Table I. Solvolysis of 1,3-Diaryl-2-propyl Tosylates; $XC_6H_4CH_2CH(OTs)CH_2C_6H_4Y$

X	Y	Solvent	Temp, °C	k_t, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
p-H	p-H	HOAc[a]	100.0[a]	$(8.98 \pm 0.05) \times 10^{-5}$	27.5	−3.7
		HCOOH	75.0	$(2.56 \pm 0.08) \times 10^{-3}$	23.7	−2.5
p-CH$_3$O	p-CH$_3$O	HOAc[a]	100.0[a]	$(1.68 \pm 0.13) \times 10^{-3}$		
		HCOOH	75.0[b]	5.24×10^{-2}	22.5	0.0
p-NO$_2$	p-NO$_2$	HOAc	100.0	$(3.71 \pm 0.06) \times 10^{-6}$	27.0	−12
		HCOOH	75.0	$(1.14 \pm 0.04) \times 10^{-5}$	26.9	−4.3
-H	p-CH$_3$O	HOAc	100.0	$(8.09 \pm 0.49) \times 10^{-4}$		
		HCOOH	75.0[b]	2.40×10^{-2}	22.3	−2.2
p-H	p-NO$_2$	HOAc	100.6[c]	$(2.10 \pm 0.02) \times 10^{-5}$	24.5	−15
		HCOOH	75.1	$(1.77 \pm 0.02) \times 10^{-4}$	26.5	0.2
p-CH$_3$O	p-NO$_2$	HOAc	100.4[c]	$(1.90 \pm 0.02) \times 10^{-4}$		
		HCOOH	75.0[b]	5.60×10^{-3}	23.9	−0.5

[a] J. J. Harper, Ph.D. Thesis, Princeton University, 1968. [b] Extrapolated from data at other temperatures. [c] Determined by an automatically recording conductometric method, as were all formolyses. *Cf.* I. Ugi and F. Beck, *Ber.*, **94**, 1839 (1961).

Table II. Calculation of k_s and Fk_Δ Terms by Multiple Substitution; Application to $XC_6H_4CH_2CH(OTs)CH_3$

X	Solvent	Temp, °C	k_s, sec^{-1}	Fk_Δ, sec^{-1}	$k_s + Fk_\Delta$, sec^{-1} Calcd	Found (k_t)[1a]
p-NO$_2$	HOAc	100.0	3.66×10^{-5}	~0	3.66×10^{-5}	3.28×10^{-5}
	HCOOH	75.0	2.42×10^{-4}	~0	2.42×10^{-4}	2.22×10^{-4}
p-H	HOAc	100.0	1.26×10^{-4}	5.02×10^{-5}	1.76×10^{-4}	1.84×10^{-4}
	HCOOH	75.0	1.03×10^{-3}	2.68×10^{-3}	3.71×10^{-3}	3.99×10^{-3}
p-CH$_3$O	HOAc	100.0	1.73×10^{-4}	2.02×10^{-3}	2.19×10^{-3}	2.21×10^{-3}
	HCOOH	75.0	1.18×10^{-3}	1.19×10^{-1}	1.20×10^{-1}	1.24×10^{-1}

taneous equations of the form of eq 2 both for acetolysis and formolysis.[4]

Table II lists the calculated values for k_s and Fk_Δ for each substituent. Furthermore, since only *diaryl* systems were used in the calculation of these terms, their accuracy and the assumptions involved can be checked by comparing their sum with the observed value of k_t for the corresponding *monoaryl* systems.[1a] This comparison (the last two columns of Table II) shows excellent agreement.

Since only diaryl systems were used in the calculations, and since the only changes made were out at the *para* position of the aromatic ring, the resulting values for k_s and Fk_Δ must be substantially free from steric effects. The close agreement between the observed and calculated values of k_t for the monoaryl systems offers further demonstration of the relative unimportance of steric effects, in agreement with the conclusion reached from the Taft treatment of these compounds.[1b]

The separation of observed rates by the multiple substitution technique into constituent k_s and Fk_Δ pathways completes the set of kinetic analyses.[1] The excellent agreement found between the results of all three methods, expressed in Table III as the per cent of each reaction proceeding through the aryl-assisted pathway, $((Fk_\Delta/k_t) \times 100)$ indicates the high degree of reliability for the rate data we have obtained, despite the assumptions inherent in the three treatments.

