Mechanisms of Substitution Reactions at Sulfonyl Sulfur. III. General Base Catalysis of the Hydrolysis of Aryl α-Disulfones[1]

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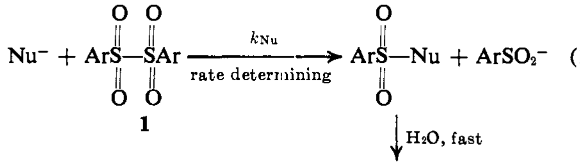
Abstract: The hydrolysis of aryl α-disulfones (**1**) has been studied in various Et_3N–Et_3NH^+ buffers in 60% dioxane and 60% glyme as solvents. Under these conditions the rate constant for hydrolysis, k_h, is the sum of a term due to the reaction of hydroxide ion with **1** and a term due to an Et_3N-catalyzed hydrolysis. Solvent isotope effect measurements show that the triethylamine-catalyzed reaction involves general base catalysis by triethylamine (eq 5) rather than nucleophilic catalysis. This appears to be the first reported example of general base catalysis of a substitution at sulfonyl sulfur. Both the reaction of **1** with hydroxide and the Et_3N-catalyzed hydrolysis show large positive ρ values, similar to other nucleophilic substitution reactions of **1**. From this and other considerations it is shown that some previously reported data (ref 5) on the alkaline hydrolysis of **1** in ethanol must be seriously in error.

We recently reported[3] that in aqueous dioxane the hydrolysis of aryl α-disulfones (**1**) can be markedly catalyzed by various added nucleophiles (F^-, AcO^-, NO_2^-) through nucleophilic catalysis of the hydrolysis *via* the mechanism shown in eq 1. In that same paper we also examined the reaction of certain other nucleophiles (N_3^-, primary and secondary *n*-alkylamines) with **1**. In these latter cases the product $ArSO_2Nu$ in eq 1 does not undergo further rapid hydrolysis under the reaction conditions involved and may be isolated. Secondary *n*-alkylamines were over ten times less reactive toward **1** than analogous primary *n*-alkylamines, presumably because replacement of hydrogens on nitrogen by alkyl groups leads to increased steric hindrance in the reaction of the amine with the α-disulfone.



$$\mathrm{Nu^- + Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\!-\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}Ar \xrightarrow[\text{rate determining}]{k_{Nu}} Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\!-\!Nu + ArSO_2^-} \quad (1)$$

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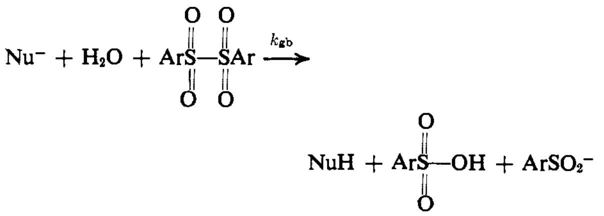
$$\downarrow \mathrm{H_2O,\ fast}$$

$$\mathrm{ArSO_3H + H^+ + Nu^-}$$

Because of this steric factor the reactivity of a tertiary *n*-alkylamine as a nucleophile in reaction 1 should be quite small indeed, and it becomes entirely possible that such a compound, being a reasonably strong base, will catalyze the hydrolysis of **1**, not by acting as a nucleophilic catalyst in the fashion shown in eq 1, but rather by functioning as a general base catalyst for the attack of water on the α-disulfone in the manner outlined in eq 2. As the results presented in this article will demonstrate, this indeed turns out to be the case. While general base catalysis by nucleophiles of substitutions of carboxylic acid derivatives is well known,[4] to our knowledge this is the first example of this phenomenon for a substitution at sulfonyl sulfur.



$$\mathrm{Nu^- + H_2O + Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\!-\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}Ar \xrightarrow{k_{gb}} NuH + Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\!-\!OH + ArSO_2^-} \quad (2)$$

