Table II. Products from Acetolysis of Substituted *threo*-3-Phenyl-2-butyl Brosylates

Substituent	Temp, °C	Product, %			Acetate configuration, %	
		Olefin	*t*-Acetate	*sec*-Acetate	*threo*	*erythro*
p-Methoxy[a]	50	0.3	0	99.7	100	0
Hydrogen[b,c]	75	35[f]	0	53[f]	96	4
Hydrogen[d,g]	50	52.6	0.1	47.3	96	4
	75	52.1	0	47.9	97	3
p-Chloro[d]	75	48	1	51	86	14
m-Chloro[d]	100	72	2	26	57	43
m-Trifluoromethyl[d]	100	76	3	21	30	70
p-Nitro[e,c]	100	68[f]		13[f]	7	93

[a] Reference 5a. [b] D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); **74**, 2129 (1952). [c] Tosylate. [d] Present study. Each run was 0.05 *M* in the substrate and 0.053 *M* in sodium acetate. [e] Reference 6. [f] Isolated yields. Other yields by glpc. [g] S. Sivaram's data.

stituent constants, σ^+ [13] (Figure 2). This result indicates that in this system considerable charge is delocalized in the transition state into the phenyl ring and its activated derivatives. Evidently the geometrical situation is more favorable for such interaction in this system than in the corresponding *trans*-2-arylcyclopentyl derivatives.[14] Data for the products of solvolysis are summarized in Table II.

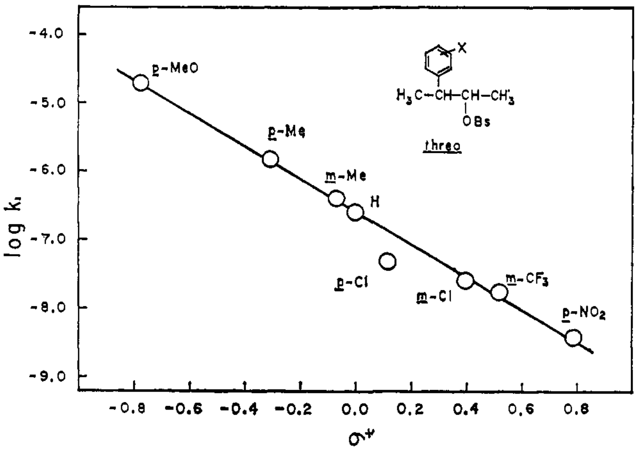

Figure 2. Rates of acetolysis at 25.0° of *threo*-3-aryl-2-butyl brosylates *vs.* the σ^+ constants ($\rho = -2.4$).

A striking feature is the regular increase in the yield of secondary acetate from *p*-nitro to *p*-methoxy. At the same time the percentage of acetate product which arises from stereochemical retention increases from 7% for *p*-nitro to 100% for *p*-methoxy. The results on the yield of acetate product were much less regular in the case of the *trans* series,[3] increasing markedly only for the *p*-methoxy derivative, the only derivative which exhibited a rate enhancement over that predicted by the correlation.

The percentage of retention in the acetate products in the *trans* series rises regularly from 0% for *p*-nitro to 98% for *p*-methoxy,[3] and in the *threo* series from 7% for *p*-nitro to 100% for *p*-methoxy. Consequently, both series exhibit a variation in the stereochemistry of substitution over almost the entire possible range from 100% inversion to 100% retention. At the same time application of the same quantitative approach, the Hammett correlation, to the data reveals only minor rate enhancement in the *trans* series, whereas major rate enhancement attributable to aryl participation is indicated in the *threo* series.

This suggests that the rate data may not reveal rate enhancements in systems which undergo substitution with retention. Such cases would be consistent with a mechanism in which stereochemistry was controlled by rapidly equilibrating cations,[1,15] or with a mechanism in which ionization occurred to an essentially unbridged ion pair, followed by bridging prior to attack of solvent,[16] or with a mechanism involving competing k_s and k_Δ processes that are comparable in magnitude.[17]

These results point up the urgent need to clarify the precise processes involved in the acetolysis of secondary alkyl arenesulfonates.

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[13] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 80, 4979 (1958).

[14] D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, 88, 5350 (1966).

