

Nucleophilic Catalysis. Part IV.¹ Acid-catalysed Hydrolyses of Some 3-Alkylsydnones

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The effects of added acids and salts on the rates of hydrolysis of a number of 3-alkylsydnones have been studied. It is shown that the acid-catalysed hydrolyses of 3-methyl- and 3-isopropyl-sydnones proceed by both an A2 mechanism and a nucleophilic catalysis pathway. On the other hand, 3-*t*-butyl- and 3-furfuryl-sydnones hydrolyse by both a 'neutral' and an A1 mechanism.

THE mesoionic 3-phenylsydnone (I; R¹ = Ph, R² = H) is hydrolysed in the presence of hydrochloric acid to form phenylhydrazine, formic acid, and carbon dioxide.^{2,3} The results of ¹⁵N-labelling experiments by Staley and Clarke⁴ ruled out the possibility of N → N aryl migration during hydrolysis and were consistent with the mechanism of hydrolysis suggested by Baker and Ollis.⁵

This has had to be modified subsequently to accommodate a nucleophilic catalysis mechanism in which the rate-limiting step involves halide-ion attack on the conjugate acid species.¹ The existence of arylhydrazides as intermediates in the hydrolysis of 3-arylsydnones has been firmly established.⁶⁻⁸

The only kinetic data previously reported for the hydrolysis of 3-alkylsydnones are from a simple comparative rate study by Garrett.⁹ He did not examine the role of halide ion in the hydrolysis or attempt to elucidate the mechanism in any detail. His data show, however, that for the hydrochloric acid-catalysed hydrolysis of a series of 3-alkylsydnones there is a change in the value of log *A* about half-way along the series 1,1-dimethylhexyl, *t*-butyl, furfuryl, isopropyl, propyl, and methyl, which suggests a possible change of mechanism.

In order to provide further evidence of the mechanism of decomposition of 3-alkylsydnones in the presence of acids, we have examined the effect of added acids and salts at relatively high electrolyte strength on the hydrolyses of 3-methyl-, 3-isopropyl-, 3-*t*-butyl-, and 3-

furfuryl-sydnones. A preliminary account of part of this work has been given.¹⁰

EXPERIMENTAL

Materials.—The sydnones were prepared by cyclodehydration of the *N*-aryl-*N*-nitrosoglycines.² After recrystallisation from benzene, 3-*t*-butylsydnone had m.p. 172° (lit.,¹¹ 168–170°); 3-furfurylsydnones, recrystallised from benzene, had m.p. 96° (lit.,¹¹ 94–95°); 3-isopropylsydnone, recrystallised from ether, had m.p. 54–56° (lit.,¹¹ 54–55°); 3-methylsydnone had b.p. 140–150°/0.1–0.2 mmHg (lit.,¹² 140–142°/0.2 mmHg).

Acid-catalysed Hydrolyses.—The acids used were of Analytical Reagent quality. Their concentrations were determined by titration with standard alkali. Sodium chloride, sodium bromide, and sodium hydrogen sulphate were dried at 120 °C. Lithium perchlorate and sodium perchlorate were dehydrated at 150 °C and kept in a vacuum at this temperature for 24 h with a diffusion pump. Anhydrous lithium chloride and lithium bromide were prepared similarly. Dioxan was purified by a standard method.

Kinetic Measurements.—The rates of hydrolysis were determined by following the decrease in the characteristic absorption of the sydnones: 3-*t*-butylsydnone, 284 nm; 3-furfurylsydnones, 286 nm; 3-isopropyl- and 3-methylsydnones, 284 nm.

Typical Run.—3-*t*-Butylsydnone (0.01 ml of stock solution in dioxan: 3 × 10⁻²M) was added to 2.99M-perchloric acid (3.0 ml) in a thermostatted stoppered cell at 59.4 ±

⁶ S. A. Zotova and V. G. Yashunskii, *Zhur. org. Khim.*, 1967, **3**, 942.

