohexene (–35.5 eu) by **1** in acetone.[14] Interestingly, the steric size of the various substituents does not appear to be reflected in the $\Delta S^{\ddagger}$ values. This suggests that the transition-state organization is similar for both *cis*- and *trans*-alkenes and enthalpy-controlled, in excellent agreement with the original predicted results of Jorgensen and Houk[8b] and those of Sarzi-Amadé et al.[8c] based on a "spiro" epoxidation mechanism.

Conclusions

The activation-parameter data have been determined for the epoxidation of five *cis*/*trans*-dialkylalkene pairs by **1**. The entropy of activation values for all ten epoxidations are essentially identical and are independent of alkene structure. Oxidation of *trans*-alkenes with **1** exhibit larger and variable $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ terms when compared to the reaction with the corresponding *cis* isomers and show a direct dependence on increasing steric interactions. The enthalpy of activation and $\Delta G^{\ddagger}$ values for oxidation of the *cis*-alkenes are essentially constant and appear independent of the R-group relative size. The experimental $\Delta\Delta G^{\ddagger}$ value for the five sets of *cis*/*trans* isomers are in excellent agreement with the predictions based on ab initio calculations performed on *cis*- and *trans*-alkene epoxidation by **1**.[8b,c]

Experimental Section

Product Studies: A solution of dimethyldioxirane (**1**, 1.1 equiv.) in acetone was added to the neat alkenes ***2cis*–*6cis*/*2trans*–*6trans*** (ca. 50 mg). The reaction mixture was stirred at room temperature and progress monitored by GC-MS. Upon completion of the reaction, GC-MS analysis showed that the epoxide was the sole product formed in quantitative yield. The solvent and remaining excess **1** were removed under reduced pressure at 0 °C. The yields of the corresponding epoxides were determined by weight and isolated in ≥85% yield. The physical and spectroscopic data for all ten compounds are in excellent agreement with published data.[3b,9–12]

Kinetic Studies: All solutions for kinetic experiments were prepared with dried HPLC-grade acetone. In general, for convenience, the reactions were studied at a 10:1 substrate to dioxirane ratio. The reactions were carried out at a constant temperature (±0.3 °C) and were followed by determining the decrease in concentration of **1** by monitoring the absorbance at 330 nm. For example, 0.400 mL of a 0.500 M solution of alkene ***2trans*** was placed in a 1-cm UV quartz cuvette with 2.400 mL dried acetone, and allowed to equilibrate. The dioxirane/acetone solution (0.200 mL, 0.070 M) was added through a syringe and the solution was mixed for 2–3 s. Upon completion of the kinetic run, the solution was analyzed by GC-MS and the expected epoxide was observed in the appropriate amount in all cases. The pseudo-first-order constants ($k_{\text{obsd.}}$) were calculated from a linear plot of the natural logarithm of the absorbance of the dioxirane against time which showed excellent linearity ($r \geq 0.99$) for all ten sets of kinetic experiments. Data were collected for at least two half-lives for all kinetic experiments. The values for the second-order rate constants were computed using the pseudo-first-order relationship: $k_2 = k_{\text{obsd.}}$/[substrate in excess]. Pseudo-first-order reaction conditions with dioxirane in excess produced k_2 values of the same magnitude within experimental error (±5%).

Preparation of Dimethyldioxirane: Dimethyldioxirane (**1**) was prepared according to work done by Murray[3a] with minor alterations.[3d,5] A 2-L three-necked round-bottomed flask was equipped with a pressure-equalizing addition funnel, a solid addition funnel, and an air condenser attached to a receiving trap in a Dewer flask at –78 °C. A solution of 60.0 mL deionized water and 45.0 mL of acetone was added to the flask containing 72.0 g of $NaHCO_3$ and 1.00 g of Na_2EDTA. "Oxone" (150 g) and a solution containing 40.0 mL of acetone and 60.0 mL of water were added, simultaneously over 30 min, while the mixture was stirred vigorously at room temperature at 110 Torr. The dioxirane was distilled from the generating flask and collected in a distillation receiving trap. The dioxirane/acetone solution was redistilled at 5 °C and 8 Torr, yielding approximately 75 mL of an acetone solution of **1**. This solution was stored in an amber bottle containing anhydrous Na_2SO_4 at –22 °C for weeks without appreciable decomposition. Typical concentrations of **1**, calculated from UV absorption at 330 nm and/or reaction methods, were determined to be 0.08–0.10 M.

Acknowledgments

Acknowledgments are made to the U.S. Army ERDEC (DAAA 15-94-K-0004) SEAS subcontract and to the Georgia State University Research Fund for support of this work.

