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Multiple Structure-Reactivity Relationships in the Acid-Catalyzed Breakdown of Meisenheimer Complexes¹

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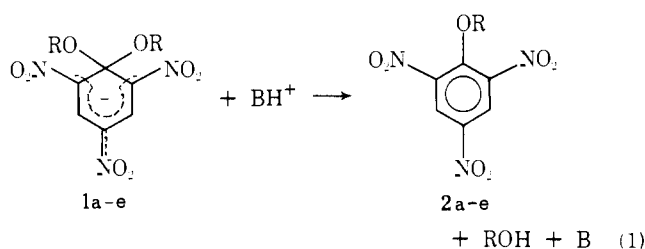
Abstract: Alkoxide ion departure from Meisenheimer complexes of the 1,1-dialkoxy-2,6-dinitro-4-X-cyclohexadienolate type is catalyzed by pyridinium ions and by H₃O⁺ with Brønsted α values ranging from 0.35 to 0.65, indicating concerted acid catalysis. α increases with increasing basicity of the leaving group and at the same time β_{1g} increases with increasing acidity of the catalyst, with $\partial\alpha/\partial pK_{1g} = -\partial\beta_{1g}/\partial pK_{BH^+} = p_{XY} = 0.12$; β_{1g} increases with the basicity of the leaving group, with $-\partial\beta_{1g}/\partial pK_{1g} = p_{Y'} = -0.34$; α also increases when the X substituent is made more electron withdrawing and this increase is accompanied by a corresponding increase in ρ with increasing acidity of the catalyst, with $\partial\alpha/\partial\sigma^- = -\partial\rho/\partial pK_{BH^+} = 1/c_4 = 0.087$ or $p_{XY} = 1/c_4\rho_{eq} = 0.014$. Qualitatively these trends in the structure-reactivity parameters can be rationalized in terms of changing bond lengths and effective charges in the transition state and are easily visualized by placing the transition state on a More O'Ferrall-Jencks diagram. The fact that $p_{XY}/p_{XY'} \gg 1$ indicates, however, that the development of effective charges and the changes in bond length are not synchronous. One contributing factor to this imbalance is attributed to an electrostatic interaction between the polar substituents on the acid catalyst and the leaving group ("Hine effect"). Other reasons for the imbalance are discussed. The water reaction also shows an increase of β_{1g} with increasing pK_{1g} which may be due to a solvation effect.

The transition state of chemical reactions has been one of the focal points of mechanistic interest for a long time. Structure-reactivity relationships have played a central role in attempts to define the structure of transition states,² and the ideas of Polanyi,³ Bell,⁴ Leffler,⁵ and Hammond⁶ have had a great influence on how chemists approach this question. In what is now commonly called the Leffler-Hammond postulate, the transition state is assumed to gradually change from a reactant-like structure in highly exothermic reactions to a product-like structure in highly endothermic reactions, with an intermediate structure in thermoneutral reactions.

There is a growing awareness that *concerted* reactions in which there is a strong coupling between two processes such as proton transfer and bond formation/cleavage between heavy atoms cannot be discussed in terms of simple Leffler-Hammond effects. For such reactions the three-dimensional energy maps introduced by Albery⁷ and made popular by More O'Ferrall⁸ and Jencks⁹ constitute a very useful framework for the interpretation of structure-reactivity effects. This approach allows one to recognize that transition state structure is not only affected by effects along the reaction coordinate ("Leffler-Hammond effects") but by effects perpendicular to it ("Thornton effects"¹⁰). Failure to take the perpendicular

effects into account may lead one to interpret certain results as being in apparent violation of the Leffler-Hammond principle^{2b,11} whereas in fact they are not.^{1b,2a}

In this paper we describe the study of reactions 1 and 2 and discuss the results within the framework of the More O'Ferrall-Jencks diagrams.



a, R = CH₂CH₃; b, R = CH₃; c, R = CH₂OCH₂CH₃; d, R = ClCH₂CH₂; e, R = HC≡CCH₂

Results

All complexes except for 3a could be isolated; 3a was generated in situ as described in the Experimental Section. The rates were determined spectrophotometrically, either in the

Table I. Rate Constants, Solvent Isotope Effects, and Brønsted α and β_{1g} Values for Reaction 1 in Water at 25 °C, $\mu = 0.2$ (KCl)

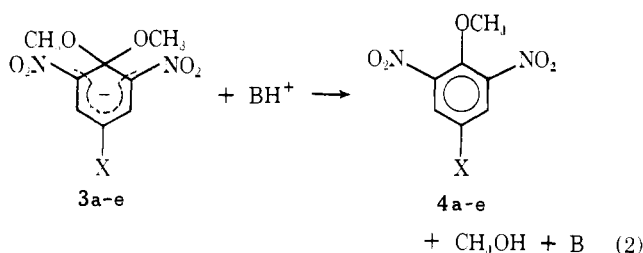
	ROH ($pK_a^{ROH} = pK_{1g}$) ^d					
	C ₂ H ₅ OH (16.0)	CH ₃ OH (15.54)	CH ₃ OCH ₂ CH ₂ OH (14.82)	ClCH ₂ CH ₂ OH (14.31)	HC≡CHCH ₂ OH (13.55)	
$k_0^{H_2O}$, s ⁻¹	3.22×10^{-4} (-0.26)	4.96×10^{-4} (-0.50)	1.65×10^{-3} (-0.82)	6.09×10^{-3} (-1.20)	5.40×10^{-2} (-1.26)	
$k_0^{D_2O}$, s ⁻¹			1.21×10^{-3}		4.19×10^{-2}	
$k_0^{D_2O}/k_0^{H_2O}$			0.73		0.77	
k_{BH^+} , M ⁻¹ s ⁻¹	$\left\{ \begin{array}{l} \gamma\text{-picoline-H}^+ \\ \text{pyridine-H}^+ \\ \text{nicotinamide-H}^+ \end{array} \right.$	3.82×10^{-2} (+0.07)	3.32×10^{-2} (-0.15)	1.10×10^{-1} (-0.47)	1.09×10^{-1} (-0.72)	6.45×10^{-1} (-0.81)
		5.36^b (+0.17)	8.30×10^{-2} (-0.05)	2.65×10^{-1} (-0.37)	2.05×10^{-1} (-0.62)	1.15 (-0.77)
		3.40^b (+0.40)	1.25 (+0.18)	3.83 (-0.14)	2.66 (-0.39)	6.05 (-0.54)
k_{H^+} , M ⁻¹ s ⁻¹ (-1.74 ^b)	8.0×10^3 (+0.96)	3.4×10^3 (+0.74)	2.9×10^3 (+0.42)	9.2×10^2 (+0.17)	8.2×10^2 (+0.02)	
k_{D^+} , ^c M ⁻¹ s ⁻¹	1.4×10^4	6.8×10^3	5.0×10^3	1.45×10^3	9.9×10^2	
k_{D^+}/k_{H^+}	2.04	2.00	1.72	1.57	1.22	
α	0.65 ± 0.02	0.62 ± 0.02	0.53 ± 0.01	0.47 ± 0.02	0.35 ± 0.01	

