Mechanisms of Substitution Reactions at Sulfonyl Sulfur. IV. Further Studies of the Catalysis of the Hydrolysis of Sulfonyl Compounds by Tertiary Amines[1a,b]

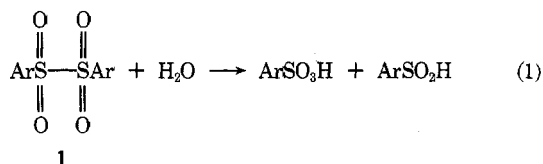John L. Kice,*[1c] Charlene A. Walters,[1d] and Suzanne B. Burton[1c]

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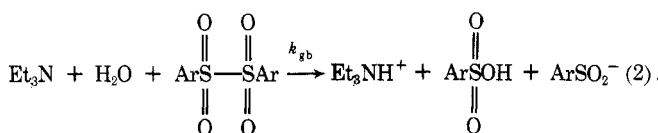
The hydrolysis of *p*-nitrophenyl *p*-toluenesulfonate (**3a**) has been studied in a series of Et_3N-Et_3NH^+ buffers in both 20% acetonitrile and 60% aqueous glyme. No evidence of any significant catalysis by triethylamine could be detected. In contrast, catalysis of the hydrolysis in 60% glyme by the less sterically hindered tertiary amine, *N*-ethylpyrrolidine (NEP), is easily detectable. The solvent isotope effect and other considerations suggest that this catalysis by NEP is nucleophilic catalysis. The catalysis of the hydrolysis of phenyl α-disulfone (**1b**) by NEP in 60% dioxane has also been investigated, and it too appears to be an example of nucleophilic catalysis. In the light of these results the earlier conclusion of Kice and Kasperek that the catalysis of the hydrolysis of **1b** by triethylamine represents general base catalysis is critically reexamined, and it is concluded that it could quite possibly represent instead a mixture of part nucleophilic catalysis and part general base catalysis.
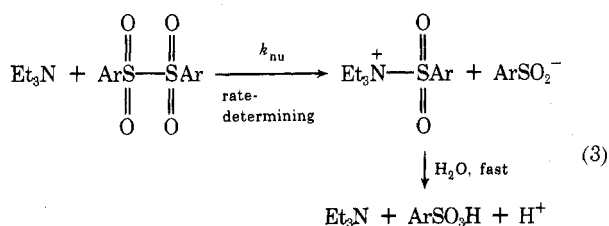
In 1970 Kice and Kasperek[2] reported that the hydrolysis of aryl α-disulfones (eq 1) could be catalyzed by triethyl-

$$ArS\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!-\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!SAr + H_2O \longrightarrow ArSO_3H + ArSO_2H \qquad (1)$$

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amine (TEA). On the basis of the magnitude of the solvent isotope effect observed for the reaction, they believed that what was involved was general base catalysis by the terti-
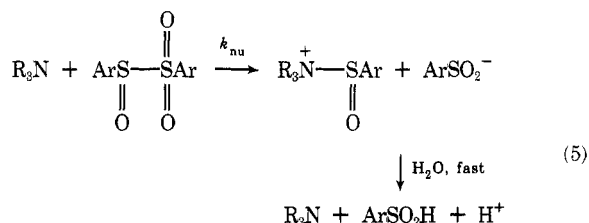
$$Et_3N + H_2O + ArS\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!-\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!SAr \overset{k_{gb}}{\longrightarrow} Et_3NH^+ + ArS\overset{\overset{O}{\|}}{}OH + ArSO_2^- \quad (2)$$

ary amine (eq 2) rather than the alternate possibility, nucleophilic catalysis (eq 3).

$$Et_3N + ArS\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!-\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!SAr \underset{\substack{\text{rate-}\\\text{determining}}}{\overset{k_{nu}}{\longrightarrow}} Et_3\overset{+}{N}\!\!-\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!SAr + ArSO_2^-$$

$$\downarrow H_2O,\ fast \qquad\qquad (3)$$
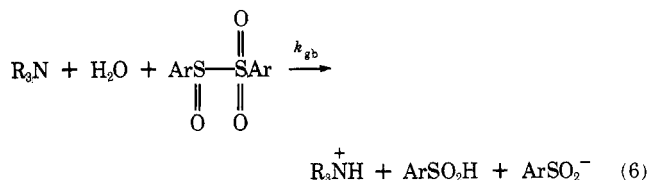
$$Et_3N + ArSO_3H + H^+$$

Subsequently, Kice and Campbell[3] investigated the catalysis by tertiary amines of an exactly analogous substitution at sulfinyl sulfur, the hydrolysis of aryl sulfinyl sulfones (eq 4). While pyridine appeared to catalyze this

$$ArS\overset{\overset{O}{\|}}{}\!\!-\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!SAr + H_2O \longrightarrow 2ArSO_2H \qquad (4)$$

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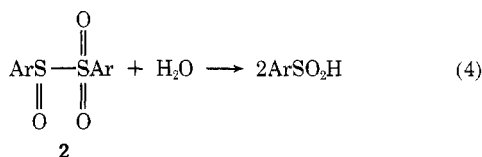
reaction by acting as a nucleophilic catalyst (eq 5), the more sterically hindered tertiary amine, *N*-benzyldiethyl-

