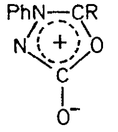
Mesoionic Compounds. Part IV.[1] Acid Catalysed Hydrolysis and Protonation Behaviour of 4,5-Diarylisosydnones

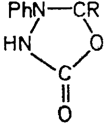
By **Emmanuel A. Isukul** and **John G. Tillett**,* Chemistry Department, University of Essex, Colchester

The acid catalysed hydrolyses of some 5-(*para*-substituted phenyl)-4-phenylisosydnones have been studied in aqueous solutions of mineral acids over a wide range of acidities. For perchloric and sulphuric acids plots of the first-order rate coefficients k_1 against [H$^+$] show maxima which are caused by extensive protonation of the substrate. Analysis of these data by Bunnett and Bunnett–Olsen criteria, solvent deuterium isotope effects, and substituent effects are consistent with an *A*-2 mechanism.

THE mesoionic 4,5-diphenylisosydnone (I; R = Ph) is hydrolysed in the presence of mineral acids to form 1-phenylbenzohydrazide and carbon dioxide.[1,2] For perchloric, sulphuric, and hydrobromic acids, plots of the first-order rate-coefficient k_1 *versus* [H$^+$] show maxima which are caused by extensive protonation of the substrate. For the acid catalysed hydrolysis in the low acidity region an *A*-2 mechanism was proposed in which initial pre-equilibrium protonation is followed by bimolecular attack of water in the rate-determining step.



(I)



(II)

In order to provide further evidence of the mechanism of decomposition of diarylisosydnones in the presence of acids, we have examined both the effect of added acids and salts at relatively high electrolyte strength on the rate of hydrolysis of a number of 4-phenyl-5-R-isosydnones (R = p-MeOC$_6$H$_4$, p-MeC$_6$H$_4$, Ph, p-ClC$_6$H$_4$, and p-NO$_2$C$_6$H$_4$), and also the protonation behaviour of these compounds in sulphuric acid.

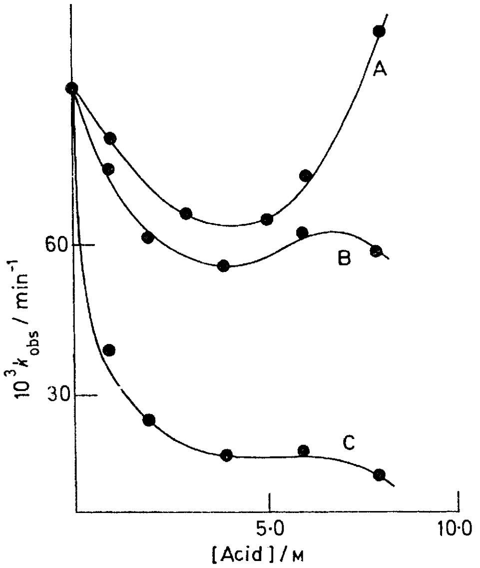
EXPERIMENTAL

Materials.—The isosydnones were prepared by the action of phosgene on the corresponding *N*-(*para*-substituted benzoyl)-*N*-phenylhydrazine hydrochloride. 4,5-Diphenylisosydnone after recrystallisation from benzene had m.p. 163° (plates) (lit.,[2,3] 162, 160°); 4-phenyl-5-p-tolylisosydnone had m.p. 193° (lit.,[3] 190—192°); 5-p-chlorophenyl-4-phenylisosydnone had m.p. 187° (lit.,[3] 188°); *5-p-nitrophenyl-4-phenylisosydnone* (yield 50%; dioxan as reaction solvent), recrystallised from benzene, had m.p. 264° (yellow prisms) (Found: C, 59·3; H, 3·3; N, 14·9; O, 22·3. $C_{14}H_9N_3O_4$ requires C, 59·3; H, 3·3; N, 14·8; O, 22·6%), $\lambda_{max.}$ 320 nm, $\nu_{max.}$ 1762 cm^{-1}; *5-p-methoxyphenyl-4-phenylisosydnone* (yield 39%; dioxan as reaction solvent), recrystallised from benzene, had m.p. 175° (grey needles) (Found: C, 67·6; H, 4·5; N, 9·7; O, 17·9. $C_{17}H_{12}N_2O_3$ requires C, 67·2; H, 4·5; N, 10·5; O, 18·2%), $\lambda_{max.}$ 313 nm, $\nu_{max.}$ 1762 cm^{-1}.