^a β_{1g} are the numbers in parentheses after the rate constants. ^b pK_{BH^+} . ^c In D₂O. ^d P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **81**, 1050 (1959); **82**, 795 (1960).

Table II. Rate Constants and Brønsted α and Hammett ρ Values for Reaction 2 in Water at 25 °C, $\mu = 0.2$ (KCl)

	X (σ^-)					ρ	ρ_n^a	
	CF ₃ (0.74)	CN (1.00)	SO ₂ CH ₃ (1.05)	NO ₂ (1.27)	SO ₂ CF ₃ (1.65)			
k_0 , s ⁻¹	1.34×10^{-1}	1.30×10^{-2}	1.06×10^{-2}	4.96×10^{-4}	2.56×10^{-4}	-2.9 ± 0.2	-0.47	
k_{BH^+} , M ⁻¹ s ⁻¹	$\left\{ \begin{array}{l} \gamma\text{-picoline-H}^+ (6.23^b) \\ \text{pyridine-H}^+ (5.36^b) \\ \text{nicotinamide-H}^+ (3.40^b) \end{array} \right.$	7.44	8.50×10^{-1}	6.50×10^{-1}	3.22×10^{-2}	2.44×10^{-2}	-2.6 ± 0.2	-0.42
		17.4	1.98	1.72	8.30×10^{-2}	6.51×10^{-2}	-2.6 ± 0.2	-0.42
k_{H^+} , M ⁻¹ s ⁻¹ (-1.74 ^b)		28.0	29.6	1.25	9.0×10^{-1}	-2.3 ± 0.2	-0.37	
α	2.4×10^5	4.7×10^4	4.2×10^4	3.4×10^3	3.3×10^3	-1.9 ± 0.2	-0.31	
	0.55 ± 0.01	0.58 ± 0.01	0.59 ± 0.01	0.61 ± 0.02	0.63 ± 0.02			

^a $\rho_n = \rho/\rho_{eq}$; see text. ^b pK_{BH^+} .



a, X = CF₃; b, X = CN; c, X = SO₂CH₃; d, X = NO₂; e, X = SO₂CF₃

stopped-flow apparatus or in a conventional spectrophotometer. Pseudo-first-order rate constants, k_{obsd} , were measured at a constant ionic strength of 0.2 M (KCl); they are summarized elsewhere^{1b} (355 rate constants).

Buffer catalysis was hardly detectable with neutral (carboxylic) or anionic (H₂PO₄⁻) acids but was appreciable with pyridinium ions. In all cases k_{obsd} obeyed the equation

$$k_{\text{obsd}} = k_0 + k_{\text{BH}^+}[\text{BH}^+] + k_{\text{H}^+}[\text{H}_3\text{O}^+] \quad (3)$$

The rate constants k_0 , k_{BH^+} , and k_{H^+} which are summarized in Tables I and II were determined as follows. Measurements in alkaline solution and in the absence of a buffer provided k_0 for the "water reaction". Typically we measured the rate at three different KOH concentrations (e.g., 0.008, 0.02, 0.04 M) and k_{obsd} was found to be independent of base concentration.

The rate constants for catalysis by the hydronium ion were

determined in dilute HCl solution in all cases except for **3a**; in such solutions eq 3 simplifies to $k_{\text{obsd}} = k_{\text{H}^+}[\text{H}_3\text{O}^+] = k_{\text{H}^+}[\text{HCl}]$. Typically k_{obsd} was measured at three or four different HCl concentrations (e.g., 0.008, 0.012, 0.016, 0.02 M) and excellent linear plots were obtained. In the case of **3a** k_{H^+} was determined in a phosphate buffer (see below).

We also determined k_{D^+} in D₂O for **1a-e**, and $k_0^{D_2O}$ for **1e** and **1c**; they are also included in Table I.

The rate constants for buffer acid catalysis, k_{BH^+} , were determined from the slopes of plots of k_{obsd} vs. $[\text{BH}^+]$ at constant pH. In most cases data at two or three different buffer ratios were collected. The slopes were the same within experimental error, showing that it is the buffer *acid* which catalyzes the reaction.

In most cases the catalytic effect of the buffer was appreciable (two- to threefold rate enhancement over $k_0 + k_{\text{H}^+}[\text{H}_3\text{O}^+]$ for $[\text{BH}^+] = 0.1$ M) but in some cases the effect was quite small, particularly with nicotinamide-H⁺ (~50% rate enhancement at $[\text{BH}^+] = 0.1$ M). Thus the possibility that at least part of the catalytic effect is due to a specific salt effect had to be considered. We determined the effect of replacing KCl with other salts as compensating electrolyte on k_{H^+} and k_{BH^+} (pyridine-H⁺) for the reaction of **1a** and on k_0 for the reaction of **1e**. NaCl, KNO₃, and (CH₃)₄NCl enhance k_{H^+} by about 10% whereas k_{BH^+} seemed to decrease slightly by not more than 10% when NaCl or (CH₃)₄NCl was used. However, this decrease is barely outside the experimental error and hardly significant. Based on these results we are confident that specific salt effects play a minor role and that our k_{BH^+} constants refer to authentic general acid catalysis. This conclusion

is further supported by the excellent adherence of k_{BH^+} to the Brønsted relationship (see below).

