The Effects of Sodium Azide on the Solvolysis of Secondary and Primary β-Arylpropyl Derivatives. Azide Ion as a Probe for k_s Processes[1]

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Abstract: The effects of sodium azide on the solvolysis of a series of 1-aryl-2-propyl and 2-aryl-1-propyl tosylates have been investigated. These compounds solvolyze with varying blends of anchimeric (k_Δ) and nucleophilic solvent assistance (k_s), and the effects of added sodium azide on rates and products vary in a manner which reflects the relative proportion of the K_s pathway. The higher the proportion of nucleophilic solvent assistance, the greater are both rate enhancement due to added azide and the percentage of azide product. The solvolyses of the β-aryl derivatives have been dissected into their component pathways (k_s and k_Δ) both in the presence and absence of azide ion. A plot of the k_s rate constants *vs.* the azide ion–water competition ratios shows marked deviation from typical carbonium ion behavior. Added azide ion can be used as a mechanistic probe for both nucleophilically assisted and unassisted processes.

Considerable evidence has accumulated which indicates that simple unhindered secondary alkyl derivatives solvolyze with appreciable nucleophilic solvent assistance.[1,3–5] The preceding paper[6] has emphasized that the presence of sodium azide produces large effects on rates and products during the solvolysis of 2-propyl and 2-octyl arenesulfonates. Such large effects are not consistent with carbonium ion reactions, but rather with a bimolecular transition state (rate-limiting attack by azide on covalent substrate[6] or ion pair[7]).

The more stable a carbonium ion, the higher is its selectivity toward different nucleophiles.[6,8] Thus high azide incorporation in the product is indicative of a relatively stable carbonium ion, provided such species are actually involved in the reaction. The high azide incorporations observed during the solvolysis of simple secondary derivatives must have a different origin; ordinary secondary carbonium ions are quite unstable. We wished to investigate the relationship between nucleophilic attack by azide (which must be responsible for the high azide incorporation with simple secondary substrates) and nucleophilic solvent participation by studying a series of compounds for which the contribution of the k_s (nucleophilic solvent assisted) process varies in a known manner.

Such a series of compounds was available from previous work in these laboratories.[4] The acetolysis and formolysis of ring-substituted 1-aryl-2-propyl tosylates (I) was shown to proceed *via* two discrete pathways: nucleophilically solvent assisted (k_s) and anchimerically assisted (k_Δ). The total solvolysis rate constant was dissected into the individual rate constants k_s and Fk_Δ by a Hammett–Taft treatment.[4] In this series of compounds the mechanism was shown to vary from almost entirely k_Δ (I, p-OCH$_3$) to virtually completely k_s (I, p-NO$_2$). In order to learn if added azide could be used as a mechanistic probe for k_s processes, we have studied the solvolysis of the β-arylpropyl tosylates I and II in 80% ethanol in the presence and absence of sodium azide.

Results and Discussion

Eight 1-aryl-2-propyl tosylates (I) were solvolyzed in 80% ethanol; the kinetic results are summarized in Table I. These data were analyzed by the method of Lancelot and Schleyer[4a] (Figure 1), and the relative magnitudes of k_s and k_Δ are indicated by the last column (% k_s) in Table I.[9]

Figure 1 and Table I show that in 80% ethanol the mechanism of solvolysis for the series of 1-aryl-2-propyl tosylates (I) varies from essentially 100% k_s (I, p-NO$_2$) to almost entirely k_Δ (I, p-OCH$_3$). In order to learn if the effects of sodium azide varied in a similar manner, several of these derivatives (I, p-OCH$_3$; I, p-CH$_3$; I, p-H; and I, p-NO$_2$) were solvolyzed in the presence of sodium azide. The rates and products for these solvolyses in the presence of sodium azide are presented in Table II.

A clear trend is observed for the effects of sodium azide on both the rates and the products. As shown in

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(2) National Institutes of Health Postdoctoral Fellows: (a) 1968–1970; (b) 1969–1970.

(3) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); (d) S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *ibid.*, **92**, 3789 (1970); (e) J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 5729 (1970); (f) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971).

(4) (a) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291, 4296 (1969); (b) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); (c) P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 4297 (1969); (d) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); (e) also see J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **92**, 7508 (1969).

(5) See also A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4521 (1969), and previous papers in this series.

(6) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 4821 (1971); preliminary communication, ref 3e.

(7) (a) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362 (1969); (b) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287, 292 (1965); (c) R. A. Sneen and J. W. Larsen, *ibid.*, **88**, 2593 (1966); (d) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 6031 (1969).

