Structural Effects on the Transition States of Imine-Forming Eliminations in N-Substituted O-(Arylsulfonyl)hydroxylamines

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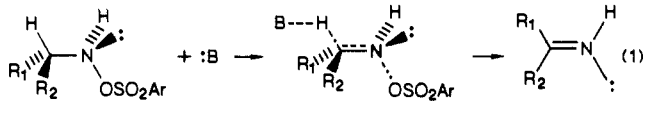
Abstract: A series of amines with various alkyl and aryl substituents at C-1 were converted to the corresponding *N*-(arylsulfonoxy)amines, which served as precursors for base-promoted, imine-forming elimination. By varying the bases used to promote the elimination and by varying the leaving groups attached to nitrogen, the Brønsted parameters β and $\beta_{lg}^{CH_3}$ were determined. These were used to locate the transition state on the More O'Ferrall–Jencks energy surface for elimination. Substituents were found to influence the structure of the activated complex markedly. Resonance effects were most important, while inductive effects had little influence.

Base-promoted elimination reactions have played an important role in the development of methods to examine and conceptualize transition-state structures.[1] These reactions are complicated by the fact that four bonds are being made or broken in the activated complex for E2 reactions. While a variety of transition state probes have been used to characterize transition states of elimination reactions, the most direct indicators of transition-state structure are the extents of bond making and bond breaking that have occurred.

Our interest in elimination reactions has focused on imine-forming eliminations in N-substituted *O*-(arylsulfonyl)-hydroxylamines.[2] These compounds undergo facile bimolecular elimination to imines in the presence of bases (eq 1).[3] Traditional



(1)

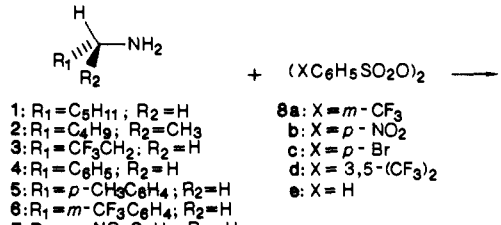
transition-state probes for these E2 reactions indicated that the activated complexes were E1-like, with loss of leaving group well in advance of proton removal.[3]

A more quantitative way to depict the bonding changes in the activated complex was to determine Brønsted parameters for proton removal and leaving group loss and use these to locate the transition state on a More O'Ferrall–Jencks (MOFJ) diagram.[4] While the Brønsted β value could be used as an effective measure of proton removal, it was necessary to develop a modified Brønsted parameter $\beta_{lg}^{CH_3}$, which used methyl-transfer equilibria as free energy models for the kinetic loss of arenesulfonate leaving groups from complicated molecules.[5] The $\beta_{lg}^{CH_3}$ parameter quantitatively describes the extent of bond breaking to arenesulfonate leaving groups in imine-forming eliminations and recently has been applied as a mechanistic probe in solvolysis reactions.[6]

By use of both β and $\beta_{lg}^{CH_3}$ to locate the transition state on the MOFJ energy surface, it is now possible to examine in detail if, and how, structural changes in the elimination precursor affect the activated complex during base-promoted E2 elimination reactions. We report that substitutions at the β-carbon of the elimination substrate cause distinct changes in the transition states of imine-forming eliminations, and these changes can be shown clearly by plotting on MOFJ diagrams.

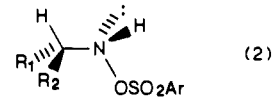
Results

A series of amines **1–7** having alkyl and aryl substituents attached to C-1 were used to evaluate structural effects on the activated complex. These amines were converted to *N*-(arylsulfonyl)oxy derivatives **9–15** by reaction with arylsulfonyl peroxides **8a–e** (eq 2). These derivatives underwent bimolecular



1: $R_1 = C_5H_{11}$; $R_2 = H$
2: $R_1 = C_4H_9$; $R_2 = CH_3$
3: $R_1 = CF_3CH_2$; $R_2 = H$
4: $R_1 = C_6H_5$; $R_2 = H$
5: $R_1 = p\text{-}CH_3C_6H_4$; $R_2 = H$
6: $R_1 = m\text{-}CF_3C_6H_4$; $R_2 = H$
7: $R_1 = p\text{-}NO_2C_6H_4$; $R_2 = H$