The intercepts of plots of k_{obsd} vs. $[\text{BH}^+]$ are given by $k_0 + k_{\text{H}^+}[\text{H}_3\text{O}^+]^{12}$ and provide another method of finding k_0 and k_{H^+} . The agreement between the k_0 and k_{H^+} values coming from the different methods was very good. A variation of this method which leads to higher accuracy because it avoids the extrapolation of k_{obsd} to zero buffer concentration is to work in a buffer which has no catalytic effect, such as $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$. This method was used for the determination of k_{H^+} for **3a** because in dilute HCl the reaction is too fast even for the stopped-flow method.

The rate constants for acid catalysis obey the Brønsted relation very well, with k_{H^+} falling on the same line as the k_{BH^+} values for the pyridine buffers. Figure 1 shows a few representative plots. In most cases we were able to determine k_{BH^+} for three different pyridinium ions (**1b**, **1c**, **1d**, **3b**, **3c**, **3d** = **1b**, **3c**) and in one case for four pyridinium ions (**1e**), but in two cases catalysis by nicotinamide was either too weak to be reliably determined (**1a**) or the rates were too fast to be measurable (**3a**). In view of the strict adherence to the Brønsted relation in all cases we are confident that the Brønsted lines defined by k_{H^+} and two k_{BH^+} values for **1a** and **3a** give just as reliable α values; all α values are summarized in Tables I and II.

Discussion

Mechanism. Murto et al.^{14,15} have studied the acid-catalyzed alkoxide ion departure from a variety of 1,1-dialkoxy-2,4,6-trinitrocyclohexadienates in aqueous solutions. Since they could not detect any buffer catalysis in dilute phosphate buffers they suggested an A1 mechanism,¹⁵ in analogy to the hydrolysis of many acetals.¹⁶ Other apparently specific acid catalyzed breakdown reactions of Meisenheimer complexes have been reported in aqueous¹⁷ as well as in methanolic¹⁸ and ethanolic¹⁹ solution.

These reports contrast with our own results which show that reactions 1 and 2 are *general* acid catalyzed, and with some recent studies by Crampton and Willison²⁰ and by Terrier et al.²¹ It appears that failure to observe general catalysis in some and perhaps most of the earlier studies is due to the use of very low buffer concentrations (0.01 M in many cases) and/or the use of inefficient catalysts which are either not acidic enough or have an unfavorable charge type. Since Meisenheimer complexes are anionic species one would expect cationic acids to be more effective than neutral or even anionic acids.²² This is borne out by our finding that in the reaction of **1e** catalysis by acetic acid is nine times less effective than that of a hypothetical pyridinium ion of the same $\text{p}K_{\text{a}}$.²³

Our Brønsted α values which lie in the range of 0.35–0.65 indicate a concerted mechanism²⁴ with a transition state like **5**. The same mechanism has been proposed for the ring opening of some spiro Meisenheimer complexes.^{20,21c} Our solvent isotope effects for the hydronium ion catalyzed pathway ($k_{\text{D}^+}/k_{\text{H}^+}$, Table I), which are comparable to those found for the spiro complexes,^{20,21c} indicate that the k_{H^+} step probably follows the same mechanism as the buffer-catalyzed steps.²⁵ It is interesting to note the increasing trend in our isotope effect values, from 1.22 for the least basic to 2.04 for the most basic leaving group. This trend toward the value expected for an A1 mechanism is analogous to the increasing trend in α with increasing basicity of the leaving group. A similar observation has been reported for acid-catalyzed aryl oxide ion departure from benzaldehyde methyl aryl acetals.²⁶

Alternative mechanisms for general acid catalysis are unattractive. Rate-limiting proton transfer can be excluded because protonation of the Meisenheimer complex on the alkoxy group is thermodynamically very unfavorable and thus should lead to an α value close to 1.²⁷ Furthermore, if there was a

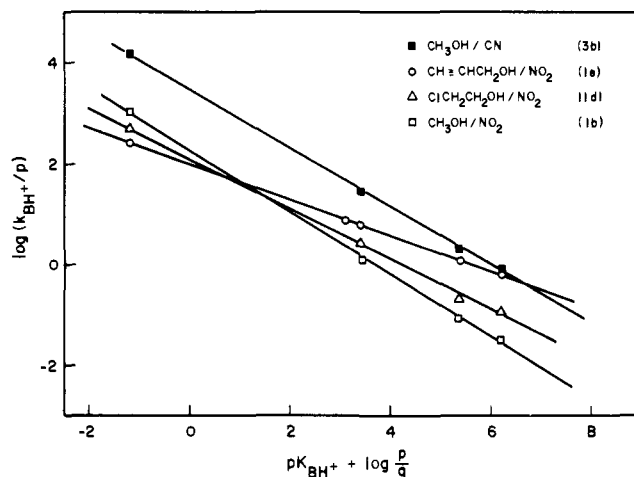
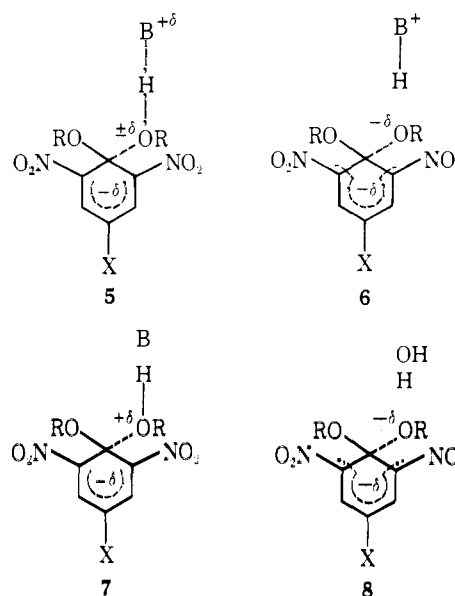


Figure 1. Representative Brønsted plots for general acid catalyzed alkoxide ion departure from Meisenheimer complexes.



trend in α it should be toward increasing values with decreasing leaving group basicity,²⁷ which is opposite to the observed trend. On the other hand, the observed trend in α is perfectly consistent with the concerted mechanism as shown below.

