study of kinetic effects that occur with biological reactions in the lipophilic layer of the stationary phase that mimics biological membranes. The low dielectric environment and the essentially two-dimensional nature of the surface layer provide reaction conditions which are not attainable in solutions. As our knowledge with regard to the surface properties and design of such stationary phases is on the increase it is likely that the high precision, speed, and convenience of HPLC will be exploited to obtain not only thermodynamic but also kinetic information of biological significance from properly designed chromatographic experiments.

Conclusions

The results presented above show that reversible reactions that are first order in eluite concentration cause the elution band to spread. If the relaxation time for the reaction is commensurate with the time for chromatographic retention, the relaxation time can be extracted from the dependence on the chromatographic velocity of the first and second moments of the chromatographic mass distribution of all forms of the eluate at the outlet of the column. The analysis is complicated by the presence of other velocity-dependent terms that contribute to band broadening. Their magnitude can be estimated from nonlinear regression of the complete expression for dependence on flow velocity of the chromatographic plate height, that is simply related to the second central moment. They can also be estimated from the band spreading of eluites with chromatographic characteristics similar to the eluite of interest.

On the other hand, numerical solution of the equations for mass conservation in the chromatograph can be used to determine rate constants. Since the change in peak shape is a dramatic function of flow velocity in the domain when the Damköhler number is near one, the relaxation time may be estimated simply by comparing the predicted and experimental profiles. The results in such a comparison of experimental and predicted results for the cis–trans isomerization of proline in Ala-Pro and Val-Pro showed good agreement.

If the relaxation time and equilibrium composition in the mobile phase are known from independent experiments, or if the reaction in the mobile phase is shown to require long times in comparison to the chromatographic elution time, the rate constants for the surface reaction can be determined. This may prove to be a superb tool for study of reactions on surfaces in contact with liquids.

Acknowledgment. This work was supported by Grants CA 21948 and GM 20993 from the National Cancer Institute and National Institute of General Medical Sciences, U.S. Department of Health and Human Resources, and by a dissertation fellowship from the American Association of University Women.

Registry No. L-Alanyl-L-proline, 13485-59-1; L-valyl-L-proline, 20488-27-1.

Boron Atom Reactions with the Epoxides: Vibrational Distributions in the Product $BO(A^2\Pi)$ State

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The results of chemiluminescence studies are reported for the reactions of boron atoms with ethylene oxide, propylene oxide, butylene oxide, diepoxybutane, cyclopentene oxide, cyclohexene oxide, 3-vinylcyclohexene oxide, and styrene oxide. The experiments were done under single-collision conditions in a beam-gas apparatus. The nascent vibrational distributions in the electronically excited product $BO(A^2\Pi)$ were determined. These distributions are well fitted by a statistical model which assumes that only those modes of the polyatomic product are excited which correspond to the conformation change in the transition from the reacting epoxide to the alkene product. Absolute cross sections for the production of the $A^2\Pi$ state of BO are also reported.

Introduction

The boron–epoxide reactions studied here are a continuation of work reported earlier.[1,2] These reactions yield BO and the corresponding alkene. The BO is produced either in the $X^2\Sigma$ or in the $A^2\Pi$ state. The ground-state channel to $BO(^2\Sigma)$ is predominant.[2] The reactions of boron atoms are the simplest of the atom–molecule reactions involving ground-state p orbitals. The large total cross sections for the reaction of boron with the epoxides[2] indicate that there is no barrier to these reactions. These results are in accord with recent MINDO computer studies.[3] In this aspect the reactions of boron with the epoxides are similar to that of the carbon atom with ethylene oxide.[4–8] The latter studies suggest that it is carbon (^1S) which reacts, and the orbital symmetry of ground-state boron (^2P) resembles that of carbon (^1S) rather than ground-state carbon (^3P) in having one occupied and two unoccupied p orbitals.

The epoxides in the present study are listed in Table I. They cover a broad range of complexity, from the simplest, ethylene oxide, to the 21-atom polyatomic 3-vinylcyclohexene oxide. The range of complexity offers a possibility to test theories which attempt to explain energy disposal in the reactions of polyatomics.[9]

Experimental Section

Details of the experimental technique used have been previously described.[1,10,11] The reactions were studied under single-collision conditions in a beam-gas apparatus. The system used in the present work is an enlarged and improved version of the earlier one with a significantly improved signal-to-noise ratio. The beam

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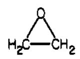
TABLE I: BO($A^2\Pi$) Vibrational Distributions, ($P(f_v)$), Average Fraction of Energy in Vibration ($\langle f_v \rangle$), and Absolute Cross Sections for the Reactions of Boron with Epoxides[a]

