Nucleophilic substitution reactions of 2-norbornyl arenesulfonates with anilines

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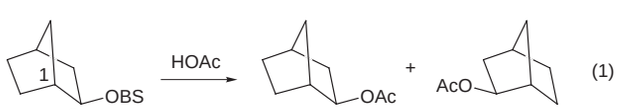
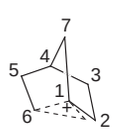
The kinetics and mechanism of the nucleophilic substitution reactions of *exo*- and *endo*-2-norbornyl arenesulfonates with anilines are investigated in methanol and acetonitrile at 60.0 °C. Rate constants for three distinct competing processes, solvolysis k_s, unimolecular k_1 and bimolecular k_2, are separately determined by plotting k_{obs} *vs.* aniline concentration [Nu], $k_{obs} = k_1 + k_2$[Nu], where $k_1 = k_s + k_n$ with k_n as the nonsolvolytic S_N1 rate constant. The k_n/k_s value ranges from 6 to 7. The extent of leaving group departure in the transition state expressed by ρ_Z (where Z is a substituent in the leaving group) is always (for k_s, k_1 and k_2) greater for *exo* than for *endo* suggesting a greater degree of bond cleavage in the *exo* system. The cross-interaction constants, ρ_{XZ}, are zero for k_s and k_n, but are the smallest ever obtained with distinctly non-zero value ($\rho_{XZ} \leqslant 0.01$) for k_2. The transition state structures of the S_N2 pathway are of a very loose, open or 'exploded' type as judged by the very small magnitudes of ρ_X (where X is a substituent in the nucleophile) and ρ_{XZ} coupled with the large values of ρ_Z. The reactions of *exo*-2-norbornyl arenesulfonates in the aprotic solvent, CH_3CN, are characterized by a much smaller ρ_Z for k_1 but a larger value of ρ_Z for k_2 than those in CH_3OH. All the experimental results support a preassociation mechanism for the bimolecular substitution process (k_2).

Introduction

The results of solvolytic studies on 2-norbornyl systems led to the non-classical carbonium ion controversy.[1] The acetolysis of chiral *exo*-2-norbornyl brosylate (*p*-bromobenzenesulfonate, BS) is *ca.* 350 times faster than that of the *endo* brosylate giving 50% rearrangement to a racemic mixture of the *exo* acetates,[2] eqn. (1). This behavior was interpreted as a result of neighboring group participation with the formation of a bridged intermediate, the norbornyl cation, **I**. The *endo* geometry does



(1)



I

not allow such anchimeric assistance, and Winstein proposed that *unassisted* ionization gives a classical carbenium ion-pair which reacts directly with a solvent molecule.[2] Brown,[3] however, suggested that it is not the *exo* rate that is unusually fast but that it is the *endo* rate that is unusually slow due to steric inhibition to ionization; the departing anion is squeezed in between the *endo*-6-hydrogen and the 2-hydrogen atom swinging towards coplanarity. A number of physical techniques have become available for the direct observation of intermediate cations derived from norbornyl derivatives.[4] Molecular orbital calculations indicate that the norbornanium ion **I** is a true intermediate on the potential energy surface.[5] The most recent theoretical studies on the transition state (TS) structure[1b] for the solvolyses of *exo*- and *endo*-2-norbornyl cations using H_2O as a leaving group led to the following conclusions: although the TS geometries show incomplete 2-norbornanium ion formation (*bridging lags behind ionization*) both cation moieties in their TS geometries benefit energetically from nonclassical stabilization by delocalization. It is also noteworthy that the *endo* TS is stabilized more through the hydrogen bonding interactions of the two closest hydrogen and oxygen (in the leaving group) atoms than is the *exo* TS in contrast to steric retardation in the *endo* TS suggested by Brown. Brown stated that 'there is an energetic bias favoring *exo* over *endo* in the absence of any bridging'. In short, the TSs are relatively early on the reaction coordinate with very little bridged norbornanium ion (**I**) character.

In this work, we carried out kinetic studies on the solvolysis in methanol–acetonitrile mixtures and the aminolysis with anilines ($XC_6H_4NH_2$; X = *p*-MeO, *p*-Me, H, *p*-Cl, *p*-Br) of the *exo*- and *endo*-2-norbornyl arenesulfonates, ($C_7H_{11}OSO_2C_6H_4Z$; Z = *p*-OMe, *p*-Me, H, *p*-Cl for *exo* and Z = H, *p*-Cl, *m*-NO_2, *p*-NO_2 for *endo*). We intended to explore the possibility of determining the cross-interaction constant, ρ_{XZ} in eqns. (2a) and (2b),[6] for

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

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

the aminolysis of *exo*- and *endo*-2-norbornyl systems by measuring the aminolysis rate constants, k_{XZ}, and subjecting them to multiple regression analysis using eqn. (2a).[6] Previous reports on the aminolysis at primary, secondary and tertiary carbon centers have shown that:[7] (i) The magnitude of ρ_{XZ} is inversely related to the tightness of S_N2 transition states (TSs), with ρ_{XZ} = 0.29–0.40, 0.10–0.13 and −0.03–−0.04 for the primary, secondary and tertiary carbon centers, respectively. (ii) The magnitude of ρ_{XZ} and hence the TS tightness varies very little with regard to the group attached to the reaction center.

The main objective of this work is to determine the ρ_{XZ} values for the *exo*- and *endo*-2-norbornyl series in methanol and acetonitrile to see if there is any S_N2 component in the aminolysis reactions, and shed more light on the mechanism of the reactions.

