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

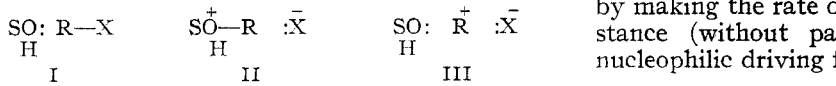
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

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.

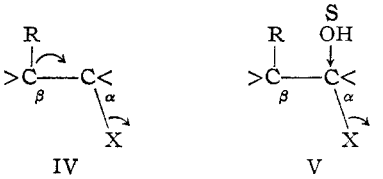
In our study of possible so-called participation[2] of carbon or hydrogen in nucleophilic replacement processes, together with the driving forces due to this participation, we have proceeded in some cases to the solvent formic acid, known to be an excellent ionizing solvent[3,4] for alkyl halides. The 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).

(3) I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946).

(4) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

(5) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

comparisons with other structures. Also reported are formolysis rates and, for comparison, acetolysis and ethanolysis rates of a series of primary *p*-toluenesulfonates, RCH_2OTs (A – D, Table III).

For the determination of formolysis rates, reaction mixtures from solvolysis of sulfonate esters in formic acid could not be titrated for generated acid by the methods employed formerly in glacial acetic acid.[6] However, by dilution of an aliquot portion of formolysis reaction mixture with 10 parts of glacial acetic acid and titration with acetic acid solutions of sodium acetate or *p*-toluenesulfonic acid using a potentiometric technique, it was possible to make reliable determinations of the extent of solvolysis. A typical set of formolysis data for a member of the series $RCH(OBs)CH_3$ is illustrated in Table I for isopropyl *p*-bromobenzenesulfonate E and the results of the rate measurements for the whole series (R = Me, Et, *i*-Pr, *t*-Bu) are summarized in Table II which also lists some rate constants for comparison purposes extrapolated from data at other temperatures with the aid of known or assumed reasonable values of $E^{\ddagger}$. Reactions were followed to 50–75% completion and first order constants were steady to ± 3% in general.

TABLE I

SOLVOLYSIS OF 0.07608 *M* ISOPROPYL *p*-BROMOBENZENESULFONATE IN FORMIC ACID AT 25.12°

Time, sec.	$10^2(RX)$ *M*	10^6k sec.$^{-1}$
0	7.048	
5400	6.537	1.39
9960	6.209	1.27
14820	5.735	1.39
21720	5.231	1.37
28380	4.812	1.34
41100	3.947	1.41
86280	2.069	1.42
	Mean	1.37 ± 0.04

For the primary *p*-toluenesulfonates, RCH_2OTs (R = H, Me, *i*-Pr), ethanolysis and acetolysis showed good first order behavior (Table II). The formolysis rates of the primary toluenesulfonates were measured similarly to those for the secondary esters but at higher temperatures, in general. At 60 or 75°, there was some tendency for formolysis rate constants to climb upward in a run, and this accounts for the usually higher mean deviations listed in Table II for these cases. This can probably, at least in part, be ascribed to the development of water in the decomposing formic acid solvent (see Experimental).

For both the secondary *p*-bromobenzenesulfonates, $RCH(OBs)CH_3$, and the primary *p*-toluenesulfonates, RCH_2OTs, the formolysis rate exceeds that for acetolysis by substantial factors. The factor is 12 at 75° in the case of CH_3OTs and rises to 226 ($10^{2.35}$) in the case of $(CH_3)_3CCH_2OTs$ (Table III). In the case of the secondary *p*-bromobenzenesulfonates, the factor at 25° varies from $10^{2.40}$ for isopropyl to $10^{3.09}$ for pinacolyl *p*-bromobenzenesulfonate (Table IV). For several of the compounds, namely, CH_3CH_2OTs, $(CH_3)_3CCH_2OTs$ and $CH_3CH(OBs)CH_3$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values in acetic and formic acid solvents (Tables III and IV) indicate that the increase in rate attending the solvent change is due essentially entirely to a change in $\Delta H^{\ddagger}$, the change in $\Delta S^{\ddagger}$ being negligible. For CH_3CH_2OTs, the available thermodynamic quantities of activation for ethanolysis (Table II) show $\Delta S^{\ddagger}$ to be essentially equal to the value in acetolysis or formolysis.

Apparent *m* values from the formic acid–acetic acid rate factors and the previously reported[4,5] **Y** values and equation 1 are given in Tables III and IV.

$$\log k_{HCOOH} - \log k_{AcOH} = m(Y_{HCOOH} - Y_{AcOH}) \quad (1)$$

The values of *m*, which measure sensitivity of solvolysis rate to ionizing power of solvent, vary from 0.295 for CH_3OTs, A, to 0.634 for neoPenOTs, D, at 75° and from 0.646 for $CH_3CH(OBs)CH_3$, E, to 0.832 for $(CH_3)_3CCH(OBs)CH_3$, H, at 25°.

