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SOLVENT EFFECTS ON THE SOLVOLYSES OF N-BENZOYL-ARENESULFONIMIDOYL CHLORIDES

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Rates of solvolyses of N-benzoyl-arenesulfonimidoyl chlorides have been studied in different compositions of aqueous organic solvents and analysed in terms of the mol fraction of organic solvent, the dielectric constant, the Kirkwood function, the polarisability, some E_T^N values, a multiparameter equation and the Grunwald-Winstein equation. All these criteria were consistent with a concerted bimolecular S_N2 mechanism of solvolysis.

Keywords: Sulfonimidoyl Chlorides; Solvolysis; Solvent effects

INTRODUCTION

Sulfonyl transfer reactions of arenesulfonyl compounds as shown in equation (1), where X is a halide or ester group and the nucleophile Y can be either a



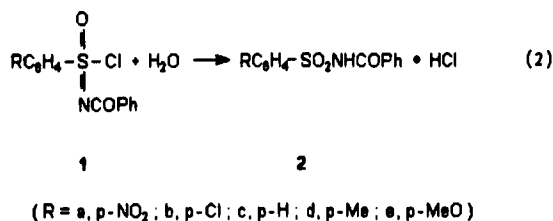
charged or a neutral species, have been reviewed by Maskill and his co-workers.¹ By analogy with acyl transfer reactions, they considered three possible mechanisms: unimolecular solvolysis, a concerted S_N2 bimolecular process or an $S_A N$ addition-elimination pathway.

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Kinetic studies on the hydrolyses of alkane and arenesulfonyl halides in both aqueous and non-aqueous solvents have led to the view that the concerted S_N2 mechanism provides the principal pathway for sulfonyl transfer in such systems. In good ionizing solvents, S-C stretching in the transition state is ahead of S-O bond formation, whilst the reverse is the case in poor ionizing solvents.¹ Although it was originally suggested that the solvolysis of a sulfonyl chloride with strongly electron donating substituents like 2,4-dimethoxybenzenesulfonyl chloride should react by an S_N1 mechanism², this is not supported by the Arrhenius data for this reaction³.

We now report a kinetic study of the solvolysis in aqueous organic solvents of a series of areneiminosulphonyl chlorides (1) (equ 2) to permit comparison of displacement reactions at sulfonic and sulfonimidic centres.



RESULTS AND DISCUSSION

The first-order rate coefficients, k_1 , for the solvolysis of N-benzoyl-p-toluene sulfonimidoyl chloride (1d) in different mol fractions of organic components (n_{cs}) in aqueous organic solvent mixtures are shown in Figure 1. It can be seen that the addition of any organic solvent reduces the rate of solvolysis compared with that observed in aqueous solution as given in Table I. Similar solvent effects were observed for all the sulfonimidoyl chlorides studied. Typical plots of the criteria used for one set of solvent (acetonitrile-water) are shown in Figures 2–4. Similar plots were obtained for other organic solvent-water mixtures. A typical plot of $\log k_1$ versus E_T^N is shown in figure 5 for acetonitrile-water mixtures. Atypical plots were obtained for aqueous DMSO and t-butanol which gave shallow reverse curvature and sigmoid behaviour respectively.