Table 1 Solvolysis rate constants, $k_s/10^{-4}$ s^{-1}, for *exo*-2-norbornyl (Z)-arenesulfonates in MeOH–MeCN mixtures

		$k_s/10^{-4}$ s^{-1}					
		Z					
MeOH (v/v%)	*T*/ °C	*p*-OMe	*p*-Me	H	*p*-Cl	ρ_Z [c]	β_Z [d]
100	50.0	0.567	0.843	1.49	3.95	1.62 ± 0.01 [b]	−0.44 ± 0.01 [b]
	60.0	1.76	2.69	4.48	11.6		
90	50.0	0.502	0.807	1.41	3.57	1.64 ± 0.01	−0.45 ± 0.01
	60.0	1.69	2.47	4.19	11.2		
80	50.0	0.471	0.774	1.32	3.44	1.68 ± 0.02	−0.46 ± 0.01
	60.0	1.56	2.25	3.91	10.7		
70	50.0	0.425	0.681	1.20	3.24	1.71 ± 0.02	−0.47 ± 0.01
	60.0	1.42	2.03	3.65	10.1		
50	50.0	0.301	0.469	0.871	2.40	1.78 ± 0.01	−0.49 ± 0.02
	60.0	0.933	1.43	2.58	7.24		
m [a]	60.0	1.24 ± 0.17 [b]	1.15 ± 0.25	1.02 ± 0.18	0.92 ± 0.12		

[a] Grunwald–Winstein coefficients with $Y_{1\text{-AdBr}}$.[19] Correlation coefficients ⩾ 0.937. [b] Standard deviation. [c] Correlation coeff. ⩾ 0.998. [d] Correlation coeff. ⩾ 0.997. The pK_a values are for methyl transfer.[20]

Table 2 Solvolysis rate constants, $k_{obs}/10^{-3}$ s^{-1}, for *exo*-2-norbornyl (Z)-arenesulfonates with added (X)-anilines in methanol at 60.0 °C

X	Z	Aniline concentration/M	$k_{obs}/10^{-3}$	$k_1/10^{-3}$ s^{-1}	$k_2/10^{-3}$ M^{-1} s^{-1}	*r*
p-OMe	H	0.119	3.701	3.51 ± 0.009	1.73 ± 0.02	0.999(6)
		0.249	3.938			
		0.300	4.042			
		0.400	4.210			
		0.501	4.367			
		0.551	4.455			
		0.600	4.544			
		0.649	4.634			
p-Me	H	0.099	3.678	3.52 ± 0.005	1.65 ± 0.01	0.999(8)
		0.149	3.771			
		0.200	3.845			
		0.300	4.024			
		0.400	4.176			
		0.449	4.260			
		0.501	4.344			
		0.549	4.431			
H	H	0.101	3.670	3.51 ± 0.006	1.64 ± 0.01	0.999(7)
		0.151	3.742			
		0.199	3.840			
		0.249	3.918			
		0.400	4.166			
		0.449	4.244			
		0.500	4.322			
		0.550	4.400			
p-Cl	H	0.093	3.642	3.50 ± 0.008	1.47 ± 0.02	0.999(6)
		0.199	3.794			
		0.299	3.920			
		0.400	4.074			
		0.501	4.238			
		0.549	4.308			
		0.599	4.380			
		0.651	4.449			

Results

The observed rate constants $k_s/10^{-4}$ s^{-1} for the solvolysis of *exo*-2-norbornyl (*Z*)-arenesulfonates in methanol–acetonitrile mixtures at 50.0 and 60.0 °C are summarized in Table 1. The Hammett (ρ_Z) and Brønsted coefficients (β_Z) together with the Grunwald–Winstein coefficients (*m*) are also given in Table 1. The first-order, k_1/s^{-1}, and second-order rate constants, k_2/M^{-1} s^{-1}, were determined from the intercept and slope of the plot of k_{obs} *versus* aniline concentration, [Nu], eqn. (3).[8] In most cases,

$$k_{obs} = k_1 + k_2[Nu] \quad (3)$$

four aniline concentrations were used in the plot, which gave good linearity and the nucleophile-independent k_1 value was obtained within experimental error (±3%). For a substrate, the intercepts for four aniline nucleophiles (X = *p*-OMe, *p*-Me, H and *p*-Cl) converged to a single point to give a k_1 value.[8] In order to test the reliability of the k_1 values determined with four [Nu] values, we have used seven or more [Nu] in two cases as shown in Tables 2 and 3. We note an excellent convergence of the intercepts to a single point for the four anilines, which agrees well with the k_1 determined with four [Nu] in Tables 4 and 5. The agreement of k_2 between those in Tables 2 and 3 and in Tables 4 and 5 is also within experimental accuracy of ±3%.

Table 3 Solvolysis rate constants, $k_{obs}/10^{-4}$ s^{-1}, for *endo*-2-norbornyl (Z)-arenesulfonates with added (X)-anilines in methanol at 60.0 °C

X	Z	Aniline concentration/M	$k_{obs}/10^{-4}$	$k_1/10^{-4}$ s^{-1}	$k_2/10^{-4}$ M^{-1} s^{-1}	r
p-OMe	*p*-NO_2	0.120	1.740	1.67 ± 0.001	0.571 ± 0.003	0.999(9)
		0.250	1.812			
		0.300	1.840			
		0.600	2.015			
		0.650	2.042			
		0.700	2.070			
		0.750	2.097			
p-Me	*p*-NO_2	0.101	1.724	1.67 ± 0.001	0.540 ± 0.001	0.999(9)
		0.200	1.776			
		0.401	1.885			
		0.501	1.940			
		0.549	1.965			
		0.600	1.993			
		0.650	2.020			
H	*p*-NO_2	0.100	1.717	1.67 ± 0.004	0.507 ± 0.0008	0.999(9)
		0.150	1.742			
		0.255	1.795			
		0.410	1.874			
		0.500	1.920			
		0.550	1.945			
		0.599	1.969			
		0.650	1.996			
p-Cl	*p*-NO_2	0.200	1.751	1.66 ± 0.007	0.470 ± 0.001	0.999(9)
		0.300	1.798			
		0.400	1.846			
		0.501	1.893			
		0.601	1.940			
		0.650	1.963			
		0.700	1.985			
		0.750	2.010			

Table 4 Second order rate constants, $k_2/10^{-4}$ M^{-1} s^{-1}, for the reactions of *exo*-2-norbornyl (Z)-arenesulfonates with (X)-anilines in methanol at 60.0 °C

