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# Transition states in Ei reactions

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## Abstract

The pyrolysis of amine oxides, sulfoxides, selenoxides, and esters to form alkenes is believed to be a concerted reaction with a cyclic transition state. Phosphine oxides, sulfones, and nitro compounds are unreactive. This study seeks to identify reasons for the lack of reactivity of the latter. Transition states were located for all substrates progressing from RHF/3-21G\* to the MP2/6-31+G(d,p) level (in certain cases). For sulfones and nitro compounds, two possible reasons for lack of reactivity were considered: (1) Atoms approaching one another in the transition state may be considered to participate in a local  $n_{\text{O}} \rightarrow \sigma_{\text{CH}}^*$  interaction. The second oxygen in the sulfone or nitro compound lowers the energy of the "non-bonded electrons" at oxygen leading to a greater mismatch in energy with the antibonding C—H orbital (in comparison to the sulfoxide or amine oxide). (2) The sulfone and nitro "lone pairs" are not really "alone," and available to react. In fact, complex bonding arrangements exist in the  $\text{SO}_2$  and  $\text{NO}_2$  groups. The situation is less clear for phosphine oxides, although ground state stability of bonds is important. Implications concerning the Hammond postulate are covered.

**Keywords:** elimination reactions, Hammond postulate, transition states

Internal elimination to form alkenes (Ei) by pyrolysis of certain "oxides" is believed to be a concerted reaction and to proceed through the cyclic five-membered transition state shown in Fig. 1.<sup>[1,2]</sup> The reaction of amine oxides (**1**), now termed the Cope Elimination, occurs

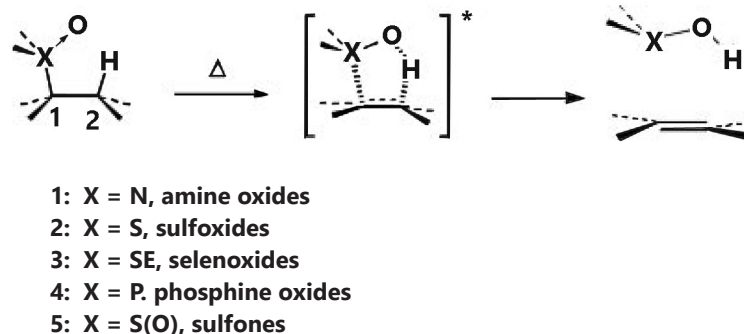
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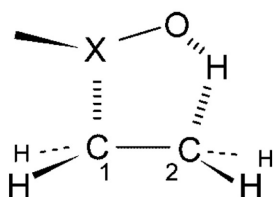
**Figure 1.** The E<sub>i</sub> reaction

at 100–130 °C.<sup>[3–5]</sup> A very low temperature reaction of **1** has been reported in dipolar aprotic solvents by Cram and coworkers.<sup>[6,7]</sup> Reactions of sulfoxides (**2**)<sup>[8–11]</sup> and selenoxides (**3**)<sup>[12–17]</sup> occur at 80–120 °C and at 0–100 °C, respectively. Jursic,<sup>[18]</sup> Jenks<sup>[19,20]</sup> and coworkers were the first to conduct detailed theoretical investigations of transition state behavior.<sup>[18–20]</sup> Pyrolysis of esters and xanthates to form alkenes require much higher temperatures. These have received intensive synthetic, theoretical, and mechanistic inquiry.<sup>[21–29]</sup>

Studies of sulfoxide pyrolysis by Kwart *et al.* suggested that bond breaking and bond making processes were not completely synchronized.<sup>[30]</sup> Kwart *et al.* found low isotope effects ( $k_H/k_D$ ) of 2.4–3.2, with normal pre-exponential factors, for phenyl heptyl sulfoxide. However, very low  $A_H/A_D$  factors are found for *t*-butyl ethyl sulfoxide.<sup>[30]</sup> Yoshimura *et al.*<sup>[31]</sup> found quite different data that are difficult to interpret.

