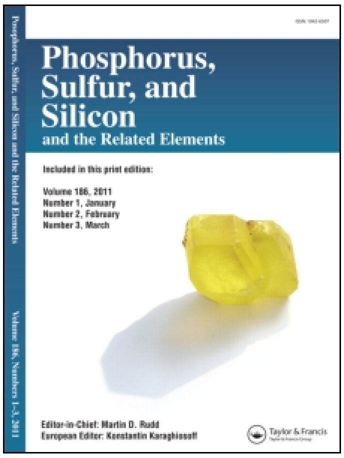

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ALKALINE HYDROLYSIS AND AMINOLYSIS OF *N*-ACYL-ARENEIMINOSULPHONATE ESTERS

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ALKALINE HYDROLYSIS AND AMINOLYSIS OF *N*-ACYL-ARENEIMINOSULPHONATE ESTERS

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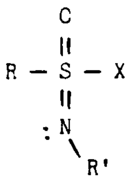
A series of *N*-acylarenesulfonimidic aryl esters has been synthesised. These esters hydrolyse in alkali by a bimolecular nucleophilic substitution mechanism with essentially exclusive S—O cleavage, an interpretation supported by activation parameters, solvent isotope effect and [^{18}O] tracer studies. The Hammett *rho* value (correlation with *sigma* values) is 1.35, for leaving group (phenolate) variation, a value much lower than those found for analogous reactions of substituted aryl arenesulfonates. Aminolyses are complex showing non-linear dependences of rate constants on amine concentrations. With respect to hydroxide ion attack the title compounds are considerably more reactive than arenesulfonates.

INTRODUCTION

Sulphonimidoyl derivatives (**1**) have been known since their synthesis in 1960 by Levchenko and her group.[1] A number of *N*-acylareneiminosulfonyl chlorides (**1**, R′ = -acyl, X = Cl)[2] have been described.[2,3] These materials have been reported as difficult to hydrolyse with water or aqueous alkali.[2] Some aryl esters (**1**, R = Ar; R′—COPh; X = —OPh or —$OC_6H_4pNO_2$) have been prepared[2] and are stable to prolonged boiling in water or dilute acid. However, they hydrolyse on gentle heating in aqueous, alcoholic alkali to benzenesulfonamides and phenols.



$$R-\overset{\overset{\displaystyle C}{\|}}{\underset{\underset{\displaystyle :N-R'}{\|}}{S}}-X$$

1

In contrast to the well-known sulfonyl (O═S═O) analogues, the S(VI) atom in **1** is chiral and this has been used elegantly by Johnson and coworkers to study nucleophilic substitution at tetracoordinate S(VI) and to prepare some inaccessible or refractory sulfoximines.[4]

To enable quantitative comparison of the sulfonimido system with the sulfonyl, we report the first kinetic studies in this area for the alkaline hydrolyses of a number

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of aryl esters of *N*-benzoyl and *N*-acetylareneiminosulfonates. Some preliminary results of studies in amine buffers are also reported.

RESULTS

Alkaline Hydrolysis

For the substituted-aryl esters of *N*-acylareneiminosulfonic acid, values of k_{obs} (the pseudo first-order rate constant measured at the wavelength given in Table I) were linearly dependent on the hydroxide ion concentration up to 0.4 M, with no indication of curvature. Second-order rate constants for hydroxide-ion attack (k_{HO^-}) were obtained, by linear least-squares regression analysis of at least 4 data points, as the slopes of plots of k_{obs} *versus* [HO$^-$], which passed through the origin within experimental error, see Figure 2. Values of k_{HO^-} are recorded in Table II at 50°C in the presence of 20% (v/v) acetonitrile, at ionic strength 0.4 M (held with KCl).

Activation parameters were obtained for the three *p*-nitrophenyl esters by measuring k_{obs} values in 0.1 M sodium hydroxide solution at $\mu = 0.4$ M in the presence of 20% v/v acetonitrile. The results are recorded in Table III.