It is instructive to compare, where possible, the *m* values based on the weakly nucleophilic acetic and formic acid solvents with those previously reported[4,5] for the more nucleophilic aqueous alcohols. For CH_3CH_2OTs and $CH_3CH(OBs)CH_3$ the present values are larger. In the case of CH_3CH_2OTs the present value, 0.374 at 75° and 0.437 at 25°, is to be compared with 0.262 at 50° in the aqueous alcohols.[5] In the isopropyl case, the present value, 0.646 at 25° and 0.536 at 75°, is to be compared with 0.408 at 70° in the aqueous alcohols.[5] On the other hand, in the case of neopentyl and pinacolyl esters, whose solvolysis is more nearly limiting[5] over the whole solvent range, the present values of *m* appear to compare well with those for other solvent ranges, including aqueous alcohols. For example, the present value of 0.634 for neoPenOTs, D, compares closely with the value of 0.712 given previously[4] for neopentyl bromide since one still needs to allow for the higher value of *m* for a bromide relative to an arylsulfonate.[5] For pinacolyl *p*-bromobenzenesulfonate, H, the 0.832 value for *m* in the present work at 25° is probably in fair agreement with the value of 0.706 previously[4] reported at 70° for another solvent range when one considers the effect of temperature on the *m* value (see isopropyl, Table IV).

It is interesting to observe the variation in the solvent rate sequence, EtOH:AcOH:HCOOH, for the several primary *p*-toluenesulfonates, A—D, as the structure becomes more and more favorable to solvolysis of the **Lim.** type (Table III). For MeOTs, A, the sequence at 75° is 81:1:12, with a minimum at acetic acid. It becomes 39:1:25 for EtOTs, B, 6.2:1:99 for *i*-BuOTs, C, and, finally with neoPenOTs, D, it is 0.28:1:226, ethanol giving the lowest solvolysis rate.[4]

For the primary *p*-toluenesulfonates, it is also instructive to observe the variation in the structural rate sequence, Me:Et:*i*-Bu:neoPen, as the solvent medium varies in the direction of the **Lim.** type of solvolysis. In Table V the present pertinent data are summarized together with some other available solvolysis rate comparisons with alkyl bromides. In absolute ethanol, the *p*-toluenesulfonates give the sequence (1, Table V)

(6) S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

TABLE II

SUMMARY OF SOLVOLYSIS RATES

Compound	Solvent	RX concn. 10^3 M	Temp., °C.	k_1 (sec.$^{-1}$)
$CH_3CH(OBs)CH_3$	EtOH		75.0[a,4]	4.5×10^{-4}
	AcOH		25.0[a,2,4]	2.43×10^{-7}
	AcOH		75.0[a,2,4]	1.18×10^{-4}
	HCOOH	8.0–9.3	25.12	$(6.20 \pm 0.10) \times 10^{-5}$
	HCOOH	4.3–4.4	39.95	$(3.50 \pm 0.19) \times 10^{-4}$
	HCOOH		25.0[a]	6.11×10^{-5}
	HCOOH		75.0[a]	1.16×10^{-3}
$CH_3CH_2CH(OBs)CH_3$	AcOH		25.0[a,2]	5.61×10^{-7}
	HCOOH	8.1–9.3	24.48	$(1.43 \pm 0.03) \times 10^{-4}$
	HCOOH		25.0[a]	1.52×10^{-4}
$(CH_3)_2CHCH(OTs)CH_3$	HCOOH	14.1–15.0	24.50	$(2.53 \pm 0.10) \times 10^{-4}$
$(CH_3)_2CHCH(OBs)CH_3$	AcOH		25.0[a,2]	1.45×10^{-6}
	HCOOH	4.0–4.3	24.92	$(8.50 \pm 0.11) \times 10^{-4}$
	HCOOH		25.0[a]	8.59×10^{-4}
$(CH_3)_3CCH(OBs)CH_3$	AcOH		25.0[a,2,4]	6.95×10^{-7}
	HCOOH	9.3–9.4	25.13	$(8.74 \pm 0.17) \times 10^{-4}$
	HCOOH		25.0[a]	8.58×10^{-4}
CH_3OTs	EtOH	3.9–6.1	75.01	$(6.87 \pm 0.06) \times 10^{-5}$
	AcOH	2.7–4.1	75.01	$(8.52 \pm 0.08) \times 10^{-7}$
	AcOH	2.7–3.3	99.60	$(7.86 \pm 0.15) \times 10^{-6}$
	HCOOH	7.4–8.5	75.01	$(1.06 \pm 0.04) \times 10^{-5}$
CH_3CH_2OTs	EtOH[b]	3.6–4.6	75.00	$(2.98 \pm 0.06) \times 10^{-5}$
	AcOH	3.0–4.5	74.56	$(7.39 \pm 0.10) \times 10^{-7}$
	AcOH	3.8–4.3	99.63	$(8.47 \pm 0.12) \times 10^{-6}$
	AcOH		75.00[a]	7.72×10^{-7}
	AcOH		25.00[a]	1.78×10^{-9}
	HCOOH	10.7–12.6	74.75	$(1.85 \pm 0.06) \times 10^{-5}$
	HCOOH	10.1	60.05	$(4.31 \pm 0.24) \times 10^{-6}$
	HCOOH		75.00[a]	1.89×10^{-5}
	HCOOH	12.1–12.2[c]	74.57	$(1.93 \pm 0.17) \times 10^{-5}$
$(CH_3)_2CHCH_2OTs$	EtOH	3.0–4.1	74.81	$(1.33 \pm 0.06) \times 10^{-6}$
	AcOH	2.0–2.1	74.71	$(2.30 \pm 0.06) \times 10^{-7}$
	AcOH	2.5–2.8	99.68	$(3.79 \pm 0.04) \times 10^{-6}$
	AcOH		75.00[a]	2.34×10^{-7}
	HCOOH	4.5–5.6	74.71	$(2.25 \pm 0.16) \times 10^{-5}$
	HCOOH		75.00[a]	2.31×10^{-5}
$(CH_3)_3CCH_2OTs$	EtOH		75.0[a,2]	1.7×10^{-8}
	AcOH		75.00[a,2]	8.35×10^{-8}
	AcOH		25.00[a,2]	3.41×10^{-11}
	HCOOH	9.7–10.0	74.67	$(1.82 \pm 0.04) \times 10^{-5}$
	HCOOH	6.3–8.2	60.05	$(3.13 \pm 0.40) \times 10^{-6}$
	HCOOH		75.0[a]	1.89×10^{-5}
	HCOOH		25.0[a]	2.28×10^{-8}