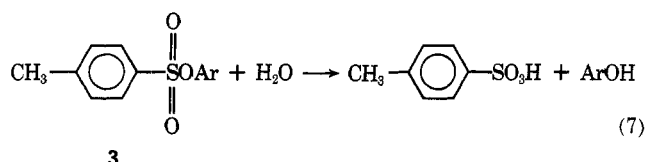$$R_3N + ArS\overset{\overset{O}{\|}}{}\!\!-\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!SAr \overset{k_{nu}}{\longrightarrow} R_3\overset{+}{N}\!\!-\!\!\overset{\overset{O}{\|}}{}SAr + ArSO_2^-$$

$$\downarrow H_2O,\ fast \qquad\qquad (5)$$

$$R_3N + ArSO_2H + H^+$$

amine, apparently catalyzed the reaction by acting as a general base catalyst (eq 6). They also noted that *N*-ben-

$$R_3N + H_2O + ArS\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!-\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}\!\!SAr \overset{k_{gb}}{\longrightarrow}$$

$$R_3\overset{+}{N}H + ArSO_2H + ArSO_2^- \quad (6)$$

zylpyrrolidine, which has essentially the same base strength as Et_2NCH_2Ph, but in which the nitrogen is less sterically hindered owing to two of the substituents on nitrogen being tied back in a ring, was a considerably better catalyst than Et_2NCH_2Ph. Were *N*-benzylpyrrolidine functioning as a general base catalyst one would not expect it to be significantly more reactive than *N*-benzyldiethylamine. On the other hand, given its less sterically hindered nitrogen, *N*-benzylpyrrolidine should almost certainly be considerably better as a nucleophilic catalyst than Et_2NCH_2Ph. Kice and Campbell accordingly concluded that the decrease in steric hindrance around nitrogen on going from Et_2NCH_2Ph to *N*-benzylpyrrolidine was apparently enough to take one from a situation where general base catalysis by the tertiary amine was faster than nucleophilic catalysis to one where k_{nu} was now larger than k_{gb}.

Nucleophilic and general base catalysis of the hydrolysis of carboxylic acid derivatives has been very extensively investigated and is a subject of great mechanistic interest.[4,5] Much less attention has been devoted to study of the same phenomena in substitutions at sulfur. Since indepth investigation of such catalysis would seem a necessary part of any complete picture of nucleophilic substitution at sulfur, further exploration of the question of catalysis by tertiary amines of the hydrolysis of sulfonyl and sulfinyl compounds certainly seems warranted.

In the present work we initially investigated whether the hydrolysis of an aryl *p*-toluenesulfonate (eq 7) would

$$CH_3-\text{\textcircled{}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}OAr + H_2O \longrightarrow CH_3-\text{\textcircled{}}-SO_3H + ArOH \qquad (7)$$
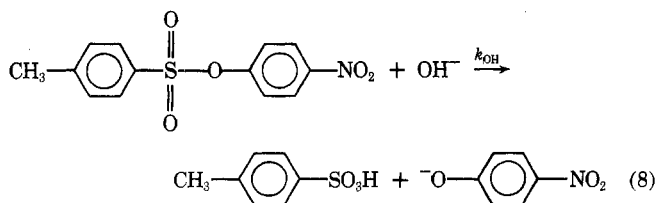
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also be subject, like the hydrolysis of 1, to catalysis by tertiary alkyl amines. Certain of our results were such as to cause us to wonder whether the triethylamine-catalyzed hydrolysis of 1 might not actually be an example of nucleophilic catalysis after all, rather than general base catalysis, as Kice and Kasperek[2] had originally thought. This led us to carry out some studies on the catalysis of the hydrolysis of 1 by *N*-ethylpyrrolidine, which, upon comparison with the earlier data[2] on the Et_3N-catalyzed hydrolysis of 1, would hopefully provide further insight on this matter. These are also described and discussed.

Results

Hydrolysis of *p*-Nitrophenyl *p*-Toluenesulfonate in $R_3N-R_3NH^+$ Buffers. The kinetics of the hydrolysis of very dilute (10^{-4} to 5×10^{-5} *M*) solutions of *p*-nitrophenyl *p*-toluenesulfonate (**3a**, Ar = $p-O_2NC_6H_4$) in various tertiary amine–tertiary alkylammonium ion buffers were followed by monitoring the increase in the absorbance of the solution at 400 nm due to the release of *p*-nitrophenolate ion on hydrolysis of **3a**. In each instance the infinity absorbance of the solution corresponded accurately with that expected from the initial concentration of **3a** in the solution. Plots of log ($A_\infty - A$) *vs.* time were nicely linear in all cases, showing that the disappearance of the ester and appearance of $p-O_2NC_6H_4O^-$ followed good first-order kinetics. From the studies of Bunnett and Bassett[6] one can be sure that the hydrolysis of **3a** under the various conditions used is occurring essentially exclusively by S–O, rather than C–O, bond cleavage. This would be true even for nucleophilic catalysis by tertiary amine, since they[6] have shown that piperidine reacts with **3a** with 90% S–O bond cleavage and less than 10% C–O bond cleavage.

