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Neighboring Methoxy Group Effect in Solvolysis Reactions of Cyclopentyl and Cyclohexyl *p*-Toluenesulfonates

Donald D. Roberts

Department of Chemistry, Louisiana Tech University,
Ruston, Louisiana 71272

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In an earlier paper from this laboratory,[1] we investigated the neighboring-group effect of a methoxy substituent upon the rates of solvolysis of *trans*-2-methoxycyclopentyl *p*-toluenesulfonate (**1**) and *trans*-2-methoxycyclohexyl *p*-toluenesulfonate (**2**). Although we found that the presence of a *trans-2*-methoxy group retarded the rate of solvolysis of both the cyclopentyl and cyclohexyl systems, it was observed that this rate retardation was insensitive to change from acetic acid (a solvent known to promote k_s solvolysis for cyclohexyl tosylate[2a−e]) to trifluoroacetic acid (a solvent known to promote $k\Delta$ solvolysis for secondary tosylates[2a−d]). On the basis of this solvolytic behavior, it was suggested, but not clearly demonstrated, that participation by the neighboring methoxy group may be involved in the solvolysis of both **1** and **2**.

Recently, in our continuing study of neighboring-group effects upon solvolyses, we became interested in a more detailed study of the methoxy group. Accordingly, we have investigated the solvolytic behavior of tosylates **1** and **2** using three probes—the effect of varying solvent ionizing power upon rate, the effect of added azide ion upon rate, and the identity of the solvolysis products in 97% aqueous TFE—to determine the absence or presence of neighboring-group assistance by a *trans*-2-methoxy group.

The first-order rate constants for solvolysis of **1** and **2** are summarized in Table 1. Reaction progress was followed by titrating the liberated *p*-toluenesulfonic acid, and strictly first-order kinetics were observed up to at least 75% conversion furnishing, within experimental error, 100% of the theoretical amount of acid present. In Table 2 we have listed the results obtained from correlations of the rate data, given in Table 1 and elsewhere, with Y_{OTs} values[3] and with Y_{OTs} and N_{OTs} values.[2b] The data showing effect of added azide ion upon rates of solvolysis of tosylate **1**, tosylate **2**, cyclopentyl tosylate (**3**), and cyclohexyl tosylate (**4**) are given in Tables 3 and 4. Product composition data for the solvolysis of **1** and **2** in 97% aqueous trifluoroethanol are given in Table 5.

Discussion

The effect of solvent on the rate of reaction of a substrate has proven to be a very useful criterion for assignment of reaction mechanism.[5−13] Therefore, we have analyzed the kinetic data of Table 1 in terms of both the two-parameter and four-parameter Grunwald−Winstein-type equations (1) and (2), where, for equation 1, k

$$\log k = mY_{\mathrm{OTs}} + \log k_0 \tag{1}$$

refers to the solvolytic rate constant in any solvent, k_0 refers to the rate constant in 80% v/v ethanol/water, and Y_{OTs} is a scale of ionizing power for tosylates.[3] For eq 2, N_{OTs} is a

$$\log k = lN_{\mathrm{OTs}} + mY_{\mathrm{OTs}} + \log k_0 \tag{2}$$

scale for solvent nucleophilicity.[2b] For comparison purposes we have carried out similar analyses for tosylates **3** and **4**, substrates known[1b,c,14] to solvolyze with significant nucleophilic-solvent assistance. The results are summarized in Table 2.

Striking differences are obvious between the results of these two analyses. While the reaction rates of both cyclopentyl and cyclohexyl tosylate are dispersed into separate correlation lines for the aqueous ethanol and carboxylic acid solvent series,[15] the reaction rates of both *trans*-2-methoxycyclopentyl and *trans*-2-methoxycyclohexyl tosylate correlate well ($r = 0.99$) against Y_{OTs} over a range of solvents varying in ionizing power from −1.75 (ethanol) to 4.57 (trifluoroacetic acid). Another noteworthy feature of Table 2 is the small response of both **1** and **2** to varying solvent nucleophilicity. As can be seen, the parent compounds, **3** and **4**, have much higher l values (0.3 and 0.3) than those for **1** and **2** (0.05 and 0.1, respectively). The relatively low m values for **1** and **2** are in the range for compounds known to solvolyze with predominantly neighboring group participation.[16a−i] These results clearly demonstrate that nucleophilic solvent assistance is not significant in the solvolysis of **1** and only slightly significant in the solvolysis of **2**.

