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KINETICS AND MECHANISM OF AMINOLYSIS OF PROPARGYL AND 1-METHYL-PROPARGYL ARENESULPHONATES

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Kinetic studies were carried out on the aminolysis of propargyl and 1-methylpropargyl arenesulphonates in acetonitrile at 45·0 °C. The cross-interaction constants, ρ_{XZ} and β_{XZ}, are similar to, but smaller than, those for the S_N2 processes at other primary and secondary carbon centers. Compared with the allyl series, the smaller magnitude of ρ_{XZ} and β_{XZ} reflects a looser transition state, which in turn leads to a lower rate despite the greater Taft's σ^* value and the lower intrinsic ($\Delta E_0^{\neq}$) and thermodynamic barriers (ΔE^0).

The sign and magnitude of cross-interaction constants, ρ_{ij} and β_{ij} in equations (1) where $i,j = X$, Y or Z in Scheme 1, have proved to be useful for predicting transition state (TS) structures and their variations with the substituents in the nucleophile X, substrate Y, and/or leaving group (LG) Z.[1] A typical S_N2 TS with three fragments, X, Y and Z, is shown in Scheme 1, where σ_i and R_i represent substituent and reaction centre i, respectively.

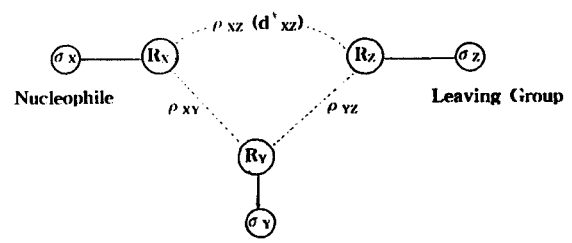
$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (1a)$$

$$\log(k_{ij}/k_{HH}) = \beta_i\,\Delta pK_i + \beta_j\,\Delta pK_j + \beta_{ij}\,\Delta pK_i\,\Delta pK_j \quad (1b)$$

The results of our studies in the past several years have led us to the following generalizations. (i) The sign of ρ_{XY} (for bond making) is negative, whereas the sign of ρ_{YZ} (for bond breaking) is positive in a normal S_N2 process.[2] (ii) The magnitude of ρ_{XY} and ρ_{YZ} is a measure of the extent of bond making and bond breaking, respectively, in the S_N2 transition state (TS).[3] (iii) The sign of ρ_{XZ} determines the type of TS variation with changes in the substituents X and Z.[1] The definition of ρ_{XZ}:

$$\rho_{XZ} = \frac{\partial^2 \log k_{XZ}}{\partial\sigma_X\,\partial\sigma_Z} = \frac{\partial\rho_Z}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Z} \quad (2)$$

postulates that if ρ_{XZ} is negative a 'later' TS ($\delta\rho_Z > 0$ and/or $\Delta\rho_X < 0$) is obtained, whereas the contrary is true for a positive ρ_{XZ}, i.e., an 'earlier' TS ($\delta\rho_z < 0$ and/or $\delta\rho_X > 0$) is obtained, with a stronger nucleophile ($\delta\sigma_X < 0$) and/or a stronger nucleofuge (i.e. a better LG) ($\delta\sigma_Z > 0$).[1] (iv) The magnitude of ρ_{XZ} provides a measure of the TS tightness; the greater the magnitude of ρ_{XZ}, the tighter is the TS, i.e. the shorter is the distance $d_{XZ}^{\neq}$.[1] (Scheme 1). Moreover, we found that for S_N2 processes at a primary carbon centre ρ_{XZ} is a relatively large positive constant value with a tight TS whereas ρ_{XZ} is relatively smaller at a secondary carbon centre with a loose TS, irrespective of the size of the group attached to the reaction centre carbon.[4]



Scheme 1

In this paper, we report the results of kinetic studies on the reactions of propargyl (2-propynyl, with a primary carbon centre) and l-methylpropargyl (1-methyl-2-propynyl, with a secondary carbon centre) arenesulphonates with anilines (AN), benzylamines

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(BA) and *N,N*-dimethylanilines (DMA) in acetonitrile at 45·0 °C.