Protonation Equilibria.—The absorbances at a number of wavelengths between 200 and 400 were recorded for various concentrations of sulphuric acid at a constant concentration of isosydnone. Measurements were carried out on a Unicam SP 800 spectrophotometer thermostatted at 25 ± 0·2°. The protonation equilibria could be more accurately studied in sulphuric acid than in perchloric acid because of the larger differences between the spectra of the substrate and its conjugate acid in the former acid. The ionisation ratio (I = [BH$^+$]/[B]) was determined from absorbance measurements from equation (1) where D_B is

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

the absorption of the neutral form, D_{HB^+} is the corresponding value of the completely protonated form, and D is the value in a solution of intermediate acidity. Absorbance measurements were made at the following wavelengths for 5-substituted 4-phenylisosydnones: 5-p-methoxyphenyl, 213 nm; 5-p-nitrophenyl, 230 nm; 5-p-tolyl, 300 nm; 5-p-chlorophenyl, 300 nm. The ionisation ratios so obtained (Table 5) were fitted by a least-squares method to equations (2)—(4).



The acid-catalysed hydrolysis of 5-p-nitrophenyl-4-phenylisosydnone: A, HCl; B, H$_2$SO$_4$; C, HClO$_4$

Acid Catalysed Hydrolyses.—The acids used were of analytical reagent quality. Their concentrations were determined by titration with standard alkali. Sodium perchlorate was a recrystallised commercial sample. It was dehydrated at *ca*. 150° and kept in a vacuum at this temperature for 24 h with a diffusion pump. Anhydrous sodium chloride and sodium hydrogen sulphate were dried similarly.

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

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

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

TABLE 1

Hydrolysis of 4-phenyl-5-*p*-tolylisosydnone

(*a*) Effect of added acids and salts at 50° *

$[HClO_4]$/M	1·00	2·00	3·00	4·00	
10^3k_1/min^{-1}	6·10	6·33	7·00	7·19	
$[HClO_4]$/M	5·00	6·00	7·00	8·00	
10^3k_1/min^{-1}	6·88	5·73	4·63	2·82	
$[H_2SO_4]$/M	1·00	2·00	3·00	4·00	
10^3k_1/min^{-1}	10·1	13·8	19·3	23·5	
$[H_2SO_4]$/M	5·00	6·00	7·00	8·00	
10^3k_1/min^{-1}	23·6	21·8	17·3	11·5	
$[NaHSO_4]$/M	1·00	2·00	3·00	4·00	5·00
10^3k_1/min^{-1}	6·65	6·71	6·80	7·00	7·18

(*b*) At constant ionic strength

$[H_2SO_4]$/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}	7·18	10·8	13·8	18·3	23·4

* $k_W = 6{\cdot}60 \times 10^{-3}$ min^{-1}.

TABLE 2

Hydrolysis of 5-*p*-chlorophenyl-4-phenylisosydnone. Effect of added acids and salts at 50° *

$[HClO_4]$/M	1·00	2·00	3·00	4·00
10^3k_1/min^{-1}	11·7	10·8	11·0	11·00
$[HClO_4]$/M	5·00	6·00	7·00	8·00
10^3k_1/min^{-1}	11·8	9·75	7·33	5·76
$[H_2SO_4]$/M	1·00	2·00	3·00	4·00
10^3k_1/min^{-1}	22·5	25·0	28·3	30·5
$[H_2SO_4]$/M	5·00	6·00	7·00	8·00
10^3k_1/min^{-1}	32·6	34·6	32·2	23·6
$[NaHSO_4]$/M	2·00	3·00	4·00	5·00
10^3k_1/min^{-1}	18·0	16·8	16·0	15·5

* $k_W = 20{\cdot}4 \times 10^{-3}$ min^{-1}.

TABLE 3

Hydrolysis of 5-*p*-methoxyphenyl-4-phenylisosydnone. Effect of added acids and salts at 50°

$[HClO_4]$/M		1·00	2·00	3·00
10^3k_1/min^{-1}	5·00	4·60	5·09	6·63
$[HClO_4]$/M	4·00	5·00	6·00	
10^3k_1/min^{-1}	5·17	3·61	2·53	
$[H_2SO_4]$/M	1·00	2·00	3·00	4·00
10^3k_1/min^{-1}	6·76	9·89	12·9	13·5
$[H_2SO_4]$/M	5·00	6·00	7·00	8·00
10^3k_1/min^{-1}	14·4	13·2	10·8	5·90
$[NaHSO_4]$/M	1·00	2·00	3·00	4·00
10^3k_1/min^{-1}	4·72	4·83	4·90	5·06

TABLE 4

Hydrolysis of 5-*p*-nitrophenyl-5-phenylisosydnone

(*a*) Effect of added salts at 50° * on the neutral reaction

Salt/M	1·00	2·00	3·00	4·00	5·00
$NaClO_4$, 10^3k_1/min^{-1}	57·4	44·5	37·2	31·2	30·8
$NaHSO_4$, 10^3k_1/min^{-1}	75·6	61·0	52·0	44·5	38·8
NaCl, 10^3k_1/min^{-1}	73·0	56·2	47·3	33·3	

* $k_W = 91{\cdot}0 \times 10^{-3}$ min^{-1}.