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Table 1. Summary of Kinetic Data

solvent	T, °C	k,[a] s^{-1}	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, eu	solvent	T, °C	k,[a] s^{-1}	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, eu
		trans-2-metho×ycyclopentyl tosylate					cyclopentyl tosylate		
EtOH	45.0	1.2×10^{-7} [b]			97TFE[c]	25.0	$(3.2 \pm 0.06 \times 10^{-5}$	19.7	−13
	50.0	$(2.0 \pm 0.05) \times 10^{-7}$	25	−13		30.0	$(5.9 \pm 0.05) \times 10^{-5}$		
	60.0	$(6.0 \pm 0.05) \times 10^{-7}$				35.0	$(9.4 \pm 0.06) \times 10^{-5}$		
	70.0	$(2.0 \pm 0.05) \times 10^{-6}$				40.0	$(1.7 \pm 0.06) \times 10^{-4}$		
90E/W[d]	45.0	$(3.5 \pm 0.04) \times 10^{-7}$				45.0	2.6×10^{4} [b]		
80E/W[d]	40.0	$(8.0 \pm 0.01) \times 10^{-7}$	22.9	−13			trans-2-metho×ycyclohe×yl tosylate		
	45.0	1.4×10^{-6} [b]			EtOH	45.0	3.2 ± 10^{-8} [b]	26	−12
	50.0	$(2.4 \pm 0.01) \times 10^{-6}$				50.0	$(6.0 \pm 0.08) \times 10^{-8}$		
	60.0	$(7.8 \pm 0.02) \times 10^{-6}$				60.0	$(2.2 \pm 0.08) \times 10^{7}$		
	45.0	$(2.8 \pm 0.1) \times 10^{-7}$				70.0	$(6.5 \pm 0.07) \times 10^{-7}$		
60E/W[d]	45.0	$(2.7 \pm 0.06) \times 10^{-6}$			90E/W[d]	45.0	$(1.8 \pm 0.03) \times 10^{-7}$		
97TFE[c]	30.0	$(7.0 \pm 0.06) \times 10^{-7}$	26.6	1	80E/W[d]	40.0	$(1.5 \pm 0.08) \times 10^{-7}$	24	−13
	40.0	$(2.0 \pm 0.05) \times 10^{-6}$				50.0	$(5.7 \pm 0.1) \times 10^{-7}$		
	45.0	4.5×10^{-6} [b]				60.0	$(1.6 \pm 0.07) \times 10^{-6}$		
	50.0	$(1.10 \pm 0.02) \times 10^{-5}$			60E/W[d]	45.0	$(2.4 \pm 0.08) \times 10^{-6}$		
	60.0	$(3.7 \pm 0.1) \times 10^{-5}$			97TFE[c]	30.0	$(3.35 \pm 0.04) \times 10^{-7}$	27	1
AcOH[e]	45.0	$(8.6 \pm 0.06) \times 10^{-8}$				40.0	$(1.2 \pm 0.1) \times 10^{-6}$		
75A/F[f]	45.0	$(1.7 \pm 0.04) \times 10^{-6}$				45.0	2.7×10^{-6} [b]		
50A/F[f]	45.0	$(5.60 \pm 0.05) \times 10^{-6}$				60.0	$(2.0 \pm (0.06) \times 10^{-5}$		
	50.0	$(5.4 \pm 0.07) \times 10^{-6}$			AcOH[g]	45.0	$(3.0 \pm 0.05) \times 10^{-8}$		
					75A/F[f]	45.0	$(7.1 \pm 0.07) \times 10^{-7}$		
					50A/F[f]	45.0	$(2.5 \pm 0.05) \times 10{-}f$		

[a] Errors reported as 1 standard deviation from the mean. [b] Either extrapolated or interpolated from collected data. [c] Percent by weight. 97TFE means 97 g of trifluoroethanol plus 3 g of water. [d] Percent by volume. For example, 90E/W means 90 volumes of ethanol plus 10 volumes of water, both at 25 °C before mixing. [e] Compares with literature[1a] value of 8.6×10^{-8}. [f] Percent by volume. For example, 75A/F means 75 volumes of acetic acid plus 25 volumes of formic acid, both at the same temperature before mixing. [g] Compares with literature[1a] value of 2.6×10^{-8}.

