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Linear Free Energy Relationship in Naphthalene System: Kinetics of Hydrolysis of 4-Substituted 1-Naphthalenesulphonyl Chlorides

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The kinetics of hydrolysis of several 4-substituted 1-naphthalenesulphonyl chlorides have been studied in aqueous acetone at three temperatures. The reaction is first order in sulphonyl chloride. Presence of electron-withdrawing substituents in the naphthyl ring enhances the rate while that of opposite ones retards it. The small ρ-values obtained in the correlation analysis using the Hammett and dual substituent parameter equations are consistent with either an S_N2 or an S_AN mechanism.

Recently Uhm *et al.*[1,2] have reported the kinetics of hydrolysis of 1- and 2-naphthalenesulphonyl chlorides. With a view to testing the applicability of the linear free-energy relationship in this reaction and thereby gaining further insight into the mechanism we have studied the kinetics of the hydrolysis of several 4-substituted 1-naphthalenesulphonyl chlorides and analysed the results using the Hammett and dual substituent parameter (DSP) equations.

Materials and Methods

All the naphthalenesulphonyl chlorides (4-X-$C_{10}H_6SO_2Cl$; X = OMe, Me, H, NHAc, F, Cl and Br) were prepared according to the literature methods[3-7]. All the other chemicals employed were of AR grade.

Rate measurement

In a typical kinetic run, the reaction was started by the addition of the required amount of water to the appropriate concentration of naphthalenesulphonyl chloride in purified acetone[8] at the temperature of the experiment. At time zero, the concentration of naphthalenesulphonyl chloride in the reaction mixture was 0.02 mol dm^{-3}. At regular time intervals, aliquots (5 ml each) were pipetted out into a separating funnel containing benzene (15 ml) and cold water (10 ml) and shaken well. The aqueous layer containing the sulphonic acid and chloride ion was separated, the organic layer further extracted with cold water (2 × 10 ml) and the chloride ion in the combined aqueous extract estimated by Volhard's method. All the reactions were homogeneous and the kinetics were followed up to 60-70% of the reaction. The correlation coefficients of all the first order plots (log [naphthalenesulphonyl chloride] versus time) were at least 0.997. The activation parameters were computed by the method of least squares from the slope and intercept of the linear Eyring's plot of log(k/T) versus 1/T.

Results and Discussion

The plots of log [naphthalenesulphonyl chloride] versus time are linear showing that the reaction is first order in [substrate]. The rate constants ($10^5 k, s^{-1}$) for the hydrolysis of 1-naphthalenesulphonyl chloride in 40, 50, 60 and 70% aq. acetone (v/v) are: 3.27 ± 0.16, 5.89 ± 0.28, 11.6 ± 0.8 and 20.3 ± 1.2 respectively at 30°C. This shows that the hydrolysis is facilitated by an increase in the water content of the solvent mixture. A good correlation exists between log k and the inverse of the dielectric constant (ε)[9] (slope = 78.6, $r = 0.992$ and $s = 0.05$) suggesting that the polarity of the solvent plays a dominant role in this reaction. However, a part of this rate enhancement may also be due to the increase in the nucleophilicity of the medium with increase in water content in the solvent mixture.

An inspection of the rate data in Table 1 shows that electron-withdrawing substituents increase the rate while those of opposite nature retard it, the order of reactivities in respect of substituents in the naphthalene ring being: Br > Cl > F > H > NHAc > Me > MeO. The data in Table 1 further show that the enthalpies of activation do not show any regular variation with the substituents in the naphthyl ring and the changes in rate are due to changes in both $\Delta H\ddagger$ and $\Delta S\ddagger$. The plot of $\Delta H\ddagger$ versus $\Delta S\ddagger$ is linear ($r = 0.997$) showing that the reaction obeys the isokinetic relationship. This indicates that all the 4-substituted 1-naphthalenesulphonyl chlorides hydrolyse via an identical mechanism[10]. The $\Delta S\ddagger$ values are negative suggesting an ordered transition state.

Correlation analysis

In general, correlation analysis in naphthalene

Table 1—Rate Constants and Activation Parameters for Hydrolysis of Naphthalenesulphonyl Chlorides[a]

Sulphonyl chloride	$10^5\ k^b s^{-1}$			$\Delta H\ddagger^c$ kJ mol^{-1}	$\Delta S\ddagger^c$ JK^{-1}mol^{-1}
	30	35	40°C		
$2\text{-}C_{10}H_7SO_2Cl$	18.6±0.90	23.4±0.91	32.9±1.4	42.4±6.8	−177±22
$4\text{-}X\text{-}1\text{-}C_{10}H_6SO_2Cl$					
X=					
MeO	4.95±0.15	7.34±0.31	10.7±0.52	58.2±6.4	−135±21
Me	5.23±0.23	8.12±0.23	12.7±0.71	67.4±6.7	−105±22
H	5.89±0.28	9.87±0.63	14.6±0.98	69.1±9.5	−98±31
NHAc	5.56±0.45	9.12±0.60	13.6±0.72	68.0±11	−102±34
F	8.41±0.76	11.3±0.64	16.5±0.53	50.5±9.5	−156±31
Cl	9.97±0.91	15.4±0.70	23.4±2.1	64.7±12	−108±38
Br	12.3±0.90	17.8±1.4	25.1±0.80	53.7±9.6	−143±31