One series of runs was carried out at 70° using 1:1, 2:1, and 4:1 $Et_3N-Et_3NH^+$ buffers in 20% acetonitrile–80% water as solvent. The ionic strength was kept constant at 0.10 by addition of lithium perchlorate. The results of these runs are listed in Table I. The values of k_1, the experimental first-order rate constant, show that at a given buffer ratio there is no dependence of k_1 on [Et_3N]. On the other hand, k_1 does increase in a linear fashion with buffer ratio. This behavior shows that under these conditions there is no detectable catalysis of the hydrolysis by triethylamine itself and that the only kinetically important term contributing to k_1 is the reaction of OH^- with **3a** (eq 8). The concentration of hydroxide ion in these solutions is, of course, directly proportional to the buffer ratio [Et_3N]/[Et_3NH^+].

$$CH_3-\text{\textcircled{}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\text{\textcircled{}}-NO_2 + OH^- \xrightarrow{k_{OH}}$$

$$CH_3-\text{\textcircled{}}-SO_3H + {}^-O-\text{\textcircled{}}-NO_2 \qquad (8)$$

Since the autoprotolysis constant for water should be several orders of magnitude smaller in a solvent like 60% dioxane or 60% glyme than it is in 20% acetonitrile, the concentration of hydroxide ion in a given $Et_3N-Et_3NH^+$ buffer should be much lower in these solvents than in 20% acetonitrile. Hopefully, therefore, it should be easier to detect any catalysis by the amine in these solvents than in

Table I
Hydrolysis of *p*-Nitrophenyl *p*-Toluenesulfonate in $Et_3N-Et_3NH^+$ Buffers in 20% Acetonitrile at 70° [a]

$Et_3N:Et_3NH^+$ buffer ratio	[Et_3N], *M*	$k_1 \times 10^5$, sec^{-1} [b]
1:1	0.100	1.97
	0.050	1.97
	0.025	2.05
	0.0125	2.09
2:1	0.100	4.25
	0.050	4.51
	0.025	4.28
	0.0125	4.38
4:1	0.100	8.18
	0.050	8.51
	0.025	8.15

[a] All runs with ionic strength of the solution held constant at 0.10 by addition of lithium perchlorate. [b] Rate constants are in each case the average of several runs.

20% acetonitrile, since the much lower hydroxide ion concentration will make eq 8 a less important contributor to the rate of hydrolysis of **3a** in any given buffer. We accordingly investigated the hydrolysis of **3a** in similar $Et_3N-Et_3NH^+$ buffers in 60% glyme as solvent. We also studied the hydrolysis in *N*-ethylpyrrolidine buffers in the same solvent. In order to get reasonable rates of reaction it was necessary to go to a considerably higher temperature, 115°, and the reactions were therefore carried out in sealed tubes. The results are listed in Table II.

From these data it is evident that even in 60% glyme there is still practically no dependence of k_1 on [Et_3N] at a given buffer ratio. On the other hand, with the sterically less hindered, but otherwise equivalent, tertiary amine *N*-ethylpyrrolidine there is a clearly detectable increase in k_1 with increasing amine concentration. As can be seen from Figure 1, which shows plots of k_1 *vs.* amine concentration for the different buffer ratios, the dependence is that which would be expected if k_1 is given by eq 9 with

$$k_1 = k_{OH}[OH^-] + k_{R_3N}[R_3N] =$$

$$k_{OH}K\frac{[R_3N]}{[R_3NH^+]} + k_{R_3N}[R_3N] \qquad (9)$$

the hydrolysis rate being the sum of the rate due to reaction with hydroxide (eq 8) and the rate due to an *N*-ethylpyrrolidine-catalyzed reaction.

From the slopes of the plots of k_1 *vs.* [*N*-ethylpyrrolidine] one can estimate the value of k_{NEP}, the rate constant for the *N*-ethylpyrrolidine-catalyzed hydrolysis of **3a** under these conditions. This is found to be 6.0×10^{-5} $M^{-1} sec^{-1}$. Because there is so little variation in k_1 with [Et_3N], a value of k_{TEA} cannot be estimated in the same way with any real accuracy. However, from Figure 1 one can say that k_{TEA} is almost certainly no larger than about $4 \times 10^{-6} M^{-1} sec^{-1}$, so that the rate constant for catalysis by *N*-ethylpyrrolidine is at least 15 times larger than the rate constant for catalysis by triethylamine.

The data in Table II on the *N*-ethylpyrrolidine-catalyzed hydrolysis of **3a** in 60% glyme–40% D_2O permit one to determine the solvent isotope effect associated with k_{NEP}. This is found to be $k_{NEP}(H_2O)/k_{NEP}(D_2O) = 1.45 \pm 0.10$.

Catalysis of the Hydrolysis of Phenyl α-Disulfone by *N*-Ethylpyrrolidine. As will be outlined in much greater detail in the Discussion, the lack of any significant catalysis of the hydrolysis of **3a** by triethylamine and the fact

Table II
Hydrolysis of p-Nitrophenyl p-Toluenesulfonate in Tertiary Amine Buffers in 60% Aqueous Glyme at 115° [a]

Amine	$R_3N:R_3NH^+$ buffer ratio	$[R_3N]$, M	$k_1 \times 10^5$, sec^{-1} [b]
Et₃N	4:1	0.08	0.72
		0.06	0.70
		0.04	0.69
		0.02	0.70
	2:1	0.08	0.41
		0.06	0.40
		0.04	0.39
		0.02	0.38
	1:1	0.05	0.23
		0.0375	0.22
		0.025	0.21
		0.0125	0.20
NEP	4:1	0.08	1.42
		0.06	1.29
		0.04	1.18
		0.02	1.05
	2:1	0.08	0.95
		0.06	0.82
		0.04	0.69
		0.02	0.58
	1:1	0.05	0.57
		0.04	0.51
		0.03	0.44
		0.0125	0.33
		0.010	0.30
	4:1	0.08	1.02 (D₂O)
		0.06	0.96 (D₂O)
		0.04	0.87 (D₂O)
		0.02	0.79 (D₂O)

[a] All runs with the ionic strength of the solution held constant at 0.05 by addition of lithium perchlorate. [b] Rate constants are average of several runs. Deviation between duplicate runs was never greater than ±3%.