Table III. Per Cent Aryl-Assisted Reaction as Determined by Several Methods; $XC_6H_4CH_2CH(OTs)CH_3$

X[a]	Solvent	Temp, °C	% aryl-assisted reaction $(Fk_\Delta/k_t) \times 100$ Hammett	Taft	Mult subst
p-H	HOAc	100.0	35	38	38
	HCOOH	75.0	78	79	72
p-CH$_3$O	HOAc	100.0	91	93	92
	HCOOH	75.0	99	99	99

[a] Where X = NO$_2$, no evidence for participation is found by any method in HOAc or in HCOOH.

It is important to emphasize that small rate enhancements, provided their extent can be reliably determined (*e.g.*, the factor of 1.6 in the acetolysis of 1-phenyl-2-propyl tosylate), correspond to quite substantial contributions of the Fk_Δ pathway (Fk_Δ/k_t = 38% for the same system).[5] It is a misconception that *large* rate enhancements *must* accompany significant neighboring group participation. The broad significance of the present results will be considered in the following communication.[6]

Acknowledgments. This research was supported by grants from the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

---

(5) Rate enhancements, k_t/k_s, are readily related to Fk_Δ/k_t by: $[(k_t/k_s) - 1]/(k_t/k_s) = Fk_\Delta/k_t$.

(6) P. von R. Schleyer and C. J. Lancelot, *J. Am. Chem. Soc.*, **91**, 4297 (1969).

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

Charles J. Lancelot,[7] Paul von Ragué Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received March 3, 1969

Participation by Neighboring Aryl Groups. IV. Correspondence of Rate and Product Data. Mechanistic Significance

Sir:

If phenonium ion intermediates are involved in solvolyses of β-arylalkyl systems, both *rates* and *products* should be affected, since both are controlled by transition states lying close to the intermediate in structure.[1] Since 1962, Brown[3] has repeatedly called attention to the "dilemma posed by the high degree of stereochemical control of substitution on the one hand, and the failure to observe significant rate enhancements on the other." This dilemma was already appreciated in 1949, by Cram and Winstein, the original workers in the field.[4]

The key to solution of the problem may possibly be found in consideration of the consequences of a dual-path solvolysis mechanism. For any general two-component reaction, $k = k_{\mathrm{I}} + k_{\mathrm{II}}$, a definite relationship exists between the fractional contribution of one component (*e.g.*, k_{I}/k) and the rate enhancement (*e.g.*, k/k_{II}): $k_{\mathrm{I}}/k = [(k/k_{\mathrm{II}}) - 1]/(k/k_{\mathrm{II}})$.[2c] Specific application to anchimerically assisted solvolysis, $k_t = Fk_\Delta + k_s$, reveals, for example, the surprising result that a titrimetric rate enhancement of only 4 ($k_t/k_s = 4$) corresponds to quite a large contribution of the anchimerically assisted component, 75% ($Fk_\Delta/k_t = 0.75$).[2c] Thus, a relatively small rate enhancement can be consistent with a major alteration of product stereochemistry.

One difficulty in the past has been that estimates of the "true" rate enhancements (corrected for inductive, steric, and other effects) have been unreliable, and have varied widely.[5] With such reliable values (*i.e.*, Fk_Δ and k_s) now available for 1-aryl-2-propyl tosylate solvolysis,[2] an opportunity is presented for the first time in β-arylalkyl systems[9] to compare quantitatively rate and product data.[10]

The acetolysis and formolysis of 1-phenyl-2-propyl tosylate can be analyzed by comparing the percentages of these reactions yielding product through phenyl-assisted pathways [$(Fk_\Delta/k_t) \times 100$] determined solely by kinetics,[2] with the stereochemical data (percentage retention of configuration) reported by Winstein[13] (Table I). The assumption was made that the aryl-assisted (Fk_Δ) pathway leads to retention of configuration in the ester product while the competing aryl-unassisted (k_s) pathway leads to inversion.[14,15] The close agreement shown in Table I demonstrates that *no major discrepancy between rate and product data, in fact, exists*, at least for the 1-phenyl-2-propyl system (our data), as well as for the primary β-arylalkyl systems examined by others.[12]

Table I. Comparison Rate and Product Data, 1-Phenyl-2-propyl Tosylate Solvolysis

Solvent	Rate enhancement (k_t/k_s)	% assisted pathway (Fk_Δ/k_t) × 100[a]	% retention configuration[13]
CH_3COOH	1.6	37 (100°)	35 (100°)
HCOOH	4.5	76 (75°)	85 (~80°)

[a] Average value from three methods; ref 2c, Table III.