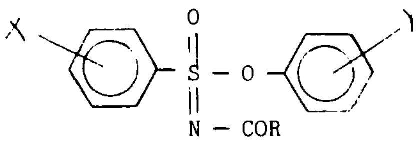
Values of $\log_{10}k_{HO^-}$ for aryl-substituted *N*-benzoylphenyliminosulfonates obeyed a Hammett relationship, the correlation being with *sigma* values (taken from reference 5), as can be seen from Figure 5. The equation followed was:

$$\log_{10}k_{HO^-} = 1.35(\pm 0.06)\sigma - 1.70(\pm 0.03)$$

The kinetic solvent isotope effect for the alkaline hydrolysis of *p*-nitrophenyl *N*-benzoylphenyliminosulfonate was determined at 50°C, ionic strength 0.4 M in the presence of 20% v/v acetonitrile. Under these conditions k_{HO^-} was 0.266

TABLE I

Analytical data for esters of *N*-acyl areneiminosulphonic acids. Except where noted, by literature references, the materials reported are novel



				Expected %				Molecular formula	Found %			
X	Y	R	M.p., °C	C	H	N	S		C	H	N	S
H	*m*-Cl	Ph	116–118	61.4	3.8	3.8	—	$C_{19}H_{14}ClNO_3S$	61.6	4.0	3.7	—
H	*p*-Cl	Ph	76–79	61.4	3.8	3.8	—	$C_{19}H_{14}ClNO_3S$	61.2	4.0	3.7	—
H	*p*-CH_3	Ph	67–69	68.4	4.9	4.0	—	$C_{20}H_{17}NO_3S$	67.9	4.9	3.6	—
H	*m*-NO_2	Ph	102–103	59.7	3.7	7.3	—	$C_{19}H_{14}N_2O_5S$	59.7	3.6	7.1	—
p-CH_3	*p*-NO_2	Ph	125–126	60.6	4.1	7.1	—	$C_{20}H_{16}N_2O_5S$	60.7	3.8	7.0	—
H	*p*NO_2	CH_3	94–95	52.5	3.8	8.4	—	$C_{14}H_{12}N_2O_5S$	52.6	3.6	8.3	—

The previously described derivatives (X = Y = H, R = Ph, m.p. 74–76°C, *liter*[2], 80–83°C) and X = H, Y = *p*NO_2, R =.Ph, m.p. 107–109°C) also had satisfactory elemental analyses.

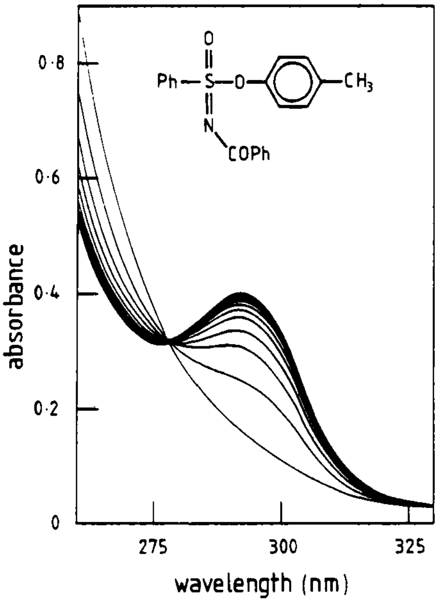


FIGURE 1 Repetitive spectral scans of the alkaline hydrolysis of *p*-tolyl *N*-benzoylphenyliminosulfonate at 50°C in 0.2 M sodium hydroxide solution, ionic strength 0.4 in the presence of 20% acetonitrile, v/v. The time between scans was approximately 1 minute, with the absorbance at ~ 300 nm increasing with time.

M^{-1} sec^{-1} (Table II) and k_{DO^-} was 0.340 M^{-1} sec^{-1} (results for three deuteroxide ion concentrations), giving a solvent kinetic isotope effect of $k_{HO^-}/k_{DO^-} = 0.78$.