In this work it also turns out to be possible to measure the reactivity of hydroxide ion toward **1** (eq 1, $Nu^- = OH^-$). Allen and Conway[5] recently reported some data for this same reaction in ethanol which seemed to us to exhibit an unusually small dependence of rate on aryl group substituent ($\rho = +0.3$), particularly given the very large (+3.5 to +5.0) ρ values found[1a,3] for the reaction of other nucleophiles with **1**, and also a much slower rate constant (k_{OH}) for hydroxide than would be expected from the k_{Nu} values for other nucleophiles[3] and the general trend of their dependence on nucleophile structure. The work reported in the present paper shows that, contrary to the report of Allen and Conway,[5] the reaction of hydroxide with **1** in 60% glyme does show a large positive ρ and also that the rate constant for hydroxide is much larger than would be predicted from Allen and Conway's data. We do *not* believe that these marked differences are due to the fact that our work was done in 60% aqueous glyme while theirs was done in ethanol, since some semiquantitative studies of the reaction rate of hydroxide with **1** in the latter solvent also reported herein clearly demonstrate that the actual rate of reaction of hydroxide with **1** in that solvent is also much faster than the values reported by Allen and Conway.[5]

Results

The rates of hydrolysis, k_h, of the different aryl α-disulfones (**1**) were determined in various Et_3N–Et_3NH^+ buffers at constant ionic strength in both 60% dioxane (v/v) and 60% glyme (v/v) using the spectrophotometric procedures outlined in an earlier paper.[3] The disappearance of **1** followed good first-order kinetics in all cases under these conditions. The results for the studies in 60% glyme are given in Table I. Those for the runs in 60% dioxane are listed in Table II.

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[1] (a) Papers I and II in this series: *J. Am. Chem. Soc.*, **91**, 5510, 5516 (1969); (b) this research supported by the National Science Foundation, Grant GP-6952.

[2] NDEA Fellow, 1966–1969.

[3] J. L. Kice, G. J. Kasparek, and D. Patterson, *J. Am. Chem. Soc.*, **91**, 5516 (1969).

[4] T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. 1, W. A. Benjamin, Inc., New York, N. Y., 1966, pp 27–118.

[5] P. Allen, Jr., and P. J. Conway, *Can. J. Chem.*, **47**, 873 (1969).

Table I. Hydrolysis of α-Disulfones in Et_3N-Et_3NH^+ Buffers in 60% Aqueous Glyme[a]

$ArSO_2SO_2Ar$, Ar =	$Et_3N:Et_3NH^+$ buffer ratio	$(Et_3N) \times 10^2$, M	$k_h \times 10^4$, sec^{-1}	$k_{Et_3N} \times 10^3$, $M^{-1}\ sec^{-1}$ [b]	$k_{OH}(OH^-) \times 10^5$, sec^{-1} [c]
p-ClC_6H_4	4:1	6.4	24.4		
		5.1	20.6		
		3.8	17.6	27	67
		2.6	13.5		
		1.3	10.3		
	1:1	6.4	15.7		
		4.8	12.3	23	16
		3.2	8.6		
		1.6	5.0		
C_6H_5	1:1	6.4	1.79		
		4.8	1.49	2.5	2.2
		3.2	1.03		
		1.6	0.59		
p-$CH_3C_6H_4$	1:1	6.4	0.37		
		4.8	0.27	0.44	0.74
		3.2	0.21		
		1.6	0.15		
p-$CH_3OC_6H_4$	1:1	6.4	0.070		
		4.8	0.058	0.078	0.20
		3.2	0.046		
		1.6	0.033		

[a] All runs at 21.3° with the ionic strength of the solution held constant at 0.08 by addition of lithium perchlorate; initial concentration of **1**, 5×10^{-5} M. [b] Calculated from the slope of a plot of k_h *vs.* (Et_3N). See Figure 1 for an example. [c] Intercept at (Et_3N) = 0.00 M; see Figure 1 for an example.