(8) R. A. Sneen, J. V. Carter, and P. S. Kay, *ibid.*, **88**, 2594 (1966).

(9) It will be shown later that $F \cong 1$ for the solvolysis of these compounds in 80% ethanol. Consequently $Fk_\Delta = k_\Delta$. See ref 4.

Table I. Conductometric Rate Constants for a Series of 1-Aryl-2-propyl Tosylates (I) in 80% Aqueous Ethanol (v/v)

I, X =	Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	% k_s
p-NO$_2$	75.0[a]	5.22×10^{-5}	21.4	−17.1	~100[b]
	75.15	$5.23 \pm 0.01 \times 10^{-5}$			
	100.18	$4.44 \pm 0.08 \times 10^{-4}$			
p-CF$_3$	75.0[a]	6.35×10^{-5}	21.6	−15.9	~100[b]
	75.15	$6.44 \pm 0.03 \times 10^{-5}$			
	100.15	$5.60 \pm 0.01 \times 10^{-4}$			
m-CF$_3$	75.0[a]	6.22×10^{-5}	20.1	−20.4	~100[b]
	75.15	$6.30 \pm 0.05 \times 10^{-5}$			
	100.20	$4.73 \pm 0.36 \times 10^{-4}$			
m-Cl	75.0[a]	6.56×10^{-5}	21.9	−15.0	~100[b]
	75.20	$6.69 \pm 0.01 \times 10^{-5}$			
	100.20	$5.99 \pm 0.02 \times 10^{-4}$			
p-Cl	75.0[a]	7.88×10^{-5}	22.1	−14.2	93
	75.20	$8.03 \pm 0.01 \times 10^{-5}$			
	100.20	$7.28 \pm 0.02 \times 10^{-4}$			
p-H	75.0	1.12×10^{-4}	22.3	−12.7	79
	75.15	$1.24 \pm 0.02 \times 10^{-4}$			
	100.20	$1.15 \pm 0.01 \times 10^{-3}$			
p-CH$_3$	75.0[a]	2.38×10^{-4}	22.1	−11.8	37
	75.15	$2.41 \pm 0.01 \times 10^{-4}$			
	100.20	$2.21 \pm 0.14 \times 10^{-3}$			
p-OCH$_3$	75.0[a]	1.28×10^{-3}	22.6	−7.3	7
	50.50	$1.01 \pm 0.02 \times 10^{-4}$			
	75.20	$1.31 \pm 0.05 \times 10^{-3}$			

[a] Calculated from data at other temperatures. [b] These values are probably slightly less than 100%[4] but the experimental error makes accurate determination of the exact percentages difficult.

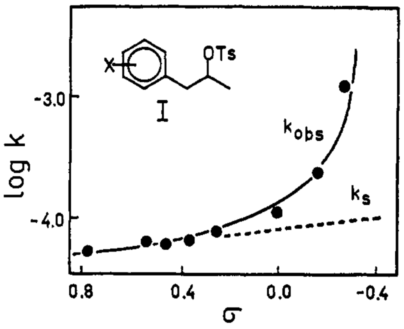

Figure 1. The dissection of the rate constants for the solvolysis of 1-aryl-2-propyl tosylates in 80% ethanol at 75°.

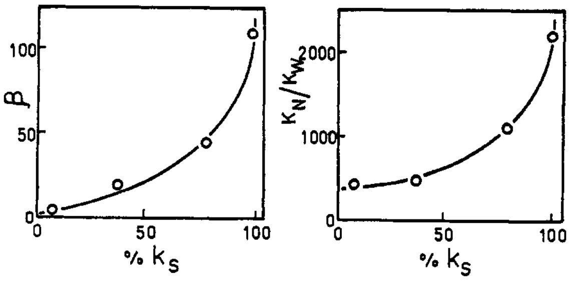

Figure 2. Plots of β (rate enhancement) and k_N/k_W (azide incorporation) *vs.* % k_s for the solvolysis of 1-aryl-2-propyl tosylates in 80% ethanol at 75°.