[a] Extrapolated or interpolated from data at other temperatures. [b] Using rate at 50° previously reported,[5] $\Delta H^{\ddagger} = 21.6$ kcal./mole; $\Delta S^{\ddagger} = -17.5$ e.u. [c] In these runs, sodium formate, 0.0946 and 0.1041 M, was included.

TABLE III

SOME COMPARISONS WITH THE PRIMARY SERIES

		Rel. rates 75°				AcOH		HCOOH	
		EtOH	AcOH	HCOOH	Apparent m[a]	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
A	H_3COTs	81	1	12	0.295	22.6	−20.9		
B	H_3CCH_2OTs	39	1	25	.374[b]	24.4	−16.7	22.1	−16.5
C	$(CH_3)_2\overset{H}{\underset{\vert}{C}}—CH_2OTs$	6.2	1	99	.546	28.2	− 8.0		
D	$(CH_3)_2\overset{CH_3}{\underset{\vert}{C}}—CH_2OTs$	0.28	1	226	.634	31.5	0.96	27.0	− 2.8

[a] From equation 1, ΔY being 3.71. [b] Value is 0.437 at 25°.

TABLE IV

SOME COMPARISONS WITH THE SECONDARY SERIES

	ROBs	Rel. k_{AcOH} 25°	Rel. k_{HCOOH} 25°	log $\frac{k_{HCOOH}}{k_{AcOH}}$	Apparent m[a]	AcOH: $\Delta H^{\ddagger}$, kcal./mole	AcOH: $\Delta S^{\ddagger}$, e.u.	HCOOH: $\Delta H^{\ddagger}$	HCOOH: $\Delta S^{\ddagger}$
E	$CH_3CH(OBs)CH_3$	1	1	2.40	0.646[b]	24.8	−5.5	21.1	−7.2
F	$CH_3CH_2CH(OBs)CH_3$	2.3	2.5	2.43	.655	23.7	−7.7		
G	$(CH_3)_2\overset{H}{\underset{|}{C}}-CH(OBs)CH_3$	6.0	14.4	2.77	.747	24.7	−2.3		
H	$(CH_3)_2\overset{CH_3}{\underset{|}{C}}-CH(OBs)CH_3$	2.9	14.4	3.09	.832	26.3	+1.5		

[a] Calculated with equation 1, ΔY being set[4] at 2.08 − (−1.633). [b] Value is 0.536 at 75°.