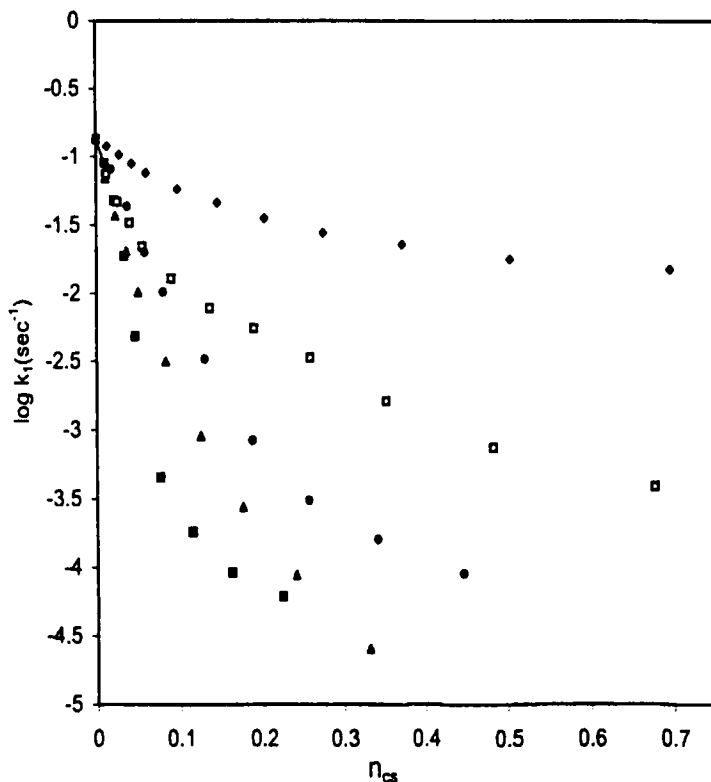


FIGURE 1 Plots of $\log k_1$ versus the mol fraction of organic components (n_{CS}) for **1d** in aqueous organic solvent mixtures. 1. DMSO, 2. DMF, 3. MeCN, 4. Dioxane, 5. *t*-Butanol.

The rapid decrease in the values of the first-order rate-coefficient with increasing mol fraction of organic solvent (Figure 1) shows that the reaction rate is sharply dependent on solvent "polarity", behaviour characteristic of reactions proceeding via a highly ionic transition state.

Koppel and Palm were amongst the first to suggest that any correlation of solvent effects must take into account both non-specific and specific effects⁴. They suggested two non-specific parameters $f(\epsilon)$ and $f(n^2)$ which reflect the polarity (or polarisation) and polarisability, respectively, of solvents. The $f(\epsilon)$ term is a dielectric constant term $(D-1)/(2D+1)$ derived by Kirkwood on the basis that solvent effects arise solely from electrostatic effects⁵.

TABLE 1 Values of $10^4 k_1(\text{sec}^{-1})$ for the hydrolyses of sulfonimidoyl chlorides in different compositions of MeCN-H₂O (v/v) at $25.0 \pm 0.1^\circ\text{C}$

%(v/v) MeCN	<i>Ia</i>	<i>Ib</i>	<i>Ic</i>	<i>Id</i>	<i>Ie</i>
0	50.7	345	489	1350	—
5	—	—	—	811	—
10	24.9	78.6	161	433	1870
15	—	—	—	199	956
20	10.0	27.9	47.0	102	395
30	4.16	8.49	13.6	32.8	101
40	1.88	2.66	4.12	8.40	30.8
50	1.27	1.48	1.84	3.10	11.7
60	0.603	0.690	0.960	1.60	4.90
70	0.293	0.330	0.410	0.90	2.40

Plots of $\log k_1$ versus D (Figure 2) show pronounced curvature for all binary aqueous-organic solvents suggesting that other factors which contribute to the overall polarity of the solvent are important. Both Amis⁶ as well as Laidler and Landskroener⁷ derived a similar relationship between $\log k_1$ and $1/D$. This correlation also fails, however, in the present case (Figure 3).

The polarisability of the solvent, α , is usually used for the $f(n^2)$ term proposed by Koppel and Palm⁴. Values of α for aqueous organic solvent have been calculated from those of water (α_w) and of the organic co-solvent (α_{cs}) assuming ideal behaviour, i.e.

$$\alpha = n_w \alpha_w + n_{cs} \alpha_{cs}$$

as described by Haak and Engberts⁸.

Plots of $\log k_1$ versus the polarisability function (Figure 4) also show very substantial curvature.

