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(28) American Can Company Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–1968; Ph.D. Thesis, Princeton University, 1969.

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Correlation of k_Δ and k_s in Solvolysis of 1-Phenyl-2-propyl Toluenesulfonate[1]

Sir:

For some years we have discussed solvolysis of 2-phenyl-1-ethyl OTs and related systems[2] which are marginal with respect to neighboring phenyl participation, in terms of a competion between anchimerically unassisted ionization (k_s) and anchimerically assisted ionization (k_Δ). The latter leads to the "nonclassical" phenyl-bridged or "ethylene phenonium" cation.[3] The two modes of ionization are associated with characteristically different $\Delta S^{\ddagger}$,[2c] β-D isotope effects,[4] phenyl substituent effects, and response to solvent nucleophilicity and ionizing power. In typical solvolysis of such simple primary systems leakage between the classical cation associated with k_s and the bridged ion or a rearranged open ion is negligible, so that product composition[2d,5] (or product stereochemistry) from suitably labeled starting material is well correlated with the proportions of k_Δ and k_s. This latter point has been especially well documented recently in the case of 2-phenyl-1-ethyl OTs.[6] The same interpretation of discrete k_Δ and k_s processes has been applied for some years in the UCLA laboratories to simple secondary 2-arylalkyl systems,[2a,3,7] and in this communication we deal further with solvolysis of 1-phenyl-2-propyl OTs (IS-OTs).[7a]

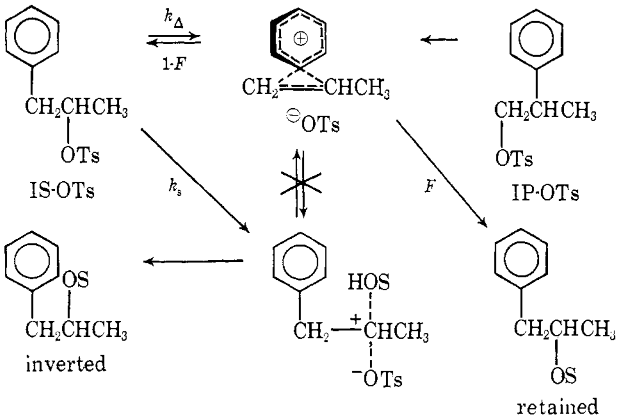
To the solvolysis of 1-phenyl-2-propyl OTs we have applied the same crucial test recently used for the 2-phenyl-1-ethyl system.[6a] On the basis of the mechanistic significance assigned to k_Δ, we should expect a quantitative correlation of k_Δ values with solvolysis rates (k_t) of neophyl OTs,[8] for which it is agreed[9] that ionization occurs with phenyl participation at a rate equal to k_t and dependent on solvent ionizing power but not nucleophilicity. On the other hand, the k_s process should depend on a blend of nucleophilicity and ionizing power for which the simple 2-propyl tosylate (2-PrOTs) should be a rather good model. Thus, k_s would be expected to correlate rather well with k_t values for 2-PrOTs. We now report the results of this kind of analysis for solvolysis of IS-OTs in EtOH, AcOH, HCOOH, and CF_3COOH.

The solvolysis rate constants (k_{ts}) in Table I for IS-OTs were dissected into k_s and Fk_Δ portions on the basis of the stereochemistry of solvolysis of IS-OTs assuming k_s leads to inversion and Fk_Δ to retention. As reported much earlier,[7a] the stereochemical outcome of solvolysis of IS-OTs shows a trend from high inversion to very substantial retention of configuration as solvent is varied from EtOH to AcOH to HCOOH (Table II). More recently, Nordlander has reported 100% retention in solvolysis of IS-OTs in CF_3COOH.[10] The derived k_s and Fk_Δ values are listed in Table II.

