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NEIGHBORING HYDROGEN, ISOTOPE EFFECT, AND CONFORMATION IN SOLVOLYSIS OF 3-METHYL-2-BUTYL *p*-TOLUENESULFONATE*[1]

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Abstract—In connection with hydrogen participation in solvolysis, 3-methyl-2-butyl *p*-toluenesulfonate is a marginal system. Comparison of the behavior of 3-D-3-methyl-2-butyl toluenesulfonate with that of the undeuterated analog discloses a substantial isotope effect on solvolysis rate, but only a small effect on product composition. The evidence points to a relatively high value of (k_Δ/k_s), the ratio of rate constants for anchimerically assisted and unassisted solvolysis processes. Conformational considerations make understandable the relatively low degree of rate acceleration displayed by 3-methyl-2-butyl toluenesulfonate.

IN connection with hydrogen participation in solvolysis, 3-methyl-2-butyl *p*-toluenesulfonate (I) is a marginal system.[2] Thus, as summarized in Table 1, acetolysis rates of the secondary alkyl *p*-bromobenzenesulfonates, $RCH(OBs)CH_3$, pass through a shallow maximum at R=*i*-Pr as R is varied from Me to *t*-Bu.[2] However, it is not easy to conclude that acetolysis of *i*-$PrCH(OBs)CH_3$ is accelerated by *tert.*-hydrogen participation, since β-Me substitution not only favors hydrogen participation, but causes several other effects[2]. For anchimerically[3] unassisted solvolysis, the sequence of rates for the various R groups, Me < Et < *i*-Pr < *t*-Bu, is predicted[2] on the basis of (i) polar and (ii) steric accelerative effects of R. The opposite order is predicted[2] from consideration of (iii) hyperconjugative and (iv) steric retarding effects of R.

The same set of effects, (i)–(iv), is associated also with change of R in the series,[4] $RCCl(CH_3)_2$, and yet the net effect of β-methyl substitution on rate of ionization in the *tertiary* series is close to zero (Table 1). Therefore, the reactivity pattern in solvolysis of $RCH(OBs)CH_3$ was taken previously as a suggestion that solvolysis rate of *i*-$PrCH(OBs)CH_3$ was influenced by a driving force due to hydrogen participation.[2c] The relatively high reactivity of the *i*-$PrCH(OBs)CH_3$ member of its series is actually obscured by the rough single-term $\rho^*\sigma^*$ correlation of solvolysis rates recently reported by Streitwieser.[5] This correlation, which takes account only of the polar effect (i) above with the aid of Taft's polar substituent constants,[6] predicts an anchimerically unassisted rate constant k_s nearly as large as the observed rate

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[1] S. Winstein *Fifteenth National Organic Chemistry Symposium of the American Chemical Society, Rochester, N.Y.* p. 29 of Abstract (1957).

[2] (a) S. Winstein *Bull. Soc. Chim. Fr.* **18**, 55 (1951); (b) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse *J. Amer. Chem. Soc.* **74**, 1113 (1952); (c) S. Winstein and H. Marshall *Ibid.* **74**, 1120 (1952).

[3] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham *Ibid.* **75**, 147 (1953).

[4] H. C. Brown and R. S. Fletcher *J. Amer. Chem. Soc.* **71**, 1845.

[5] A. Streitwieser, Jr. *Ibid.* **78**, 4935 (1956).

[6] R. W. Taft, Jr. *Ibid.* **75**, 4231 (1953).

constant for acetolysis of *i*-PrCH(OBs)CH$_3$ (Table 1). However, the single-term $\rho^*\sigma^*$ correlation fails rather badly to account for the rate sequence in the *tertiary* series, RCCl(CH$_3$)$_2$ (Table 1).