Table 2. Summary of Parameters Derived from Correlation Equations

		equations						
		mY_{OTs} (1)			$lN_{OTs} + mY_{OTs}$ (2)			
tosylates	solvents	m	r[a]	std err[b]	l	m	r[a]	std err[b]
1[c]	set A[d−f]	0.42	0.99	0.05	0.04	0.5	0.98	0.1
2[g]	set A[d,e]	0.49	0.99	0.06	0.1	0.6	0.99	0.1
cyclopentyl	set B[h,i]	0.5	0.87	0.5	0.3	0.7	0.96	0.3
cyclohexyl	set B[h,i]	0.6	0.91	0.5	0.3	0.8	0.97	0.3

[a] Correlation coefficient. [b] Standard error of log $k(\pm)$. [c] *trans*-2-Methoxycyclopentyl *p*-toluenesulfonate. [d] EtOH, 90E/W, 80E/W, 60E/W, 97TFE, 75A/F, 50A/F, HCOOH, TFA. [e] Rate constants for HCOOH and TFA taken from Table 1 of ref 1a. [f] Excluded AcOH; the observed value for AcOH lies 0.75 log units below the correlation line. This result can be accounted for by enhanced ion-pair return in acetic acid. [g] *trans*-2-Methoxycyclohexyl *p*-toluenesulfonate. [h] EtOH, 80E/W, 50E/W, 97TFE, AcOH, HCOOH, TFA. [i] Rate constants for HCOOH and TFA taken from Table 1 of refs 18 and 1a, respectively.

Table 3. Effect of Added Sodium Azide upon Solvolysis Rates of 1−3 in 80% Aqueous EtOH at 45 °C

compd	M	k_{obsd}[a] (s^{-1})	(k_t/k^0)[b]
1[c]	0.00	1.4×10^{-6} [d]	
	0.02	$(1.5 \pm 0.04) \times 10^{-6}$	1.07
	0.04	$(1.5 \pm 0.03) \times 10^{-6}$	1.07
	0.06	$(1.5 \pm 0.02) \times 10^{-6}$	1.07
2[e]	0.00	$(2.8 \pm 0.1) \times 10^{-7}$	
	0.005	$(3.2 \pm 0.2) \times 10^{-7}$	1.14
	0.02	$(5.0 \pm 0.3) \times 10^{-7}$	1.8
	0.04	$(5.5 \pm 0.06) \times 10^{-7}$	1.9
	0.06	$(5.6 \pm 0.0.2) \times 10^{-7}$	2.0
3[f,g]	0.0	4.9×10^{-5} [d]	
	0.02	$(5.7 \pm 0.1) \times 10^{-5}$	1.2
	0.04	$(8.8 \pm 0.2) \times 10^{-5}$	2.0
	0.06	$(1.20 \pm 0.03) \times 10^{-4}$	2.5

[a] Errors reported as 1 standard deviation from the mean. [b] Ratio of observed rate constant at some concentration of salt to observed rate constant at zero salt concentration. [c] *trans*-2-Methoxycyclopentyl p-toluenesulfonate. [d] Taken from Table 1 of ref 20. [e] *trans*-2-Methoxycyclohexyl *p*-toluenesulfonate. [f] Cyclopentyl p-toluenesulfonate. [g] At 30 °C.

The effect of added azide ion on the rates of reaction—the azide probe[16]—has also proven to be a very useful criterion for assessing the magnitude of nucleophilic solvent assistance. Accordingly, we have analyzed the kinetic data of Table 3 in terms of rate enhancement (k_t/k^0)[1b,17c] and diversion of product to alkyl azide (% infinity titer)[1b,17c,f] due to added azide. The results given in Table 4 are complicated. The enhancement rates for **1** are slight: no greater than those for 2-adamantyl tosylate, a system known[19] to solvolyze via a k_c pathway, and some 2.3-fold lower (at 0.06 M NaN_3) than those for cyclopentyl tosylate, a system known[1d,20] to solvolyze with nucleophilic solvent assistance. On the other hand, major amounts of alkyl azide formation are shown for **1**. The enhancement rates for **2** are appreciable, about the same as those for cyclohexyl tosylate, a system known[1b,15,20] to solvolyze with nucleophilic solvent assistance, but some 1.6-fold lower (at 0.06 M NaN_3) than those for isopropyl tosylate, a system known[1b−d,17d] to solvolyze via a k_s pathway. Major amounts of alkyl azide formation are also shown for **2**. A possible explanation for these results is that the 2-methoxy substituent participates as a neighboring group in the solvolysis transition state involving preassociation with the salt.[21−23] Under these conditions, attack by azide anion should be favored over

