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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen.[1] V. Driving Forces in the Wagner–Meerwein Rearrangement[2,3]

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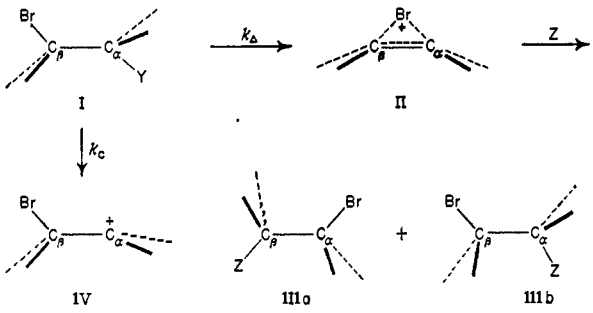
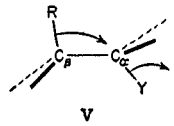
Participation by a β-H, R or unsaturated group and its associated electron cloud in a nucleophilic replacement process has important analogies to the similar participation of functional neighboring groups. The driving force due to so-called participation of carbon in the rate-determining ionization can be substantial, and some orientation as to the order of magnitude of driving forces attained is supplied by rate measurements now reported. Solvolysis rate constants for a primary series and another secondary series of arylsulfonates illustrate the trends expected on the basis of participation. Driving forces decrease in the order of C_α: primary > secondary, and increase as C_β is substituted with conjugating groups in the order: $CH_3 < C_6H_5 \cong (CH_3)_2 < (C_6H_5)_2$. These effects modify tremendously the usual trends in reactivity with α- or β-substitution in the absence of driving forces due to participation.

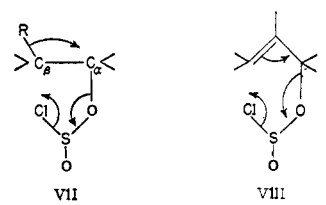
Our work reported in another series of papers[5] has made it clear that participation of a functional neighboring group (*e.g.*, Br) and its associated electron cloud in nucleophilic displacement processes at a nearby center is a general phenomenon. The stereochemistry[6] of replacement processes (I → III) are often controlled by this phenomenon and, also, the driving forces[7] due to this kind of participation are often of an important magnitude. Estimating k_c, the specific rate constant of ionization to IV without participation of the neighboring group, and defining the driving force L as $RT \ln k_\Delta/k_c$, one arrives at semi-quantitative figures for driving forces.



The participation of functional neighboring groups in displacement reactions is part of a more general phenomenon which includes participation of the electrons associated with a neighboring β-H, R, Ar or vinyl group. In this paper we are concerned with this participation as it applies to the Wagner–Meerwein rearrangement (V).



For the Wagner-Meerwein rearrangement there are conceivable special mechanisms which may prove to be operative for certain circumstances in the way of structure or conditions. One of these



(1) Previous papers in this series: (a) I, Winstein and Adams, THIS JOURNAL, **70**, 838 (1948); (b) II, Winstein and Schlesinger, *ibid.*, **70**, 3528 (1948); (c) III, Winstein and Trifan, *ibid.*, **71**, 2953 (1949); (d) IV, Winstein, Walborsky and Schreiber, *ibid.*, **72**, 5795 (1950).

(2) Supported in part by the Office of Naval Research and the Research Corporation.

(3) The material of this paper was presented in summary: (a) before the Organic Division of the American Chemical Society at St. Louis, September, 1948; (b) at the Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of abstracts; and (c) at Montpellier, France, April 26, 1950 [*Bull. soc. chim. France*, **18**, 55 (1951)].

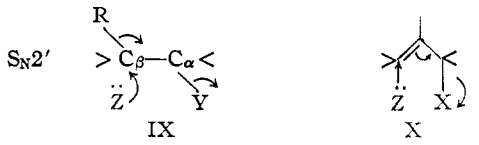
(4) Taken in part from Ph.D. theses, U. C. L. A., of Betsy Morse, 1949, and E. Grunwald, 1947.

(5) Winstein and Boschan, THIS JOURNAL, **72**, 4669 (1950), and previous papers.

(6) *E.g.*, Winstein, Hess and Buckles, *ibid.*, **64**, 2796 (1942).

(7) (a) Winstein, Grunwald and Ingraham, *ibid.*, **70**, 821 (1948); (b) Winstein and Grunwald, *ibid.*, **70**, 828 (1948).

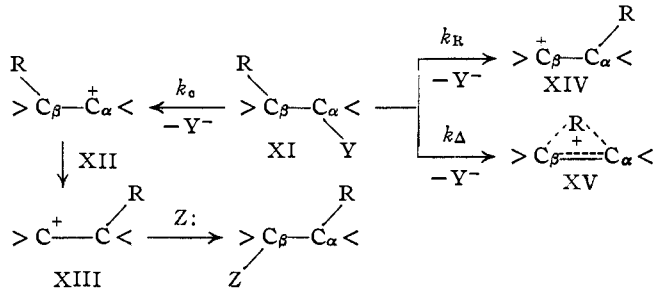
is S_Ni', illustrated by VII,[8] analogous to the S_Ni' mechanism in the allylic[9] rearrangement field (VIII). Another conceivable special mechanism is S_N2' illustrated by IX, analogous to S_N2' with allylic[10] materials (X). This is the type mechanism for which negative evidence was obtained by Bartlett and Pöckel[11] in the rearrangement of camphene hydrochloride.



IX X

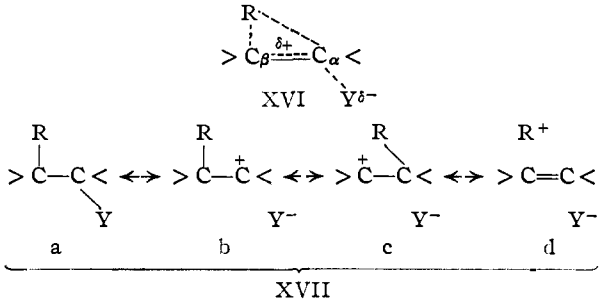
However, the most general mechanisms for the Wagner–Meerwein rearrangement would appear to involve preliminary ionization.[12–15] Whitmore,[14] who in 1932 formulated a consistent picture at the time of various rearrangements, visualized the Wagner–Meerwein rearrangement in terms of formation of a carbonium ion with the original structure XII, which rearranges, by shift of a β-electron pair and the accompanying group, to a carbonium ion with a rearranged structure XIII. The question has sometimes been raised whether rearrangement accompanies or occurs subsequent to ionization[16] and each alternative has at times been suggested.[15–17]

Our view has been[3] that it is possible for participation of the electron cloud associated with a neighboring H, R or Ar group to occur in the rate-determining ionization producing either the rearranged ion XIV (specific reaction rate constant k_R) or an ion XV (specific reaction rate constant k_Δ) with a bridged structure. This latter type formulation for a carbonium ion has been mentioned or proposed[18] a number of times, and evidence on this matter is presented in later papers in this series. On the other hand, migration of a group may also occur subsequent to ionization to an unrearranged carbonium ion XII (rate constant k_c).