TABLE 1. SUMMARY OF STRUCTURAL RATE SEQUENCES IN SOLVOLYSIS

	Relative Rates			
	RCH(OBs)CH$_3$ AcOH, 25°		RCCl(CH$_3$)$_2$ 80% EtOH, 25°	
R	Obs.[2]	Calc.[a]	Obs.[4]	Calc.[b]
Me	1·0	1·0	1·00	1·0
Et	2·3	2·2	1·65	2·1
i-Pr	6·0	5·0	0·95	4·6
t-Bu	2·9	13·1	1·21	11·5

[a] $\log k/k^0 = -3{\cdot}49\sigma^*$; Ref. 5
[b] $\log k/k^0 = -3{\cdot}3\sigma^*$; Ref. 5

As indicated previously,[2c] comparison of the behavior of 3-D-3-methyl-2-butyl *p*-toluenesulfonate with that of the undeuterated analog is helpful here, and we can now outline the results of this study.

TABLE 2. SUMMARY OF k^H/k^D FACTORS IN SOLVOLYSIS OF 3-DEUTERO-3-METHYL 2-BUTYL[a] *p*-TOLUENESULFONATE

Temp. °C	80% EtOH	AcOH	HCOOH
75°	1·85 ± 0·04	1·93 ± 0·10	
50°		2·06 ± 0·08	
25°	2·05[b]	2·15[b]	2·13 ± 0·10
25° (corr.)[c]	2·14[b]	2·26[b]	2·24

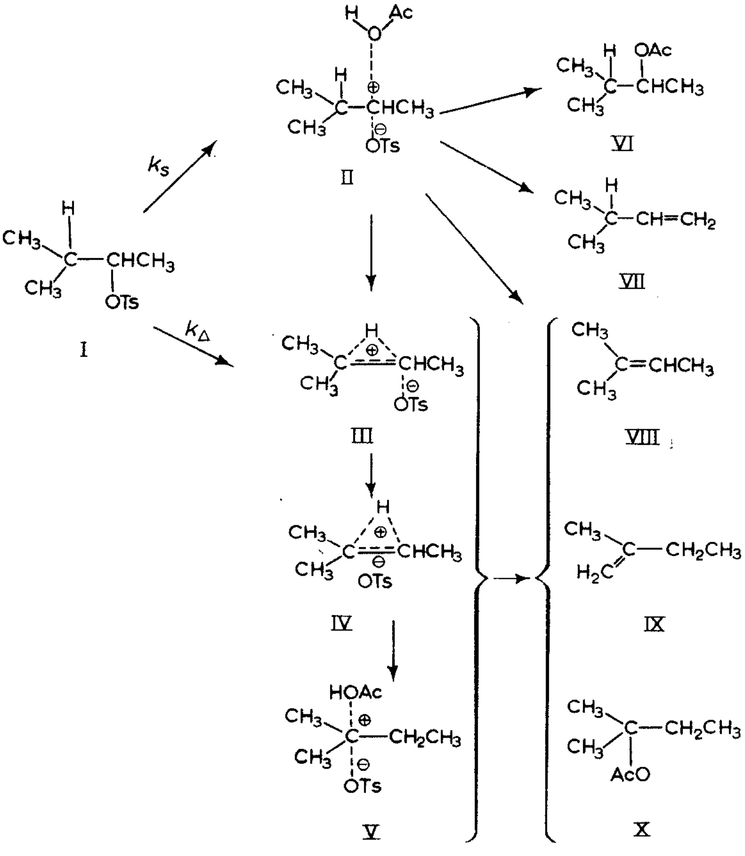
[a] A deuterium analysis of 0·94 deuterium atom per molecule of the 3-D-3-methyl-2-butanol was kindly determined through the courtesy of Dr. N. R. Trenner of Merck and Co., Rahway, N.J.

[b] Extrapolated from the data at the other temperatures.

[c] Corrected approximately for deuterium content of the deuterated toluenesulfonate during main portion of rate runs.