⁷ J. Kenner and K. Mackay, *Nature*, 1947, **160**, 465.

⁸ I. M. Hunsberger, personal communication quoted in ref. 4.

⁹ E. R. Garrett, *J. Pharm. Sci.*, 1964, **53**, 42.

¹⁰ S. Aziz and J. G. Tillett, *Tetrahedron Letters*, 1969, 2855.

¹¹ L. B. Kier and D. Dharvan, *J. Pharm. Sci.*, 1962, **51**, 1058.

¹² D. L. Hammick and D. J. Voaden, *J. Chem. Soc.*, 1961, 3303

¹ Part III, S. Aziz, A. F. Cockerill, and J. G. Tillett, *J. Chem. Soc. (B)*, 1970, 416.

² J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 1925, 899.

³ R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 1946, 591.

⁴ J. Staley and D. C. Clarke, *J. Org. Chem.*, 1964, **29**, 2493.

⁵ W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15.

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0.03 °C. The cell contents were shaken rapidly and readings of optical density (D) taken at intervals. Results are in Table 1.

Values of the first-order rate-coefficients (k_1), calculated from the usual equation or graphically from the plot of $\log (D_t - D_\infty)$ against time, are in Tables 2–5.

TABLE 1

t/min	0	20.0	67.4	142	178	220
D	0.808	0.780	0.719	0.631	0.592	0.550
$10^2 k_1/\text{min}^{-1}$	—	0.176	0.173	0.174	0.175	0.175
t/min	256	300	347	378	532	∞
D	0.516	0.479	0.439	0.418	0.316	0
$10^5 k_1/\text{min}^{-1}$	0.175	0.174	0.176	0.174	0.176	—

Mean $k_1 = 0.00175 \text{ min}^{-1}$; k_1 (graphical) 0.00174 min^{-1} .

TABLE 2

Hydrolysis of 3-methylsydnone (k_1 in min^{-1}) in water and at 70.0 °C unless indicated otherwise

(a) Effect of added acids					
[Acid]/M	0.500	1.00	1.00	1.50	2.00
HClO_4 , $10^5 k_1$	—	1.84	2.30 †	—	5.30
H_2SO_4 , $10^5 k_1$	—	3.22	—	—	10.3
HCl , $10^5 k_1$	1.28	3.07	—	5.99	9.36
HBr , $10^5 k_1$	—	3.68	—	—	12.7
(b) At constant ionic strength					
[Acid]/M	3.00	4.00	5.00	5.50	6.00
HClO_4 , $10^5 k_1$	11.1	22.7	36.1	—	72.2
H_2SO_4 , $10^5 k_1$	24.9	50.7	—	126	—
HCl , $10^5 k_1$	21.5	52.2	107	—	235
HBr , $10^5 k_1$	41.5	127	304	—	—
(c) Effect of added salts and perchloric acid (2.00M)					
[Salt]/M	1.00	2.00	3.00	4.00	—
NaClO_4 , $10^5 k_1$	—	10.8	—	20.0	—
NaHSO_4 , $10^5 k_1$	9.98	—	19.2	—	—
NaCl , $10^5 k_1$	10.4	—	37.2	—	—
NaBr , $10^5 k_1$	—	35.3	—	92.1	—
(d) With perchloric acid (1.00M) at different temperatures					
$T/^\circ\text{C}$	60.0	65.0	70.0	78.0	80.0
$10^5 k_1$	0.84	1.46	1.84	5.07	6.14

† In 99.9% D_2O .

TABLE 3

Hydrolysis of 3-isopropylsydnone (k_1 in min^{-1})

(a) Effect of added acids						
Acid/M	1.00	1.00	2.00	3.00	4.00	5.00
HClO_4 , $10^5 k_1$	1.84	2.83 †	4.70	10.8	20.0	32.2
HCl , $10^5 k_1$	2.30	—	7.68	19.0	32.6	89.8
HBr , $10^5 k_1$	4.53	—	11.2	33.8	99.6	261
(b) With perchloric acid at different temperatures						
$T/^\circ\text{C}$	59.9	70.0	80.0	85.1	90.2	—
$10^5 k_1$	—	4.70	16.5	28.4	47.6	—

† In 99.9% D_2O .