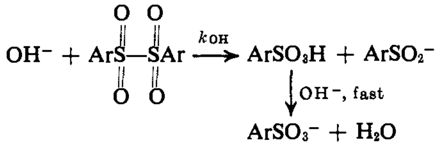
Table II. Hydrolysis of α-Disulfones in Et_3N-Et_3NH^+ Buffers in 60% Dioxane[a]

$ArSO_2SO_2Ar$, Ar =	$Et_3N:Et_3NH^+$ buffer ratio	$(Et_3N) \times 10^2$, M	$k_h \times 10^3$, sec^{-1}	$k_{Et_3N} \times 10^2$ $M^{-1}\ sec^{-1}$ [b]
p-ClC_6H_4	1:1	6.0	11.6	
		5.0	10.3	
		4.0	8.4	17
		3.0	6.8	
		2.0	4.9	
	1:1	6.0	5.7 (D_2O)	
		5.0	4.5 (D_2O)	
		4.0	3.6 (D_2O)	9.0 (D_2O)
		3.0	3.0 (D_2O)	
		2.0	2.1 (D_2O)	
C_6H_5	1:1	6.0	2.0	
		4.0	1.5	2.7
		3.0	1.23	
		2.0	0.91	
	1:1	6.0	0.92 (D_2O)	
		5.0	0.78 (D_2O)	
		4.0	0.63 (D_2O)	1.4 (D_2O)
		3.0	0.49 (D_2O)	
		2.0	0.38 (D_2O)	
p-$CH_3C_6H_4$	1:1	6.0	0.40	
		5.0	0.34	0.55
		3.0	0.23	
		2.0	0.18	
p-$CH_3OC_6H_4$	1:1	6.0	0.079	
		5.0	0.074	
		4.0	0.063	0.11
		3.0	0.048	
		2.0	0.042	

[a] All runs at 21.3° with the ionic strength of the solution held constant at 0.10 by addition of lithium perchlorate. [b] Calculated from the slope of a plot of k_h *vs.* (Et_3N).

Since the rate of spontaneous hydrolysis of the various α-disulfones[1a] at 21.3° is in every instance much smaller than the measured k_h values in Tables I and II, it is clear that the spontaneous hydrolysis makes a negligible contribution to the total rate under these conditions, and k_h should therefore presumably be given by eq 3, where k_{Et_3N} is the rate constant for the triethylamine-catalyzed reaction, and k_{OH} is the rate constant for the reaction of hydroxide ion (arising from the equilibrium $Et_3N + H_2O \rightleftarrows Et_3NH^+ + OH^-$) with **1** (eq 4).

$$k_h = k_{OH}(OH^-) + k_{Et_3N}(Et_3N) \qquad (3)$$



$$OH^- + Ar\overset{O}{\underset{O}{S}}-\overset{O}{\underset{O}{S}}Ar \xrightarrow{k_{OH}} ArSO_3H + ArSO_2^- \qquad (4)$$
$$ArSO_3H \xrightarrow{OH^-,\ fast} ArSO_3^- + H_2O$$

Equation 3 predicts that a plot of k_h *vs.* (Et_3N) for runs at a given Et_3N–Et_3NH^+ buffer ratio should be linear with a slope equal to k_{Et_3N} and an intercept on the k_h axis equal to $k_{OH}(OH^-)$. The magnitude of the intercept should be directly proportional to the buffer ratio (Et_3N)/(Et_3NH^+). The slope should, of course, be independent of the buffer ratio. The data for the hydrolysis of *p*-chlorophenyl α-disulfone (**1a**, Ar = *p*-ClC_6H_4) in 60% glyme given in the first part of Table I, and presented graphically in Figure 1, show that these expectations are indeed realized. Thus, the intercept (6.7×10^{-4} sec^{-1}) for the runs in the 4:1 Et_3N–Et_3NH^+ buffer is, within experimental error, four times larger than the intercept (1.6×10^{-4} sec^{-1}) for the runs in the 1:1 Et_3N–Et_3NH^+ buffer, while the slopes of the two plots, 2.7×10^{-2} and 2.3×10^{-2} M^{-1} sec^{-1}, are, within experimental error, the same. We therefore believe that eq 3 correctly predicts the dependence of k_h on the various reaction variables, and that the slope and intercept of plots of the type shown in Figure 1 can be equated with k_{Et_3N} and $k_{OH}(OH^-)$, respectively.[6]

