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.

---

[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.

Charles J. Lancelot,[20] Paul von Ragué Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received March 3, 1969

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]

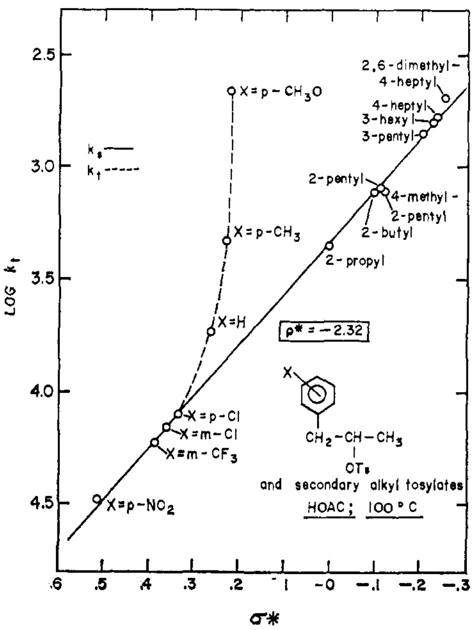


Figure 1. Acetolysis (100°) of β-aryl and simple secondary systems. For nonparticipating systems: $k_t = k_s$.

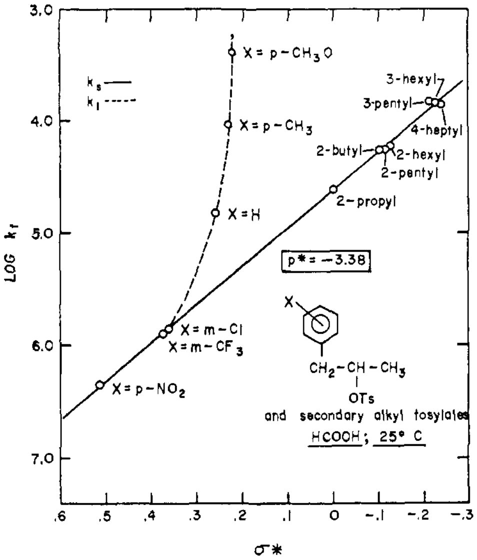


Figure 2. Formolysis (25°) of β-aryl and simple secondary systems. For nonparticipating systems: $k_t = k_s$.

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,

---

[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]

Table I. Solvolysis Rates (k_t) for a Series of Secondary Alkyl Tosylates; RCH(OTs)R′[a,b]

R	R′	Solvent	Temp, °C	k_t, sec^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
CH_3	CH_3	HOAc	75.0	$(3.60 \pm 0.07) \times 10^{-5}$	24.7	−8.3
			100.0	$(4.22 \pm 0.10) \times 10^{-4}$	(25.4)[6]	(−5.8)[6]
		HCOOH	25.0[7]	2.38×10^{-5}		
			50.10	$(5.28 \pm 0.15) \times 10^{-4}$	19.5	−13.3
			75.12	$(4.88 \pm 0.02) \times 10^{-3}$		
CH_3CH_2	CH_3	HOAc	75.0	$(6.58 \pm 0.05) \times 10^{-5}$	24.9	−6.6
			100.0	$(7.61 \pm 0.10) \times 10^{-4}$	(26.4)[6]	(−1.8)[6]
		HCOOH	25.0[7]	5.50×10^{-5}		
$CH_3(CH_2)_2$	CH_3	HOAc	75.0	$(6.42 \pm 0.15) \times 10^{-5}$	25.4	−5.1
			100.0	$(8.06 \pm 0.10) \times 10^{-4}$		
		HCOOH	25.0[7]	5.35×10^{-5}		
$CH_3(CH_2)_3$	CH_3	HCOOH	25.0[7]	5.43×10^{-5}		
CH_3CH_2	CH_3CH_2	HOAc	75.0	$(1.20 \pm 0.02) \times 10^{-4}$	24.6	−7.7
			100.0	$(1.46 \pm 0.01) \times 10^{-3}$		
		HCOOH	25.0[7]	1.41×10^{-4}		
			75.72	$(1.83 \pm 0.09) \times 10^{-2}$		
$CH_3(CH_2)_2$	CH_3CH_2	HOAc	75.0	$(2.24 \pm 0.04) \times 10^{-4}$	25.1	−4.5
			100.0	$(1.62 \pm 0.03) \times 10^{-3}$		
		HCOOH	25.0[7]	1.38×10^{-4}		
			75.72	$(2.33 \pm 0.05) \times 10^{-2}$		
$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	HOAc	75.0	$(1.31 \pm 0.01) \times 10^{-4}$	25.9	−2.1
			100.0	$(1.73 \pm 0.03) \times 10^{-3}$		
		HCOOH	25.0[7]	1.32×10^{-4}		
$(CH_3)_2CHCH_2$	CH_3	HOAc	75.0	$(6.51 \pm 0.48) \times 10^{-5}$	25.8	−4.1
			100.0	$(7.76 \pm 0.06) \times 10^{-4}$		
		HCOOH	75.72	$(1.25 \pm 0.02) \times 10^{-2}$		
$(CH_3)_2CHCH_2$	$(CH_3)_2CHCH_2$	HOAc	75.0	$(1.54 \pm 0.01) \times 10^{-4}$	26.3	−0.8
			100.0	$(2.02 \pm 0.02) \times 10^{-3}$		

[a] Several investigators have reported data for some of the compounds in this table, *e.g.*, ref 5, 6, and 7. For consistency, we have used Peterson's formolysis data at 25°,[7] and our own data otherwise. [b] All formolyses were followed conductometrically with a self-balancing, recording Wheatstone bridge.