In the case of amine oxides, Kwart *et al.* found very low but constant  $k_H/k_D$  values (2.2) over a large temperature range.<sup>[30]</sup> Kwart envisioned an envelope-shaped transition state due to the steric problem of locating hydrogen between closely spaced carbon and oxygen. Calculations of the present study predict isotope effects of 2.9 for sulfoxide **2**, and 2.8 for amine oxide **1**.

A long-standing mystery is why phosphine oxides (**4**) and sulfones (**5**) do not easily undergo similar reactions.<sup>[1]</sup> In one of the few known cases of a phosphine oxide E<sub>i</sub> reaction, Bailey *et al.*<sup>[32]</sup> found reaction at 325 °C. In the sole case of an E<sub>i</sub> for sulfones, Jenks and co-workers<sup>[33]</sup> carried out experimental as well as theoretical studies of sulfone pyrolysis. High temperatures again were necessary.

**Table 1.** Effect of method and basis set on transition structure bond distances (nm)

Compound	Method/Basis set <sup>a</sup>	C <sub>1</sub> —X	C <sub>1</sub> —C <sub>2</sub>	C <sub>2</sub> —H	X—O	O—H
Amine oxide, <b>1-ts</b>	(A)	0.179	0.143	0.151	0.134	0.112
<b>1-ts</b>	(B)	0.205	0.141	0.137	0.135 <sup>b</sup>	0.124
<b>1-ts</b>	(C)	0.198	0.141	0.142	0.135	0.120
<b>1-ts</b>	(D)	0.198	0.141	0.141	0.136	0.120
Sulfoxide, <b>2-ts</b>	(A)	0.228	0.141	0.140	0.155	0.121
<b>2-ts</b>	(B)	0.242	0.141	0.137	0.158 <sup>b</sup>	0.125
<b>2-ts</b>	(C)	0.234	0.141	0.140	0.159	0.121
Selenoxide, <b>3-ts</b>	(B)	0.248	0.142	0.135	0.171 <sup>b</sup>	0.127
Phosphine oxide, <b>4-ts</b>	(A)	0.216	0.143	0.175	0.156 <sup>b</sup>	0.103
<b>4-ts</b>	(B)	0.235	0.141	0.150	0.158	0.116
<b>4-ts</b>	(C)	0.229	0.141	0.153	0.160	0.113
<b>4-ts</b>	(D)	0.230	0.142	0.151	0.159	0.114
Sulfone, <b>5-ts</b>	(B)	0.246	0.140	0.135	0.155	0.129
Nitro, <b>6-ts</b>	(B)	0.221	0.139	0.137	0.127	0.127
<b>6-ts</b>	(C)	0.209	0.139	0.139	0.128	0.124

a. A=RHF/6-31+G(2d,p); B=B3LYP/6-31+G(2d,p); C=MP2/6-31+G(2d,p) D=QCISD/6-31+G(d,p).

b. The starting material X-O bond distance is: X=N, 0.136 nm; S, 0.151 nm; Se, 0.166 nm; P, 0.149 nm.

### Nature of the transition states

Transition states were located for all substrates **1-5**, and the structures were calculated to be planar in all cases.<sup>[18,20]</sup> For **2**, The resulting C<sub>2</sub>—C<sub>1</sub>—S bond angle is *ca.* 98° using most basis sets. The hydrogens of the developing H<sub>2</sub>C=CH<sub>2</sub> unit remain *ca.* 17° from planarity at the transition state, with the hydrogens at C<sub>1</sub> were somewhat closer to planarity than the hydrogens at C<sub>2</sub>, perhaps due to carbanionic character in the latter (Table 2). The C<sub>1</sub>—C<sub>2</sub> bond distance at the transition state (0.141 nm) is midway between single (*ca.* 0.152 nm) and double bond distances (0.134 nm) and remarkably similar for reactive versus unreactive 'oxides'.<sup>[28]</sup> For **2-ts** and **3-ts**, the C<sub>2</sub>—H—O angle is fairly close to linearity (*ca.* 155°), but for the amine oxide, **1-ts**, the C<sub>2</sub>—H—O angle is 144°. The greater congestion imposed by the short C—N bond leads to lack of space between oxygen and C<sub>2</sub>, which forces

