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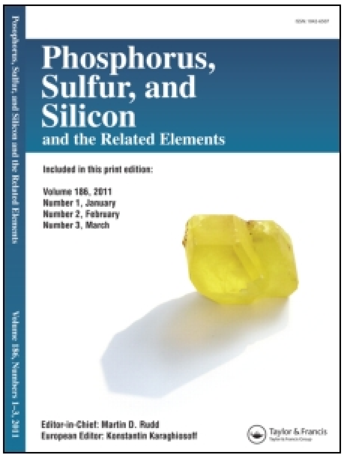

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Solvent Effects on the Alkaline Hydrolyses of 4-Nitrophenyl N-Aroyl-Areneiminosulfonates

Halil Kutuk[a]; John G. Tillett[a]
[a] Department of Biological and Chemistry Sciences, University of Essex, Colchester, United Kingdom

To cite this Article Kutuk, Halil and Tillett, John G.(2001) 'Solvent Effects on the Alkaline Hydrolyses of 4-Nitrophenyl N-Aroyl-Areneiminosulfonates', Phosphorus, Sulfur, and Silicon and the Related Elements, 176: 1, 95 — 109
To link to this Article: DOI: 10.1080/10426500108055106
URL: http://dx.doi.org/10.1080/10426500108055106

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Phosphorus, Sulfur and Silicon, 2001, Vol. 176, pp. 95–109

1042-6507/01 $12.00 + .00

SOLVENT EFFECTS ON THE ALKALINE HYDROLYSES OF 4-NITROPHENYL N-AROYL-ARENEIMINOSULFONATES

Halil Kutuk[a,*] *and John G. Tillett*
Department of Biological and Chemistry Sciences,
University of Essex, Wivenhoe Park, Colchester, CO4 3SQ,
United Kingdom

(Received April 24, 2001)

Second-order rate constants have been determined for the alkaline hydrolyses of N-aroyl-p-toluenesulfonimidic esters in aqueous organic solvents. Rate minima were observed with decreasing water concentration in aqueous acetonitrile, dioxane and t*-butanol mixtures whereas rates of hydrolysis decrease continuously in MeOH-H_2O and increase in DMSO-H_2O. Solvent effects, Arrhenius parameters, and substituent effects are consistent with either an addition-elimination or a concerted S_N2-type mechanism.*

Keywords: Alkaline hydrolysis; solvent effects; sulfonimidic esters

INTRODUCTION

An earlier report from this laboratory established second order kinetics for the alkaline hydrolysis of N-benzoyl-areneiminosulfonates in aqueous 20% (v/v) acetonitrile.[1] Hydrolysis was shown to proceed via S-O bond-fission to give the corresponding N-benzoylsulfonamide product.

Although a solvent effect study on the solvolyses of the analogous sulfonimidoyl chlorides has recently been reported,[2] there are no such data available for the alkaline hydrolyses of sulfonimidic esters. To provide further information about the mechanism of such reactions, we now report a kinetic study of the alkaline hydrolysis of a series of p-nitrophenyl N-aroyl-areneiminosulfonates **1(a–e)** in binary aqueous

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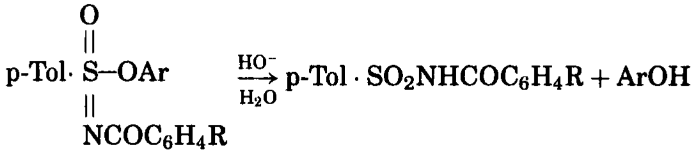
[a] Present address: Ondokuz Mayis University, Faculty of Arts and Sciences, Chemistry Department, 55139 Kurupelit, Samsun, Turkey.

[*] Corresponding author. E-mail: hkutuk@omu.edu.tr

organic solvents at different temperatures (Eq. 1).



$$\text{p-Tol}\cdot\underset{\underset{\text{NCOC}_6\text{H}_4\text{R}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}\text{—OAr} \xrightarrow[\text{H}_2\text{O}]{\text{HO}^-} \text{p-Tol}\cdot\text{SO}_2\text{NHCOC}_6\text{H}_4\text{R} + \text{ArOH} \qquad (1)$$

1 2

$(R = a, p\text{-}NO_2; b, p\text{-}Cl; c, p\text{-}H; d, p\text{-}Me; e, MeO)$

$(Ar = p\text{-}NO_2C_6H_4\text{-})$

Results and Discussion

The second-order rate coefficients for the alkaline hydrolysis of p-nitrophenyl N-benzoyl-p-tolueneiminosulfonate (**1c**) in different mole fractions of organic components (n_{cs}) in a number of aqueous organic solvent mixtures are shown in Figures 1(a–c) and Tables I–V. The rates of hydrolysis of **1c** in aqueous acetonitrile go through a minimum (around $n_{cs} \sim 0.3$) with decreasing water content (Figure 1a). Similar behavior is observed for aqueous dioxane and *t*-butanol although the mole fraction of the organic component at the minima are around 0.2 and 0.12 respectively. The values of $\log k_2$ for the hydrolysis of **1c** decrease with added methanol throughout the range studied (n_{cs}, 0.23–0.80; (Figure 1b), but increase with added DMSO (n_{cs}, 0.10–0.50; (Figure 1c)). The alkaline hydrolysis of p-nitrophenyl acetate in aqueous MeCN mixtures shows similar behavior to that observed for the hydrolysis of **1** (Figure 2); (Table VI).