Influence of Temperature.—The entropies (ΔS) and energies of activation (ΔE) were calculated by use of the equation $k = (e \cdot kT/h) \exp (\Delta S/R) \exp (-\Delta E/RT)$ by a least-squares procedure (Table 6).

TABLE 4

Hydrolysis of 3-*t*-butylsydnone (k_1 in min^{-1}) in water and at 75.0 °C unless otherwise indicated

(a) Effect of added acids						
[Acid]/M	0.490	0.99	1.49	1.98	2.49	2.98
HClO_4 , $10^5 k_1$	0.743	1.88	3.23	6.48	11.0	15.9
H_2SO_4 , $10^5 k_1$	0.722	1.59	2.92	4.91	8.57	12.4
HCl , $10^5 k_1$	0.726	1.32	2.27	3.63	5.51	7.20
HBr , $10^5 k_1$	—	1.51	2.98	4.97	8.58	12.5
(b) At constant ionic strength						
$[\text{HClO}_4]/\text{M}$	0.490	0.990	1.24	1.49	1.98	—
$[\text{LiClO}_4]/\text{M}$	1.49	0.990	0.74	0.49	—	—
$10^5 k_1$	1.77	3.39	4.22	4.86	6.48	—
$10^5 k_2/\text{l mol}^{-1} \text{ min}^{-1}$	3.63	3.42	3.27	3.40	3.25	—
(c) With perchloric acid (0.990M) at different temperatures						
$T/^\circ\text{C}$	60.0	64.4	70.0	75.0 †	80.0	—
$10^5 k_1$	0.227	0.398	1.02	1.88	3.22	—
(d) Kinetic solvent isotope effect at 59.4 °C						
Solvent	Catalyst	$10^5 k_1$	$k_1(\text{D}_2\text{O})/k_1(\text{H}_2\text{O})$	—	—	—
H_2O	2.99M- HClO_4	1.80	—	—	—	—
D_2O	2.99M- HClO_4	3.11	1.73	—	—	—

† Neutral rate, $k_1 = 0.157 \times 10^{-3} \text{ min}^{-1}$.

TABLE 5

Hydrolysis of 3-furfurylsydnone (k_1 in min^{-1}) in water and at 60.0 °C unless otherwise indicated

(a) Effect of added acids						
[Acid]/M	0.490	0.990	1.49	1.99	2.49	2.99
HClO_4 , $10^5 k_1$	4.14	6.20	10.3	14.9	25.4	45.9
H_2SO_4 , $10^5 k_1$	4.10	6.10	9.66	14.3	22.7	36.8
HCl , $10^5 k_1$	3.87	5.36	7.80	11.0	15.3	21.2
(b) At constant ionic strength						
$[\text{HClO}_4]/\text{M}$	0.490	0.99	1.49	1.99	2.98	—
$[\text{LiClO}_4]/\text{M}$	2.49	1.99	1.49	0.99	—	—
$10^5 k_1$	10.4	17.1	24.2	30.9	45.9	—
$10^5 k_2/\text{l mol}^{-1} \text{ min}^{-1}$	21.1	17.3	16.3	15.9	15.5	—
(c) Kinetic solvent isotope effect						
Solvent	Catalyst	$10^5 k_1$	$k_1(\text{D}_2\text{O})/k_1(\text{H}_2\text{O})$	—	—	—
H_2O	—	2.34	—	—	—	—
D_2O	—	2.35	1.00	—	—	—
H_2O	1.49M- HClO_4	10.3	—	—	—	—
D_2O	1.49M- HClO_4	16.6	1.60	—	—	—
H_2O	1.49M- H_2SO_4	9.66	—	—	—	—
D_2O	1.49M- H_2SO_4	12.7	1.32	—	—	—
H_2O	1.49M- HCl	7.80	—	—	—	—
D_2O	1.49M- HCl	9.58	1.24	—	—	—
(d) Effect of added salts with perchloric acid (0.240M)						
$[\text{LiClO}_4]/\text{M}$	—	0.99	1.99	2.98	—	—
$[\text{LiCl}]/\text{M}$	—	—	—	—	0.99	1.99
$10^5 k_1$	3.24	4.39	5.46	7.80	4.39	5.45
(e) At different temperatures						
$T/^\circ\text{C}$	50.5	54.3	60.0	64.9	70.3	—
$10^5 k_1$ (acid)	1.22	2.21	4.16	7.97	16.07	—
$10^5 k_1$ (neutral)	0.650	0.962	2.02	3.43	6.23	—
(f) Effect of added perchloric acid (1.99M) in different solvents						
Solvent	H_2O	20% Dioxan	40% Dioxan	60% Dioxan	—	—
$10^5 k_1$	11.0	7.06	6.73	6.67	—	—