Dependence of k_{Et_3N} on Aryl Group Structure. The k_{Et_3N} values in Tables I and II for the various α-disulfones show that the rates of the Et_3N-catalyzed reactions depend markedly on the nature of the substituent present in the aromatic ring of the α-disulfones, electron-withdrawing substituents increasing k_{Et_3N} and electron-donating ones decreasing it. Plots of log k_{Et_3N} *vs.* σ for the data for the two solvents indicate a ρ value of +4.3 in 60% dioxane and one of +4.9 in 60% glyme. Because of the very limited number of substituents used to establish the correlation, the difference between these two ρ values may not be significant. However, the important point is that, like all of the other nucleophilic substitution reactions of **1** studied previously,[1a,3] the triethylamine-catalyzed hydrolysis also shows a large positive ρ value.

Solvent Isotope Effect for k_{Et_3N}. The solvent isotope effect associated with k_{Et_3N} was determined in 60% dioxane for both *p*-chlorophenyl α-disulfone (**1a**) and the phenyl compound (**1b**, Ar = C_6H_5). In both instances k_{Et_3N} was significantly smaller in 60% dioxane–40% D_2O than it was in 60% dioxane–40% H_2O, the measured solvent isotope effect being $(k_{Et_3N}{}^{H_2O}/k_{Et_3N}{}^{D_2O}) = 1.9$ in each case.

Dependence of k_{OH} on Aryl Group Structure. Inspection of Table I reveals that k_{OH}, like k_{Et_3N}, is also increased markedly by the substitution for hydrogen of an electron-withdrawing group (*p*-Cl) in the aromatic rings of the α-disulfone and is correspondingly decreased by substitution of electron-donating groups (*p*-CH_3 or *p*-CH_3O) for hydrogen. A plot of log $k_{OH}(OH^-)$ for the data in the 1:1 Et_3N–Et_3NH^+ buffer *vs.* σ indicates that ρ for the reaction of hydroxide with **1** in 60% glyme is +3.7, a value somewhat smaller than that (+5.0) found[3] for reaction of fluoride ion with the same α-disulfones in 60% dioxane, but still *an order of magnitude larger* than that claimed[5] to have been observed for the hydroxide–**1** reaction in ethanol.

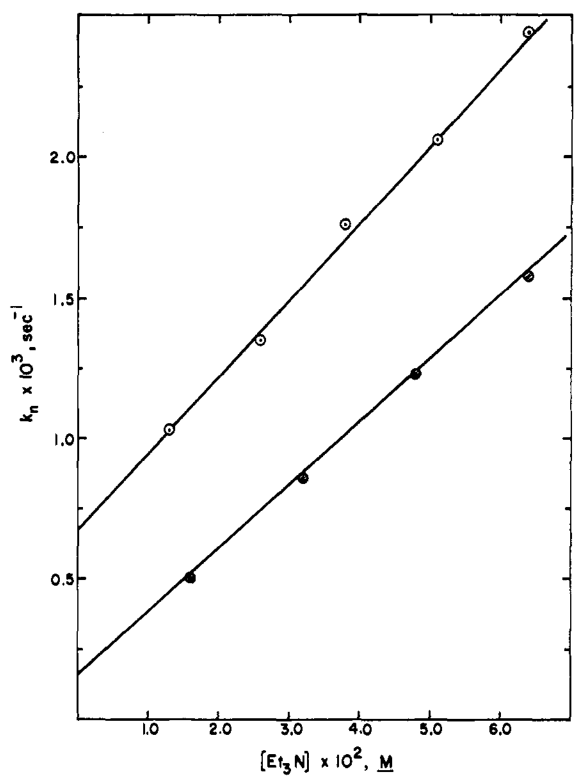
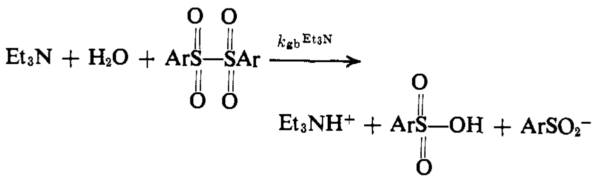