Table III
Hydrolysis of Phenyl α-Disulfone in N-Ethylpyrrolidine Buffers in 60% Dioxane [a]

| NEP:NEPH⁺ buffer ratio	[NEP], M	$k_1 \times 10^3$, sec^{-1} [b]
1:1	0.06	9.2
	0.05	8.0
	0.04	6.2
	0.03	4.2
	0.02	3.0
	0.06	6.5 (D₂O)
	0.05	5.4 (D₂O)
	0.04	4.4 (D₂O)
	0.03	3.2 (D₂O)
	0.02	2.0 (D₂O)

[a] All runs at 25° with ionic strength of the solution held constant at 0.10 by addition of lithium perchlorate. [b] Rate constants are average of several runs. Deviation between duplicate runs was never greater than ±6%.

that catalysis by N-ethylpyrrolidine was detectable in 60% glyme led us to wonder whether the catalysis of the hydrolysis of aryl α-disulfones, 1, by triethylamine observed by Kice and Kasperek[2] might not be nucleophilic catalysis rather than the general base catalysis (eq 2) they had suggested. To get information that might help to resolve this point, the catalysis of the hydrolysis of phenyl α-disulfone (1b, Ar = C₆H₅) by N-ethylpyrrolidine was studied in 60% dioxane under the same conditions used earlier[2] to study the catalysis of the same hydrolysis by Et₃N. The results are shown in Table III. Plots of k_1 vs. [N-ethylpyrrolidine] (Figure 2) are nicely linear and indicate that k_{NEP} in 60% dioxane–40% H₂O is 0.15 M^{-1} sec^{-1} with $k_{NEP}(H_2O)/k_{NEP}(D_2O)$ equal to 1.38 ± 0.05.

The value which we find for k_{NEP}, the catalytic constant for N-ethylpyrrolidine, is about six times larger than the catalytic constant for triethylamine measured by Kice and Kasperek.[2] As a check on their work we briefly reinvestigated the catalysis of the hydrolysis of 1b by triethylamine in 60% dioxane in a 1:1 Et₃N–Et₃NH⁺ buffer and from a plot of k_1 vs. [Et₃N] obtained a value of k_{TEA} about 15% smaller than the one they reported, but one which was still in sufficiently close agreement with their value to show clearly that N-ethylpyrrolidine is definitely a markedly better catalyst for the hydrolysis of 1b than is triethylamine, despite the fact that both amines are of essentially equal base strength.

Discussion

Catalysis of the Hydrolysis of p-Nitrophenyl p-Toluenesulfonate (3a). In Et₃N–Et₃NH⁺ buffers no significant catalysis of the hydrolysis of 3a by triethylamine itself can be detected either in 20% acetonitrile or 60% aqueous glyme as solvent. In contrast, with the sterically less hindered tertiary amine, N-ethylpyrrolidine (NEP), a kinetic term due to catalysis by the amine is easily detected (see Figure 1). While catalysis of the hydrolysis of 3a by NEP could, in principle, represent either nucleophilic catalysis or general base catalysis, several factors suggest rather strongly that nucleophilic catalysis (eq 10) is what is involved.

$$\text{ArSO}_3\text{H} + \text{H}^+ + \text{Et—N} \bigcirc$$
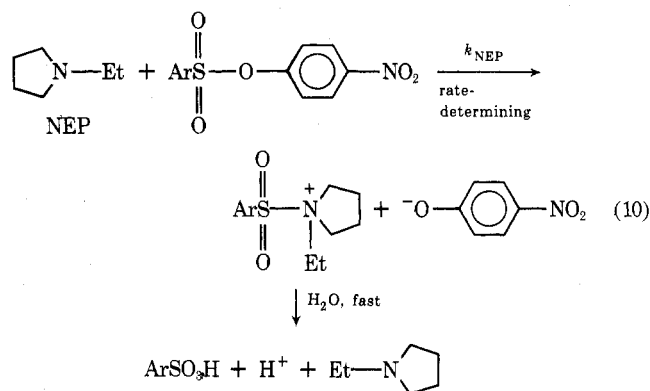
First, there is no appreciable difference in the base strength of NEP and triethylamine. This is evident from the fact that the intercepts on the k_1 axis in Figure 1, which are proportional to [OH⁻] present in solutions of a given buffer ratio, are only 30% larger for each NEP–NEPH⁺ buffer than for the corresponding Et₃N–Et₃NH⁺ buffer. This corresponds to a difference in the pK_a of NEPH⁺ and Et₃NH⁺ of only 0.10 pK unit. This is also in accord with data in the literature[7] that indicate that there is little difference between the pK_a of Et₃NH⁺ and N-ethyl-2-methylpyrrolidinium ion. If NEP were functioning as a general base catalyst for the hydrolysis of 3a, the catalytic rate constant for NEP should presumably be approximately the same as for triethylamine. The fact that k_{NEP} for the hydrolysis of 3a is at least 15 times larger than k_{TEA} is therefore hardly consistent with general base catalysis.