Table I. Summary of Rate Constants for 1-phenyl-2-propyl (IS) and 2-phenyl-1-propyl (IP) Tosylates

Solvent	ROTs	Temp, °C	k	10^7k, sec^{-1}
EtOH	IS	50.0	k_{ts}	1.41[a]
AcOH	IS	50.0	k_{ts}	0.585[a]
AcOH	IS	75.0	k_{ts}	13.1 ± 0.1
AcOH	IP	75.0	k_{tp}	0.62 ± 0.02[b]
AcOH	IS + IP[c]	75.0	$k_r + k_{tp}$	3.34 ± 0.02
HCOOH	IS	50.0	k_{ts}	304[d]
CF_3COOH	IS	50.0	k_{ts}	3470 ± 20
CF_3COOH	IS	25.0	k_{ts}	260 ± 14
CF_3COOH	IP	25.0	k_{tp}	13 ± 1[b]
CF_3COOH	IS + IP[e]	25.0	$k_r + k_{tp}$	137 ± 2

[a] Reference 7a. [b] Calculated value using $k_{obsd} = k_{tp}F_p + k_{ts}(1 - F_p)$ where F_p is the mole fraction of IP-OTs in the tosylate mixture; $[(k_r + k_{tp})/k_{tp}] = 5.4 \pm 0.2$ in AcOH compared to the value of 6.1 ± 0.4 reported[7a] for ROBs. [c] $F_p = 0.783$. [d] Reference 11a. [e] $F_p = 0.50$.



To obtain k_Δ from Fk_Δ, F, the fraction of ion pairs giving product instead of ion-pair return, needs to be

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(1) Research sponsored by the National Science Foundation.

(2) S. Winstein, *et al.*: (a) *Bull Soc. Chim. France*, **18**, 55 (1951); (b) *J. Am. Chem. Soc.*, **75**, 147 (1953); (c) *ibid.*, **78**, 4801 (1956); (d) *Helv. Chim. Acta*, **41**, 807 (1958); (e) *J. Am. Chem. Soc.*, **87**, 3504 (1965).

(3) (a) D. J. Cram, *ibid.*, **71**, 3863 (1949); (b) D. J. Cram, *ibid.*, **86**, 3767 (1964); (c) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967).

(4) W. H. Saunders, *et al.*, *ibid.*, **80**, 242 (1958); **82**, 3586 (1960).

(5) C. C. Lee, *et al.*, *Can. J. Chem.*, **35**, 1417 (1957); *Tetrahedron*, 7, 206 (1959).

(6) (a) A. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968); (b) J. E. Nordlander and W. G. Deadman, *Tetrahedron Letters*, 4409 (1967); *J. Am. Chem. Soc.*, **90**, 1590 (1968); (c) R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968); (d) J. L. Coke, *et al.*, *J. Am. Chem. Soc.*, **91**, 1154 (1969); (e) M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969); (f) R. J. Jablonski and E. I. Snyder, *ibid.*, in press.

(7) (a) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1140 (1952); S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952); (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (c) S. Winstein and R. Baker, *ibid.*, **86**, 2071 (1964).

(8) (a) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956); (b) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957); (c) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

(9) H. C. Brown, *et al.*: (a) Special Publication No. 16, The Chemical Society, London, 1962, p 140; (b) *J. Am. Chem. Soc.*, **87**, 1280 (1965); (c) *ibid.*, **87**, 2137 (1965); (d) *ibid.*, **89**, 370 (1967); (e) *ibid.*, **90**, 2082 (1968).

(10) J. E. Nordlander and W. J. Kelly, *ibid.*, **91**, 996 (1969).

Table II. Data for Solvolysis of 1-phenyl-2-propyl Tosylate at 50.0°

Solvent	Stereochemistry[a] % inv	% ret	10^6k, sec^{-1} k_s	Fk_Δ	k_Δ	F
EtOH	93	7	1.31	0.099	0.099	*Ca.* 1.0
AcOH	65	35	0.38	0.205	1.11	0.185[d]
HCOOH	15	85	46.0	258	258	1.0
CF_3COOH	0	100[b]	6.6[c]	3463	36,800	0.0943[e]

[a] Reference 7a. [b] Reference 10. [c] Extrapolated value from plot of log k_s *vs.* log k_t for 2-propyl OTs in Figure 1. [d] 75.0°. [e] 25.0°.

