Nucleophilic Substitution Reactions of 2-Chloro-2-Propen-1-yl Arenesulfonates with Anilines and N,N-Dimethylanilines in Acetonitrile

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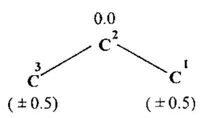
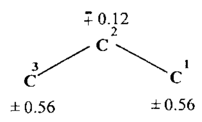
Kinetic studies are carried out on the reactions of 2-chloro-2-propen-1-yl arenesulfonates with anilines and N,N-dimethylanilines in acetonitrilile at 45.0 °C. The 2-chloro substituent is found to deactive the allyl moiety with considerable decrease in the rates. The sign and magnitude of the cross-interaction constant ($\rho_{XZ} \cong 0.3$) and the inverse secondary kinetic isotope effect ($k_H/k_D \cong 0.92$) support an S_N2 mechanism with a relatively tight transition state. The possibility of an S_N2' mechanism can be safely precluded based on the ρ_{XZ} values observed.

Introduction

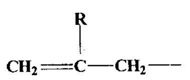
In the simplest π-MO method, Hückel MO (HMO) theory, a substituent on the central carbon (C^2) of the allyl system should have practically no effect on the reactivity and hence on the transition state (TS) structure, as HMO formal charge distribution on an allylic ion (cation or anion) indicate, I.[1] However, according to a more advanced π-MO method due to Pople,[1,2] the central carbon has a small opposite formal charge relative to the two terminal carbon atoms, II; in the allyl anion the central carbon has formal charge of +0.12 whereas in the allyl cation it reverses to −0.12. Therefore this model predicts that an electron donor on C^2, *e.g.* IIIb, will stabilize the anionic form in contrast to a destabilizing effect of an electron acceptor, *e.g.* IIIc, compared with allyl anion IIIa. In our previous work,[3,4] we found that the donor group CH_3 has little destabilizing effect on the net negatively charged allyl moiety in the TS of the aminolysis of IIIa and IIIb derivatives, eq. (1), due to most probably the steric effect of the R=CH_3 group in the TS. The fact that the TS is tight with negative charge on the reaction center, C^1, is confirmed by the relatively large positive ρ_{XZ}, eqs. (2),[5] which had a typical value corresponding to the nucleophilic substitution at a primary carbon center ($\rho_{XZ} \cong 0.3$-0.4).[6] It has been shown experimentally that the ρ_{XZ} values for the direct nucleophilic substitutions at secondary carbon centers have *ca.* one-third ($\rho_{XZ} \cong 0.11$-0.13)[7] of those for the primary carbon center ($\rho_{XZ} \cong 0.30$-0.40)[6] indicating much looser TSs for displacements at secondary than primary carbons.



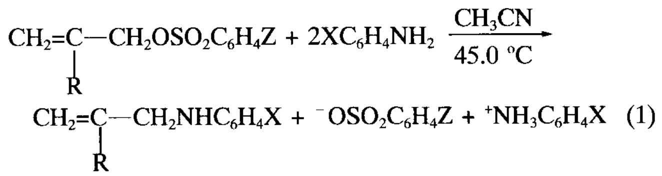
I



II



III (a) R = H
(b) R = CH_3
(c) R = Cl



$$CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}{-}CH_2OSO_2C_6H_4Z + 2XC_6H_4NH_2 \xrightarrow[45.0\ ^\circ C]{CH_3CN} CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}{-}CH_2NHC_6H_4X + {}^-OSO_2C_6H_4Z + {}^+NH_3C_6H_4X \quad (1)$$

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \qquad (2a)$$

$$\rho_{XZ} = \frac{\partial\rho_Z}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Z} \qquad (2b)$$

In this work, we carried out the kinetic studies on the nucleophilic substitution at an allyl derivative with an electron acceptor group on C^2, IIIc, under the same reaction conditions with those used in the studies of the corresponding systems of IIIa and IIIb. The purpose of this work is to confirm the deactivating effect of an electron acceptor group (R = Cl) on C^2 in reaction (1). We used substituted anilines (AN) and N,N-dimethylanilines (DMA) as nucleophiles, and determined the cross-interaction constants, ρ_{XZ}, between substituents in the nucleophile (X) and nucleofuge (Z) in order to show that the TS tightness, or the sign and magnitudes of ρ_{XZ}, remains essentially unchanged irrespective of a variation of the R group on C^2.