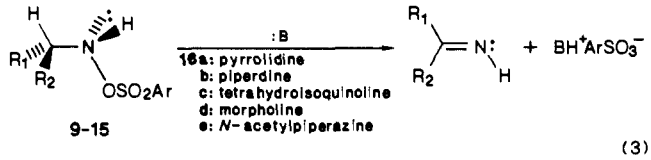
8a: X = *m*-CF_3
b: X = *p*-NO_2
c: X = *p*-Br
d: X = 3,5-$(CF_3)_2$
e: X = H



(2)

9: $R_1 = C_6H_{11}$; $R_2 = H$
10: $R_1 = C_4H_9$; $R_2 = CH_3$
11: $R_1 = CF_3CH_2$; $R_2 = H$
12: $R_1 = C_6H_5$; $R_2 = H$
13: $R_1 = p\text{-}CH_3C_6H_4$; $R_2 = H$
14: $R_1 = m\text{-}CF_3C_6H_4$; $R_2 = H$
15: $R_1 = p\text{-}NO_2C_6H_4$; $R_2 = H$

elimination to imines when treated with amine bases **16a–e** (eq 3). Rates of elimination were measured conductometrically in



16a: pyrrolidine
b: piperdine
c: tetrahydroisoquinoline
d: morpholine
e: *N*-acetylpiperazine

9-15

(3)

2.25 M aqueous THF–ethyl acetate (3:1)[5] (TEW) under pseudo-first-order conditions with respect to the promoting base. Good first-order behavior was observed through at least 2 half-lives in all cases. The second-order rate constants, k_2, were obtained by dividing the pseudo-first-order rate constants, k_{obsd}, by the base concentrations. These values were occasionally checked by plotting k_{obsd} versus the base concentrations. The slopes of these plots yielded k_2 values indistinguishable from those determined from k_{obsd} directly. Brønsted plots of k_2 versus the pK_a's of the promoting bases gave β, the extent of proton removal in the activated complex. The rate data are collected in Table I, a typical Brønsted plot is shown in Figure 1, and the Brønsted β parameters are shown in Table III.

The extent of leaving-group loss in the activated complex was measured by converting each amine to a series of *N*-(arylsulfonyl)oxy derivatives **9a–e** to **15a–e** by reaction with arylsulfonyl peroxides **8a–e**. Morpholine was used as the promoting base for these eliminations, and second-order rate constants were deter-

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Table I. Rate Constants for Elimination in *N*-[[[(Trifluoromethyl)phenyl]sulfonyl]oxy]amines **9a–15a** Promoted by Bases **16a–e** in TEW at −10 °C[a]

		$k_2 \times 10^3$[b]					
base	pK_a[c]	**9a**	**10a**	**11a**	**13a**	**14a**	**15a**
16a	11.27	8.88	4.22	13.5	52.7	186	1050
16b	11.12	4.47	3.37	9.72	24.4	60.9	306
16c	9.41	2.73	1.81	6.33	11.7	28.6	88.2
16d	8.33	1.39	1.04	3.71	7.79	13.6	37.4
16e	7.94	1.02	0.64	1.71	1.96	6.83	22.6

[a] Data for **12a** reported previously in ref 5. [b] Rate constants are the average of several runs (two to four). Agreement between runs was found to be better than ±2%. [c] pK_a (25 °C) were taken from Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; IUPAC Analytical Division Butterworth: London, 1965.

Table II. Rate Constants for *N*-(Arylsulfonoxy)amines **9a–e** to **15a–e** in TEW at −10 °C Promoted by Morpholine

		$k_2 \times 10^3$[a]						
leaving group $XC_6H_4SO_3$	pK_{lg}	**9**	**10**	**11**	**12**	**13**	**14**	**15**
X = *m*-CF_3	−1.33	2.29	1.48	3.71	6.65	7.79	13.6	37.4
X = *p*-NO_2	−2.36	4.24	2.72	7.43	11.7	10.8	26.4	60.4
X = *p*-Br	−0.74	0.92	0.54	1.63	3.02	2.80	5.71	18.6
X = 3,5-$(CF_3)_2$	−2.59	10.8	8.09	19.4	32.0	28.8	57.0	161.
X = H	0.0	0.369	0.21	0.75	2.00	1.40	2.37	11.2

[a] Reported rate constants are the average of several (two to four) runs. Agreement between runs was found to be better than ±2%.