The 3-D-3-methyl-2-butanol was prepared from the Grignard reagent from 2-D-2-propyl bromide and acetaldehyde. The isotope factors obtained from comparison of first order solvolysis rate constants of 3-D-3-methyl-2-butyl *p*-toluenesulfonate and its undeuterated analog I are sizable, being 2·25 in acetic and formic acid solvents (Table 2). As summarized in Table 3, essentially the whole of the product from solvolysis of 3-methyl-2-butyl *p*-toluenesulfonate (I) in acetic acid at 75° in the presence of a slight excess of sodium acetate involves either loss or migration of the *tertiary* hydrogen atom. Only 1 per cent of 3-methyl-1-butene (VII) and 3 per cent of unrearranged acetate VI were observed. From the 3-D-3-methyl-2-butyl ester, 59 per cent elimination was observed instead of 70 per cent with the undeuterated analog. Also, the percentages of 3-methyl-1-butene (VII) and unrearranged acetate VI were increased to 2 and 6·5 per cent, respectively.

TABLE 3



	Product per cent from 3-H	Product per cent from 3-D
VI	3	6·5
VII	1	2
VIII	54	44
IX	15	13
X	27	34·5

The small response of the observed kinetic isotope factor to solvent variation and the small isotope effect on product composition suggest that solvolytic processes involving nucleophilic attack on hydrogen or carbon are relatively unimportant in acetic acid solvent. It seems best to discuss the acetolysis of 3-methyl-2-butyl toluenesulfonate (I) in terms of two independent solvolytic processes, anchimerically unassisted solvolysis with rate constant k_s, and anchimerically assisted solvolysis with rate constant k_Δ. From intermediate II in the anchimerically unassisted solvolysis is obtained unrearranged acetate VI, 3-methyl-1-butene (VII) and 2-methyl-2-butene (VIII), together with a certain amount of rearranged olefin IX and rearranged acetate X as a result of *tertiary* hydrogen involvement with C_α in a step subsequent to the rate-determining one. Anchimerically assisted ionization through a transition state such as III leads to 2-methyl-2-butene (VIII), rearranged olefin IX and rearranged acetate X. A substantial ratio of (k_Δ/k_s) in acetolysis of 3-methyl-2-butyl toluenesulfonate

(I) is indicated by the composition of observed acetolysis products together with the size of the observed kinetic isotope factor.

The observed kinetic isotope factors are of a different order of magnitude from those for the secondary hydrogen isotope effects observed in solvolysis of systems[7–10] whose structure[2] does not favor anchimerically assisted ionization. As summarized in Table 4, the factor per β-deuterium atom varies from 1·10 to 1·28 for a *primary* to a *tertiary* deuterium atom adjacent to a *tertiary* center and is ca. 1·2 for a *secondary* deuterium atom adjacent to a *secondary* center. The factor observed for the *tertiary* deuterium atom in the 3-methyl-2-butyl system, 2·25, is of the same order as that observed in the intermolecular electrophilic substitution of triphenylcarbonium ion on 2-D-2-propanol.[11,12]

In using the observed isotope factors, it helps to distinguish between three factors: (i) I, the overall isotope factor; (ii) I_Δ, the isotope factor for anchimerically assisted ionization, namely k_Δ^H/k_Δ^D; (iii) I_s, the isotope factor for the anchimerically unassisted solvolysis, namely k_s^H/k_s^D. I may be expressed as in equation (1), three other useful derived equations being (2), (3), and (4). Using equation (2) with an anticipated value for I_s of the order of

$$I = \frac{k^H}{k^D} = \frac{k_\Delta^H + k_s^H}{k_\Delta^D + k_s^D} = \frac{1 + (k_\Delta^H/k_s^H)}{(k_\Delta^D/k_s^H) + (k_s^D/k_s^H)} \tag{1}$$

$$I_s = \frac{k_s^H}{k_s^D} = I\left[\frac{1 + (k_\Delta^D/k_s^D)}{1 + (k_\Delta^H/k_s^H)}\right] \tag{2}$$

$$I = \frac{k^H}{k^D} = I_\Delta\left[\frac{1 + (k_\Delta^H/k_s^H)}{(k_\Delta^H/k_s^H) + (I_\Delta/I_s)}\right] \tag{3}$$

$$I_\Delta = \frac{k_\Delta^H}{k_\Delta^D} = \frac{I(k_\Delta^H/k_s^H)}{1 + (k_\Delta^H/k_s^H) - (I/I_s)} \tag{4}$$

1·3, k_Δ^H/k_s^H is estimated to be of the order of 6, if it is to be roughly twice the value of k_Δ^D/k_s^D as the product compositions tend to indicate. On this basis, the I_Δ value, relating to anchimerically assisted solvolysis, is predicted by equation (4) to be of the order of 2·6.

