Mesoionic Compounds. Part 5.[1] The Acid-catalysed Hydrolysis of Diarylisosydnones

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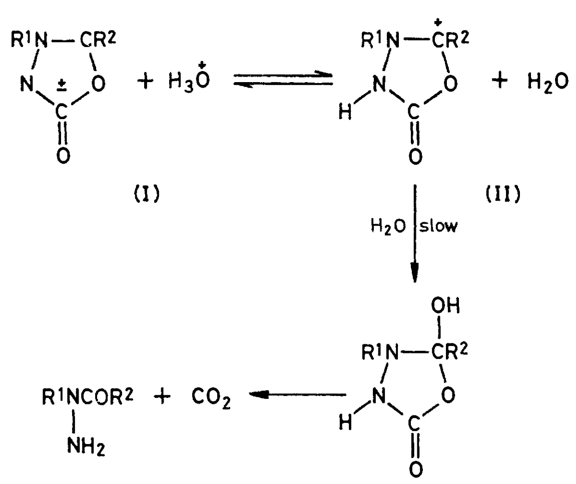
The acid-catalysed hydrolyses and protonation behaviour of some 4-(*para*-substituted phenyl)-5-phenylisosydnones have been studied in aqueous solutions of mineral acids. For perchloric and sulphuric acid, plots of the first-order rate coefficients k_1 against $[H^+]$ show maxima which arise from extensive protonation of the substrates. Analyses of the kinetic data by Bunnett and Bunnett–Olsen criteria are consistent with a bimolecular mechanism. Oxygen-18 tracer studies establish that the acid-catalysed hydrolyses of diarylisosydnones proceed through two different pathways involving attack of water at both the C-5 and the C-2 carbonyl carbon atom.

ALTHOUGH the kinetics of hydrolysis of diarylisosydnones (I) have been intensively studied and the products of hydrolysis are well known, the mechanism of hydrolysis is not clearly understood. Several groups of workers [1-3] have assumed that hydrolysis occurs *via* an *A*-2 mechanism in which initial pre-equilibrium protonation is followed by attack of a water molecule at C-5 of the *N*-protonated conjugate acid (II) (Scheme 1). On the other hand, isosydnones undergo nucleophilic attack by alcohols and amines at the C-2 carbonyl carbon to give the corresponding urethanes and amides respectively.[2]



SCHEME 1

In order to provide more information about the site of nucleophilic attack on the isosydnone ring in acid-catalysed hydrolysis we have determined the point of bond fission by an oxygen-18 tracer method and examined the effects of substituents on the acid-catalysed hydrolyses of a number of 4-R-5-phenylisosydnones (R = C_6H_5, *p*-MeC_6H_4, *p*-ClC_6H_4, or *p*-BrC_6H_4).

EXPERIMENTAL AND RESULTS

Materials.—The isosydnones were prepared by the action of phosgene on the corresponding *N*-benzoyl-*N*-(*para*-substituted) phenylhydrazine hydrochloride. 4,5-Diphenylisosydnone after recrystallisation from benzene had m.p. 163° (plates) (lit.,[2,4] 162, 160°); 5-phenyl-4-*p*-tolylisosydnone had m.p. 181° (lit.,[5] 181—183°); 4-*p*-chlorophenyl-5-phenylisosydnone had m.p. 163° (plates) (lit.,[5] 162°); 4-p-*bromophenyl-5-phenylisosydnone* had m.p. 267—270° (plates) (Found: C, 52.8; H, 2.8; N, 8.8. $C_{14}H_7BrN_2O_2$ requires C, 53.0; H, 2.8; N, 8.8%), $\lambda_{max.}$ 295 nm, $\nu_{max.}$ 1 766 cm^{-1}.