**Table 2.** Mulliken charge densities and calculated activation energies for the E<sub>i</sub> reaction [B3LYP/6-31+G(2d,p)]

Structure	X	C <sub>1</sub> <sup>a</sup>	C <sub>2</sub> <sup>a</sup>	H <sup>b</sup>	O	Activation energy, (kcal/mol)
<b>1-ts</b>	0.16	0.10	-0.33	0.37	-0.38	20
<b>2-ts</b>	0.44	0.13	-0.36	0.39	-0.56	26
<b>3-ts</b>	0.45	0.02	-0.26	0.39	-0.54	21
<b>4-ts</b>	0.61	0.08	-0.33	0.39	-0.25	54
<b>5-ts</b>	0.68	0.17	-0.27	0.42	-0.57	43
<b>6-ts</b>	0.01	0.20	-0.23	0.41	-0.25	42

a. Combined charges are shown for the (CH<sub>2</sub>) group of atoms.

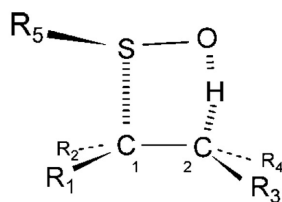
b. Hydrogen undergoing bond breakage in the transition state.

hydrogen outward from linearity, as recognized by Kwart *et al.*<sup>[30]</sup> The nonlinear C—H—O atoms are, in general, consistent with low isotope effects.<sup>[34,35]</sup>

The transition states for the phosphine oxide **4-ts** and for the sulfone **5-ts** were easily located and found to be similar to **1-ts** and to **2-ts** in geometry and in calculated charge densities (Tables 1 and 2). No obvious stereoelectronic reasons for the lack of reactivity of **4** and **5** seem evident. All methods and basis sets placed a slight positive charge density on C<sub>1</sub> and somewhat more negative charge density on C<sub>2</sub>, the carbon losing hydrogen (Table 2).

For **1-3**, the calculated reactivities [B3LYP/6-31+G(2d,p)], seem roughly in accord with experiment, except that the amine oxide (**1**) persistently comes out rather low in activation energy (Table 2).<sup>[1,18]</sup> Selenoxides **3** are predicted to be the next most reactive, followed by sulfoxides **2**.<sup>[20]</sup> The calculated activation energy for **2** compares favorably with experimental activation enthalpies (25–28 kcal) determined in systems that form simple unstabilized alkenes.<sup>[1]</sup> In contrast, the phosphine oxide **4** and the sulfone **5** gave high activation energies in accord with their lack of reactivity.<sup>[33]</sup>

Transition structure bond distances were found to be somewhat different using different methods and basis sets (*cf.* Table 1). Some transition structures were determined at the presumably more accurate MP2/6-31+G(2d,p) and at the QCISD/6-31+G(d,p) level (both with difficulty). The MP2 and QCISD data were in between Hartree–Fock and density functional data, but rather similar to the latter. All subsequent