(*b*) At constant ionic strength at 50°

$[H_2SO_4]$/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}	38·8	41·5	46·1	50·7	55·3
$[HCl]$/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}	33·3	57·4	52·0	46·5	39·1

Kinetic Measurements.—The rates of hydrolysis were determined spectrophotometrically by following the decrease in the characteristic absorption of the isosydnones: 4,5-diphenyl, 297 nm; 5-*p*-chlorophenyl-4-phenyl, 303 nm; 5-*p*-nitrophenyl-4-phenyl, 320 nm; 4-phenyl-5-*p*-tolyl, 300 nm; 5-*p*-methoxyphenyl-4-phenyl, 313 nm.

Procedure.—4,5-Diphenylisosydnone (10 μl of stock solution in dioxan; $6{\cdot}0 \times 10^{-3}$M) was added to the reaction solution containing acid (3·0 ml) thermostatted to 0·03° in a stoppered cell. The cell contents were shaken rapidly and readings of optical density (D) taken at intervals. Values of the first-order rate coefficients were determined graphically from plots of log $(D_t - D_\infty)$ *versus* time and are shown in the Figure and Tables 1—4.

TABLE 5

Analysis of rate data for the hydrolysis of 5-*para*-substituted 4-phenylisosydnones in H_2SO_4 by use of the Bunnett w treatment and Bunnett–Olsen linear free energy relationship

Substituent	w	ϕ
MeO	3·4	0·81
Me	3·2	0·78
H		0·90 *
Cl	2·8	0·65
NO_2	2·1	0·63

* From ref. 1.

DISCUSSION

Protonation Behaviour.—One way of avoiding the necessity of establishing unique scales of acidity for different types of substrate is to analyse protonation data in terms of the H_0 acidity scale according to equation (2) where M is a measure of the protonation

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

behaviour of B relative to Hammett bases (primary aromatic amines) used for the determination of H_0 (if $M = 1$, B is a Hammett base). The 4,5-diarylisosydnones do not behave like Hammett bases, plots of log I *versus* H_0 giving straight lines of slopes considerably less than unity ranging from 0·55 to 0·59 (Table 6).

TABLE 6

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

Substituent	Equation (2)		Equation (3)		Equation (4)	
	M	$(H_0)_{\frac{1}{2}}$	c	d/c	ϕ	$\mathrm{p}K_{\mathrm{BH^+}}$
MeO	0·55	−2·62	0·92	−2·07	0·52	−1·62
	±0·04	±1·0	±0·02	±0·05	±0·03	±0·07
Me	0·56	−2·86	0·92	−2·19	0·53	−1·74
	±0·02	±0·07	±0·2	±0·02	±0·02	±0·03
H [a]	0·55	−3·33	0·94	−2·49	0·46 [b]	−2·18 [b]
	±0·03	±0·29	±0·07	±0·36		
Cl	0·58	−3·54	0·96	−2·62	0·50	−2·20
	±0·03	±0·07	±0·02	±0·04	±0·02	±0·04
NO_2	0·59	−3·86	0·97	−2·82	0·49	−2·42
	±0·02	±0·07	±0·05	±0·02	±0·02	±0·05

[a] Data from ref. 1. [b] Graphical.

Slopes of similar magnitude have been observed for the protonation of amides,[4] sulphoxides,[5] acetates,[6] and hydroxamic acids.[7] Because diarylisosydnones do not

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[4] 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.

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

[6] 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**, 6492.

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

behave like Hammett bases, the pK data obtained do not represent the thermodynamic pK values but correspond to the H_0 values for half-protonation[8] [*i.e.* $(H_0)_{\frac{1}{2}}$].

The protonation data has also been analysed in terms of the amide acidity formation, H_A[9] [equation (3)], and

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

using Bunnett and Olsen's approach[10] [equation (4)].

$$\log I + H_0 = \Phi(H_0 + \log [H^+]) + pK_{BH^+} \qquad (4)$$

The slopes of the plot of log I *versus* H_A lie close to unity in the range 0·92—0·97 and are similar to these obtained for the protonation of hydroxamic acids[7] (0·94—1·02). The values of $-d/c$ should represent thermodynamic pK values.