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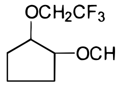
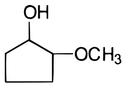
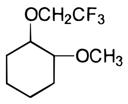
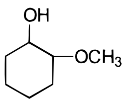
Table 4. Summary of Parameters Derived from Salt Effect Data

compd	T, °C	concn, M	(k_t/k^0)[a]	% infinity titer[b]
2-Ac-OTs[c]	75	0.00		100
		0.02	1.08	99.9
		0.04	1.12	99.6
		0.06	1.16	99.3
Me_2CH-OTs[d]	54.6	0.00		96
		0.02	1.35	68
		0.04	2.17	46
		0.06	2.88	36
c-Hexyl-OTs[e]	60	0.00		100
		0.02	1.49	99
		0.04	1.60	89
		0.06	1.73	85
c-Pentyl-OT[s]	30	0.00		100
		0.02	1.16	95
		0.04	1.80	48
		0.06	2.50	45
1[g]	45	0.00		100
		0.02	1.07	60
		0.04	1.07	62
		0.06	1.08	45
2[h]	45	0.00		100
		0.005	1.03	100
		0.02	1.61	66
		0.04	1.77	58
		0.06	1.80	45

[a] Ratio of observed rate constant at some concentration of NaN_3 to observed rate constant at zero NaN_3 concentration. [b] Calculated by dividing the observed by the theoretical yield of acid. [c] 2-Adamantyl tosylate, data taken from ref 17d. [d] Data taken from ref 17d; see also ref 17f. [e] Cyclohexyl tosylate, data taken from ref 1b. [f] Cyclopentyl tosylate, data taken from Table 3. [g] *trans*-2-Methoxycyclopentyl tosylate, data taken from Table 3. [h] *trans*-2-Methoxycyclohexyl tosylate, data taken from Table 3.

Table 5. Summary of Product Runs (% Yield) for *trans*-2-Methoxycyclopentyl and *trans*-2-Methoxycyclohexyl Tosylates in 97% Aqueous TFE

			
tosylate **1** products		tosylate **2** products	
60	40	none detected[a]	>98[b]

[a] At least no more than 2% of product. [b] At least 98% of product.

that by solvent. This explanation is consistent with the analysis of the solvent parameters for **1** and **2**.

The products found for the solvolysis of **1** and **2** in 97% aqueous trifluoroethanol are listed in Table 5 and are interesting. For example, *trans*-2-methoxycyclopentyl tosylate yielded a 3:2 mixture of 1-(2,2,2-trifluoroethoxy)-2-methoxycyclopentane and 2-methoxycyclopentanol, while *trans*-2-methoxycyclohexyl tosylate yielded the alcohol 2-methoxycyclohexanol but no detectable ether product. On the basis of the low nucleophilicity of 2,2,2-trifluoroethanol, relative to that of water,[24] the product results suggest that nucleophilic solvent assistance in the solvolysis of **1** must be relatively weak. On the other hand, the product results suggest that nucleophilic solvent assistance in the solvolysis of **2** is stronger. This interpretation is consistent with the relative magnitudes of both the l values (listed in Table 2) and the (k_t/k^0) values (listed in Table 4) for **1** and **2.**

In conclusion, we propose that *trans*-2-methoxycyclopentyl tosylate solvolyses mainly via an unstable, bridged ion pair that is stabilized by weak nucleophilic solvation and relatively strong electrophilic solvation. We further propose that *trans*-2-methoxycyclohexyl tosylate also solvolyzes via an unstable, bridged ion pair that is stabilized by relatively strong electrophilic solvation and weak nucleophilic solvation. The nucleophilic solvation for **2**, however, is more significant than it is for **1**.

Experimental Section

***trans*-2-Methoxycyclopentanol** was prepared as before[1a] in 63% yield: bp 96 °C at (27 mm); ^1H NMR ($CDCl_3$) δ 1.5−1.61 (m, 2H), 1.64−1.75 (m, 2H), 1.86−2.0 (m, 2H), 3.33 (s, 3H), 3.53−3.6 (m, 1H), 4.0−4.07 (m, 1H), 4.08−4.1 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.9, 32.35, 56.97, 76.72, 88.75.