Table III. Brønsted Coefficients β and $\beta_{lg}^{CH_3}$ for C–H Removal and Leaving-Group Loss in Base-Promoted Eliminations in N-Substituted *N*-(Arylsulfonoxy)amines

arylsulfonoxy substrate	β[a]	$\beta_{lg}^{CH_3}$[a]
9	0.24 ± 0.04	0.51 ± 0.06
10	0.22 ± 0.02	0.55 ± 0.07
11	0.22 ± 0.04	0.49 ± 0.06
12	0.30 ± 0.09[b]	0.42 ± 0.05
13	0.32 ± 0.07	0.45 ± 0.07
14	0.35 ± 0.06	0.49 ± 0.05
15	0.43 ± 0.06	0.41 ± 0.07

[a] The reported errors are 1 standard deviation from the least-squares value. [b] These data were reported in ref 5.

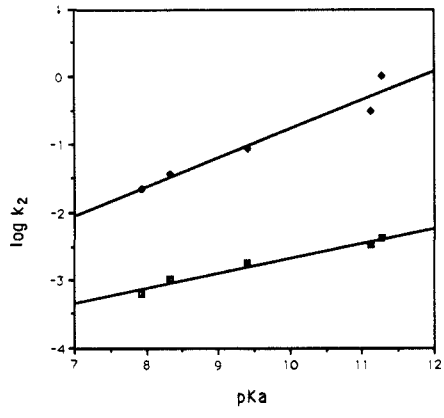


Figure 1. Brønsted plots of second-order rate constant versus pK_a's of the promoting bases **16a–e** for imine-forming eliminations from **10a** (□) and **15a** (■). The slopes of the plots are β, the extent of C–H cleavage in the activated complexes.

mined as described above. Modified Brønsted plots of k_2 versus pK_{lg}[5] gave $\beta_{lg}^{CH_3}$, the extent of leaving-group loss for each substrate. The rate data are collected in Table II, a typical modified Brønsted plot is shown in Figure 2, and the Brønsted parameters are recorded in Table III.

Discussion

The Brønsted parameters β and $\beta_{lg}^{CH_3}$, determined for each *N*-(arylsulfonoxy)amine substrate, provide a direct means of assessing the bonding changes occurring in the activated complex. The β parameter can be taken as a measure of the amount of base–hydrogen bond formation (and by inference the amount of carbon–hydrogen bond breaking). The parameter $\beta_{lg}^{CH_3}$ is a

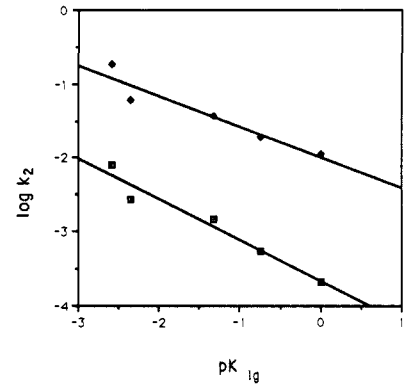


Figure 2. Modified Brønsted plot of second-order rate constants versus pK_{lg} of arenesulfonate leaving groups for morpholine-promoted, imine-forming eliminations from **10** (□) and **15** (■). The slopes of the plots are $\beta_{lg}^{CH_3}$, the extent of N–O cleavage in the activated complex.