Plots of $\log k_1$ versus E_T^N (Figure 5) show curvature for all binary aqueous-organic solvents. Generally E_T^N values reflect a combination of both non-specific and specific contributions to "polarity"⁹. In order to better compare non-electrostatic forces on the reaction, isodielectric rate constants (k_1^{iso}) were calculated, for four pairs of binary solvents for which literature data were available, from plots of $\log k_1$ versus mol fractions of organic solvents (n_{cs}) using values directly read from plots of D versus n_{cs}

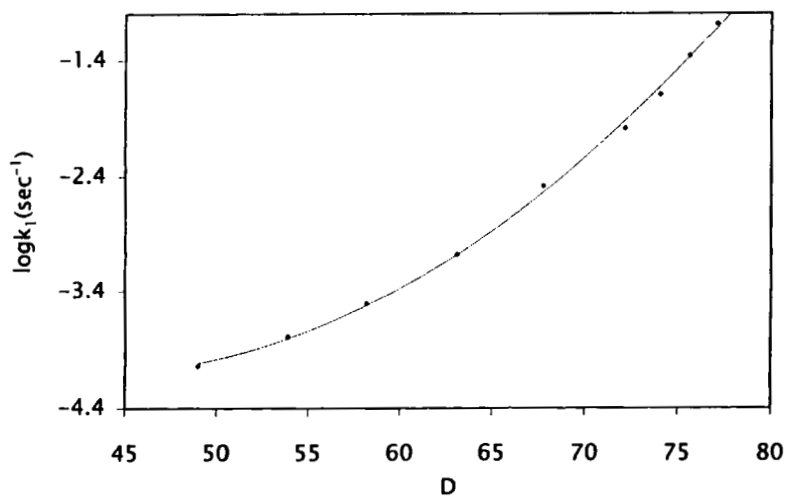


FIGURE 2 Plot of $\log k_1$ versus D (dielectric constant) for the solvolysis of **1d** in MeCN-H₂O % (v/v)

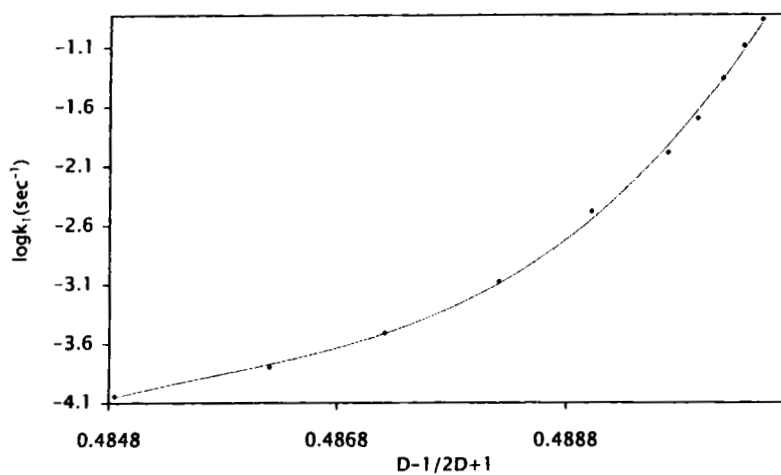


FIGURE 3 Plot of $\log k_1$ versus $D-1 / 2D+1$ for the solvolysis of **1d** in MeCN-H₂O % (v/v)