Protonation Equilibria.—The absorbances at a number of wavelengths between 200 and 450 nm were recorded for solutions containing various concentrations of sulphuric acid and a fixed concentration of isosydnone. Measurements were carried out on a Unicam SP 800 spectrometer thermostatted at 25 ± 0.2°. The ionisation ratio ($I = [BH^+]/[B]$) was determined from absorbance measurements from equation (1) where D_B is the absorption of the neutral

$$\log I = \log [(D_B - D)/(D - D_{BH^+})] \qquad (1)$$

form, D_{BH^+} the corresponding value of the completely protonated form, and D the value in a solution of intermediate acidity. Absorbance measurements were made at the following wavelengths for 4-substituted 5-phenylisosydnones: 4-*p*-tolyl, 220; 4-*p*-chlorophenyl, 212; 4-*p*-bromophenyl, 218 nm. The ionisation ratios so obtained were fitted by a least squares method to equations (2)—(4) (Table 1).

TABLE 1

Protonation equilibria of 4-(*para*-substituted phenyl)-5-phenylisosydnones

Substituent	Equation (2)		Equation (3)		Equation (4)	
	M	$(H_0)_{\frac{1}{2}}$	c	d/c	ϕ	pK_{BH^+}
Me	0.54	−3.06	0.90	−2.22	0.55	−1.80
	±0.02	±0.05	±0.02	±0.02	±0.01	±0.03
H [a]	0.55	−3.3	0.94	−2.49	0.46	−2.18 [b]
	±0.03	±0.29	±0.07	±0.36		
Cl	0.64	−3.36	1.04	−2.54	0.44	−2.66
	±0.02	±0.05	±0.04	±0.09	±0.02	±0.04
Br	0.59	−3.46	0.96	−2.60	0.49	−2.28
	±0.01	±0.03	±0.04	±0.08	±0.01	±0.01

[a] Data from ref. 4. [b] Graphical.

Kinetic Measurements.—The kinetics of hydrolysis were followed spectrophotometrically at appropriate wavelengths in the u.v. region using methods previously described.[1] A Unicam SP 800 spectrometer fitted with a thermostatted cell block (±0.03°) and an external recorder were used. Values of the first-order rate coefficients (k_1), calculated from the usual equation or graphically, are shown in Tables 2—4.

Bond Fission Studies.—The isosydnones (0.5 g) were hydrolysed in acidic solutions of aqueous dioxan (60 : 40

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[1] Part 4, E. A. Isukul and J. G. Tillett, *J.C.S. Perkin II*, 1975, 230.

[2] M. Hashimoto and M. Ohta, *Bull. Chem. Soc. Japan*, 1961, **34**, 668.

[3] P. B. Talukdar, S. Banerjee, and A. Chakraborty, *Indian J. Chem.*, 1972, **10**, 610.

[4] A. J. Buglass and J. G. Tillett, *J.C.S. Perkin II*, 1973, 1687.

[5] A. R. McCarthy, W. D. Ollis, A. N. M. Barnes, L. E. Sutton, and C. Ainsworth, *J. Chem. Soc.* (*B*), 1969, 1185.

v/v, 5.0M-HCl) using water enriched with oxygen-18. After 24 h at 60° the reaction solution was cooled and a stream of air bubbled through the solution to precipitate the corresponding *N*-aroyl-*N*-arylhydrazine hydrochloride. This was filtered off, washed several times with ether, and dried at 100° for several hours before analysis for oxygen-18 content by conversion into carbon dioxide. Authentic samples of the hydrolysis product were also exposed to the hydrolysis procedure to check the extent of oxygen-18 enrichment occurring by oxygen exchange of the product with the solvent.

