

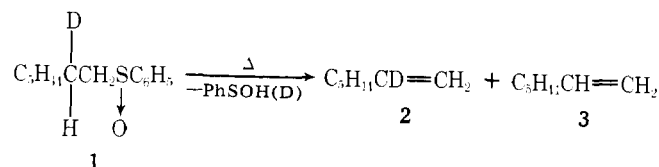
Communications to the Editor

Transition-State Structures in Sulfoxide and Amine Oxide Thermolysis

Sir:

Thermolysis of sulfoxides with one or more hydrogens at the β carbon normally results in stereospecific formation of olefins,¹⁻³ which may be reacted reversibly or with external reagents in situ, to form new products.⁴⁻⁷ The operation of steric strain acceleration effects^{1,2} and polar effects² has been documented. In some cases, activation parameters appear to increase with increasing temperatures; this, together with marked changes in the product olefin composition, has been interpreted^{1,2} as a mechanistic change from a concerted process involving a cyclic transition state—analogueous to that for amine oxide thermolysis⁸—to a less concerted, heterolytic,² or radical pair¹ process at higher temperatures. We have now obtained evidence demonstrating that the transition states of the β -elimination in comparable, regular, alkyl sulfoxides and amine oxides are, in fact, markedly different.

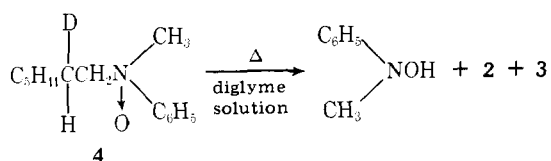
The temperature dependence of the kinetic deuterium isotope effect⁹⁻¹⁴ in such hydrogen-transfer reactions has proven to be extremely valuable as a probe of transition-state geometry, where the possibilities have been previously sorted out by traditional kinetic studies. This mechanistic criterion was applied in studies of the decomposition of the deuterated sulfoxide **1** in diglyme solution over a 100 °C range of thermostatically controlled temperatures in which a mixture of deuterated (**2**) and nondeuterated (**3**) olefins is formed.



Analysis of this thermolysis product composition by means of the high-precision mass spectrometric technique previously developed¹⁵ provided a very accurate measure of the temperature dependence of the isotope effect; see Table I.

Apparently, the activation energy difference, $[\Delta E_a]_{\text{D}}^{\text{H}}$, is identical with the zero point energy difference of the C-H and C-D bond being broken in the rate-determining step; $A_{\text{H}}/A_{\text{D}}$, moreover, is within theoretical limits¹⁶ of the value for linear hydrogen transfer in a symmetrical transition state with no evidence of tunneling. This result is apparently in keeping with what has been established for concerted, pericyclic transition states such as prevail in a retro-ene reaction mechanism.^{9,11}

A parallel study of the thermolysis of the deuterated amine oxide **4** was carried out and the isotope effect measured in precisely the same way; see Table II. The unusual temperature



independence of $k_{\text{H}}/k_{\text{D}}$ (i.e., $[\Delta E_a]_{\text{D}}^{\text{H}} = 0$) and the fact that the value of $A_{\text{H}}/A_{\text{D}}$ (~ 2.2 over a 120 °C temperature range) is far greater than the theoretical maximum (1.2)^{16,17} for a classical linear H-transfer process is possibly indicative of¹³⁻¹⁶

Table I. Temperature Dependence of the Kinetic Deuterium Isotope Effect in Thermolysis of Sulfoxide **1**

| T, K | $k_{\text{H}}/k_{\text{D}}$ | Computed by regression analysis |
|---------------|-----------------------------|---|
| 403 | 3.168 | $[E_a]_{\text{D}}^{\text{H}} = 1.15 \text{ kcal/mol}$ $A_{\text{H}}/A_{\text{D}} = 0.76$ Correln coeff = 0.9997 |
| 423 | 2.944 | |
| 443 | 2.773 | |
| 463 | 2.634 | |
| 483 | 2.486 | |
| 503 | 2.381 | |

Table II. Temperature Dependence of the Kinetic Deuterium Isotope Effect in Thermolysis of Amine Oxide **4**

| T, K | $k_{\text{H}}/k_{\text{D}}$ | T, K | $k_{\text{H}}/k_{\text{D}}$ |
|---------------|-----------------------------|---------------|-----------------------------|
| 363 | 2.204 | 443 | 2.213 |
| 383 | 2.199 | 463 | 2.209 |
| 403 | 2.223 | 483 | 2.214 |
| 423 | 2.200 | | |

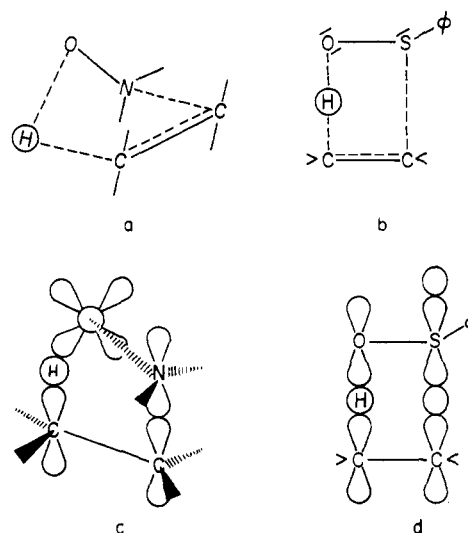


Figure 1.

a bent, cyclic transition state.¹⁸ This picture stands in contrast to the planar, pericyclic transition state of linear H transfer corroborated by the results in Table I for sulfoxide thermolysis.