Results and Discussion

The second-order rate constants, k_2, for the reactions of 2-Chloro-2-propen-1-yl arenesulfonates with anilines (eq. (1)) and DMAs are summarized in Table 1. The effects of various substituents in the nucleophile (X) and nucleofuge (Z) on the rates are in accord with those for a typical nucleophilic substitution reaction. The rates are faster with anilines than with the corresponding reactions of DMAs

Table 1. The Second Order Rate Constants, $k_2/10^5$ dm^{-1} s^{-1}, for the Reactions of 2-Chloro-2-propen-1-yl Arenesulfonates with Anilines and N,N-Dimethylanilines in Acetonitrile at 45.0 °C

	X	Z			
		p-CH_3	H	p-Cl	p-NO_2
Aniline	p-OMe	28.5	43.1	97.3	553
	p-Me	19.5	30.0	66.8	398
	H	8.45	13.2	30.8	205
	p-Cl	3.26	5.25	12.9	89.1
N,N-Dimethyl-aniline	p-Me	12.5	19.7	48.9	343
	H	5.94	8.41	21.6	156
	p-Br	0.718	1.24	3.21	25.6
	m-NO_2	0.0179	0.0313	0.0907	0.873

even though DMAs have slightly greater basicities ($pK_a = 4.6$ and 4.8 for AN and DMA respectively). The rate retardation for the DMAs relative to ANs reflects the steric effect of the N,N-dimethyl group, which is greater for $R = CH_3$ and $R = H^{3,4}$ than Cl with typical k_{DMA}/k_{AN} values of 0.36, $0.50^{3,4}$ and 0.64, respectively. The greater k_{DMA}/k_{AN} value for R = Cl than R = H suggests a somewhat looser TS for R = Cl than R = H. The rate ratio $S = k(R = Cl)/k(R = H)$ of *ca.* 0.05 (for X = Z = H) is an order of magnitude smaller than $S = k(R = CH_3)/k(R = H)$ of 0.47 indicating that the R = Cl group deactivates the allyl moiety. This means that the allyl moiety becomes negatively charged in the TS and the central carbon (C^2) has formal positive (+0.12 in II) charge which is destabilized by an electron acceptor substituent, R = Cl.

The selectively parameters, ρ_X (β_X) and ρ_Z (β_Z), in Table 2 are quite similar in magnitude with those corresponding value for $R = CH_3$.[4] The cross-interaction constants, ρ_{XZ} (= 0.33 and 0.29 for ANs and DMAs), are also within the range of values ($\rho_{XZ} = 0.3$-0.4)[6,7] for the nucleophilic substitution (S_N2) reactions at a primary carbon center. However, close examination of the magnitude of ρ_{XZ} reveals that the ρ_{XZ} for R = Cl is somewhat smaller than those for R = H (ρ_{XZ} = 0.37 and 0.30)[3] and $R = CH_3$ ($\rho_{XZ} = 0.40$ and 0.37,[4] respectively, with ANs and DMAs) under the same reaction conditions. This is in line with a somewhat looser TS for R = Cl than those for R = H and $R = CH_3$, as suggested by the lower steric effect of the N,N-dimethyl group represented by the greater k_{DMA}/k_{AN} ratio (*vide supra*).

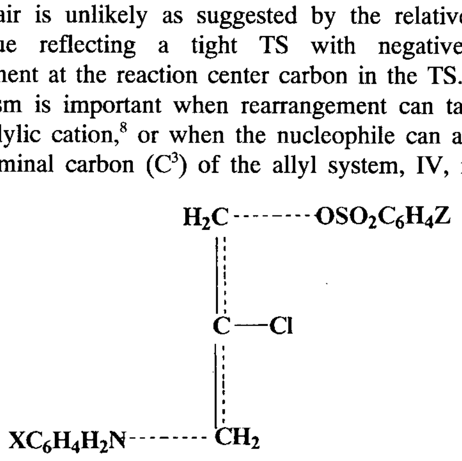
This is also supported by the magnitude of secondary kinetic isotope effects, k_H/k_D, involving deuterated aniline nucleophiles[7] in Table 3. We note that the k_H/k_D values are less unity (< 1.0) with somewhat greater value (0.92-0.93) than those for R = H (k_H/k_D = 0.87-0.90).[3] The inverse isotope effects ($k_H/k_D < 1.0$) are in accord with our proposed mechanism of the direct nucleophilic didplacement (S_N2 mechanism)[7] and the relatively greater k_H/k_D value supports the somewhat loose TS for R = Cl than for R = H.