	$P(f_v)$						$\langle f_v \rangle$				absolute cross section, Å^2
	$v' = 0$	$v' = 1$	$v' = 2$	$v' = 3$	$v' = 4$	$v' = 5$	exptl	calcd	δH	H	
ethylene oxide (1)	0.31	0.31	0.18	0.11	0.063	0.031	0.102	0.097	0.004	0.013	0.0073
propylene oxide (2)	0.39	0.28	0.16	0.10	0.051	0.023	0.091	0.090	0.005	0.002	0.0070
butylene oxide (3)	0.41	0.26	0.15	0.10	0.053	0.026	0.090	0.089	0.005	0.0005	0.0052
diepoxybutane (4)	0.35	0.30	0.17	0.10	0.056	0.021	0.096	0.089	0.005	0.011	0.0061
cyclopentene oxide (5)	0.40	0.30	0.13	0.082	0.045	0.036	0.088	0.089		0.008	0.0044
cyclohexene oxide (6)	0.48	0.26	0.13	0.076	0.038	0.014	0.073	0.072		0.001	0.0038
3-vinylcyclohexene oxide (7)	0.46	0.28	0.13	0.074	0.034	0.016	0.073	0.072	0.001	0.002	0.0044
styrene oxide (8)	0.50	0.29	0.11	0.059	0.026	0.018	0.066	0.067		0.004	0.0065

[a] The experimental uncertainty δH^{9c} is given for reactants for which two or three spectra were taken. For other reactants δH is expected to be slightly larger than the typical value of 0.005. Values of quality of fit[9c,24] $H \leq \delta H$ imply an acceptable fit within experimental error (see text).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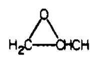
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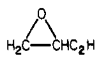
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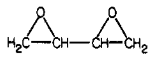
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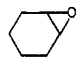
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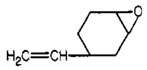
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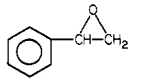
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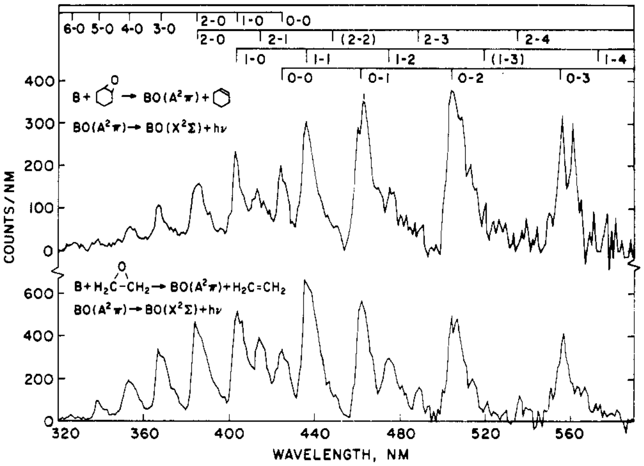

Figure 1. Chemiluminescence spectra observed in the reactions of boron with ethylene oxide and cyclohexene oxide under single-collision conditions. Spectra shown are not corrected for spectral response of detection, but thermal background of boron oven has been subtracted. Resolution is 1 nm. Vibrational assignments are made in accord with ref 17.

of boron atoms was produced by heating a graphite-lined tantalum crucible to 2350 K by electron bombardment of the exterior of the crucible. It has been shown that thermal vaporization of boron produces essentially monatomic boron.[12] The reaction zone was contained in a cylindrical light baffle designed to minimize the background of stray light from the glowing boron oven. The light from the reaction zone was detected by a spectrometer with a cooled photomultiplier-pulse counting system.

Results of the Experimental Work

Sample chemiluminescence spectra for the reactions of boron with ethylene oxide and cyclohexene oxide are shown in Figure 1. In these spectra the background (from the glowing boron oven) has been subtracted. The increased noise at the longer wavelengths is due to the spectral distribution of the subtracted thermal background. The resolution of the spectrometer used to obtain the data in Figure 1 was 1 nm. For other scans used in this study the resolution ranged from 0.5 to 2.8 nm. The spectra show vibrational excitation in the $A^2\Pi$ state up to $v' = 6$. The signal to noise was adequate for quantitative treatment up to $v' = 5$.

From the known Franck–Condon factors and the electronic transition moments of BO,[13-16] the relative cross sections for the production of the specific vibrational states[17] of BO($A^2\Pi$) have been determined (Table I and Figures 2–4). The procedure was

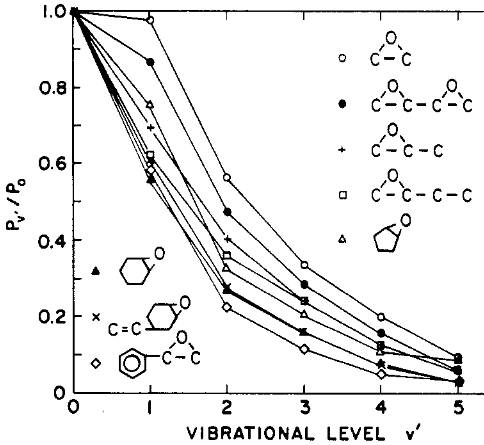

Figure 2. Nascent vibrational energy distribution of BO($A^2\Pi$, v') from reactions of boron with indicated epoxides. Lines are to aid the eye.