On the other hand, the fact that k_{NEP} is much larger than k_{TEA} is easily explained if NEP is acting as a nucleophilic catalyst for the hydrolysis of 3a, since the nitrogen atom in NEP is significantly less sterically hindered than the one in triethylamine and its reactivity in a nucleophilic substitution such as eq 10 might therefore be expected to be significantly larger.

Nucleophilic catalysis by NEP is also consistent with the solvent isotope effect for k_{NEP}. The measured value of $k_{NEP}(H_2O)/k_{NEP}(D_2O)$ of 1.45 ± 0.10 seems too small to be consistent with general base catalysis, since solvent
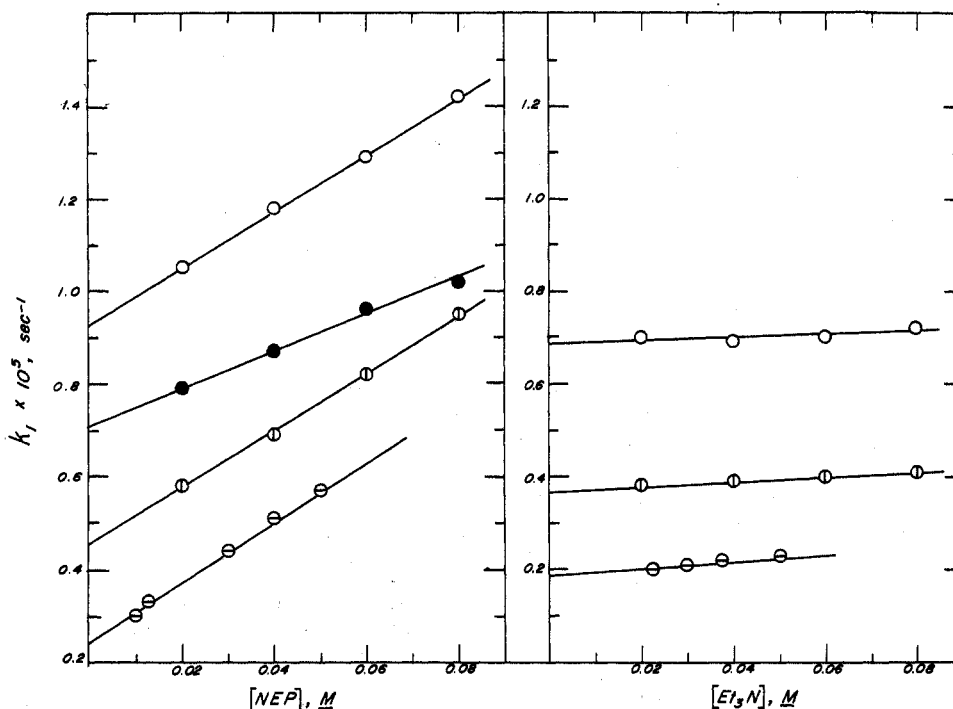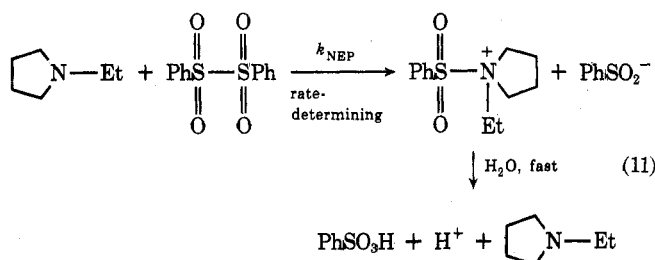
Figure 1. Rates of hydrolysis of **3a** in 60% glyme in N-ethylpyrrolidine (NEP) and triethylamine buffers *vs.* amine concentration: O, 4:1 $R_3N-R_3NH^+$ buffer; ⊙, 2:1 buffer; ⊖, 1:1 buffer; ●, 4:1 buffer in 60% glyme–40% D_2O. All runs at constant ionic strength of 0.05.

isotope effects for general base catalyzed reactions involving amine catalysts normally range between 1.9 and 4.4.[8] It can be reconciled with nucleophilic catalysis by NEP involving the mechanism shown in eq 10.[9]

Catalysis of the Hydrolysis of Phenyl α-Disulfone by N-Ethylpyrrolidine. The results in Figure 2 indicate that NEP is a substantially better catalyst than triethylamine for the hydrolysis of phenyl α-disulfone (**1b**) and also that the solvent isotope effect, $k_{NEP}(H_2O)/k_{NEP}(D_2O)$, associated with catalysis by NEP is relatively small, being only 1.4. Just as in the case of catalysis of the hydrolysis of **3a**, these two factors suggest that the catalysis of the hydrolysis of **1b** by NEP is nucleophilic catalysis (eq 11) and not

$$\text{N—Et} + \text{PhS—SPh} \xrightarrow[\text{rate-determining}]{k_{NEP}} \text{PhS—N}^{+} + \text{PhSO}_2^{-}$$

$$\downarrow \text{H}_2\text{O, fast} \qquad (11)$$

$$\text{PhSO}_3\text{H} + \text{H}^+ + \text{N—Et}$$

general base catalysis. In connection with the solvent isotope effect it is worth recalling that $k(H_2O)/k(D_2O)$ for nucleophilic catalysis by pyridine of the hydrolysis of **2** in the same solvent was 1.44.[3]