TABLE V

SUMMARY OF RATE COMPARISONS FOR SOLVOLYSIS OF PRIMARY DERIVATIVES

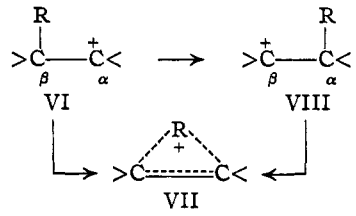
		R = CH_3— A	CH_3CH_2— B	$(CH_3)_2\overset{H}{\underset{|}{C}}-CH_2$— C	$CH_3-\overset{CH_3}{\underset{|}{C}}-CH_2$— D
1	ROTs, EtOH, 75°	4000	1750	80	1
2	RBr, 50% EtOH[3], 95°	310	160	12	1
3	RBr, 70% EtOH[3], Ag^+, 64°	62	77	6.5	1
4	RBr, 70% Dioxane,[7] Hg^{++}, 25°		7	1	
5	ROTs, AcOH, 75°	10	9	2.8	1
6	RBr, HCOOH,[3] 95°	0.64	1		0.57
7	ROTs, HCOOH, 75°	0.56	1.0	1.22	1.0

of steeply descending rates, 4000:1750:80:1. The bromides in 50% EtOH at 95° are reported by Dostrovsky, Hughes and Ingold[3] (2, Table V) to give the rate sequence, 310:160:12:1, the factor between Me and neoPen now being only *ca.* 300. The sequence is successively further compressed for the reaction of bromides with silver ion in 70% EtOH (3, Table V), or with mercuric ion in 70% dioxane[7] (4, Table V), and for the acetolysis of *p*-toluenesulfonates (5, Table V). The most limiting solvolysis appears to be the formolysis of the toluenesulfonates, the sequence (7, Table V) being 0.56:1.0:1.22:1.0.

The tendency for α-methyl substitution to become rate enhancing as the solvent changes in the direction of the **Lim.** type of solvolysis, and the R part of the solvolysis transition state (I↔II↔III), becomes more and more electron deficient, was illustrated previously[5] with the sequence, Me:Et:*i*-Pr, in several solvents. This can be more strikingly demonstrated with the aid of the present data and some from the literature summarized in Table VI. Thus the rate sequence Me:Et:*i*-Pr either descends as in 1:0.37:0.28 for RBr in EtOH at 50°, or has a minimum, as in 1:0.9:46 for ROTs in AcOH at 75°, or rises, as in 1:1.8:364 for ROTs in HCOOH at 75°.

Judging by the rate comparisons in Table VI, a *p*-toluenesulfonate may tend to exceed a bromide in the approach of solvolysis to the **Lim.** type. Also, from Tables V and VI, various solvent media line up approximately in the order, EtOH<80% EtOH<50% EtOH<Ag^+, 70% EtOH<H_2O<AcOH<HCOOH, for increasing approach of the solvolysis to the **Lim.** type.

Our present chief interest in the here reported solvolysis rates is with respect to driving forces due to participation of carbon or hydrogen in cases such as $(CH_3)_2CHCH(OBs)CH_3$, G, $(CH_3)_2C(CH_3)$-$CH(OBs)CH_3$, H, and $(CH_3)_2C(CH_3)CH_2OTs$, D, which we originally expected might lead to the appearance of a driving force due to participation (IV). Even if a substantial activation energy is



intrinsically associated with carbonium ion rearrangement VI→VIII or VI→VII→VIII where C_α and C_β are symmetrically or equivalently substituted, unsymmetrical substitution such that VIII is more stable than VI could make this activation energy disappear. It could become energetically profitable to couple, to a certain extent, the migration VI→VIII or VI→VII with the ionization of the original C_α–X linkage (IV).

The relative solvolysis rates of the series of secondary *p*-bromobenzenesulfonates, $RCH(OBs)CH_3$ (E-H, Table IV), with R = Me, Et, *i*-Pr, *t*-Bu, are 1:2.0:6.0:3.5 in acetolysis[2] at 49.6°. These calculate to be 1:2.3:6.0:2.9 at 25°, as summarized in Table IV. In formic acid as a solvent at 25°, the sequence becomes 1:2.5:14.4:14.4 (Table IV) the relative values for E and F remaining the same, but the values for G and H going higher. While we have seen some cases of rearrangement associated with large driving forces,[2] the rate sequence E-H, even in formic acid, shows

(7) O. T. Benfey, THIS JOURNAL, **70**, 2163 (1948).

TABLE VI

SUMMARY OF RATE COMPARISONS FOR Me, Et AND *i*-Pr DERIVATIVES

	R =	Me	Et	*i*-Pr
1	RBr, EtOH,[5] 50°	1	0.37	0.28
2	ROTs, EtOH, 75°	1	0.44	2.2
3	RBr, 80% EtOH,[5] 50°	1	0.39	0.54
4	RBr, HOH,[5] 50°	1	1.08	11
5	ROTs, AcOH, 75°	1	0.9	46
6	RBr, HCOOH,[8] 100.2°	1	1.7	45
7	RBr, Hg^{++}, 70% dioxane,[7] 25°		1	145
8	ROTs, HCOOH, 75°	1	1.8	364

that any driving force associated with the rearrangement accompanying solvolysis[2] reactions of methylisopropylcarbinyl and pinacolyl derivatives[9] and other reactions,[10] such as the conversion of the carbinols to halides, is not large.