Alkaline Hydrolysis: Product Analysis

The site of bond fission in the alkaline hydrolysis of *p*-nitrophenyl *N*-benzoyl phenyliminosulfonate was determined by means of a macroscopic experiment in [^{18}O]-enriched water as follows. A solution of *p*-nitrophenyl *N*-benzoylphenyliminosulfonate (0.002 mol) in acetonitrile (6 mL) and 1 M NaOH (6 mL) was heated at 50°C for 15 min and then left with stirring at room temperature for 48 h for complete hydrolysis. Some of the organic solvent was removed by rotovap and the solution remaining adjusted to ~ pH4 (with HCl), extracted with ether (4 × 30 mL) and the ethereal extracts combined, dried over $MgSO_4$ and evaporated to yield a pale yellow oil which, on recrystallisation from toluene, gave yellow, crystalline *p*-nitrophenol, m.p. 110–112°C. The experiment was repeated using 1 M NaOH prepared in 10.05% [^{18}O]-enriched H_2O and the *p*-nitrophenol products from the two isolations subjected to mass spectrometry. The observed ratio of 141/139 peak intensities (*p*-nitrophenol parent ion) was 1.17% for the system $Na^{16}OH/H_2{}^{16}O$/ester and 1.50% for the system with 10.05% [^{18}O]-enrichment. For aryl—C—O cleavage one calculates that the theoretical 141/139 ratio is 10.85% (and 0.80% for S—O cleavage). Comparing the [^{18}O]-enriched and "control" runs, the maximum amount of C—O cleavage is of the order of 3.5%. Within the limits imposed by the spectrometer used (AEI MS12), alkaline hydrolysis occurs with S—O fission, essentially exclusively.

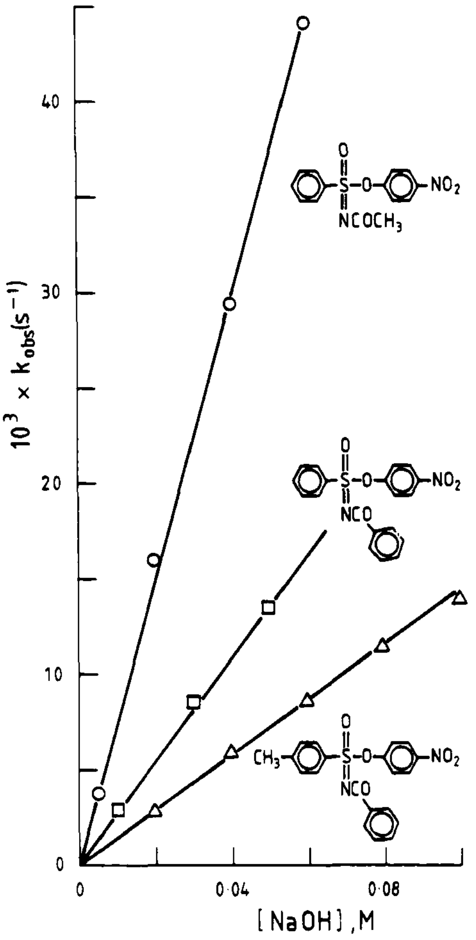


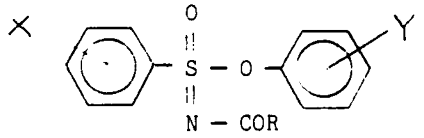
FIGURE 2 Plots of k_{obs} *versus* hydroxide ion concentration at 50°C, ionic strength 0.4 M in the presence of 20% v/v acetonitrile for: —○—○—, 4-nitrophenyl *N*-acetylbenzeneiminosulfonate; —□—□—, 4-nitrophenyl *N*-benzoylbenzeneiminosulfonate; —△—△—, 4-nitrophenyl *N*-benzene-*p*-tolueneiminosulfonate. Points are experimental; lines are by least squares regression analysis for the values of k_{HO^-} given in Table II.