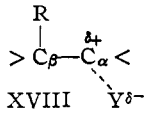
One of the keys to understanding the Wagner–Meerwein phenomenon is the assessment of the magnitude of the driving force due to so-called participation of carbon or hydrogen in the rate-determining ionization and here, as with functional neighboring groups,[7] rate measurements are helpful. This paper and the next two in the series report the results of a survey of solvolysis rates of a number of compounds of interest in the Wagner–Meerwein connection.

If there is participation[19] by neighboring carbon in the rate-determining ionization, whether the carbonium ion is best described by a structure of the type XIV or by one of the bridged type XV, the transition state for ionization of XI is the type XVI, structures such as XVIIa-d contributing to the hybrid. If there is no such participation, the



XVI XVII

transition state is the type XVIII. The effects of methyl substitution on C_α and C_β closely correspond to those observed in functional group participation.[7] Alpha and beta substitution will both increase k_R or k_Δ, while alpha substitution will increase k_c more than k_R or k_Δ. Thus, the driving force due to participation will be increased by beta substitution and decreased by alpha substitution, and we can anticipate that it will increase as we proceed from a tertiary cleaving group to a primary. In this paper are reported rates of solvolysis of a series of primary arylsulfonates and a similar series of secondary arylsulfonates, which furnish some orientation on the order of magnitude of driving forces due to participation.



XVIII

Unfortunately, the very variation of structure designed to vary the driving force due to participation changes other factors which affect rate, such as inductive effects, hyperconjugation[20] effects and steric effects and these need to be considered in interpreting the rates obtained.

To make the solvolyses of the compounds in question and the reference compounds used in estimating k_c as nearly limiting[21] (Lim.) with re-

(8) Wallis and Bowman, *J. Org. Chem.*, **1**, 383 (1936).
(9) Roberts, Young and Winstein, THIS JOURNAL, **64**, 2157 (1942).
(10) Kepner, Young and Winstein, *ibid.*, **71**, 115 (1949).
(11) Bartlett and Pöckel, *ibid.*, **60**, 1585 (1938).
(12) Meerwein and van Emster, *Ber.*, **53**, 1815 (1920); **55**, 2500 (1922).
(13) Ingold, "Annual Reports," **25**, 124 (1928).
(14) Whitmore, THIS JOURNAL, **54**, 3274 (1932).
(15) Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 173 (1946).
(16) *E.g.*, Skell and Hauser, THIS JOURNAL, **64**, 2633 (1942).
(17) Swain, *ibid.*, **70**, 1119 (1948).
(18) (a) Winstein and Lucas, *ibid.*, **60**, 836 (1938); (b) Nevell, de Salas and Wilson, *J. Chem. Soc.*, 1188 (1939); (c) Watson, "Annual Reports," 197 (1939); 120 (1941); (d) Eyring, *Ind. Eng. Chem.*, **35**, 511 (1943); (e) Dewar, *J. Chem. Soc.*, 406 (1946); (f) Walsh, *ibid.*, 89 (1947); (g) Arcus, *Chemistry and Industry*, 442 (1947).

(19) Participation amounts to delocalization of the C_β–R bonding electron pair as electron deficiency is created by ionization. Now in hyperconjugation,[20] involving β-linkages, there is also delocalization. Whether, in general, hyperconjugation and participation should be considered to merge depends on the still unsettled preferred geometry in hyperconjugation.
(20) (a) Baker and Nathan, *J. Chem. Soc.*, 1844 (1935); (b) Mulliken, Rieke and Brown, THIS JOURNAL, **63**, 41 (1941).
(21) Winstein, Grunwald and Jones, *ibid.*, **73**, 2700 (1951).