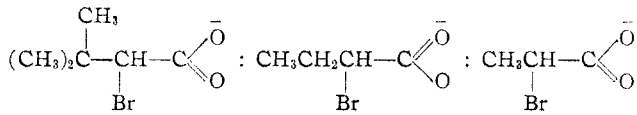
Whether the increased rates of G and H are to be ascribed to a driving force due to participation of hydrogen or carbon, is not easy to decide. This is because it is difficult to recognize small driving forces due to participation promoted by variation of the state of substitution of C_β since a number of other effects are associated with such variation. Variation of RX from $H_3C-\overset{\beta}{C}<\overset{\alpha}{}\overset{}{X}$ to $(CH_3)_3C-\overset{\beta}{C}<\overset{\alpha}{}\overset{}{X}$ would decrease the extent of departure of the solvolysis from the **Lim.** category[5] and thus the amount of nucleophilic assistance from solvent (II); this would contribute a downward trend in the rate sequence. A small upward trend would be expected from the sequence of relative electron supply, *t*-Bu > *i*-Pr > Et > Me, by alkyl groups in the so-called inductive effect.[11] A small downward trend would be expected if the hyperconjugative order of alkyl groups observed in other electron-demanding reactions[12] prevailed. Steric hindrance to solvation[5] of the transition state for solvolysis would also contribute a downward trend. In this connection, the general upward trend of $\Delta S^\ddagger$ values for acetolysis of the members of the series, E-H, (−5.47, −7.75, −2.27, 1.55 e.u.) (Table IV), is in line with decreasing solvation. The $\Delta H^\ddagger$ values (24.8, 23.7, 24.7, 26.3 kcal./mole) show the upward trend which would be expected on this basis but not sufficiently to give the downward trend in rate anticipated if solvation were the governing consideration.

The same general group of effects are involved in variation of R in tertiary halides, $RCX(CH_3)_2$, and some assistance may be derived from comparison of the results with the series of secondary *p*-bromobenzenesulfonates, E-H, with those from solvolysis of tertiary halides, $RCX(CH_3)_2$. With tertiary halides, in 80% ethanol at 25°, with R = Me, Et, *i*-Pr, *t*-Bu, the rate sequence is 1:1.7:0.9:1.2 for X = Cl[13]; it is 1:1.8:1.2:1.7 for X = Br.[14] For X = Cl, the activation energy[15] $E^\ddagger$ (23.1, 22.9, 23.3, 23.8 kcal./mole), shows somewhat the same trend as the $\Delta H^\ddagger$ values in the series E-H.

While the sequence of rates for the tertiary series begins similarly to the E-H series with a small rise from Me to Et there is a drop from R = Et to R = *i*-Pr instead of a rise. Also, there is a slight rise from R = *i*-Pr to R = *t*-Bu, ascribed by Brown and Fletcher[13] to B-strain. As has been emphasized previously[16] the rate sequence here is very constant. This can be taken as an indication that ionization rates may be expected to be insensitive to β-methyl substitution[15,16] (in the absence of important steric effects).

While the net balance of the effects of varying R from Me to *t*-Bu in the tertiary series of halides $RCHCl(CH_3)_2$ is not necessarily required to be the same as in the secondary series, E-H, comparison of the rise in rate from Et to *i*-Pr or *t*-Bu in AcOH and more so in HCOOH with the effect in the tertiary series, suggests that the E-H rate sequence is indeed influenced by a driving force due to participation in the last two members.

Some support for a driving force due to participation of methyl in the solvolysis of $(CH_3)_2C(CH_3)$-$CH(OBs)CH_3$ comes from the first order rates of solvolysis of the α-bromoacid anions, $RCHBrCO_2^-$. These are secondary bromides whose solvolysis involves participation of the carboxylate ion group,[17] and which is less conducive to neighboring methyl participation. Here, variation of R gives the sequence of relative rates in water at 70°



	$(CH_3)_2C(CH_3)CHBrCO_2^-$	:	$CH_3CH_2CHBrCO_2^-$	:	$CH_3CHBrCO_2^-$
10^4k	2.1[18]	:	4.2[19]	:	2.7[19,20]

In water at 25°, there is obtained the comparison

	$(CH_3)_3CCHBrCO_2^-$	:	$CH_3CHBrCO_2^-$
10^7k	1.7[21]	:	2.75[22]

In this series, the change of R from Me to Et produces again the usual small increase in rate already illustrated, but the change of R to *t*-Bu does not produce an increase, as in the series E-H, but, instead, a small decrease.