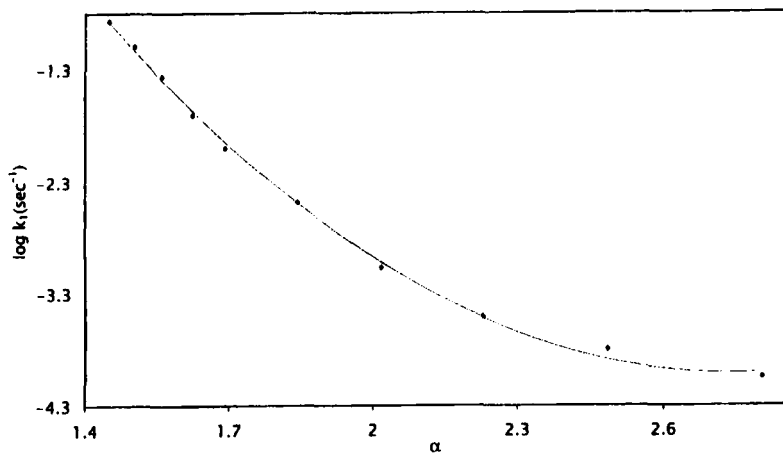


FIGURE 4 Plot of $\log k_1$ versus α for the solvolysis of **1d** in MeCN-H₂O % (v/v)

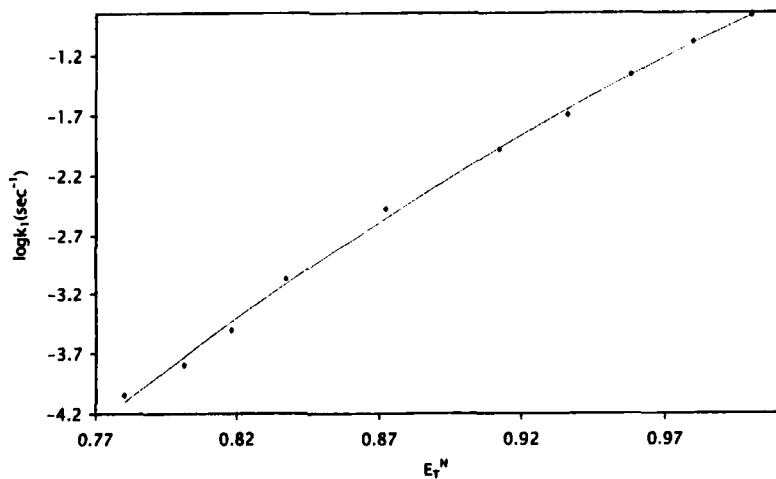


FIGURE 5 Plot of $\log k_1$ versus E_T^N for the solvolysis of **1d** in MeCN-H₂O % (v/v)

in Table II. The plot of $\log k_1^{\text{iso}}$ versus E_T^N shows quite a good correlation of slope -6.2 ($r = 0.996$).

TABLE II Isodielectric rate-coefficients for the solvolysis of **1d** at 25.0°C

<i>Solvent</i>	$n_{cs} (D=57)$	$\text{Log} k_I^{\text{iso}}$	E_T^N
DMSO-H ₂ O	0.696	-1.827	0.521
DMF-H ₂ O	0.320	-2.720	0.644
<i>t</i> -Butanol-H ₂ O	0.074	-3.240	0.729
MeCN-H ₂ O	0.278	-3.594	0.812

Gonçalves and his co-workers¹⁰ have suggested a multiple regression equation to correlate the effect of solvents on the solvolysis of tert-butyl halides in hydroxylic solvents as shown in (equation 3).

$$\text{Log} k_1 = a_0 + a_1 f(\epsilon) + a_2 g(n) + a_3 E_T^N + a_4 C \quad (3)$$

In equation (3), $f(\epsilon)$ is the Kirkwood function of the relative permittivity, $(D-1) / (2D+1)$, $g(n)$ is a function of the refractive index, $(n^2-1) / (n^2+2)$, E_T^N is the normalized Dimroth and Reichardt parameter and C is the cohesive energy density. A slightly modified form of equation (3) was adopted for the solvolysis of *N*-benzoyl-*p*-toluenesulfonimidoyl chloride in binary aqueous organic solvents as shown in equation (4).

$$\text{Log} k_1 = a_0 + a_1 f(\epsilon) + a_2 g(\alpha) + a_3 E_T^N \quad (4)$$

Here $f(\epsilon)$ is the Kirkwood parameter, α is the polarisability and E_T^N is the normalized Dimroth and Reichardt parameter. The multiple regression analysis gave a good correlation in all the binary organic solvent-water systems as shown in Table III.