***trans*-2-Methoxycyclopentyl tosylate (1)** was prepared as before[1a] in 61% yield. Purification by column chromatography gave a lightly colored oil: ^1H NMR ($CDCl_3$) δ 1.5−1.75 (m, 4H), 1.8−1.98 (m, 2H), 2.43 (s, 3H), 3.15 (s, 3H), 3.67−3.76 (m, 1H), 4.71−4.8 (m, 1H), 7.33 (d, 2H), 7.79 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 21.8, 29.78, 30.69, 57.19, 86.1, 86.39, 128.1, 130.2, 134.4, 145.1.

***trans*-2-Methoxycyclohexanol** was prepared as before[1a] in 80% yield: bp 73 °C (10 mm); ^1H NMR ($CDCl_3$) δ 1.2−1.33 (m, 4H), 1.65−1.78 (m, 2H), 1.94−2.04 (m, 1H), 2.06−2.17 (m, 1H), 2.89−3.0 (m, 1H), 3.17 (s, 1H), 3.34 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 23.72, 23.8, 28.22, 32.0, 56.1, 73.51, 84.95.

***trans*-2-Methoxycyclohexyl tosylate (2)** was prepared as before[1a] in 50% yield. Purification by column chromatography gave a semisolid: ^1H NMR ($CDCl_3$) δ 1.12−1.3 (m, 3H), 1.48−1.69 (m, 3H), 1.87−2.05 (m, 2H), 2.4 (s, 3H), 3.04−3.13 (m, 1H), 3.12 (s, 3H), 4.29−4.4 (m, 1H), 7.28 (d, 2H, 7.78 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 21.7, 22.2, 22.8, 28.5, 30.8, 57.5, 80.0, 84.3, 128.0, 130.0, 134.8, 144.8.

Cyclopentyl tosylate (3) was prepared as before[1a] in 60% yield: mp 29.0−29.2 °C; ^1H NMR ($CDCl_3$) δ 1.49−1.6 (m, 2H), 1.66−1.84 (m, 6H), 2.45 (s, 3H), 4.9−5.0 (m, 1H), 7.34 (d, 2H), 7.78 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 21.9, 23.2, 33.3, 85.8, 127.9, 130.1, 135.0, 144.8.

Solvents. Acetic acid solvent was prepared from 994.9 mL of glacial acetic acid and 5.1 mL of acetic anhydride. Formic acid solvent was prepared by storing practical-grade formic acid over boric anhydride for several days, decanting, and distilling from fresh anhydride. Ethanol solvent was prepared according to the method of Fieser.[25] 2,2,2-Trifluoroethanol (Aldrich Chemical Co.) was redistilled prior to use. The water solvent was purified by passage through ion-exchange cartridges.

Rate Measurements. The rates of solvolysis were followed titrimetrically. Reaction solutions were 0.01 M. Rate measurements were made by either the aliquot or ampule technique. Both the titrating solutions and indicators used were prepared as previously described.[1b]

Treatment of Kinetic Data. First-order rate constants were calculated by using the integrated first-order equation $k_t = 1/t \ln [mL_4/(mL_4 - mL_t)]$. Multiple determinations (8−12) were made for each kinetic run. The activation parameters listed in Table 1 were obtained by regression analysis of ln (k_t/T) versus $1/T$. The m and l values recorded in Table 2 were also obtained by regression analysis.

Product Studies. The products of solvolysis were determined by examination of 270 MHz spectra of the oil isolated from the buffered reaction mixture in 97% aqueous trifluoroethanol after 10 half-lives at 45 °C. For the solvolysis products of **1**, the percentages were based on the 2:3 ratio of the integrated peak areas for the δ 3.33 methoxy signal (assigned to the alcohol product on the basis of the 1:3 ratio of the integrated peak areas for the δ 4.1 hydroxy peak and the δ 3.30 methoxy peak) and the δ 3.35 methoxy signal (assigned to the ether product on the basis of the 2:3 ratio of the integrated peak areas for the δ 3.84 CF_3CH_2- peak and the δ 3.35 methoxy peak). Identification of the solvolysis product of **2** was accomplished by comparing the ^1H NMR spectrum of the isolated product with that of *trans*-2-methoxycyclohexanol.

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