TABLE 6

Arrhenius parameters for the hydrolysis of 3-alkylsydnone

Substituent	Catalyst	$E_a/\text{kcal mol}^{-1}$	$\Delta S/\text{cal mol}^{-1} \text{ K}^{-1}$
Methyl	1.00M- HClO_4	23.4 ± 0.6	-19.9 ± 1.7
Isopropyl	2.00M- HClO_4	26.2 ± 0.8	-10.2 ± 2.4
<i>t</i> -Butyl	0.99M- HClO_4	31.7 ± 1.2	10.1 ± 3.5
Furfuryl	0.99M- HClO_4	28.3 ± 0.7	5.6 ± 2.0
Furfuryl	Neutral	25.5 ± 0.5	-4.2 ± 1.5

DISCUSSION

3-Methyl- and 3-Isopropyl-sydnone.—The kinetic forms observed for the hydrolyses of 3-methyl- and 3-isopropyl-sydnone are so similar that the illustrations for most of the ensuing discussion could be taken from the data for either compound. In contrast to the behaviour of 3-arylsydnone the hydrolyses of these alkylsydnone is catalysed by both perchloric acid and sulphuric acid as well as hydrochloric and hydrobromic acids.

The Proton Transfer.—The values obtained [Tables 2(a) and 3(a)] for the deuterium kinetic solvent isotope effect [$k_1(\text{D}_2\text{O})/k_1(\text{H}_2\text{O})$] for the perchloric acid-catalysed hydrolysis of both 3-methylsydnone (1.25) and 3-isopropylsydnone (1.5) are characteristic¹³ of reactions which proceed by specific hydrogen ion catalysis and suggest a similar rapid pre-equilibrium proton transfer to that observed for 3-arylsydnone.¹

In a study of the hydrochloric acid-catalysed hydrolyses of a series of 3-alkyl- and 3,4-dialkyl-sydnone, Garrett and his co-workers^{9,14} assumed protonation on position 2 of the sydnone ring. Olah and his co-workers have recently shown, however, that the protonation of 3-phenylsydnone in $\text{FSO}_3\text{H-SbF}_5$ solution occurs exclusively on the carbonyl oxygen atom.¹⁵ A possible explanation of this apparent contradiction is to be found in studies of the protonation of amides for which similar conflicting evidence has been found.¹⁶ Liler has concluded from n.m.r. studies that the *N*-protonated conjugate acid of amides, which is the dominant form in dilute and moderately concentrated acid, is converted into the *O*-protonated form in highly concentrated and anhydrous acid owing to a medium effect arising from cation hydration.¹⁷ We have assumed therefore, as did earlier workers, that the acid-catalysed hydrolyses of 3-alkylsydnone proceed through the *N*-protonated conjugate acid.^{14,18}

