Nuclear Magnetic Resonance Study of Conformational Isomerization in Acetone Diperoxide

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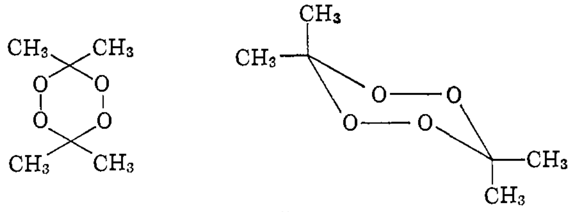
Abstract: The nuclear magnetic resonance spectrum of acetone diperoxide has been measured between −16 and 30°. The spectra were used to calculate the rate constants for the chair-to-chair conformational isomerization, and the activation energy, E_a, for this process was determined to be 12.3 kcal./mole with a frequency factor of 3.95×10^{10} sec.$^{-1}$. The activation free energy, enthalpy, and entropy are also calculated. Possible reaction paths for the isomerization process are discussed.

The use of the n.m.r. technique has permitted studies of conformational isomerization in a number of six-membered ring systems. Acetone diperoxide (1,1,-4,4-tetramethyl-2,3,4,5-tetraoxacyclohexane) (I) presents a particularly suitable case for such a study since the absence of α-hydrogen atoms eliminates strong proton coupling which leads to more complex spectra and line broadening making accurate kinetic measurements difficult. A study of conformational isomerism in I also is of interest because it presents an opportunity to compare the six-membered ring containing four oxygen atoms to the cyclohexane system.

Diperoxides are produced frequently in olefin ozonolyses. A study of their properties is of importance to the field of ozone chemistry as well as to the chemistry of rubber and other materials susceptible to attack by ozone. Acetone diperoxide itself is produced by ozonolysis of tetramethylethylene.[1]



I

Results and Discussion

The n.m.r. spectra of I at a number of temperatures are shown in Figure 1. At temperatures below 30°, the n.m.r. spectrum consists of two peaks due to the axial and equatorial methyl groups. At 30° the two lines coalesce to give a single peak which is broadened owing to intraconversion between the two conformers. At temperatures below 0° the two peaks have reached their maximum separation and appear as two, sharp, clean absorptions with a chemical-shift difference which is considerably greater than the line width. The chemical-shift difference between axial and equatorial methyl groups of 0.44 p.p.m. is close to that reported for the axial and equatorial protons of cyclohexyl fluoride (0.46 p.p.m.[2]) and cyclohexane (0.47,[3] 0.478,[4] 0.445[5] p.p.m.).

Peak separation measurements in the temperature range between complete separation and coalescence were used to calculate the activation energy for the isomerization process using the method of Gutowsky and Holm.[6] According to this method the isomerization process is treated as a typical rate process with the temperature dependence given by

$$k = \nu_0 \exp(-E_a/RT)$$

where k is the isomerization rate constant, ν_0 is the frequency factor, and E_a is the activation energy for the isomerization. In this treatment $k = 1/2\tau$ where τ is the residence time as defined by Gutowsky and Holm.[6] The temperature dependence equation can be written[6] as

$$\log \frac{1}{\tau\delta\omega} = \log \frac{2\nu_0}{\delta\omega} - E_a/2.3RT$$

where $\delta\omega$ is the separation of the two peaks assuming no exchange. The limiting separation for long exchange lifetimes, *i.e.*, $\tau \rightarrow \infty$, is $\delta\omega_\infty$. T_2, the transverse relaxation time, is defined as