TABLE 2

Hydrolysis of 4-*p*-chlorophenyl-5-phenylisosydnone

(a) Effect of added acids at 50.1°

[HCl]/M		1.00	2.00	3.00
10^3k_1/min^{-1}	25.6	31.0	38.0	44.9
[HCl]/M	4.00	5.00	6.00	7.00
10^3k_1/min^{-1}	53.0	60.2	75.5	75.5
[H_2SO_4]/M	1.00	2.00	3.00	4.00
10^3k_1/min^{-1}	28.7	33.0	38.4	45.3
[H_2SO_4]/M	5.00	6.00	7.00	8.00
10^3k_1/min^{-1}	52.0	54.9	47.7	37.7
[$HClO_4$]/M	1.00	2.00	3.00	4.00
10^3k_1/min^{-1}	16.1	14.4	13.8	15.4
[$HClO_4$]/M	5.00	6.00	7.00	8.00
10^3k_1/min^{-1}	19.6	19.1	14.8	8.52

(b) Effect of added salts at 50.1° on the neutral reaction

[Salt]/M	1.00	2.00	3.00	4.00	5.00
NaCl, 10^3k_1/min^{-1}	15.0	11.5	9.21	8.00	7.52
$NaHSO_4$, 10^3k_1/min^{-1}	23.1	22.5	20.4	18.5	17.0
NaBr, 10^3k_1/min^{-1}	11.0	8.64	7.48		
$NaClO_4$, 10^3k_1/min^{-1}	10.6	6.58	4.41	2.88	2.11

(c) At constant ionic strength at 50.1°

[HCl]/M		1.00	2.00	3.00	4.00
[NaCl]/M	5.00	4.00	3.00	2.00	1.00
10^3k_1/min^{-1}	7.52	18.1	27.5	40.0	52.0
[H_2SO_4]/M		1.00	2.00	3.00	4.00
[$NaHSO_4$]/M	5.00	4.00	3.00	2.00	1.00
10^3k_1/min^{-1}	17.0	22.5	30.2	35.9	43.6
[$HClO_4$]/M		1.00	2.00	3.00	4.00
[$NaClO_4$]/M	5.00	4.00	3.00	2.00	1.00
10^3k_1/min^{-1}	2.11	7.30	9.00	13.0	15.0

TABLE 3

Hydrolysis of 4-*p*-tolyl-5-phenylisosydnone

(a) Effect of added acids at 50.1°

[H_2SO_4]/M		1.00	2.00	3.00	4.00
10^3k_1/min^{-1}	5.89	10.5	14.7	17.6	21.9
[H_2SO_4]/M	5.00	6.00	7.00	8.00	
10^3k_1/min^{-1}	24.8	24.2	17.3	14.7	
[HCl]/M	1.00	2.00	3.00	4.00	5.00
10^3k_1/min^{-1}	12.2	15.8	20.3	25.2	30.0
[HCl]/M	6.00	7.00	8.00		
10^3k_1/min^{-1}	36.0	41.1	49.5		

(b) Effect of added acids and salts at different temperatures

T/°C	40.0	45.0	55.0	60.0
10^3k_1/min^{-1} (2.00M-H_2SO_4)	5.47	9.51	32.8	31.5
10^3k_1/min^{-1} (2.00M-$NaHSO_4$)	5.73	8.67	18.5	25.6

Analysis for ^{18}O.—In all experiments carbon dioxide was analysed with an A.E.I. MS 12 mass spectrometer equipped with a digital ion current meter. The vacuum line and pyrolysis tube used were a modification of those of Williams and Hager.[6] Samples were converted into carbon dioxide by heating with mercury(II) chloride by the method of Rittenburg and Ponticorvo.[7] To obtain reproducible results it was found necessary to use a $HgCl_2$: isosydnone ratio of $\geqslant 100$ as previously observed by Shain and Kirsch.[8]