Figure 1. Plot of k_h *vs.* [Et_3N] for the Et_3N-catalyzed hydrolysis of **1a** in 60% glyme: ○, runs in 4:1 Et_3N–Et_3NH^+ buffer; ●, runs in 1:1 buffer.

Discussion

Mechanism of the Triethylamine-Catalyzed Hydrolysis of α-Disulfones. The triethylamine-catalyzed hydrolyses of both **1a** and **1b** in 60% dioxane show a solvent isotope effect of $(k_{Et_3N}{}^{H_2O}/k_{Et_3N}{}^{D_2O}) = 1.9$. In our opinion, a solvent isotope effect of this magnitude demonstrates that catalysis of these hydrolyses by triethylamine must involve general base catalysis of the attack of water on **1** (eq 5) rather than nucleophilic



$$Et_3N + H_2O + Ar\overset{O}{\underset{O}{S}}\text{—}\overset{O}{\underset{O}{S}}Ar \xrightarrow{k_{gb}{}^{Et_3N}} Et_3NH^+ + Ar\overset{O}{\underset{O}{S}}\text{—}OH + ArSO_2^- \tag{5}$$

catalysis (eq 1, Nu^- = Et_3N). Thus, hydrolyses in which amines act as nucleophilic catalysts normally exhibit solvent isotope effects in the range 0.9–1.3,[7] while those in which they act as general base catalysts

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[6] In 60% dioxane the slopes of plots of k_h *vs.* (Et_3N) for the various α-disulfones are found to be independent of Et_3N:Et_3NH^+ buffer ratio, just as in 60% glyme. The magnitudes of the intercepts are erratic, however, and not proportional to (Et_3N)/(Et_3NH^+) as they were in 60% glyme. This was shown to be due to the presence of very small but variable amounts of an impurity in the dioxane which, in a 1:1 Et_3N–Et_3NH^+ buffer or any more basic medium, is completely converted to its conjugate base. The conjugate base ofthe impurity is a very effective catalyst for the hydrolysis of **1**. We know it is the conjugate base which is the catalyst and not the impurity itself since in less basic buffers, such as a 10:1 AcO^-–AcOH buffer, we did not observe any such effect.[3] (We suspect the trace impurity is some peroxidic species since anions of the type YOO^-, being α-effect nucleophiles, should be very reactive toward sulfonyl sulfur.) The net result of all this is that, while we can measure k_{Et_3N} for each α-disulfone accurately in 60% dioxane, we cannot determine $k_{OH}(OH^-)$ for any of them in this solvent with confidence. This is the reason that only values of k_{Et_3N} are shown in Table II.

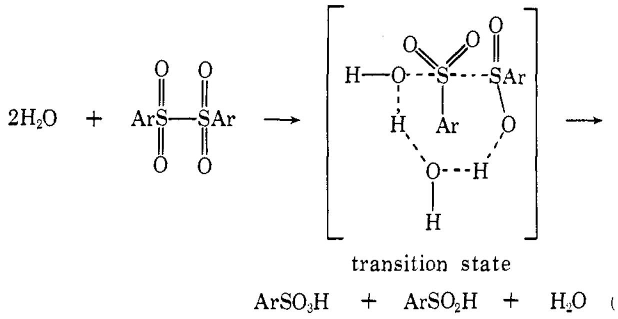
[7] Perhaps the example most directly relevant to the present discussion, since it also involves a tertiary *n*-alkylamine, is nucleophilic catalysis of the hydrolysis of *p*-nitrophenylacetate by trimethylamine. There (k_{H_2O}/k_{D_2O}) is 0.9.[8]

[8] M. L. Bender, E. J. Pollock, and M. C. Neveu, *J. Am. Chem. Soc.*, **84**, 595 (1962).