[15] S. Winstein and B. K. Morse, *ibid.*, 74, 1133 (1952).

[16] See ref 3 for a fuller consideration of the possibilities.

[17] This problem of an objective approach to rate enhancements in the acetolysis of secondary β-arylakyl arenesulfonates and the precise processes involved in such solvolyses is considered in an accompanying group of publications by C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4291, 4294, 4296, 4297 (1969).

[18] Purdue Research Foundation Fellow, 1966–1968; Postdoctoral Research Associate, 1968–1969, on a Grant (GP 6492 X) supported by the National Science Foundation.

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Participation by Neighboring Aryl Groups. I. Determination of Assisted and Nonassisted Solvolysis Rates by Hammett Correlation[1]

Sir:

Phenonium ions were first postulated as intermediates in the solvolysis of β-arylalkyl systems in order to explain the remarkable stereochemical product control by the aryl groups.[2] For example, acetolysis of *erythro*-3-phenyl-2-butyl tosylate gave acetate (68% yield) with 96% retention of configuration.[2] In contrast, the observed rate enhancements, if any, produced by β-aryl groups are typically quite small. In fact, if titrimetric rates are compared, both diastereomeric 3-phenyl-2-butyl tosylates acetolyze almost two times *slower* than the parent 2-butyl tosylate.[3]

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[1] This set of four communications was presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN 4, and at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 1968.

[2] D. J. Cram, *J. Am. Chem. Soc.*, 71, 3863 (1949); 74, 2129 (1952).

[3] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952).

It is this apparent discrepancy between product and rate data which has been chiefly responsible for the current controversy concerning the definition of the role of β-aryl groups in solvolysis reactions.[4-10]

However, other factors must be taken into account. Since β-aryl groups introduce steric, inductive, as well as potential anchimeric assistance effects, and the possibility of internal return exists, it is clear that the "raw" rate data must be corrected to obtain the "true" rate enhancement values. Unfortunately, estimates of the magnitudes of the corrections needed vary widely,[4] and it is clear that more accurate evaluation methods must be employed.

We describe here the first of three approaches to determine the true rate enhancements. In this series of analyses, the measured titrimetric rates, k_t, in the absence of added salt, were taken as the total solvolysis rate. We have employed Winstein's definitions whereby the anchimerically unassisted pathway is designated k_s, while the aryl-assisted route is designated k_Δ.[9] However, in the event of internal return, only that fraction of the aryl-assisted reaction which yields product, Fk_Δ, will contribute to the total titrimetric rate, k_t, the balance, $(1 - F)k_\Delta$, undergoing ion-pair return.[9,10b] Thus, the working relationship may be expressed as $k_t = Fk_\Delta + k_s$.[11]

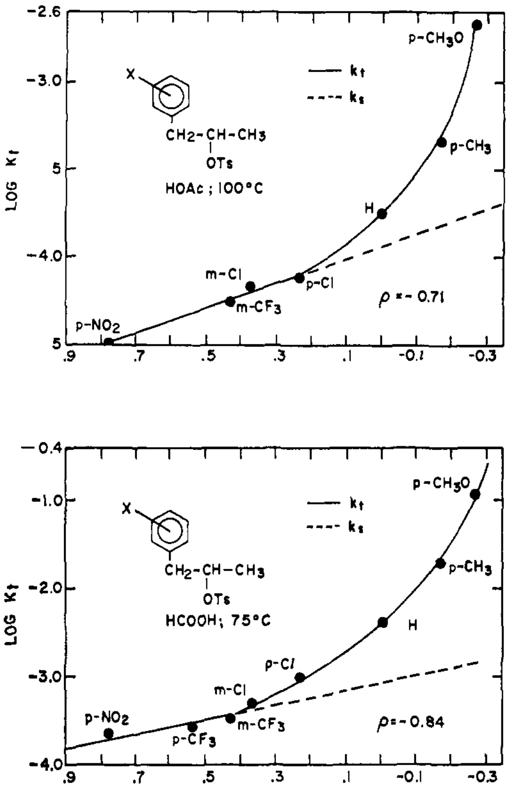
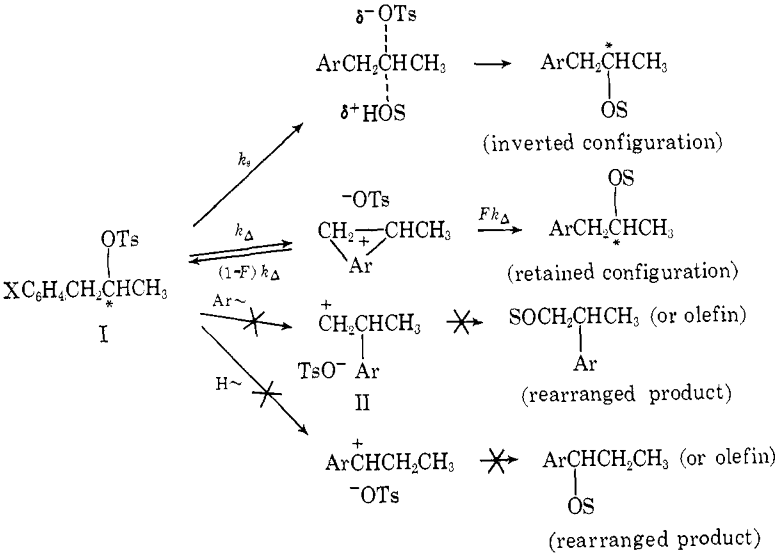