TABLE 4

Hydrolysis of 4-*p*-bromophenyl-5-phenylisosydnone

(a) Effect of added acids and salts at 50.1° *

[H_2SO_4]/M	1.00	2.00	3.00	4.00	
10^3k_1/min^{-1}	28.9	33.4	40.3	44.9	
[H_2SO_4]/M	5.00	6.00	7.00	8.00	
10^3k_1/min^{-1}	50.1	53.0	49.5	43.0	
[HCl]/M	1.00	2.00	3.00	4.00	
10^3k_1/min^{-1}	31.1	36.7	40.3		
[HCl]/M	5.00	6.00	7.00	8.00	
10^3k_1/min^{-1}	53.0	64.4	80.6	92.1	
[$HClO_4$]/M	1.00	2.00	3.00	4.00	
10^3k_1/min^{-1}	17.4	10.3	10.3	14.3	
[$HClO_4$]/M	5.00	6.00	7.00	8.00	
10^3k_1/min^{-1}	18.0	18.6	12.5	6.31	
[$NaHSO_4$]/M	1.00	2.00	3.00	4.00	5.00
10^3k_1/min^{-1}	21.2	22.5	19.6	18.4	14.4

* k_{H_2O} 22.4 × 10^{-3} min^{-1}.

Typically, isosydnone (5—10 mg) together with mercury(II) chloride was placed in a break-seal ampoule which was evacuated, sealed, and heated for 1—1.5 h at 400—500°. After cooling, the ampoule was placed in the vacuum line, the seal broken, and the hydrogen chloride generated was trapped by passage through benzoquinone.[9] The gaseous products were distilled through a series of traps at −72, −135, and −196°. Before the trap at −196° was put in place, a small amount of non-condensable gas was pumped from the −135° trap and discarded. The reproducibility of the analysis procedure was checked using tank carbon dioxide before and after each analysis. The mean of at least ten measurements of peak heights at 44, 45, and 46 mass units was calculated and the ^{18}O content determined by Klein's formula.[10] Each determination was carried out in duplicate and the accuracy was better than ±5%.

TABLE 5

^{18}O Tracer studies in acidic, aqueous dioxan (60 : 40 v/v; 5.0M-HCl)

Isosydnone	H_2O	Hydrolysis product	Product after equilibration
4,5-Diphenyl	3.1	2.56	0.34
	1.7	1.50	0.38
4-Phenyl-5-*p*-tolyl	3.1	2.80	0.37
	1.7	1.71	0.31
5-*p*-Nitrophenyl-4-phenyl	3.1	2.70	0.36
	1.7	1.71	0.27

DISCUSSION

Protonation Behaviour.—The protonation data were analysed using equations (2)—(4). Equation (2) avoids the necessity of establishing a unique scale of acidity for each different type of substrate. The protonation data are analysed in terms of the H_0 acidity scale where M is a

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[6] F. R. Williams and L. P. Hager, *Science*, 1958, **128**, 1434.

[7] D. R. Rittenburg and L. Ponticorvo, *Internat. J. Appl. Radiation Isotopes*, 1956, **1**, 208.

[8] S. A. Shain and J. F. Kirsch, *J. Amer. Chem. Soc.*, 1968, **70**, 5848.

[9] D. R. Henberg and L. Ponticorvo, *Internat. J. Appl. Radiation Isotopes*, 1956, **1**, 208.

[10] F. S. Klein, 'Stable Isotopes of Oxygen,' YEDA Research and Development Co. Ltd., Israel.

measure of the protonation behaviour of B relative to Hammett bases (primary aromatic amines) used for the

$$\log I = M(\mathrm{p}K - H_0) \quad (2)$$

$$\log I = cH_A + d \quad (3)$$

$$\log I + H_0 = \phi(H_0 + \log[\mathrm{H}^+]) + \mathrm{p}K_{\mathrm{BH}^+} \quad (4)$$

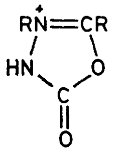
determination of H_0 (for Hammett bases, $M = 1$). Table 1 shows that 4-(*para*-substituted phenyl)-5-phenylisosydnones do not behave like Hammett bases. The values of the slope M are considerably less than unity and range from 0.54 to 0.64. These values are very similar to those observed for 5-(*para*-substituted phenyl)-4-phenylisosydnones (0.55—0.59).[1] Slopes of similar magnitude have been observed for the protonation of amides,[11] hydroxamic acids,[12] sulphoxides,[13] and acetates.[14] Because the diarylisosydnones do not behave like simple Hammett bases, the pK values obtained represent the H_0 value for half-protonation and do not correspond to thermodynamic pK_a values.[15]