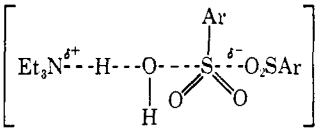
are characterized by much larger solvent isotope effects in the range 1.9–4.4.[9]

While there are many examples of general base catalysis of the hydrolysis of carboxylic acid derivatives,[4] the Et_3N-catalyzed hydrolysis of **1** represents, to our knowledge, the first example of general base catalysis of the hydrolysis of a sulfonyl derivative. That such catalysis can be observed is interesting in its own right, but it would seem to take on heightened significance in the light of the recent interest[10,11] in enzyme-catalyzed hydrolyses of various sulfonyl derivatives and comparison of their behavior with that of analogous enzyme-catalyzed hydrolyses of carboxylic acid derivatives, for the present work shows that the possibility of general base catalysis must be allowed for in considering the hydrolyses of sulfonyl derivatives and may under appropriate circumstances be responsible for certain aspects of the pH–rate profile observed.

The ρ value (+4.3) associated with the Et_3N-catalyzed hydrolysis of **1** in 60% dioxane is significantly larger than that for the spontaneous hydrolysis of **1** in the same solvent (ρ = +3.5).[1a] This is reasonable in terms of the mechanisms proposed for the two reactions. The spontaneous hydrolysis is thought[1a] to involve a mechanism (eq 6) in which one has the transfer of a proton to the departing $ArSO_2$ group in the rate-determining step, so that it is in effect displaced as the sulfinic acid $ArSO_2H$. If, on the other hand, there is no such proton transfer to the departing $ArSO_2$ group in the Et_3N-catalyzed reaction, $ArSO_2$ will be displaced as the sulfinate ion $ArSO_2^-$, and the transition state will have a structure, **2**, in which the electron density on one of the sulfur atoms is significantly greater than it is in the transition state of the spontaneous hydrolysis, thereby accounting for the larger positive value of ρ observed for the Et_3N-catalyzed reaction.



$$2H_2O + ArSO_2{-}SO_2Ar \longrightarrow [\text{transition state}] \longrightarrow ArSO_3H + ArSO_2H + H_2O \quad (6)$$



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Reaction of α-Disulfones with Hydroxide Ion. In 60% glyme the reaction of hydroxide with the α-disulfones (eq 4) also has a large positive ρ value, +3.7. While this is somewhat smaller than the ρ of +5.0 found[3] for the reaction of fluoride ion with **1** (eq 1, $Nu^- = F^-$), it is over an order of magnitude larger than the value of ρ which Allen and Conway[5] claimed was associated with eq 4 in ethanol as solvent. Since we felt it was extremely unlikely that a change from ethanol to 60% glyme would lead to this large a change in ρ, we began to suspect that Allen and Conway's measurements were in some way seriously in error. As the discussion in the ensuing paragraphs will demonstrate, we have now shown fairly convincingly that this must be the case.

The intercepts of plots of the type shown in Figure 1 are, of course, equal to $k_{OH}(OH^-)$. In order to evaluate k_{OH} one must know (OH^-), which in the Et_3N–Et_3NH^+ buffers in question is given by

$$(OH^-) = \frac{K_w(Et_3N)}{K_a^{Et_3NH^+}(Et_3NH^+)}$$

where K_w is the autoprotolysis constant of water and $K_a^{Et_3NH^+}$ is the acid dissociation constant of Et_3NH^+. Unfortunately neither K_w nor $K_a^{Et_3NH^+}$ are known in 60% glyme. They are, however, known in 60% dioxane,[12,13] and, hopefully, in view of the structural similarity of dioxane and glyme, should not be too different in the two solvents. Using the values for K_w and $K_a^{Et_3NH^+}$ in 60% dioxane, (OH^-) for a 1:1 Et_3N–Et_3NH^+ buffer is calculated to be 2×10^{-8} *M*. Using this value, k_{OH} for the reaction of hydroxide with phenyl α-disulfone (**1b**) in 60% glyme at 21.3° would be estimated to be $1 \times 10^3\ M^{-1}\ sec^{-1}$. While this value is admittedly approximate, due to the uncertainty in K_w and $K_a^{Et_3NH^+}$, it is probably correct to within at least an order of magnitude. It is clearly much larger than the value of k_{OH} of $7.1\ M^{-1}\ sec^{-1}$ claimed by Allen and Conway[5] for the same reaction in ethanol at 23°.