RESULTS AND DISCUSSION

The second-order rate constants, k_2, for the aminolyses of propargyl and 1-methylpropargyl arenesulphonates are summarized in Tables 1 and 2. In both cases, the rate is faster with benzylamine, a stronger nucleophile, than with aniline. However, for propargyl arenesulphonate, the rate is *ca* 2–3 times lower with *N,N*-dimethylaniline reflecting steric hindrance of the dimethyl group in the TS. The rate ratios, k_{DMA}/k_{AN}, in Table 3 indicate that the steric rate retardation becomes enhanced as the degree of bond formation in the TS increases with a weaker nucleophile and/or nucleofuge; for this reaction ρ_{XZ} in equation (2) is positive (see below) so that a weaker nucleophile (X = *p* – Cl) and/or a weaker nucleofuge (Z = *p* – CH_3) should lead to a greater degree of bond formation [statement (iii) in the Introduction]. This steric rate retardation effect of the *N,N*-dimethyl group for the reactions of the propargyl series is, however, seen to be somewhat greater than the corresponding steric effect for the reactions of the allyl series[5] (Table 3); the rate ratios, k_{DMA}/k_{AN},vary from 0·33 to 0·48 as the substituent X is changed from *p*-Cl to *p*-CH_3O for propargyl benzenesulphonates in contrast to the corresponding changes from 0·48 to 0·64 for the allyl series (the magnitude of ρ_{XZ}, ρ_X and ρ_Z indicates that the degree of bond formation in the TS is similar for the two series).

This suggests that an acetylene group, HC≡C, is sterically more demanding than a vinyl group, CH_2=CH. This could be a reason why the rate constants for the propargyl series are in general *ca* 5 times lower than those for the corresponding allyl series. This is, however, in contrast to faster rates expected for propargyl rather than allyl based on the greater electron-withdrawing power (Taft's polar substituent constants, σ^*, are 2·18 and 0·56 for CH≡C and CH_2=CH group respectively),[6] the lower intrinsic barrier, $\Delta E_0^{\neq}$ (our MP2/6–31 + G* *computations on the identity chloride* exchange reactions gave $\Delta E_0^{\neq} = 6{\cdot}87$ and 8·21 kcal mol^{-1} (1 kcal = 4·184 kJ) for propargyl and allyl, respectively)[7] and the exothermicity (or lower thermodynamic barrier, ΔE_0) the reaction (the enthalpies of reaction propargyl and allyl benzenesulphonates with aniline are $\Delta H^{\circ} = -8{\cdot}0$ and $-6{\cdot}3$ kcal mol^{-1}, respectively by AM1 calculations).[8]

The Hammett and Brønsted coefficients, ρ_X, β_X, ρ_Z and β_Z, are given in Tables 4 and 5. The magnitudes of both ρ_X (allowing for the fall-off factor of *ca* 2·8 for the intervening CH_2 in BA)[1] and β_X are greater for BA than for AN, reflecting a tighter TS for the BA series. However, the magnitudes of β_X and β_Z suggestt that the TS for the DMA is looser than that for the AN series.

Finally, the rate data in Tables 1 and 2 were subjected

Table 1. Second-order rate constants, $k_2 \times 10^4$ dm^3 mol^{-1} s^{-1}, for the reactions of propargyl arenesulphonates with anilines (AN), benzylamines (BA) and *N,N*-dimethylanilines (DMA) in acetonitrile at 45·0 °C

		Z			
Nucleophile	X	*p*-CH_3	H	*p*-Cl	*m*-NO_2
AN	*p*-CH_3O	10·4	16·1	31·1	102
	p-CH_3	6·45	10·3	19·6	65·2
	H	3·22	5·19	10·5	35·7
	p-Cl	1·25	2·17	4·58	16·5
BA	*p*-CH_3O	67·8	120	263	1351
	p-CH_3	57·9	102	221	1167
	H	43·0	75·8	175	893
	p-Cl	28·5	52·3	121	638
DMA	*p*-CH_3O	4·78	7·73	17·6	75·5
	p-CH_3	2·74	4·60	10·5	47·2
	H	1·19	2·09	4·88	21·9
	p-Cl	0·406	0·714	1·75	8·57