[a]Solvent: 60% acetone-40% water (v/v); [b]the error quoted in *k* is the 95% confidence limit of the 'Student t'[20]; [c]the precision of $\Delta H\ddagger$ and $\Delta S\ddagger$ values were calculated by the method of Petersen *et al.*[21].

derivatives is performed employing either Hammett or DSP equations[11,12]. The use of σ_{41}(FM) (ref. 13) and σ^+_{41} (ref. 14) parameters in Hammett equation affords poor correlations of the rate data the results being: σ, ρ, r, n: σ_{41}(FM), 0.602, 0.939, 6: σ^+_{41}, 0.270, 0.795, 6 (acetamido substituent not included in the correlation). The failure of σ_{41}(FM) and σ^+_{41} constants to afford good correlation of the rate data may be ascribed to the fact that the blend of resonance and inductive effects making up these constants and the blend of these effects operating in the 4,1-naphthalene series of the present study are fortuitously different.

Hence, with a view to obtaining a better correlation of the rate data and separating the contribution of inductive and resonance effects, the rate data have been analysed employing, σ_I, σ^0_R, σ_R and σ^+_R constants[15] in DSP equation (1).

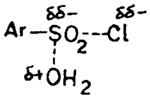
$$\log k = \rho_I\sigma_I + \rho_R\sigma_R + h \qquad \ldots (1)$$

The correlation of the rate data with σ_I and σ_R constants is found to be better than that with other combinations ($\sigma_I\sigma^0_R$ or $\sigma_I\sigma^+_R$) and the results are given in Eq. (2).

$$\log k_{35^\circ C} = 0.849\,\sigma_I + 0.668\,\sigma_R - 3.9936 \qquad \ldots (2)$$
$$(\pm 0.094)\ (\pm 0.100)$$
$$F=40,\ R=0.982,\ n=7$$

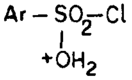
The above correlation is justified by >99.5% confidence level (CL) of the F-test while the ρ_I and ρ_R values are justified by >99.9% and >99.5% CL of student's t-test respectively. The magnitudes of ρ_I and ρ_R constants show that the inductive effect contributes slightly more than the resonance effect.

The ρ-values (with σ_{41}(FM) and ρ^+_{41}) and the ρ_I and ρ_R values in Eq. (2) are all positive indicating that the reaction is facilitated by a decrease in electron density at the sulphonyl reaction center. This observation rules out an *S*N1 mechanism involving the rate-limiting formation of the cationic intermediate ($Ar-SO_2^+$) as this would be facilitated by electron-releasing substituents present in the naphthyl ring resulting in a negative ρ-value. The observed positive ρ-values can be accounted for by either an *S*N2 mechanism with bond-making more advanced than bond-breaking in the transition state (1) or an S_AN mechanism proceeding through the intermediate (2). Generally, as the bond formation progresses far more than the bond cleavage in the S_AN mechanism, a good deal of negative charge builds up in the transition state resulting in large ρ-value (>2.0)[16,17]. Such a situation prevails for an S_AN mechanism involving a rate-limiting formation of the intermediate (2). However, if the S_AN mechanism involves the formation of intermediate (2) in a pre-equilibrium step followed by a rate-limiting formation of hydrolytic products from the intermediate (2), the ρ-value of the overall reaction would be the sum of the ρ-values of the equilibrium (ρ_{eq}) and rate-limiting (ρ_{r1}) steps. As ρ_{eq} and ρ_{r1} would be of different magnitudes and sign (ρ_{eq} and ρ_{r1} would be positive and negative respectively) it is possible for an S_AN mechanism to give a small ρ-value. Hence the low positive ρ-value obtained in the present study, although does not favour an S_AN mechanism with



$$Ar-\overset{\delta\delta-}{\underset{\delta+OH_2}{SO_2}}\cdots\overset{\delta\delta-}{Cl}$$

(1)



$$Ar-\underset{+OH_2}{\bar{S}O_2}-Cl$$

(2)

rate-limiting formation of intermediate (**2**), is unable to distinguish between an S_AN mechanism involving a pre-equilibrium step and an S_N2 mechanism.

The data in Table 1 show that the 1-naphthalenesulphonyl chloride is less reactive than the corresponding 2-isomer. This is explicable by (i) the steric effect of the *peri*-hydrogen (8-H) in the 1-isomer in destabilising the sterically crowded transition state by introducing steric strain and causing steric inhibition to solvation and (ii) the greater polarisability of the 1-position of naphthalene[12,18] relative to the 2-position leading to a decrease in the electron-deficiency of the sulphonyl group and hence a lower reactivity for the 1-isomer. It is pertinent to note that the reactivities of these two sulphonyl chlorides towards S_N2 displacement with aniline also show the same trend[19].

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