	$k_2/10^{-4}$ M^{-1} s^{-1}					
	Z					
X	*p*-OMe	*p*-Me	H	*p*-Cl	ρ_Z[a]	β_Z[b]
p-OMe	5.94	8.79	17.8	45.7	1.79	−0.491
p-Me	5.59	8.35	17.0	43.3	1.79	−0.492
H	5.14	7.77	15.9	40.4	1.80	−0.494
p-Cl	4.65	6.92	14.1	36.5	1.81	−0.495
p-Br	4.63	6.89	13.9	36.4	1.81	−0.496
k_1 (intercepts)	13.0	20.2	35.2	74.0	1.49 ± 0.06 (r = 0.998)	
ρ_X[c]	−0.211	−0.209	−0.208	−0.194		
β_X[d]	0.077	0.075	0.073	0.070		

[a] Correlation coeff.: $r \geqslant 0.999$. [b] Correlation coeff.: $r \geqslant 0.984$. [c] Correlation coeff.: $r \geqslant 0.999$. [d] Correlation coeff.: $r \geqslant 0.998$.

Tables 4 and 5 also list the ρ_X (β_X) and ρ_Z (β_Z) values. Variations of these with different substituents are admittedly small, but definite trends can be clearly seen. The k_1 and k_2 values for *exo*-2-norbornyl arenesulfonates are also determined in acetonitrile (Table 6). In order to test steric effects of the nucleophile in the TS, the k_2 values are also determined with *N*,*N*-dimethylanilines for Z = H, as shown in Table 6. The salt effect on the solvolysis of *exo*-2-norbornyl arenesulfonates was examined with KCl at 60.0 °C in methanol. The results are given in Table 7. The steep initial increases in k_s are noted indicating that there is a special salt effect due to internal return of the solvent separated ion-pairs.[9] Kinetic solvent isotope effects, k_H/k_D, on the solvolysis rates of *exo* compounds at 60.0 °C were determined and the results are given in Table 8. It is apparent that $k_H/k_D \cong 1.0$ indicating that there is no kinetic isotope effect. In addition we have determined secondary kinetic isotope effects (SKIEs) in methanol (Table 9) and in acetonitrile with deuterated anilines[7b] (Table 10). Normal SKIEs are obtained with the k_H/k_D values, in all cases, greater than one.

The activation parameters, $\Delta H^‡$ and $\Delta S^‡$, were determined for the solvolysis of *exo*-2-norbornyl arenesulfonates in MeOH–MeCN mixtures with the k_s values at two temperatures, 50.0 and 60.0 °C. The results are shown in Table 11. Since k_s at two temperatures are used, the $\Delta H^‡$ and $\Delta S^‡$ values provide rough estimates only.

Discussion

Solvolysis

The relatively large magnitude of ρ_Z (1.6–1.8) and β_Z (−0.44–−0.49) for the solvolysis of *exo*-2-norbornyl arenesulfonates in MeOH–MeCN mixtures at 60.0 °C in Table 1 suggests extensive

Table 5 Second order rate constants, $k_2/10^{-5}$ M^{-1} s^{-1}, for the reactions of *endo*-2-norbornyl (Z)-arenesulfonates with (X)-anilines in methanol at 60.0 °C

	$k_2/10^{-5}$ M^{-1} s^{-1}					
	Z					
X	H	*p*-Cl	*m*-NO_2	*p*-NO_2	ρ_Z[a]	β_Z[b]
p-OMe	0.604	1.13	4.50	5.55	1.237	−0.320
p-Me	0.583	1.09	4.36	5.36	1.239	−0.320
H	0.552	1.02	4.11	5.07	1.240	−0.320
p-Cl	0.508	0.953	3.81	4.70	1.241	−0.321
p-Br	0.508	0.953	3.80	4.67	1.240	−0.321
k_1 (intercepts)	2.89	5.32	14.7	16.7	0.97 ± 0.03 (r = 0.999)	
ρ_X[c]	−0.151	−0.149	−0.146	−0.146		
β_X[d]	0.054	0.055	0.053	0.052		

[a] Correlation coeff.: $r \geqslant 0.999$. [b] Correlation coeff.: $r \geqslant 0.998$. [c] Correlation coeff.: $r \geqslant 0.999$. [d] Correlation coeff.: $r \geqslant 0.998$.

Table 6 Second order rate constants, $k_2/10^{-5}$ M^{-1} s^{-1}, for the reactions of *exo*-2-norbornyl (Z)-arenesulfonates with (X)-anilines in acetonitrile at 60.0 °C

	$k_2/10^{-5}$ M^{-1} s^{-1}					
	Z					
X	*p*-OMe	*p*-Me	H	*p*-Cl	ρ_Z[a]	β_Z[b]
p-OMe	1.00	1.58	3.51	10.2	2.035	−0.557
p-Me	0.975	1.53	3.41 (3.39)[e]	9.97	2.042	−0.559
H	0.925	1.45	3.24 (3.20)	9.58	2.053	−0.562
p-Cl	0.862	1.36	3.03 (2.99)	9.09	2.068	−0.567
p-Br	0.861	1.35	3.02 (2.98)	9.08	2.069	−0.567
k_1(intercepts)	3.74	4.31	5.14	8.22	0.67 ± 0.07 (r = 0.989)	
ρ_X[c]	−0.135	−0.134	−0.129	−0.101		
β_X[d]	0.049	0.048	0.047	0.036		

[a] Correlation coeff.: $r \geqslant 0.999$. [b] Correlation coeff.: $r \geqslant 0.984$. [c] Correlation coeff.: $r \geqslant 0.999$. [e] With DMA.