Since we thought it unlikely that a change from ethanol to 60% glyme as solvent would result in a large increase in k_{OH}, we decided to attempt to measure k_{OH} in ethanol ourselves. Because of the slowness with which α-disulfones dissolve in ethanol, we proceeded as follows. A cell containing a 0.01 *M* solution of sodium hydroxide in ethanol was brought to temperature (21.3°) and enough of a solution of the α-disulfone in glyme was added so that the final solution was 10^{-4} *M* in α-disulfone and contained 1% glyme. The entire procedure of adding the α-disulfone and mixing took less than 10 sec, and yet by the time it was complete the reaction had gone to completion. This shows that k_{OH} in ethanol at 21.3° for **1c** (Ar = p-$CH_3C_6H_4$) is *at least* $50\ M^{-1}\ sec^{-1}$, which is much larger than the value of $6.5\ M^{-1}\ sec^{-1}$ at 23° claimed by Allen and Conway.[5] We conclude that the data reported by those authors are almost certainly in error, and we believe that a careful quantitative reinvestigation of the system will reveal that eq 4 has a large positive ρ in ethanol, just as it does in 60% glyme. A suspected source of their experimental difficulty is discussed in ref 14.

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[9] For a tabulation of much of the pertinent data, see S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 281 (1967).

[10] J. H. Heidema and E. T. Kaiser, *J. Am. Chem. Soc.*, **90**, 1860 (1968).

[11] G. Tomalin, M. Trifunac, and E. T. Kaiser, *ibid.*, **91**, 722 (1969).

[12] H. S. Harned and L. D. Fallon, *ibid.*, **61**, 2374 (1939).

[13] P. Rumpf, G. Girault-Vexlearschi, and R. Schaal, *Bull. Soc. Chim. Fr.*, **22**, 554 (1955).

[14] As noted earlier, aryl α-disulfones dissolve very sluggishly in ethanol. Because these α-disulfones are often obtained in the form of extremely small crystals, it is not always apparent on mixing them with ethanol that one has a suspension rather than a solution. If this were the case in Allen and Conway's[5] work, then, given the very fast rate of reaction of **1** with hydroxide, what they might well have been measuring was the rate of solution of **1**, rather than the rate of its reaction with hydroxide ion. Since the rate of solution might well be effectively independent of the structure of the aryl group in **1** within the limits of structural variation examined, this could account for the fact that they found essentially no dependence of rate on the nature of the aryl group.

Experimental Section

Preparation and Purification of Materials. The preparation and purification of the α-disulfones and the method of purifying the dioxane used have already been described.[1a] Glyme (Ansul Co.) was purified by first distilling it from sodium and then distilling it from lithium aluminum hydride immediately before use. Triethylamine (Eastman Kodak) was distilled under nitrogen from barium oxide before being used.

Procedure for Kinetic Runs. The same general procedure previously used[3] for runs at 21.3° was also employed in the present work. The various Et_3N–Et_3NH^+ buffer solutions required were prepared by adding the calculated amount of standard perchloric acid to a standard solution of triethylamine in water. The ionic strength was maintained constant by addition of lithium perchlorate. The hydrolyses were followed spectrophotometrically in the manner previously described.[3]

Solvolyses of Tertiary α-Arylcycloalkyl and -polycycloalkyl Chlorides. Effects of Ring Size and Substituents in the Aryl Ring on the Solvolysis Rates