Nature of the Catalysis of the Hydrolysis of Phenyl α-Disulfone by Triethylamine. A *priori* there are three possibilities for catalysis of the hydrolysis of phenyl α-disulfone (**1b**) by triethylamine (TEA): (1) general base catalysis (eq 2); (2) nucleophilic catalysis (eq 3); or (3) a mixture of the two, the catalytic rate constants for eq 2 and eq 3 adventitiously being approximately the same. Based on the size of their measured solvent isotope effect, $k_{TEA}(H_2O)/k_{TEA}(D_2O) = 1.9$, Kice and Kasperek[2] concluded that catalysis by triethylamine was general base catalysis. This conclusion must now be carefully reexamined in the light of the following aspects of the present results. First, while NEP is at least 15 times more reactive
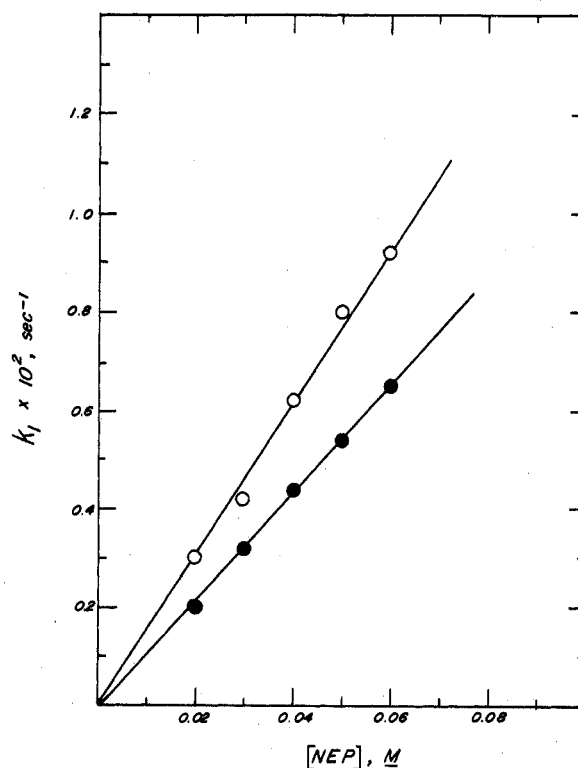

Figure 2. Catalysis of the hydrolysis of **1b** by NEP. Plot of k_1 *vs.* [NEP] for runs in a 1:1 NEP–NEPH$^+$ buffer at a constant ionic strength of 0.10: O, 60% dioxane–40% H_2O; ●, 60% dioxane–40% D_2O.

than Et_3N as a catalyst for the hydrolysis of the aryl p-toluenesulfonate **3a**, it is only 6 to 7 times more reactive than Et_3N as a catalyst for the hydrolysis of **1b**. Second, while with **1b** catalysis by Et_3N is *easily* detected in 1:1 Et_3N–Et_3NH^+ buffers in competition with direct alkaline hydrolysis, catalysis by Et_3N is not significant in comparison with alkaline hydrolysis in the same buffers in the hydrolysis of **3a**.

If the catalysis of the hydrolysis of 1b by Et$_3$N is general base catalysis it seems rather surprising that Et$_3$N does not catalyze the hydrolysis of 3a at all effectively. Usually, all else being equal, the poorer the leaving group in a hydrolysis the more important general base catalysis, and certainly p-O$_2$NC$_6$H$_4$O$^-$ is a poorer leaving group than PhSO$_2^-$. On the other hand, if catalysis of the hydrolysis of 1b by Et$_3$N were nucleophilic catalysis, one could understand how k_{NEP}/k_{TEA} might be considerably larger for the hydrolysis of 3a than for the hydrolysis of 1b. For example, the rate constant for nucleophilic catalysis could well be more sensitive to changes in the steric requirements of the nucleophile the greater the extent of nucleophile–sulfonyl group bond formation in the rate-determining transition state, and with the poorer leaving group in 3a the extent of N–SO$_2$ bond formation in that transition state could well be further advanced than for 1b.

There is, however, one major problem associated with interpreting the catalysis of the hydrolysis of 1b by triethylamine as nucleophilic catalysis, and that is the size of the solvent isotope effect, k_{TEA}(H$_2$O)/k_{TEA}(D$_2$O) = 1.9. This seems abnormally large to be associated with a mechanism where catalysis by Et$_3$N involves exclusively nucleophilic catalysis.

At first sight one therefore seems left with a not very satisfying pair of alternatives. On the one hand, if one assumes that the catalysis of the hydrolysis of 1b by Et$_3$N is general base catalysis because of the magnitude of the solvent isotope effect, it is not clear why similar catalysis by Et$_3$N should be so unimportant in the hydrolysis of 3a. On the other hand, if one assumes that the catalysis of the hydrolysis of 1b by Et$_3$N is nucleophilic catalysis, one has to write off the solvent isotope effect as somehow being anomalous in this particular case. However, before concluding that these are the only possible explanations for the data, one should explore whether or not the entire situation may not be better explained by assuming that catalysis of the hydrolysis of 1b by Et$_3$N in 60% dioxane represents the sum of the contribution from two separate reactions, one a nucleophile-catalyzed reaction (eq 3) and the other a general base catalyzed reaction (eq 2), and that these two processes have approximately equal rate constants in 60% dioxane–40% H$_2$O. First, such a situation could account for the observed solvent isotope effect for k_{TEA}, because k_{TEA} as measured would be the sum of k_{nu} (eq 3) and k_{gb} (eq 2), and, while k_{gb} would be markedly lowered on transfer to 60% dioxane–40% D$_2$O, k_{nu} would not be greatly affected, the net result being that k_{TEA}(H$_2$O)/k_{TEA}(D$_2$O) as measured would appear to be intermediate in value between that expected for nucleophilic catalysis and that usual for general base catalysis. Second, because of the considerations outlined earlier, k_{nu} for TEA could well be much smaller relative to k_{nu} for NEP for catalysis of the hydrolysis of 3a than it is for catalysis of the hydrolysis of 1b, so that while k_{NEP}/k_{TEA} for 1b is given by k_{nu} (for NEP)/[k_{gb} + k_{nu}] (for TEA), with k_{nu} and k_{gb} for TEA being roughly equal in magnitude, k_{NEP}/k_{TEA} for 3a is effectively given by k'_{nu}(NEP)/k'_{gb}(Et$_3$N), k'_{nu} for TEA being of negligible importance, and the net result is that k_{NEP}/k_{TEA} could easily be two to three times larger for 3a than it is for 1b.