Table 7 Solvolysis rate constants, $k_s/10^{-3}$ s^{-1}, for the reactions of *exo*-2-norbornyl (Z)-arenesulfonates with added KCl (M) in methanol at 60.0 °C

	$k_s/10^{-3}$ s^{-1}			
	[KCl]			
Z	0	0.01	0.03	0.04
p-OMe	0.176	1.25	1.47	1.56
p-Me	0.269	1.98	2.34	2.46
H	0.448	3.19	3.49	3.59
p-Cl	1.16	4.13	4.45	4.56

Table 8 Kinetic solvent isotope effects on the solvolysis rate constants of *exo*-2-norbornyl (Z)-arenesulfonates in MeOH at 60.0 °C

Z	$k_H/10^{-4}$ s^{-1}	$k_D/10^{-4}$ s^{-1}	k_H/k_D
p-OMe	1.76 ± 0.02[a]	1.71 ± 0.02	1.03 ± 0.01[b]
p-Me	2.69 ± 0.02	2.59 ± 0.02	1.04 ± 0.01
H	4.48 ± 0.03	4.39 ± 0.01	1.02 ± 0.01
p-Cl	11.6 ± 0.04	11.4 ± 0.01	1.02 ± 0.01

[a] Standard deviation. [b] Standard error.

Table 9 Secondary kinetic isotope effects for the reactions of *exo*-2-norbornyl (Z)-arenesulfonates with deuterated anilines in MeOD at 60.0 °C

X	Z	$k_H/10^{-4}$ M^{-1} s^{-1}	$k_D/10^{-4}$ M^{-1} s^{-1}	k_H/k_D
p-OMe	*p*-OMe	5.94 ± (0.02)[a]	5.29 ± (0.02)	1.12 ± 0.005[b]
p-OMe	*p*-Cl	45.7 ± (0.1)	41.2 ± (0.1)	1.11 ± 0.004
p-Cl	*p*-OMe	4.65 ± (0.02)	4.18 ± (0.02)	1.11 ± 0.007
p-Cl	*p*-Cl	36.5 ± (0.3)	33.0 ± (0.4)	1.10 ± 0.009

[a] Standard deviation. [b] Standard error.

Table 10 Secondary kinetic isotope effects for the reactions of *exo*-2-norbornyl (Z)-arenesulfonates with deuterated anilines in MeCN at 60.0 °C

X	Z	$k_H/10^{-6}$ M^{-1} s^{-1}	$k_D/10^{-6}$ M^{-1} s^{-1}	k_H/k_D
p-OMe	*p*-OMe	10.0 ± (0.26)[a]	9.09 ± (0.01)	1.10 ± 0.029[b]
p-OMe	*p*-Cl	102 ± (3)	92.7 ± (0.01)	1.10 ± 0.003
p-Cl	*p*-OMe	8.62 ± (0.01)	7.91 ± (0.03)	1.09 ± 0.004
p-Cl	*p*-Cl	90.9 ± (0.1)	81.9 ± (0.1)	1.11 ± 0.002

[a] Standard deviation. [b] Standard error.

leaving group departure in the TS. The magnitudes are comparable to those for the solvolysis of α-*tert*-butylbenzyl arenesulfonates in the same solvent mixtures (ρ_Z = 1.4–1.7 and β_Z = −0.46–−0.53 at 55.0 °C).[10] They are also similar to those for the ethanolysis of 1-adamantyl toluene-*p*-sulfonates (ρ_Z = 1.8 and β_Z = −0.60 at 25.0 °C)[11] taking into account the fact that the numerical values of ρ and β decrease with increasing temperature. Extensive bond cleavage in the TS suggests an S_N1 pathway for the solvolysis of *exo*-2-norbornyl arenesulfonates similar to the two examples of solvolysis described above which are believed to proceed by a limiting S_N1 mechanism.[10,11] In addition, the large Grunwald–Winstein *m* values (Table 1) also support the proposed mechanism. For the solvolysis of α-*tert*-butylbenzyl[10] and 1-adamantyl arenesulfonates,[11] the *m* values

Table 11 Activation parameters ($\Delta H^{\ddagger}$/kcal mol^{-1} and $\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}) for the solvolysis of *exo*-2-norbornyl (Z)-arenesulfonates in MeOH–MeCN mixtures at 60.0 °C

MeOH (v/v %)	Activation parameter	Z			
		p-OMe	*p*-Me	H	*p*-Cl
100	$\Delta H^{\ddagger}$	23.6	24.2	22.9	22.4
	$\Delta S^{\ddagger}$	−5	−3	−5	−5
90	$\Delta H^{\ddagger}$	25.3	23.2	22.6	23.8
	$\Delta S^{\ddagger}$	0	−6	−6	0
80	$\Delta H^{\ddagger}$	24.9	22.1	22.5	23.6
	$\Delta S^{\ddagger}$	−1	−9	−7	−1
70	$\Delta H^{\ddagger}$	25.2	22.7	−23.2	23.7
	$\Delta S^{\ddagger}$	−1	−7	−5	−1
50	$\Delta H^{\ddagger}$	23.6	23.1	22.5	23.0
	$\Delta S^{\ddagger}$	−7	−7	−8	−4

were 0.8–1.3 at 35.0 °C and 1.6 at 25.0 °C in MeOH–MeCN mixtures, respectively. The second-order interaction expansion, eqn. (2a), can be extended to any two rate variables, *e.g.* σ, pK_a, Y (ionizing power), n (nucleophilicity), T (temperature) *etc.*[6c] Expansion using σ_Z and Y in eqn. (2a) instead of σ_X and σ_Z yields eqns. (4a) and (4b).[6c,10,11]

$$\log k_s = \rho_Z\sigma_Z + mY + \Theta\sigma_Z Y + constant \qquad (4a)$$

where

$$\Theta = \frac{\partial^2 \log k}{\partial\sigma_Z\,\partial Y} = \frac{\partial m}{\partial\sigma_Z} = \frac{\partial\rho_Z}{\partial Y} \qquad (4b)$$

Subjecting the k_s data in Table 1 to multiple regression analysis using eqn. (4a) gave $\Theta = -0.58$ ($r = 0.995$). This value is again similar to that for the S_N1 solvolysis of α-*tert*-butylbenzyl arenesulfonates[10] ($\Theta = -0.55$). The negative sign of Θ reflects the fact that a stronger nucleofuge ($\delta\sigma_Z > 0$) leads to a lower susceptibility to the ionizing power of solvent ($\delta m < 0$), or alternatively, a stronger ionizing medium ($\delta Y > 0$) leads to a lower degree of leaving group departure ($\delta\rho_Z < 0$). These are the results of the delocalized structure of the anionic leaving group, arenesulfonates, which are better stabilized in a weakly ionizing medium; this is again indicative of a well developed anionic charge *i.e.* ion-pair character in the TS.