Preassociation mechanisms,²⁴ with transition state **6** or **7**, are also unattractive. **6** implies that in the reverse reaction (base-catalyzed nucleophilic attack by ROH) the addition of RO^- to the aromatic ring is faster than diffusional separation of $\text{RO}^- \cdot \text{HB}^+$. This is inconsistent with known reactivities.²⁸ **7** implies transition state stabilization (rate enhancement) when R becomes more electron donating. Our results (Table I) show, however, that, except for the hydronium ion catalyzed reactions, the rates *decrease* as R becomes more electron donating. Furthermore, our α values are inconsistent with those expected for **6** ($\alpha \approx 0.2$)²⁴ or **7** ($\alpha \approx 0.8$).²⁴

The mechanism of the water reaction (k_0) is probably a simple alkoxide ion departure, assisted by water solvation as shown in **8**, but without a proton transfer taking place in the rate-determining step. Such a proton transfer from water to the leaving group would not confer any significant driving force or, for most leaving groups, would even be thermodynamically unfavorable and thus would violate Jencks' libido rule.^{9,29} The fact that the points for $k_0/[\text{H}_2\text{O}] = k_0/55$ deviate positively from the Brønsted plots by factors of 20 to 10^4 supports the notion of a different mechanism for the water reaction. The

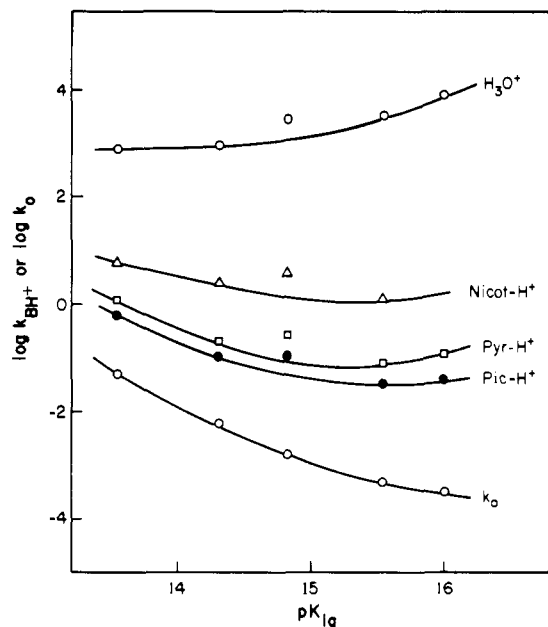


Figure 2. Dependence of rate constants for the acid-catalyzed reactions and the water reaction on the pK of the leaving alcohol. The slope of a tangent to any point of a curve defines a β_{1g} .

solvent isotope effects, $k_0(D_2O)/k_0(H_2O)$, have values (Table 1) typical for similar water reactions^{16b,20,21c} but do not permit firm mechanistic conclusions since the solvent isotope effects on the general acid catalyzed processes are often of the same order of magnitude.^{16b}

Structure-Reactivity Relationships. A. Effect of Changing Leaving Group. The following observations are noteworthy. (1) The Brønsted plots for acid catalysis form a series of lines of different slopes = α (Figure 1: **1b**, **1d**, and **1e**) whereby α decreases with decreasing basicity of the leaving group (Table 1). (2) The Brønsted lines intersect at a point around $pK_{BH^+} \approx 1$. There is a reversal of the reactivity order at this point: with acid catalysts of $pK_{BH^+} > 1$ (all buffer acids used) leaving groups depart more easily when they become less basic whereas the opposite is true for $pK_{BH^+} < 1$ (H_3O^+). This reversal, which appears to violate the reactivity-selectivity principle,^{2a,2b} is a consequence of the concerted nature of the mechanism as further elaborated upon below. (3) Plots of $\log k$ vs. pK_{1g} are curved (Figure 2) with $\beta_{1g}^{30} = \partial \log k / \partial pK_{1g}$ increasing with increasing pK_{1g} , i.e., $p_{xy'}^{31} = -\partial \beta_{1g} / \partial pK_{1g} = -0.34$, corresponding to an anti-Hammond effect.³¹ (4) Comparison of the plots in Figure 2 for different catalysts shows that β_{1g} increases with increasing acidity of the catalyst. Approximate β_{1g} values are summarized in Table 1 (numbers in parentheses after rate constants).

The changes in α with pK_{1g} , and the changes in β_{1g} with pK_{BH^+} , are related through the Cordes^{9,31,32} equation

$$\frac{\partial \alpha}{\partial pK_{1g}} = \frac{\partial \beta_{1g}}{-\partial pK_{BH^+}} = \frac{1}{c_5} = p_{xy'}^{31} \quad (4)$$

A plot of α vs. pK_{1g} (not shown) is linear within experimental error, with a slope $p_{xy'} = 0.12$.

Our results seem typical for reactions in which an alkoxide ion is expelled from an addition compound by a concerted acid catalyzed pathway, such as alkoxide expulsion from addition compounds of a phthalimidium ion^{33a} ($p_{xy'} = 0.07$), from formaldehyde^{33b} ($p_{xy'} = 0.09$), from tosylhydrazone addition compounds³⁴ ($p_{xy'} = 0.05$), from 2-alkoxy-2-phenyl-1,3-dioxolanes³⁵ ($p_{xy'} = 0.08$), and aryl oxide ion expulsion from benzaldehyde aryl methyl acetals²⁶ ($p_{xy'} \approx 0.2$).

A convenient way to visualize these structure-reactivity

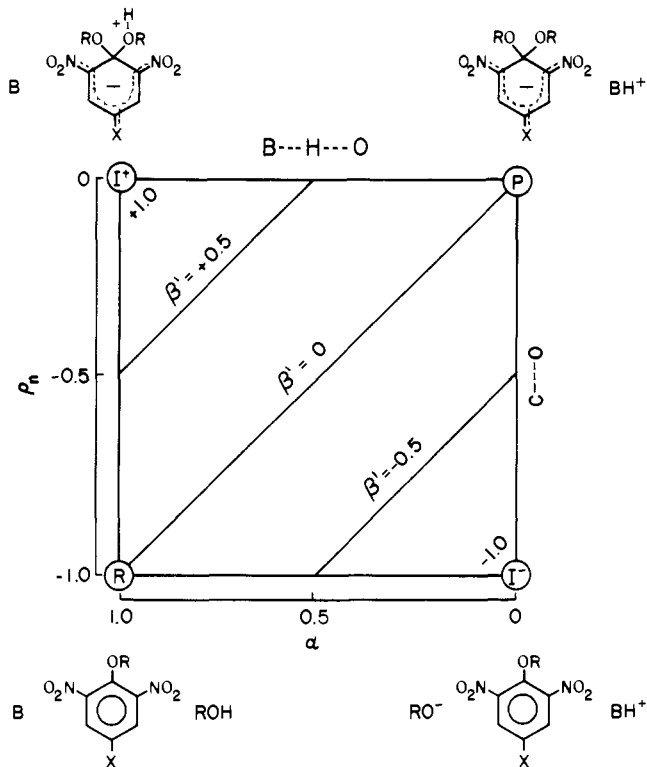


Figure 3. More O'Ferrall-Jencks structure-reactivity diagram. The horizontal axis refers to proton transfer and is defined by the observed α ; the vertical axis refers to C-O bond cleavage or formation and is defined by the observed normalized ρ value. The diagonal $1^+ - 1^-$ is defined by $\beta' = \beta_{1g}$ or β_{nuc} .