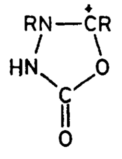
Because of the structural similarity of isosydnones to amides it is of interest to analyse the ionisation data in terms of the amide acidity function H_A [16] [equation (3)]. The slopes (c) of the plots of log I against H_A (Table 1) are close to unity and lie in a similar range (0.90—1.04) to that observed for 5-aryl(substituted 4-phenyl)isosydnones.[1] These values are similar in magnitude to those observed for the protonation of hydroxamic acids (0.94—1.02) and suggest that the protonation behaviour of isosydnones is similar to that of amides and related compounds. The value of $-d/c$ should represent the thermodynamic pK value and is less negative than the apparent values based on equation (2). A further method of determining pK values is to use the linear free energy approach of Bunnett and Olsen [17] [equation (4)]. Provided the plot of the left hand side of equation (4) *versus* (H_0 + log [H$^+$]) is linear, thermodynamic quantities can be calculated because the intercept of the plot represents the pK_{BH^+} value referred to infinite dilution in water as the standard state. The slope (ϕ) is a measure of the susceptibility of the equilibrium to changing acid concentration. The values of the pK determined in this way (—1.80 to —2.28) (Table 1) are somewhat less negative than that based on the H_A scale [equation (2)].

If values of pK_{BH^+} for the 4-(*para*-substituted phenyl)-5-phenylisosydnones obtained by the Bunnett and Olsen method are plotted as a function of σ, the Hammett substituent constant, a poor correlation is obtained. A plot of pK_{BH^+} values against σ^+ values,[18] however, gives an approximately linear correlation of slope —0.42 (with some scatter). A better correlation of pK_{BH^+} with σ^+ than σ was also found for 5-(*para*-substituted phenyl)-4-phenylisosydnones with a slope of —0.53.[1] However, this correlation must be regarded as an approximate one because it was obtained from data for only a small number of substituents.

Previously we have shown that a *p*-methoxyphenyl group in the 5-position enhances the basicity of the isosydnone ring by a resonance effect. Such an effect requires coplanarity of both the phenyl and isosyndnone ring and indicates that charge delocalisation between the two rings has an important effect on basicity. This is in marked contrast to substituent effects with *e.g.* primary benzamidinium cations where pK_{BH^+} values are correlated better by σ than σ^+ substituent constants and where resonance interactions are thought to be unimportant.[19]

There is no direct evidence available to indicate whether protonation of isosydnones occurs on nitrogen or oxygen. Olah *et al.* showed that the protonation of 3-phenylsydnone in FSO_3H–SbF_3 solution occurs exclusively on the carbonyl oxygen atom.[20] It seems reasonable to suppose that the *N*-protonated conjugate acid (I) and the *O*-protonated form (II) can exist, in equilibrium, in aqueous solution.


(I)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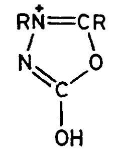
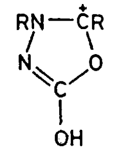

(II)


(IV)

Both these forms are resonance stabilised *e.g.* as in (III) and (IV). Electron releasing substituents will have a greater stabilising effect on (III) and (IV) in the 5- rather than the 4-position and the relative magnitude of the observed substituent effects in 4-(*para*-substituted phenyl)-5-phenyl- and 5-(*para*-substituted phenyl)-4-phenyl-isosydnones suggests that (III) and (IV) are important resonance forms.

Bond Fission Studies.—Diarylisosydnones are hydrolysed in aqueous acid to the corresponding *N*-aroyl-*N*-arylhydrazine and carbon dioxide [equation (5)]. The results of oxygen-18 tracer experiments (Table 5) show

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[11] J. T. Edward and I. C. Wang, *Canad. J. Chem.*, 1962, **40**, 966; R. B. Homer and R. B. Moodie, *J. Chem. Soc.*, 1963, 4377; A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, 1963, **19**, 465.