Values of pK determined from equation (4) are somewhat less negative than those given by equation (3).* The values of Φ for 5-aryl-4-phenylisosydnones are in the same range as those observed for amides (0·42—0·55) and hydroxamic acids[7] (0·51—0·57).

If values of pK_{BH^+} for the 5-(*para*-substituted phenyl)-4-phenylisosydnones obtained by the Bunnett and Olsen method are plotted as a function of σ, the Hammett substituent constant, a rather poor overall correlation is observed. A plot of pK_{BH^+} values against σ^+ values,[11] however, gives an approximately linear relation (although with some scatter) of slope 0·5, the point for the *p*-methoxy-substituent now falling on the line. It seems therefore that resonance interactions of the 5-phenyl group with the isosydnone ring do have an important effect on the basicity of the molecule. This is in marked contrast to observations with *e.g.* primary benzamidinium cations whose pK_{BH^+} values are correlated better by σ than by $\sigma^{\pm}$ substituent constants and where such interactions are thought to be unimportant.[12]

Rate Dependence on Acidity.—The kinetic behaviour observed for the hydrolyses of 4-phenyl-5-*p*-tolyl-, -*p*-methoxyphenyl-, and -*p*-chlorophenyl-isosydnones is so similar that all three may be discussed together. The first-order rate coefficients for the hydrolyses of these three compounds at various acidities in perchloric and sulphuric acids are shown in Tables 1—3. Their overall kinetic behaviour is similar to that observed for the hydrolysis of 4,5-diphenylisosydnone.[1] All the compounds have a high 'neutral' rate of hydrolysis. In sulphuric acid the rate of hydrolysis at first steadily increases with increasing acid concentration but then reaches a maximum. In perchloric acid the rate of hydrolysis first goes through a shallow minimum and then increases to a maximum, which is below the neutral rate, particularly so in the case of 5-*p*-chlorophenyl-4-phenylisosydnone.

The acid rate profile (Figure) for the hydrolysis of 4-*p*-nitrophenyl-4-phenylisosydnone is somewhat different to that observed for the three isosydnones discussed above. The most striking difference is that rate minima are observed in *ca.* 4·0M-perchloric, -sulphuric, and -hydrochloric acid. Interpretation of this kinetic behaviour is complicated by the presence of a very rapid neutral hydrolysis. From the data in Table 4(a) it can be seen that sodium hydrogen sulphate, perchlorate, and chloride all exert a large negative salt effect on this reaction. Furthermore, the magnitude of these salt effects is so large that at low concentrations of perchloric, sulphuric, and hydrochloric acids, the weak positive catalytic effect of the acid is outweighed by the large negative salt effect of the anion of the acid on the neutral rate and so the overall rate of hydrolysis is reduced. Eventually a point is reached (at *ca.* 4·0M-acid) where the two effects balance and a rate minimum is observed. This conclusion was confirmed by determining the rates of hydrolysis of 5-*p*-nitrophenyl-4-phenylisosydnone in mixtures of hydrochloric acid and sodium chloride, and sulphuric acid and sodium hydrogen sulphate at constant ionic strength (5·0M). Under these conditions the neutral rate will have a constant depressed value, any ionic strength effect on the acid rate will be constant and the expected linear dependence of rate on acid concentration is observed [Tables 4(b)]. At acidities above the rate minimum acid catalysis begins to dominate as the salt effect 'flattens out,' the overall rate at first increases (Figure) and then reaches a maximum.

The rate maxima observed by all the isosydnones studied could arise in two main ways, either because of extensive protonation as in the hydrolysis of *e.g.* amides,[13] or from the superposition of a specific salt effect on an acid-catalysed reaction (often accompanied by a considerable effect on a concurrent neutral reaction) such as observed in the hydrolysis of some sulphites.[14]

Evidence bearing on the course of the observed rate maximum can be obtained from a study of the effect of added salts under conditions of constant ionic strength. In mixtures of sulphuric acid and sodium hydrogen sulphate at constant hydrogen sulphate ion concentration (5·00M) [Table 1(b)] the rate of hydrolysis of 4-phenyl-5-*p*-tolylisosydnone at first increases linearly with increase in acid concentration but then reaches a maximum. Similar behaviour has been observed in the hydrolyses of the unsubstituted 4,5-diphenylisosydnone[1] and hydroxamic acids[7] under conditions of constant ionic strength, and is characteristic of extensive

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* A referee has pointed out that such deviations are to be expected because equation (4) is only an empirical equation and has no greater significance than direct acidity function correlations.