Table II. Solvolysis of 1-Aryl-2-propyl Tosylates[a] (I) in 80% Ethanol at 75° in the Presence of Sodium Azide

I, X = a	[NaN$_3$]	$k_{obsd} \times 10^4$, sec^{-1}	% RN$_3$[b]	% ROH[b]	% ROEt[b]
p-NO$_2$	0.00	0.52 ± 0.01	(0)	(100)	
	0.02	1.84 ± 0.25	(71)	(29)	
	0.04	2.63 ± 0.15	(80)	(20)	
	0.06	4.15 ± 0.12	(86)	(14)	
p-H	0.00	1.24 ± 0.02	0.0	46	54
	0.02	2.20 ± 0.22	42 (40)	25	32
	0.04	3.22 ± 0.02	61 (58)	18	21
	0.06	4.19 ± 0.54	71 (67)	12	17
p-CH$_3$	0.00	2.40 ± 0.01	0.0	54	46
	0.02	3.18 ± 0.03	27 (28)	39	35
	0.04	4.28 ± 0.06	46 (44)	27	27
	0.06	5.19 ± 0.10	55 (53)	21	24
p-OCH$_3$	0.00[c]	1.01 ± 0.02	0	49	51
	0.02[c]	1.03 ± 0.01	30 (39)	32	38
	0.04[c]	1.21 ± 0.02	46 (56)	27	27
	0.06[c]	1.26 ± 0.07	53 (62)	21	26

[a] Tosylate 0.01 *M* in all cases. [b] Numbers in parentheses from titration; all other data were obtained by glpc. [c] 50°.

Figure 2, the rate enhancements as measured by β, eq 1,[10] and the product distribution, as measured by

$$k/k_0 = 1 + \beta[\mathrm{NaN_3}] \qquad (1)$$

eq 2,[7a] both increase as the relative proportion of k_s increases.

$$\frac{k_N}{k_W} = \frac{\%\ \mathrm{RN_3[H_2O]}}{\%\ \mathrm{ROH[NaN_3]}} \qquad (2)$$

These results demonstrate that the use of sodium azide can function, at least in a qualitative manner, as a probe for k_s processes.

Each of the products (alkyl azide, ether, and alcohol) presumably arises by two different pathways: direct displacement on neutral substrate (or ion pair[7]) and attack on phenonium ion. In order to obtain a more exact relationship between k_s and azide effects it was necessary to dissect the rates and the products with regard to these two pathways. Scheme I illustrates the kinetic model we used for this purpose. Here f_N, f_W, and f_E represent the fractions of phenonium ion III

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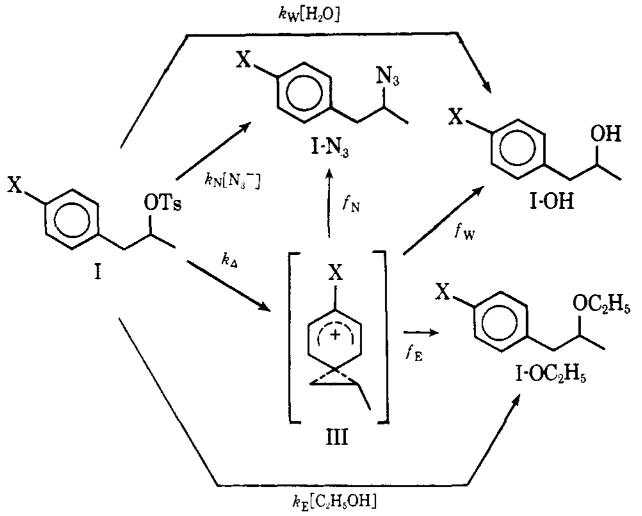
(10) This equation takes the form of Winstein's equation[11] for salt effects. However, we do not believe that these large rate enhancements are a consequence of the types of salt effects which Winstein discussed. Consequently the symbol β has been used in place of Winstein's *b*. See also ref 6.

(11) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2780 (1956).

Scheme I. A Kinetic Model for the Solvolysis of 1-Aryl-2-propyl Tosylates in Aqueous Ethanol in the Presence of Sodium Azide



which are diverted to azide, alcohol, and ether product, respectively, and these quantities are related by eq 3.

$$f_N + f_W + f_E = F \cong 1 \tag{3}$$

According to Scheme I the observed rate constant, k_{obsd}, is equal to the sum of the individual rate constants (eq 4), where k_s is the sum of the pseudo-first-

$$k_{obsd} = k_s + k_\Delta + k_N[N_3^-] \tag{4}$$

order rate constants for displacement by ethanol and water (eq 5). The product distributions are given by