$$T_2 = \frac{2}{\Delta\omega_{1/2}}$$

where $\Delta\omega_{1/2}$ is the width at half-height of the individual peaks at complete separation ($\tau \rightarrow \infty$) in radians per second. In the present case $2/(T_2\delta\omega)$ is small, *i.e.*, <0.12, and $\delta\omega/\delta\omega_\infty$ is found to be equal to 1 (*i.e.*, see Figure 2 in ref. 6). Thus $\delta\omega_\infty$ can be used for $\delta\omega$ in the subsequent treatment. Values of $1/\tau\delta\omega$ were obtained from a plot of $1/T_2\delta\omega$ *vs.* $1/\tau\delta\omega$ for different ratios of $\delta\omega_e/\delta\omega$ as given in Figure 3 of the Gutowsky and Holm paper. The $\delta\omega_e$ values are from the experimentally observed line separations over the temperature range used. In order to facilitate use of Gutowsky and Holm's graph for $1/\tau\delta\omega$, a plot of the experimental values of $\delta\omega_e/\delta\omega$ *vs.* temperature was made (Figure 2) and values of $\delta\omega_e/\delta\omega$ then were chosen to correspond to those plotted in Figure 3 of ref. 6. The values of $1/\tau\delta\omega$ thus obtained could then be plotted *vs.* $1/T$ to obtain E_a, the activation energy for the isomerization process. A straight-line plot was obtained (Figure 3). E_a was calculated to be 12.3 kcal./mole, and ν_0, the frequency factor, was calculated to be

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(1) R. Criegee, G. Blust, and H. Zinke, *Chem. Ber.*, **87**, 766 (1954).

(2) F. A. Bovey, F. W. Anderson, F. P. Hood, III, and R. L. Kornegay, *J. Chem. Phys.*, 40, 3099 (1964).

(3) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **84**, 386 (1962).

(4) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, **41**, 2041 (1964).

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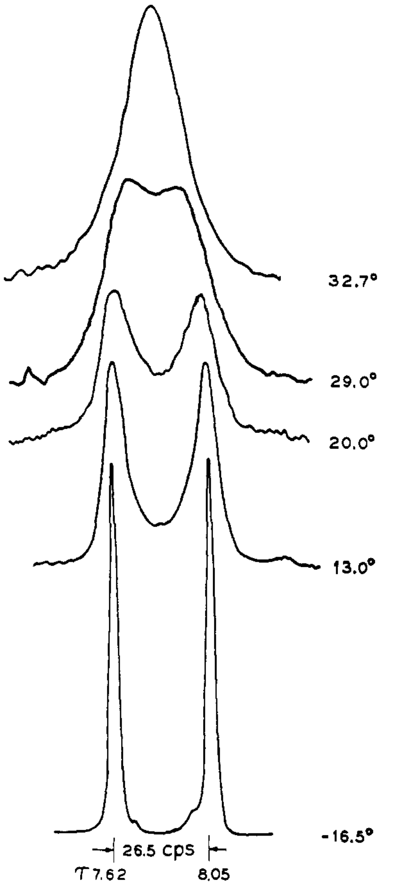

Figure 1. Nuclear magnetic resonance spectra of acetone diperoxide at various temperatures.

3.95×10^{10} sec.$^{-1}$ using the least-squares method. A summary of the data obtained is given in Table I.

The Eyring formulation was then used to calculate values for the free energy, enthalpy, and entropy of activation

$$k = \kappa \frac{k_B}{h} T e^{-\Delta F^*/RT}$$

where k is the rate constant, k_B is the Boltzmann constant, h is Planck's constant, ΔF^* is the free energy of activation, and κ is the transmission coefficient which was taken to be 1. Taking logarithms and rearranging gives

$$\Delta F_T^* = 2.3RT\left(\log \frac{k_B}{h} + \log T - \log k\right)$$

or

$$\Delta F_T^* = 2.3RT(10.32 + \log T - \log k)$$

Values of k, the rate constant for conversion from chair-to-chair forms, were calculated from $k = 1/2\tau$ and the previously obtained values of $1/\tau\delta\omega$. The enthalpy and entropy values were obtained from

$$\Delta H^*_T = E_a - RT$$

and

$$\Delta S^*_T = (\Delta H^*_T - \Delta F_T^*)/T$$

The values obtained for ΔF^*, ΔH^*, and ΔS^* near the coalescence temperature are given in Table I. The free energy of activation was found to increase slightly with increasing temperature.