Table II. Least-Squares ρ^* Values for Taft Plots for Solvolysis of Secondary Tosylates

Reaction	ρ^* value	Correl coeff	ρ^*, alkyl groups only
HOAc, 100° (Figure 1)	−2.32	−0.998	−2.60[8]
HCOOH, 25° (Figure 2)	−3.38[a]	−0.998	−3.41[a]
HCOOH, 75°	−2.88	−0.996	−2.98

[a] Peterson, *et al.*,[7] have reported ρ^* as −3.50.

Table III. Partitioning of Rates for 1-Aryl-2-propyl Tosylates, $XC_6H_5CH_2CH(OTs)CH_3$

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	1.38×10^{-4}	1.2	2.07×10^{-3}	18	16	94
	HCOOH[b]	25	3.98×10^{-6}	1.3	3.85×10^{-4}	123	98	99
		75	1.12×10^{-3}	1.3	1.23×10^{-1}	140	110	99
p-CH_3	HOAc	100	1.35×10^{-4}	1.2	3.37×10^{-4}	2.9	3.5	71
	HCOOH[c]	25	3.80×10^{-6}	1.3	8.62×10^{-5}	29	24	96
		75	1.10×10^{-3}	1.2	1.86×10^{-2}	21	18	94
H	HOAc	100	1.15×10^{-4}	1.0	6.90×10^{-5}	0.6	1.6	38
	HCOOH[c]	25	3.02×10^{-6}	1.0	1.05×10^{-5}	3.5	4.5	78
		75	8.91×10^{-4}	1.0	3.10×10^{-3}	3.5	4.5	78

[a] Based on k_s for X = H at the temperature and in the solvent indicated. [b] $\Delta S_s^\ddagger = -7.5$ eu; $\Delta S_\Delta^\ddagger = +3.5$ eu. [c] $\Delta S_s^\ddagger \approx -7$ eu; $\Delta S_\Delta^\ddagger \approx -5$ eu.

expanding the range of aliphatic substrates studied in acetic acid to include many γ-branched derivatives, also gave a ρ^* of −2.6.[8]

The reliability of the Taft correlation used to detect and to assess the anchimeric assistance (Figures 1 and 2) provided by β-aryl groups has been further increased in the present study through the inclusion of the data for *deactivated* 1-aryl-2-propyl derivatives,[1] thus extending the range of available σ^* constants.[9] Table II, listing the least-squares ρ^* values obtained and the correlation coefficients (>0.996) for these plots (Figures 1 and 2), shows that points for the deactivated 1-aryl-2-propyl derivatives indeed would lie very close to lines determined solely by the alkyl systems. This confirms our conclusion[1] that these deactivated systems solvolyze entirely *via* the anchimerically unassisted (k_s) pathway.

Figures 1 and 2 reveal significant deviations from the ρ^* line for the points representing 1-phenyl-, 1-p-tolyl-, and 1-p-anisyl-2-propyl tosylates. These deviations are not caused by steric factors because the deactivated aryl derivatives, with the same bulk in the vicinity of the reaction site, fall nearly exactly on the line. Furthermore, alkyl systems containing the isobutyl group, which is bulkier than the benzyl group,[11] also fall well on the line both in acetolysis (Figure 1) and in for-

[9] σ^* constants for the benzyl groups were calculated from ionization constant data for the corresponding arylacetic acids.[3,10]

[10] G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution, Butterworth & Co. (Publishers), Ltd., London, 1961.

[11] The Taft steric substituent constant, E_s, for the isobutyl group (−0.93) is more than double that of the benzyl group (−0.35).[3]

molysis. It must be concluded that the solvolysis of the deviate aryl derivatives contains a contribution from the anchimerically assisted (Fk_Δ) path. As was the case in the Hammett treatment of these substrates, k_s for each deviate point is found by extrapolation to the ρ^* line, and Fk_Δ is readily calculated as the difference between k_s and k_t. Table III lists the derived values of all pertinent rate constants, the rate enhancement, k_t/k_s, and the per cent reaction proceeding *via* Fk_Δ. The rate enhancements (k_t/k_s) are found to vary from a factor of 1.6 (1-phenyl-2-propyl tosylate, HOAc) to a factor of 100 (1-anisyl-2-propyl tosylate, HCOOH). The significance of these results is discussed in the last paper[12] of the present series.