The rate/product comparison for β-arylalkyl systems is more complicated than implied above, because *all* products, olefins as well as esters, must be taken into account, and the mechanisms responsible for their formation identified. The aryl-unassisted (k_s) process can give rise to olefins as well as inverted ester, but also through the intervention of artifacts,[16] some ester of retained configuration.[15] Neighboring hydride participation can also occur;[17] olefins are usually the chief products from this route. Such participation also influences k_t, and must be taken into account. Finally, the phenyl-assisted route (Fk_Δ) seems to be the cleanest process of all since ester with retained configuration is the overwhelmingly major product, although trace amounts of olefin, tending to be of the terminal rather than the internal type, have also been found.[18,19] A complete rate/product comparison must take all these complications and others[15] into account, and must be based on 100% product balance. In practically no case in the literature is all of the necessary data available. In the absence of such data, we propose the use of the *percentage yield of ester with retained configuration* as a better approximation for the Fk_Δ product than "% retention," used in Table I. Few olefins arise from the phenonium ion; it is probable that olefins are lost by polymerization, etc., more than are esters. Table II

---

(1) For leading references, see the first of the present set of papers.[2a]

(2) (a) C. J. Lancelot and P. von R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4291 (1969); (b) *ibid.*, 91, 4294 (1969); (c) *ibid.*, **91**, 4296 (1969).

(3) Footnote 6, paper I.[2a]

(4) D. J. Cram, *J. Am. Chem. Soc.*, 71, 3863 (1949).

(5) For example, in the acetolysis of 3-phenyl-2-butyl tosylate, the highest rate enhancement yet reported is a factor of 43,[6] based on *ionization* rates [$(k_\Delta + k_s)/k_s$]. However, estimates of the corresponding *titrimetric* rate enhancement [$(Fk_\Delta + k_s)/k_s$; $F \sim 0.25$] have varied from ten[6] to near unity.[7] Reliable methods[2] give estimates in the range 2.5–4.0.[8]

(6) D. J. Cram and J. A. Thompson, *J. Am. Chem. Soc.*, **89**, 6766 (1967).

(7) See J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968), footnote 27.

(8) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) C. J. Kim and H. C. Brown, *ibid.*, 91, 4289 (1969).

(9) *Cf.* also ref 8.

(10) Such quantitative correspondence of rate and product data has been shown for a number of primary and a few secondary systems, with remotely substituted "neighboring" groups.[11] In such systems, the neighboring groups have small inductive and steric effects. These are negligible in the case of primary but not in the case of secondary substrates. Thus, rate constants in the absence of anchimeric assistance could be estimated reliably for such primary cases, but uncertainty remained in the secondary estimates.[11b,d] In other primary systems, with neighboring groups nearer the reaction site, product composition also has been found to correlate with kinetics.[12]

(11) (a) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956); R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**: (b) 3105, (c) 3114 (1957); (d) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (e) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (f) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965); (g) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1314 (1965); (h) R. Muneyuki and H. Tanida, *ibid.*, **90**, 656 (1968).

(12) (a) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, 41, 807 (1958); (b) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3504 (1965); (c) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); (d) R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968); (e) J. L. Coke, *et al.*, *J. Am. Chem. Soc.*, **91**, 1154, 4284 (1969).

(13) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952).