There is a steep initial solvolysis rate increase for the *exo* compound as the salt, KCl, is added as shown in Table 7. This indicates that the ion-pair formed through an S_N1 process is solvent-separated and internal return of the ion-pair to the substrate is prevented by the very poor nucleophile, Cl^-.[9] However, nucleophilic attack by Cl^- can not be entirely precluded.

There is practically no kinetic solvent isotope effect in the solvolysis of the *exo* compound in MeOH, $k_H/k_D \cong 1.0$ (Table 8). This means that in the ionization of the substrate, *i.e.* in the TS, solvent participation is not significant, or the two opposing effects of hydrogen-bonding and steric crowding of the OH (OD) bond nearly cancel out. Similar kinetic solvent isotope effects ($k_H/k_D \cong 1.0$) were observed in the solvolysis of α-*tert*-butylbenzyl arenesulfonates[10] in MeOH.

The activation parameters, $\Delta H^{\ddagger}$ (22–25 kcal mol^{-1}) and $\Delta S^{\ddagger}$ (0–−9 e.u.) in Table 11, are within the ranges of values which are normally obtained in the S_N1 process. For example, for the solvolysis of 1-[11] and 2-adamantyl,[12] and α-*tert*-butylbenzyl arenesulfonates,[10] the $\Delta H^{\ddagger}$; $\Delta S^{\ddagger}$ values were 22–24; +7–−5, 29–30; +4–−2, and 21–23 kcal mol^{-1}; +2–−6 cal deg^{-1} mol^{-1}, respectively.

S_N1 Mechanism

The intercept, k_1 in eqn. (3), corresponds to a first-order component representing concurrent zeroth-order reaction in aniline. As shown above (Results section), k_1 is independent of the amount and nature of the nucleophile so that it constitutes an S_N1 component including k_s when methanol is used as a reaction medium. However for an inert solvent, CH_3CN, k_1 represents a true S_N1 reactivity, k_n.[8] We have collected in Table 12 the k_s and k_1 values together with the corresponding ρ_Z values. The *exo*/*endo* rate ratios in methanol are *ca.* 120–180 for k_s, and 120–140 for k_1. First we note that the k_1 values for both *exo* and *endo* in MeOH are *ca.* 7–8 times greater than those corresponding k_s values. But if we subtract k_s from k_1, the true S_N1 rate constant k_n is obtained, which leads to $k_n/k_s \cong 6$–7. Thus trapping of carbocation is faster by 6–7 times by stronger nucleophiles, anilines, than by methanol solvent. The ρ_Z values derived with k_s are quite similar to those with k_1. When the pure S_N1 component, $k_n = k_1 - k_s$, is used, ρ_Z hardly changes (1.47 ± 0.07 and 0.96 ± 0.04 for *exo* and *endo*, respectively). Since trapping of the ion-pair by either aniline or methanol occurs after the TS, nearly the same ρ_Z values for k_s and k_n are consistent with the rate-limiting ionization for both *exo*- and *endo*-2-norbornyl arenesulfonates. However, there is a significant difference in the ρ_Z values between *exo* (~1.5) and *endo* (~1.0). Thus the S_N1 TS for *endo* is formed somewhat earlier along the reaction coordinate than for *exo*, which is in agreement with the results of the recent *ab initio* studies by Schreiner *et al.*;[1b] the C_2-OH_2 separations in TS_{exo} and TS_{endo} are 3.104 Å and 2.396 Å respectively with H_2O as a leaving group.

The S_N1 rates of *exo* in the inert solvent, MeCN, are much slower than those in the protic solvent, MeOH, $k_{MeOH}/k_{MeCN} \cong 30$–90. The ρ_Z value for the S_N1 component of the *exo* compound in MeCN is much smaller, $\rho_Z = 0.67$, than that in MeOH ($\rho_Z \cong 1.5$). The earlier TS along the reaction coordinate in MeCN may reflect the greater stability of the 2-norbornanium ion in MeCN than in MeOH. For the S_N2 reactions, k_2, which are believed to proceed by a preassociation mechanism (*vide infra*), the leaving group departure is nearly complete (*i.e.* a nucleophile associated with an ion-pair) in the TS.[13] The ρ_Z value is greater in MeCN ($\rho_Z = 2.05$) than in MeOH ($\rho_Z = 1.80$) suggesting that the intermediate, associated nucleophile-ion-pair, is more stable in MeCN than in MeOH. Thus the earlier TS on the reaction coordinate in MeCN is in accord with the Bell–Evans–Polanyi (BEP) principle.[14] Since the slower S_N1 (k_1) reaction in MeCN has a lower ρ_Z (=0.67) than in MeOH ($\rho_Z \cong 1.5$), the reactivity–selectivity principle (RSP) is violated.[15]

Thus, the aprotic solvent, MeCN, seems to cause a shift of the TS structure towards the less ionized form, perpendicular to the reaction coordinate. The magnitude of ρ_Z for the S_N1 TSs in MeOH at 60.0 °C, ($\rho_Z \cong 1.5$ and 1.0 for *exo* and *endo*, respectively) is significantly smaller than that for the S_N2 component of the aminolysis reactions in Tables 4 and 5 ($\rho_Z \cong 1.8$ and 1.2 for *exo* and *endo*). We believe that the S_N2 component of the aminolysis proceeds by a preassociation mechanism[13] so that in the S_N2 TS the development of anionic charge may be nearly complete (*vide infra*). Thus the S_N1 TSs for both *exo* and *endo* occur considerably in advance of formation of the bridged nonclassical structure of the intermediate, **I**. However, the *exo* form is somewhat nearer to the bridged structure (larger ρ_Z) than the *endo* form. These are again in agreement with the theoretical results.[1b] One noteworthy fact is that ρ_Z for the S_N2 component of the *exo* compound in MeCN is quite large ($\rho_Z \cong 2.0$) relative to that for the S_N1 component in MeCN ($\rho_Z \cong 0.7$, Table 12). This may reflect that the ion-pair and hence the anionic leaving group, $OSO_2C_6H_4Z^-$, is more stabilized, and hence the S_N1 TS is formed much earlier on the reaction coordinate in MeCN than in MeOH. If we take the magnitude of ρ_Z as a measure of the ionization, the rates are faster as the extent of ionization becomes greater, which may suggest that the rates become faster as the extent of the development of the bridged structure is greater, since a greater contribution of such nonclassical delocalized structure will stabilize the TS to a greater extent.