[8] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223.

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

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

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conversion of the substrate into its conjugate acid. The pK_{BH^+} values of isosydnones (Table 6) also predict such behaviour.

Mechanism of Hydrolysis.—The values of the kinetic isotope effect (k.s.i.e.), $k_\psi^{D_2O}/k_\psi^{H_2O} = 1·69$, for the acid-catalysed hydrolysis of 4-phenyl-5-*p*-tolylisosydnone in sulphuric acid solution at an acidity (2·00M) too low to give substantial protonation is characteristic of reactions which proceed by a rapid pre-equilibrium protonation.[15]

At the present time there is no direct evidence as to whether initial protonation of isosydnones occur on nitrogen or on oxygen. We have assumed, as did earlier workers,[2,16] that the acid-catalysed hydrolyses of isosydnones proceeds through the *N*-protonated conjugate acid (II).

The values of the k.s.i.e. for the acid-catalysed hydrolysis of 4-phenyl-5-*p*-tolylisosydnone at higher acidities are 1·16 and 0·92 at 4·0 and 6·0M-sulphuric acid respectively. A similar fall of the k.s.i.e. with increasing acidity for the hydrolysis of amides has been discussed by Bell [17] and by Wiberg.[18] At relatively low acidity the magnitude of the k.s.i.e. is determined by the isotope effect on the equilibrium step and a 'normal' value is obtained. At higher acidities, however, where most of the substrate is converted into its conjugate acid, the observed k.s.i.e. is determined by the relative nucleophilicities of H_2O and D_2O and so $k_\psi^{D_2O}/k_\psi^{H_2O} < 1$.

Before any attempt is made to analyse the kinetic data shown in Tables 1—4 and the Figure the pseudo-first-order rate constants of hydrolysis, k_1, must be corrected first for the high neutral rate with its attendant salt effect and secondly for the extent of protonation. Table 5 shows the results of plotting ($\log_{10}k_\psi - \log\,[SH^+]/[S]$) against $\log_{10}a_w$ (Bunnett *w* function) [19] and against ($H_0 + \log\,[H^+]$) (Bunnett–Olsen linear free energy relationship) [20] for the hydrolyses of five isosydnones in sulphuric acid.

For the hydrolysis of all the isosydnones studied the values of *w* lie in the range 1·2—3·3 said to be characteristic of water acting as a nucleophile in the rate-determining step. The values of ϕ, however, are all $>0·58$, and fall in the region normally associated with water acting as a proton transfer agent. O'Connor and Barnett have recently observed similar conflicting conclusions from *w* and ϕ treatments in the hydrolysis of *N*-substituted 4-chlorobenzamides [21] and have suggested that the limits of Φ for this mechanism for amides should be $0·47 \leqslant \Phi \leqslant 0·98$. In view of the similar kinetic behaviour of amides and isosydnones it seems reasonable to assume that the upper limit of Φ suggested by Bunnett and Olsen (0·58) for reactions in which water is involved as a nucleophile in the rate-determining step should also be raised in a similar way for isosydnones.

Effect of Substituents.—To compare the effect of substituents on the rate-limiting step and to enable comparison of relative reactivities without the complication of different extents of protonation we have converted the observed 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 (5). The data are shown in

$$k_p = k_\psi([S] + [SH^+])/[SH^+] \qquad (5)$$

Table 7. 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 the mechanism.

TABLE 7

Analysis of substituent effects

Substituent	10^3k_1/ min^{-1} [a]	10^3k_1/ min^{-1} [b]	10^3k_ψ/ min^{-1}	[S]/ [SH$^+$]	10^3k_p/ min^{-1}	σ [c]
p-MeO	9·89	4·80	9·70	9·60	10·3	−0·268
p-Me	13·8	6·91	13·5	10·0	14·9	−0·170
H	16·3	8·23	16·0	15·9	27·1	0
p-Cl	25·0	17·98	27·5	26·3	249	+0·227
p-NO_2	61·0	60·98	91·0	48·8	445	+0·778

[a] In 2·00M-H_2SO_4. [b] In water + 2·00M-$NaHSO_4$. [c] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

The values of k_p correlate better with σ than with σ^+ in contrast to the effects of substituents on the protonation equilibria. It seems therefore that resonance interactions of the 5-phenyl group with the isosydnone ring are much more important in the protonation equilibrium than in the rate-limiting step. The value of ρ (+0·71) is similar to that found for the rate-limiting step of the hydrolysis of amides (+1·2) [22] and hydroxamic acids (+0·64).[7]

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