Mechanism in Perchloric Acid.—The rates of hydrolysis in perchloric acid of both 3-methylsydnone and 3-isopropylsydnone at first increase linearly with acid concentration but above ca. 2.0M-acid increase more rapidly than does acid concentration [Tables 2(a) and 3(a)]. This is probably due to a positive salt effect superimposed on a linear dependence of rate on stoichiometric acidity and is characteristic of many reactions hydrolysing by an A2 mechanism, e.g., the acid-catalysed hydrolysis of ethyl acetate,¹⁹ methyl phosphate,²⁰ and dialkyl sulphites.²¹

Application of Bunnett's treatment²² to the kinetic data for the perchloric acid-catalysed hydrolysis of

3-methyl- and 3-isopropyl-sydnone leads to *w* values of 3.45 and 3.88 which fall into the range expected for an A2 mechanism. Further confirmation of this mechanism comes from values of the entropy of activation [−19.9 and −10.2 cal mol^{−1} K^{−1} respectively (Table 6)] which are consistent with a bimolecular mechanism.²³

Nucleophilic Catalysis.—The order of effectiveness of the catalysing acids, $\text{HBr} > \text{HCl} > \text{H}_2\text{SO}_4 > \text{HClO}_4$, and the magnitude of the relative effects, suggests the occurrence of nucleophilic catalysis in which anions possessing nucleophilic properties compete with the solvent for the conjugate acid, thereby providing an additional, more favourable, reaction path than that followed in the absence of such anions. Similar behaviour was observed in the hydrolyses of 3-arylsydnone¹ and of diazo-ketones,²⁴ dialkyl sulphites,²¹ and methyl toluene-*p*-sulphinate.²⁵

Further evidence of the role of nucleophiles in the hydrolysis of 3-methyl- and 3-isopropyl-sydnone can be obtained from a study of the effect of added salts on the perchloric acid-catalysed reaction [Table 2(c)]. The salts used seemed to fall into two clearly defined classes. The first, in which effects are small, includes sodium perchlorate and sodium bisulphate. Sodium chloride and sodium bromide fall into a second category and have a very marked positive catalytic effect. This effect is much too large to be ascribed to a simple salt effect and must arise from additional specific anion or nucleophilic catalysis.

A general expression for the first-order rate-coefficient (k_1) for the hydrolysis of sydnone in acidic solutions containing halide ions can be written as equation (1), where terms represent reaction of the neutral species

$$k_1 = k_0 + k_{\text{H}^+}[\text{H}^+] + k_0'[\text{X}^-] + k_{\text{X}^-}[\text{H}^+][\text{X}^-] \quad (1)$$

with water, an acid-catalysed reaction, a halide ion-catalysed reaction, and halide ion attack on the conjugate acid species respectively.

For the hydrolyses of 3-methyl- and 3-isopropyl-sydnone, k_0 and k_0' are effectively zero, and equation (1) reduces to (2). Each term may be subject to ionic-

$$k_1 = k_{\text{H}^+}[\text{H}^+] + k_{\text{X}^-}[\text{X}^-][\text{H}^+] \quad (2)$$

strength effects. If, however, the halide-ion concentration is kept constant as in mixtures of hydrochloric acid and sodium chloride of constant ionic strength, k_1 varies linearly as a function of acid concentration as predicted by equation (2) [Table 2(b)].

One possible reaction scheme for the hydrolyses of

¹³ F. A. Long and J. G. Pritchard, *J. Amer. Chem. Soc.*, 1956, **78**, 2663.

¹⁴ E. R. Garrett and P. J. Mehta, *J. Pharm. Sci.*, 1967, **56**, 1468.

¹⁵ G. A. Olah, D. P. Kelly, and N. Swein, *J. Amer. Chem. Soc.*, 1970, **92**, 3133.

¹⁶ Cf. C. O'Connor, *Quart. Rev.*, 1970, **24**, 553.