TABLE III Correlation of rates of solvolysis of **1d** at 25.0°C, using Equation (5)

<i>Solvent</i>	a_0	a_1	a_2	a_3	<i>Corr. coeff.</i>
MeCN-H ₂ O	340.82	660.87	2.33	12.43	0.9997
	1319.27	2650.94	13.79	—	0.9760
	-11.51	—	-0.621	11.58	0.9993
	-81.94	141.49	—	-11.70	0.9995
Dioxane-H ₂ O	14.613	-40.941	-1.055	6.055	0.9994
	90.659	-175.91	-3.715	—	0.9974
	-8.131	—	-0.287	7.663	0.9992

<i>Solvent</i>	a_0	a_1	a_2	a_3	<i>Corr. coeff.</i>
DMF-H ₂ O	-16.24	14.236	-	8.331	0.9991
	313.44	-646.45	-1.195	4.367	0.9950
	1210.11	-2454.8	-4.835	-	0.9850
	-6.501	-	0.064	5.385	0.9940
DMSO-H ₂ O	6.696	-26.744	-	5.301	0.9940
	4.432	-16.382	0.059	2.630	0.9993
	242.42	-494.34	-0.586	-	0.9971
	-3.721	-	0.081	2.719	0.9993
<i>t</i> -Butanol-H ₂ O	26.562	-60.84	-	2.40	0.9993
	526.259	-1047.33	-10.237	1.451	0.9987
	544.277	-1080.46	-10.642	-	0.9954
	-0.292	-	-1.984	2.327	0.9353
	-116.96	230.5	-	3.108	0.9222

Chastrette and his co-workers¹¹ examined the E_T values by using factorial analysis and multiple regression. The results obtained show that, for aprotic solvents, the parameter E_T is a measure of the polarity, of the polarisability and the cohesion of the solvent to the extent of 43, 39, and 18 %, respectively. Chastrette et al¹¹ also reported that the effect of the cohesion of the solvent on the rate of solvolysis is low compared to that of the polarity and polarisability. Values of C are not available for binary aqueous organic solvents and they were assumed to be negligible.

The solvolysis of tert-butyl chloride was the standard system used by Grunwald and Winstein to establish the Y scale of solvent-ionising power¹². Subsequently, equation (5) was proposed¹³ for the correlation of S_N2 solvolyses, where k and k_0 are specific rates of solvolysis of the RX substrate in the solvent under consideration and in 80 % (v/v) ethanol, respectively, l is the sensitivity to changes in solvent nucleophilicity (N) and m is the sensitivity to changes in solvent ionising power (Y).

$$\text{Log}(k/k_0)_{RX} = lN + mY \quad (5)$$

The plots of $\text{log} k_1$ versus Grunwald-Winstein Y values for the hydrolysis of N -benzoyl- p -toluenesulfonimidoyl chloride in both dioxane-water¹⁴ and acetonitrile-water mixtures¹⁵ are not linear. These observations indi-

cate that the reaction rate depends not only on the ionising power of the solvent but also on the nucleophilicity of the solvent.

The plots of $\log k_1$ versus $lN + mY$ values for the solvolyses of N-benzoyl-p-substituted benzenesulfonimidoyl chlorides in acetonitrile-water % (v/v) are given in Table IV. Values of m between 0.26 and 0.54 and values of l between 3.81 and 7.11 were obtained. Values of l are quite large and consistent with an S_N2 mechanism (water attack at the sulfur atom in the rate-determining step).