$$k_s = k_W[H_2O] + k_E[C_2H_5OH] \tag{5}$$

eq 6–8. Combination of eq 5, 7, and 8 leads to eq 9,

$$\frac{\%\ RN_3}{100} = \frac{k_N[N_3^-] + f_N k_\Delta}{k_{obsd}} \tag{6}$$

$$\frac{\%\ ROH}{100} = \frac{k_W[H_2O] + f_W k_\Delta}{k_{obsd}} \tag{7}$$

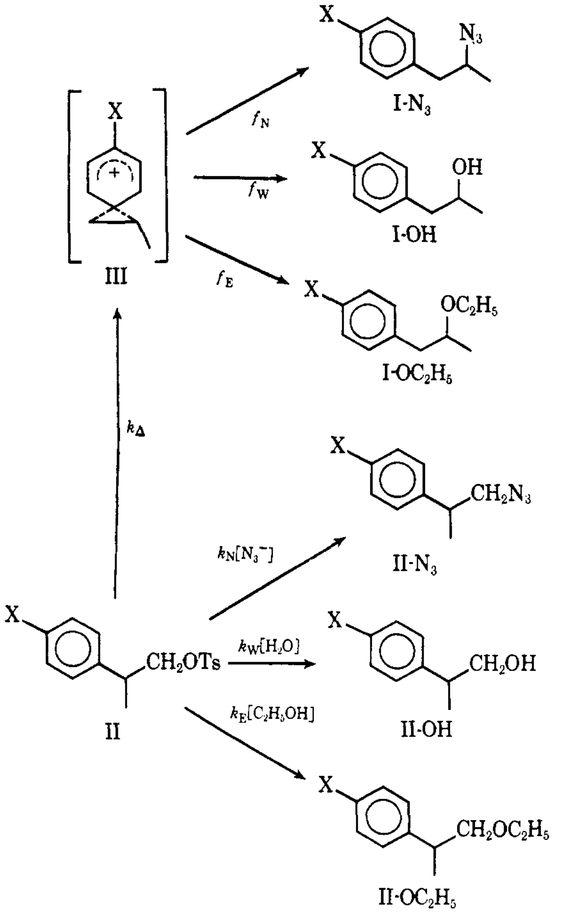
$$\frac{\%\ ROC_2H_5}{100} = \frac{k_E[C_2H_5OH] + f_E k_\Delta}{k_{obsd}} \tag{8}$$

$$\frac{\%\ ROH + \%\ ROC_2H_5}{100} = \frac{k_s + (f_W + f_E)k_\Delta}{k_{obsd}} \tag{9}$$

which relates the rates and products for processes not involving azide ion.

The key to the separation of the various pathways lies in the independent determination of the products arising from attack on phenonium ion III (*i.e.*, in obtaining the values of f_N, f_W, and f_E). A convenient method for accomplishing this independent determination was made available by an alternative mode of generating the appropriate phenonium ions (III): solvolysis of the isomeric 2-aryl-1-propyl tosylates (II) (Scheme II). It was hoped that secondary products (*e.g.*, I-N_3) would arise only from phenonium ion III and that f_N, f_W, and f_E could be obtained directly. We therefore solvolyzed the requisite 2-aryl-1-propyl tosylates (II) in 80% ethanol. The complete product distributions are shown in Table III, and pertinent rate data are summarized in Table IV.

Scheme II. A Kinetic Model for the Solvolysis of 2-Aryl-1-propyl Tosylates in Aqueous Ethanol in the Presence of Sodium Azide



The kinetic studies demonstrated, in agreement with related findings of Winstein,[12] that there is little or no ion pair return from phenonium ion to the secondary tosylate I in this solvent system. Had such ion pair return taken place, a steady increase in the instantaneous rate constants would have been observed during the course of the reaction.[12] However, the instantaneous rate constants remained reasonably constant through 95% of the reaction (see Experimental Section). Furthermore, since primary tosylate (II) leads to significant amounts of primary azide product (Table III), the absence of primary azide products (<1%) in the solvolysis of the 1-aryl-2-propyl tosylates (I) indicates that there is also no significant ion pair return from phenonium ion III to the primary tosylate II. Consequently, as illustrated in Scheme II, the distributions of secondary products arising from solvolysis of the primary tosylates (II) are those resulting from attack on the appropriate phenonium ions III (Table III).

Simple algebraic manipulation of eq 3–9 permits a complete dissection of the rate processes shown in Scheme I. A key assumption we have made is that the magnitude of k_s (*i.e.*, k_W and k_s) is not affected by sodium azide. This assumption appears to be justified by the constancy of k_s in the available cases:[13] 1-*p*-nitrophenyl-2-propyl tosylate and 2-phenyl-1-propyl tosylate (Table V).

(12) S. Winstein and T. C. Schreiber, *J. Amer. Chem. Soc.*, **74**, 2171 (1952).

(13) See also Tables I and II in ref 6a. For 2-octyl brosylate in 75% dioxane and for 2-propyl tosylate in 75% dioxane and 80% ethanol added sodium azide causes no appreciable variation in k_s as measured by (% ROH + % ROC_2H_5)(k_{obsd}).