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Abstract: A series of α-arylcyclobutyl (**1-Z**), -cyclopentyl (**2-Z**), -cyclohexyl (**3-**, Z), -7-norbornyl (**4-Z**), and -2-adamantyl (**5-Z**) chlorides, in which the aryl rings are variously substituted for the study of substituent effects, was prepared and their solvolysis rates in 90% aqueous acetone were studied. The reactivities decrease in the sequence **2-Z** > **5-Z** > *t*-cumyl chlorides (**6-Z**) > **1-Z**–**3-Z** > **4-Z**; and for the parent α-phenyl (R = H) compounds, the relative rates at 25° are 369 for **2-H**, 23.4 for **5-H**, 6.68 for **6-H**, 1.40 for **1-H**, 1.00 for **3-H**, and 2.04×10^{-3} for **4-H**. The ρ–σ^+ treatments gave straight lines in all the systems and the ρ values obtained are −4.48 for **1-Z**, −4.10 for **2-Z**, −4.65 for **3-Z**, −5.64 for **4-Z**, −4.83 for **5-Z**, and −4.54 for **6-Z**. The rate-increasing effects arising from the transformation of the secondary cycloalkyl systems into the tertiary α-arylcycloalkyl system, k_ϕ/k_H, are 2.8×10^1 for the cyclobutyl, 4.6×10^3 for the cyclopentyl, 4.0×10^2 for the cyclohexyl, 1.7×10^3 for the isopropyl, 6.3×10^7 for the 7-norbornyl, and 1.4×10^5 for the adamantyl system. The relative importance of several factors governing the solvolysis reactivities is discussed.

Ring compounds exhibit a significant change in the facility of their solvolysis reactions with ring size, from small to large, and with cycle number, from monocyclic to polycyclic. In order to account for this change, a number of important factors and concepts of structure–reactivity relationships in organic chemistry have been introduced and demonstrated.[1] For example, the solvolysis reactivities of secondary cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl *p*-toluenesulfonates in acetic acid have been found to be cyclopentyl–cyclobutyl > cyclohexyl ≫ cyclopropyl.[2–4] The solvolysis rates of tertiary α-methylcyclobutyl, -cyclopentyl, and -cyclohexyl chlorides in 80% ethanol have been found to be in the sequence cyclopentyl > cyclohexyl > cyclobutyl, and Brown has attempted with considerable success to rationalize these results in terms of "I strain."[5] The 7-norbornyl derivatives are extraordinarily unreactive in solvolysis; for example, 7-norbornyl brosylate solvolyzes (in acetic acid) 10^4 times more slowly than *n*-butyl brosylate,[6] 10^7 times more slowly than cyclohexyl brosylate, and 10^6 times more slowly than 2-adamantyl brosylate.[7] Substitution of a methyl group for the hydrogen at the reaction center of the 7-norbornyl derivative caused a rate enhancement of 5.1×10^7 (at 50°), the greatest yet reported.[8] Therefore, the effect of aryl substitution at the reaction center must be of considerable interest.

We have studied the rates and products in hydrolysis reactions of tertiary α-aryl-substituted cycloalkyl chlorides of the following fundamental ring systems in 90% aqueous acetone: α-arylcyclobutyl (**1-Z**), -cyclopentyl (**2-Z**), -cyclohexyl (**3-Z**), -7-norbornyl (**4-Z**), and -2-adamantyl (**5-Z**) chlorides. Combination of the present results with the reported data provides both the effect of aryl substitution and the relative effect of methyl and aryl substitutions. In addition, since sufficient varieties of substituents have been introduced into the aryl rings, it is possible to investigate whether or not linear free energy relationships are obtained by treatments of the rates with the Hammett–Brown relationship, $\log (k/k_0) = \rho\sigma^+$, and where obtained, the reaction constants, ρ, will be discussed as a measurement of the electron demand of a cationic center in a ring system. Although the objective was different, a recent study based on substantially the same technique was made of the substituent effect on the solvolysis of **2-Z**,

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