TABLE IV Parameters of Equation (6) for the hydrolyses of (1a-e) in MeCN-H₂O % (v/v) at 25.0°C

Substituents	Slope	l	m	intercept	corr. coeff.
1e	1.000	6.21±1.31	0.54±0.13	0.63±0.06	0.9987
1d	0.998	6.84±0.64	0.43±0.07	0.70±0.04	0.9994
1c	1.000	6.48±0.49	0.38±0.06	0.27±0.03	0.9997
1b	1.000	7.11±1.46	0.26±0.16	0.74±0.09	0.9972
1a	1.000	3.81±1.01	0.40±0.11	-1.79±0.06	0.9974

The values of the entropy and enthalpy of activation are shown in Table V and VI for the solvolysis of (1d) and (1e), respectively. The values of the entropies of activation are significantly large and negative, reflecting a more heavily solvated transition state. Negative entropies of activation are characteristic of a loss of transitional degrees of freedom upon formation of the activated complex. The enthalpies of activation are lower than typical S_N1 values. Maskill et al.³ reported similar ΔH^\ddagger and ΔS^\ddagger values for the solvolysis of arenesulfonyl chlorides in aqueous trifluoroethanol (e.g. 2,4-dimethoxybenzenesulfonyl chloride in 50 % THF (v/v), $\Delta H^\ddagger = +70 \text{ kJ.mol}^{-1}$ and $\Delta S^\ddagger = -82 \text{ JK}^{-1}\text{mol}^{-1}$) for which they suggested an S_N2 mechanism.

TABLE V Arrhenius parameters for the hydrolysis of 1d in different compositions of organic solvents-water (v/v) at 25.0°C

Organic solvents	% (v/v)	$\Delta H^\ddagger (\text{kJ.mol}^{-1})$	$\Delta S^\ddagger (\text{JK}^{-1}\text{mol}^{-1})$
Acetonitrile	20	47.41±0.75	-124.1±2.5
	40	65.60±1.21	-83.4±3.9
	70	60.20±0.17	-120.5±0.5

Organic solvents	% (v/v)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)
DMSO	20	51.81±0.17	-92.2±0.5
	40	58.72±1.09	-73.6±3.7
	60	42.51±1.21	-132.0±3.9
	80	40.40±0.46	-143.1±1.5
Dioxane	20	46.93±0.17	-126.0±0.5
	40	65.52±0.63	-83.2±1.9
	60	63.90±0.38	-108.1±1.2
	70	65.05±0.75	-114.5±2.5
<i>t</i> -Butanol	20	38.04±0.67	-161.5±2.2
	40	76.92±1.09	-58.1±3.5
	60	71.61±1.04	-85.0±3.4
DMF	20	55.62±1.04	-89.9±3.5
	40	64.21±0.08	-69.6±0.3
Water	-	31.63±0.33	-155.4±1.0

TABLE VI Arrhenius parameters for the hydrolysis of **1e** in different compositions of MeCN-H₂O (v/v) at 25.0°C

MeCN % (v/v)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)
20	46.42±0.54	-116.1±1.8
40	65.71±0.54	-72.6±1.8
70	61.50±0.42	-107.7±1.4

Electron-donating substituents produce the highest rate of hydrolysis (i.e. **1e** faster than **1a**) and the solvolysis rates give a curved Hammett plot as shown in Figure 6. The data may, however, be explained by supposing that, in solvolysis, bond-making and bond-breaking are comparable. For such systems, as has been pointed out by Swain and Langsdorf,¹⁶ the reactivity may be increased by both electron-attracting and electron-donating substituents. Electron-donating substituents may lead to a transition state in which bond-breaking has progressed to a greater extent than bond-formation. With electron-attracting substituents, bond-formation is more extensive than bond-breaking. Rogne¹⁷ reported a similar plot for the hydrolysis of sulfonyl chlorides in water which proceeds via an S_N2 mechanism.