TABLE I Kinetic Data for the Alkaline Hydrolysis of **1c** in MeCN-H_2O % (v/v) at 30.0°C

Acetonitrile % (v/v)	n_{cs}	$10^2k_2(M^{-1}sec^{-1})$	D^a
20	0.080	2.72	65.60
30	0.129	1.70	60.60
35	0.157	1.38	58.00
40	0.187	1.15	55.85
45	0.221	1.02	53.50
50	0.257	0.98	51.30
60	0.341	0.97	47.40
65	0.391	1.03	45.60
70	0.446	1.22	43.80

[a] At 30.0°C.

TABLE II Kinetic Data for the Alkaline Hydrolysis of **1c** in Dioxane-H_2O % (v/v) at 30.0°C

Dioxane % (v/v)	n_{cs}	$10^2k_2(M^{-1}sec^{-1})$	D^a
20	0.050	3.82	60.00
30	0.083	2.88	51.20
35	0.102	2.53	46.90
40	0.124	2.34	42.60
50	0.175	2.24	34.20
60	0.241	2.32	25.80
67	0.399	2.77	20.20
70	0.331	3.49	18.12
75	0.390	4.47	14.70

[a] At 30.0°C.

TABLE III Kinetic Data for the Alkaline Hydrolysis of **1c** in *t*-Butanol-H_2O % (v/v) at 30.0°C

t-Butanol % (v/v)	n_{cs}	$10^2k_2(M^{-1}sec^{-1})$	D^a
20	0.046	1.82	63.00
25	0.060	1.20	59.20
30	0.076	0.97	55.30
33	0.086	0.88	53.00
40	0.114	0.80	47.30
45	0.136	0.79	43.20
50	0.161	0.84	39.34
60	0.224	1.06	31.10
70	0.310	1.42	23.90

[a] At 30.0°C.

TABLE IV Kinetic Data for the Alkaline Hydrolysis of **1c** in DMSO-H_2O % (v/v) at 30.0°C

DMSO % (v/v)	n_{cs}	$10^2k_2(M^{-1}sec^{-1})$	D^a
30	0.098	7.10	77.08
40	0.145	8.96	76.17
50	0.203	13.2	74.67
55	0.237	17.1	73.77
60	0.276	22.9	72.57
65	0.321	35.9	70.83
70	0.373	58.1	68.83
75	0.433	99.5	66.47
80	0.504	193	63.83

[a] At 25.0°C.

TABLE V Kinetic Data for the Alkaline Hydrolysis of **1c** in MeOH-H_2O % (v/v) at 30.0°C

MeOH % (v/v)	n_{cs}	$10^2k_2(M^{-1}sec^{-1})$	D^a
40	0.229	32.1	60.60
50	0.304	27.6	56.20
60	0.400	24.5	51.40
65	0.453	22.9	48.70
70	0.501	22.0	47.00
75	0.572	20.6	44.00
80	0.641	19.2	40.72
85	0.717	18.4	38.10
90	0.801	17.5	35.58

[a] At 30.0°C.

In water-rich solvent mixtures, the rate of reaction can be expressed as a function of the dielectric constant of the relevant mixture. The rates of hydrolysis of **1** decrease with decreasing dielectric constant for MeCN-H_2O, dioxane-H_2O, *t*-butanol-H_2O and MeOH-H_2O mixtures (Figures 3 and 4) whereas for DMSO-H_2O values of k_2 increase (Figure 5).

According to the theory for ion-dipole interactions, $\log k_2$ can be shown to depend on dielectric constant as in equation 2[3].

$$\log k_D = \log k_\infty + Ze\mu/DkTr^2 \quad (2)$$

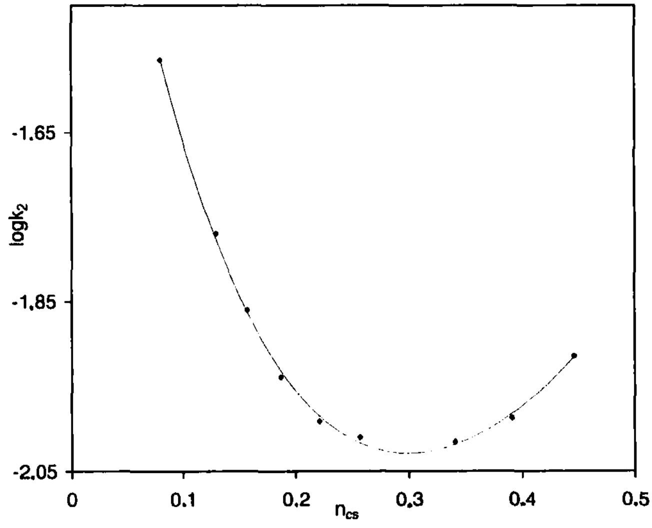


FIGURE 1a Plot of $\log k_2$ versus mol fraction of MeCN(n_{cs}) for the alkaline hydrolysis of **1c** at 30.0°C.

