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

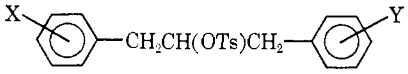
Received March 3, 1969

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.

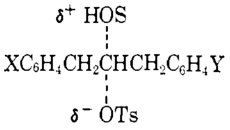


I

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

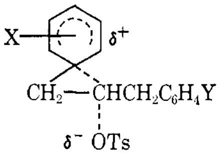
$$k_t = sk_0 + \Delta k_0$$
$$k_t = k_0(s + \Delta) \tag{1}$$

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.*, $Fk_\Delta = \Delta k_0$).

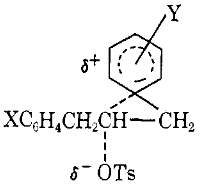


$$\underset{\delta^- \,\text{OTs}}{\overset{\delta^+ \,\text{HOS}}{XC_6H_4CH_2CHCH_2C_6H_4Y}}$$

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 ≠ 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}.

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_3O	*p*-CH_3O	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_3O	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_3O	*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	$k_s + Fk_\Delta$, sec^{-1} 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_3O	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_3O	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