Excellent agreement is found between the k_s and Fk_Δ values as determined by both the Taft (Table III) and the Hammett (ref 1, Table II) treatments. A third treatment,[13] not dependent on the possibly questionable choice of σ constants,[14] confirms the validity of these values.

Acknowledgments. This research was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the Petroleum Research Fund, administered by the American Chemical Society. We thank Mr. Paul Garrison and staff, FMC Corporation, Princeton, N. J., for the figures in this and the preceding paper.[1]

---

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

[13] C. J. Lancelot and P. von R. Schleyer, *ibid.*, **91**, 4296 (1969).

[14] C. G. Swain and E. C. Lupton, Jr., *ibid.*, **90**, 4328 (1968).

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

Charles J. Lancelot,[15] Jon J. Harper,[8] Paul von Ragué Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

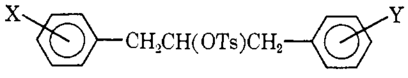
Received March 3, 1969

Participation by Neighboring Aryl Groups. III. Accurate Determination of Inductive and Anchimeric Assistance Effects by a Novel Multiple Substitution Technique

Sir:

We have employed a multiple substitution technique, the last and most novel of three methods,[1] to separate the observed solvolysis rate constants (k_t) for a series of β-arylalkyl tosylates into their constituent anchimerically unassisted (k_s) and assisted (Fk_Δ) rate components, $k_t = k_s + Fk_\Delta$.[2]

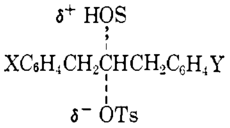
The systems examined are 1,3-diaryl-2-propyl derivatives, I. While *both* aryl rings in such compounds can exert inductive and steric effects simultaneously, *only one* of the β-aryl groups can participate at any given instant. If both rings were to bridge in the transition state, carbon would be hexacoordinate, if partial attachment of the leaving group is included; this situation is impossible. Thus, the β-aryl groups must participate *competitively*, but both rings exert inductive/steric effects *cooperatively*. This is the key principle of the present method.


I

It is convenient, in applying this method, to choose 2-propyl tosylate as the nonparticipating reference compound, and to designate its rate constant k_0. The solvolysis rate of any substituted 2-propyl tosylate can be expressed as some function of k_0. For example, eq 1 applies to 1-aryl-2-propyl tosylates. Here, the anchimerically unassisted rate constant, k_s, is related to k_0 by the inductive/steric factor, s (*i.e.*, $k_s = sk_0$), and Fk_Δ is similarly related to k_0 by the anchimeric assistance factor, Δ (*i.e.*, $Fk_\Delta = \Delta k_0$).

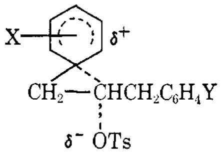
$$k_t = sk_0 + \Delta k_0$$

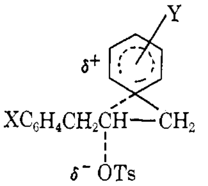
$$k_t = k_0(s + \Delta) \tag{1}$$



$$\begin{array}{c} \delta^+\ \mathrm{HOS} \\ \vdots \\ \mathrm{XC_6H_4CH_2CHCH_2C_6H_4Y} \\ \vdots \\ \delta^-\ \mathrm{OTs} \end{array}$$

II


III


IV

The utility of this treatment lies in its application to 1,3-diaryl-2-propyl tosylate solvolysis data. Here, three transition states, II–IV, are possible. In the anchimerically unassisted transition state, II, the inductive/steric effects of the aryl groups operate simultaneously, and $(k_s)_X(k_s)_Y$, or $k_0(s_Xs_Y)$, describes this component of the total rate constant. The anchimerically assisted transition states, III and IV, represent participation of either *one or the other* aryl ring (factors Δ_X or Δ_Y), modified by the inductive/steric effects (factors s_Y or s_X)[3] of the nonparticipating ring. The contributions of III and IV to the total rate constant are, respectively, $k_0(\Delta_Xs_Y)$ and $k_0(\Delta_Ys_X)$. Equation 2 summarizes the situation.[4]

$$k_t = k_0(s_Xs_Y + \Delta_Xs_Y + \Delta_Ys_X) \tag{2}$$

Since each aryl group in I introduces two unknowns (an s and a Δ), six unknowns will result from the selection of three aryl groups, but six rate expressions of the form of eq 2 also result, since six 1,3-diaryl-2-propyl systems are possible, three symmetrical (I; X = Y) and three unsymmetrical (I; X $\neq$ Y). We have chosen the p-anisyl, phenyl, and p-nitrophenyl groups for study. The data from these compounds (Table I) was used to solve a set of simul-

---

[1] (a) C. J. Lancelot and P. von R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4291 (1969); (b) C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *ibid.*, **91**, 4294 (1969).

[2] 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] It is assumed that the inductive/steric factors for a given aryl ring are virtually the same whether in II or in III or IV.

[4] Values of k_0 used are:[1b] HOAc, 100°, 4.22×10^{-4} sec^{-1}; HCOOH, 75°, 4.83×10^{-3} sec^{-1}.