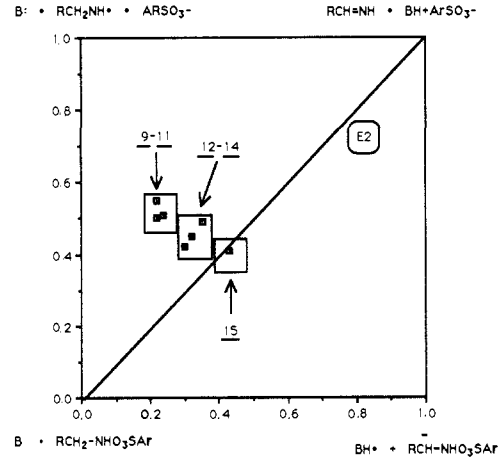


Figure 3. MOFJ energy surface for base-promoted, imine-forming eliminations from *N*-(arylsulfonoxy)amines. The abscissa is β and leads to the carbanionic E1cb intermediate (lower right). The ordinate is $\beta_{lg}^{CH_3}$ and leads to the cationic E1 intermediate (upper left). The solid diagonal line represents the synchronous, concerted E2 mechanism. The β and $\beta_{lg}^{CH_3}$ parameters determined for **9–15** are plotted to locate the position of the transition state on the energy surface.

measure of the extent of cleavage of the N–O bond. Taken together they can be used to locate the transition state on the MOFJ energy surface. The transition-state descriptors for each (arylsulfonoxy)amine **9–15** are plotted in the MOFJ diagram in

Figure 3. The reactants are shown in the lower left corner of this diagram, and the products are shown in the upper right. The abscissa, β, represents the amount of C–H breakage, and the ordinate, $\beta_{lg}^{CH_3}$, represents the amount of N–O cleavage at the transition state. Thus labeled, the lower right of the diagram is the carbanionic intermediate in a stepwise E1cb process, while the upper left is the cationic intermediate in a stepwise E1 process.

The plot reveals that the structure of the *N*-(arylsulfonoxy)-amine precursor has a significant effect in determining the structure of the activated complex for elimination. Substrates **9–11**, which have saturated groups attached to C-1, exhibit similar transition states. They are classified as E1-like in that loss of leaving group is the leading event in the transition state (49–55% N–O cleavage), while proton removal lags behind (22–24% C–H cleavage). Given the error inherent in the determinations of β and $\beta_{lg}^{CH_3}$, the activated complexes for this group are indistinguishable. (The boxes surrounding the groups of points in Figure 3 approximate the errors in the determinations of β and $\beta_{lg}^{CH_3}$.) Of note, however, is that inductive effects appear to play an insignificant role in affecting the structure of the activated complex. Attachment of either one (in **9**) or two (in **10**) alkyl groups at C-1 or attachment of an electron-withdrawing trifluoroethyl group (in **11**) gives activated complexes that are, within experimental error, identical.

Aromatic rings attached to C-1 in **12–14** cause a pronounced perpendicular shift of the transition state in the E1cb direction. Proton removal in the activated complex is greater (30–35%) than for alkyl substituents, and loss of leaving group is less advanced (42–49%). Error analysis shows that these changes are clearly distinguishable. Inductively electron-donating (in **13**) or -withdrawing (in **14**) groups attached to the aromatic ring do not cause significant changes in the activated complex, reinforcing the notion that inductive effects are relatively unimportant in influencing transition states in these eliminations.

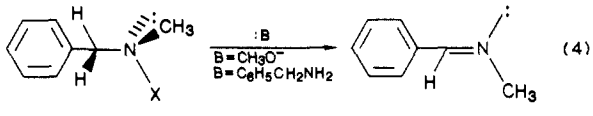
Attachment of a *p*-nitrophenyl group (in **15**) to C-1 causes a further shift toward the E1cb corner, and the transition state is a nearly synchronous E2 process with proton removal (43%) and leaving group loss (41%) occurring to nearly equal extents in the activated complex. The transition state for **15** is clearly distinguishable from those of the other aromatic groups **12–14** discussed above.

The collective data for **9–15** represents one of the most complete studies on the effects of substrate structure on transition states for elimination reactions that is available for systems in which base, solvent, leaving group, and temperature are held constant.[7] Because the extent of *both* C–H and N–O bond cleavage at the transition state are determined for each substrate, a much clearer understanding of substituent effects is possible. The results indicate that substituents at C-1 of *N*-(arylsulfonoxy)amines affect both proton removal and N–O cleavage. In terms of the MOFJ diagram in Figure 3, placement of alkyl groups at C-1 would be expected to destabilize the lower right (E1cb) corner and stabilize the upper left (E1) corner. The result is a decided shift of the transition state in the E1 direction. These alkyl-substituted substrates, **9–11**, have the most E1 character of any eliminations that have been examined. The lack of significant inductive effect on the activated complex results from the E1-like nature of the activated complex. The extent of proton removal (and, by inference, the amount of negative charge) is low on C-1, the site closest to the alkyl group(s), and there is little charge for the inductive effect to act on. Furthermore the alkyl substituents are insulated by the saturated carbon, C-1, from the site of leaving-group loss from nitrogen, thus little inductive influence is experienced at the electron deficient nitrogen. The net result is very little change in the transition state.