TABLE I

SOLVOLYSIS RATES OF *p*-TOLUENESULFONATES AND *p*-BROMOBENZENESULFONATES

Compound	Concn. *M*	Temp., °C.	Solvent	k_1(sec.$^{-1}$)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$(CH_3)_3CC_2HOTs$	....	49.60[a]	AcOH	2.17×10^{-9}	31.5	−1.0
	0.0403	74.71	AcOH	$(7.7 \pm 0.4) \times 10^{-8}$		
	.0796	74.71	AcOH	$(8.32 \pm 0.08) \times 10^{-8}$		
	.418	99.58	AcOH	$(1.72 \pm 0.06) \times 10^{-6}$		
	.0796	99.58	AcOH	$(1.60 \pm 0.13) \times 10^{-6}$		
	.0555	99.58	EtOH	$(4 \pm 1) \times 10^{-7}$		
$(C_6H_5)_2CHCH_2OTs$	....	49.60[a]	AcOH	1.15×10^{-7}	27.1	−6.4
	.0155	74.71	AcOH	$(2.61 \pm 0.05) \times 10^{-6}$		
	.0144	99.58	AcOH	$(3.81 \pm 0.27) \times 10^{-5}$		
	.0080	99.58	EtOH	2×10^{-5}		
$(CH_3)_2C_6H_5CCH_2OTs$	....	49.60[a]	AcOH	9.92×10^{-7}	25.7	−6.4
	.0411	74.71	AcOH	$(1.93 \pm 0.05) \times 10^{-5}$		
	.0524	99.58	AcOH	$(2.47 \pm 0.05) \times 10^{-4}$		
	.0426	74.72	EtOH	$(5.2 \pm 0.2) \times 10^{-6}$		
$(C_6H_5)_3CCH_2OTs$	.0087	49.60	AcOH	$(1.68 \pm 0.09) \times 10^{-5}$	25.2	−2.5
	.0085	74.72	AcOH	$(3.09 \pm 0.11) \times 10^{-4}$		
	.0107	49.60	EtOH	$(7.5 \pm 0.4) \times 10^{-6}$		
$CH_3CH(OBs)CH_3$	.0427	34.94	AcOH	$(1.02 \pm 0.01) \times 10^{-6}$	24.8	−5.5
	....	49.60[a]	AcOH	6.44×10^{-6}		
	.0267	70.0[b]	AcOH	6.90×10^{-5}		
$CH_3CH_2CH(OBs)CH_3$	.0229	40.0	AcOH	$(4.05 \pm 0.02) \times 10^{-6}$		
	....	49.60[a]	AcOH	1.29×10^{-5}		
	.0281	70.0	AcOH	$(1.23 \pm 0.01) \times 10^{-4}$	23.7	−7.7
	.0369	70.0	AcOH 0.025 *M* KOAc	$(1.27 \pm 0.02) \times 10^{-4}$		
$(CH_3)_2CHCH(OBs)CH_3$	.0162	34.94	AcOH	$(5.85 \pm 0.05) \times 10^{-6}$		
	....	49.60[a]	AcOH	3.83×10^{-5}		
	.0162	70.0	AcOH	$(4.02 \pm 0.09) \times 10^{-4}$	24.7	−2.3
	.0157	70.0	AcOH 0.025 *M* KOAc	$(4.14 \pm 0.04) \times 10^{-4}$		
$(CH_3)_3CCH(OBs)CH_3$	....	49.60[a]	AcOH	2.27×10^{-5}		
	.0343	50.0	AcOH	$(2.37 \pm 0.03) \times 10^{-5}$		
	.0226	70.0[b]	AcOH	(2.73×10^{-4})	26.3	1.5
$(CH_3)C_6H_5CHCH(OTs)CH_3$(I)	.035	49.60	AcOH	$(2.38 \pm 0.05) \times 10^{-6}$	26.3	−2.9
	.030	74.71	AcOH	$(4.95 \pm 0.17) \times 10^{-5}$		
$(CH_3)C_6H_5CHCH(OTs)CH_3$(II)	.029	49.60	AcOH	$(2.72 \pm 0.05) \times 10^{-6}$	26.5	−2.1
	.032	74.72	AcOH	$(5.77 \pm 0.26) \times 10^{-5}$		
$(C_6H_5)_2CHCH(OBs)CH_3$	....	49.60[a]	AcOH	1.17×10^{-5}		
	.0145	49.30	AcOH	$(1.134 \pm 0.015) \times 10^{-5}$		
	.0145	74.81	AcOH	$(2.31 \pm 0.05) \times 10^{-4}$	25.7	−1.7
	.0244	74.81	EtOH	$(1.12 \pm 0.04) \times 10^{-4}$		
$(CH_3)_2(C_6H_5)CCH(OBs)CH_3$	.0104	24.95	AcOH	$(2.03 \pm 0.03) \times 10^{-5}$	23.6	−1.0
	.0292	24.95	AcOH	$(2.05 \pm 0.02) \times 10^{-5}$		
	.0147	49.61	AcOH	$(4.64 \pm 0.08) \times 10^{-4}$		
	.0274	49.61	AcOH	$(4.67 \pm 0.09) \times 10^{-4}$		

[a] Extrapolated from data at other temperatures. [b] Previously reported.[48]

spect to the solvent role and thus to bring out most clearly the assistance derived from participation, we have studied acetolysis of benzenesulfonates.[7a] Also, in some cases we have compared the acetolysis rates with rates of ethanolysis.

Table I lists first order rates of acetolysis and ethanolysis for four primary toluenesulfonates including neopentyl, prepared by conventional methods. The value of the ratio of acetolysis rate to ethanolysis rate (*ca.* 2–4) suggest that the acetolysis reactions approach the desired type. Acetolysis rates, if not available at 49.60°, have been extrapolated to this temperature for comparison, the figures being given in Table I. In Table II, the acetolysis rates at 49.60° relative to neopentyl *p*-toluenesulfonate are given for the four primary *p*-toluenesulfonates A, B, C and D. It is clear that substantial increases of rate attend the structural changes represented by the sequence A:B:C:D. Thus β,β-diphenylethyl toluenesulfonate B, is some 50 times as reactive as neopentyl A, neophyl C some 500 times and the β,β,β-triphenylethyl D more reactive by a factor of nearly 4 powers of ten.

Table I also lists first order rates of acetolysis of a number of secondary *p*-toluenesulfonates or *p*-bromobenzenesulfonates, E – M. The esters were derived from alcohols prepared by conventional methods, except for the *dl*-3-phenyl-2-butanols I and II which were furnished by Dr. Donald Cram. The configurations indicated in Table III for 3-phenyl-2-butyl *p*-toluenesulfonates

TABLE II

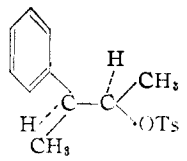
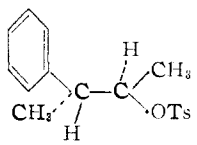
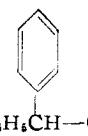
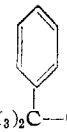
RELATIVE ACETOLYSIS RATES OF PRIMARY *p*-TOLUENESULFONATES

		Rel. k_{AcOH} 49.6°	10^n rel. k or est. k/k_c
A	$(CH_3)_2\overset{CH_3}{\overset{|}{C}}—CH_2OTs$	1	1
B	$C_6H_5—\overset{H}{\overset{|}{C}}—CH_2OTs$	53	5.3×10^3
C	$(CH_3)_2\overset{H}{\overset{|}{C}}—CH_2OTs$	460	4.6×10^3
D	$(C_6H_5)_2\overset{H}{\overset{|}{C}}—CH_2OTs$	7.7×10^3	7.7×10^6

J I and J II are based on Cram's stereochemical evidence.[22] Acetolysis rate constants adjusted to 49.60° are given in Table I and the relative rates compared to isopropyl *p*-bromobenzenesulfonate E are shown in Table III (allowing a factor of 3

TABLE III

RELATIVE ACETOLYSIS RATES OF SECONDARY *p*-TOLUENESULFONATES AND *p*-BROMOBENZENESULFONATES

		Rel. k_{AcOH} 49.6°	k/k_H	10^n k/k_H or est. k/k_c
E	$CH_3—CH(OBs)CH_3$	1.0		
F	$CH_3—CH_2—CH(OBs)CH_3$	2.0		
G	$(CH_3)_2\overset{H}{\overset{|}{C}}—CH(OBs)CH_3$	6.0		
H	$(CH_3)_2\overset{CH_3}{\overset{|}{C}}—CH(OBs)CH_3$	3.5		
J I		1.1	0.55	6
J II		1.3	0.63	6
K	 $C_6H_5CH—CH(OBs)CH_3$	1.8	1.8	180
M	 $(CH_3)_2C—CH(OBs)CH_3$	73	12.2	120

(22) Cram, THIS JOURNAL, **71**, 3863, 3883 (1949).

between acetolysis rates of *p*-bromobenzenesulfonates and *p*-toluenesulfonates). In the series E — H of bromobenzenesulfonates, $RCH(OBs)CH_3$, variation of R from CH_3 to *t*-Bu leads to the sequence of relative rates: 1:2:6:3.5. Other substitution of C_β also gives little effect on rate until M, $(CH_3)_2C(C_6H_5)CH(OBs)CH_3$, is reached, this having a relative rate of 73.