When it comes to deciding the extent to which ionization in the primary series, A-D (Table III), is assisted by participation of hydrogen in isobutyl C or carbon in neopentyl D, it is difficult indeed

(8) L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 945 (1940).

(9) There are indications (H. Marshall, unpublished work), that the solvolysis even of *s*-butyl *p*-bromobenzenesulfonate is accompanied by some rearrangement.

(10) (a) P. G. Stevens, W. E. Higbee and R. T. Armstrong, THIS JOURNAL, **60**, 2658 (1938); (b) F. C. Whitmore and H. S. Rothrock, *ibid.*, **55**, 1106 (1933); (c) F. C. Whitmore and F. Johnston, *ibid.*, **60**, 2265 (1938).

(11) C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

(12) (a) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940); (b) P. B. D. De la Mare and P. W. Robertson, *ibid.*, 279 (1943); (c) E. Berliner and F. Berliner, THIS JOURNAL, **68**, 2355 (1946); **71**, 1195 (1949).

(13) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

(14) H. C. Brown and A. Stern, *ibid.*, **72**, 5068 (1950).

(15) E. D. Hughes, C. K. Ingold, R. J. L. Martin and D. F. Meigh, *Nature*, **166**, 679 (1950).

(16) S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

(17) E. Grunwald and S. Winstein, *ibid.*, **70**, 841 (1948).

(18) Extrapolated with aid of data of J. Gripenberg, E. D. Hughes and C. K. Ingold.[21]

(19) G. S. Simpson, THIS JOURNAL, **40**, 674 (1918).

(20) The same value is obtained by extrapolation from 59.7° using the data of A. F. Chadwick and E. Pacsu [*ibid.*, **65**, 392 (1943)].

(21) J. Gripenberg, E. D. Hughes and C. K. Ingold, *Nature*, **161**, 480 (1948).

(22) Extrapolated from data of A. F. Chadwick and E. Pacsu (see ref. 20).

to select a reference value[2] of k_c, the rate of ionization, without such assistance. With bromides in formic acid at 95°, Dostrovsky, Hughes and Ingold[3] report the sequence (Table V) Me, 0.64: Et, 1:neoPen,0.57; they regard the so-called unimolecular mechanism as important throughout the series. In formic acid at 75°, the rates of the *p*-toluenesulfonates, A-D give the sequence (Table V), Me, 0.56:Et, 1:*i*-Bu, 1.22:neoPen, 1.0, and the additional information that there is a maximum in rate at isobutyl. Considering the major changes in the sequence, Me:Et:*i*-Bu:neoPen, on going from ethanol to acetic acid to formic acid, there is no reason to suppose that a limiting sequence has been reached in formic acid. In acetic acid, $\Delta H^{\ddagger}$ increases by some 9 kcal./mole on going from MeOTs to neoPenOTs but there is a nearly completely balancing increase in $\Delta S^{\ddagger}$ of some 20 e.u. (Table III). While the data in formic acid are less complete, the behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ appears to be quite parallel. Thus there is nothing like a constant $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the primary series as virtually obtains in the case of the tertiary halides,[15] $RCCl(CH_3)_2$.

It seems very doubtful that the formolysis of MeOTs could be anything close to limiting in character, for, if it were, EtOTs would be even more so, and its rate would be expected to be larger by the kind of factor characteristic for an α-methyl group, at least 10^4. Instead, the ratio of rates in formic acid at 75° is 1.8. Thus the solvolysis of MeOTs must be very far from limiting. While the factor due to an α-methyl group, even for solvolyses in the **Lim.** category, will vary somewhat with temperature, solvent and structure, very large decreases in the factor may be used for diagnosis. Such decreases will occur, for example, when the solvolysis of one or both of the substances involved in the comparison either are far from **Lim.** with respect to the solvent or involve participation.[2,16]

Summarized in Table VII are the actual or estimated rate ratios in formic acid, EtOTs/MeOTs, *i*-PrOTs/EtOTs, $(CH_3)_2CHCH(OTs)CH_3$/*i*-BuOTs and pinacolylOTs/neoPenOTs, showing the effect, on formolysis rate, of α-methyl substitution in the members of the primary series A-D.