**Table 3.** Bond distances (nm) in substituted sulfoxides transition structures [B3LYP/6-31+G(2d,p)]

Structure <sup>a</sup>	C <sub>1</sub> —S	C <sub>1</sub> —C <sub>2</sub>	C <sub>2</sub> —H	S—O	O—H
<b>2-ts</b> R <sub>5</sub> =CH <sub>3</sub>	0.242	0.141	0.137	0.158	0.125
<b>2a-ts</b> (syn) <sup>b</sup> R <sub>1</sub> =R <sub>5</sub> =CH <sub>3</sub>	0.251	0.141	0.133	0.158	0.128
<b>2b-ts</b> (anti) R <sub>2</sub> =R <sub>5</sub> =CH <sub>3</sub>	0.247	0.141	0.135	0.158	0.126
<b>2c-ts</b> R <sub>1</sub> =R <sub>2</sub> =R <sub>5</sub> =CH <sub>3</sub>	0.256	0.142	0.131	0.158	0.130
<b>2d-ts</b> (syn) R <sub>3</sub> =R <sub>5</sub> =CH <sub>3</sub>	0.244	0.141	0.135	0.158	0.127
<b>2e-ts</b> (anti) R <sub>4</sub> =R <sub>5</sub> =CH <sub>3</sub>	0.245	0.141	0.135	0.158	0.127
<b>2f-ts</b> R <sub>3</sub> =R <sub>4</sub> =R <sub>5</sub> =CH <sub>3</sub>	0.245	0.141	0.133	0.158	0.128
<b>2g-ts</b> (anti) R <sub>2</sub> =CF <sub>3</sub> , R <sub>5</sub> =CH <sub>3</sub>	0.241	0.141	0.139	0.158	0.122
<b>2h-ts</b> (anti) R <sub>4</sub> =CF <sub>3</sub> , R <sub>5</sub> =CH <sub>3</sub>	0.232	0.141	0.144	0.158	0.118
<b>2i-ts</b> R <sub>5</sub> =CF <sub>3</sub>	0.250	0.141	0.130	0.156	0.133

a. Substituents R<sub>1</sub> to R<sub>4</sub>, are hydrogen, unless otherwise specified.

b. "Syn" refers to the orientation of the C<sub>1</sub> or C<sub>2</sub> substituent and the S—CH<sub>3</sub> group in the cyclic transition structure.

data in this paper will refer to the more accessible B3LYP/6-31+G(2d,p) calculations, unless otherwise specified.<sup>[18]</sup>

Steric problems to coplanarity in the sulfoxide **2** can be imposed by adding substituents to C<sub>1</sub> or to C<sub>2</sub> (Table 3). Methyl substitution at C<sub>1</sub> for **2a-ts** (C<sub>1</sub> methyl syn to S—CH<sub>3</sub>) leads to a C<sub>2</sub>—H—O—S dihedral angle of 10°, i.e., still close to planarity. However, in **2a-ts**, the C—S bond distance has extended to 0.251 nm, compared to 0.242nm for **2-ts**. The transition state avoids steric hindrance by adjusting bond distances, whereas ground state molecules usually modify bond angles or torsional interactions.<sup>[36]</sup> The anti structure **2b-ts** shows a less extended C<sub>1</sub>—S bond (0.247 nm).

## Reactivity

A possible reason for the ease of reaction of selenoxides concerns the weak and easily broken C—Se bond.<sup>[14,15]</sup> In order to roughly estimate the effect of C<sub>1</sub>—X bond strength on reactivity, heterolytic

bond dissociation energies were determined by calculation on ground state molecules. Experimental values seemed rather variable and often involve compounds of inappropriate structure.<sup>[37–39]</sup> Heterolytic bond dissociation energy for  $\text{H}_3\text{C—Se(O)CH}_3$  (to form  $\text{CH}_3^+$  and  $^-\text{O—SeCH}_3$ ) indeed was low (229 kcal) compared to the analogous sulfoxide (239 kcal) or amine oxide (240 kcal). For the phosphine oxide, the  $\text{H}_3\text{C—P(O)(CH}_3)_2$  dissociation energy (257 kcal) was high and consistent with its lack of reactivity. For the sulfone, the carbon–sulfur bond dissociation energy is very low, 220 kcal. Thus, the weak bond should make **5** highly reactive, which is not the case. However, the same stabilization that  $\text{CH}_3\text{SO}_2^-$  enjoys relative to  $\text{CH}_3\text{SO}^-$  should reduce the ability of its oxygen to bond to hydrogen in the transition state. It is noteworthy that the C—S bond distance is longer, but the O—H distance is less fully established for the sulfone **5-ts** compared to the sulfoxide **2-ts** (Table 1).