It is clear that the solvolysis of the primary *p*-toluenesulfonates A — D is associated with rearrangement. Neopentyl derivatives give rearranged tertiary amyl compounds in solvolytic reactions[15,23] and acetolysis of neopentyl toluenesulfonate A should be no exception. From acetolysis of β,β-diphenylethyl toluenesulfonate B was isolated a high yield of *trans*-stilbene, the olefin derived after migration of a phenyl group, a result which recalls the reported dehydrations of β,β-diphenylethyl alcohol to stilbene.[24] We assume solvolysis of neophyl toluenesulfonate C largely involves migration of the phenyl group, by analogy with the almost exclusive formation of β,β-dimethylstyrene in the dehydration of neophyl alcohol.[24a] The situation is similar in the case of the triphenylethyl[25] derivative D. All four toluenesulfonates are written in Table II to indicate the migrating group on this basis. With the secondary arylsulfonates (Table III), rearrangement attends the solvolysis of most of the materials. The acetolysis products from methyl-*i*-propylcarbinyl (G) and pinacolyl (H) *p*-bromobenzenesulfonates are at least largely rearranged.[26]

With the 3-phenyl-2-butyl *p*-toluenesulfonates J I and II, at least a very substantial part of solvolysis involves phenyl group migration.[22] This same thing is true for 1,1-diphenyl-2-propyl *p*-bromobenzenesulfonate[27] K and is assumed for 3-methyl-3-phenyl-2-butyl *p*-bromobenzenesulfonate M. On this basis, compounds G — M are written in Table III to indicate the migrating group.

In discussing the significance of the substantial enhancement of rates in the primary series A — D and the effects in the secondary series E — M, we must first consider the possibility that participation is not the governing consideration. With the highly branched structures involved we must consider possible enhancement of rate due to relief of steric strain[28] in ionization without participation. For example, in the series of alkyl chlorides, $R_1R_2R_3CCl$, substantial enhancement of solvolysis rate is observed by the time (i-Pr)$_3$CCl[28b,d] is reached. If the governing consideration was simply steric acceleration of rate, then an effect observed in the primary series A — D should be accentuated, if anything, by α-methyl substitution to a more substituted structure. This

(23) (a) Whitmore and Fleming, *J. Chem. Soc.*, 1269 (1934); (b) Whitmore, Wittle and Popkin, THIS JOURNAL, **61**, 1586 (1939); (c) Dostrovsky and Hughes, *J. Chem. Soc.*, 164, 166, 171 (1946).

(24) (a) Ramart and Amagat, *Ann. chim.*, [20] **8**, 263 (1927); (b) Kharasch and Clapp, *J. Org. Chem.*, **3**, 355 (1938).

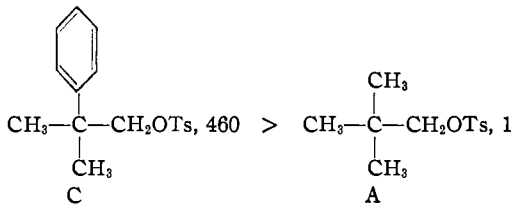
(25) Danilov, *C. A.*, **18**, 1488 (1924).

(26) D. Gelfer and H. Marshall, unpublished work.

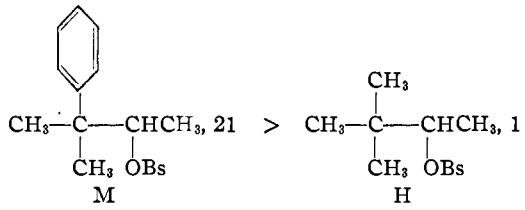
(27) Kurt Schreiber, unpublished work.

(28) (a) Brown, *Science*, **103**, 385 (1946); (b) Bartlett, Paper before 10th National Organic Symposium, Boston, Mass., June, 1947, p. 22 of Abstracts; (c) Brown and Fletcher, THIS JOURNAL, **71**, 1845 (1949); (d) Bartlett, Paper delivered at Montpellier, France, April 28, 1950.

is just the opposite of what is observed to be the effect of α-methyl substitution. For example, the C:A comparison gives relative rates

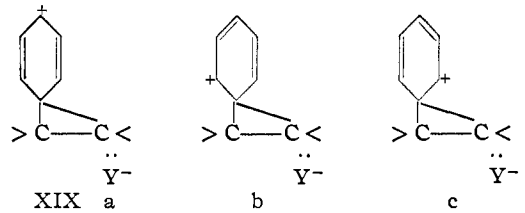


The analogous comparison (M:H) in the secondary series gives relative rates



Alpha methyl substitution acts to depress markedly the enhancement of rate attending the change of a β-CH_3 to a β-phenyl group. This can be accounted for on the basis of participation. In fact, the main trends in rate in the A – D series and much of the trend in the E – M series are well explained by participation.

It appears that rearrangement is attended by substantial driving forces in the primary series A – D. The main trend in rate is due to changes in $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ being -4.1 ± 2.3 e.u. for the series. The C:A comparison (460:1) shows the serious increase in rate when phenyl is the migrating group rather than methyl. This much greater driving force for a migrating phenyl over migrating methyl may be understood on the basis, long realized, that the migration represents internal electrophilic displacement and has some analogy to external electrophilic substitution on the benzene ring or on saturated carbon (for example, the reaction of RHgI or ArHgI with triiodide ion[29]). The superiority of phenyl over alkyl lies in the availability of an electron supply for contribution of structures of the type XIXabc to the transition state. The stabilization of the transition state by this device apparently usually outweighs the advantage of leaving the aryl group on C_β for conjugation purposes.[30] The relative rates in the A – D series in Table II represent the first approximation to values of k/k_c, and the approximation may be improved. One correction has to do with the electron-attracting inductive effect usually attending the replacement of a hydrogen atom by a phenyl substituent. A crude estimate of one power of ten for the depressing effect of a phenyl substituent on k_c may be obtained from the fact that a phenyl substituent in acetic acid is *ca.* one-fourth as acid strengthening (logarithmically) as a chlorine substituent and the estimate that the latter decreases k_c by 4 powers of ten.[7a] Applying this correction for one phenyl substituent in C, two in B and 3 in D gives the steeper rate sequence, A:B:C:D, of 1:*ca.* 5×10^3: *ca.* 5×10^3: 8×10^6. Thus, on this basis, β,β,β-triphenylethyl *p*-toluenesulfonate D is *ca.* 10^7 as reactive as it would be without participation.