Figure 1. Log k_t vs. σ; 1-aryl-2-propyl tosylates.

The unsymmetrical 1-aryl-2-propyl system (I) was chosen for study because it is structurally disposed against both aryl participation[7,13] and aryl rearrangement,[14] and it is less prone to potentially complicating hydride shift processes.[13,14] This simplifies the kinetic analysis, for the finding of *any* anchimerically assisted contribution (Fk_Δ) to the total solvolysis rate (k_t) for members of this system can be explained *only* by aryl bridging, since there is neither steric nor electronic driving force for the formation of the less stable, primary cation (II) by aryl migration.



Hammett plots (Figure 1) of the acetolysis and formolysis data (Table I) for a series of 1-phenyl-2-propyl

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[4] Recent papers contain comprehensive bibliographies.[5-10]

[5] D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964); D. J. Cram and J. Thompson, *ibid.*, **89**, 6766 (1967); **91**, 1778 (1969).

[6] (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 140 ff; (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965); (c) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967); (d) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968).

[7] J. E. Nordlander and W. E. Deadman, *ibid.*, **90**, 1590 (1968).

[8] M. D. Bentley and M. J. S. Dewar, *ibid.*, **90**, 1075 (1968).

[9] A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

[10] (a) R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968); (b) J. F. Coke, *et al.*, *J. Am. Chem. Soc.*, **91**, 1154, 4284 (1969).

[11] Alternatively, the total rate, k, may be determined polarimetrically (k_α), or from label scrambling[10b] or salt effect data (k_{ext}),[12] in which cases the anchimerically assisted ionization rate, k_Δ, is measured directly.

[12] S. Winstein, R. Baker, and S. Smith *J. Am. Chem. Soc.*, **86**, 2072 (1964), and earlier papers in this series.

[13] J. E. Nordlander and W. J. Kelly, *ibid.*, **91**, 996 (1969).