Table 2. Second-order rate constants, $k_2 \times 10^4$ dm^3 mol^{-1} s^{-1}, for the reactions of 1-methylpropargyl arenesulphonates with anilines and anilines and benzylamines in acetonitrile at 45·0 °C

		Z			
Nucleophile	X	*p*-CH_3	H	*p*-Cl	*p*-NO_2
AN	*p*-CH_3O	1·43	2·06	3·86	16·2
	p-CH_3	0·965	1·39	2·61	11·8
	H	0·556	0·827	1·63	6·97
	p-Cl	0·289	0·428	0·834	3·72
BA	*p*-CH_3O	4·13	6·28	10·9	40·9
	p-CH_3	3·47	5·41	9·75	34·8
	H	2·72	4·16	7·53	28·7
	p-Cl	1·86	2·94	5·42	21·5

Table 3. Rate ratios (k_{DMA}/k_{AN}) for reactions of propargyl Z-benzenesulphonates in acetonitrile at 45·0 °C

	Z			
X	*p*-CH_3	H[a]	*p*-Cl	*m*-NO_2
p-CH_3O	0·45	0·48 (0·64)	0·57	0·74
H	0·37	0·40 (0·50)	0·46	0·61
p-Cl	0·32	0·33 (0·48)	0·38	0·52

[a] Values in parentheses are those for reactions of allyl arenesulphonates under the same reaction conditions.

to multiple regression analyses using equations (1) with $i, j = X, Z$, and the derived cross-interaction constants, ρ_{XZ} and β_{XZ}, are summarized in Table 6. The lower ρ_{XZ} values for the BA series in Table 6 are due to the fall-off of *ca* 2·8 by an intervening CH_2 group between the substituent (X) and the reaction centre (N) in BA.[1] The magnitudes of ρ_{XZ} and β_{XZ} for the reactions of propargyl and 1-methylpropargyl arenesulphonates with anilines are similar to those for other corresponding reactions at primary ($\rho_{XZ} \approx 0{\cdot}30$–$0{\cdot}33$ and $\beta_{XZ} \approx 0{\cdot}20$ at 65·0 °C)[4a] and secondary carbon centres ($\rho_{XZ} \approx 0{\cdot}10$ and $\beta_{XZ} \approx 0{\cdot}06$ at 65·0 °C, respectively).[4b]

The magnitude of ρ_{XZ} provides a measure of the TS tightness. The greater the $|\rho_{XZ}|$, the tighter is the TS. We found an interesting, unexpected, result concerning the TS tightness for S_N2 processes at primary and secondary carbon centres: the magnitude of ρ_{XZ} is a relatively large constant value (*ca* 0·29–0·40 in MeCN or MeOH at 45·0–65·0 °C) at a primary carbon whereas it is smaller constant value (*ca* 0·10–0·11 in MeCN at 65·0 °C) at a secondary carbon centre, irrespective of the size of the group attached to the reaction centre carbon (Table 7). These constant ρ_{XZ} values suggest that the TS is tight or loose ($d^{\ddagger}_{XZ}$ in Scheme 1 is short or long), depending on whether the reaction centre (R_Y) carbon is primary or secondary, but the TS tightness varies very little regardless of the group attached to R_Y. These approximate constancies of the TS tightness have been supported by the results of high-level *ab initio* MO calculations on the chloride exchanges at various primary and secondary carbon centres.[9] The results of MP2/6–31 + G*//MP2/6–31 + G* level calculations have indicated that the distances between the chlorine nucleophile and chlorine LG are indeed approximately constant at *ca* 4·7 and *ca* 4·8 Å for the primary and secondary carbon centres, respectively. This 0·1 Å difference in the TS tightness corresponds to a difference in the magnitude of ρ_{XZ} of *ca* 0·2. It is therefore gratifying to find in this work that the magnitude of ρ_{XZ} for propargyl (primary carbon centre) and 1-methylpropargyl (secondary carbon centre) falls within the range of the respective constant value for the reactions with anilines in acetonitrile in Table 7.