The rate constant for neopentyl *p*-toluenesulfonate A is used as the reference compound because the solvolysis of, for example, ethyl *p*-toluenesulfonate is far from limiting[21] in type, This rate constant may be high as an estimate of k_c because of whatever driving force may already be in evidence in the neopentyl case. Thus the estimated values of k/k_c in the last column of Table II represent lower limits.

Going over to the secondary compounds, we consider first the series, $RCH(OBs)CH_3$ (E – H). The compounds $(CH_3)_2CH\text{-}CH(OBs)CH_3$ (G) and $(CH_3)_2C(CH_3)CH(OBs)CH_3$ (H) have structures which we originally expected might lead to the appearance of a driving force due to participation. However, the departure from constancy in the rate sequence, E:F:G:H, of 1:2:6:3.5 is very slight and there are several effects outside of participation, the net result of which could conceivably give the observed trend. While there may be some rate enhancement in G and H, and this matter is discussed further in a following article which reports more data, any such assistance from participation is small.

Driving forces become more clearly indicated as we move down the E – M series in Table III. The diastereomeric 3-phenyl-2-butyl *p*-toluenesulfonates J I and II are, in a sense, borderline. They are approximately equal to *i*-Pr (E) in reactivity and *ca.* half as reactive as *s*-butyl (F); $k/k_H = 0.55$ or 0.63 for J I and J II, respectively. Correction for the effect a phenyl group may have on k_c raises the estimated k/k_c to *ca.* 6.

With 1,1-diphenyl-2-propyl *p*-bromobenzenesulfonate K, the driving force is larger. The acetolysis rate is already larger than that of the isopropyl compound and correction for the effect of two phenyl groups on k_c gives a corrected relative reactivity of 180. The situation is similar with 3-methyl-3-phenyl-2-butyl *p*-bromobenzenesulfonate M whose rate is 73 times that of the isopropyl standard and 12.2 times that of $(CH_3)_2CHCH(OBs)CH_3$ (k_H). Correcting k/k_H by the factor for a phenyl group gives a value of 120, which is a lower limit to k/k_c to the extent a driving force exists in the reference compound G. For the cases J – M, $\Delta S^{\ddagger}$ is -1.9 ± 0.6 e.u., the rate trend being mainly due to changes in $\Delta H^{\ddagger}$.

The estimates for k/k_c in the last columns of Tables II and III are apt to be low because the

(29) J. Keller, Dissertation, U. C. L. A., 1948.

(30) We prefer this viewpoint to the one of Dewar, who explains the greater migration aptitude of phenyl by the greater electron attraction of cationic phenyl over cationic alkyl in a π-complex. Carried further, this viewpoint predicts incorrectly relative migration aptitudes of substituted aryl groups. [Dewar, "The Electronic Theory of Organic Chemistry," Oxford Univ. Press, Oxford, 1949, p. 215.]

values employed for k_c have probably been too high for still other reasons. Substitution of a hydrogen by carbon can be expected to reduce k_c slightly for hyperconjugative reasons, Further, this will increase steric hindrance to solvation and reduce k_c.

Besides the greater driving force for migrating phenyl *vs.* methyl, the estimated values of k/k_c illustrate other features in line with participation. Alpha-methyl substitution decreases (by a factor of *ca.* 30 or 40) the apparent driving force. For example, the k/k_c estimates are: B, $5.3 \times 10^3 >$ K, 180; C, $4,6 \times 10^3 >$ M, 120. The effect of a β-methyl group is illustrated by the k/k_c values: M, 120 > J, 6. Beta-substitution increases the apparent driving forces pretty much in the order of relative power for conjugation with a cationic or olefinic center. Reference to B, C, D and J, K, M gives the order of relative effectiveness of β-substituents other than the migrating group: $(C_6H_5)_2 > (CH_3)_2 \cong (C_6H_5) > CH_3$.

Looking not at driving forces but at over-all reactivities, we notice how the phenomenon of participation markedly affects the reactivity pattern in solvolysis. The effect of an α-methyl group, which ordinarily, in solvolysis of the limiting[21] or near-limiting variety, has a large rate-enhancing effect, may vary widely. As the comparisons show, introduction of an α-methyl group into neopentyl *p*-bromobenzenesulfonate still increases the acetolysis rate by a factor of 3500, but the effect is reduced to a factor of 34 in β,β-diphenylethyl. Similarly, a β-methyl group which usually has a small effect in solvolysis may have a large effect in cases of participation. This is illustrated by the comparison

$(CH_3)_3CCH(OBs)CH_3$, 3500 > $(CH_3)_3CCH_2OBs$, 1

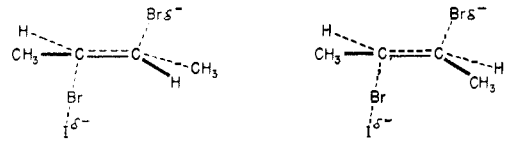
$(CH_3)_2(C_6H_5)CH(OBs)CH_3$, 156 > $(CH_3)_2C(C_6H_5)CH_2OBs$, 1

$(C_6H_5)_2CHCH(OBs)CH_3$, 34 > $(C_6H_5)_2CHCH_2OBs$, 1

$(CH_3)_2C(C_6H_5)CH(OTs)CH_3$, 60 > $CH_3CH(C_6H_5)CH(OTs)CH_3$, 1

While we believe the large rate trends observed involve participation and the driving forces have mainly the electronic origin discussed, nevertheless the observed rates (involving participation) can be influenced by steric effects to an extent we still have to assess. If steric strain is relieved by migration of a group from C_β to C_α, there can be an enhancement of rate of a reaction involving participation. To put it another way, participation may provide a mechanism for relief of steric strain.[28d]

As we mentioned already in connection with functional neighboring groups,[31] in a reaction involving participation, the bonds on C_α and C_β are becoming more eclipsed and interaction between groups, one on C_α and one on C_β, can increase on going to the transition state. The observed rates of reactions involving participation will reflect this interaction and further consequences of it, such as steric inhibition of resonance in the transition state.[32] While the cases are not quantitatively comparable, we can obtain some idea of the order of magnitude this effect may reach from existing information on other reactions. Thus for CH_3,CH_3 interaction, we know that *meso*-2,3-dibromobutane reacts with iodide ion to eliminate bromine only 1.8 times as rapidly as the *dl*-dibromide.[33] Similarly, it is interesting to note in



the case of the 3-phenyl-2-butyl *p*-toluenesulfonates J, that the diastereomer J I which eclipses the two methyl groups as a phenyl group participates is *ca.* 0.9 as reactive as the other diastereomer J II.