TABLE VII

SOME RATE FACTORS DUE TO α-METHYL SUBSTITUTION

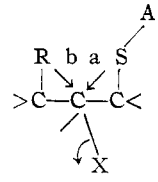
Compound pair	Ratio of solvolysis rates HCOOH 75°	HCOOH 25°
CH_3CH_2OTs/CH_3OTs	1.8	
$CH_3CH(OTs)CH_3/CH_3CH_2OTs$	200	
$(CH_3)_2CHCH(OTs)CH_3/(CH_3)_2CHCH_2OTs$	2240	5200
$(CH_3)_3C(CH_2)CH(OTs)CH_3$/ $(CH_3)_3C(CH_3)CH_2OTs$	4180	12,500

The latter two are similarly high, being 2240 and 4180 at 75° and 5200 and 12,500 at 25°. These are of the order of 10^4. On the other hand, the factor *i*-Pr/Et is *ca.* 200, and this seems much too low for the solvolysis of EtOTs to be anything close to limiting in type. With the bromides in formic acid[8] at 100.2°, the factor *i*-Pr/Et is 26. On this basis, the formolysis of EtOTs (and also EtBr) is far from the **Lim.** category and is higher than it would be were it limiting. The rate of neoPenOTs, with its very large steric hindrance[3] to back-side solvent entry, is just as high. In view of the results of variation of R in $RCCl(CH_3)_2$ from Me to *t*-Bu, the simplest explanation for the rate of neoPenOTs is that there is some assistance from participation of carbon in this case (IV).

In the case of *i*-BuOTs, the hindrance[3] at the α-carbon atom is very much less than it is for neoPenOTs, so the same argument used above with neoPen does not apply. The solvolysis rates would be consistent with some successful competition, in the rate-determining step, of hydrogen participation leading to rearrangement (observed in certain solvolysis type reactions of *i*-Bu derivatives[23]) with solvent participation (IV and V).

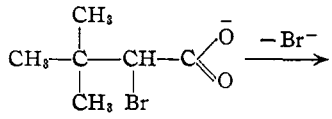
The solvolysis–rearrangement reactions of some of the arylsulfonates are being further scrutinized. Also, rates of solvolysis of, for example, methylisopropylcarbinyl *p*-bromobenzenesulfonate, deuterated at the position of the potentially participating hydrogen atom, are being determined.

Competition between Wagner–Meerwein Rearrangement and Neighboring Functional Group Participation.—When participation by different groups is possible, a knowledge of the driving forces due to the respective competing participations helps one to understand which participation will predominate in the rate-determining ionization. As an example of one kind of competition we can take the one between a functional neighboring group[6,16,17] (a) and carbon (b) as symbolized in IX. To be more specific let us take the carboxylate

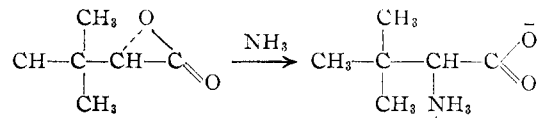


IX

ion group as the neighboring functional group and solvolysis of α-bromo-*t*-butylacetic acid anion X as the specific example. In the ammonolysis of



X



XI XII

this material with the neopentyl type structure, one could anticipate either a Wagner–Meerwein rearrangement or solvolysis with participation of the carboxylate-ion group[17] by way of the α-lactone XI. Actually, we now know that the driving force from participation of a carboxylate-ion group is substantial in a structure of this kind.[17] Also, the driving force due to participation of carbon in a structure of this kind is small. Therefore, it is

(23) *E.g.*, (a) E. Linneman and Zotta, *Ann.*, **162**, 12 (1872); (b) L. Henry, *Compt. rend.*, **145**, 899, 1247 (1907).

clear why the carboxylate-ion group controls matters and holds structure in the rate-determining step. It is at least not surprising that the α-carboxylate-ion group continues to preserve structure until XI is attacked by ammonia to give the unrearranged aminoacid[24] XII (with retained configuration).

Experimental

Arylsulfonates.—Methyl *p*-toluenesulfonate, b.p. 136.5–137.5° (2 mm.), $n^{25}D$ 1.5142, equiv. wt. in ethanol 184.2 (calcd. 186.2) was purified Eastman Kodak Co. material. Ethyl *p*-toluenesulfonate, m.p. 33.5–34.2°, equiv. wt. 199.7 (EtOH), 202.8 (AcOH), (calcd. 200.3), was employed. The neopentyl *p*-toluenesulfonate, m.p. 48–49°, isopropyl *p*-bromobenzenesulfonate, m.p. 32.5–33.5°, 2-butyl *p*-bromobenzenesulfonate, m.p. 31–32°; pinacolyl *p*-bromobenzenesulfonate, m.p. 53–54°; and methyl-*i*-propylcarbinyl *p*-bromobenzenesulfonate, $n^{25}D$ 1.5298, were similar to the samples previously employed.[2,4]

Isobutyl *p*-Toluenesulfonate.—This material, m.p. 12.0–12.5°, was prepared in the conventional manner.

Anal. Calcd. for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06. Found: C, 57.97; H, 7.26.