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

Table I. Solvolysis Rates of 1-Aryl-2-propyl Tosylates; $XC_6H_4CH_2CH(OTs)CH_3$

X	Solvent	Temp, °C	k_t, sec^{-1}	Rel rates		$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
				HOAc, 100°	HCOOH, 75°		
p-CH_3O	HOAc	100.0[a,b]	2.21×10^{-3}	12		24.1	−6.4
	HCOOH[14]	24.12	$(3.89 \pm 0.04) \times 10^{-4}$			22.7	2.3
		34.92	$(1.53 \pm 0.01) \times 10^{-3}$				
		75.00[b]	1.24×10^{-1}		31		
p-CH_3	HOAc	101.1[c]	$(4.72 \pm 0.03) \times 10^{-4}$	2.6			
	HCOOH	25.16	$(9.00 \pm 0.01) \times 10^{-5}$			21.7	−4.4
		50.00	$(1.66 \pm 0.05) \times 10^{-3}$				
		75.00[b]	1.97×10^{-2}		4.9		
H	HOAc	100.0[d]	1.84×10^{-4}	1.0		26.5	−5.0
	HCOOH	25.12	$(1.35 \pm 0.02) \times 10^{-5}$			22.4	−5.6
		50.00	$(3.04 \pm 0.01) \times 10^{-4}$				
		75.00[b]	3.99×10^{-3}		1.0		
p-Cl	HOAc	100.0	$(7.82 \pm 0.07) \times 10^{-5}$	0.42			
	HCOOH	50.16	$(6.86 \pm 0.02) \times 10^{-5}$			23.0	−6.7
		75.28	$(9.75 \pm 0.51) \times 10^{-4}$				
		75.00[b]	9.48×10^{-4}		0.24		
m-Cl	HOAc	100.3	$(6.86 \pm 0.14) \times 10^{-5}$	0.38			
	HCOOH	50.11	$(3.26 \pm 0.10) \times 10^{-5}$			23.2	−6.2
		75.12	$(4.92 \pm 0.08) \times 10^{-4}$				
		75.00[b]	4.86×10^{-4}		0.12		
m-CF_3	HOAc	100.4	$(5.68 \pm 0.06) \times 10^{-5}$	0.31			
	HCOOH	50.11	$(2.36 \pm 0.05) \times 10^{-5}$			22.9	−9.1
		75.12	$(3.28 \pm 0.05) \times 10^{-4}$				
		75.00[b]	3.23×10^{-4}		0.081		
p-CF_3	HCOOH	75.04	$(2.55 \pm 0.20) \times 10^{-4}$		0.064		
p-NO_2	HOAc	100.2	$(3.28 \pm 0.11) \times 10^{-5}$	0.18		26.0	−9.8
		124.7[c]	$(3.04 \pm 0.06) \times 10^{-4}$				
	HCOOH	50.00	$(1.32 \pm 0.03) \times 10^{-5}$			24.8	−4.4
		75.00	$(2.22 \pm 0.10) \times 10^{-4}$		0.056		

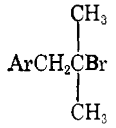
[a] Reference 14. [b] Calculated from data at other temperatures. [c] Determined by a conductometric method, as were all formolyses. [d] J. J. Harper, Ph.D. Thesis, Princeton University, 1968; W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, 95, 834 (1962), give $\Delta H^{\ddagger}$ = 23.7 kcal/mol and $\Delta S^{\ddagger}$ = −12.8 eu while S. Winstein, *et al.*,[14] give $\Delta H^{\ddagger}$ = 27.3 kcal/mol and $\Delta S^{\ddagger}$ = −2.7 eu.

Table II. Partitioning of Rates for 1-Aryl-2-propyl Tosylates; $XC_6H_4CH_2CH(OTs)CH_3$

X	Solvent	Temp, °C	k_s, sec^{-1}	Rel[a] k_s	Fk_Δ, sec^{-1}	Rel[a] Fk_Δ	k_t/k_s	$Fk_\Delta/k_t \times 100$
p-CH_3O	HOAc	100	1.86×10^{-4}	1.6	2.02×10^{-3}	17.3	12	91
	HCOOH[b]	50	1.2×10^{-4}	1.7	8.94×10^{-3}	132	76	99
		75	1.41×10^{-3}	1.7	1.23×10^{-1}	146	88	99
p-CH_3	HOAc	100	1.55×10^{-4}	1.3	3.17×10^{-4}	2.7	3.0	67
	HCOOH[c]	50	9.8×10^{-5}	1.4	1.56×10^{-3}	22.6	17	94
		75	1.17×10^{-3}	1.4	1.85×10^{-2}	21.8	17	94
p-H	HOAc	100	1.17×10^{-4}	1.0	6.70×10^{-5}	0.6	1.6	36
	HCOOH[c]	50	6.9×10^{-5}	1.0	2.35×10^{-4}	3.7	4.4	77
		75	8.50×10^{-4}	1.0	3.14×10^{-3}	3.4	4.7	79