In comparison to alkyl substituents at C-1, changes in the transition state caused by aromatic groups at C-1 are due to resonance interactions in the activated complex. In terms of Figure 3, aromatic groups stabilize the E1cb corner by resonance delocalization of the developing negative charge. It is not clear what effect aromatic groups would have on the E1 corner, but the effect is likely to be small because of the saturated methylene group interposed between the phenyl ring and the site of ionization. The result is a net shift of the transition state in the E1cb direction. The activated complex is still E1-like, but less so than for alkyl substituents at C-1. Resonance delocalization results in increased proton removal from C-1, and consequently less loss of leaving group is required at the transition state. The lack of an appreciable inductive influence on the transition state when electron-withdrawing or -donating substituents are attached to the aromatic ring support an E1-like transition state with little charge development and hence little inductive influence.

The effect of a *p*-nitrophenyl substituent attached to C-1 (in **15**) clearly shows the importance of resonance in determining the structure of the activated complex. The electron-withdrawing resonance effect of the *p*-nitro group causes a further perpendicular shift in the E1cb direction to a nearly synchronous E2 reaction. Resonance stabilization of developing charge facilitates proton removal and decreases leaving group loss in the activated complex. This latter effect may be amplified by resonance interaction through the developing double bond, which would decrease electron density on nitrogen and thus retard loss of the leaving group.

In addition to the structural effects reported here, Cho has recently investigated the effects of leaving-group ability and base strength on the transition states of imine-forming eliminations in *N*-methylbenzylamine derivatives (eq 4).[8] By use of a combi-



X=Cl, Br, OSO_2Ar (4)

nation of kinetic deuterium isotope effects, Hammett ρ values, and $\beta_{lg}^{CH_3}$ values, it was determined that as the leaving group becomes better (Cl < Br < OSO_2Ar) the activated complex becomes more E1-like. Use of a weaker base ($C_6H_5CH_2NH_2$ < CH_3O^-) to promote the elimination also gave a shift to a more E1-like activated complex. These qualitative changes are expected from consideration of the effects of these changes on the MOFJ energy surface for eliminations.[8]

It was earlier shown that solvent can also play a major role in determining the structure of the activated complex in imine-forming eliminations.[4] In the present study it was found that for **15a** the transition-state parameters β and $\beta_{lg}^{CH_3}$ changed from 0.43 and 0.40, respectively, in TEW to 0.17 and 0.50, respectively, in methanol. The change to the more polar solvent causes a marked shift from a nearly synchronous to a *very* E1-like transition state. This change induced by solvent is much larger than changes caused by structural changes in the precursor.

From these results a fairly comprehensive view of imine-forming eliminations has emerged. Because of the generally weak bond from nitrogen to halide and arenesulfonate leaving groups,[4,8] these eliminations tend to be E1-like.[9] Transition states can, however, be shifted considerably by the choice of precursors and conditions. The use of nonconjugating groups at C-1, relatively weak amine bases, arenesulfonate leaving groups, and polar solvents all accentuate the E1 character of the transition state. Conversely, the use of conjugating groups at C-1, strong alkoxide bases, poorer leaving groups like chloride and bromide, and less polar solvents cause transition states to be shifted to the E2 type, or even somewhat E1cb-like. It is also pertinent that only perpendicular shifts of transition states are noted. Although it is tempting to suggest that the data for **12–14** show a trend of earlier and later transition states in this series, these points lie within experimental error. Thus no evidence for changes to "earlier" or "later" was found. These may be improper descriptions for changes in

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transition states for elimination reactions.