However if we account for the small depression of the magnitude accompanying a temperature rise (from 45·0 to 65·0 °C) (a 20 °C rise in temperature resulted in a decrease in ρ_{XZ} by 0·27), the values observed in Table 6 are lower by approximately 10–20% than those for other corresponding reactions. This means that the TSs for the aminolysis reactions of propargyl and 1-methylpropargyl are looser than those for other corresponding S_N2 reactions at the primary and secondary carbon centres. In a looser TS, C_α—LG bond stretching is greater, resulting in a higher intrinsic barrier so that the rate becomes lower.[16] A greater degree of steric hin-

Table 4. Hammett (ρ_X and ρ_Z)[a] and Brønsted (β_X and β_Z)[a] coefficients for the reactions Z-substituted propargyl benzenesulphonates with X-substituted anilines, benzylamines and *N*,*N*-dimethylanilines in acetonitrile at 45·0 °C

Nucleophile	Z	ρ_X	β_X	X	ρ_Z	β_Z
AN	*p*-CH_3	−1·84	0·66	*p*-CH_3O	1·13	−0·31
	H	−1·75	0·63	*p*-CH_3	1·14	−0·31
	p-Cl	−1·66	0·60	H	1·19	−0·32
	m-NO_2	−1·58	0·58	*p*-Cl	1·27	−0·34
BA	*p*-CH_3	−0·76	0·77	*p*-CH_3O	1·48	−0·40
	H	−0·73	0·72	*p*-CH_3	1·49	−0·40
	p-Cl	−0·68	0·66	H	1·50	−0·41
	m-NO_2	−0·66	0·65	*p*-Cl	1·53	−0·41
DMA	*p*-CH_3	−2·11	0·59	*p*-CH_3O	1·37	−0·37
	H	−2·08	0·57	*p*-CH_3	1·41	−0·38
	p-Cl	−2·01	0·55	H	1·44	−0·39
	m-NO_2	−1·90	0·52	*p*-Cl	1·51	−0·41

[a] Correlation coefficients >0·995.

Table 5. Hammett (ρ_X and ρ_Z)[a] and Brønsted (β_X and β_Z)[a] coefficients for the reactions Z-substituted 1-methylpropargyl benzenesulphonates with X-substituted anilines and benzylamines in acetonitrile at 45·0 °C

Nucleophile	Z	ρ_X	β_X	X	ρ_Z	β_Z
AN	*p*-CH_3	−1·39	0·50	p-CH30	1·12	−0·30
	H	−1·36	0·49	*p*-CH_3	1·16	−0·31
	p-Cl	−1·32	0·47	H	1·17	−0·32
	p-NO_2	−1·28	0·46	*p*-Cl	1·18	−0·32
BA	*p*-CH_3	−0·69	0·68	*p*-CH_3O	1·05	−0·28
	H	−0·67	0·66	*p*-CH_3	1·05	−0·28
	p-Cl	−0·62	0·63	H	1·08	−0·29
	p-NO_2	−0·55	0·52	*p*-Cl	1·12	−0·30

[a] Correlation coefficients >0·995.

Table 6. Cross-interaction constants, ρ_{XZ} and β_{XZ}, for aminolysis of propargyl and 1-methylpropargyl benzenesulphonates in acetonitrile at 45·0 °C

Substrate	Nucleophile	ρ_{XZ}[a]	β_{XZ}[a]
Propargyl	AN	0·29 (0·999)	0·17 (0·992)
	BA	0·10 (0·999)	0·21 (0·992)
	DMA	0·25 (0·999)	0·13 (0·993)
1-Methyl	AN	0·10 (0·999)	0·06 (0·996)
Propargyl	BA	0·04 (0·999)	0·11 (0·999)

[a] Correlation coefficientst are given in parentheses.

Table 7. ρ_{XZ} values for reactions of $ROSO_2C_6H_4Z$ with $XC_6H_4NH_2$.