A more subtle way of enhancing the leaving group ability of sulfur is to replace the  $\text{S(O)—CH}_3$  group of **2-ts** with  $\text{S(O)—CF}_3$ , as in **2i-ts**. Table 3 lists the changes in bond distances relative to **2-ts**.

In **2i-ts**, the C—S distance is lengthened to 0.250 nm, compared to 0.242 for the parent compound, **2-ts**. The less basic oxide oxygen shows a larger O—H separation in the transition structure and the C—H bond is correspondingly less extended, rather similar to **5-ts**. The positive charge on the carbon bearing sulfur,  $\text{C}_1$ , is somewhat increased. The activation energy for **2i** is **less** than that of **2** by *ca.* 1.5 kcal, perhaps due to a slight ground state destabilization of **2i** imposed by the  $\text{S—CF}_3$  group. In contrast, the sulfone, **5**, may experience ground state stabilization due to the bonding arrangements in the  $\text{SO}_2$  group (see below).

## Nitro compounds

At the suggestion of a colleague, nitro compounds (**6**) were investigated in order to provide another case of an  $\text{XO}_2$  system versus an  $\text{X—O}$  system (i.e., **1**), similar to sulfones (**5**) versus sulfoxides (**2**). Experimentally, pyrolysis of nitroethane to form alkenes occurs with high activation energy (41.5–47 kcal/mol).<sup>[40]</sup> This reaction is seldom used preparatively, perhaps because of reluctance of chemists to heat nitro

compounds strongly. Batt<sup>[40]</sup> has suggested a free radical process for the mechanism of elimination, but the mechanism was considered to be uncertain.

Nitroethane, **6**, is calculated to form ethylene by a planar cyclic Ei transition state. The activation energy (42 kcal) is much higher than the amine oxide **1** case (*ca.* 20 kcal), similar to **5** versus **2**.

## Rationale

The first attempt to explain the lack of reactivity of **4**, **5**, and now **6**, involves the interaction of the "oxide" oxygen with C<sub>2</sub>—H in the transition state. Although the quantum calculations necessarily involve multi-center orbitals encompassing many atoms, Hoffman has emphasized the advantage of considering localized orbitals centered on individual atoms in arriving at a concept of chemical reactions.<sup>[41,42]</sup> The use of the "Natural Bond Order" (NBO) approach provides a method of approximating localized interactions.<sup>[43,44]</sup> The orbital on oxygen that forms a bond to hydrogen might be approximated as a non-bonding orbital, i.e., an 'n' orbital. The C—H bond into which the n electrons formally move involves a local antibonding orbital,  $\sigma^*_{\text{CH}}$ . The local HOMO/ LUMO interaction might be described as a local  $n_{\text{o}} \rightarrow \sigma^*_{\text{CH}}$  interaction.

One interpretation of high reactivity of **1-3** centers on the local HOMO. The oxygen lone pair electrons are not engaged in substantial chemical bonding, and should be high in energy.<sup>[42]</sup> The energy difference between the lone pair and the putative (C—H)\* antibonding orbital is not large, i.e., the  $n_{\text{o}} \rightarrow \sigma^*_{\text{CH}}$  transition state interaction is relatively favorable. For **5** and **6**, the second oxygen lowers the energy of the HOMO by virtue of its electronegativity. A considerably higher energy mismatch occurs between these orbitals and the putative (C—H)\* and the formation of the transition state occurs less readily. A similar interpretation may be used to account for the weak hydrogen bonds of nitromethane or dimethyl sulfone to alcohols or water.<sup>[45,46]</sup> However, the high reactivity of **2h** should be remembered.