Finally, for the S_N1 process, the rate constant, k_1, is independent of the aniline nucleophile so that $\rho_X = 0$. This

Table 12 The solvolysis (k_s) and first order rate constants (k_1) for the reactions of *exo*- and *endo*-2-norbornyl (Z)-arenesulfonates with aniline in MeOH and MeCN at 60.0 °C

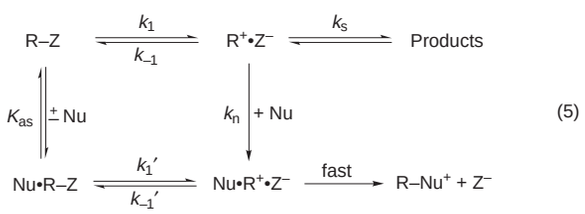
	Z						
	p-OMe	*p*-Me	H	*p*-Cl	*m*-NO_2	*p*-NO_2	ρ_Z[a]
	$k_s/10^{-5}$ s^{-1}						
exo (MeOH)	17.6	26.9	44.8	116			1.61 ± 0.07[a] (0.998)[b]
endo (MeOH)			0.364	0.64	1.95	2.23	1.02 ± 0.01 (0.999)
	$k_1/10^{-5}$ s^{-1}						
exo (MeOH)	130	202	352	740			1.49 ± 0.06 (0.998)
endo (MeOH)			2.89	5.32	14.7	16.7	0.97 ± 0.03 (0.999)
exo (MeCN)	3.74	4.31	5.14	8.22			0.67 ± 0.07 (0.989)

[a]Standard deviation. [b] Correlation coefficient.

means that the cross-interaction constants, ρ_{XZ}, are zero [eqn. (2b)] for the S_N1 as well as solvolysis processes.[6]

S_N2 Mechanism

The results in Tables 2 and 3 clearly show that there are two distinct pathways in the aminolysis of 2-norbornyl arenesulfonates in both MeOH and in MeCN (Table 12). Recently similar separation of the nucleophilic reaction rates into two distinct, S_N1 and S_N2, components has been reported for the Menschutkin reaction of 1-arylethyl bromides with pyridine.[8] In this report they showed that the dependence of the S_N1 rate on the aryl substituent, ρ_Y where Y is the aryl substituent, is much greater than that of the S_N2 rate. This means, as normally expected, that the positive charge development on the benzylic carbon in the TS is much greater in the S_N1 TS, $\rho_Y = -5.0$ (S_N1) *vs.* -2.9–-2.6 (S_N2). This is, however, quite in contrast to our results of $\rho_Z \cong 1.5$ (S_N1) and 1.8 (S_N2) for the *exo* and $\rho_Z \cong 1.0$ (S_N1) and 1.2 (S_N2) for the *endo* compound. This type of abnormal substituent effect in the aminolysis of 2-norbornyl arenesulfonates can only be accounted for by a preassociation mechanism, eqn. (5).[13]



(5)

The upper route is the normal S_N1 pathway, and the lower route is the preassociation pathway. If the leaving group, Z^-, returns (k_{-1}) faster than the intermediate (IP) reacts with solvent (k_s) many ionization events lead to no product, whereas if ionization occurs in the presence of aniline (k_1') product will be formed, and an increase in the rate of substrate disappearance is possible even if there is no nucleophilic assistance to ionization by anilines. The preassociation step, K_{as} and association of the Nu to the ion-pairs, k_n, occur in a diffusion limited or fast process and k_1' is the rate-limiting step. This mechanism exhibits second-order kinetics, and therefore, is an S_N2 process, but structural effects on rates will be very similar to those on S_N1 reactions, since the R^+Z^- pair consists of essentially the two free ions.[13]

In this mechanism, the leaving group, Z^-, is a fully developed anionic species so that ρ_Z should be much greater than the developing anionic charge on the leaving group in the S_N1 TS, k_1. The preassociation mechanism is also supported by the unusually small magnitude of ρ_X (-0.02 and -0.15 for *exo* and *endo* with Z = H, respectively) and β_X (0.07 and 0.05, respectively for *exo* and *endo* with Z = H) reflecting a very small extent of bond formation in the TS. In fact, an insignificant amount of bond making coupled with almost complete leaving group departure in the TS leads to a very loose, open or 'exploded' TS structure for this process.

We have attempted to determine the ρ_{XZ} values for this S_N2 pathway by subjecting 20 k_2 values in Tables 4–6 to multiple regression using eqn. (2a).[6] The magnitudes of the ρ_{XZ} values are indeed insignificantly small but are distinctly nonzero, as expected from the inverse proportionality between the magnitude of ρ_{XZ} and the TS tightness, $\rho_{XZ} = 0.009$ ($r = 0.9999$), 0.005 ($r = 0.9999$) and 0.004 ($r = 0.9999$) for *exo* in MeCN, *exo* in MeOH and *endo* in MeOH, respectively. The magnitudes of ρ_{XZ} obtained in this work for the aminolysis of *exo*- and *endo*-2-norbornyl arenesulfonates are considered to be the limiting minimum values that can possibly be determined in a bimolecular process being less than 0.01.