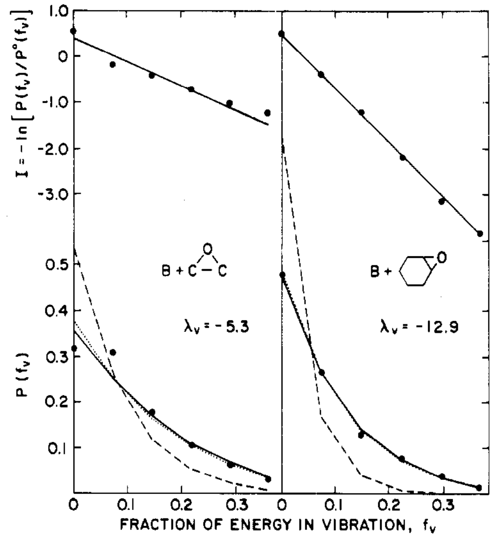

Figure 3. Lower plots: vibrational energy distributions of BO($A^2\Pi$, v') from reactions of boron with ethylene oxide and cyclohexene oxide. Points are measured distribution; ----, prior distribution $P^0(f_v)$; —, optimized distribution $P^T(f_v) = P^0(f_v)\exp(-\lambda_0 - \lambda_v f_v)$; ····, calculated distribution $P^a(f_v)$ using only active vibrational modes as discussed in test. Upper plots: surprisal I for measured distributions (points) and optimized distribution $P^T(f_v)$ (line).

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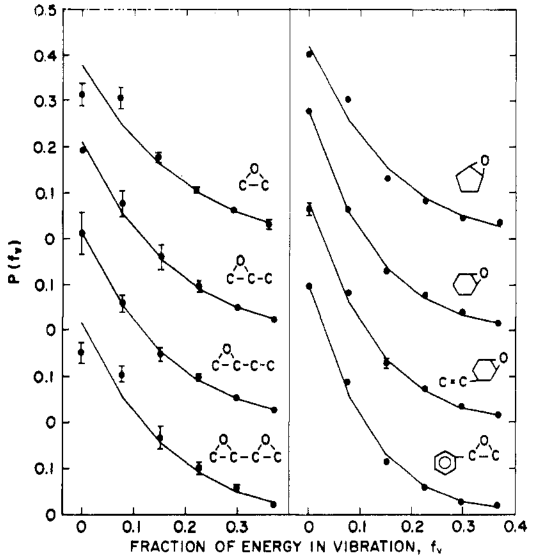

Figure 4. Measured distributions (points) and calculated distributions $P^a(f_v)$ for BO($A^2\Pi$, v') from reactions of boron with all epoxides studied. Error bars of $\pm\sigma$ are shown for all reactions where more than one run was made. Zeroes of successive curves are offset by 0.2 for clarity.

straightforward for levels $v' = 5$ through $v' = 1$ which are each represented by a single, not seriously overlapped band (the 5–0, 4–0, 3–0, 2–0, and 1–1 bands). Smaller contributions from minor bands were calculated and appropriately subtracted. For the $v' = 0$ vibrational level an average was obtained from the 0–1, 0–2 and 0–3 bands.[18]

From one to four runs were made for each compound. These were analyzed individually and the resulting distributions were averaged. The distributions in Figure 4 show error bars of $\pm\sigma$ for those reactions where more than one run was made.

The experimental values of $\langle f_v \rangle$, the average fraction of reaction exoergicity which appears as BO($A^2\Pi$) vibration, are shown in Table I. The reaction exoergicities on which these are based are discussed in Appendix A.

With the method described in the earlier experiments,[1] the absolute cross sections for the production of BO($A^2\Pi$) were also measured. The results are included in Table I. Reproducibility of measurements is within ±25%, but uncertainties associated with the technique limit the accuracy of the absolute cross sections to within a factor of 2.[1] The vibrational distribution measurements are considerably more accurate (average uncertainty less than ±10%). The distributions are therefore reported in relative values.

Discussion

Vibrational Distributions. While the differences in vibrational distributions between one compound and another are sometimes slight, nevertheless, there is a significant trend toward a decreased degree of vibrational excitation in the BO($A^2\Pi$) produced from the larger epoxides[19] (see Figure 2). This trend is also shown in the values of $\langle f_v \rangle$ in Table I. Since the total energy available in all reactions studied here is approximately the same (see Appendix A), the above result may be interpreted as an indication that the greater number of vibrational modes of the larger alkene products act as a more effective sink for the energy of the reaction. This conclusion, however, is not obvious from an information theoretical analysis.[20,21]

To perform an information theoretical analysis one must calculate the equal-probability-of-states or prior distribution. The prior vibrational energy distribution of the diatomic in a diatomic-polyatomic product pair[22] can be calculated by integrating the appropriate product rotational and translational state densities over product rotational energies and explicitly summing over levels of the vibrational modes of the polyatomic product. This procedure can be used for polyatomics which are not too large (i.e., for which the number of modes is not too large to perform the nested summations required) and it employs the rigid-rotor quantized harmonic oscillator or RRQHO approximation. With this procedure, the unnormalized expression for the vibrational distribution $P^0(f_v)$ for nonlinear polyatomics is

$$P^0(f_v) \propto \sum_{f_{V_1=0}}^{f_{V_1\max}} \dots \sum_{f_{V_s=0}}^{f_{V_s\max}} (1 - f_v - \sum_{i=1}^{s} f_{V_i})^3 \qquad (1)$$

$$f_{V_i\max} = (h\nu_i/E)\ \mathrm{Int}[(1 - f_v - \sum_{j=1}^{i-1} f_{V_j})E/h\nu_i]$$