Table 2. The Hammett (ρ_X and ρ_Z) and Brϕnsted (β_X and β_Z) Coefficients for Reactions of Z-Substituted 2-Chloro-2-propen-1-yl Arenesulfonates with X-Substituted Anilines and N,N-Dimethylanilines

	Z	ρ_X	β_X	X	ρ_Z	β_Z
Aniline	p-Me	-1.93	0.70	p-OMe	1.38	-0.37
	H	-1.87	0.68	p-Me	1.40	-0.38
	p-Cl	-1.79	0.65	H	1.48	-0.40
	p-NO$_2$	-1.62	0.58	p-Cl	1.54	-0.42
N,N-Dimethy-aniline	p-Me	-3.06	0.63	p-Me	1.54	-0.42
	H	-3.01	0.61	H	1.56	-0.43
	p-Cl	-2.94	0.60	p-Br	1.66	-0.45
	p-NO$_2$	-2.79	0.57	m-NO$_2$	1.80	-0.49

*Correlation coefficients: > 0.998

The possibility of an S_N2' mechanism (IV), in which the allylic system reacts with rearrangement of double bond, can be safely precluded since formation of a carbonium ion and/or ion-pair is unlikely as suggested by the relatively large ρ_{XZ} value reflecting a tight TS with negative charge development at the reaction center carbon in the TS. An S_N2' mechanism is important when rearrangement can take place in the allylic cation,[8] or when the nucleophile can attack the other terminal carbon (C^3) of the allyl system, IV, in which case the distance between the two substituents X and Z is longer by two C···C bonds so that the magnitude of ρ_{XZ} should be reduced to *ca.* 1/2-1/4 than that for the S_N2 reactions at a primary carbon center ($\rho_{XZ} = 0.3$-0.4).[9] The large ρ_{XZ} of ~0.3 observed in this work in fact provides a mechanistic criterion for rejecting the S_N2' mechanism.



IV

We conclude that the much slower rates for the substrate with R = Cl than for the substrate with $R = CH_3$ (an order of magnitude lower) reflect deactivating effect of an electron acceptor group (R = Cl) at the central carbon of the negatively charged allyl moiety in the relatively tight S_N2 TS. The ρ_{XZ} values obtained (0.33 and 0.29 with ANs and DMAs) are well within the range for those of S_N2 reaction at a primary carbon center.

Experimental

Materials. Anilines were Tokyo Kasei G.R. grade and N,N-dimethylanilines were Aldrich G.R. grade. Merck G.R. grade acetonitrile was redistilled three times before use. 2-Chloro-2-propen-1-ol, pyridine and arenesulfonyl chlorides used in the preparation of substrates were Aldrich G.R. grade.

Preparation of Substrates. To a round bottom flask containing methylene chloride, 2-chloro-2-propen-1-ol (5 mmol) was dissolved and triethylamine (7 mmol) was added keeping temperature to 0-5 °C. To this arenesulfonyl chloride (5 mmol) was added and reacted for one hour.

Table 3. Secondary Kinetic Isotope Effects for the Reactions of 2-Chloro-2-propen-1-yl Arenesulfonates with Deuteriated Anilines in MeCN at 45.0 °C

X	Z	k_H(dm^3 mol^{-1} s^{-1})	k_D(dm^3 mol^{-1} s^{-1})	k_H/k_D
p-MeO	p-Me	$2.85\pm(0.03)^a\times10^{-4}$	$3.09\pm(0.03)^a\times10^{-4}$	0.920 ± 0.005^a
p-MeO	p-NO$_2$	$55.3\pm(0.2)\times10^{-4}$	$60.2\pm(0.3)\times10^{-4}$	0.920 ± 0.006
p-Cl	p-Me	$0.326\pm(0.002)\times10^{-4}$	$0.350\pm(0.004)\times10^{-4}$	0.930 ± 0.012
p-Cl	p-NO$_2$	$8.91\pm(0.04)\times10^{-4}$	$9.57\pm(0.03)\times10^{-4}$	0.931 ± 0.005

[a] Standard deviation.