The definitive, but with magnitude of less than 0.01, ρ_{XZ} values for the aminolysis of 2-norbornyl arenesulfonates are in contrast to the vanishingly small ρ_{XZ} values for the similar reactions of 1-adamantyl[11] and α-*tert*-butylbenzyl arenesulfonates.[10] For these latter two S_N1 reactions, the plots of k_{obs} against the aniline concentrations, [Nu], led to zero or negative slope so that the k_2 components were non-existent for all the aniline nucleophiles. Thus, $k_2 = 0$ and $\rho_X = 0$, so that ρ_{XZ} ($=\partial\rho_X/\partial\sigma_Z$) is zero.[6,10,11]

The *exo* rates using bulky DMA instead of aniline are practically the same as those with the corresponding anilines (Table 6). This is also consistent with the preassociation mechanism proposed, since the TS is very loose and a steric effect cannot be expected.

Very small normal secondary kinetic isotope effects ($k_H/k_D \cong 1.1$) involving deuterated aniline nucleophiles in Tables 9 and 10 are also in accord with the open TS structure with aniline associated with the ion-pair. In this type of structure there will be scarcely any steric crowding effect, but very weak H···O bonding leading to the very small k_H/k_D (>1.0) value. The ratio of the norbornanium cation, **I**, trapped by the aniline and by methanol, k_n/k_s, is quite similar for *exo* (6.8 with Z = H) and *endo* (6.6 with Z = *p*-NO_2). However, the ratio of k_2/k_s (using a first-order rate constant for the reaction of solvent, MeOH) is also similar or slightly greater for *exo* (3.5 with Z = H) than for *endo* (2.3 with Z = *p*-NO_2). These results suggest that the concurrent S_N1 and S_N2 mechanisms operating in

the nucleophilic substitution reactions of *exo*- and *endo*-2-norbornyl arenesulfonates are quite similar, *i.e.* there is no mechanistic difference between the *exo* and *endo* systems, and the difference between the two is only in the progress of reaction along the reaction coordinate; the TS_{exo} is invariably later on the reaction coordinate than the TS_{endo}. According to recent theoretical studies, the TS_{endo} becomes more stabilized as the C_6H_{endo}–oxygen (of the leaving group) bond length becomes shorter due to the increased hydrogen-bonding type interaction of the oxygen atom in the TS *vs.* the ground state.[1b] This could be the reason why the TS_{endo} is earlier on the reaction coordinate (with smaller ρ_Z values indicating bond cleavage has progressed to a lesser extent) than the TS_{exo}.

A similar reasoning may be applicable to the increased k_{exo}/k_{endo} ratio for the stronger nucleophile and nucleofuge; the ratio increases from *ca.* 270 to 400 when substituents X = *p*-Br and Z = H are changed to X = *p*-OMe and Z = *p*-Cl. A greater degree of leaving group departure for a stronger nucleofuge should reduce the stability of the TS_{endo} acquired by the CH_{endo}–oxygen hydrogen-bonding interaction due to the increased distance, and leads to a smaller k_{endo} relative to the increased k_{exo}.

Conclusions

The three distinct competing processes, solvolysis k_s, unimolecular k_n, and bimolecular k_2 can be separated, and the ratio of k_n/k_s is *ca.* 6–7. In all the three processes, the leaving group departure in the TS, measured by the magnitude of ρ_Z, is greater for the *exo* than the *endo* system. For the bimolecular process, the ρ_{XZ} value is the smallest ever obtained ($\rho_{XZ} \leqslant 0.01$) but is distinctly nonzero in contrast to those for the k_n and k_s pathways for which $\rho_{XZ} = 0$. All the experimental evidence can be accommodated with a preassociation mechanism for the S_N2 process in which the transition state has an open, 'exploded' structure.

Experimental

Materials

The norborneol, pyridine and arenesulfonyl chlorides that were used in the preparation of substrates were Aldrich GR grade. Tokyo Kasei GR grade anilines were used after redistillation or recrystallization. Merck GR grade acetonitrile was used after three distillations and Merck GR grade methanol was used as purchased.

Preparation of substrates[16]

Norborneol (5 mmol), pyridine (7.5 mmol) and arenesulfonyl chloride (6 mmol) were added to a three-neck flask at 0 °C. After 48 h at 5 °C, the reaction was hydrolyzed with excess dilute aqueous HCl. The reaction mixture was kept at 0–5 °C for 1 or 2 h, neutralized with NaOH and water and then the solvents were removed by drying over dry $MgSO_4$ followed by distillation under reduced pressure. The 2-norbornyl arenesulfonates thus obtained were identified by IR, ^1H and ^{13}C NMR (JEOL 400 MHz) spectroscopy as follows. *J* Values are given in Hz.

***exo*-Norbornyl benzenesulfonate.** Liquid, ν_{max}(KBr)/cm^{-1} 2955–2872 (CH), 1560, 1448, (aromatic C=C), 1357, 1882 (S=O), 756–680 (=CH); δ_H 7.90 (2H, d, *o*-H, *J* 8.06), 7.65 (1H, t, *p*-H, *J* 7.33), 7.55 (2H, t, *m*-H, *J* 8.06), 4.46 (1H, d, CHO, *J* 6.59), 2.35–0.98 (10H, m, cyclic ring); δ_C 137.51, 133.58, 129.23, 127.59, 85.80, 42.12, 39.60, 35.34, 34.98, 27.84, 23.88.

***exo*-Norbornyl tosylate.** Liquid, ν_{max}/cm^{-1} 2961–2878 (CH), 1603, 1449 (aromatic C=C), 1357, 1177 (S=O), 816 (=CH); δ_H 7.70 (2H, d, *m*-H, *J* 8.06), 7.26 (2H, d, *o*-H, *J* 8.06), 4.36 (1H, s, CHO), 2.36 (3H, s, CH_3), 2.26–0.96 (10H, m, cyclic ring); δ_C 144.49, 134.53, 129.80, 127.59, 85.41, 42.04, 39.58, 35.31, 34.95, 27.84, 23.85, 21.58.