The NBO program provides a quantitative measure of these interactions, which is termed the "stabilization energy."<sup>[44]</sup> Unfortunately, the program identifies different interactions in **1-ts-6-ts** as important



in the transition state. For **2-ts** and **3-ts**, the "oxide" interacts with  $\sigma_{\text{CH}}^*$  with "stabilization energy,"  $n_{\text{o}} \rightarrow \sigma_{\text{CH}}^*$  of 107 and 102 kcal. In contrast, ground state molecules rarely show any "stabilization energy" of more than *ca.* 10kcal.

For the S-CF<sub>3</sub> sulfoxide, **2i-ts**,  $n_{\text{o}} \rightarrow \sigma_{\text{CH}}^*$  drops to 84 kcal. For the C<sub>2</sub>—CF<sub>3</sub> substituted sulfoxide, **2h-ts**, in which the C<sub>2</sub>—H bond is "activated" by CF<sub>3</sub>,  $n_{\text{o}} \rightarrow \sigma_{\text{CH}}^*$  increases to 147 kcal.

However, for both **1-ts** and **4-ts**, the program considers the transition state to be so advanced that a lone pair is present at C<sub>2</sub>, which interacts with an antibonding H—O localized orbital, i.e.,  $n_{\text{C}} \rightarrow \sigma_{\text{OH}}^*$ , with **1-ts** showing the larger "stabilization energy" (177 vs. 107 kcal). For **5-ts** and **6-ts**, the dominant interaction is considered to be between the incipient C<sub>1</sub>—C<sub>2</sub>  $\pi$  bond with  $\sigma_{\text{OH}}^*$ . Due to the variability of the presumed dominant interaction, and the fact that the numerical data are extremely variable depending upon method and basis set, no detailed interpretation seems worthwhile.

Gas phase proton affinity data are a way to gauge the ability of a ground state "oxide" to interact with a proton donor. Nitromethane has an exceedingly low proton affinity (180 kcal), with phenyl methyl sulfone (194 kcal) somewhat higher. Dimethyl sulfoxide (211 kcal) and trimethyl amine oxide (235 kcal) show high proton affinities.<sup>[47,48]</sup> Trimethyl phosphine oxide is remarkably high (217 kcal), although much lower than the amine oxide. Other work shows that trimethyl phosphine oxide hydrogen bonds to alcohols more weakly than trimethyl amine oxide.<sup>[49]</sup>

A second interpretation for the unreactivity in **5** and **6** involves the putative "lone pairs" shown in Lewis structures found in textbooks. The "lone pairs" on the oxygens are not in fact "alone." The X atom and two oxygens are engaged in complex bonding arrangements not only in the *y* direction (formal textbook *p* orbitals), but also in the *x-z* plane. The Lewis structures commonly shown for the sulfone and nitro group in textbooks are inadequate and give rise to false expectations.<sup>[50]</sup> As the transition state forms, the benefit from the developing O—H bond is opposed by the loss of bonding among the XO<sub>2</sub> electrons. In contrast, the visual representation of the lone pair of the sulfoxide oxygen seems more classical in nature.<sup>[51]</sup>

For the phosphine oxide, **4**, the reason for the lack of reactivity is less clear, although the high ground state bond energy of the C—P

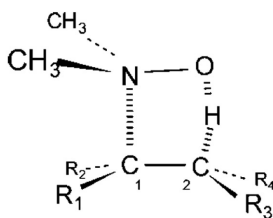
and "P=O" bonds are certainly a factor.<sup>[50]</sup> Calculated results for the hypothetical reaction  $(\text{CH}_3)_{2(3)}\text{X}+\text{O}\rightarrow(\text{CH}_3)_{2(3)}\text{X}-\text{O}$  are: X=N (-106 kcal), S (-131), Se (-129), and P (-178). This illustrates an extremely high stabilization of the phosphorus—oxygen bond. In the Ei reaction, the phosphorus—oxygen bond changes from its initial state to essentially a P—O single bond in the initial product. The product of elimination,  $\text{R}_2\text{P}-\text{OH}$ , is unstable relative to  $\text{R}_2\text{PH}=\text{O}$ .<sup>[50]</sup> However, the calculated energy difference in these two structures is *ca.* 6 kcal, and this relatively small value probably does not play a large role in the very high activation energy. Despite the stability of the O—H bond in  $\text{R}_2\text{P}-\text{O}-\text{H}$ , the so-called "P=O" double bond is preferred in the ultimate product,  $\text{R}_2\text{PH}=\text{O}$ .