Checking the progress of reaction by TLC the reaction was quenched by adding ice, and extracted three times with methylene chloride. After washing the extract with cold hydrochloric acid (2N), washed twice with saturated aqueous NaCl solution, desiccated with anhydrous $MgSO_4$ and solvent was then removed under reduced pressure. The yields were better than 85% in all case. The residue was then subjected to column chromatography for separation. The IR, H and ^{13}C NMR (JEOL 400 MHz) analytical data are as follows:

2-chloro-2-propen-1-yl benzenesulfonate. Liquid, IR (cm^{-1}, KBr), 1448, 1639 (aromatic C=C), 1184, 1367 (S=O), 689-832 (=CH), δ_H 7.90 (2H, d, ortho, J=7.81 Hz), 7.64 (1H, t, para, J=7.32), 7.53 (2H, t, meta, J=7.81), 5.47 (1H, s, vinyl), 5.36 (1H, s, vinyl), 4.56 (2H, s, $-CH_2O-$) δ_C 135.57, 134.01, 133.43, 129.19, 127.71, 116.78, 70.98.

2-chloro-2-propen-1-yl tosylate. Liquid, IR (cm^{-1}), 2939 (CH aliphatic), 1590, 1640 (aromatic C=C), 1179, 1364 (S=O), 833 (=CH), δ_H 7.80 (2H, d, meta, J=8.30 Hz), 7.36 (2H, d, ortho, J=7.81), 5.50 (1H, s, vinyl), 5.39 (1H, s, vinyl), 4.56 (2H, s, $-CH_2O-$), 2.45 (3H, s, methyl) δ_C 145.10, 133.52, 132.49, 129.84, 127.85, 116.53, 70.77, 21.60.

2-chloro-2-propen-yl p-chlorobenzenesulfonate. Liquid, IR (cm^{-1}, KBr), 3112 (CH), 1475, 1581 (aromatic C=C), 1371, 1184 (S=O), 829 (=CH), δ_H 7.87 (2H, d, ortho, J=8.30 Hz), 7.55 (2H, d, meta, J=8.79 Hz), 5.53 (1H, s, vinyl), 5.43 (1H, s, vinyl), 4.62 (2H, s, $-CH_2O-$), δ_C 140.66, 134.18, 133.34, 129.55, 129.29, 177.23, 71.32.

2-chloro-2-propen-1-yl p-nitrobenzenesulfonate. mp 68-69 °C, IR (cm^{-1}, KBr), 3102 (CH), 1608, 1637 (aromatic C=C), 1533, 1380 (N=O), 1186, 1355 (S=O), 833 (=CH), δ_H 8.42 (2H, d, ortho, J=8.79), 8.15 (2H, d, meta, J=8.79), 5.57 (1H, s, vinyl), 5.46 (1H, s, vinyl), 4.72 (2H, s, $-CH_2O-$), δ_C 150.75, 141.54, 133.10, 129.23, 124.38, 118.12, 72.13.

Kinetic Procedure. The procedure adopted is as described previously.[3,4,10] Rates were reproducible to within ±3%.

Product Analysis. 2-Chloro-2-propen-1-yl benzenesulfonate was reacted with aniline in acetonitrile under the same conditions used in the kinetic measurements. After over 10 half-lifes, salt was filtered off and solvent was removed from the filtrate under reduced pressure. Yield was in the range reported on the substrate preparation. Anilide was separated by column chromatography. The analytical data are as follows:

$CH_2=C(Cl)-CH_2-NHC_6H_5$. Liquid, IR (cm^{-1}), 3160 (NH), 3015-3075 (CH), 745, 910 (phenyl), 670-752 (=C-H), δ_H 7.18 (2H, t, meta, J=8.30), 6.74 (1H, t, para, J=7.33), 6.62 (2H, d, ortho, J=8.30), 5.42 (1H, s, vinyl), 5.31 (1H, s, vinyl), 3.92 (2H, s, $-CH_2N-$), δ_C 146.66, 139.10, 129.18, 118.12, 112.96, 112.39, 50.15.

Secondary Kinetic Isotope Effect. Secondary kinetic isotope effects, k_H/k_D, were determined as described previously.[11]

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