evaluated. As previously outlined,[7a] F may be indirectly approximated from a kinetic analysis of the solvolysis of the isomeric 2-phenyl-1-propyl OTs (IP-OTs). The solvolysis of IP-OTs (k_{tp}) is accompanied by rearrangement (k_r) due to ion-pair return to the somewhat more reactive IS-OTs. The latter then solvolyzes with a first-order rate constant equal to k_{ts} (eq 1). Using the rate constants in Table I, the F values, namely $[k_{tp}/(k_r + k_{tp})]$, may be calculated, and these, along with the derived k_Δ values, are listed in Table II. Ion-pair return, measured by $(1 - F)$, is large in AcOH and CF_3COOH; it is negligible in HCOOH[7a] and fairly small in EtOH.[7a]

$$\text{product} \xleftarrow{k_{tp}} \text{IP-OTs} \xrightarrow{k_r} \text{IS-OTs} \xrightarrow{k_{ts}} \text{product} \qquad (1)$$

As illustrated in Figure 1, a good linear free energy correlation exists between log k_Δ for the secondary IS-OTs and log k_t for neophyl tosylate.[6a,8] The slope of the least-squares line is 1.12 with a mean deviation of 0.14 log unit for the four points. Similarly log k_s is linear in log k_t for 2-propyl OTs. The slope of the least-squares line is 0.914 with a mean deviation of 0.05 log unit for the AcOH, HCOOH, and EtOH points. With the aid of this line the value of 6.6×10^{-6} sec^{-1} is estimated for k_s in CF_3COOH. Thus (k_Δ/k_s) is 5600, somewhat lower than for phenylethyl OTs in CF_3COOH.[6a]

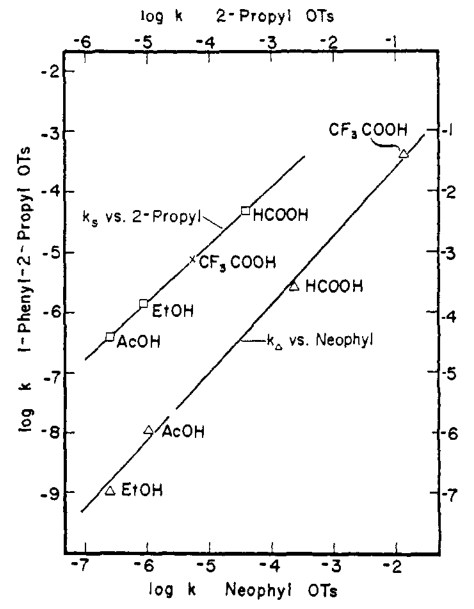

Figure 1. 1-Phenyl-2-propyl OTs *vs.* neophyl OTs and 2-propyl OTs at 50°.

It should be obvious that the present results support strongly the description of the solvolysis of the secondary IS-OTs in terms of discrete k_Δ and k_s processes. Similar support has come from the recent work of Schleyer[11] on aryl-substituted 1-phenyl-2-propyl OTs systems. Estimating k_s from a $\rho\sigma$ line for electron-attracting substituents which make k_Δ negligible, Fk_Δ for the unsubstituted 1-phenyl-2-propyl system is evaluated as that part of the solvolysis rate in excess of k_s. The estimates of the Fk_Δ and k_s contributions to k_t in AcOH and HCOOH reproduce well our reported stereochemical results.[7a]

As regards solvent variation, we have shown that k_Δ for IS-OTs correlates well with neophyl OTs. For aryl-substituent effects we would also expect log k_Δ for substituted IS-OTs systems to correlate with log k_t for substituted neophyl systems, the slope of the plot being equal to the ratio of substituent sensitivities of the two systems.[12] Shown in Figure 2 is a plot of log k_Δ for substituted 1-aryl-2-propyl OTs systems in HCOOH[11a] *vs.* log k_t for the acetolysis of the substituted neophyl analog.[6e,8,13] As expected, a good straight line is obtained for the *p*-MeO, *p*-Me, *p*-H, and *p*-Cl points.[14] The slope of the line is 0.87, the mean deviation of the fit of the points being 0.053 log unit.