relationships is to consider the transition state to be located on a More O'Ferrall-Jencks diagram. We shall use the version of Jencks and Jencks³¹ (Figure 3) where the axes are defined by the *observed* structure-reactivity parameters rather than by bond lengths. Thus the horizontal proton transfer axis is defined by α and the vertical axis for C-O bond cleavage by ρ_n , which is a normalized ρ value which puts it on the same scale as α ³¹ (more on this below). Note that in such a diagram $\beta' = \beta_{1g}$ or β_{nuc} , which corresponds to the charge on the oxygen atom that is "seen" by the substituent on the leaving group, increases from -1 in the 1^- corner to zero on the R-P diagonal to $+1$ in the 1^+ corner.

In Figure 4a we have illustrated the effects of changing the leaving group. As a starting point for discussion we assume a diagonal reaction coordinate with a transition state in the center. An electron-withdrawing substituent on ROH (lower pK_{1g}) will stabilize the 1^- corner (negative charge on oxygen) and destabilize the 1^+ corner (positive charge on oxygen) and thus induces a perpendicular shift of the transition state toward the 1^- corner (arrow 1).³⁶ On the other hand, the relative energies of R and P remain about the same (no charge on oxygen) and thus there is no significant effect along the reaction coordinate. Hence the change which results from a lowering of pK_{1g} is essentially completely determined by the perpendicular effect; it leads to a transition state with less proton transfer and more negative charge on oxygen which is consistent with the observed decrease in α and β_{1g} .

The effect of changing the acid catalyst is illustrated in Figure 4b; increasing the acidity raises the energy of the right-hand edge relative to the left-hand edge of the diagram. This produces a perpendicular shift toward the 1^+ corner (arrow 2)³⁶ and a shift along the reaction coordinate toward the P corner (arrow 3).³⁶ The resulting vector (arrow 4) indicates that there is no significant shift along the proton transfer

axis and α should remain constant, as observed; it also indicates an increase in (positive) charge on oxygen which is consistent with the observed increase in β_{1g} .

Push by Remaining Alkoxy Group. Our reaction series (1a–e) differs from the examples cited from the literature^{26,33–35} in that a change in the leaving group is accompanied by a change in the alkoxy group that is left behind. If “push”^{34,37} by this latter group were significant and depended on the alkyl substituent, this would affect our results in a way which is again most easily visualized with the help of a More O’Ferrall–Jencks diagram (Figure 4c). Making the alkyl group more electron withdrawing would decrease the push which translates into a lowering of the energy of the top edge relative to the lower edge of the diagram. This produces a perpendicular effect toward the I⁺ corner (arrow 5)³⁶ and a shift along the reaction coordinate toward the R corner (arrow 6).³⁶ with a net effect as shown by arrow 7. The overall effect of making the alkyl group more electron withdrawing is found by combining arrows 1 (from Figure 4a) and 7 to produce arrow 8. Thus push leads to a reduction in the extent by which α changes with changing pK_{1g} , i.e., a reduction in p_{xy} so that our experimental value of 0.12 constitutes a lower limit for the true p_{xy} .³⁸ Preliminary results on reactions where the remaining group is being kept constant and the leaving group varied suggest that there is probably some weak but significant push.³⁹

Structure–Reactivity Relationships. B. Effect of Changing the X Substituent. Our findings can be summarized as follows. (1) Making the X substituent more electron withdrawing leads to an increase in α (Table II); the effect is relatively small but it appears to lie outside the experimental error.⁴⁰ (2) Hammett plots (not shown) from which the negatively deviating nitro group has been omitted⁴² are linear. The ρ values are summarized in Table II. There is a trend for ρ to increase (to become less negative) with increasing strength of the catalyst. Similar trends have been reported for phenoxide ion departure from substituted benzaldehyde methyl phenyl acetals.²⁶

The change of α with σ^- , and the dependence of ρ on pK_{BH^+} , are related through the Cordes^{9,31,32} equation

$$\frac{\partial \alpha}{\partial \sigma^-} = \frac{\partial \rho}{-\partial pK_{BH^+}} = \frac{1}{c_4} \quad (5)$$

From a plot of α vs. σ^- (not shown) we obtain $1/c_4 = 0.087$. For the purpose of our discussion below it is advantageous to use normalized ρ values, ρ_n ; ρ_n is defined as ρ/ρ_{eq} where ρ_{eq} refers to the equilibrium addition of methoxide ion to 1-methoxy-2,6-dinitro-4-X-benzene. For lack of a ρ_{eq} value in water we use $\rho_{eq} = 6.2$ calculated on the basis of Terrier’s^{18b} data in methanol; ρ_n values are also summarized in Table II. Normalization of eq 5 gives $p_{xy}^{31} = 1/c_4\rho_{eq} = 0.014$. This compares with $p_{xy} = 0.08$ for the substituted benzaldehyde methyl phenyl acetals.²⁶ In view of the known tendency of ρ values to be somewhat higher in organic solvents compared to water,^{42a} the true ρ_{eq} may be somewhat smaller than the assumed value of 6.2 which would make p_{xy} somewhat larger than 0.014.

It is again easy to visualize the structure–reactivity relationships described by eq 5 with the help of a More O’Ferrall–Jencks diagram (Figure 4d). A more electron-withdrawing X substituent will lower the energy of the upper edge relative to the lower edge of the diagram. The result is a shift along the reaction coordinate toward R (arrow 9)³⁶ and a shift perpendicular to the reaction coordinate toward I⁺ (arrow 10).^{36,43} The result (arrow 11) is a transition state in which proton transfer has made greater progress but where C–O bond breaking is about the same; this is consistent with the observed increase in α and with the fact that the Hammett plots are linear (constant ρ).