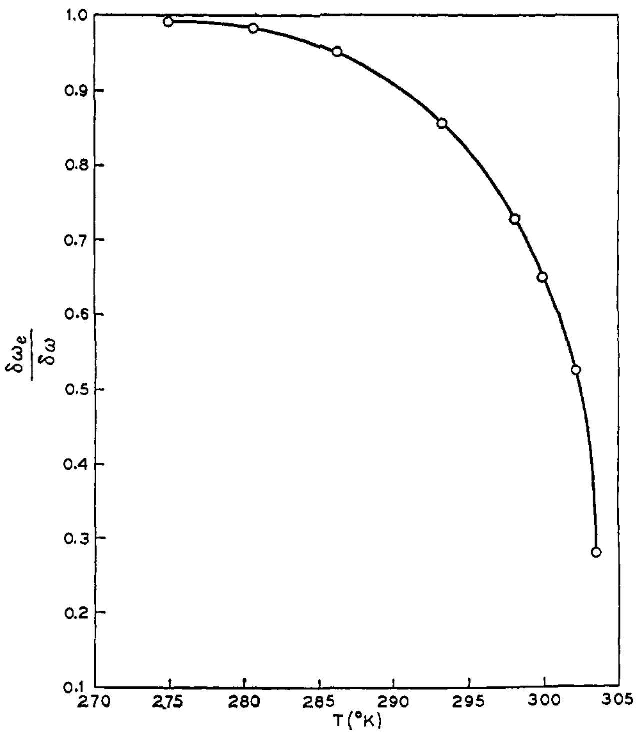

Figure 2. Plot of experimental values, $\delta\omega_e/\delta\omega$, vs. temperature for acetone diperoxide.

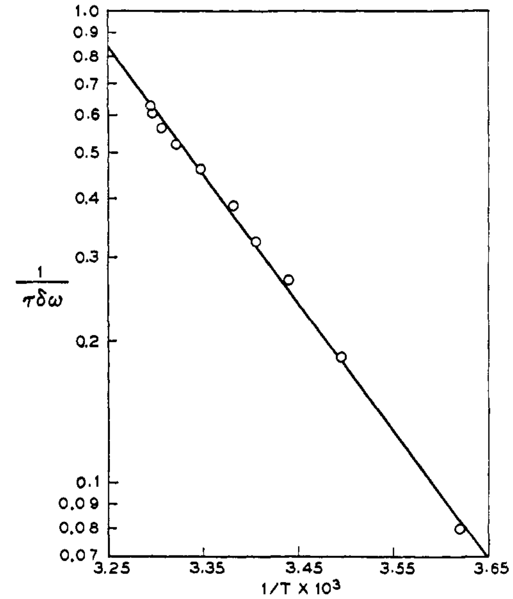

Figure 3. Temperature dependence of the conformer isomerization rate constant ($1/2\tau$) for acetone diperoxide.

In these calculations a reaction pathway was assumed which involves only a single barrier between chair conformers. A transmission coefficient of 1 was used; that is, it was assumed that all reacting molecules continue on to their conformers. While in most cyclohexane conformer isomerizations it is reasonable to assume that the molecules pass through a metastable boat form, such an assumption may be unwarranted in the present case. An examination of molecular models suggests that the true boat form is incapable of existence. A similar conclusion was reached by Claeson, Androes, and Calvin for 3,3,6,6-tetramethyl-1,2-dioxane.

Table I

Compound	Temp., °K.	E_a, kcal./mole	ν_0, sec.$^{-1}$	ΔS^*_{cc}, e.u	ΔS^*_{cb}, e.u.	ΔF^*_{cc}, kcal./mole	ΔF^*_{cb}, kcal./mole	ΔH^*, kcal./mole	Ref.
Tetramethyldithiane	271	16.1	2.10×10^{14}	6.7	. . .	13.8	. . .	15.6	7
Tetramethyldioxane	285	18.5	4.0×10^{16}	14.4	. . .	14.6[a]	. . .	17.9	7
Acetone diperoxide	303	12.3	3.95×10^{10}	−12.1	−10.7	15.4	15.0	11.7	This work

[a] Transmission coefficient taken as one-half.

The values of ΔF^*, ΔH^*, and ΔS^* found by these latter workers are also given in Table I for comparison purposes. Such a comparison suggests that the acetone diperoxide isomerization follows a different reaction pathway than that proposed[7] for tetramethyldithiane (II) or tetramethyldioxane (III). The negative ΔS^* obtained for acetone diperoxide suggests a barrier form with a greater degree of order than the starting form. In the case of II and III positive activation entropies were found which were attributed to a boat form for the barrier form for II, and a flexible form involving five coplanar atoms in the case of III.

