Notes

Absence of Catalysis of the Hydrazinolysis of Phenyl α-Disulfone by Triethylamine and Its Mechanistic Implications for the Ordinary Hydrazinolysis[1a]

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Kice and Legan[2] studied the kinetics of the reaction of various amino compounds with phenyl α-disulfone (1), $PhSO_2SO_2Ph$, in 60% aqueous dioxane as solvent at a constant ionic strength of 0.04, with the amino compound present in large stoichiometric excess over the α-disulfone. With most amino compounds the experimental first-order rate constant, k_{exp}, was, as expected, strictly proportional to the first power of the concentration of the amino compound, i.e., $k_{exp} = k_a[\text{amino}]$, but with hydrazine k_{exp} appeared to have a different form (eq 1)

$$k_{exp} = k_a[NH_2NH_2] + k_b[NH_2NH_2]^2 \qquad (1)$$

with the k_b term contributing about one-third of the total value of k_{exp} at 0.04 *M* NH_2NH_2 in a 1:1 NH_2NH_2–$NH_2NH_3^+$ buffer. Kice and Legan[2] suggested that the k_b term probably represented general base catalysis by a second molecule of hydrazine of the attack of a molecule of hydrazine on 1.

If this interpretation is correct then hydrazinolysis of 1 in the presence of the much stronger base triethylamine ought to lead to marked catalysis of the hydrazinolysis by Et_3N, with k_{exp} being given by

$$k_{exp} = k[NH_2NH_2][Et_3N] \qquad (2)$$

We have now determined the kinetics of the hydrazinolysis of 1 in a series of 1:1 Et_3N–Et_3NH^+ buffers containing 0.01 *M* NH_2NH_2 and 0.01–0.04 *M* triethylamine. The results are shown in Table I. It is evident that there is no dependence of k_{exp} on $[Et_3N]$ and that the rate is the same as that found[2] in the absence of triethylamine at the same hydrazine concentration. Clearly, then, the *apparent* $k_b[NH_2NH_2]^2$ term in eq 1 observed by Kice and Legan[2] was *not* the result of general base catalysis by hydrazine of the reaction of hydrazine with 1.

Table I
Kinetics of the Hydrazinolysis of Phenyl α-Disulfone in Et_3N–Et_3NH^+ Buffers in 60% Dioxane at 25° [a]

$[NH_2NH_2]$, *M*	$[Et_3N]$, *M*	$[Et_3NH^+]$, *M*	$[LiClO_4]$, *M*	k_{exp}, sec^{-1}
0.01	0.01	0.01	0.03	0.18
	0.02	0.02	0.02	0.20
	0.04	0.04	0.00	0.19

[a] All runs with initial concentration of $1\ 3 \times 10^{-5}$ *M*.

To explore the matter further we have reexamined the hydrazinolysis of 1 in both 1:1 and 2:1 NH_2NH_2–$NH_2NH_3^+$ buffers, but using a significantly higher total ionic strength of about 0.10, so that $NH_2NH_3^+$ was always present at a lower concentration than Li^+, something that was not true in the earlier study.[2] The results are shown in Table II. It is clear that under these conditions $k_{exp}/[NH_2NH_2]$ is effectively constant and that there is no significant contribution to the rate from a term of the form $k_b[NH_2NH_2]^2$.

Table II
Kinetics of the Hydrazinolysis of Phenyl α-Disulfone in NH_2NH_2–$NH_2NH_3^+$ Buffers in 60% Dioxane at 25° [a]

$[NH_2NH_2]$, *M*	$[NH_2NH_3^+]$, *M*	$[LiClO_4]$, *M*	k_{exp}, sec^{-1}	$k_{exp}/[NH_2NH_2]$, *M*$^{-1}$ sec^{-1}
0.02	0.01	0.09	0.37	19
0.04	0.02	0.08	0.75	19
0.08	0.04	0.06	1.55	19
0.01	0.01	0.095	0.18	18
0.02	0.02	0.09	0.40	20
0.04	0.04	0.08	0.81	20

[a] All runs with initial concentration of $1\ 3 \times 10^{-5}$ *M*.

Salomaa and coworkers[3] have shown that *apparent* catalysis by a buffer component is *sometimes* observed in experiments in dioxane–water solvents, as a consequence of salt effects, when maintenance of a constant ionic strength is achieved by a systematic variation in the concentration of both buffer component and inert salt, rather than by use of a large constant excess of inert salt. The results in Table II suggest that an effect of this type might well have been responsible for the apparent $k_b[NH_2NH_2]^2$ term observed by Kice and Legan,[2] although a more extensive investigation of the salt effects associated with the hydrazinolysis would, of course, be necessary to establish this with certainty.

In any event, the important point of the present work is that the variation in $k_{exp}/[NH_2NH_2]$ with $[NH_2NH_2]$ observed by Kice and Legan[2] under their particular reaction conditions actually has nothing to do with the concentration of free hydrazine base and is definitely not the result of general base catalysis of the hydrazinolysis of 1 by a second hydrazine molecule, as was originally suggested.[2]

Experimental Section

The kinetics of the reactions were followed by the same stopped-flow procedure described by Kice and Legan.[2] The triethylamine was purified in the manner described by Kice, Walters, and Burton.[4] The purification of the other reagents followed previously described procedures.[2]

Registry No.—Phenyl α-disulfone, 10409-06-0; NH_2NH_2, 302-01-2; Et_3N, 121-44-8.

References and Notes

(1) (a) This research supported by the National Science Foundation, Grant GP-35927X. (b) Address correspondence to Department of Chemistry, Texas Tech University, Lubbock, Texas 79409.
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