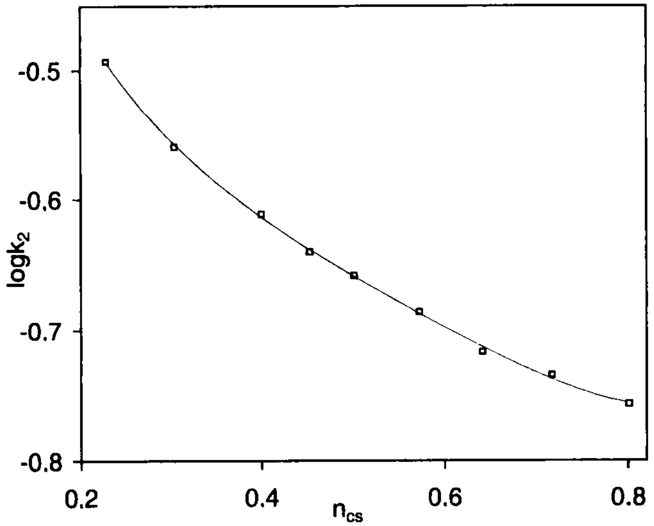


FIGURE 1b Plot of logk_2 versus mol fraction of MeOH(n_{cs}) for the alkaline hydrolysis of **1c** at 30.0°C.

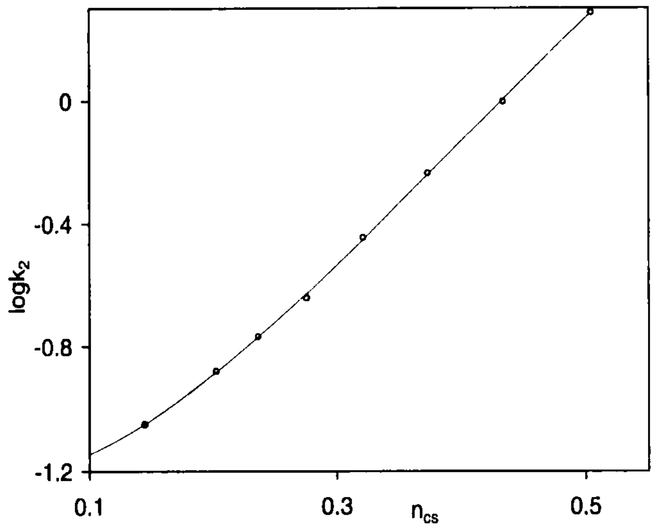


FIGURE 1c Plot of logk_2 versus mol fraction of DMSO(n_{cs}) for the alkaline hydrolysis of **1c** at 30.0°C.

TABLE VI Kinetic Data for the Alkaline Hydrolysis of p-Nitrophenyl Acetate in Different Compositions of MeCN-H_2O % (v/v) at Different Temperatures

		$\log k_2$				
Acetonitrile % (v/v)	n_{cs}	T°C 21.5	25.0	29.0	33.0	D^a
0	0.000	0.880	0.973	1.061	1.158	78.35
20	0.080	0.760	0.847	0.936	1.025	72.20
40	0.187	0.534	0.621	0.728	0.823	63.10
50	0.257	0.415	0.528	0.651	0.784	58.20
60	0.341	0.387	0.505	0.638	0.762	53.90
80	0.580	0.608	0.731	0.865	0.993	45.24

[a] At 25.0°C.

Here $\log k_D$ and $\log k_\infty$ refers to rate constants in solvent mixtures of dielectric constant D and infinity respectively, Ze is the charge of the ion, k is the Boltzmann constant, r is the distance of approach necessary for reaction to occur between the ion and the molecule, and μ is the dipole moment of the reacting molecule. Plots of $\log k_2$ versus 1/D for the alkaline hydrolysis of **1c** gave shallow curves in the water rich region for MeCN-H_2O, dioxane-H_2O, *t*-BuOH-H_2O, and MeOH-H_2O with negative slopes. Typical plots are shown in Figures 6