	R	Solvent	T (°C)	ρ_{XZ}	Ref.
Primary compounds	CH_3	MeCN	65·0	0·32	10
		MeOH	65·0	0·30	10
	C_2H_5	MeCN	65·0	0·34	10
		MeOH	65·0	0·33	10
	$CH_2=CHCH_2$	MeCN	45·0	0·37	5
	$CH_2=C(CH_3)CH_2$	MeCN	45·0	0·40	11
	$(CH_3)_3CCH_2$	MeOH	55·0	0·31	4a
	$(CH_3)_3SiCH_2$	MeCN	65·0	0·33	12
		MeOH	65·0	0·31	12
	$CH\equiv CCH_2$	MeCN	45·0	0·29	This work
Secondary compounds	$(CH_3)_2CH$	MeCN	65·0	0·10	13
	Cyclobutyl	MeCN	65·0	0·11	14
	Cyclopentyl	MeCN	65·0	0·11	14
	Cyclohexyl	MeCN	65·0	0·11	14

drance seems to result in a looser TS for propargyl, which in turn leads to a lower rate. This is supported by the smaller ρ_{XZ} and β_{XZ} values in Table 6, indicating a looser TS with a lower rate for the DMA rather than the AN series.

We conclude that the cross-interaction constants for the reactions of propargyl and 1-methylpropargyl arenesulphonates are similar to, but smaller than, those for the S_N2 processes at other primary and secondary series, respectively. Compared with the allyl series, the smaller magnitude of ρ_{XZ} and β_{XZ} reflects a looser TS for the propargyl series, which in turn leads to a lower rate despite the greater Taft's polar constant, σ^*, and the lower intrinsic ($\Delta E_0^{\neq}$) and thermodynamic barriers (ΔE^0).

EXPERIMENTAL

Materials. Merck GR-grade acetonitrile was used after three distillations. The nucleophiles, aniline and benzylamine, were GR-grade reagents from Tokyo Kasei and were redistilled or recrystallized before use. *N,N*-Dimethylanilines were prepared from anilines using dimethylsulphate by the known method.[17] Substrate propargyl arenesulphonates were prepared[18] from propargyl alcohol as follows. Benzenesulphonyl chloride dissolved in dry diethyl ether was mixed with propargyl alcohol in dry diethyl ether at 0 °C and the mixture was shaken occasionally. Aqueous potassium hydroxide was added dropwise to a mixture, then poured into 100 ml of 1N sulphuric acid. The organic layer was separated and washed several times with water and dried with anhydrous magnesium sulphate. After removal of the solvent, the product was confirmed by (NMR analyses with a Jeol 400 MHz instrument. A similar method was used for the preparation of the other substrates. The NMR spectroscopic data are as follows.

Propargyl benzenesulphonate: liquid; δ 7·95 (2H, d, *ortho*, J = 7·33 Hz), 7·68 (1H, t, *para*, J = 7·33 Hz), 7·57 (2H, t, *meta*, J = 8·06 Hz), 4·73 (2H, d, CH_2, J = 2·20 Hz), 2·47 (1H, t, CH, J = 2·220 Hz).

Propargyl tosylate: liquid; δ 7·82 (2H, d, *ortho*, J = 8·06 Hz), 7·36 (2H, d, *meta*, J = 8·06 Hz), 4·07 (2H, d, CH_2, J = 2·20 Hz), 2·47 (1H, t, CH, J = 2.20 Hz), 2·46 (3H, s, CH_3).

Propargyl *p*-chlorobenzenesulphonate: liquid, δ 7·88 (2H, d, *ortho*, J = 8·80 Hz), 7·54 (2H, d, *meta*, J = 8·80 Hz), 4·75 (2H, d, CH_2, J = 2·20 Hz), 2·49 (1H, t, CH, J = 2·20 Hz).

Propargyl *p*-nitrobenzenesulphonate: m.p. 62–63 °C; δ 8·54 (2H, d, *meta*, J = 8·06 Hz), 8·29 (2H, d, *ortho*, J = 8·06 Hz), 4·87 (2H, d, CH_2, J = 2·20 Hz), 2·49 (1H, t, CH, J = 2·20 Hz).