Here $f_v = E_v/E$ is the ratio of vibrational energy E_v of the diatomic to the total available energy E; V_i and ν_i represent the vibrational quantum number and frequency of the ith mode of the polyatomic product; s is the number of modes of the polyatomic; and the limits $V_{i_{\max}}$ are given by the integral portion of the expression shown above, based simply on conservation of energy. For larger polyatomics the prior distribution is more readily calculated from the Whitten–Rabinovitch approximation[23] for the density of vibrational states $\rho_V(f_V)$ and numerically integrating the expression

$$P^0(f_v) \propto \int_0^{1-f_v} \mathrm{d}f_V (1 - f_v - f_V)^3\, \rho_V(f_V) \qquad (2)$$

The two methods of calculating the prior distribution give equivalent results (within 3% for ethylene oxide).

To illustrate the nature of the results the surprisal plots for the ethylene oxide and cyclohexene oxide reactions are shown in Figure 3. The negative temperature parameter λ_v giving the best fit of the trial function[9c,24] $P^T(f_v) = P^0(f_v) \exp[-\lambda_0 - \lambda_v f_v]$ to the data has the value $\lambda_v = -5.3$ for the ethylene oxide reaction and $\lambda_v = -12.9$ for the cyclohexene oxide reaction. This shows that in both reactions the vibrational excitation of the BO($A^2\Pi$) state is higher than predicted by a simple statistical distribution and, furthermore, that the deviation is greater in the reaction with the more complex cyclohexene oxide. Thus the simple statistical model which incorporates all the vibrational modes does not fit the observed results.

A somewhat different approach based on the concept of "active" vibrational modes provides an additional insight into the nature of these reactions. Earlier work from this laboratory[1] had suggested a calculation of the vibrational distribution using a physically reasonable scheme of limited energy sharing where only a few modes of the polyatomic product participate. The number of participating modes was treated as a variable and the RRHO approximation for classical harmonic oscillators was used. It was suggested that specific geometry changes in the transition from epoxide to alkene correspond to participating modes. The greater data base made available in this work justifies a more rigorous approach with predictive capability. We first identify all the differences in geometry between the epoxide reactant and the alkene (or alkene derivative) product and associate these changes

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(18) The intensity of the 0–1 band was obtained by subtracting the predicted intensity due to the 1–2 and 2–3 bands from the measured intensity in the 457–490-nm range. The values for the $v' = 0$, 1, and 2 levels were checked and the $v' = 0$ and 1 values were somewhat modified by calculating the total chemiluminescence in the range 400–433 nm (due to the overlapped 1–0, 2–1, and 0–0 transitions) and comparing with the total measured.

(19) The earlier experiments of Hosseini et al.[1] indicated that the halogenated propylene oxides, whose masses ranged up to the largest masses studied here but which are structurally analogous to the relatively light propylene oxide, have vibrational distributions similar to that for propylene oxide. Hence the trend reported here is correlated to the structural complexity, not to the mass of the epoxide.

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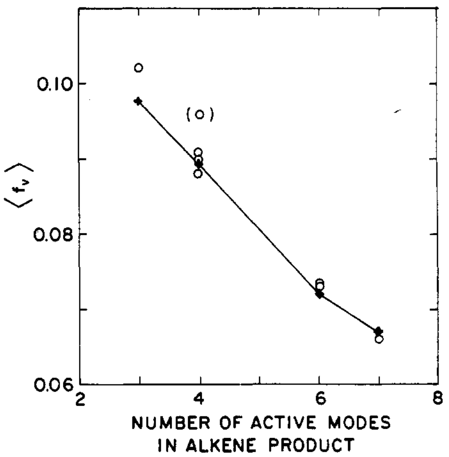

Figure 5. Average fraction of energy in BO($A^2\Pi$) vibration $\langle f_v \rangle$ as a function of number of active modes resulting from transition from epoxide to alkene (see text): +, from calculated distributions $P^a(f_v)$; lines are to aid the eye; O, experimentally measured $\langle f_v \rangle$ for all reactions studied (choice of active modes described in appendix C). Parenthetical point corresponds to diepoxybutane reaction which may be more exoergic than assumed (see text and Appendix A).

with normal modes (or combinations of normal modes) of the product. Using only these modes, we calculate a BO($A^2\Pi$) vibrational distribution $P^a(f_v)$ from eq 1. Since in each reaction all the active modes are identified, there are no variable parameters in the calculated vibrational distributions. The reasoning involved in the choice of active vibrational modes and additional comments on the individual reactions are included in Appendix C.