¹⁷ M. Liler, *Chem. Comm.*, 1971, 115; *J. Chem. Soc. (B)*, 1971, 334.

¹⁸ E. B. Roche and L. B. Kier, *Tetrahedron*, 1968, **24**, 1673.

¹⁹ R. P. Bell, A. L. Dowding, and J. A. Noble, *J. Chem. Soc.*, 1955, 3106.

²⁰ C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, 1958, 3574.

²¹ C. A. Bunton, P. B. D. de la Mare, and J. G. Tillett, *J. Chem. Soc.*, 1958, 4754; 1959, 1766; G. E. Manser, A. D. Mesure, J. G. Tillett, and R. C. Young, *J. Chem. Soc. (B)*, 1968, 267.

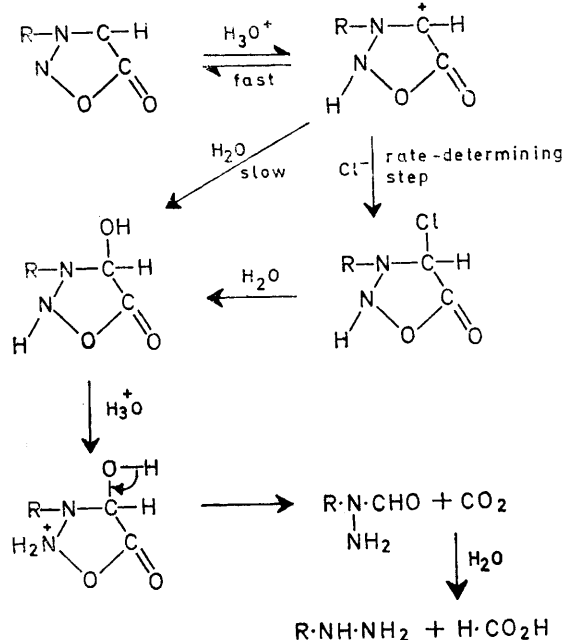
²² J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, and 4978.

²³ L. L. Scholenger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.

²⁴ J. B. N. F. Engberts and B. Zwannenberg, *Tetrahedron*, 1968, **24**, 1737.

²⁵ C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, 1962, 2562.

3-methyl- and 3-isopropyl-sydnone is a modified version (Scheme 1) of that suggested for 3-phenylsydnone.



SCHEME 1

3-*t*-Butyl- and 3-Furfuryl-sydnone.—The behaviour of 3-*t*-butylsydnone and 3-furfurylsydnone is both very similar in acid solution but differs significantly from that observed for the hydrolysis of other alkyl or arylsydnone. Both of these sydnone hydrolyse by a pH-independent mechanism (*i.e.*, a spontaneous or 'neutral' hydrolysis) as well as by an acid-catalysed pathway.

The values obtained [Tables 4(e) and 5(c)] for the kinetic deuterium solvent isotope effect in perchloric acid (1.73 and 1.60) do properly represent the solvent isotope effect on the acid-catalysed reaction because the isotope effect on the neutral hydrolysis is negligible (see later). The values obtained are similar to those observed for the hydrolyses of other 3-alkylsydnone and are again characteristic of reactions which proceed by a rapid pre-equilibrium proton transfer.¹³

The most striking feature of the effect of different acids on the hydrolysis of these compounds is the order of effectiveness of the acids, *viz.*, $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HBr} > \text{HCl}$. This is in marked contrast to that observed for 3-methyl- and 3-isopropyl-sydnone which was related to the nucleophilic power of the acid anion. This important difference suggests that there might be a change in mechanism on going from primary and secondary alkylsydnone to tertiary alkylsydnone.