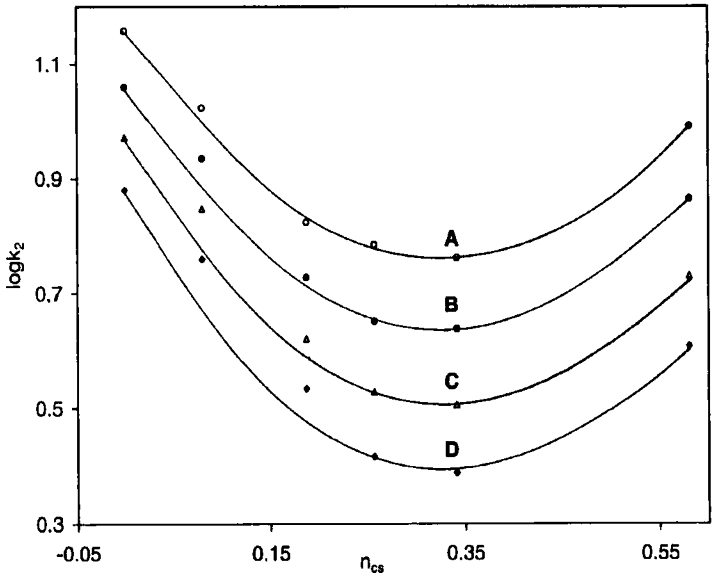


FIGURE 2 Plot of $\log k_2$ versus mol fraction of MeCN(n_{cs}) for the alkaline hydrolysis of p-nitrophenyl acetate. **A**.33.0°C, **B**.29.0°C, **C**.25.0°C, **D**.21.5°C.

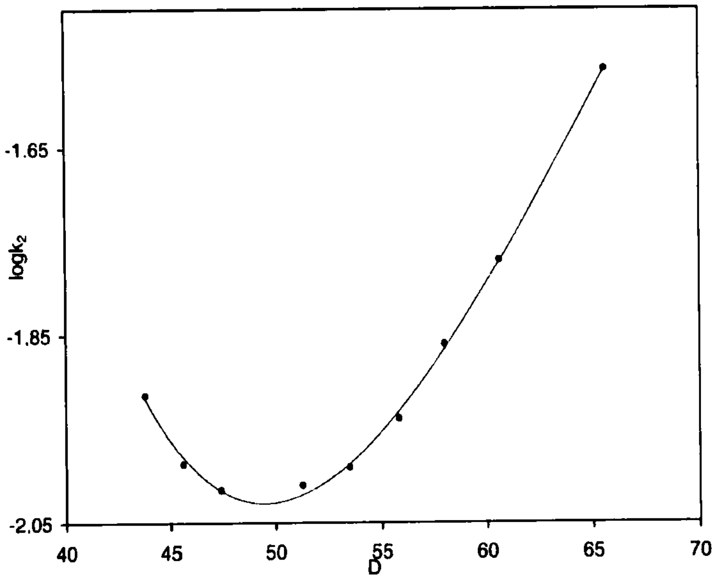


FIGURE 3 Plot of logk_2 versus D (dielectric constant) for the alkaline hydrolysis of **1c** in MeCN-H_2O mixtures at 30.0°C.

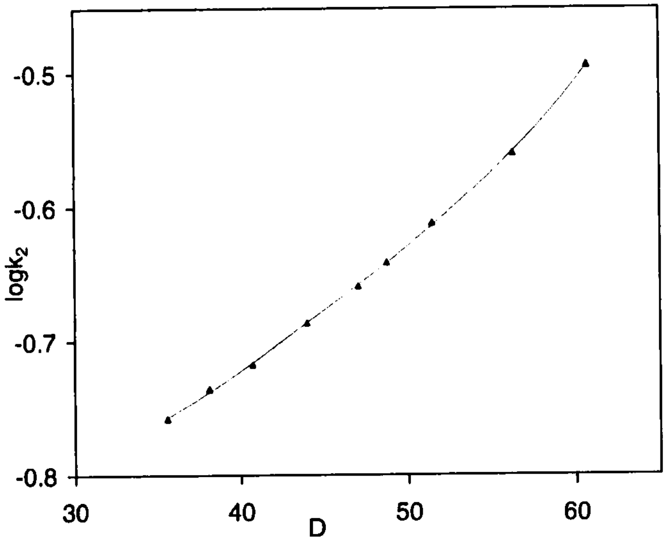


FIGURE 4 Plot of logk_2 versus D (dielectric constant) for the alkaline hydrolysis of **1c** in MeOH-H_2O mixtures at 30.0°C.

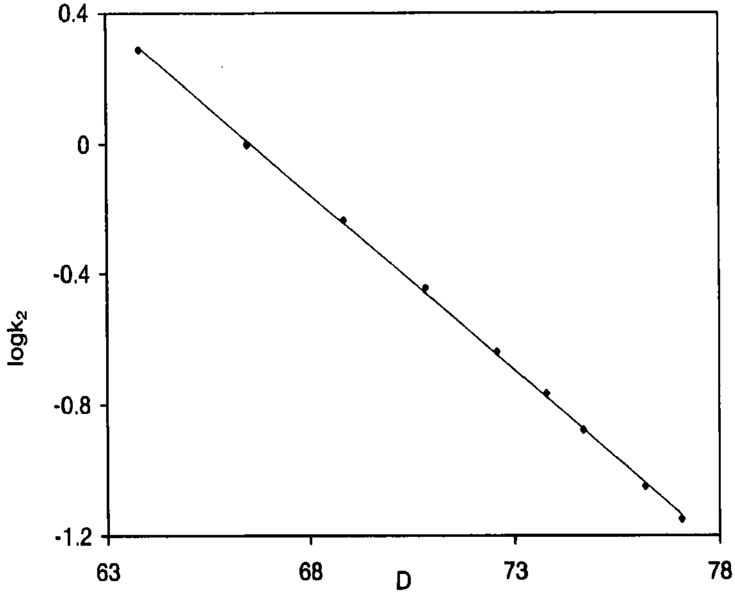


FIGURE 5 Plot of $\log k_2$ versus D (dielectric constant) for the alkaline hydrolysis of **1c** in DMSO-H_2O mixtures at 30.0°C.