That the CH_3, C_6H_5 interaction of this kind can be serious, we know, for example, from the factor of *ca.* 70 which exists between acyl migration rates of benzoyl-ψ-ephedrine and benzoylephedrine,[34]

That the C_6H_5, C_6H_5 interaction is similarly serious we know, for example, from the factor of *ca.* 20 between equilibrium constants in the reaction of the *dl*- and *meso*-stilbene glycols with acetone,[35] the substantial difference in rate of reaction with potassium iodide between *meso*- and *dl*-stilbene dibromides,[36] and the inertness of *meso*-stilbene dichloride to elimination with pyridine relative to the *dl*-isomer.[37]

Participation by neighboring carbon in the rate-determining ionization step is important not only to our understanding of reactivity but also for stereochemical reasons. The general principle, applicable to the Walden inversion,[38] elimination (E2)[39] and rearrangement,[40] that activation energy is minimized when the incoming and leaving electron clouds in each unit displacement on a carbon atom have a *trans* relationship, will hold here, Therefore, definite evidence of a driving force due to participation should also be associated with Walden inversion at C_α.

Experimental

Neopentyl *p*-Toluenesulfonate.—Neopentyl alcohol, b.p. 110–111.5°, m.p. 51.6° (reported 52°)[41] was prepared by reduction of pivalyl chloride with lithium aluminum hydride by the procedure of Nystrom and Brown.[42] The *p*-toluenesulfonate, m.p. 48–49°, was prepared in 78% yield.

Anal. Calcd. for $C_{12}H_{18}SO_3$: C, 59.48; H, 7.79. Found: C, 59.51; H, 7.84.

2,2-Diphenylethyl *p*-Toluenesulfonate.—The alcohol, m.p. 59.1–59.5° (reported 59–60°),[43] was prepared in 84%

(31) Winstein and Seymour, THIS JOURNAL, **68**, 119 (1946).

(32) Pollak and Curtin, *ibid.*, **72**, 961 (1950).

(33) (a) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930); (b) Young, Eighth Nat. Org. Symposium, St. Louis, Mo., Dec., 1939, Abstracts of Papers, pp. 92–95.

(34) Welsh, THIS JOURNAL, **71**, 3500 (1949).

(35) Hermans, *Z. physik. Chem.*, **113**, 338 (1924).

(36) Young, Pressman and Coryell, THIS JOURNAL, **61**, 1640 (1939).

(37) Pfeiffer, *Ber.*, **45**, 1816 (1912).

(38) Hughes, Ingold, *et al.*, *J. Chem. Soc.*, 1252 (1937).

(39) (a) Winstein, Pressman and Young, THIS JOURNAL, **61**, 1645 (1939); (b) Hughes, Ingold, *et al.*, *J. Chem. Soc.*, 2093 (1948).

(40) Bartlett and Pöckel, THIS JOURNAL, **59**, 820 (1937).

(41) Huntress and Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941.

(42) Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

(43) Bergmann, *J. Chem. Soc.*, 412 (1936).

yield by reduction of diphenylacetic acid with lithium aluminum hydride, the reaction mixture being worked up with potassium hydroxide solution. Some less pure material, m.p. 53–54°,[44] used in some of the earlier work, was prepared from methyl benzhydryl ether by cleavage with excess sodium under nitrogen and treatment with formaldehyde. The *p*-toluenesulfonate, m.p. 116°, equivalent weight in acetolysis within 0.3% of theory, was prepared in the usual way.

Anal. Calcd. for $C_{21}H_{20}SO_3$: C, 71.56; H, 5.72. Found: C, 71.31; H, 5.71.

Neophyl *p*-Toluenesulfonate.—The alcohol was prepared in 62% yield by the oxidation of neophylmagnesium chloride according to the directions of Whitmore, Weisgerber and Shabica.[45] The toluenesulfonate, m.p. 74–75°, was prepared in the conventional manner. The equivalent weight in acetolysis agreed to 0.05 and 1.7% with the calculated value in different runs.

Anal. Calcd. for $C_{17}H_{20}SO_3$: C, 67.08; H, 6.62. Found: C, 66.96; H, 6.79.

2,2,2-Triphenylethyl *p*-Toluenesulfonate.—Triphenylmethylsodium was prepared in anhydrous ether according to the method of Hauser[46] from 1.5% sodium amalgam and trityl chloride, which had been recrystallized from ligroin and acetyl chloride. The solution of triphenylmethylsodium was decanted under nitrogen from the excess sodium and a threefold excess of formaldehyde, generated by heating dried polyoxymethylene, was passed over the vigorously stirred solution. Addition of ice water, drying of the ether layer over potassium carbonate, and removal of the ether, followed by several recrystallizations of the residue from methanol, gave triphenylethanol, m.p. 104–105° (reported 107°).[47] The toluenesulfonate, m.p. 106°, equivalent weight in solvolysis within 1.8% of theoretical, was prepared in 51% yield.

Anal. Calcd. for $C_{27}H_{24}SO_3$: C, 75.67; H, 5.65. Found: C, 75.65; H, 5.80.

Isopropyl and Pinacolyl *p*-Bromobenzenesulfonates.—These materials, m.p. 32.3–34.1° and 53.2–53.5°, respectively, have been described previously.[48]

2-Butyl *p*-Bromobenzenesulfonate.—Prepared in 50% yield from 2-butanol, this material tended to be a viscous oil, $n^{25}D$ 1.5323, d^{25}_4 1.4394; equiv. wt., calcd. 293.2; obsd. 299.6 (solvolysis in 80% acetone), 299.4 (acetolysis), m.p. 31–32° after crystallization.

Anal. Calcd. for $C_{16}H_{13}SO_3Br$: C, 40.96; H, 4.47. Found: C, 40.77; H, 4.47.