Amine Buffers

Some preliminary studies in amine buffers were made. In piperidine buffers (up to 0.90 M piperidine as free base form) the reaction of *p*-nitrophenyl *N*-benzoylphenyliminosulfonate exhibited specific base catalysis (50°C, μ = 1.0 M, 20% v/v acetonitrile). However, complex amine dependencies were detected for *p*-nitrophenyl *N*-acetylphenyliminosulfonate in triethylamine, piperidine and morpholine buffers (above conditions, except at 40°C). The reactions had clean isosbestic points and obeyed good pseudo-first-order kinetics (amine in excess) but plots of k_{obs} *versus* [amine] showed saturation phenomena for triethylamine and piperidine (see Figure 3) whilst for morpholine the k_{obs} versus [amine] plot was curved but in the opposite sense (Figure 4). For triethylamine and piperidine the data could be analysed in

TABLE II

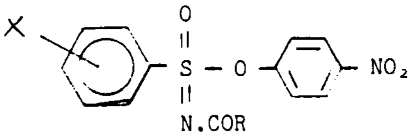
Kinetic data for alkaline hydrolyses of aryl esters of *N*-acylareneiminosulfonic acid at 50.0°C, μ = 0.4 M (held with KCl) in the presence of 20% v/v acetonitrile



X	Y	R	λ_{kin} (nm)	k_{HO^-} (M^{-1} sec^{-1})
H	4-NO_2	Ph	400	0.266
H	3-NO_2	Ph	285	0.202
H	3-Cl	Ph	275	0.0588
H	4-Cl	Ph	280	0.0384
H	H	Ph	275	0.0177
H	4-CH_3	Ph	280	0.0139
4-CH_3	4-NO_2	Ph	400	0.141
H	4-NO_2	CH_3	400	0.735

TABLE III

Temperature dependences and activation parameters for alkaline hydrolyses in 20% (v/v) acetonitrile, 0.4 M (held with KCl) media containing 0.1 M sodium hydroxide for *p*-nitrophenyl *N*-acyl-areneiminosulfonates



T°C	k_{obs} (sec^{-1})		
	X = H; R = Ph	X = *p*-CH_3; R = Ph	X = H; R = CH_3
20.3	0.0341	—	—
24.6	—	0.0175	0.140
29.8	—	0.0266	—
30.0	0.0695	—	—
31.0	—	—	0.226
35.3	0.0973	—	—
37.4	—	—	0.345
37.8	—	0.0538	—
40.1	0.135	—	—
43.0	—	0.0756	—
45.3	0.186	—	—
45.5	—	—	0.581
50.0	—	0.140	0.737
E_a (kcal · $mole^{-1}$)	12.6 ± 0.1	15.6 ± 0.4	12.5 ± 0.2
$\Delta H^\ddagger$ (kcal · $mole^{-1}$)	11.4 ± 0.1	14.4 ± 0.4	11.3 ± 0.2
$\Delta S^\ddagger$ (cal · deg^{-1} mol^{-1})	−26.1 ± 0.4	−18.1 ± 1.2	−24.1 ± 0.6
k at 25°C	0.0482 sec^{-1}	0.0178 sec^{-1}	0.147 sec^{-1}

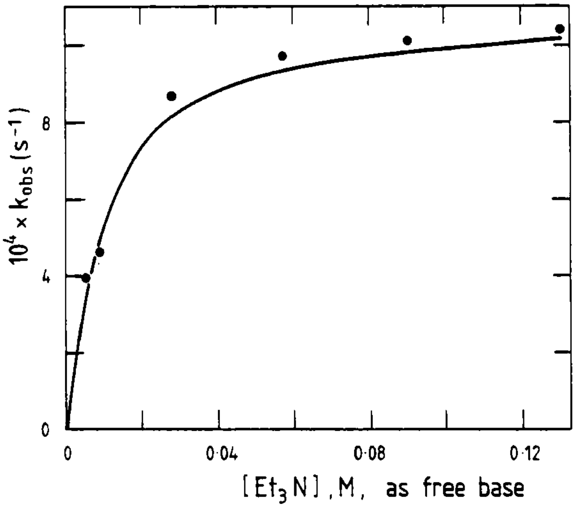


FIGURE 3 Plot of k_{obs} *versus* triethylamine concentration (free base form) for 4-nitrophenyl *N*-acetylphenyliminosulfonate at 40°C, ionic strength 1.0 M, 90% free base in the presence of 20% v/v acetonitrile. Points are experimental; the line is calculated using equation (1) and the values of k_{max} and K given in the text.