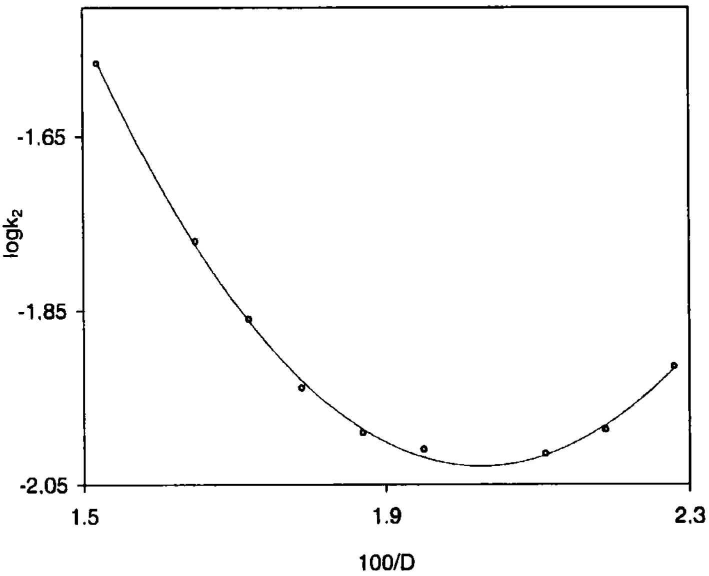


FIGURE 6 Plot of $\log k_2$ versus 1/D for the alkaline hydrolysis of **1c** in MeCN-H_2O mixtures at 30.0°C.

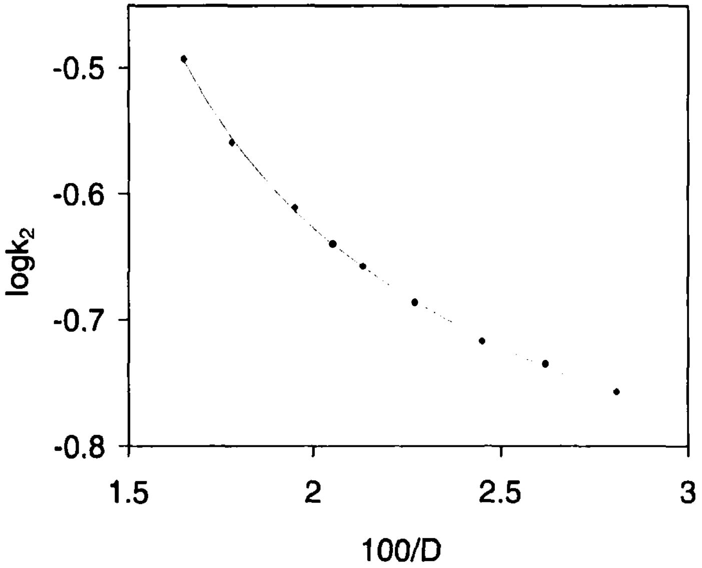


FIGURE 7 Plot of logk$_2$ versus 1/D for the alkaline hydrolysis of **1c** in MeOH-H_2O mixtures at 30.0°C.

and 7, for MeCN-H_2O and MeOH-H_2O respectively. The corresponding plot for the hydrolysis of **1c** in DMSO-H_2O mixtures (n_{cs}, 0.10–0.50) is, however, linear of positive slope.

According to Laidler et al.,[4] the slope of the plot of In*k* against 1/D for an ion A of charge Z_A ($\mu_A = 0$) and a neutral dipolar molecule B of dipole moment μ_B is given by Eq. 3.

$$\mathrm{dln}k/\mathrm{d}(1/D) = 1/kT[Z_A^2e^2/2(1/r_A - 1/r^{\neq}) + 3/4(\mu_B^2/r_B^3 - \mu^{\neq 2}/r^{\neq 3})] \qquad (3)$$

Data for the alkaline hydrolysis of methyl propanoate in aqueous acetone mixtures has been correlated by Eq. 2.[5] The negative slope is consistent with the prediction from Eq. 3 if the first term dominated and $r_A > r^{\neq}$, which has been attributed to specific solvation of the hydroxide ion by hydrogen bonding.[6] The negative slopes observed for the hydrolysis of **1c** in MeCN-H_2O, dioxane-H_2O, *t*-BuOH-H_2O, and MeOH-H_2O mixtures can be explained in a similar way. In DMSO-H_2O mixtures, however, the solvation of hydroxide ion is drastically reduced,[7] $r^{\neq} > r_A$ and values of k_2 for the hydrolysis of **1c** increase with decreasing values of dielectric constant throughout the solvent composition range studied (Figure 8). Measurements of enthalpies of transfer for the alkaline hydrolysis of ethyl acetate in aqueous DMSO have shown that