***exo*-Norbornyl *p*-methoxybenzenesulfonate.** Liquid, ν_{max}(KBr)/cm^{-1} 2960–2878 (CH), 1597, 1498 (aromatic C=C), 1354, 1262 (S=O), 870 (=CH); δ_H 7.77 (2H, d, *m*-H, *J* 8.80), 6.95 (2H, d, *o*-H, *J* 8.80), 4.35 (1H, d, CHO, *J* 6.59), 3.83 (3H, s, OMe) 2.28–0.93 (10H, m, cyclic ring); δ_C 163.52, 129.80, 128.93, 114.38, 85.25, 55.68, 42.04, 39.60, 35.31, 34.98, 27.87, 23.90.

***exo*-Norbornyl *p*-chlorobenzenesulfonate.** Mp 58–59 °C; ν_{max}(KBr)/cm^{-1} 2963–2878 (CH), 1580, 1490 (aromatic C=C), 1364, 1242 (S=O), 1185 (C-Cl), 872 (=CH); δ_H 7.84 (2H, d, *m*-H, *J* 8.06), 7.52 (2H, d, *o*-H, *J* 8.80), 4.47 (1H, d, CHO, *J* 5.13), 2.36–0.97 (10H, m, cyclic ring); δ_C 140.09, 136.17, 129.50, 129.06, 86.12, 46.12, 39.63, 35.34, 34.98, 27.82, 23.88.

***endo*-Norbornyl benzenesulfonate.** Liquid, ν_{max}/cm^{-1} 2954–2871 (CH), 1620, 1400 (aromatic C=C), 1210, 1180 (S=O), 650 (=CH); δ_H 7.87 (2H, d, *o*-H, *J* 7.33), 7.60 (2H, d, *m*-H, *J* 7.33), 7.51 (1H, t, *p*-H, *J* 7.70), 4.77 (1H, t, CHO, *J* 5.13), 2.30–1.07 (10H, m, cyclic ring); δ_C 137.11, 133.40, 129.00, 127.66, 83.27, 42.46, 39.49, 37.62, 36.16, 29.85, 20.67.

***endo*-Norbornyl *p*-chlorobenzenesulfonate.** Liquid, ν_{max}/cm^{-1} 2965–2870 (CH), 1595, 1490 (aromatic C=C), 1363, 1230 (S=O), 1181 (=C–Cl), 850 (=CH); δ_H 7.84 (2H, d, *m*-H, *J* 8.43), 7.52 (2H, d, *o*-H, *J* 8.43), 4.81 (1H, t, CHO, *J* 5.13), 2.36–1.10 (10H, m, cyclic ring); δ_C 139.99, 135.59, 129.32, 129.00, 83.62, 42.52, 41.05, 37.59, 36.99, 29.83, 20.64.

***endo*-Norbornyl *p*-nitrobenzenesulfonate.** Mp 68–69 °C; ν_{max}/cm^{-1}, 2950–2869 (CH), 1610, 1470 (aromatic C=C), 1185, 1080 (S=O), 1532, 1351 (N=O), 849 (=CH); δ_H 8.40 (2H, d, *m*-H, *J* 8.79), 8.11 (2H, d, *o*-H, *J* 8.30), 4.89 (1H, t, CHO, *J* 5.13), 2.39–0.81 (10H, m, cyclic ring); δ_C 142.78, 128.92, 128.84, 124.19, 84.62, 42.46, 39.49, 37.55, 37.13, 29.78, 19.86.

***endo*-Norbornyl *m*-nitrobenzenesulfonate.** Mp 57–58 °C; ν_{max}/cm^{-1}, 2950–2870 (CH), 1610, 1470 (aromatic C=C), 1110, 1030 (S=O), 1535, 1357 (N=O), 850 (=CH); δ_H 8.76 (1H, s, *o*-H) 8.50 (1H, d, *o*-H, *J* 7.81), 8.24 (1H, d, *p*-H, *J* 7.81), 2.25–0.81 (10H, m, cyclic ring); δ_C 139.22, 133.01, 130.79, 130.49, 130.40, 122.85, 122.79, 84.59, 42.26, 39.49, 37.54, 37.13, 29.77, 19.86.

Kinetic procedures

Rates were measured conductimetrically as described previously.[7d,10,17] The k_{obs} values used in the determination of k_1 and k_2 were the averages of more than two runs and the k_1 and k_2 values obtained were reproducible to within ±3%. Kinetic isotope effects were determined as described previously.[7b,18]

Product analysis

Norbornyl arenesulfonates and anilines were reacted for over 15 half-lives under the same reaction conditions as for the kinetic measurements. The salt was removed by filtration and anilides and ethers obtained by removing the solvent under reduced pressure from the filtrate and were purified by column chromatography. The analytical data are as follows.

***exo*-$C_7H_{11}NHC_6H_5$.** Liquid, δ_H 7.16 (2H, t, *m*-H, *J* 8.06), 6.67 (1H, t, *p*-H, *J* 7.33), 6.56 (2H, d, *o*-H, *J* 8.79), 3.54 (1H, br s, NH), 2.28–1.16 (10H, m, cyclic ring); δ_C 147.63, 129.17, 116.87, 113.12, 56.59, 41.19, 41.13, 35.64, 35.34, 28.47, 26.39.

***exo*-Norbornyl methyl ether.** Liquid, δ_H 3.82 (1H, d, CHO, *J* 6.59), 3.67 (3H, s, OMe), 2.21–0.88 (10H, m, cyclic ring).

***endo*-$C_7H_{11}NHC_6H_5$.** Liquid, δ_H 7.16 (2H, t, *m*-H, *J* 7.81), 6.67 (1H, t, *p*-H, *J* 7.32), 6.56 (2H, d, *o*-H, *J* 7.81), 3.23 (1H, br s, NH), 2.28–1.16 (10H, m, cyclic ring); δ_C 128.96, 116.72, 112.95, 102.83, 63.69, 56.52, 41.02, 35.49, 29.65, 28.35.

***endo*-Norbornyl methyl ether.** Liquid, δ_H 5.02 (1H, d, CHO, *J* 5.37), 3.26 (3H, s, OMe), 2.25–1.23 (10H, m, cyclic ring).

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