It is tempting to suggest that the barrier form for acetone diperoxide is a rigid, planar, or near-planar form thus accounting for the negative ΔS^*. Bovey[4] and Harris[8] have pointed out that based on symmetry grounds alone only a transition *via* planar form would be expected to give a negative ΔS^*_{cb} in the cyclohexane case. Such a transition would require a ΔH^* of at least 30 kcal.[9] in cyclohexane.

It seems likely, however, that not all of the same considerations apply to the acetone diperoxide case since the six-membered framework now incorporates four oxygen atoms with smaller bond angles involved. It may be that steric strain in the ground state of I raises it to a higher energy level so that the ΔH^* involved in reaching a planar-like barrier state is considerably less than the 30 kcal. calculated for cyclohexane.[9] Again, the use of a molecular model suggests that the pathway from chair to chair may be narrowly defined because of a combination of restricted bond angles and repulsive forces. Initial movement of one end of the chair form to give a form with five atoms coplanar followed by a subsequent motion toward the barrier state would also seem to be precluded by steric considerations. It may be that both ends of the molecule must move simultaneously or near simultaneously in order to reach the barrier state for isomerization. Such a requirement would contribute toward a negative activation entropy.

The fact that ΔH^* for I is quite a bit lower than that for II or III is also consistent with the proposed, highly strained ground state for I which achieves some relief from steric strain in the transition state.

A consideration of symmetry factors alone does not predict the observed ΔS^* for I. A calculation of ΔS^* was made from[8]

$$\Delta S^* = R \ln \left(\frac{\omega_2}{\sigma_2}\right) \Big/ \left(\frac{\omega_1}{\sigma_1}\right)$$

where ω and σ refer to the statistical weight and symmetry number, respectively. Using $\omega_1 = 2$ and $\sigma_1 = 4$ for the ground chair state and $\omega_2 = 1$ and $\sigma_2 = 8$ for the planar transition state gives a value of −2.76 e.u. for ΔS^*. The failure of symmetry considerations alone to predict ΔS^* has been observed in other cases. For example, perfluorocyclohexane has an activation entropy of −10 e.u.,[10] which is considerably lower than any of the values reported for cyclohexane. Yet symmetry considerations would predict the same activation entropy for both molecules. It is clear that other factors, such as rotational and vibrational influences, should be considered in attempting to predict ΔS^* in more complex systems.

An alternative proposal for the reaction pathway for isomerization in I is one which follows more closely the mechanism proposed[2-4] for the cyclohexane system. Such a pathway would most likely involve a twist boat form as an intermediate. This intermediate would then be separated from the chair conformers by equal transition barriers. While models indicate that the true boat form would incorporate strong steric interactions, they suggest that the twist boat form may be a reasonable intermediate.[11] If we assume that a molecule in the twist boat form has an equal chance of passing over either barrier to the chair form, then the rate of chair-to-boat isomerization, k_{cb}, must be twice that of the observed chair-to-chair rate, k_{cc}. This description is equivalent to using a transmission coefficient of one-half for the chair-to-chair isomerization.

If one refers to the equation given above for the calculation of ΔF^*_T (ΔF^*_{cc}), it is seen that ΔF^*_{cb} is related to ΔF^*_{cc} by

$$\Delta F^*_{cb} = \Delta F^*_{cc} - 2.3RT \log 2$$

where the transmission coefficient for the chair-to-boat path is taken to be 1. Likewise, we have

$$\Delta S^*_{cb} = \Delta S^*_{cc} + 2.3R \log 2$$

From these relationships we find at 303 °K.

$$\Delta F^*_{cb} = 15 \text{ kcal./mole}$$

$$\Delta S^*_{cb} = -10.7 \text{ e.u.}$$

The barrier state involved in reaching the intermediate twist boat form may be the cyclohexane-like form proposed by others.[2-4] Again, however, when symmetry factors alone are considered, the experimentally observed negative ΔS^* is not predicted by such a barrier form.