Methyl-*i*-propylcarbinyl *p*-Toluenesulfonate.—This material, m.p. 20.1–20.8°, was prepared in the usual manner.

Anal. Calcd. for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.49. Found: C, 59.48; H, 7.76.

Solvents.—Absolute ethanol[2,5] contained less than 0.012% water as shown by Karl Fischer titration.

The acetic acid[2,5] solvent titrated 0.0066 *M* in acetic anhydride.

Formic acid (Baker and Adamson C.P., 98–100%) was purified in 4-l. batches. The low-boiling components were distilled off through a 2-foot helixes-packed column until the head temperature reached 99°. After cooling, pure boric anhydride (4 g. per gram of water, calculated on the basis of 2% water) was added. After it had stood three days at room temperature, the formic acid was decanted and distilled from some fresh boric anhydride; b.p. 30–31° (50 mm.). The acid content, determined by titration with standard sodium hydroxide, was 99.95 and 100.3%, while the water content determined by Karl Fischer titrations at 0° were 0.08 and 0.19% by weight for two batches, respectively.

Methods of Rate Measurements.—Rates in acetic acid and ethanol were measured by the usual ampoule technique.[2,5]

In formic acid, the reagents were weighed out and made up to volume with formic acid at 23–26°. For the 25° runs, the volumetric flask was immersed in the desired thermostat. The samples were withdrawn with a 5-ml. calibrated automatic pipet, delivered into a beaker containing 50 ml. of anhydrous acetic acid and titrated potentiometrically as described below. The time of delivery into the acetic acid was used in the rate calculations, and the time called zero for the first sample. For most of the runs above 25°, the contents of the volumetric flask were transferred into a container[25] which was fitted with a spiral condenser and a calcium chloride tube and was immersed in the desired thermostat. Approximately 10-ml. samples were withdrawn and cooled in ice for 45 seconds; a 5-cc. aliquot from a calibrated automatic pipet was delivered into a beaker containing 50 ml. of anhydrous acetic acid and titrated potentiometrically as described below. The time of removal of the 10-ml. sample was used in the calculations and the time called zero for the first sample.

In the case of formolysis of ethyl *p*-toluenesulfonate at 60°, the development of water in the formic acid was followed by Karl Fischer titration, the time in hours and the % water at several points being: 0 hours, 0.08%; 48 hours, 0.23%; 100 hours, 0.76%.

Potentiometric Titration.—A Beckman *p*H meter, model H-2 with standard glass and calomel electrodes, was employed.[26] The electrodes were connected to the *p*H meter by a crude Wheatstone bridge. The glass electrode was attached directly to the *p*H meter, and the calomel electrode to the negative side of a dry cell and to one side of a 50,000 ohm variable resistor (R). The middle pole of R was connected to the *p*H meter (normal connection of the calomel electrode), and the side pole of R to the positive side of the dry cell. The buret tip was coated with Descicote [National Technical Laboratories, Pasadena, California], and the beaker was set in a copper cup, which was grounded. The electrodes were immersed in the stirred solution to be titrated, and the mv. reading adjusted with R and the standardization knob on the *p*H meter, to an arbitrary setting of 700 mv. on the 800 mv. scale. The solution was titrated with *ca.* 0.05 *N* sodium acetate in acetic acid and the mv. readings plotted against volume of added base. From the inflection points of the curve, the concentration of acid generated in the reaction was calculated.

For formolysis runs in the presence of formate ion the titrating solution was *ca.* 0.05 *N* *p*-toluenesulfonic or perchloric acid in acetic acid. The *p*H meter was adjusted to an arbitrary setting of 700 mv. as above, this time however, using the 1400 mv. scale.

Check on Titration Procedure.—The potentiometric titration procedure used on formic acid diluted with acetic acid was checked by titration of aliquots of a glacial acetic acid solution of *p*-toluenesulfonic acid, first in the usual[5] way with brom phenol blue indicator, and then potentiometrically after the proper addition of formic acid. On a solution, 0.04221 ± 0.00002 *N* by the indicator method, the potentiometric method gave 0.04196 ± 0.00012, while on one 0.004222 ± 0.000005, the potentiometric method gave 0.004143 ± 0.000032.

A formic acid solution of *p*-toluenesulfonic acid was titrated after various times at 75°, the normalities, 0.03234, 0.03240, 0.03244 and 0.03245, being obtained after 0, 10, 157 and 1265 minutes, respectively.

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(24) E. Abderhalden, W. Faust and E. Haase, *Z. physiol. Chem.*, **228**, 187 (1934).

(25) An open system was employed, since ampoules occasionally burst due to the pressure developed from decomposition of the formic acid.

(26) The electrodes, especially the calomel, deteriorate slowly in the solvent used.