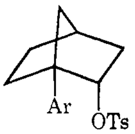
[a] Based on k_s phenyl for each solvent at the temperature indicated. [b] $\Delta S_s^{\ddagger} = -10$ eu, $\Delta S_\Delta^{\ddagger} = +2$ eu. [c] $\Delta S_s^{\ddagger} \sim -10$ eu, $\Delta S_\Delta^{\ddagger} \sim -5$ eu.

tosylate derivatives (I) reveal features expected on the basis of the behavior of the extreme model systems, III,[6d,15] IV,[16] V,[17] and VI.[18]

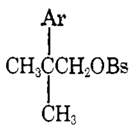


$$ArCH_2\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}Br$$

III

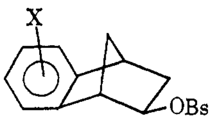


IV



$$CH_3\overset{\overset{\large Ar}{|}}{\underset{\underset{\large CH_3}{|}}{C}}CH_2OBs$$

V



VI

When the substituents, X, in I are sufficiently deactivating, no participation by aryl is observed, and the compounds react by the unassisted pathway (k_s). Rate data from such compounds, when plotted against σ constants (Figure 1), give correlation lines with low slopes ($\rho = -0.71$, acetolysis; -0.84, formolysis), reflecting the (relatively minor) inductive effects of the β-aryl rings. *The extrapolation of these correlation lines defines the k_s contributions for the other substituents.* III ($\rho = -1.11$,[15] -0.65[6d]) and IV ($\rho = -1.06$)[16] are models for such anchimerically unassisted behavior.

Activation of the aryl rings in I by sufficiently electron-releasing substituents, X, facilitates participation. The values of k_t for such substrates necessarily deviate (Figure 1) from the k_s line defined by the deactivated compounds: the extent of this deviation is a measure of Fk_Δ. Model substances V[17] and VI,[18] solvolyzing by anchimerically assisted pathways, give ρ values near −3. These values are substantially larger in absolute magnitude than those from III and IV, due to the greater delocalization of positive charge into the bridging aryl rings.

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(15) A. Landis and C. A. VanderWerf, *J. Am. Chem. Soc.*, 80, 5277 (1958); *cf.* M. M. Tessler and C. A. VanderWerf, *J. Org. Chem.*, **30**, 405 (1965).

(16) D. C. Kleinfelter and P. von R. Schleyer, 138th National Meeting of the American Chemical Society, New York, N. Y. Sept 1960, Abstracts, p 43P; D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960; *Dissertation Abstr.*, **22**, 428 (1961); J. A. Berson in "Molecular Rearrangements" Part I, P. de Mayo, Ed., Interscience Publishers, Inc.,New York, N. Y., 1963, p 182.

(17) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3432 (1957).

(18) H. Tanida, private communication; *cf.* D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 1901 (1968); H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, **90**, 2688 (1968); H. C. Brown and G. L. Trittle, *ibid.*, **90**, 2689 (1968); H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

Both in acetic and in formic acids, participation in I is observed for phenyl, *p*-tolyl, and *p*-anisyl groups. Estimates for k_s and for Fk_Δ for these compounds are compiled in Table II. Although the rate enhancement (k_t/k_s) for the acetolysis of I (X = H) is small (1.6), it is seen that 36% ($Fk_\Delta/k_t \times 100$) of the reaction is passing through the assisted (k_Δ) pathway. For formolysis of I (X = OCH_3), where $k_t/k_s = 88$ at 75°, virtually the entire reaction (99%) is assisted. In consonance with earlier suggestions[7,19] the anchimerically unassisted (k_s) processes have more negative activation entropies than their assisted (Fk_Δ) counterparts.

The following papers provide further discussion and analysis.

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.

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[19] S. Winstein and R. Heck *J. Am. Chem. Soc.*, **78**, 4801 (1956); D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963).

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

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Participation by Neighboring Aryl Groups. II. Accurate Determinations of Inductive and Anchimeric Assistance Effects by a Hammett–Taft Correlation

Sir:

We present here the second of three methods[1] for partitioning the observed solvolysis rate constants (k_t) of a set of 1-aryl-2-propyl tosylates into the constituent anchimerically unassisted (k_s) and assisted (Fk_Δ) constants.[2] The rate constants for the arylalkyl and related model alkyl systems are correlated by use of Taft σ^* constants.[3] An anchimerically unassisted Taft ρ^* line is established through the use of simple secondary aliphatic tosylates, which contain no neighboring groups capable of anchimeric assistance.[4] Accordingly, substrates whose rate constants deviate from this ρ^* correlation line must be solvolyzing under influences other than purely inductive ones.