In evaluating the effect of increasing the acidity of the catalyst one only needs to refer to Figure 4b again (resulting arrow

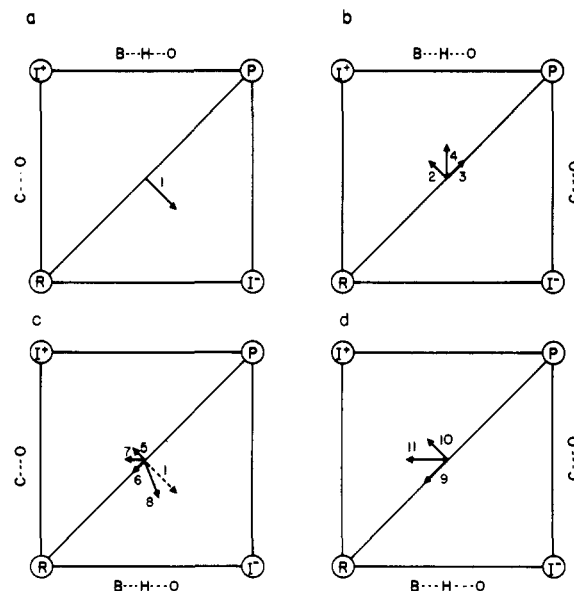


Figure 4. Structure–reactivity diagrams, defined as in Figure 3, showing the effects of making the alkyl and the X group more electron withdrawing and of making BH^+ more acidic; see text.

4) which predicts a shift toward less negative ρ_n values, again as observed.

Imbalance in the Transition State. The definition of the axes of the structure–reactivity diagrams (see Figure 3) requires that the equation

$$\rho_n + \alpha = \beta_{1g} \quad (6)$$

hold and implies that charge development in the transition state is synchronous with bond cleavage/formation. Our experimental results do not fit eq 6 well, implying that one, two, or all three parameters do not accurately measure the changes as assumed. For example, in the reaction of **1b** with $PicH^+$ we have $\rho_n + \alpha = 0.15$ whereas $\beta_{1g} = -0.15$, for the reaction of **1b** with H_3O^+ we have $\rho_n + \alpha = 0.28$ whereas $\beta_{1g} = 0.74$. In the first example the oxygen atom seems to bear a charge which is 0.30 units less positive than implied by $\rho_n + \alpha$, in the second a charge which is 0.46 units more positive than indicated by $\rho_n + \alpha$. A practical consequence of this nonadherence to eq 6 is that structure–reactivity relationships referring to changes in the leaving group (“central atom effects”³¹) cannot be described by the same diagram as those referring to changes in the X substituent (“end atom effects”³¹).

A quantitative measure of these charge imbalances is obtained by differentiating eq 6 with respect to pK_{BH^+} ; since $\partial\alpha/\partial pK_{BH^+} = 0$ (linear Brønsted plots), this affords $\partial\rho_n/\partial pK_{BH^+} = \partial\beta_{1g}/\partial pK_{BH^+}$ or $p_{xy'} = p_{xy}$. The extent by which the ratio $p_{xy'}/p_{xy}$ differs from 1 is a measure of the imbalance. In our system $p_{xy'}/p_{xy} = 0.12/0.014 = 8.55$,⁴⁴ in the case of the substituted benzaldehyde methyl aryl acetals²⁶ $p_{xy'}/p_{xy} = 0.2/0.08 = 2.5$.

Possible reasons for these imbalances have been discussed by Jencks et al.^{31,45} One factor which tends to increase $p_{xy'}$ and decrease p_{xy} is the “Hine effect”,^{31,46} which can be visualized as an electrostatic interaction between electron-donating substituents in the leaving group and electron-withdrawing substituents in the acid catalyst. This effect, which depends only on the distance between the interacting substituents but not on the position of the proton, stabilizes the transition state relative to the separated reactants;⁴⁷ it becomes more pronounced with increasing acidity of the catalyst and increasing basicity of the leaving group and leads to increases in α and β_{1g} with increasing pK_{1g} which are on top of those brought about

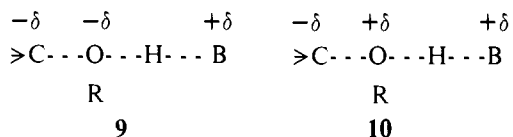
by changes in the bond length, α . It thus tends to make $p_{xy'}$ larger by an amount $p_{xy'}$ (electrostatic) which is equal to τ in the Hine equation³¹ and probably in the order of 0.024.⁴⁶ A factor which might enhance $p_{xy'}$ (electrostatic) somewhat in our system but not in others^{26,33-35} is that making R more electron donating in the leaving group has the same electron-donating effect on the remaining alkoxy group, thereby increasing the leaving group basicity over what would be predicted based on pK_{1g} (defined as pK_a^{ROH}). However, this effect on the total $p_{xy'}$ is counteracted by the push factor (Figure 4c).

Changing the X substituent leads to a "Hine effect" of its own inasmuch as the basicity of the leaving group increases when X is made less electron withdrawing; it leads to $1/c_4$ (electrostatic) < 0 or p_{xy} (electrostatic) < 0 and thus tends to counteract p_{xy} which arises from bond length changes (Figure 4d). Assuming that the leaving group pK follows a Hammett relationship with a ρ value between -1 and -1.5 ⁴⁸ this would lead to $1/c_4$ (electrostatic) = -0.024 to -0.036 or p_{xy} (electrostatic) = -0.004 to -0.006 if τ is again assumed to be 0.024.

With the above estimates for $p_{xy'}$ (electrostatic) and p_{xy} (electrostatic) we can estimate a corrected $p_{xy'}/p_{xy}$ ratio of about 5.0–4.8⁵⁰ compared to the experimental ratio of 8.55; the corrected ratio is still $\gg 1$ and suggests that additional factors are responsible for the imbalance.