Table III. Solvolysis of 2-Aryl-1-propyl Tosylates (II) in 80% (v/v) Ethanol in the Presence of Sodium Azide at 75° [a]

II, X =	[NaN$_3$]	Primary (2-aryl-1-propyl) products, % RN$_3$	ROH	ROEt	Secondary (1-aryl-2-propyl) products, % RN$_3$	ROH	ROEt	f_N	f_W	f_E
H	0.00	0	1	9	0	42	48	0.00	0.47	0.53
	0.02	21	3	7	10	31	30	0.14	0.44	0.42
	0.04	37	2	5	12	22	22	0.21	0.39	0.39
	0.06	49	2	4	12	16	17	0.27	0.35	0.38
p-CH$_3$	0.00	0	1	2	0	49	49	0.00	0.50	0.50
	0.02	3	1	2	5	43	47	0.05	0.45	0.50
	0.04	7	1	2	10	39	41	0.11	0.43	0.46
	0.06	11	1	2	12	36	39	0.14	0.41	0.45
p-OCH$_3$	0.00	0	~0.1	~0.2	0	45	55	0.00	0.45	0.55
	0.02	1	~0.1	~0.2	23	34	42	0.23	0.34	0.42
	0.04	3	~0.1	~0.2	34	28	36	0.35	0.28	0.37
	0.06	4	0.1	0.2	41	22	33	0.43	0.23	0.34

[a] All product data obtained by glpc.

Table IV. Solvolysis Rates of 2-Aryl-1-propyl Tosylates (II) in 80% Ethanol

II, X =	Temp, °C	k_{obsd}, sec^{-1} [a]	k_s, sec^{-1} [b]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
p-OCH$_3$	75.0[c]	4.90×10^{-4}	1.47×10^{-6}	22.0	−10.8
	49.38	3.56×10^{-5}			
	51.7	$4.77 \pm 0.01 \times 10^{-5}$			
	75.50	$5.12 \pm 0.05 \times 10^{-4}$			
p-CH$_3$	75.0[c]	4.55×10^{-5}	1.37×10^{-6}	23.9	−10.2
	75.22	$4.65 \pm 0.01 \times 10^{-5}$			
	100.56	$5.16 \pm 0.03 \times 10^{-4}$			
H	75.0[c]	7.93×10^{-6}	7.93×10^{-7}	22.5	−17.6
	74.85	$7.82 \pm 0.36 \times 10^{-6}$			
	100.50	$7.84 \pm 0.20 \times 10^{-5}$			
	100.50[d] (0.02 *M* NaN$_3$)	$1.17 \pm 0.02 \times 10^{-4}$			
	100.50[d] (0.04 *M* NaN$_3$)	$1.49 \pm 0.03 \times 10^{-4}$			
	100.50[d] (0.06 *M* NaN$_3$)	$1.87 \pm 0.02 \times 10^{-4}$			

[a] Duplicate runs; determined conductometrically unless otherwise noted. [b] Calculated from the data in Table III using eq 10. [c] Extrapolated from the rates at other temperatures. [d] These runs were made titrimetrically in the presence of added azide.

Table V. Individual Rate Constants for the Various Processes in the Solvolyses of β-Aryl-Substituted Propyl Tosylates (I and II) in the Presence of Sodium Azide

Compd, X = (temp, C°)	sec^{-1}	$k_{obsd} \times 10^4$, sec^{-1}	$k_s \times 10^4$, sec^{-1}	$k_\Delta \times 10^4$, sec^{-1}	$k_N[N_3^-] \times 10^4$, sec^{-1}	$k_N \times 10^4$,[a] l. mol^{-1} sec^{-1}
	0.00	0.52	0.52		0.00	
I, *p*-NO$_2$	0.02	1.83	0.52		1.31	58.1
(75)	0.04	2.63	0.43		2.20	
	0.06	4.15	0.57		3.58	
	0.00	1.24	0.89	0.35	0.00	
I, H	0.02	2.21	*b*	0.44	0.88	47.9
(75)	0.04	3.23	*b*	0.46	1.88	
	0.06	4.19	*b*	0.45	2.86	
	0.00	2.41	0.87	1.54	0.00	
I, *p*-CH$_3$	0.02	3.18	*b*	1.56	0.76	43.9
(75)	0.04	4.20	*b*	1.63	1.78	
	0.06	5.19	*b*	1.73	2.59	
	0.00	1.01	0.07	0.94	0.00	
I, *p*-CH$_3$O	0.02	1.03	*b*	0.89	0.11	5.1
(50)	0.04	1.21	*b*	0.89	0.25	
	0.06	1.26	*b*	0.90	0.29	
	0.00	0.82	0.09	0.73	0.00	
II, (100)	0.02	1.17	0.11	0.82	0.24	15.2
	0.04	1.15	0.11	0.84	0.56	
	0.06	1.87	0.12	0.85	0.91	

[a] Determined by the slope of a plot of $k_N[N_3^-]$ *vs.* [NaN$_3$]. [b] Assumed to be independent of [NaN$_3$] (see text).