The first correlation of secondary alkyl solvolysis rates with Taft σ^* constants is due to Streitwieser.[5] However, a variety of cyclic, acyclic, and branched substrates was used, and the resultant scatter of the points gave rise to a rather ill-defined ρ^* line. Nevertheless, certain compounds suspected of anchimeric assistance did deviate significantly from the line, and in this manner Streitwieser estimated the acceleration factor for several β-arylalkyl derivatives.[5a]

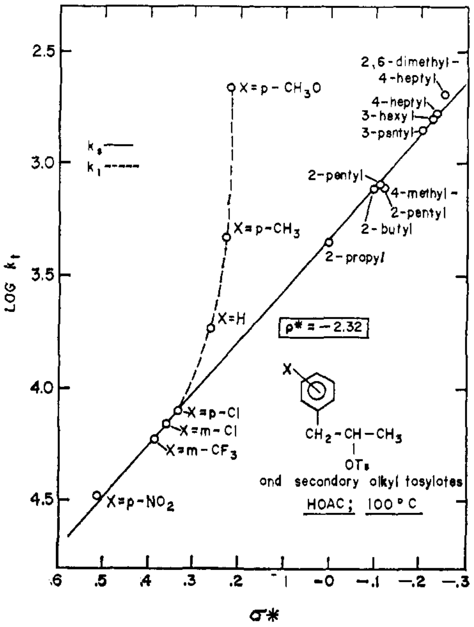

Figure 1. Acetolysis (100°) of β-aryl and simple secondary systems. For nonparticipating systems: $k_t = k_s$.

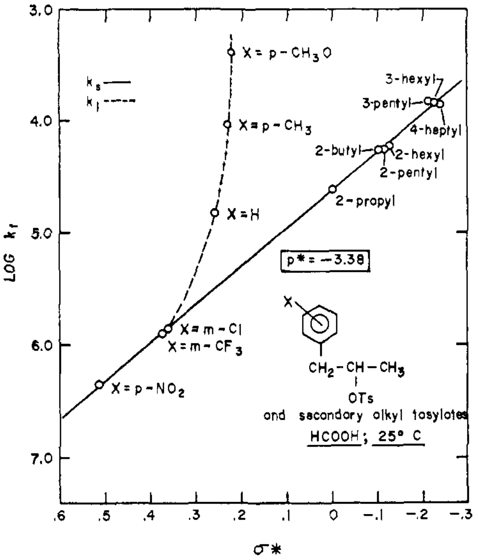

Figure 2. Formolysis (25°) of β-aryl and simple secondary systems. For nonparticipating systems: $k_t = k_s$.

More recent Taft correlations of aliphatic solvolysis rates[6–8] have concentrated on a somewhat narrower range of acylic systems. Pritzkow and Schöppler,[6] and later Peterson and coworkers,[7] found a reasonably good correlation, with a ρ^* value of −2.6, for the acetolysis of secondary systems without β-alkyl branching, and Peterson[7] extended his treatment to other solvents. Recent work in this laboratory,

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[1] C. J. Lancelot and P. von. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4291 (1969).

[2] See A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); E. F. Jenny and S. Winstein, *Helv. Chim Acta*, **41**, 807 (1958), and papers cited therein.

[3] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 556 ff.

[4] In order to ensure the absence of either hydrogen or alkyl participation, and the minimization of steric effects, aliphatic substrates are chosen which either are unbranched or are branched no closer than the γ-carbon atom.

[5] (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 122, 146; (b) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **78**, 4935 (1956).

[6] W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962).

[7] P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.*, **87**, 5169 (1965).

[8] J. J. Harper, Ph.D. Thesis, Princeton University, 1968. Some of these data are included in Table I. Unsatisfactory results are obtained when systems with β-alkyl branching are included.[4]