The intimate mechanistic details of the formation of final products from anchimerically assisted ionization are still not clear.[1,13] The formulation in Table 3 leaves open the question of the number of intermediates such as III, IV, and V which require explicit mention and what their roles are in formation of olefins VIII and IX and rearranged acetate X. Further, III, IV, and V are arbitrarily written only as intimate ion pairs. Under the same conditions as those employed in acetolysis of 3-methyl-2-butyl toluenesulfonate (I), *t*-amyl chloride, which gives rise to *t*-amyl cationic

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[7] V. J. Shiner, Jr. *J. Amer. Chem. Soc.* **75**, 2925 (1953).

[8] V. J. Shiner, Jr. *Ibid.* **76**, 1603 (1954).

[9] E. S. Lewis and C. E. Boozer *Ibid.* **76**, 791 (1954).

[10] A. Streitwieser, Jr., R. H. Jagow and S. Suzuki *Ibid.* **77**, 6713 (1955).

[11] P. D. Bartlett and J. D. McCollum *Ibid.* **78**, 1441 (1956).

[12] The similarity in k_H/k_D factors may be more than coincidental, since the bonding situation of the hydrogen or deuterium atom in question may be geometrically similar in the transition states for the two reactions. See S. Winstein, T. G. Traylor and C. S. Garner *J. Amer. Chem. Soc.* **77**, 3741 (1955), for remarks on electrophilic substitution. This point was also made independently to one of us (S.W.) by Dr. E. S. Lewis of Rice Institute of Technology.

[13] S. Winstein and N. J. Holness *J. Amer. Chem. Soc.* **77**, 5562 (1955).

species of the type of V, gives rise to 2-methyl-2-butene (VIII), 2-methyl-1-butene (IX) and *t*-amyl acetate (X) in the proportions, 59 : 26 : 15, respectively. Both the proportion of elimination and the IX : X ratio are considerably higher than in acetolysis of I.

TABLE 4. ISOTOPE EFFECTS (k_H/k_D) PER DEUTERIUM ATOM IN VARIOUS SYSTEMS AT 25°

System	80% EtOH	AcOH	HCOOH	Ref
$CH_3CH_2CCl(CD_3)_2$	1·10			7
$CH_3CD_2CCl(CH_3)_2$	1·19			7
$(CH_3)_2CDCCl(CH_3)_2$	1·28			8
$CH_3CH_2CD_2CH(OTs)CD_3$	1·08	1·13	1·13	9
trans-2-D-*cyclo*pentyl OTs		1·19		10
cis-2-D-*cyclo*pentyl OTs		1·24		10
$(CH_3)_2CDCH(OTs)CH_3$	2·15	2·27	2·24	
$(C_6H_5)_3C^{\oplus} + DC(OH)(CH_3)_2$		1·84[a,b]		11

[a] In H_2O-H_2SO_4 medium.

[b] From deuterium analyses of products; a value of 2·58 obtained from rate measurements.

The indicated relatively high k_Δ/k_s and yet the low degree of rate acceleration in acetolysis displayed by 3-methyl-2-butyl toluenesulfonate (I) becomes more understandable on the basis of conformational degeneracy[13] of the solvolysis, and differing effects of β-methyl substitution on the intrinsic rate constants associated with the different conformations of toluenesulfonate I, namely IA, B, and C.