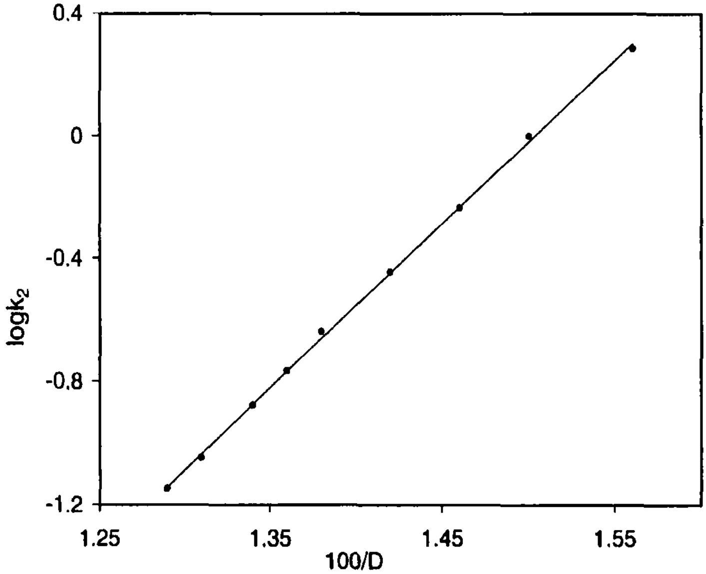


FIGURE 8 Plot of $\log k_2$ versus 1/D for the alkaline hydrolysis of **1c** in DMSO-H_2O mixtures at 30.0°C.

increased reaction rates observed with increasing DMSO concentration arise principally from an entropy effect rather than a large enthalpy of derivation of the hydroxide ion which is compensated by desolvation of the transition state.[8]

The rate minima observed for the hydrolysis of **1c** in MeCN-H_2O, dioxane-H_2O, and *t*-BuOH-H_2O mixtures when the composition of organic solvent is 30 mole% or lower is not specific to the present reaction but is a characteristic feature of many reactions in aqueous organic solvents. The reaction of nucleophiles with substituted phenyl acetate in DMSO-H_2O[9] and MeCN-H_2O[10] (Figure 2) and the alkaline hydrolysis of phosphorus (V) esters in various mixed solvents[11,12] shows such behavior.

It has been suggested that the addition of small quantities of an organic solvent to water induces rigidification of the water structure as the organic molecules gradually fill the cavities between the hydrogen bond structure of water.[13] Various physicochemical properties of aqueous organic mixtures also show extreme at the solvent composition corresponding to the rate minima. For aqueous MeCN mixtures, where the stoichiometric ratio of 1:2 for MeCN-H_2O is reached at 33.3 mole% MeCN. Symons reported spectroscopic evidence for the formation of 1:2 MeCN-H_2O complexes.[14]

TABLE VII Arrhenius Parameters for the Alkaline Hydrolysis of **1c** in Different Compositions of Organic Solvents-Water (v/v) (30.0°C)

Organic solvents	% (v/v)	$\Delta H^{\neq}$ ($kJmol^{-1}$)	$\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)
Acetonitrile	20	62.2 ± 0.08	−69.6 ± 0.29
	30	63.8 ± 0.33	−68.1 ± 1.13
	40	73.0 ± 0.46	−41.4 ± 1.55
	50	73.8 ± 0.46	−39.7 ± 1.55
	60	76.8 ± 0.42	−30.1 ± 1.42
	70	80.5 ± 0.21	−16.1 ± 0.67
Dioxane	30	54.9 ± 1.04	−93.1 ± 3.47
	50	59.7 ± 0.46	−79.4 ± 1.46
	70	59.1 ± 0.67	−77.8 ± 2.13
Methanol	40	41.9 ± 0.88	−116 ± 2.88
	60	44.0 ± 0.25	−111 ± 0.79
	80	45.7 ± 0.71	−108 ± 2.34
Dimethylsulfoxide	30	59.1 ± 0.79	−71.9 ± 2.55
	50	58.2 ± 0.08	−69.8 ± 0.29
	70	55.2 ± 0.67	−67.3 ± 2.17
t-butanol	25	56.6 ± 0.88	−95.0 ± 2.84
	40	59.8 ± 0.33	−87.6 ± 1.04
	70	63.3 ± 0.54	−71.5 ± 1.84

DMSO also forms complexes with two and three water molecules.[15] The absence of a rate minimum in the hydrolysis of **1c** in aqueous DMSO mixtures suggests that differential desolvation of the rather large transition state begins to occur significantly below 30 mole% DMSO.