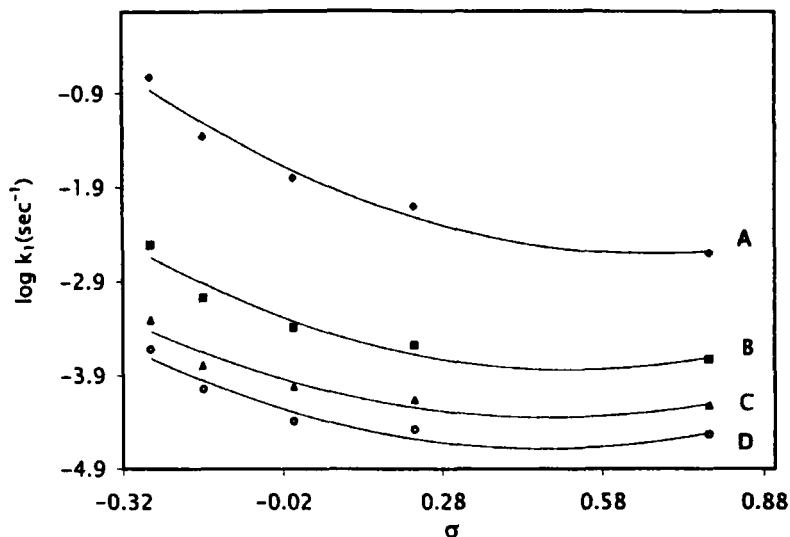
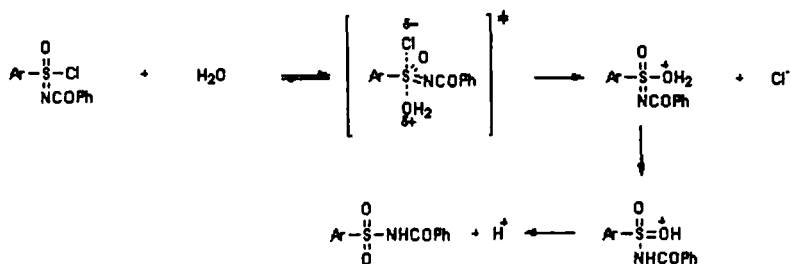


FIGURE 6 Plot of $\log k_1$ versus Hammett σ values for the solvolyses of **1a-e** in MeCN-H₂O % (v/v). A. 10 %, B. 40 %, C. 60 %, D. 70 %

All the above evidence is consistent with the hydrolysis of sulfonimidoyl chlorides proceeding via an S_N2-type mechanism via a trigonal bipyramidal transition state.



SCHEME

EXPERIMENTAL

Sulfonimidoyl chlorides (**1a-e**) were prepared from the corresponding p-substituted benzenesulfinyl chlorides which were synthesized following the procedure of Levchenko and her co-workers¹⁸. This involved reaction of p-substituted benzenesulfinyl chloride with the N-chlorobenzamide¹⁹ in the presence of pyridine to give the sulfonimidoyl chloride. N-Benzoyl-p-methoxybenzenesulfonimidoyl chloride (**1e**) crystallized from diethylether, had m.p. 110–111°C. Anal. Calculated for C₁₄H₁₂NO₃SOCl: C, 54.3; H, 3.9; N, 4.5; S, 10.4. Found: C, 54.2; H, 3.8; N, 4.5; S, 10.6.

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), DMF (99.9 %, HPLC grade, b.p. 153°C), *t*-Butanol (99.5 %, HPLC grade, b.p. 83 °C).

Kinetic Procedure

The rates of hydrolysis of N-benzoyl-p-substituted- benzenesulfonimidoyl chlorides (**1a-e**) were followed spectrophotometrically at 260–286 nm using a Perkin-Elmer model 554 spectrometer with a thermostatted cell compartment ($\pm 0.05^\circ\text{C}$). Good first-order behaviour was observed with clean isosbestic points. Values of k_f were calculated from the standard equation using a least-squares procedure.

Product Analysis

The products of the hydrolysis of three typical N-benzoyl-p- substituted benzenesulfonimidoyl chlorides isolated and recrystallized from ethanol, were found to be (**2d**), m.p. 147°C (Lit²⁰, m.p. 147°C), (**2e**), m.p. 148°C (Lit²¹, m.p. 146–147 °C) and (**2a**), m.p. 199–200°C (Lit¹⁸, m.p. 198–199°C).

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