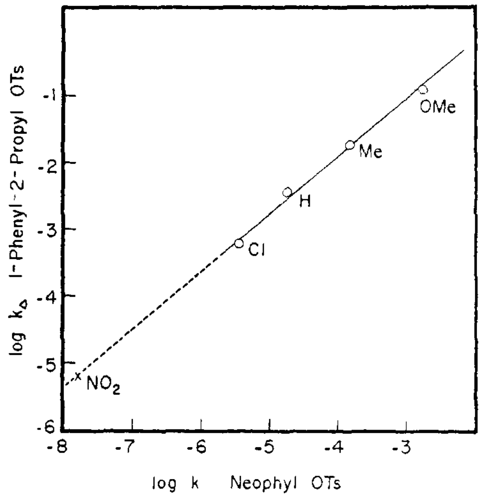

Figure 2. *para*-Substituted 1-phenyl-2-propyl OTs in HCOOH *vs. para*-substituted neophyl OTs in AcOH at 75°.

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(11) (a) C. J. Lancelot and P. Schleyer, *J. Am. Chem. Soc.*, **91**, 4291 (1969); (b) P. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969).

(12) Such a correlation has been demonstrated by Coke[6e] for the 2-phenyl-1-ethyl system.

(13) H. Tanida, *et al.*, *J. Org. Chem.*, **34**, 1086 (1969); Tanida's rate constant of 7.60×10^{-8} sec^{-1} for *p*-nitroneophyl brosylate in AcOH at 75.0° was corrected for the observed 72% aryl participation, and divided by a factor of 3.4 to obtain k_Δ for the tosylate.

(14) Since Schleyer's k_s line[11a] is based on substituents which do not represent really "pure" k_s points, we have improved slightly the k_Δ, k_s dissection by a successive approximation procedure. We estimate that formolysis of the *m*-chloro-1-phenyl-2-propyl OTs is *ca.* 30% k_Δ, while that of the *p*-nitro is *ca.* 5% k_Δ.

The k_Δ values in solvolysis of simple secondary β-arylalkyl systems other than IS-OTs are also correlated well with k_t for the neophyl system. This is true, for example, for the 1-*p*-anisyl-2-propyl OTs[7a,15] and threo-3-phenyl-2-butyl OTs[3,7b,15] systems. The same general picture of competing k_Δ and k_s routes, with little or no leakage between them, and with (k_Δ/k_s) dependent on structure and solvent, applies generally to the simple primary and secondary β-arylalkyl systems.

Quite a different description of the solvolysis of simple primary and secondary β-arylalkyl systems has been evolved by Brown.[9] Since he does not recognize discrete k_Δ and k_s processes, his resulting treatments of rates, phenyl-substituent effects, solvent effects, and stereochemistry are unacceptable.

[15] (a) A. Diaz, unpublished work; (b) S. Winstein, James Flack Norris Award Address, American Chemical Society Meeting, Miami, Fla., April 11, 1967.

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Metal Ion Promoted Hydrolysis of Fluorocarbons

Sir:

The catalytic effect of the hydronium ion on the hydrolysis of a number of fluoro complexes (both cationic and anionic) is well documented.[1] This type of catalysis is also found for the hydrolysis of certain organic fluorides.[2] The theory of hard and soft acid–base behavior interprets this as a specific type of hard acid–hard base interaction. It leads to the anticipation that hard acids other than the hydronium ion should also prove capable of promoting the hydrolysis of suitable fluorocarbons. In particular, the metal cations which are hard acids should show such activity. We have obtained unequivocal experimental proof that this is indeed the case.

Our study has examined the effects of Zr(IV), Th(IV), Ti(IV), Al(III), and Be(II) on the acid hydrolysis of PF_6^-, BF_4^-, $AsF_5(OH)^-$, and benzyl fluoride. Accelerative effects have been general, though dependent upon the media and conditions. Some of the most striking results are found, however, with benzyl fluoride, and these are summarized in Table I.

The data in Table I represent the first quantitative evidence for metal ion catalyzed hydrolytic displacement of fluoride from the C–F linkage.