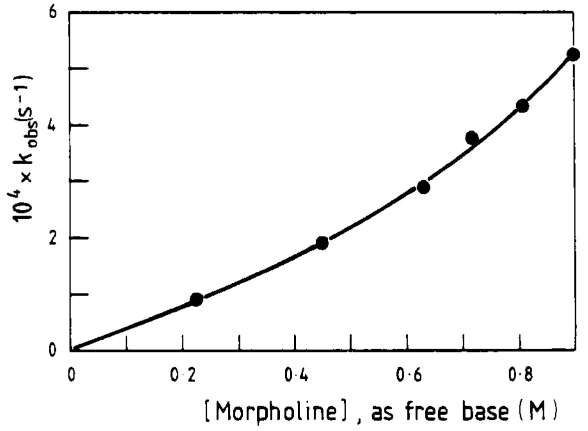


FIGURE 4 Plot of k_{obs} *versus* morpholine concentration (as free base form) for 4-nitrophenyl *N*-acetylphenyliminosulfonate at 40°C, ionic strength 1.0 M, 90% free base in the presence of 20% v/v acetonitrile. Line is notional to assist visualisation.

terms of equation (1), by appropriate linearisation and plotting ($[\mathrm{B}]_{\text{free}}/k_{\text{obs}}$ *versus* $[\mathrm{B}]_{\text{free}}$). This yielded the kinetic

$$k_{\text{obs}} = \frac{k_{\text{max}}[B]_{\text{free}}}{K + [B]_{\text{free}}} \qquad (1)$$

parameters k_{max} (sec^{-1}), $k_B = k_{\text{max}}/K$ (M^{-1} sec^{-1}) and $K(M)$ with values of 1.1×10^{-3}, 0.113 and 9.96×10^{-3}, respectively, for triethylamine and 1.87×10^{-2}, 3.9×10^{-2} and 0.477, respectively, for piperidine. The rate constants for the reaction of *p*-nitrophenyl *N*-acetylphenyliminosulfonate observed in morpholine

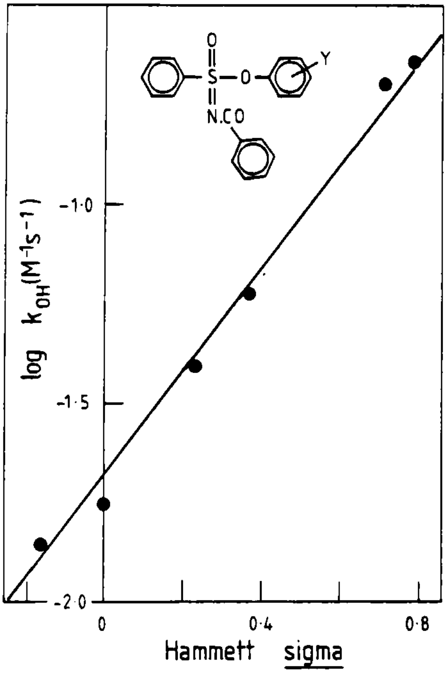


FIGURE 5 Plot of $\log_{10} k_{HO}$ *versus* Hammett *sigma* constants for aryl *N*-benzoylphenyliminosulfonates at 50°C, ionic strength 0.4 M in the presence of 20% v/v acetonitrile. Points are experimental; line is by least squares linear regression analysis with slope (ρ) = 1.35.

buffers (90% free base, 20% v/v acetonitrile, μ = 1.0 M, 40°C, λ_{kin} = 410 nm) were as follows ([morpholine] as free base, k_{obs}): 0.90 M, 5.26×10^{-4} s^{-1}; 0.81 M, 4.34×10^{-4} s^{-1}; 0.72 M, 3.77×10^{-4} s^{-1}; 0.63 M, 2.92×10^{-4} s^{-1}; 0.45 M, 1.91×10^{-4} s^{-1}; 0.225 M, 0.90×10^{-4} s^{-1}.

DISCUSSION

Alkaline hydrolysis of 4-nitrophenyl *N*-benzoylphenyliminosulfonate occurs with essentially completely S—O fission from the results of the studies in [^{18}O]-enriched solvent.