The best proposal for the reaction pathway is probably one incorporating aspects of both of those considered above. The isomerization could then be considered to involve a twist boat intermediate which is separated

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(11) Such a procedure is somewhat deficient since the models used do not adequately account for the lone-pair electrons on oxygen.

from the chair by a narrowly defined barrier form. These restrictions on the barrier form probably arise from the angle strain associated with the presence of the oxygen atoms as well as effects of the oxygen lone-pair electrons.

An assignment of the observed chemical shift values in I is made possible if the method discussed by Jackman[12] is followed. Jackman has presented arguments relating the long-range shielding effect to the diamagnetic anisotropy of the carbon–carbon single bond in the cyclohexane system. According to these arguments the 2,3 and 5,6 bonds (where the protons under discussion are at position 1) have the greatest effect on shielding differences between axial and equatorial protons and lead to a deshielding of the equatorial proton at 1 and a shielding of the axial proton. If these same arguments are applied to I where the 2,3 and 5,6 bonds are now oxygen–oxygen bonds, that is, if it is assumed that the electrons in these bonds are axially symmetrical, then the equatorial methyl group protons are more deshielded and absorb at 7.62 and the axial protons occur at 8.05. The center of the two absorptions occurs at 7.83 compared to 8.65 for tetramethyldioxane[7] where there is only one peroxy bond.

Experimental Section

The spectra were determined on a Varian A-60 high-resolution n.m.r. spectrometer equipped with a Varian V-6057 variable-temperature accessory. Temperatures were determined by measuring the peak separation in a methanol sample both before and after measurements on the acetone diperoxide sample at each temperature. Temperature could be controlled to ±0.1° at the low temperatures and to ±0.5° at the high temperatures. The samples of acetone diperoxide used were 4.2% solutions in deuteriochloroform sealed in Varian n.m.r. tubes. Chemical-shift values given are τ values relative to external tetramethylsilane.

The maximum errors in E_a and ν_0 were determined from the lines drawn on the log $1/\tau\delta\omega$ *vs.* $1/T$ plot using the maximum possible experimental errors at the temperature extremes. The maximum error in E_a was found to be ±0.9 kcal. and the maximum range for ν_0 was calculated to be from 1.15×10^{10} to 2.05×10^{11} sec.$^{-1}$.

Preparation of 1,1,4,4-Tetramethyl-2,3,4,5-tetraoxacyclohexane. The Criegee[1] method was used. Tetramethylethylene was ozonized in pentane solution using a Welsbach Model T-23 ozonator. The white solid formed was filtered off and purified by gas chromatography using a 20-ft., 10% cyanosilicone column at 90°. The purified material had m.p. 133–134° (lit.[13] m.p. 132°). The infrared spectrum of this material was identical with the published spectrum for acetone diperoxide.[14]

Acknowledgment. The authors are grateful to Professor F. A. L. Anet, Dr. F. A. Bovey, and Dr. S. Meiboom for helpful discussions.

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Substituent Effects in Unimolecular Ion Decompositions. II. A Linear Free Energy Relationship between Acyl Ion Intensities in the Mass Spectra of Substituted Acylbenzenes[1,2]

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. Received August 23, 1965

Abstract: A linear relationship between the intensities of the fragments corresponding to the benzoyl ion and the acetyl ion in the mass spectra of substituted benzophenones and acetophenones has been found and explained on the basis of a kinetic argument. Much of the data can be correlated by the common relationhips of solution chemistry. Both the extent of this correlation and individual failures of relationship may be used to establish features of the structures of the ions involved. The new technique appears to have some generality for the prediction of spectra and the elucidation of mechanisms and structures of unimolecular ion decompositions.

Investigation of organic ion reactions in the gas phase, as observed in mass spectra, has been hampered by a scarcity of applicable techniques. The few available include the determination of elemental compositions by high-resolution spectroscopy,[3] the elucidation of decomposition pathways with metastable ions,[4] determination of structural detail by specific labeling with stable isotopes,[5] and assignment of structure on the agreement of appearance potentials with calculated internal energies of ions.[6]

In solution organic chemistry, correlation of data by linear free-energy relationships, particularly the Hammett equation, has been widely applied in the study of

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