[12] A. J. Buglass, K. Hudson, and J. G. Tillett, *J. Chem. Soc.* (*B*), 1971, 123.

[13] P. Haake and R. D. Cook, *Tetrahedron Letters*, 1968, 427.

[14] K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, 1967, **89**, 2686; C. A. Lane, M. F. Cheung, and G. F. Dorsey, *ibid.*, 1968, **90**, 4492.

[15] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 233.

[16] K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957.

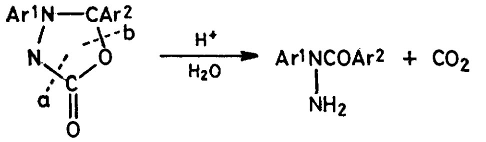
[17] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.

[18] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

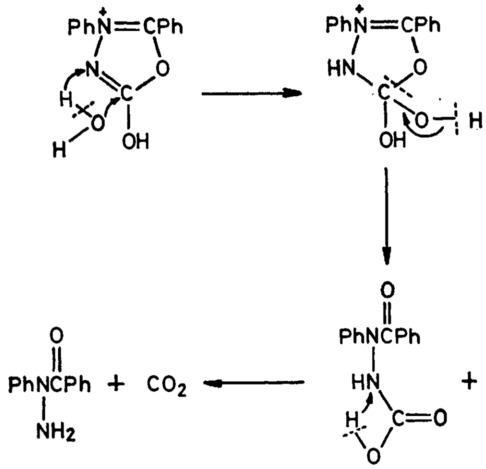
[19] K. Yates and J. B. Stevens, *Canad. J. Chem.*, 1965, **43**, 529.

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

that after hydrolysis of isosydnones in enriched water, the hydrazide product shows substantial incorporation (>70%) of oxygen-18. Subsidiary experiments indicate that very little of this incorporation is due to oxygen exchange of the product with the solvent after hydrolysis. This establishes that the main reaction pathway involves fission of the isosydnone ring at positions a and b [equation (5)], with attack of the water molecule occurring at C-5 rather than at the C-2 carbonyl carbon (Scheme 1). One possible mechanism for the minor pathway is shown in Scheme 2 which involves attack of a water molecule on the *O*-protonated conjugate acid.



(5)



Scheme 2

Rate Dependence on Acidity.—The kinetic behaviour observed for the hydrolysis of 4-*p*-tolyl-, 4-*p*-chlorophenyl-, and 4-*p*-bromophenyl-isosydnone is similar to that observed for 4,5-diphenylisosydnone and the 5-(*para*-substituted phenyl)-4-phenylisosydnones. Whilst in hydrochloric acid the rate of hydrolysis increases steadily with increasing concentration of acid, in sulphuric acid the rate of hydrolysis at first increases with acid concentration but then reaches a maximum. In perchloric acid the rate of hydrolysis first goes through a shallow minimum and then through a maximum which is below the neutral rate (Tables 2—4). All the compounds have a high neutral rate which is markedly depressed by added anions [Table 2(b)]. This salt effect is responsible for the rate minimum at low concentrations of perchloric acid where it outweighs the weak positive catalytic effect of the acid. Consistent with this view, the rates of hydrolysis in mixtures of perchloric acid and sodium perchlorate at constant perchlorate ion concentration (5.00M) [Table 2(c)] increase linearly with increase in acid concentration.