The mechanism is likely to be a direct nucleophilic attack at S(VI).* In agreement with this is the magnitude of the kinetic solvent isotope effect ($k_{DO^-}/k_{HO^-} = 1.38$) which is normal for such a process (*cf.* the reported value for 4-nitrophenyl benzenesulfonate of $k_{DO^-}/k_{HO^-} = 1.26$ and $k_{HO^-} = 1.7 \times 10^{-2}$ $l \cdot mol^{-1}$ s^{-1}, 20% dioxan-water (v/v), 25°C, μ = 1.02). The activation entropies are quite markedly negative (Table III) also in line with an associative transition-state.

The Hammett analysis (Figure 5) shows a good correlation with Hammett *sigma* values with a positive *rho* value, as found for arylsulfonate esters reacting by

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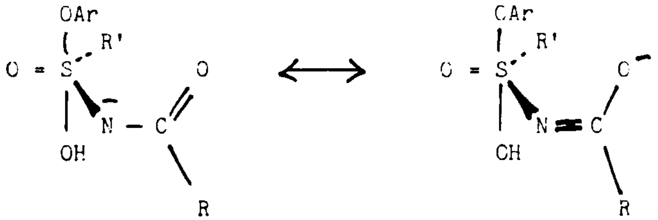
*Much more complicated mechanisms, involving attack at C=O can be envisaged also.

nucleophilic attack of hydroxide ion at sulfur.[6,7] However, the *rho* value for k_{HO^-} with aryl *N*-benzoylphenyl-iminosulfonate was very low ($\rho = 1.35$) compared to those reported for aryl phenylsulfonates[7] ($\rho = 2.75$, $PhSO_2OAr$), aryl *p*-biphenylsulfonates[7] ($\rho = 2.56$, $pPh\text{-}C_6H_4SO_2OAr$) and aryl *N*,*N*-dimethylaminosulfonates[6] ($\rho = 2.4$, Me_2NSO_2OAr).

If the sulfonimidic aryl esters (O=S=N.COR) behave similarly to sulfonates (O=S=O), attack of hydroxide ion is likely to be dominated by the electrophilicity of the sulfur. The difference in *rho* values for the systems must reflect the differences electron-withdrawing power and negative charge dispersal ability of the S=O and S=N.COR systems. On going from $—SO_2—$ to O=S=N.COR there is a lower electronegativity (O *cf.* N) but this is offset by two features peculiar to the N system, which can bear a substituent (O cannot, of course). The RCO-group is strongly electron-withdrawing (inductive) and can delocalise charge by resonance. Thus, when a hydroxide ion-derived adduct (or the transition-state leading to it) is formed, the additional negative charge in the molecule can be dispersed in which case the substituted-OAr group contributes relatively less (than in $—SO_2—$ cases) to the stabilisation of the transition-state (or bipyramidal intermediate, if this exists); hence $\rho_{S=N} < \rho_{S=O}$. If the loss of aryloxide ion from the S(VI) centre were significantly involved in the transition-state, the correlation would have been with *sigma-minus* values—not with σ constants as observed. Thus, it is likely that the rate-determining step is attack of HO^- ion at sulfur.



2 **3**

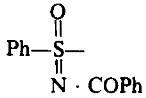
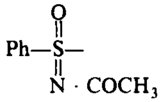
The relative reactivities of sulfonic and sulfonimidic sites can now be compared quantitatively. For *p*-nitrophenyl esters, the rate constants (k_{HO^-}) at 25°C are summarised in Table IV.

Clearly, the reactivity depends markedly on the nature of the *N*-acyl group, but for either *N*-acetyl or *N*-benzoyl substitution the S(VI) site is *more* reactive than the sulfonyl by 28- and 86-fold, respectively, under fairly comparable conditions. This higher reactivity can be ascribed to the extra stabilisation (by charge dispersal) of the transition-state formed by HO^- attack (*cf.* **2** and **3**) for the sulfonimides.