Values of the entropy and enthalpy of activation are shown in Table VII for the alkaline hydrolysis of **1c** in different compositions of aqueous organic solvents. Similar data for the alkaline hydrolysis of p-nitrophenyl acetate in aqueous acetonitrile are shown in Table VIII. In water-rich solvents the values of the entropies of activation for the hydrolysis of **1c** are significantly large and negative, characteristic of an associative transition state. They become less negative in the organic solvent rich region, especially in acetonitrile-water ($\Delta S^{\neq} = -16.1$, $JK^{-1}mol^{-1}$, 70% v/v acetonitrile, $\Delta S^{\neq} = -69.6$ JK^{-1} mol^{-1}, 20% v/v acetonitrile). Similar changes have been reported for the alkaline hydrolysis of carboxylic esters in aqueous organic solvents; Ethyl benzoate[16] [EtOH, $\Delta S^{\neq} = -80.26$ to -51.83 $JK^{-1}mol^{-1}$ (0.35–0.85 mol fraction)], [DMSO, $\Delta S^{\neq} = -108.7$–87.8 $JK^{-1}mol^{-1}$ (0.32–0.59 mol fraction)], ethyl acetate[17] [DMSO, $\Delta S^{\neq} = -133.8$–-100.3 $JK^{-1}mol^{-1}$ (0.20–0.60 mol fraction)], methyl benzoate[18] [DMSO, $\Delta S^{\neq} = -91.96$ and -91.96 $JK^{-1}mol^{-1}$ (0.10–0.55 mol fraction)].

TABLE VIII Arrhenius Parameters for the Alkaline Hydrolysis of p-Nitrophenyl Acetate in Different Compositions of Acetonitrile-Water (v/v) (25.0°C)

Acetonitrile % (v/v)	$\Delta H^{\neq}$ (kJmol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
0	38.7 ± 0.92	−96.6 ± 3.05
20	37.3 ± 0.46	−103 ± 1.55
40	41.1 ± 0.58	−95.0 ± 1.96
50	52.7 ± 0.88	−57.9 ± 2.88
60	54.0 ± 0.38	−54.1 ± 1.25
80	55.2 ± 0.33	−45.5 ± 1.13

The substantial change in $\Delta S^{\neq}$ particularly for the hydrolysis of **1c** in aqueous acetonitrile raises the possibility of a change in mechanism in organic rich solvent mixtures.

For this reason substituent effects were studied in both 30% acetonitrile (v/v), 70% acetonitrile (v/v), and 60% methanol (v/v) for the alkaline hydrolysis of p-nitrophenyl N-aroyl-p-tolueneiminosulfonates. The Hammett analyses (Table IX) show very good correlation with Hammett sigma values giving positive rho values. In 30% MeCN (v/v), $\rho = 1.07$ (r = 0.998), in 70% MeCN (v/v), $\rho = 1.15$ (r = 0.999), and in 60% MeOH (v/v), $\rho = 1.67$ (r = 0.998).

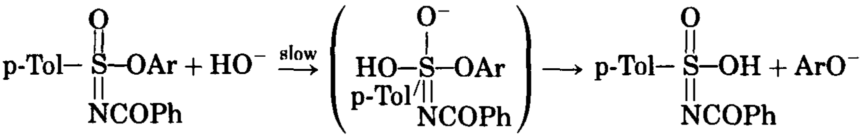
The rho values in 30% MeCN (v/v) and 70% MeCN (v/v) are essentially identical which implies the same mechanism in both solvent compositions. Rogne[19,26] reported a value of $\rho = 1.564$ for the alkaline hydrolysis of aromatic sulfonyl chlorides in water and concluded that in the transition state, bond-formation predominates. Said and Douglas[1] reported for the hydrolysis of aryl N-benzoylphenyliminosulfonates in 20% MeCN (v/v) ($\mu = 0.4$), a value of $\rho = 1.35$. The rho value for alkaline hydrolysis of p-nitrophenyl N-(p-substituted-benzoyl)-p-tolueneiminosulfonates obtained in the present work is much lower than expected when compared to that reported for arylphenylsulfonates[20] ($\rho \simeq 2.75$), aryl p-biphenylsulfonates[20] ($\rho = 2.56$),

TABLE IX Values of 10^3k_2(M^{-1}sec^{-1}) and Hammett σ Values for the Alkaline Hydrolyses of p-Nitrophenyl N-(p-Substitutedbenzoyl)-p-tolueneiminosulfonates (**1a–e**)

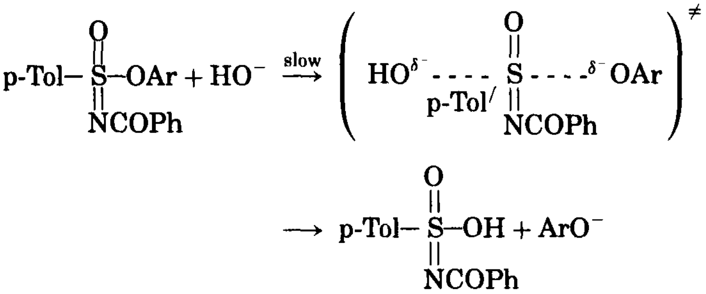
Substituent	30% (v/v) MeCN	70% (v/v) MeCN	60% (v/v) MeOH	σ
p-MeO	9.32	6.50	7.66	−0.268
p-Me	11.96	8.53	11.24	−0.170
p-H	17.00	12.2	18.10	0.000
p-Cl	27.59	21.5	43.29	0.227
p-NO_2	123.5	104.4	435.1	0.778

and aryl N,N-dimethylaminosulfonates[21] ($\rho = 2.40$). If the sulfonimidic aryl esters behave like sulfonates, attack of hydroxide ion is dominated by the electrophilicity of the sulfur atom. Douglas and Said[1] suggested that the differences in electron-withdrawing power and negative charge dispersing ability between the S=O and the S=NCOR system, arise from not only the electronegativity of the nitrogen atom compared to the oxygen atom, but also the ability of nitrogen to bear a substituent. The benzoyl group is strongly electron-withdrawing and can therefore delocalize the charge by resonance.