The results of such calculations for the ethylene oxide and cyclohexene oxide reactions are shown as dotted lines in Figure 3. As can be seen these plots are almost indistinguishable from the optimized curves $P^T(f_v)$. The calculated and measured distributions for all reactions studied are shown in Figure 4. The persuasion or quality of fit function $H^{9c,24}$ defined as $H = \sum_v P(f_v) \ln [P(f_v)/P^a(f_v)]$ is given in Table I. Here we also show the measure of experimental uncertainty[9c] $\delta H = {}^1/_2 \sum_v P(f_v)[\delta P(f_v)/P(f_v)]^2$ for those reactions for which $\delta P(f_v)$, taken to be the standard deviation, was available.

For most reactions reported here, H is comparable to or less than δH, implying an acceptable fit within experimental error. Exceptions are the ethylene oxide and diepoxybutane reactions which show a curved pattern of the data points which is not reproduced by the calculation. A slight curvature is also observed in the propylene oxide reaction but here the fit is within experimental error. It may be that a more detailed calculation (of the same type we have performed) which would explicitly include upper limits on rotational energy due to conservation of angular momentum and/or lower limits on translational energy due to the requirement of surmounting a centrifugal barrier would more accurately describe the experimental data. Alternately, there may be more subtle dynamical effects which a statistical approach does not take into account.

It is interesting to note that the calculated distributions represent the "best" fits with respect to the number of vibrational modes chosen to participate in the energy sharing. The calculated distributions would not fit the data as well had one more or one less vibrational mode been included in the calculation. The one exception is diepoxybutane, for which one less vibrational mode gives an equally good fit. Possible error in the exoergicity assumed for the diepoxybutane reaction (see Appendix A) may produce a discrepancy between the calculated and measured distributions for that reaction. If a slightly larger (2–4 kcal/mol) exoergicity is assumed, the calculated vibrational distribution for the correct number of vibrational modes is in fact optimal.

The value of $\langle f_v \rangle$ is given for all experimental and calculated distributions in Table I. It is also shown graphically in Figure 5 as a function of number of active modes in the alkene product. The measurements show tight clustering about the calculated values.

Absolute Cross Sections for the Formation of BO($A^2\Pi$). The trend in the absolute cross sections is toward smaller values for the cyclic reactants. The reductions in cross section are, however, not as dramatic as were observed for the halogenated epoxides.[1]

Limitations to reaction imposed by entrance and exit channel centrifugal barriers are expected to be the same for all reactions studied here, since the reduced masses of the reactants and products are chiefly determined by the light boron reactant and the BO product. The exoergicities are likewise nearly the same for all the reactions. The observed trends in the reactivity must, therefore, be due to other factors. Mass in fact may hinder reactivity. The greater moment of inertia of the larger epoxides may reduce their ability to rotate into a more favorable orientation during the limited collision time. The trend may also be due to a greater degree of steric hindrance in the more structurally complex reactants. Steric hindrance considerations may be particularly important since orbital correlations suggest that reactions producing BO($A^2\Pi$) result from an off-axis attack of boron on ethylene oxide (see Appendix B). Since rotation can occur between the epoxide and the phenyl group in styrene oxide, it is likely that inertial and steric factors do not hinder its reactivity even though the molecule is as massive as the cyclic epoxides.

Symmetry Considerations

In our analysis we have chosen only those vibrational modes corresponding to changes in equilibrium geometry between reactants and products. Restrictions on vibrational excitation may also emerge from certain symmetry considerations. Recently, for example, Miller[25] deduced such restrictions to excitation of certain vibrational modes from an analysis of dynamical effects of symmetry along a reaction path. His analysis is most likely to be valid for relatively slow processes.

An implicit assumption in our choice of active modes is that no additional nuclear motions are necessary to overcome any barriers in the reaction path. That this is a good assumption is suggested by Appendix B, which shows that (for certain approach geometries) all orbitals correlate smoothly from reactants to products. Hence no additional symmetry-breaking nuclear motions are required.

Dynamic Considerations

Additional insight into the reaction process may be gained by comparing the results reported here with other reactions for which energy disposal has been explained by dynamic modeling. Conservation of linear momentum following an impulsive release of energy[26] appears to govern the (nonstatistical) energy disposal in a number of alkali atom–alkyl halide,[26,27] and alkaline earth–alkyl halide[27-30] reactions. The following considerations show that an impulsive mechanism does not govern the energy disposal in the reactions studied here. In our experiments the vibrational distributions peak at $v' = 0$ and decrease monotonically; and the values of $\langle f_v \rangle$ are constant for more massive substituents on the epoxide reactants. By contrast, in the impulsive process, the distribution peaks sharply at a higher v and the $\langle f_v \rangle$ values increase dramatically for more massive substituents on the alkyl halide reactants.[27-29] The model which best fits our experimental results suggests that the energy is released not impulsively but gradually enough for it to couple into the degrees of internal motion required to form the alkene product. The collision complex, however, does not last long enough to allow significant coupling to the other modes. Still it should be pointed out that to the extent to which the dynamics of a particular reaction are not completely averaged during the collision process, values of $\langle f_v \rangle$ may be skewed to lower

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or higher values for very heavy or very light (e.g., hydrogen[31,32]) transferred atoms.[33] Hence the excellent fit provided by the proposed model may be in part due to the fortuitous closeness of the mass of the transferred atom (oxygen) to those of the reacting atom (boron) and the atom to which the oxygen is initially bound (carbon).