1-methylpropargyl benzenesulphonate: liquid; δ 7·95 (2H, d, *ortho*, J = 7·33 Hz), 7·65 (1H, t, *para*, J = 7·33 Hz), 7·55 (2H, t, *meta*, J = 7·33 Hz), 5·20 (1H, q, CH, J = 6·6, 2·20 Hz), 2·39 (1H, d, CH, J = 2·20 Hz), 1·59 (3H, d, CH_3, J = 6·59 Hz).

1-Methylpropargyl tosylate: m.p. 47–48 °C; δ 7·82 (2H, d, *ortho*, J = 8·06 Hz), 7·34 (2H, d, *meta*, J = 8·06 Hz), 5·16 (1H, q, CH, J = 6·6, 2·20 Hz), 2·45 (3H, s, CH_3), 2·41 (1H, d, CH, J = 2.20 Hz), 1·57 (3H, d, CH_3, J = 6·59 Hz).

1-Methylpropargyl *p*-chlorobenzenesulphonate: m.p. 74–75 °C; δ 7·88 (2H, d, *ortho*, J = 8·79 Hz), 7·53 (2H, d, *meta*, J = 8·79 Hz), 5·21 (1H, q, CH, J = 6·6, 2·20 Hz), 2·43 (1H, d, CH, J = 2·20 Hz), 1·61 (3H, d, CH_3, J = 6·59 Hz).

1-Methylpropargyl *p*-nitrobenzenesulphonate: m.p. 112–113 °C; δ 8·39 (2H, d, meta, J = 8·79 Hz), 8·15 (2H, d, *ortho*, J = 8·79 Hz), 5·30 (1H, q, CH, J = 6·6, 2·20 Hz), 2·42 (1H, d, CH, J = 2·20 Hz), 1·65 (3H, d, CH_3, J = 6·60 Hz).

Kinetic procedures. Rates were measured conductimetrically and k_2 values were determined with at least four nucleophile concentrations using the procedure described previously.[4,5] The k_2 values were reproducible to within 3%.

Product analysis. Propargyl tosylate was reacted with excess aniline with stirring for more 15 half-lives at 45·0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography. The same method was used for the preparation of the other products. Analysis of the products gave the following results.

$CH{\equiv}CCH_2NHC_6H_5$; liquid; δ 6·64–7·23 (5H, m, aromatic), 3·95 (2H, d, CH_2, $J = 2·20$ Hz), 3·88 (1H, broad, s, NH), 2·21 (1H, t, CH, $J = 2·20$ Hz).

$CH{\equiv}CCH_2NHCH_2C_6H_5$; liquid; δ 7·29–8·39 (5H, m, aromatic), 3·70 (2H, s, CH_2, $J = 2·20$ Hz), 3·65 (1H, broad, s, NH), 3·43 (2H, d, CH_2, $J = 2·20$ Hz), 2·27 (1H, t, CH, $J = 2·20$ Hz).

$CH{\equiv}CCH(CH_3)NHC_6H_5$; liquid; δ 6·85–7·45 (5H, m, aromatic), 4·15 (1H, d, CH, $J = 2·20$ Hz), 3·65 (1H, broad, s, NH), 2·35 (1H, t, CH, $J = 2·20$ Hz), 1·30 (3H, s, CH_3).

$C_6H_5NH_3^+ {}^- OSO_2C_6H_4CH_3$; m.p. 226–228 °C; δ 7·12–7·46 (9H, m, aromatic), 2·14 (3H, s, CH_3).

$C_6H_5CH_2NH_3^+ {}^- OSO_2C_6H_4CH_3$; m.p. 202–204 °C; δ 7·01–7·45 (9H, m, aromatic), 4·35(2H, s, CH_2), 3·45 (3H, broad, NH_3^+), 2·37 (3H, s, CH_3).

$C_6N_5NH_3^+(CH_3)_2CH_2C{\equiv}CCH^-OSO_2C_6H_4CH_3$; m.p. 261–264 °C; δ 7·13–7·87 (9H, m, aromatic), 5·21 (2H, d, CH_2, $J = 2·20$ Hz), 3·87 (6H, s, $2CH_3$), 2·57 (1H, t, CH, $J = 2·20$ Hz), 2·34 (3H, s, CH_3).

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