The anchimerically assisted ionization of toluenesulfonate I is conformationally homogeneous,[13] k_Δ being given by equation (5), where N_B is the mole fraction of conformation B and k_Δ^B is the rate constant for anchimerically assisted ionization for this conformation. On the other hand, anchimerically unassisted solvolysis of toluenesulfonate I is conformationally degenerate,* k_s being given by equation (6). Steric considerations suggest that B is the least populated of

$$k_\Delta = N_B k_\Delta^B \tag{5}$$

$$k_s = N_A k_s^A + N_B k_s^B + N_C k_s^C \tag{6}$$

the three conformations of I. This contributes to a low value of k_Δ. On the other hand, A is predicted to be the most populated conformation of I and yet associated with a relatively low k_s^A value by analogy with the behavior of conformationally more homogeneous *cyclo*hexyl systems.[13,14]

Solvolysis rates of *trans*-2-methyl*cyclo*hexyl[1,15] toluenesulfonate (XII) are ca. one-third of the values for the *trans*-4-*t*-butyl*cyclo*hexyl[13] analog, a β-methyl group on an *equatorial* toluenesulfonate being noticeably rate-depressing. Analogy between conformations IA and XIIA predicts that k_s^A for IA is lower than k_s^A for the 2-butyl

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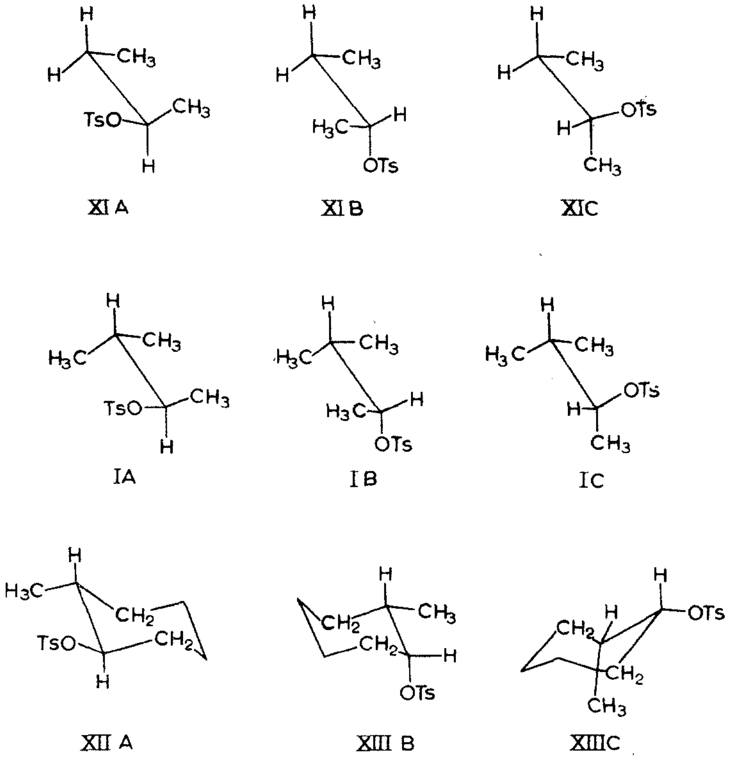
* As pointed out previously,[2b] β-hydrogen hyperconjugation and hydrogen participation both involve delocalization of β-bonding electrons. Where geometry is proper, as in conformation IB, hydrogen hyperconjugation and participation can merge. Equation (6) assumes that the approximation of distinct anchimerically unassisted and assisted solvolysis processes is valid even for conformation IB.

[14] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall *J. Amer. Chem. Soc.* 74, 1127 (1952).

[15] R. Heck unpublished work.



XI A XI B XIC

IA IB IC

XII A XIII B XIIIC

FIG. A

system XI. With the *cis*-2-alkyl*cyclo*hexyl toluenesulfonates, such as *cis*-2-methyl-*cyclo*hexyl[1,15] XIII or neomenthyl,[1,10,16,17] the proportion of conformation B is considerably higher than for the 3-methyl-2-butyl one and thus k_Δ given by equation (5) is higher. This makes the β-methyl group more rate-enhancing in the *cyclo*hexyl than in the 2-butyl system and thus anchimeric acceleration due to participating β-hydrogen more pronounced.

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[16] J. Schwartz Unpublished work.

[17] S. Winstein 1, 2- and 1, 3-Hydrogen Shift. *Symposium on Molecular Rearrangements*. Queen Mary College, Univ. of London (1954).