For the benzyl fluoride studies the procedure of Swain and Spalding[2a] was used for introduction of the sample, whereby an aliquot of a solution of benzyl fluoride dissolved in a nonaqueous solvent is added to the previously thermostated solution of the other reagents. Our observed rate constant of 1.05×10^{-3} min^{-1} for the reaction in 3 *M* $HClO_4$ with 10% acetone at 25° is in reasonable agreement with their value of 1.19×10^{-3} min^{-1} for the reaction in the same medium at 25.1°. We chose the 2 *M* acid concentration for these initial data so that hydrolysis of the catalyst ions, especially Zr(IV), would be retarded.

Table I. Comparison of Half-Lives for the Metal Ion Catalyzed and Uncatalyzed Acid Hydrolysis of Benzyl Fluoride at 25°

Hydrolysis medium	Catalyst	Catalyst Ratio[a]	$t_{1/2}$, min
2 *M* HCl (5% ethanol)	None	. . .	1850
	Th(IV)	10.4	9.0
2 *M* $HClO_4$ (5% ethanol)	None	. . .	1650
	Th(IV)	10.4	7.5
2 *M* HCl (10% acetone)	None	. . .	3000[b]
	Th(IV)	10.4	11
	Zr(IV)	10.4	33.5
	Al(III)	10.3	350
2 *M* $HClO_4$ (10% acetone)	None	. . .	2210
	Th(IV)	9.8	9.1
	Zr(IV)	9.8	28
1 *M* HCl (10% acetone)	Th(IV)	10.3	20.5

[a] Total metal ion concentration/total fluoride. Initial benzyl fluoride was approximately 0.004 *M* in each run. [b] Based on the first 20% of reaction. The first-order plot was nonlinear during later stages of the hydrolysis, presumably from the loss of HF.

The experimental technique used to obtain the rate data consisted of quenching an aliquot of the reaction mixture in an acetate–citrate buffer to give a solution of pH 5.0 followed by the measurement of the potential of an Orion 94-09 fluoride electrode *vs.* sce. The fluoride ion concentration of the resulting solution was then obtained by comparison with standard calibration curves obtained with sodium fluoride solutions obtained under identical conditions of pH, buffer composition, and catalyst concentrations.

A commercial sample of benzyl fluoride (Columbia Organic Chemicals, Co., Inc., Columbia, S. C.) has been used without further purification due to the reported tendency of benzyl fluoride to decompose *via* polymerization upon distillation except under special conditions.[2a] Recovery of fluoride upon complete hydrolysis has typically amounted to 97% of theoretical for C_7H_7F. Catalyzed hydrolyses, all of which have been conducted with pseudo-first-order concentrations of catalyst, have produced first-order plots which are somewhat nonlinear with respect to unhydrolyzed benzyl fluoride. This problem appears to arise from the amount and kind of organic solvent used and is being investigated further.

The results here suggest strongly that the hard and soft acid–base theory may well provide a valuable guide in the development of metal-catalyzed substitution processes on saturated carbon.

[1] See, for example: (a) M. Anbar and S. Guttman, *J. Phys. Chem.*, **64**, 1896 (1960); (b) S. C. Chan, *J. Chem. Soc.*, 2375 (1964); (c) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956); (d) A. E. Gebala and M. M. Jones, *J. Inorg. Nucl. Chem.*, **31**, 771 (1969); (e) L. N. Devonshire and H. H. Rowley, *Inorg. Chem.*, **1**, 680 (1962).

[2] (a) C. G. Swain and R. E. T. Spalding, *J. Am. Chem. Soc.*, **82**, 6104 (1960); (b) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1677 (1952); (c) C. W. L. Bevan and R. F. Hudson, *ibid.*, 2187 (1953).

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Received May 23, 1969

Mass Spectrometric Evidence for the Gaseous AlOCN Molecule

Sir:

In connection with the investigation of the vapor components over the aluminum nitride–graphite system,[1,2] a molecule containing one atom each of

[1] K. A. Gingerich, *Naturwissenschaften*, 54, 646 (1967).

[2] K. A. Gingerich, submitted for publication.