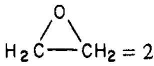
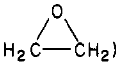
Conclusions

The excellent agreement between the predictions of the model and the experimental data strongly suggests that in the course of the reaction only those vibrational modes of the polyatomic molecule are excited which correspond to changes in the equilibrium geometry. This implies that the duration of energy release is sufficient for the energy to enter the modes strongly coupled to the reaction process. It seems reasonable that in such a moderately fast collision the modes which are not as strongly coupled remain relatively inert and, therefore, initially they do not share in the energy released in the reaction.

Acknowledgment. We thank Mary Beth Tabacco for assistance in this project. This work was supported in part by the Air Force Office of Scientific Research and by the National Science Foundation.

Appendix A. Reaction Exoergicities

To illustrate the method of determining reaction exoergicities we show the calculations for the reaction of boron with ethylene oxide.

	ΔH	ref
$B + O = BO(X^2\Sigma)$	$-D_0^\circ(BO)$	34
$BO(X^2\Sigma) = BO(A^2\Pi)$	$h\nu_{00}$	17
$^1/_2O_2 = O$	$\Delta H_f^\circ(O)$	35
 $= 2H_2 + 2C + O_2$	$-\Delta H_f^\circ$ ()	36
$2H_2 + 2C = H_2C{=}CH_2$	$\Delta H_f^\circ(H_2C{=}CH_2)$	36

An additional −5.6 kcal/mol must be included to take into account the initial translational energy in the reaction coordinate.

In the above calculation the heats of formation are referred to 298 K. To give the exoergicity to the alkene product in its translational and rotational ground state, we adjusted the above calculated value by $-3RT$ which is −1.8 kcal/mol. A small correction was also introduced for the active vibrational modes involved in the calculation. The modes *not* included in the statistical analysis were assumed to remain at 298 K.

Heats of formation are available for the pairs ethylene oxide/ethylene,[36] propylene oxide/propylene,[36] and butylene oxide[37]/butylene,[36] giving net exoergicities of −47.6, −46.0, and −46.2 kcal/mol, respectively. Heats of formation are not available for the other reactant/product pairs. In these cases the butylene oxide/butylene values were used. This is likely to be a good approximation where the substituent groups contain only carbon and hydrogen. However, for the diepoxybutane we might expect the presence of the additional electron-withdrawing oxygen atom to lead to a somewhat larger exoergicity. This results from a tendency of the additional oxygen to destabilize the (reacting) epoxide group. (The electron-rich double bond of the alkene product is not destabilized.) However, this effect should be small compared to the total exoergicity. Therefore, the known butylene oxide/butylene values were used in this case. If the total energy is treated as a variable, the best fit to the statistical model is obtained with a value 3.1 kcal/mol larger. This slight deviation is in the expected direction.

Appendix B. Orbital Correlations

Orbital correlations from reactants to products for the reaction of boron with ethylene oxide suggest that reaction to BO($A^2\Pi$) can occur only when the boron is positioned away from the symmetry axis of ethylene oxide. With boron positioned on the axis, ground-state reactants correlate only to BO($X^2\Sigma$) or to excited products above BO($A^2\Pi$).

The ethylene oxide molecule (C_{2v} symmetry) has orbital occupation[38] $1a_1^2\ldots 6a_1^2\ 1a_2^2\ 1b_1^2\ 2b_1^2\ 1b_2^2\ 2b_2^2\ 3b_2^2$. In an approach along the axis of symmetry, the boron ^2P state splits into three states having occupancies $1a_1^2\ 2a_1^2\ 3a_1$, $1a_1^2\ 2a_1^2\ 1b_1$, and $1a_1^2\ 2a_1^2\ 1b_2$. The combined reactant orbital occupations in C_{2v} symmetry are thus

$B\text{-}C_2H_4O$:

$1a_1^2\cdots 8a_1^2\ 9a_1$	$1a_2^2\ 1b_1^2\ 2b_1^2$	$1b_2^2\cdots 3b_2^2$	$^2A_1$
$1a_1^2\cdots 8a_1^2$	$1a_2^2\ 1b_1^2\ 2b_1^2\ 3b_1$	$1b_2^2\cdots 3b_2^2$	$^2B_1$
$1a_1^2\cdots 8a_1^2$	$1a_2^2\ 1b_1^2\ 2b_1^2$	$1b_2^2\cdots 3b_2^2\ 4b_2$	$^2B_2$

The product ethylene orbital occupation in C_{2v} symmetry (where the axis and plane of symmetry are as for ethylene oxide) is $1a_1^2\ldots 4a_1^2\ 1a_2^2\ 1b_1^2\ 1b_2^2\ 2b_2^2$.[38] The BO($X^2\Sigma$) orbitals ($1\sigma^2\ldots 4\sigma^2\ 5\sigma\ 1\pi^2\ 2\pi^2$)(39) become, in C_{2v} symmetry, $1a_1^2\ldots 4a_1^2\ 5a_1\ 1b_1^2\ 1b_2^2$. These combine to