Methyl-*i*-propylcarbinyl *p*-Bromobenzenesulfonate.—The necessary carbinol, b.p. 111.8–111.9 (754 mm.) was prepared from acetaldehyde and isopropylmagnesium bromide, The bromobenzenesulfonate was prepared in 55% yield in the form of a viscous oil, which could not be induced to crystallize, $n^{24}D$ 1.5292, d^{24}_4 1.389; equiv. wt., calcd. 307.2; found 309.6 (acetolysis).

Anal. Calcd. for $C_{11}H_{15}SO_3Br$: C, 43.00; H, 4.92. Found: C, 43.07; H, 5.20.

From the refractive indices and densities of the two esters described above, the molar refraction of the p-$BrC_6H_4SO_3$ group is found to be 43.79 ± 0.22.

3-Phenyl-2-butanols and 3-Phenyl-2-butyl *p*-Toluenesulfonates.—The alcohols, b.p. of both racemates, 114° (20 mm.), were obtained by the saponification of the acid phthalates furnished by Dr. Donald Cram. The distilled alcohols were converted to toluenesulfonates by the conventional procedure.

I. Racemate I from acid phthalate, m.p. 130–131°, gave rise to *p*-toluenesulfonate, m.p. 51°, in 58% yield.

Anal. Calcd. for $C_{17}H_{20}SO_3$: C, 67.08; H, 6.62. Found: C, 67.24; H, 6.57.

II. Racemate II from acid nitrophthalate, m.p. 156–157°, gave rise to *p*-toluenesulfonate, m.p. 42.5–43° in 48% yield.

Anal. Found: C, 67.09; H, 6.75.

Toluenesulfonate I displayed equivalent weights in acetolysis within 0.68–0.75% of theoretical and toluenesulfonate II within 0.78–2.0%.

1,1-Diphenyl-2-propanol and *p*-Bromobenzenesulfonate.—1,1-Diphenylacetone was prepared by addition of a solution of diphenylacetyl chloride, prepared from 106 g. (0.5 mole) of diphenylacetic acid, in 250 ml. of benzene in a nitrogen atmosphere, to a solution of dimethylcadmium in benzene prepared from 24 g. (1 mole) of magnesium and excess methyl iodide according to the directions of Cason.[49] The addition required 15 minutes and the reaction mixture was allowed to stand 1 hour at room temperature. Decomposition was effected with ice and hydrochloric acid. The organic layer was washed with water, sodium hydroxide solution, water, sodium sulfite solution and again with water, and finally dried over magnesium sulfate. Removal of the solvent on the steam-bath and distillation *in vacuo* yielded 66 g. of 1,1-diphenylacetone, b.p. 142–144° (2 mm.).

In more recent work, 1,1-diphenylacetone, b.p. 138–145° (1.5–3 mm.), m.p. 57–60° (reported 61°),[50] was prepared from phenylacetone by the method of Schultz and Mickey.[51]

The 66 g. of liquid ketone was dissolved in 120 ml. of anhydrous ether and added over 30 minutes to 3.8 g. of lithium aluminum hydride suspended in 120 ml. of ether. After stirring for 20 minutes, the reaction mixture was decomposed with water and cold dilute sulfuric acid. The organic layer was washed with water and potassium carbonate solution and dried over potassium carbonate. Evaporation of the ether left 62.9 g. of crude liquid 1,1-diphenyl-2-propanol. Similar reduction of 190 g. (0.90 mole) of solid ketone yielded 164 g. (84.5%) of 1,1-diphenyl-2-propanol, m.p. 62° from Skellysolve B (reported 62–63°).[52]

Preparation of the *p*-bromobenzenesulfonate from the carbinol in the usual way, allowing a reaction period of four days in the refrigerator, gave rise to the ester in 69% yield, m.p. 98–99°; equiv. wt., 428.8 (ethanolysis), 433.1 (acetolysis); calcd., 431.3.

Anal. Calcd. for $C_{21}H_{19}BrO_3S$: C, 58.47; H, 4.44. Found: C, 58.47; H, 4.61.

2-Phenyl-2-methyl-3-butanol and Derivatives.—To a methyl Grignard solution, prepared from methyl iodide (5 g., 0.055 mole), magnesium (5 g., 0.037 mole) and ether (100 cc.), was added 2-phenyl-2-methylpropionaldehyde (5 g., 0.034 mole) (kindly furnished by Mr. Lee Kent) in ether (50 cc.). The resulting mixture was stirred for one hour at room temperature after the addition was complete and it was then poured into ice-water containing sulfuric acid (15 cc., 6 *N*). The ether layer was separated, and the aqueous layer extracted with ether. The combined ethereal layers were washed with 5% sodium bicarbonate solution and dried over sodium sulfate. The ether was distilled on a steam-bath, the last traces under reduced pressure at room temperature. The residual oil, 3.9 g., represented a 71% yield of crude carbinol based on the starting aldehyde.

The crude alcohol (0.7 g., 4.3 mmol.) in 5 cc. of anhydrous pyridine was mixed with 0.9 g., 4.8 mmol., of *p*-nitrobenzoyl chloride and allowed to stand at room temperature for 12 hr. There was obtained in the usual way 0.9 g. (65%) of *p*-nitrobenzoate, m.p. 94–100°, m.p. 105.5–106.4° after several recrystallizations from ethanol.

Anal. Calcd. for $C_{18}H_{19}O_4N$: C, 68.67; H, 6.11. Found: C, 68.81; H, 6.03.

The crude 2-phenyl-2-methyl-3-butanol was left with *p*-bromobenzenesulfonyl chloride in pyridine for one week. Working up in the usual way gave a precipitate which was filtered and dissolved several times in chloroform and reprecipitated with petroleum ether (20–40°). The material crystallized slowly in the cold to yield 0.9 g. (28%) of *p*-bromobenzenesulfonate, m.p. 55–56°, decomposing after several days at room temperature. The equivalent weight of this material in acetolysis was 389 (calcd. 383.3).

Anal. Calcd. for $C_{17}H_{19}O_3SBr$: C, 53.27; H, 5.00. Found: C, 53.21; H, 4.97.

3,3-Diphenyl-2-butanol.—A 67-g. quantity of 3,3-diphenyl-2-butanone, m.p. 40.4–41° (reported 41–41.5°),[53]

(44) Kostanecki and Lampe, *Ber.*, **39**, 4019 (1906).

(45) Whitmore, Weisgerber and Shabica, THIS JOURNAL, **65**, 1469 (1943).