The infrared stretching frequencies of the X→O bond correlate quite well with reactivity in the Ei reaction. The experimental infrared "P=O" stretch (*ca.* 1200  $\text{cm}^{-1}$ ),<sup>[49,52]</sup> is higher energy than the S—O stretch of sulfoxides (1060–1045  $\text{cm}^{-1}$ ), and much higher than the N—O stretch in amine oxides (*ca.* 970–950  $\text{cm}^{-1}$ ) and Se—O in selenoxides (822  $\text{cm}^{-1}$ ).<sup>[53,54]</sup> However, the "P=O" stretch is lower in energy than the nitro absorptions (1550 *asym* and 1360  $\text{cm}^{-1}$  *sym*) and one sulfone band (1310 and 1160  $\text{cm}^{-1}$ )<sup>[55,56]</sup>.

### Hammond postulate

The widely-used Hammond postulate predicts that the transition structure of exothermic reactions resemble starting material in geometry and endothermic transition structures resemble products.<sup>[57–61]</sup> The preceding discussion shows quite a number of instances of variable behavior. Unreactive substrates form transition structures that resemble product in some degrees of freedom, but reactant in others (Table 1). For the developing  $\text{C}_1-\text{C}_2$   $\pi$  bond, little difference is seen between reactive and unreactive molecules. For the reactions of this study, a More O'Farrell<sup>[62]</sup> plot in three dimensions is probably of greater value, although this treatment lacks predictive capacity.<sup>[63]</sup>

In fact, a case could be made for a more intuitive approach. A structural change stabilizing a certain part of the transition structure, *e.g.*, the carbanionic center,  $\text{C}_2$ , *lengthens* the  $\text{C}_2-\text{H}$  bond undergoing scission. Examples (Table 3) include the sulfoxide **2h-ts**, where  $\text{C}_2-\text{CF}_3$

**Table 4.** Bond distances (nm) in substituted amine oxide transition structures [B3LYP/6-31pG(2d,p)]

Structure <sup>a</sup>	C <sub>1</sub> —N	C <sub>1</sub> —C <sub>2</sub>	C <sub>2</sub> —H	N—O	O—H
<b>1-ts</b>	0.205	0.141	0.137	0.135	0.124
<b>1a-ts</b> , <sup>b</sup> R <sub>1</sub> =R <sub>2</sub> =CH <sub>3</sub>	0.226	0.143	0.126	0.134	0.136
<b>1b-ts</b> , R <sub>3</sub> =CH <sub>3</sub>	0.208	0.141	0.135	0.134	0.127
<b>1c-ts</b> , R <sub>3</sub> =R <sub>4</sub> =CH <sub>3</sub>	0.210	0.141	0.133	0.134	0.128
<b>1d-ts</b> , R <sub>3</sub> =CF <sub>3</sub>	0.188	0.142	0.147	0.136	0.116

a. The R groups are hydrogen unless otherwise specified.

b. The transition state of the compound with a single methyl, R<sub>1</sub>=CH<sub>3</sub>, R<sub>2</sub>=H, was optimized at the pBN/DN\*\* level; the data are: 0.220, 0.142, 0.133, 0.135, and 0.130 nm, respectively, in the five categories of the table.

stabilizes the carbanionic center C<sub>2</sub> and the C<sub>2</sub>—H bond distance extends to 0.144nm in the transition structure compared to 0.137nm in the unsubstituted case, **2-ts**. Groups of opposite charge character, i.e., the methyls attached to C<sub>2</sub> in **2d-ts** – **2f-ts**, lead to a contraction of C<sub>2</sub>—H, ultimately to 0.133 nm.