The simplest explanation for the remaining imbalance is that the original premise underlying eq 6, namely, that charge development and bond formation/cleavage are synchronous, is invalid. For example, it is unlikely that ρ_n is an exact measure of both C–O bond breaking and charge transfer from the ring to the oxygen atom because the charge is not only borne by the X substituent but is strongly delocalized. Also, there is considerable uncertainty as to how accurately α measures the degree of proton transfer in the transition state even for simple proton transfer reactions.⁵¹

That eq 6 cannot be of general validity can be appreciated on its most fundamental level if one realizes that it would imply that the transition state can be described by only two independent parameters, e.g., by two bond lengths. This would require that the distance between >C and B were fixed and independent of substituents; this is unlikely. Allowing for a variation in the distance between >C and B would, for example, permit a change in transition state structure from **9** to **10** where the C–O and B–H bond lengths are the same as in **9** (presumably implying same α and ρ_n) but where the O–H bond has become shorter, implying more transfer of positive charge to the oxygen atom and thus a larger β_{1g} . In terms of a structure–reactivity diagram a change from **9** to **10** could be visualized as being a motion, perpendicular to the reaction coordinate, of the >C–OR entity toward the proton of a stronger acid.⁴⁵ This would be consistent with our observation of a change from $\rho_n + \alpha > \beta_{1g}$ for weak acids to $\rho_n + \alpha < \beta_{1g}$ for H_3O^+ .



Other possible explanations for the remaining imbalances have been discussed by Jencks et al.^{31,45} We shall mention one, namely, the possibility that a water molecule between the acid and oxygen is carrying the extra positive charge in cases where $\alpha + \rho_n > \beta_{1g}$.

Water Reaction. The most noteworthy feature about the water reaction is that the plot of $\log k_0$ vs. pK_{1g} shows curvature in the same direction as the analogous plots for the acid-catalyzed reactions (Figure 2), i.e., β_{1g} increases with pK_{1g}

(Table I). For the acid-catalyzed reactions the curvature was easily rationalized on the basis of the structure–reactivity diagram in Figure 4a. The same rationalization cannot be used for the water reaction since its mechanism is presumably a simple C–O bond cleavage process; in fact the curvature is opposite to what one would expect on the basis of the Lefler–Hammond postulate.

There is evidence that solvation effects can significantly perturb β_{1g} values in the expulsion of alkoxide ions.^{33b,34,52} In our case an attractive interpretation of the increase in β_{1g} is in terms of solvation of the leaving alkoxide ion which becomes of increasing importance as the basicity of the leaving group increases. This solvation would increasingly counteract the destabilization of the transition state which arises from the increasingly less electron-withdrawing substituents on the leaving group as pK_{1g} increases. As pK_{1g} is increased, this would lead to increasingly larger positive deviations from a presumably linear plot of $\log k_0$ vs. pK_{1g} , just as observed. Note that this is similar to the "Hine effect" which adds increasingly to the stabilization of the transition state of the acid-catalyzed reactions as the pK_{1g} increases.

Another factor which might contribute to the curvature is an increasing push by the remaining alkoxy group as pK_{1g} is increased.⁵³

Experimental Section

Materials. All inorganic salts were analytical grade and used without further purification except for tetramethylammonium chloride, which was recrystallized twice from ethanol. Analytical reagent grade methanol was fractionally distilled and stored over 4A molecular sieves. All the other alcohols were Aldrich reagent grade and were used without further purification. SIC D₂O of 99.8% isotopic purity and Aldrich DCI solution ($>99\%$ D) was used for the isotope effect studies. Pyridine, γ -picoline, and 3-chloropyridine were first dried over BaO and then fractionally distilled and stored under nitrogen in the cold. Buffer solutions were always freshly prepared before each series of kinetic runs. Nicotinamide (Aldrich, $\geq 98\%$) was used without further purification. Dioxane was purified by the method of Fieser⁵⁴ and freshly distilled as needed.

The potassium salts of the 1,1-dialkoxy-2,4,6-trinitrocyclohexadienates (**1a–e**) were prepared by adding 2 equiv of KOH to 1 equiv of picryl chloride, each dissolved in a minimal amount of the respective alcohol. The solution was kept in an ice bath. A precipitate was formed which was thoroughly washed with benzene and ether and recrystallized from an acetonitrile–benzene mixture. The sodium salts of the 1,1-dimethoxy-2,6-dinitro-4-X-cyclohexadienates (**3b**, **3c**, **3e**) were prepared by adding 1 equiv of sodium methoxide dissolved in a minimal amount of methanol to 1 equiv of the respective 2,6-dinitro-4-X-anisole⁵⁵ dissolved in a minimal amount of dry dioxane. A precipitate formed which was washed thoroughly with benzene and ether. Attempts to isolate **3a** were not successful; it was generated in situ in Me_2SO from 2,6-dinitro-4-trifluoromethylanisole⁵⁵ and NaOMe.

Structural proof for the various Meisenheimer complexes was obtained by ¹H NMR and, in some cases, ¹³C NMR. Chemical shifts in $\text{Me}_2\text{SO}-d_6$ relative to internal Me_4Si are summarized in Tables III and IV. The ¹H NMR shifts compare well with those (**1a**, **1b**, **3a–e**) reported in the literature.^{28,56} The integration was also consistent with the structural assignments in all cases. In **1c** and **1d** the two methylene groups have the same ¹H NMR chemical shift; however, their ¹³C shifts are distinctly different and consistent with expectation based on the spectra of appropriate model compounds.⁵⁷ The ring carbon ¹³C NMR shifts of **1c** and **1d** are also consistent with those reported by Olah et al.⁵⁸ for **1b**.

Kinetics. Those reactions which were slow enough for the conventional spectrophotometric method were initiated by syringing 5–30 μL of a concentrated solution of the Meisenheimer complex in Me_2SO into the appropriate buffer solution which had been equilibrated at 25 °C in the spectrophotometer cuvette. When rapid mixing was essential the use of a "plumper" (CalBiochem) allowed us to reduce the mixing time to about 2 s. The fast reactions were monitored in a Durrum-Gibson stopped-flow apparatus. The kinetics was monitored at or near the absorption maximum of the complex, usually between 490 and 560 nm; thus it was immaterial whether the end product was

Table III. NMR Chemical Shifts for the Potassium 1,1-Dialkoxy-2,4,6-trinitrocyclohexadienates in Me₂SO-*d*₆

	B	A	A	C	B	A	B	A	B	A
shift	CH ₃ CH ₂	CH ₃	CH ₃ OCH ₂	CH ₂	ClCH ₂	CH ₂	HC≡C	CH ₂		
¹ H NMR										
A	3.23	3.03			3.34			3.60		4.09
B	1.03				3.34			3.60		3.21
C					3.19					
ring	8.53	8.62			8.56			8.53		8.60
¹³ C NMR										
A					65.4			67.2		
B					72.4			44.8		
C					59.3					
ring					102.9			101.6		
ring					119.6			118.6		
ring					130.9			129.6		
ring					131.2			131.2		