An explanation that attributes the catalysis of the hydrolysis of 1b by Et$_3$N to a mixture of part nucleophilic catalysis (eq 3) and part general base catalysis (eq 2) can thus apparently be accommodated to the various experimental results more easily than alternate explanations which assume that the catalysis is either entirely nucleophilic or entirely general base.

However, it is also clear from the work to date that the question of just what type of catalysis will be observed in any particular tertiary amine catalyzed hydrolysis of a sulfonyl derivative is a complex one and that considerable further study of additional appropriate systems will be necessary before one can develop a detailed understanding of this area.

Experimental Section

Preparation and Purification of Materials. The preparation and purification of phenyl α-disulfone (1b) followed previously described procedures.[2] p-Nitrophenyl p-toluenesulfonate was prepared in the following manner. To 13.3 g (0.096 mol) of p-nitrophenol in 50 ml of dimethylformamide was added 3.8 g of sodium hydroxide in 12.5 ml of water. To this solution was then added 18.1 g (0.098 mol) of p-toluenesulfonyl chloride in 50 ml of dimethylformamide and the resulting mixture was stirred at room temperature for 30 min. It was then poured over a 100-ml volume of ice and the white crystals of p-nitrophenyl p-toluenesulfonate which separated were collected by suction filtration. After recrystallization from 95% ethanol they melted at 93–95° (lit.[6] mp 96–97°). Triethylamine (Matheson Coleman and Bell) was purified by refluxing it over barium oxide and then fractionally distilling it under a nitrogen atmosphere immediately prior to use. N-Ethylpyrrolidine (Adams Chemical Co.) was purified in an exactly similar manner. Acetonitrile was purified by being fractionally distilled from over phosphorus pentoxide. Glyme (Ansul Chemical Co.) was distilled from sodium and then distilled from lithium aluminum hydride just prior to use. Dioxane was purified as previously described.[2] Reagent grade lithium perchlorate and perchloric acid were used without further purification.

Procedure for Kinetic Runs. Hydrolysis of p-Nitrophenyl p-Toluenesulfonate in 20% Acetonitrile. Buffer solutions having the appropriate Et$_3$N–Et$_3$NH$^+$ ratio were prepared by the addition of the standard aqueous perchloric acid to a standard aqueous solution of triethylamine. Lithium perchlorate was used where needed to adjust the ionic strength to the desired level. A sample of p-nitrophenyl p-toluenesulfonate (3a) was weighed out and dissolved in a known volume of acetonitrile. To initiate a kinetic run 20 ml of the appropriate Et$_3$N–Et$_3$NH$^+$ buffer solution containing the proper concentration of Et$_3$N was pipetted into a flask together with 4 ml of acetonitrile and 1 ml of the standard solution of 3a in acetonitrile. After mixing, aliquots of the solution were placed in a series of tightly stoppered (polyethylene stoppers) glass vials and the vials were shut so that there would be no loss of solvent or amine when the vial was subsequently heated to the reaction temperature of 70°. The vials were then placed in a constant-temperature bath at 70°. At appropriate intervals a vial was removed, cooled in ice water, opened, and the absorbance of the solution in it read at 400 nm. The absorbance increases with time owing to the formation of p-nitrophenolate ion, which absorbs strongly at 400 nm. The initial concentration of 3a used was normally about 10^{-4} M and in each instance the final absorbance of the solution at 400 nm corresponded within 2–3% of that expected for the formation of 1 mol of p-nitrophenolate ion for each mole of 3a present initially.

Hydrolysis of p-Nitrophenyl p-Toluenesulfonate in 60% Aqueous Glyme. Aqueous buffer solutions of either Et$_3$N–Et$_3$NH$^+$ or NEP–NEPH$^+$ were made up by adding the proper amount of standard perchloric acid to aqueous solutions containing known amounts of freshly distilled tertiary amine. (To get reproducible results it was very important to use freshly distilled amines.) A standard solution of lithium perchlorate in water was also prepared. The proper volumes of amine buffer and of lithium perchlorate solution were then mixed with the proper volumes of freshly distilled glyme and water to give a final solution containing 60% glyme (v/v). A very small volume of a relatively concentrated glyme solution of 3a sufficient to give a concentration of 3a in the initial kinetic solution of 5 × 10^{-5} M was then added, and aliquots of the final solution were then placed in a series of constricted tubes, which were carefully degassed and sealed under vacuum. The sealed tubes were placed in a constant-temperature bath at 115°. At appropriate intervals a tube was removed, cooled, opened, and the absorbance of the contents measured at 400 nm. As in the runs in 20% acetonitrile the infinity absorbance of the solution corresponded very closely to that expected for the formation of 1 mol of p-O$_2$NC$_6$H$_4$O$^-$ for each mole of 3a present initially.