In contrast, olefin-forming eliminations can be generally characterized as having E1cb-like transition states. Such would be predicted on the basis of the above influences. The bond from carbon to leaving group is much stronger effectively making the leaving group poorer, alkoxide bases are most commonly used to promote these eliminations, and a large number of studies, on which the E1cb-like characterization is based, used β-phenylethyl substrates with a conjugating phenyl group in the β-position (equivalent to C-1 in imine-forming eliminations).[1] It has been suggested that alkyl substitution at the β-position leads to a shift of the transition state in the E1 direction,[10] but insufficient data are available to confirm this suggestion.

Experimental Section

Morpholine, piperidine, pyrrolidine, benzylamine, hexylamine, and *p*-methylbenzylamine were purchased from Aldrich Chemical Co. Tetrahydroisoquinoline was a gift from Kawaken Chemicals. Purification was accomplished by conversion to the hydrochloride salts, recrystallization, regeneration of the free amine with potassium hydroxide, and distillation. *p*-Nitrobenzylamine hydrochloride (Aldrich) was converted to the free amine and purified by Kugelrohr distillation. All amines were stored and handled under nitrogen to minimize the absorption of carbon dioxide.

1-Acetylpiperazine (16e) was prepared by the monoacetylation of piperazine by the method of Baltzy and Buck.[11] A large amount of unreacted piperazine was separated from the reaction mixture as the dihydrochloride, and the 1-acetylpiperazine was crystallized as its hydrochloride, 36%, mp 149 °C (lit.[12] mp 150 °C). The free base was obtained by treatment with potassium hydroxide and purified by Kugelrohr distillation. Spectral data (IR, ^{1}H NMR) were identical with those reported for **16e**.[11]

2-Hexylamine (1) was prepared by reduction of 2-hexanone ketoxime.[13]

3,3,3-Trifluoropropylamine (3) was prepared from 3,3,3-trifluoropropene (SCM Specialty Chemicals) in a multistep sequence. Addition of HBr across the double bond was carried out photochemically[14] to give a mixture of 2-bromo-3,3,3-trifluoropropane (35%) and the desired 1-bromo-3,3,3-trifluoropropane (65%). After separation by spinning band distillation, the 1-bromo isomer was converted to the Grignard reagent and carbonated with carbon dioxide to yield 4,4,4-trifluorobutanoic acid.[15] Conversion to the acid chloride with catechol-phosphoryl trichloride[16] followed by Curtius rearrangement[17] gave 3,3,3-trifluoropropylamine identical with that reported in the literature.[17]

***m*-Trifluorobenzylamine (6)** was prepared by the reduction of α,α,α-trifluoro-*m*-toluonitrile (Aldrich) with LAH.[18]

Arylsulfonyl peroxides (8a–e) were prepared as described earlier.[3b,4] All peroxides were of greater than 98% purity. Peroxides **8c** and **8e** were found to partially decompose after several weeks of storage at −20 °C. Therefore only fresh preparations were used in the kinetic studies reported here.

Solvents. Tetrahydrofuran and ethyl acetate were purified as described earlier.[3b]

Kinetic Studies. Rates of reaction were measured conductometrically as described previously.[4] Constant voltage was supplied by a Wavetek function generator. A Commodore 64 microcomputer was interfaced to the system to apply voltage to the apparatus at timed intervals, read the voltage across a fixed resistor in series with the conductivity cell after AC/DC and A/D conversion of the signal, and plot and store the data. We have noted,[19] as have others,[20] that different batches of solvents give slightly different rate constants for bimolecular eliminations. These differences are small and reproducible (<10%) for a given batch of solvent. Even though individual rate constants were dependent on the solvent batch, the slopes of the derived Brønsted plots were not, if the same batch of solvent were used for all of the rate constant determinations in a series. Therefore when a series of reactions was carried out to determine a particular β or $\beta_{lg}^{CH_3}$ value, a single batch of solvent was used throughout. Thus correlations from Tables I and II to obtain β and $\beta_{lg}^{CH_3}$ were carried out with single solvent batches. It is not correct to correlate the data in these tables horizontally because rate constants taken horizontally were obtained in different solvent batches.

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