[1] For selected reviews, see: a) R. Curci, in: *Advances in Oxygenated Processes*, vol. 2 (Ed.: A. Baumstark), JAI Press, Greenwich, CT, **1990**; b) W: Adam, L. Hadjiarapogolonu, R. Curci, R. Mello, in: *Organic Peroxides* (Ed.: W. Adam), John Wiley & Sons, Chichester, England **1992**, chapter 4; c) W. Adam, L. Hadjiarapoglou, *Top. Curr. Chem.* **1993**, *164*, 45–62; d) R. Curci, A. Dinoi, M. Rubino, *Pure Appl. Chem.* **1995**, *67*, 811–822.

[2] a) S. E. Denmark, Z. Wu, *J. Org. Chem.* **1998**, *63*, 2810–2811; b) M. Frohn, Z.-X. Wang, Y. Shi, *J. Org. Chem.* **1998**, *63*, 6425–6426; c) D. Yang, M.-K. Wong, Y.-C. Yip, *J. Org. Chem.* **1995**, *60*, 3887–3889; d) W. Adam, L. Hadjiarapoglou, A. Smerz, *Chem. Ber.* **1991**, *124*, 227–232; e) R. Curci, M. Fiorentino, L. Troisi, J. D. Edwards, R. H. Pater, *J. Org. Chem.* **1980**, *45*, 4758–4760.

[3] a) R. Murray, R. Jeyaraman, *J. Org. Chem.* **1985**, *50*, 2847–2853; b) A. Baumstark, P. C. Vasquez, *J. Org. Chem.* **1988**, *53*, 3437–3439; c) A. Baumstark, E. Michelena-Baez, A. M. Navarro, H. D. Banks, *Heterocycl. Commun.* **1997**, *3*, 393–396; d) W. Adam, L. Hadjiarapogolonu, J. Bialas, *Chem. Ber.* **1991**, *124*, 2377.

[4] W. R. Winkeljohn, P. C. Vasquez, L. Strekowski, A. Baumstark, *Tetrahedron Lett.* **2004**, *45*, 8295–8297.

[5] A. Baumstark, C. J. McCloskey, *Tetrahedron Lett.* **1987**, *28*, 3311–3314.

[6] Z.-X. Wang, Y. Tu, M. Frohn, J.-R. Zhang, Y. Shi, *J. Am. Chem. Soc.* **1997**, *119*, 11224–11235.

[7] A. Baumstark, P. J. Franklin, P. C. Vasquez, B. S. Crow, *Molecules* **2004**, *9*, 117–124.

[8] a) R. D. Bach, J. L. Andres, A. L. Owensby, H. B. Schlegel, J. W. McDouall, *J. Am. Chem. Soc.* **1992**, *114*, 7207–7217; b) C. Jenson, J. Liu, K. N. Houk, W. L. Jorgensen, *J. Am. Chem. Soc.* **1997**, *119*, 12982–12983; c) M. Freccero, R. Gandolfi, M. Sarzi-Amade, A. Rastelli, *Tetrahedron* **1998**, *54*, 6123–6134.

[9] E. Michelena-Baez, A. M. Navarro-Eisenstein, H. D. Banks, P. C. Vasquez, A. Baumstark, *Het. Commun.* **2000**, *6*, 119–122.

[10] A. T. Bottini, R. L. VanEtten, *J. Org. Chem.* **1965**, *30*, 2994–2997.

[11] R. W. Murray, W. Kong, S. N. Rajadhyaksha, *J. Org. Chem.* **1993**, *58*, 315–321.

[12] D. R. Paulson, F. Y. N. Tang, G. F. Moran, A. S. Murray, B. P. Pelka, E. M. Vasquez, *J. Org. Chem.* **1975**, *40*, 184–186.

[13] The k_2 values at 23 °C for eight of the epoxidations are in excellent agreement with previously reported values. The values for ***3cis***[3b] and ***3trans***[5] are slightly lower than previously reported, presumably reflecting a systematic error in previous temperature measurement.

[14] R. W. Murray, D. Gu, *J. Chem. Soc., Perkin Trans. 2* **1993**, 2203–2207.

[15] R. W. Murray, *Chem. Rev.* **1989**, *89*, 1187–1201.

[16] Relative gas-phase activation enthalpies for the epoxidation of alkenes by dioxirane are reported by Sarzi-Amadé et al.[8c] as theoretical $\Delta\Delta G^{\ddagger}$ values. The reported relative experimental $\Delta\Delta G^{\ddagger}$ values appear to be calculated partially based on rate-constant data. The experimental $\Delta\Delta G^{\ddagger}$ values (vide infra) from the Arrhenius approach agree with the calculated $\Delta\Delta G^{\ddagger}$ values reported by Sarzi-Amadé et al.

Received: May 15, 2006