Hydrolysis of Phenyl α-Disulfone in NEP–NEPH$^+$ Buffers in Aqueous Dioxane. A 1:1 standard buffer of NEP–NEPH$^+$ in 60% dioxane was prepared from purified N-ethylpyrrolidine and

standard perchloric acid, and 1:1 buffers of varying NEP concentration were prepared from this by appropriate dilution. The proper volume of a standard solution of lithium perchlorate in 60% dioxane was added to these solutions as required to achieve the desired ionic strength. The procedure used for following the kinetics of the disappearance of **1b** in 60% dioxane has already been described.[10] The hydrolyses were all slow enough at 25° to be followed by conventional, rather than stopped-flow, spectrophotometry.

Besides the various runs in 1:1 NEP-NEPH[+] buffers we also carried out a single series of runs in 60% dioxane in a set of 1:1 Et₃N–Et₃NH^{+} buffers of varying triethylamine concentration in order to verify that we could obtain kinetic results on this system in adequate agreement with those reported earlier by Kice and Kasperek.[2]

Registry No. 1b, 10409-06-0; **3a,** 1153-45-3.

References and Notes

(1) (a) This research was supported by the National Science Foundation, Grants GP-25799 and GP-35927X. (b) Preceding paper in this series: *J. Amer. Chem. Soc.,* **92,** 3393 (1970). (c) University of Vermont. (d) NDEA Fellow, Oregon State University, 1968–1971.

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The Addition of 2,4-Dinitrobenzenesulfenyl Chloride to 1-Phenylpropyne and Related Compounds

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Electrophilic additions of 2,4-dinitrobenzenesulfenyl chloride (1) to 1-phenylpropyne (4) and its ring-substituted derivatives (*p*-OCH₃, *p*-Cl, and *m*-Cl) have been studied kinetically in acetic acid. The effects of the ring substituents on the reaction rate of 4 conformed to the Hammett $\rho\sigma$ relationship with the reaction constant $\rho = -1.46$ at 40°. Additions of 1 to phenylacetylene (5), 1-hexyne (7), and 2-heptyne (6) were also studied for the sake of comparison. It was found that the methyl substitution on the acetylenic carbon enhances the reactivity by a factor of 10 to 20. The secondary kinetic isotope effects were examined for 5 and styrene (10) with use of α- and β-deuterated substrates. The value $k_H/k_D \sim 0.95$ for each deuteration was obtained. These results were compared with those found in the related electrophilic addition reactions. It is concluded that the sulfenyl sulfur attacks the isolated π bond of phenylacetylenes to form an unsaturated episulfonium ion.

Electrophilic addition reactions of acetylenes are closely related to those of olefins in character. The acid-catalyzed hydration of both phenylacetylene[1] and styrene[2] involves a carbonium ion intermediate stabilized by the benzyl conjugation. Yates, *et al.*,[3] have recently compared the reactivities of some olefin–acetylene pairs in electrophilic addition reactions, pointing out the similarity and the difference of the two systems. Intermediacy of an episulfonium ion was concluded in the additions of sulfenyl halides to both classes of compounds.[3-9]

We have recently found that 2,4-dinitrobenzenesulfenyl chloride (1) adds exclusively to the terminal double bond of phenylallene, whose nodal plane is orthogonal to that of the phenyl ring.[10] This aroused our interest in the problem as to which of the two acetylenic π bonds of phenylacetylene (parallel or orthogonal to the phenyl $p\pi$ orbitals) is the more amenable to the electrophilic attack of sulfur. The phenyl group could stabilize the unsaturated episulfonium ion either by conjugation with the intact double bond as in 2 or by interaction with the ring as in 3.

Hassner, *et al.*,[11] have recently suggested the intermediacy of iodonium ion of type 2 in the ionic addition of IN₃ to 1-phenylpropyne to explain the orientation. Their claim was later criticized in a review.[12] Nevertheless, the possible intermediacy of the onium ion of type 2 will be well conceivable in some cases, because the intermediate 2 is considered to be more stable owing to the conjugation.

In the present paper, we will report the results of the

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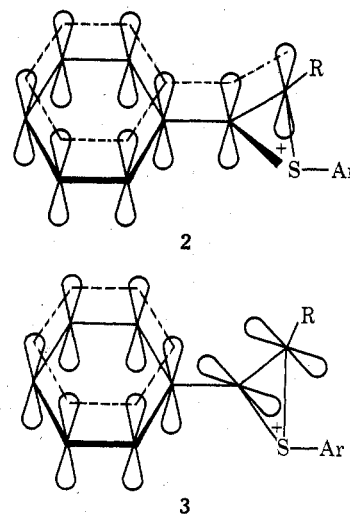
kinetic studies on the electrophilic addition of 1 to 1-phenylpropyne (4) and its related compounds 5-7. The secondary isotope effects on the reaction rate of 5 were also measured with use of phenylacetylene-β-*d* (5β), in comparison with those observed for the styrene system. The kinetic information obtained here has provided a useful basis to determine which form of intermediate, 2 or 3, is the more closely related to the transition state of the reaction.