(14) In *all* cases where rate enhancements are compared with product distributions, it is essential to use the *titrimetrically* determined solvolysis rate constants, k_t. Although this gives an incomplete measure of the *total* anchimerically assisted ionization rate (k_Δ) in the event of internal return, nevertheless it leads to the correct determination of the fraction of the assisted path (Fk_Δ) which leads to substitution and elimination product.[2a]

(15) A. Streitwieser, Jr., *et al.*, *J. Am. Chem. Soc.*, **87**, 3682, 3686 (1965); H. Weiner and R. A. Sneen, *ibid.*, **87**, 287, 292 (1965); R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969); M. C. Whiting, *et al.*, *J. Chem. Soc.*, 355, 365 (1968).

(16) Attack of tosylate by toluenesulfonic acid, formed during the reaction, followed by substitution with inversion; addition of solvent to the product olefin; racemization of acetate under the reaction conditions.[15]

(17) D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964); **74**, 2137 (1952).

(18) See S. Winstein and R. Baker, *ibid.*, **86**, 2071 (1964).

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

summarizes the available data on two secondary β-arylalkyl systems.

Table II. Refined Comparison, Rate and Product Data, Secondary β-Arylalkyl Systems

Arenesulfonate	Solvent	Rate enhancement (k_t/k_s)	% assisted pathway [$F(k_\Delta/k_t) \times 100$][2c]	% yield of ester with retained configuration
1-Phenyl-2-propyl	HOAc	1.6[2]	37	25[a]
	HCOOH	4.5[2]	76	68[13]
	CF_3COOH	564[19]	99.8	~100[19]
threo-3-Aryl-2-butyl, Ar =				
p-$CH_3OC_6H_4$	HOAc	363[c]	99.7	99.7[18]
C_6H_5	HOAc	4[8a]	75	78[b]
p-$NO_2C_6H_4$	HOAc	1.0[6]	~0	1[6]
	HCOOH	1.0[6]	~0	4[6]

[a] Calculated from stereochemical data of Winstein[13] (Table I) plus product analyses repeated in these laboratories: 70% secondary ester + 30% various olefins. [b] Includes 49% ester with retained configuration + 29% olefin demonstrated to arise *via* hydride participation.[17] [c] Determined by a Hammett-Taft treatment, using data extrapolated from other temperatures.[13,18] See ref 2b, footnote 8. σ^* constant for p-$CH_3OC_6H_4CH(CH_3)$ estimated as -0.13.

The close agreement between rate and product data in Table II has major implications, for it suggests that the assumed *separation* and *independence* of the aryl-unassisted (k_s) and aryl-assisted (Fk_Δ) pathways (implicit in the mathematical form of the equation, $k_t = Fk_\Delta + k_s$) actually exist; that is, such a separation is more than just a convenient way of formulating these reactions. Indeed, these solvolyses actually do appear to involve two discrete pathways, between which there is no crossover. It is important to rationalize this striking result.

To do this, it is necessary first to consider the nature of the aryl-unassisted process. If this involves essentially open carbonium ions or ion pairs ("k_c" in the original terminology of Winstein)[20] then there is no reason why crossover should not occur, for the interconversion between open and bridged cations should be extremely easy, and should involve only very small activation energies.[21]

However, if such crossover were to take place, there would be no reason to expect correspondence of rate and product data. Such correspondence would *only* be possible in the highly fortuitous circumstance that the differences in rate-determining and product-determining transition state energies of the two pathways matched exactly and compensated for the loss of mechanistic independence due to the crossover equilibria.

In fact, there are indications that correspondence of rates and products does *not* occur in tertiary systems,[22] where open carbonium ions probably are involved.

If the aryl-unassisted solvolysis involves instead transition states and intermediates strongly bound at the rear to the solvent, rather than open ions or ion pairs, then crossover cannot occur. Interconversion of strongly bound intermediates (aryl-bound and solvent-bound) should require high activation energies. Thus, such strongly covalently solvated species are much more nearly compatible with our results than are open, essentially unsolvated carbonium ions or ion pairs.

This conclusion is consistent with current theory concerning the nature of the solvolysis of *primary* systems: predominate solvent participation must occur in the aryl-unassisted pathway, since primary cations are far too unstable to exist in solution.[23,24] However, *secondary* aliphatic systems are not thought to solvolyze in a manner similar to primary: they "approach the **Lim.** category in acetic acid and more closely in formic acid."[23] While Sneen and Streitwieser have presented evidence that the solvolysis of simple secondary arenesulfonates under these conditions proceeds through rate-limiting ion-pair formation, neither author has suggested that solvent participates nucleophilically in this process.[15] Although Winstein at one time defined the k_s process as "solvent assisted,"[25] he has been less definite in his most recent papers, and the k_s process termed merely "anchimerically unassisted."[12c,18] We have used this definition of k_s until now in the present set of communications.