(46) Hauser and Hudson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 286.

(47) Schlenk and Ochs, *Ber.*, **49**, 610 (1916).

(48) Grunwald and Winstein, THIS JOURNAL, **70**, 846 (1948).

(49) Cason, *ibid.*, **68**, 2078 (1946).

(50) Tiffeneau, *Compt. rend.*, **143**, 127 (1898).

(51) Schultz and Mickey, *Org. Syntheses*, **29**, 38 (1949).

(52) Levy, Callais and Abragam, *Bull. soc. chim.*, **43**, 874 (1928).

(53) Tiffeneau and Levy, *ibid.*, [4] **41**, 1362 (1927); **45**, 732 (1929).

in 200 ml. of anhydrous ether was added to 11.4 g. of lithium aluminum hydride suspended in 360 ml. of ether with stirring over a 40-minute period and the reaction mixture was stirred one hour longer. Then it was decomposed with water and cold dilute sulfuric acid. The ether layer was separated, washed with water and dried over potassium carbonate. Evaporation of the ether left 58.2 g. of crude 3,3-diphenyl-2-butanol.

Attempts to prepare the toluenesulfonate or *p*-bromobenzenesulfonate from the above material were without success. Distillation of the alcohol gave, as a main fraction, material, b.p. 125–126° (0.7 mm.), which did not crystallize and which was somewhat impure, probably containing olefin (% C: calcd., 84.91; found, 86.60. % H: calcd., 8.00; found, 8.15). Attempted preparation of the toluenesulfonate from this material gave a solid, m.p. 94–96°, which analyzed near that of an olefin $C_{16}H_{16}$.

Product of Acetolysis of β,β-Diphenylethyl *p*-Toluenesulfonate.—In this experiment, for which we are indebted to Mr. William Beidler, a solution of 8.8 g. (0.02 mole) of toluenesulfonate in 500 ml. of glacial acetic acid was held at 100° for 35 hours. It was cooled and poured into water to yield 3.75 g. (83.5%) of a white solid after washing with water and drying, m.p. 122.8–124°, m.p. 123–124° after recrystallization from ethanol, no depression on admixture with Eastman Kodak Co. *trans*-stilbene, m.p. 123–124°. Further dilution and neutralization of the aqueous acetic acid phase and extraction with ether gave rise to 0.60 g. of more solid, m.p. 114–121°.

Rate Measurements.—Acetic acid solvent, usually 0.2% in acetic anhydride, was prepared as previously described.[7a] Absolute ethanol was prepared from commercial absolute ethanol with sodium and ethyl phthalate.[54] Titrations in acetic acid were carried out with standard sodium acetate in acetic acid.[7a] In ethanol, brom thymol blue was used as indicator.

The sealed-ampoule technique was used in the rate runs, and acetolyses were followed to 70–90% completion, except with neopentyl *p*-toluenesulfonate which was followed to 17% completion at 75° and 44% at 100°. Good first-order behavior was observed in acetolysis, the mean deviation in the constants obtained from the integrated first-order expression being shown in Table I.

The ethanolyses were followed less nearly to completion, especially with neopentyl *p*-toluenesulfonate, and the ethanolysis rate constants listed in Table I are much less precise than for acetolysis. These were considered sufficient for the purpose and were not studied further.

(54) Fieser, "Experiments in Organic Chemistry," The Macmillan Co., New York, N. Y., 1937, pp. 359, 360, 368.

LOS ANGELES 24, CALIF. RECEIVED JUNE 11, 1951

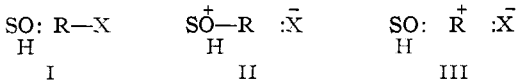
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen. VI. Formolysis and Other Solvolysis Rates of Some Simple Secondary and Primary Benzenesulfonates[1]

BY S. WINSTEIN AND HENRY MARSHALL

Formolysis and, in some cases, other solvolysis rates of the simple series of secondary *p*-bromobenzenesulfonates, RCH(OBs)CH_3 and the simple series of primary *p*-toluenesulfonates, RCH_2OTs, with R equal to Me, Et, *i*-Pr or *t*-Bu, have been determined in connection with the study of possible driving forces due to participation of carbon or hydrogen in the case of some of the members of the series. While such driving forces in the case of the methylisopropylcarbinyl and pinacolyl derivatives are small, contrast of the rate trend with change in R in the series RCH(OBs)CH_3 with the analogous trends in other series, gives some indication that there is some assistance to ionization from participation. Similarly, the indications are that the ionization of neopentyl derivatives is assisted by participation. A knowledge of the respective driving forces enables one to understand which participation will predominate when there are different possible competing participations. This is illustrated in the case of solvolysis of α-bromo-*t*-butylacetic acid anion.

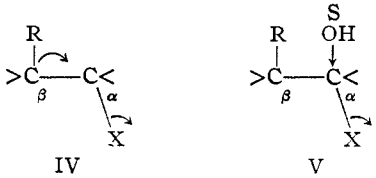
In our study of possible so-called participation[2] of carbon or hydrogen in nucleophilic replacement processes, together with the driving forces due to this participation, we have proceeded in some cases to the solvent formic acid, known to be an excellent ionizing solvent[3,4] for alkyl halides. The change from acetic acid to formic acid is one which makes solvolysis more nearly limiting[5] (**Lim.**) in character. In other words, there is a decrease (or virtual disappearance) of the driving force due to covalent



I II III

bond formation between R of RX and a solvent molecule SOH, indicated by the structure II contributing to the hybrid transition state (contributing structures I, II and III) for the rate-determining step of the solvolysis. There is an increase in the positive charge of the R portion of the RX molecule in the transition state, and internal electron supply becomes more important. Among the modes of internal electron supply is that due to participation of carbon or hydrogen (IV), and thus the effects on rate due to neighboring group participation (IV) may appear.

A change in solvent such as the one from acetic to formic acid helps to disclose driving forces due to participation, not only by allowing neighboring group participation (IV), where this is possible, to displace so-called solvent participation (V), but by making the rate of solvolysis of a reference substance (without participation) less assisted by nucleophilic driving force (II).



IV V

In the present paper we report and discuss the formolysis rates of the series of simple secondary alkyl *p*-bromobenzenesulfonates, RCH(OBs)CH_3 (E — H, Table IV), which were studied both to obtain more evidence on driving forces in the case of some of the members of the series, and to make available the necessary information for later rate

(1) Research supported by the Office of Naval Research.

(2) S. Winstein, B. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952).

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