$BO(X^2\Sigma)\text{–}C_2H_4$:

$$1a_1^2\ldots 8a_1^2\ 9a_1\ 1a_2^2\ 1b_1^2\ 2b_1^2\ 1b_2^2\ldots 3b_2^2 \qquad 2A_1$$

which correlates to the reactant $^2A_1$ state. The BO($A^2\Pi$) orbitals ($1\sigma^2\ldots 5\sigma^2\ 1\pi^2\ 2\pi$)[39] become, in C_{2v} symmetry, $1a_1^2\ldots 5a_1^2\ 1b_1\ 1b_2^2$ and $1a_1^2\ldots 5a_1^2\ 1b_1^2\ 1b_2$. These combine with the ethylene orbitals to

$BO(A^2\Pi)\text{–}C_2H_4$:

$1a_1^2\cdots 9a_1^2$	$1a_2^2\ 1b_1^2\ 2b_1$	$1b_2^2\cdots\cdots\cdots 3b_2^2$	$^2B_1$
$1a_1^2\cdots 9a_1^2$	$1a_2^2\ 1b_1^2\ 2b_1^2$	$1b_2^2\ 2b_2^2\ 3b_2$	$^2B_2$

neither of which correlates to the reactants. (Presumably the reactants correlate to the higher BO $^2\Pi$ state $1\sigma^2\ldots 4\sigma^2\ 1\pi^2\ 2\pi^2\ 3\pi$.)[39] Thus we see that for axially symmetric approach of boron to ethylene oxide, the reactants correlate to BO($X^2\Sigma$) but not to BO($A^2\Pi$).

By reducing the symmetry to planar (C_s), i.e., allowing the boron to approach off-axis, the reactants can correlate to BO($A^2\Pi$). This occurs for either of the two possible C_s planes chosen. For the symmetry plane coplanar with the epoxide ring, the ethylene oxide orbitals become $1a'^2\ldots 9a'^2\ 1a''^2\ldots 3a''^2$. The boron states become $1a'^2\ 2a'^2\ 3a'$, $1a'^2\ 2a'^2\ 1a''$, and $1a'^2\ 2a'^2\ 4a'$. The combined reactant orbital occupations for this C_s plane are

$B\text{–}C_2H_4O$:

$1a'^2\cdots 11a'^2\ 12a'$	$1a''^2\cdots 3a''^2$	$1^2A'$
$1a'^2\cdots 11a'^2$	$1a''^2\cdots 3a''^2\ 4a''$	$^2A''$
$1a'^2\cdots 11a'^2\ 13a'$	$1a''^2\cdots 3a''^2$	$2^2A'$

The product ethylene orbitals in the corresponding C_s plane are $1a'^2\ldots 6a'^2\ 1a''^2\ 2a''^2$. In C_s symmetry the BO($X^2\Sigma$) orbitals become $1a'^2\ldots 5a'^2\ 6a'\ 1a''^2$ and the combination is $BO(X^2\Sigma)\text{–}C_2H_4$ $1a'^2\ldots 11a'^2 12a' 1a''2\ldots 3a''^2$, $^2A'$. This still correlates to one of the $^2A'$ reactant states, as it should. In addition, in C_s symmetry the BO($A^2\Pi$) orbitals become $1a'^2\ldots 6a'^2\ 1a''$ and $1a'^2\ldots 5a'^2\ 7a'\ 1a''^2$. These combine with the ethylene orbitals to

$BO(A^2\Pi)\text{–}C_2H_4$:

$1a'^2\cdots\cdots\cdots 12a'^2$	$1a''^2\ 2a''^2\ 3a''$	$^2A''$
$1a'^2\cdots 11a'^2$	$13a'\ 1a''^2\ 2a''^2\ 3a''^2$	$^2A'$

The latter $^2A'$ product state correlates to the second reactant $^2A'$ state. It can be shown that for the other possible C_s plane the

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correlations are identical. Thus for any off-axis approach of boron to ethylene oxide the reactants correlate to $BO(A^2\Pi)$.

Appendix C. Choice of Active Vibrational Modes in Polyatomic Products

Ethylene. A comparison of bond distances and angles for ethylene oxide and ethylene[40] shows that the carbon–carbon distance changes from 1.47 to 1.34 Å and the out-of-plane H_2C–C angle changes from 158 to 180°. By contrast the H–C distance changes very little (1.080 to 1.086 Å) and the HCH angle remains unchanged at 117°. Viewed perpendicular to the plane of the four hydrogens, the HCH angle in ethylene oxide is only slightly larger, at 120.6°. The C–C bond shortening which occurs in the process of reaction is, therefore, actually a motion of the two CH_2 groups closer to each other. The change in the in-plane bond angles is negligible. This motion is not described well by the C=C stretch (ν_2, a_g) or the CH_2 scissors (ν_3, a_g) normal modes of ethylene[41,42] since they involve considerable change in the in-plane bond angles nsee ref 42 for the local-mode nomenclature). The best description is provided by a combination of $\nu_2 + \nu_3$ modes which preserves the in-plane bond angles as desired. The out-of-plane motion (change in the H_2–C–C angle) corresponds to the symmetric CH_2 wag (ν_7, b_{1u}). It could also be manifested as the asymmetric CH_2 wag (ν_8, b_{2g}) as a result of a boron atom approach from one end (see Appendix B). This could introduce a phase difference in the out-of-plane motions at the two ends of the ethylene molecule. The change in geometry from ethylene oxide to ethylene can thus be accounted for by the $\nu_2 + \nu_3$ combination (2965 cm^{-1}), ν_7 (949 cm^{-1}), and ν_8 (943 cm^{-1}).[42]