Structural changes stabilizing the somewhat cationic center, C<sub>1</sub>, *lengthen* the C<sub>1</sub>—X bond, as first predicted by Swain and Thornton<sup>[64]</sup> in 1962. Methylation at C<sub>1</sub> as in **2b-ts** (anti structure), results in extension of C—S (to 0.247 nm). The dimethyl analog, **2c-ts** shows further extension, although now relief of steric hindrance is an issue. In contrast, the C<sub>1</sub>—CF<sub>3</sub> analog, **2g-ts**, shows a slightly shortened bond distance of 0.241 nm. Often these changes occur in an inverse complementary fashion, i.e., as the C—S extends, C—H becomes less extended.

The data on substituted amine oxides (Table 4) complement the sulfoxide data. However, relief of steric hindrance is of greater significance in these more compact structures.

## Computational techniques

The Gaussian 03 program was generally used.<sup>[65]</sup> Transition states for **1-6** were located by a trial-and-error search of likely geometries at the RHF/3-21G\* level, followed by moving up in stages to RHF/6-31+G(2d,p) and to B3LYP/6-31+G(2d,p) and higher methods and basis sets, using force constants determined from frequency calculations at the preceding level. Attempts to locate transition states at high levels, directly, were time consuming and not generally successful, even using good geometries, but without force constants. It was necessary to use the "noeigentest" calculation option to determine any transition state successfully. A single imaginary major frequency was observed in each case (the program at times reported very low frequencies that were imaginary). IRC determinations indicated that the transition state thus located was on the reaction pathway (one method and basis set each for **1-5**, usually RHF/ 6-31+G(2d,p)). "QST2" was successful in locating a transition state, but offered few advantages over trial-and-error searches, in our hands. Although Truhlar and coworkers<sup>[66-68]</sup> disparage the use of the B3LYP method, or even of MP2 (they favor MPW1K, which is not available to us), they find QCISD acceptable. Calculations using the MP2 and QCISD methods were successful in some cases, but frequencies could not be determined with our equipment. The "activation energies" quoted in the paper represent transition state energies minus starting material energies (the "sum of electronic and free energies" data were used, which includes a zero-point energy correction). The frequency component is thus not scaled. For **1**, the activation energy using a scaled zero-point energy (scaling factor 0.9804) was 19.85 kcal versus 19.76 kcal using the "sum of electronic and free energies data." For **6**, the difference in activation energy using these two calculation methods was likewise small. The isotope effects were evaluated using the difference in energy of the transition state versus starting materials using the "read isotopes" method of substitution (evaluated at temperature of 110 °C, which is near temperatures used experimentally). The "sum of electronic and free energies" data again were used from the frequency calculation. The  $k_H/k_D$  values were calculated from  $e^{-\Delta E/kT}$  at  $T=110$  °C (converted to Kelvin) as before.

Charge densities were also evaluated using the NPA technique.<sup>[43,44]</sup> These agreed with the Mulliken charge data reported in Table 2

in important aspects ( $C_1$  overall slightly positive;  $C_2$  overall negative). However, charges on X and O were calculated to be extremely large.

Although Hartree–Fock calculations (RHF/6-31+G(2d,p) gave isotope effects similar to the density functional data, activation energies were way off. Incorporation of a second diffuse function [B3LYP/6-31++G(2d,p)] or B3LYP/6-311+G(2d,p), produced small changes and was not further investigated.

The Spartan<sup>®</sup> calculations were performed at the pBp/DN\*\* level. <sup>[51]</sup> Images from Spartan graphically illustrate the complex bonding patterns of  $XO_2$  groups.

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