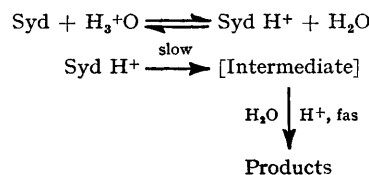
In a recent study of electrolyte effects on acid-catalysed reactions, Bunton and his co-workers suggested the generalisation that for A1 reactions the catalytic effect of added acids decreases in the sequence $\text{HClO}_4 > \text{HCl} \sim \text{H}_2\text{SO}_4$, whereas for A2 reactions the relative order is $\text{H}_2\text{SO}_4 > \text{HCl} \sim \text{HBr} > \text{HClO}_4$.²⁶ On the basis of this criterion the order of effectiveness of acids on the hydrolysis of 3-*t*-butyl- and 3-furfuryl-sydnone at

moderately high acidity again suggests that both hydrolyse by an A1 mechanism.

Further information about the mechanism of hydrolysis is provided by the effect of added salts. Lithium perchlorate and lithium chloride have a similar effect on the acid-catalysed hydrolysis of 3-furfurylsydnone at relatively low concentrations of added salt (<2.0M) [Table 5(d)], but above this the perchlorate begins to exert a larger effect. Such behaviour is consistent with the relative effects of added salts on A1 reactions as observed by Bunton *et al.*²⁶

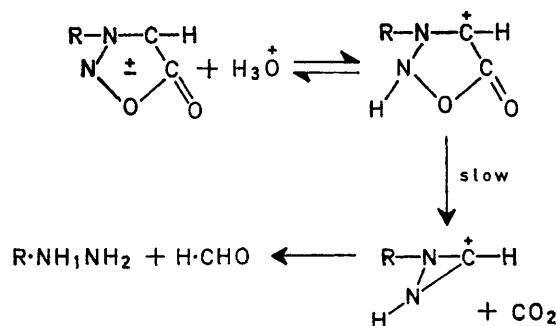
The Bunnett *w* values for the hydrolysis of both *t*-alkylsydnone are *ca.* 0 (the plot for 3-furfurylsydnone showing considerable scatter) and are therefore consistent with the suggested A1 mechanism. The values of the entropy of activation (+10.1 cal mol⁻¹ K⁻¹, +5.6 cal mol⁻¹ K⁻¹) are also in the range associated with a unimolecular mechanism.²³ Further evidence for this mechanism is provided by solvent effects. Thus the rate of hydrolysis of 3-furfurylsydnone in aqueous dioxan [Table 5(f)] increases with increasing water content, and a similar increase in the rate of hydrolysis of 1,1-dimethylhexylsydnone in aqueous ethanol with increasing polarity of the solvent has been reported by Garrett.⁹

The evidence presently available suggests that the acid-catalysed hydrolysis of 3-*t*-butyl- and 3-furfurylsydnone, in marked contrast to that of 3-arylsydnone and 3-methyl- and 3-isopropyl-sydnone, follows an A1 mechanism which can be generalised as in Scheme 2.



SCHEME 2

If it is assumed that protonation again occurs on the 2-nitrogen atom, one possible reaction sequence (Scheme 3) involves the formation of a cyclic carbonium ion. Garrett and Mehta have shown that 4-methyl-3-*t*-butyl-



SCHEME 3

sydnone hydrolyses more quickly than 3-*t*-butylsydnone.¹⁴ This is consistent with the greater stabilisation of the bridged carbonium ion by the methyl groups.

²⁶ C. A. Bunton, J. H. Crabtree, and L. Robinson, *J. Amer. Chem. Soc.*, 1968, **90**, 1258.

It is noteworthy that the acid-catalysed hydrolysis of the related diaziridine ring is also thought to involve a unimolecular mechanism.²⁷

The lack of any isotope effect on the spontaneous hydrolysis of furfurylsydnone [Table 5(c)] and the value

of the entropy of activation ($-4.2 \text{ cal mol}^{-1} \text{ K}^{-1}$) possibly suggests that this reaction may also proceed *via* a unimolecular mechanism.

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²⁷ Cf. E. Schmitz, *Angew. Chem. Internat. Edn.*, 1964, **3**, 333.

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