Our preliminary studies show that aminolysis of the sulfonimido-centre is complex. Non-linear buffer kinetics of the type seen for triethylamine and piperidine (Figure 3) could imply a change in rate-determining step with buffer concentration or specific solvent-amine effects at the high levels of amine used. In view of the change in the nature of curvature seen on going to morpholine the system is clearly complicated and not further discussed here, but a referee has noted the difference in basicity between triethylamine and piperidine, on the one hand, and morpholine on the other.

TABLE IV

Rate constants for hydroxide-ion attack on *p*-nitrophenyl esters of some S(VI) acids at 25°C. ($R—OC_6H_4pNO_2$)

R	k_{HO^-} ($l \cdot mol^{-1} s^{-1}$)	Medium	Reference
$PhSO_2—$	0.017	20% dioxan (v/v) $\mu = 1.02$ M	7
 $Ph—\overset{O \atop \|}{\underset{\| \atop N \cdot COPh}{S}}—$	0.482	20% acetonitrile $\mu = 0.4$ M	this work
 $Ph—\overset{O \atop \|}{\underset{\| \atop N \cdot COCH_3}{S}}—$	1.47	20% acetonitrile $\mu = 0.4$ M	this work

EXPERIMENTAL

Materials. Solvents used were of Analar quality or purified after Vogel[8] before use. Esters were prepared from *N*-acyl iminosulfonyl chlorides, which were synthesised after the procedure of Levchenko *et al.*[9] This involved reaction of the appropriate sulfinyl chloride with an appropriate *N*-chloroamide in the presence of pyridine to give the iminosulfonyl chloride followed by reaction with sodium aryloxide in benzene. The *N*-chloroamides,[10] sulfinyl chlorides,[11] *N*-benzoyl-benzeneiminosulfonyl chloride,[9] *N*-benzoyl-*p*-tolyliminosulfonyl chloride[9] and *N*-acetyl-benzeneiminosulfonyl chloride[9] were prepared as described in the literature.

The following general method described for phenyl *N*-benzoyl-benzeneiminosulfonate, was used to prepare esters of iminosulfonic acids. A benzene solution of *N*-benzoyl-benzeneiminosulfonyl chloride (0.005 mol) was added to a suspension of sodium phenoxide (0.005 mol) in benzene (15 mL). The reaction mixture was refluxed (20 min) and the NaCl filtered off and washed with a small amount of dried diethyl ether. Benzene was removed by rotovap and the crude oil crystallised on treatment with a small amount of methanol and cooling. The product was recrystallised from methanol to give 0.9 g (56%), m.p. 74–76°C, liter[9], 80–83°C. This procedure was used for the other esters, except that the reflux time required for the 4-nitrophenyl esters was 90 min. Analytical data for the esters are collected in Table I.

N-Benzoylbenzenesulfonamide (m.p. 146–147°C, liter.[12], 145.5–146°C) and *N*-acetyl-benzenesulfonamide (m.p. 124–126°C) were prepared by refluxing benzenesulfonamide with equimolar quantities of acid chloride and pyridine in benzene for 24 h, followed by filtration and solvent removal to give product which was recrystallised from ethanol.

Buffer components were from analytical grade material and water for kinetic studies was redistilled twice from glass.

Methods-Kinetic Measurements. Rate measurements were carried out spectrophotometrically using a Pye-Unicam SP 8100 spectrophotometer with the cuvette compartment thermostatted to within ±0.1°C by means of a Churchill Thermocirculator. Substrate (20–50 μL) was added from a Hamilton syringe to the flattened tip of a teflon stirring rod to 3.0 mL of the appropriate medium in a 1 cm pathlength quartz cuvette at the correct temperature.

The optimum wavelengths for kinetic study (Table II) were determined by repetitive spectral scanning of a reacting mixture, usually using a Carlo Erba Spectracomp 601 instrument. A typical example of a repetitive spectral scan study is shown in Figure 1. This shows that the alkaline hydrolysis is a clean A → B reaction with no spectrophotometrically detectable intermediates. Pseudo-first-order rate constants (k_{obs}) were obtained from semilogarithmic plots with hydroxide ion or amine concentrations in excess over substrate. Good linearity of semilogarithmic plots to > 90% of total reaction was obtained.

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