Table IV. ¹H NMR Chemical Shifts for the Sodium 1,1-Dimethoxy-2,6-dinitro-4-X-cyclohexadienates in Me₂SO-*d*₆

X	SO ₂ CF ₃	NO ₂	CN	SO ₂ CH ₃ ^a	CF ₃
δOCH ₃	3.05	3.03	3.00	3.02	3.00
δH _(ring)	8.15	8.62	8.12	8.25	8.02

^a δ of CH₃ in SO₃CH₃: 3.02.

the respective aryl alkyl ether (typical product in acidic solution) or the picrate ion (typical product in basic solution). Excellent first-order plots were obtained over 3–4 half-lives. The pH of the reaction was measured with a Corning Model 12 research pH meter according to standard procedures.

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Tetraoxysulfuranes from Phenols. Synthesis and the Dehydration of Alcohols¹

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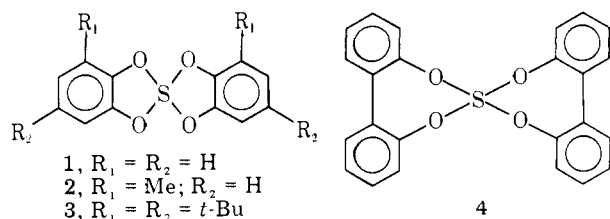
Abstract: Lithium salts of phenols react with SF₄ to form tetraoxysulfuranes. Reaction of **1** with alcohols bearing β-hydrogen atoms leads to olefins by what appears to be a cyclic elimination mechanism from a sulfurane generated by ligand exchange with the alcohol. Borneol and isoborneol give rearrangement products. The products from methanol are guaiacol, dimethyl ether, and dimethyl sulfite in addition to catechol and *o*-phenylene sulfite.

Introduction

Since the isolation of SCl₄³ and SF₄⁴ there has been a continued interest in the generation of stable sulfuranes functionalized with ligands other than halogens⁵ and in studies of their structure-reactivity relationships and their stereochemical dynamics. Extensive examples of the chemical reactivity of a number of oxysulfuranes have been reported.⁶ A suggestion of the extension of the concept of pseudorotation developed for pentacoordinate phosphorus compounds to tetra-coordinate sulfur(IV)⁷ stimulated a number of workers⁸⁻¹⁴ to look for examples of this phenomenon in the sulfuranes. In this report we describe a general synthesis of tetraoxysulfuranes of phenols, some reactions of catechol spiro-sulfurane **1** with alcohols, and an NMR spectrum of **1** which requires that pseudorotation be occurring in this sulfurane.

Results and Discussion

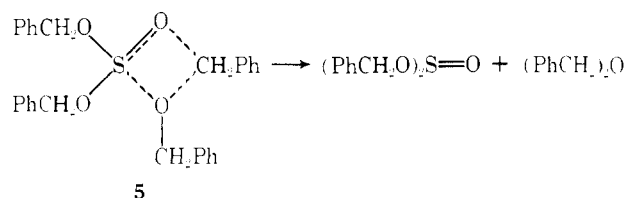
The reaction of sulfur tetrafluoride with lithium salts of phenols provides a general route to stable symmetrical tetraoxysulfuranes. For example, tetraoxysulfurane **1** is formed



by addition of a premeasured quantity of sulfur tetrafluoride to the lithium salt of catechol in scrupulously dry ether at -78 °C under a rigorously dry and oxygen-free nitrogen atmosphere. After removal of excess sulfur tetrafluoride by the nitrogen stream, the inorganic salt is removed by room temperature filtration in a glovebag filled with dry, oxygen-free nitrogen, and the sulfurane is isolated by crystallization at -78 °C. The method is of general utility, and we have also obtained sulfuranes **2**, **3**, and **4** in good yield.

The nature of the intermediates in the reaction of the lithium salts with sulfur tetrafluoride is not clear; however, catechol itself does not react with SF₄ suggesting the importance of the nucleophilicity of the oxygen in the reaction or a coordination of the lithium atom with the departing fluorine atoms. When

the lithium salt of benzyl alcohol was allowed to react with sulfur tetrafluoride under the same conditions, the isolated products were dibenzyl sulfite and dibenzyl ether, presumably arising from collapse of an intermediate sulfurane. This could occur by an electrocyclic mechanism through **5** as previously



postulated for the formation of ethers from dialkoxysulfuranes.^{6b,15}

The tetraoxysulfuranes reported here are exceptionally susceptible to hydrolysis, as has been observed by others.¹⁶

The molecular ion of **1** occurs at *m/e* 248.017 (calcd 248.016), and the 60-MHz spectrum shows a single aromatic proton peak. At 220 MHz this peak is resolved into an AA'BB' pattern centered at 6.95 ppm downfield from internal Me₄Si. The AA'BB' patterns for *o*-phenylene sulfite and catechol, compounds which are always isolated together with the sulfurane, occur at 7.14 and 6.82 ppm, respectively. The 220-MHz NMR is inconsistent with all alternative covalent non-tetra-coordinate sulfur compounds of the correct molecular weight and further requires a structure in which all chemically identical protons are magnetically equivalent or one in which structural interconversions make these protons magnetically equivalent on a time average.

All tetravalent sulfur(IV) compounds for which structures have been determined have been shown to possess a trigonal bipyramidal geometry about sulfur.^{11a,b,12,17} Assuming that tetraaryloxysulfuranes are trigonal bipyramidal, rapid conformational averaging is required in order to account for the AA'BB' coupling pattern. In the absence of such averaging, an ABCD pattern would be expected as a result of inherent differences between apical and equatorial positions.¹⁸

The 220-MHz NMR spectrum of sulfurane **2** at 18 °C shows aromatic absorption centered about 6.82 ppm downfield from Me₄Si and a methyl singlet at 2.25 ppm well separated from the methyl peaks of the 3-methylcatechol, 2.20 ppm, and 3-methyl-*o*-phenylene sulfite, 2.34 ppm, which occur with and cannot readily be separated from the sulfurane. The temper-