Since the implicit assumption of our approach is that appreciable vibrational energy can be deposited only in the active polyatomic modes, it may be interesting to calculate how much energy is associated with the displacements from the equilibrium ethylene structure. When the potential energy formula for classical harmonic oscillators is used the $\nu_2 + \nu_3$ combination and the out-of-plane ν_7 or ν_8 displacement correspond to a potential energy of 0.26 and 0.25 eV, respectively. This is a significant fraction of the 2.06-eV total energy available in the reaction.

Propylene. Here also similar shortening of the C–C bond occurs as discussed for ethylene. Again, the motion is best represented by a combination of two normal modes which minimizes in-plane angular motion. For propylene this is the $\nu_6 + \nu_8$ (a′) combination, where ν_6 is the C=C stretch and ν_8 is the CH_2 scissors.[41] For the out-of-plane motion, we use ν_{17} (CH_2 wag, a″) and ν_{19} (C–H out-of-plane bend, a″). In addition, the presence of the CH_3 group "anchors" one corner of the molecule so that a twist about the double bond, ν_{20} (C=CH_2 twist, a″) may also result. These out-of-plane modes may be introduced in varying degrees depending on the phase relationship of the motions involved. No other bond distances or angles are expected to change in the transition from propylene oxide to propylene; therefore, the complete set of frequencies in this case is $\nu_6 + \nu_8$ (3063 cm^{-1}), ν_{17} (1166 cm^{-1}), ν_{19} (936 cm^{-1}), and ν_{20} (578 cm^{-1}).[41,43]

Butylene. With respect to changes in geometry, this case is identical with propylene. The presence of a C_2H_5 group instead of CH_3 does not change the analysis. The values of the frequencies for propylene are used since those for butylene are not readily available. The values are expected to be similar.[43]

Butadiene Oxide. The changes here are the same as for butylene.

Cyclopentene. For this and for the two other cycloalkenes, the C–C bond shortening is represented by the same combination of frequencies ($\nu_6 + \nu_8$) as for propylene. The out-of-plane motion of the two ethylenic hydrogens is represented by using (twice) the propylene C–H out-of-plane bend (ν_{19}) and the C=C twist is represented by the propylene C=C twist (ν_{20}). The C=C twist frequency is undoubtedly modified by the presence of the ring structure, but the insensitivity of the calculation to the value of frequency used should make this a good approximation. Thus the values used are $\nu_6 + \nu_8$ (3063 cm^{-1}), ν_{19} (936 cm^{-1}), ν_{19} (936 cm^{-1}), and ν_{20} (578 cm^{-1}).

Cyclohexene and 3-Vinylcyclohexene. These two are treated identically. In addition to the four modes mentioned for cyclopentene, other modes are possible due to the differences between a quasi-boat configuration favored by the epoxide and a quasi-chair configuration favored by the alkene. The motion required to effect this transition can be resolved into two modes which are analogous to two of the CCC deformation + CC torsion modes[42] of cyclohexane (ν_6, a_{1g} and ν_{32}, e_u). Hence the six frequencies used are 3063, 936, 936, 578, 383, and 248 cm^{-1}.

Styrene. In addition to the four frequencies chosen for propylene, butylene, etc., other modes must be used to account for the transition from the staggered conformation of styrene oxide (with the terminal carbon out of the plane of all other carbons) to the styrene planar structure,[44] a result of the interaction between the π electrons of the double bond and the benzene ring. Another consequence of this interaction is a shortening of the C–phenyl bond to 1.48 Å.[44] The close proximity of two of the hydrogens in the styrene structure must also result in a C–C–C bending to minimize the H–H interaction. Appropriate frequencies were not available for styrene so the analogous frequencies for butadiene[42] were used. These are the C–C torsion (ν_{13}, a_u, 162 cm^{-1}), the C–C stretch (ν_7, a_g, 1196 cm^{-1}), and the C–C–C deformation (ν_9, a_g, 512 cm^{-1}). Combined with the other frequencies (3063, 1166, 936, and 578 cm^{-1}) a total of seven modes are used.

Registry No. BO, 12505-77-0; boron, 7440-42-8; ethylene oxide, 75-21-8; propylene oxide, 75-56-9; butylene oxide, 106-88-7; diepoxybutane, 1464-53-5; cyclopentene oxide, 285-67-6; cyclohexene oxide, 286-20-4; 3-vinylcyclohexene oxide, 106-86-5; styrene oxide, 96-09-3.

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