The rate maxima observed in the sulphuric and hydrochloric acid catalysed hydrolyses of the isosydnones studied are considered to arise from extensive protonation as in the hydrolysis of amides [21] and related compounds.[13]

Mechanism of Hydrolysis.—The value of the kinetic isotope effect (k.s.i.e.), $k_\psi^{D_2O}/k_\psi^{H_2O} = 1.48$ for the acid-catalysed hydrolysis of 5-phenyl-4-*p*-tolylisosydnone in sulphuric acid at an acidity (2.00M) too low to give substantial protonation is characteristic of reactions which proceed *via* a rapid pre-equilibrium protonation.[22]

Before the kinetic data in Tables 2—4 can be analysed, the pseudo first-order rate constants of hydrolysis, k_1, must be corrected first for the high neutral rate with its accompanying salt effect and secondly for the extent of protonation. Plots of $\log_{10}k_\psi - \log [SH^+]/[S]$ against $\log a_w$ gives values of the Bunnett *w* function [23] slightly higher than those obtained for the corresponding 5-(*para*-substituted phenyl)-4-phenylisosydnones. Analysis of the data in terms of the Bunnett–Olsen linear free energy relationship [24] gives ϕ values of *ca*. 0.5, slightly lower than for the corresponding 5-*substituted* isosydnones. Both these plots show considerable scatter which partly arises from the difficulty in accurately determining the acid-catalysed rate in the presence of a large neutral rate of hydrolysis. The values of ϕ obtained fall in the range associated with water involved as a nucleophile. The magnitude of the entropy of activation (-20.9 cal mol^{-1} K^{-1}) for the acid-catalysed hydrolysis of 5-phenyl-4-*p*-tolyl isosydnone in the low acidity region is also consistent with a bimolecular mechanism.[25] The values of *w* obtained fall in the range associated with water acting as a proton transfer agent. Similar conflicting conclusions from *w* and ϕ treatments in borderline cases have been observed by Hyland and O'Connor.[26]

Table 6

Analysis of substituent effects for 4-(*p*-substituted phenyl)-5-phenylisosydnones

Substituent	*p*-Me	H [a]	*p*-Cl	*p*-Br
10^3k_1 (2.00M-H_2SO_4)/min^{-1}	14.7	16.3	33.0	33.4
$10^3k_{H_2O}$/min^{-1}	5.98	7.93	25.6	26.2
$10^3k_{H_2O}$ (2.00M-$NaHSO_4$)/min^{-1}	8.51	8.23	22.5	22.5
10^3k_ψ/min^{-1}	6.14	8.07	10.5	10.9
[S]/[SH$^+$]	11.42	16.9	24.5	25.6
10^4k_p/min^{-1}	7.62	14.4	26.8	29.1
σ	-0.170	0	0.227	0.232

[a] Data from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

Substituent Effects.—To compare the effect of substituents on the rate-limiting step and to allow

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[21] J. T. Edward, H. P. Hutchinson, and S. C. R. Meacock, *J. Chem. Soc.*, 1955, 2520; J. T. Edward and S. C. R. Meacock, *ibid.*, 1957, 2000.

[22] C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 42, 3207, 3214.

[23] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **81**, 4956, 4968, 4973, 4978.

[24] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1917.

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comparison of relative reactivities without the complication of different extents of protonation we have converted the first-order rate coefficients k_ψ for acid hydrolysis, into specific first-order rate coefficients for the hydrolysis of the protonated substrate k_p, by means of equation (6). The data are shown in Table 6. Although only a limited number of substituents have been studied, the values of k_p for 4-(*para*-substituted phenyl)-5-phenylisosydnones correlate better with σ than with σ^+ giving a value of ρ_4 of *ca.* 1.0, identical to that found (ρ_5) for 5-(*para*-substituted phenyl)-4-phenylisosydnones (this latter value was incorrectly reported in our earlier paper [1] to be +0.71). Thus substituents in the 4- and 5-positions of the isosydnone ring seem to exert very similar electronic effects on the rate of hydrolysis. The observed substituent effects are as expected for the rate-limiting step of an *A*-2 reaction; electron-withdrawing substituents accelerate the hydrolysis and electron-donating substituents retard it, providing further support for such a mechanism for both the major and minor pathways.

$$k_p = k_\psi([S] + [SH^+])/[SH^+] \qquad (6)$$

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