We are thus faced with a dilemma. Either the current theory of nucleophilically unassisted secondary solvolysis is incorrect, or we lack a satisfactory explanation for the experimentally observed correspondence of rate and product data. Since, in our opinion, the nature of the secondary solvolysis has not been correctly interpreted,[26] we therefore propose that k_s for simple secondary as well as for primary β-arylalkyl systems should be strongly accelerated by solvent assistance.[27]

If this proposal is correct, then the detection of any rate enhancement due to anchimeric assistance, *no matter how small*, is indicative of strong (not weak!) participation by the neighboring group. Such participation must be strong in order to compete with the already efficient solvent assistance. This picture of competition between two *strongly assisted* processes, k_s (solvent assisted) and k_Δ (neighboring group assisted), explains well why these processes are found to be discrete; since the transition states and the intermediates for k_s and k_Δ are both strongly bound, crossover between them is not observed. Likewise, rapidly equilibrating classical or partially bridged ion formulations[3] appear highly unlikely. These are essentially open carbonium ion processes, and open carbonium ions are not energetically accessible to the systems under consideration.

Acknowledgments. We wish to acknowledge many discussions and exchanges of information with Professor H. C. Brown and Dr. C. J. Kim. Professor

---

(20) S. Winstein and L. L. Ingraham, *J. Am. Chem. Soc.*, **77**, 1738 (1955), define k_c as the "ionization rate corresponding to no anchimeric assistance and no assistance from covalent solvation of C_α by a solvent molecule in the transition state."

(21) Evidence supporting this expectation is abundantly available from results of experiments in strong acid media. See G. A. Olah C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 5571 (1966); G. A. Olah, M. B. Comisarow, and C. J. Kim, *ibid.*, **91**, 1458 (1969).

(22) *Cf.* H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968). It is desirable to study such systems in greater detail, under strictly identical conditions.

(23) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); *cf.* ref 8a.

(24) Simple primary cations have never been observed even in strong media; see M. Saunders and E. L. Hagen, *ibid.*, **90**, 6881 (1968).

(25) *E.g.*, S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958), define k_Δ, k_s, and k_c, respectively, as the anchimerically assisted, the solvent assisted, and the totally unassisted routes.

(26) Experimental evidence to support this contention will be presented shortly.

(27) For this reason also we propose a return to the original definition of k_s,[25] as the solvent-assisted process.

James Coke and Professor Saul Winstein provided helpful comments. This research was supported by grants from the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (AI-07766).

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

Paul von Ragué Schleyer, Charles J. Lancelot[28]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received March 5, 1969

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]

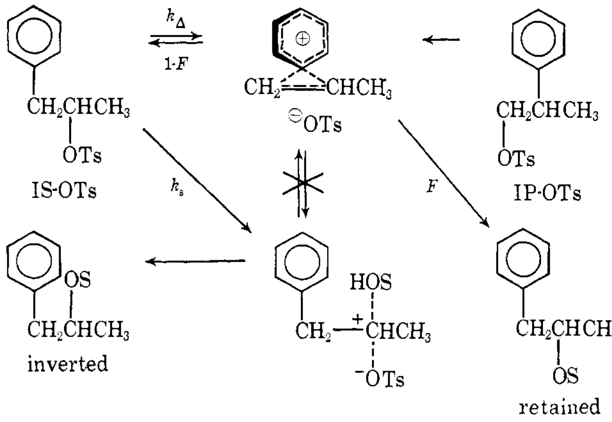
To the solvolysis of 1-phenyl-2-propyl OTs we have applied the same crucial test recently used for the 2-phenyl-1-ethyl system.[6a] On the basis of the mechanistic significance assigned to k_Δ, we should expect a quantitative correlation of k_Δ values with solvolysis rates (k_t) of neophyl OTs,[8] for 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

---

[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).