The origin of these differences in transition-state geometry can be rationalized with the aid of scalar diagrams. If it is assumed that the bonds in the reactant which are changed in the product have been half-altered or half-broken in these transition state constructions, it can be perceived that the rather short C-N bond does not permit a planar structure of linear H transfer (Figure 1a), but the markedly longer C-S distance does (Figure 1b).¹⁹ Moreover, the 2p orbital developing on N concomitantly with the breaking of the C-N bond (Figure 1c) clearly experiences repulsive interaction with the filled oxygen orbitals at the relatively short O-N distance. These circumstances must bring about a staggering of p orbital conformations reminiscent of the O-O interactions in peroxides²⁰ which enforce a skewed conformation in cyclic hydrogen bonding of peracids.²¹ This factor also tends to accommodate angular H transfer from the p orbital on carbon emerging from the in-

cient formation of the olefin product (Figure 1c). A similar effect does not seem to occur in the sulfoxide case since the large, diffuse 3p orbital developing on sulfur (Figure 1d) experiences little repulsive interaction with the more remote oxygen at a dihedral angle of 90° ²² and is, therefore, of diminished influence on the attainment of the planar orbital arrangement necessary for linear H transfer. An alternative interpretation may be based on the relatively short O-N bond compared with the longer C-S distance. The longer S-X bond distance together with the more easily compressed X-S-Y compared with X-N-Y angles argues for a sulfoxide transition state that can more readily attain the planarity requirement for the pericyclic process than the amine oxide transition state.

It has been noted¹⁴ that the large variation in rates correlated with certain structural changes in the sulfoxide substrate (e.g., steric acceleration) may be due to the oxygen and carbon centers being forced into closer proximity. This shortens the distance of separation of these centers in the transition state and results in the observation of quantum mechanical tunneling in H transfer. Possibly, this is also causing the variation of activation parameters (curvature of the Arrhenius plot) noticed before.² We are presently studying these aspects, and their mechanistic origin(s) more closely.

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- Note that C-N is ~ 1.5 , C-S is ~ 1.8 Å (see P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, 46 (1950)); for the transition states this difference will be larger, owing to the larger polarizability of C-S bonds. This leads to a much greater β -C-O distance for the sulfoxide transition state (2.5-3 Å) compared with that in amine oxides assuming a planar transition state (~ 2 Å).
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- A repulsive S-X interaction in RSXR has been discussed by H. E. Van Wart, A. Lewis, H. A. Scheraga, and F. D. Saeva, *Proc. Natl. Acad. Sci., U.S.A.*, **70**, 2619 (1973), originating in the repulsion between the 3p lone pairs which is minimal at a dihedral angle of 90° . D. B. Boyd, *J. Am. Chem. Soc.*, **94**, 8799 (1972), has deduced there is also an attractive component involving $3p_\pi-3d_\pi$ overlap between the sulfur atoms. A composite of these

effects would suggest, therefore, that the 90° planar representation of the five-membered pericyclic transition state in Figure 1d corresponds to an energy minimum among alternative structures of the transition state. This assumes, of course, that RSSR' and RSOR' exhibit comparable overall molecular geometries as concluded by J. P. Snyder, *ibid.*, **99**, 2931 (1977).

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Hydrogen Atom Transfer Reactions in the Photochemistry of Tetrasubstituted Cyclopropenes¹

Sir:

The photochemical behavior of the cyclopropene ring has been shown to be remarkably dependent on the multiplicity of the excited state involved.²⁻⁴ Singlet states react by σ -bond cleavage to give products which are explicable in terms of the chemistry of vinylcarbenes,² while triplet states, generated by sensitization techniques, give high yields of cyclopropene dimers.^{3,5-9} We now wish to report that the triplet states of tetrasubstituted cyclopropenes which possess γ hydrogens undergo an intramolecular hydrogen-transfer reaction by a mechanism analogous to the well-known Norrish type II photoreaction of carbonyl compounds. In this communication we describe some of the salient features of this reaction.

Direct irradiation of 1,2-diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (**1a**) in benzene with Pyrex-filtered light afforded a 1:1 mixture of 1,2,6-triphenyl-3-methyl-1,3-hexadiene (**2**) and 1,2-diphenyl-3-(3-phenylpropyl)-1,3-butadiene (**3**). The formation of **2** and **3** can be most economically accounted for by ring opening of the excited singlet state of **1** to