The dissection was carried out as follows. Equation 9 was solved for k_Δ, and the resulting value of k_Δ was used to solve eq 6 for $k_N[N_3^-]$. The values of $k_N[N_3^-]$ were then plotted against the concentration of sodium azide to give k_N as the slope of the resulting straight line. The results of this dissection are summarized in Table V. Data for the primary 2-phenyl-1-propyl tosylate are also included in this table; separation of the rate processes for this compound follows directly from the secondary–primary product distribution (see Table III and Scheme II) according to eq 10–12.

$$k_s = (\%\ \text{II-OH} + \%\ \text{II-OC}_2\text{H}_5)(k_{\text{obsd}})/100 \quad (10)$$

$$k_\Delta = (\%\ \text{I-OH} + \%\ \text{I-OC}_2\text{H}_5 + \%\ \text{I-N}_3)/100 \quad (11)$$

$$k_N[N_3^-] = (\%\ \text{II-N}_3)(k_{\text{obsd}})/100 \quad (12)$$

This dissection process allows direct comparison of the displacement pathways (k_N and k_s) without interference from the anchimerically assisted (k_Δ) pathway. In order to allow comparison with the carbonium ion reactions discussed in the previous paper,[6] we have converted the values of k_s (the pseudo-first-order rate constant for the nucleophilically solvent assisted process) for the tosylates in 80% ethanol to estimates of k_s for the corresponding chlorides in 80% acetone at 25°; these estimates are presented together with values of k_N/k_W (the azide competition ratio)[6,8] in Table VI. A log–log plot of k_s *vs.* k_N/k_W for these compounds is shown in Figure 3 which also shows (as the dotted line) the stability–selectivity correlation for carbonium ion reactions. This carbonium ion line does not correlate the k_s points at all. Figure 3 shows that such a plot *can differentiate between the two mechanistic types.* Sneen, Carter, and Kay[8] suggested that deviations from the carbonium ion stability–selectivity plot (the dotted line in Figure 3) can "serve as useful diagnostics for the intermediacy of ion pairs." This suggestion was based on the contention that 2-octyl mesylate (which does not fall on the carbonium ion line) solvolyzed by displacement on an ion pair.[7a] However, we have shown[6] that an alternative interpretation (direct displacement on neutral substrate) for the mechanism of 2-octyl solvolysis is possible.[14]

Table VI. Rates of k_s Processes for the Solvolysis of Alkyl Chlorides in 80% Acetone at 25° and Competition Ratios for Azide Ion and Water

Alkyl chloride	k_s,[a] sec^{-1}	k_N/k_W[b]
2-Propyl[c]	1.05×10^{-9}	740[g]
2-Octyl[d]	9.56×10^{-10}	770[g]
1-*p*-Nitrophenyl-2-propyl[e]	8.08×10^{-11}	2360[h,i]
1-Phenyl-2-propyl[e]	1.42×10^{-10}	1380[h]
1-*p*-Tolyl-2-propyl[e]	1.39×10^{-10}	1023[h]
1-*p*-Anisyl-2-propyl[e]	1.34×10^{-10}	957[h]
2-Phenyl-1-propyl[f]	1.99×10^{-12}	4500[j]
2-*p*-Tolyl-1-propyl[f]	2.17×10^{-12}	1870[j]
2-*p*-Anisyl-1-propyl[f]	2.34×10^{-12}	7400[k]

[a] The rates were estimated from the rates of the corresponding tosylates relative to 2-propyl tosylate in 80% ethanol. [b] Values of k_N/k_W were calculated using eq 2 and the appropriate product data. [c] The rate of the chloride in 80% acetone was calculated from the rate in 80% ethanol [E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937)] using m = 0.43 (determined for the bromide[3b]). [d] The rate of the chloride in 80% acetone was estimated from the relative rates of 2-octyl tosylate and 2-propyl tosylate in ethanol [W. Hückel and Y. Riad, *Justus Liebigs Ann. Chem.*, **678**, 19 (1964); W. Hückel and K. Tomopulos, *ibid.*, **610**, 78 (1957)]. [e] Values of k_s were calculated from the data in Table I. [f] Values of k_s for the tosylates in 80% ethanol were taken from Table IV. [g] Reference 3e. [h] Calculated from the data in Tables IV and V using eq 7. [i] Equal amounts of alcohol and ether products were assumed. [j] From the product data in Table III; average values. [k] From the product data in Table III; 0.06 M NaN$_3$ only.