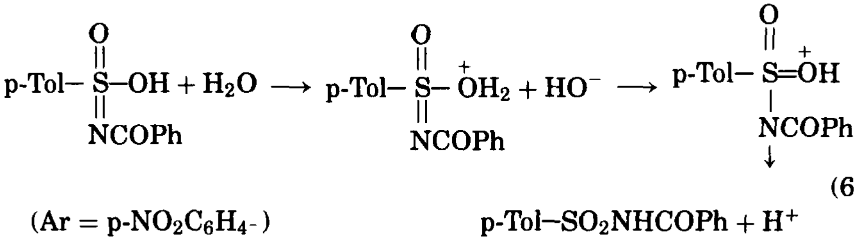
The overall evidence is consistent with the alkaline hydrolyses of sulfonimidic esters proceeding via either an addition-elimination or a concerted S_N2-type mechanism as shown in Eqs. 4 and 5 respectively. (Followed in both case by Eq. 6.)



$$\text{p-Tol}-\underset{\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{OAr} + \text{HO}^- \xrightarrow{\text{slow}} \left(\text{HO}-\underset{\text{p-Tol}/\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}^-}{|}}{\text{S}}}-\text{OAr} \right) \longrightarrow \text{p-Tol}-\underset{\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{OH} + \text{ArO}^- \qquad (4)$$



$$\text{p-Tol}-\underset{\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{OAr} + \text{HO}^- \xrightarrow{\text{slow}} \left(\text{HO}^{\delta^-}\text{----}\underset{\text{p-Tol}/\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}\text{----}{}^{\delta^-}\text{OAr} \right)^{\neq} \longrightarrow \text{p-Tol}-\underset{\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{OH} + \text{ArO}^- \qquad (5)$$



$$\text{p-Tol}-\underset{\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{OH} + \text{H}_2\text{O} \longrightarrow \text{p-Tol}-\underset{\underset{\text{NCOPh}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\overset{+}{\text{O}}\text{H}_2 + \text{HO}^- \longrightarrow \text{p-Tol}-\underset{\underset{\underset{\text{p-Tol}-\text{SO}_2\text{NHCOPh} + \text{H}^+}{\downarrow}}{\underset{\text{NCOPh}}{|}}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}=\overset{+}{\text{O}}\text{H} \qquad (6)$$

($Ar = p\text{-}NO_2C_6H_4\text{-}$)

EXPERIMENTAL

Sulfonimidic esters (**1a–e**) were prepared from the corresponding N-acyl iminosulfonyl chlorides which were synthesized following the procedure of Levchenko and her co-workers[22] as described previously.[23] This involved reaction of p-toluenesulfinyl chloride with the appropriate N-chloramide in the presence of pyridine to give the iminosulfonyl chloride followed by reaction with sodium p-nitrophenoxide in benzene. The N-chloroamides[24,25] and p-nitrophenyl N-benzoyl-p-tolueneiminosulfonate[1] were prepared as described in the literature.

Materials

MeCN (99.9 + %, HPLC grade, b.p. 82°C), DMSO (99.9%, ACS spectrophotometric grade, b.p. 189°C), 1,4-Dioxane (99.8%, HPLC grade, b.p. 100–102°C), *t*-Butanol (99.5%, HPLC grade, b.p. 83°C), CH_3OH (99.9%, HPLC grade, b.p. 64.6°C).

Kinetic Procedure

The rates of hydrolysis of 4-nitrophenyl-N-aroyl-p-tolueneiminosulfonates (**1a–e**) were followed spectrophotometrically at 400 nm using a Perkin-Elmer model 554 spectrometer with a thermostated cell compartment (±0.05°C). Good first-order behavior was observed with clean isosbestic points. Values of k_1 were calculated from the standard equation using a least-squares procedure. These rate coefficients, k_1, divided by the sodium hydroxide concentration give the second-order rate coefficients. The sodium hydroxide concentrations were determined by titration against a hydrochloric acid solution at given temperatures using phenolphthalein as the indicator.

Product Analysis

The products of hydrolysis were determined by comparing the UV spectrum obtained at the completion of kinetic experiment with the spectrum of expected products, run the same concentrations and under the same conditions. Thus, for the hydrolysis of p-nitrophenyl N-benzoyl-p-tolueneiminosulfonate, the UV spectrum recorded at the end of the reaction was identical with that of a 1:1 mixture of p-nitrophenol and N-benzoyl-p-toluenesulfonamide, whose concentrations were equal to the initial concentration of the ester.

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