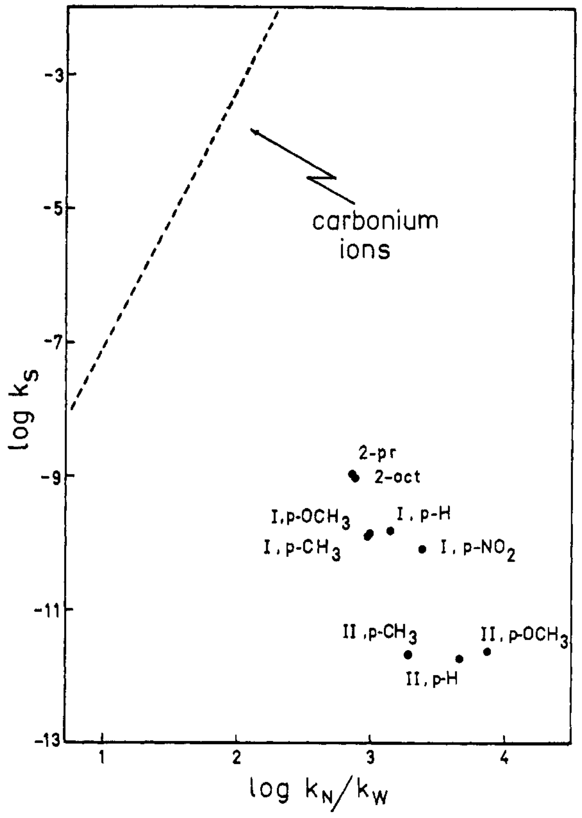


Figure 3. A plot of log k_s *vs.* log k_N/k_W for primary and secondary alkyl chlorides in 80% acetone at 25°.

Conclusions

Two situations give high azide incorporation: (1) the solvolysis of derivatives capable of giving rather stable cations,[6,8] (2) the solvolysis of unhindered primary and secondary substrates. Our results indicate that azide incorporation values alone are not sufficient evidence for assignment of a mechanistic pathway.[15] However, the analysis of azide incorporations in conjunction with solvolysis rates (Figure 3) can accomplish this end. In the previous paper[6] we showed that solvolysis in the presence of sodium azide could be used as a quantitative probe for carbonium ion reactions. The present results demonstrate that azide ion can also provide a probe for nucleophilic solvent assistance (k_s) in the solvolysis of primary and secondary derivatives.

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(14) From the values of f_N and f_W (Table V) selectivity ratios (k_N/k_W) can also be calculated for the phenonium ions: III, p-OCH$_3$ 348; III, p-CH$_3$ 61; and III, H 148. These ratios, when plotted against the values of k_Δ estimated for the chlorides corresponding to I, increase the scatter found in Figure 3. The selectivities of the phenonium ions (III) are considerably greater than predicted from the carbonium ion stability–selectivity relationship. This suggests an interesting possibility. The enhanced selectivity may result from S$_N$2 character in attack on the phenonium ion (III) where the aryl moiety acts as the leaving group.

(15) Professor D. E. Sunko has reached a similar conclusion (private communication).

Experimental Section

Materials. 1-Phenyl-2-propyl Tosylate (I-H). Commercial 1-phenylacetone (Aldrich) was reduced with lithium aluminum hydride to give an alcohol which was treated with tosyl chloride in pyridine. The resulting tosylate was recrystallized at −80° from pentane, mp 91.2–92.4° (lit. mp 90.7–91.6°,[16] 93.5–95°[17]).

1-(*p*-Tolyl)-2-propyl Tosylate (I-*p*-CH_3). Treatment of *p*-tolylacetonitrile (Aldrich) with sodium ethoxide and ethyl acetate followed by hydrolysis with aqueous sulfuric acid gave *p*-tolylacetone,[18] bp 105° (12 mm). The ketone was reduced with lithium aluminum hydride to give the alcohol, which was treated with tosyl chloride in pyridine. The resulting tosylate was recrystallized at −80° from pentane, mp 48.8–50.0° (lit.[17] mp 49–50°).

1-(*p*-Anisyl)-2-propyl Tosylate (I-*p*-OCH_3). Reaction of *p*-methoxybenzyl alcohol with concentrated hydrochloric acid followed by reaction with sodium iodide and sodium cyanide in acetone gave *p*-anisylacetonitrile.[19] This compound (without further purification) was treated with sodium ethoxide and ethyl acetate followed by hydrolysis with aqueous sulfuric acid[18] to give *p*-anisylacetone, bp 109–112° (1.5 mm). Reduction of the ketone with lithium aluminum hydride was followed by treatment with tosyl chloride in pyridine. The resulting tosylate was recrystallized at −80° from pentane–ether, mp 74.5–75.5° (lit.[17] 77–78°).

2-Phenyl-1-propyl Tosylate (II-H). Commercial 2-phenylpropionaldehyde (Aldrich) was reduced with lithium aluminum hydride. The resulting alcohol was treated with tosyl chloride in pyridine to give the tosylate,[12] which was purified by low-temperature recrystallization from pentane: mp 50.5–51.5° (lit.[17] 50–50.5°); nmr ($DCDl_3$) δ 1.27 (d, 3 H, J = 7 Hz), 2.38 (s, 3 H), 3.07 (q, 1 H, J = 7 Hz), 4.07 (d, 2 H, J = 7 Hz), and 7.4 (m, 9 H).

2-(*p*-Tolyl)-1-propyl Tosylate (II-*p*-CH_3). Reaction of 1-*p*-tolylacetone (Aldrich) with methylenetriphenylphosporane gave 2-*p*-tolylpropene which was taken to the next step without purification.[20] Hydroboration[21] of the olefin was followed by treatment with tosyl chloride in pyridine. The resulting tosylate was recrystallized from pentane at −80°: mp 34.5–35.5° (lit.[17] 42.5–43°); nmr ($CDCl_3$) δ 1.23 (d, 3 H, J = 7 Hz), 2.27 (s, 3 H), 2.38 (s, 3 H), 3.03 (q, 1 H, J = 7 Hz), 4.06 (d, 2 H, J = 7 Hz), 7.02 (s, 4 H), 7.48 (q, 4 H). *Anal.* Calcd for $C_{17}H_{20}O_3S$: C, 67.10; H, 6.58. Found: C, 67.04; H, 6.63.

2-(*p*-Anisyl)-1-propyl tosylate (II-*p*-OCH_3) was prepared from *p*-anisyl methyl ketone (Aldrich) as described in the preparation of II-*p*-CH_3: mp 36.5–38.5° (lit.[17] mp 37–39°); nmr ($CDCl_3$) δ 1.25 (d, 3 H, J = 7 Hz), 2.43 (s, 3 H), 3.04 (q, 1 H, J = 7 Hz), 3.78 (s, 3 H), 4.05 (d, 2 H, J = 7 Hz), 6.93 (q, 4 H), 7.50 (q, 4 H). *Anal.* Calcd for $C_{17}H_{20}O_4S$: C, 63.80; H, 6.28. Found: C, 63.61; H, 6.11.

The 1-(*p*-nitro-, *p*-trifluoromethyl-, *m*-trifluoromethyl-, *m*-chloro-, and *p*-chloro-)phenyl-2-propyl tosylates were prepared by C. J. Lancelot.[22] The techniques used for determination of products and rates are described in the preceding paper.[6]

The absence of internal return in the solvolysis of the 2-aryl-1-propyl tosylates (II) was demonstrated by the constancy of the instantaneous rate constants, calculated with eq i. Tables VII

$$k = \frac{2.303}{t_2 - t_1}\left(\log \frac{V_\infty - V_1}{V_\infty - V_2}\right) \qquad \text{(i)}$$

and VIII present the instantaneous rate constants for typical kinetic runs.

Table VII. Instantaneous Rate Constants for the Solvolysis of 2-*p*-Anisyl-1-propyl Tosylate in 80% Ethanol at 75.15°

Time, min	Conductance, $\text{ohm}^{1} \times 10^5$	$k \times 10^4$, sec^{-1}
0.00	6.00	5.21
3.27	10.00	5.19
6.08	13.10	5.25
8.93	16.00	5.22
12.17	19.00	5.11
16.08	22.20	5.25
19.88	25.00	5.25
27.19	29.50	5.21
33.15	32.50	5.20
40.53	35.50	5.24
50.09	38.50	5.18
63.29	41.40	5.27
89.10	44.58	
∞	47.09	

Table VIII. Instantaneous Rate Constants for the Solvolysis of 2-Phenyl-1-propyl Tosylate (II, *p*-H) in 80% Ethanol at 100.5°

Time, min	Titer, ml	$k \times 10^4$, sec^{-1}
0.00	0.24	1.11
19.50	0.61	1.25
47.85	1.10	1.09
78.39	1.49	0.95
122.29	1.88	1.57
157.09	2.27	1.13
220.73	2.62	1.03
343.35	3.00	
∞	3.27	

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