1253. k_{OTs}/k_{Br} *Ratios and the Separation of Charges in the Transition States of Solvolytic Displacements*

By H. M. R. HOFFMANN

The scope of the k_{OTs}/k_{Br} ratio as a mechanistic criterion is explored for solvolytic displacements. For these reactions, ratios rise steeply along the series Et, Pr^i, Bu^t, indicating increasing charge separation between carbon and the leaving group in the transition state. Along the β-methylated series, ratios increase for formolyses, but decrease for hydrolyses, this difference being ascribed to the difference in solvent type. It is suggested that, in general, the faster an S_N1 (and $E1$) reaction, the more ionic its transition state. An attempt is made to estimate charge-development in the transition state from the value of k_{OTs}/k_{Br}.

Some limitations of the k_{OTs}/k_{Br} ratio as a mechanistic criterion are discussed. They arise from solvation differences in the transition and initial states of RBr and ROTs, *i.e.*, from disturbances due to $\Delta\Delta F_s^‡$ (*e.g.*, for carbonium ions with strongly dispersed charges and formed in highly polar solvents) and to $\Delta\Delta F_v$ (*e.g.*, for structurally ordered solvents).

THE k_{OTs}/k_{Br} ratios of the preceding Paper[1] referred mainly to substitutions of charge-type 1 of the Hughes–Ingold classification,[2] *i.e.*, reactions

$$N^- + R{-}X \longrightarrow R{-}N + X^- \quad (X = OTs\ \text{or}\ Br) \qquad (1)$$

Clearly, for these displacements the ratios reflect charge separation between carbon and the leaving group in the transition state in good approximation, *i.e.*, toluene-*p*-sulphonate ion is an electronically versatile leaving group and the ratio k_{OTs}/k_{Br} is dominated by changes in $\Delta\Delta F_g^‡$, with little disturbance from $\Delta\Delta F_v$ and $\Delta\Delta F_s^‡$.

We here discuss ratios, which are all greater than unity, refer to sovolyses, and so belong to another charge-type. Tables 1—3 give the results for some formolyses, hydrolyses, and ethanolyses, respectively.

TABLE 1

k_{OTs}/k_{Br} ratios for the formolysis of some alkyl derivatives. Comparison with the rates of gas-phase elimination of alkyl bromides

	Me	Et	Pr^n	Bu^i	Neopentyl	$PhCH_2CH_2$	Pr^i	2-Pentyl
10^5k_1 (sec.$^{-1}$) ROTs at 75°	1·06 [a]	1·89 [a]	1·32	2·31 [a]	1·89 [a]	4·10 [b]	464 [c]	14·10 [d]
,, RBr at 95°...	0·174 [e]	0·270 [e]	0·185 [e]	0·326	0·153 [e]	0·186	10·5 [f]	22·4 [g]
k_{OTs}/k_{Br} at 95°	24 [h]	41	47	58	90	152	360 [f,c]	498 [g]
Rel. k for gas-phase elimination of RBr at 400° ...	—	1 [i]	3 [i]	5·3 [i]	—	2 [j]	138 [i]	300 [k]

[a] Ref. 3. [b] Ref. 4. Ref. 5 gives $k_1 = 3·80 \times 10^{-5}$ sec.$^{-1}$ at 75·25°. [c] From ref. 3, assuming $k_{OBr}/k_{OTs} = 2·5$. [d] Extrapolated from data in ref. 6. [e] Ref. 7. [f] At 100·2°; ref. 8. [g] At 98°; ref. 6. [h] At 75°. Ref. 9. [j] Estimated from ref. 10. [k] For Bu^s; ref. 9.

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[1] H. M. R. Hoffmann, preceding Paper.

[2] C. K. Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, ch. 7.

[3] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1120.

[4] S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, 1956, **78**, 4801.

[5] W. H. Saunders, S. Ašperger, and D. H. Edison, *J. Amer. Chem. Soc.*, 1958, **80**, 2421.

[6] E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, 1954, **76**, 791.

[7] I. Dostrovsky and E. D. Hughes, *J.*, 1946, 171.

[8] L. C. Bateman and E. D. Hughes, *J.*, 1940, 940, 945.

[9] C. H. DePuy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.

[10] B. Stephenson, Ph.D. Thesis, University of London, 1957.

TABLE 2

$k_{\mathrm{O\cdot SO_2Ph}}/k_{\mathrm{Br}}$ ratios for the aqueous hydrolysis of some alkyl compounds at 50°
(all data from refs. 11 and 12)

	Me	Et	$\mathrm{Pr^n}$	$\mathrm{Bu^i}$	Neopentyl	Pr
10^5k (sec.$^{-1}$) $\mathrm{ROSO_2Ph}$	19·7	18·5	13·2	2·27	0·55	1160
$\Delta S^{\ddagger}$ (e.u.)	−11·58	−10·30	−12·33	−6·6	−2·8	−3·86
10^5k (sec.$^{-1}$) RBr	1·11	1·096	0·78	0·186	0·0972	11·0
$\Delta S^{\ddagger}$ (e.u.)........................	−6·65	−7·10	−10·12	−2·64	−1·37	−1·43
$k_{\mathrm{O\cdot SO_2Ph}}/k_{\mathrm{Br}}$	17·8	16·9	16·9	12·2	5·65	105

TABLE 3

$k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios for the ethanolysis of some alkyl derivatives at 50°

	Me	Et	$\mathrm{Pr^i}$	$p\text{-}\mathrm{NO_2C_6H_4CH_2}$	$p\text{-}\mathrm{MeC_6H_4CH_2}$	MeCHPh	$\mathrm{Bu^t}$
10^5k (sec.$^{-1}$) ROTs	0·645 [a]	0·219 [a]	0·814 [a]	24·6 [b]	41·0 [c]	9840 [d]	>40,000 [d]
10^5k (sec.$^{-1}$) RBr	0·0393 [e]	0·0145 [e]	0·0112 [e]	1·20 [b]	0·184 [c]	11·62 [f]	11·85 [f]
$k_{\mathrm{OTs}}/k_{\mathrm{Br}}$	16	15	73	20 [b, g]	223 [c, g]	845	>4000

[a] Ref. 13. [b] At 75°. [c] At 25°. [d] Estimated from ref. 1. [e] Ref. 14. [f] Ref. 15. [g] Ratios of limited accuracy.

These Tables have in common that the ratios rise steeply along the α-methylated series, Et, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$.* The increasing ionic character of the solvolysis transition state along this series can also be inferred from criteria developed earlier in these laboratories.[2,16]

(i) Sensitivity to added lyate ion (or other nucleophiles) decreases from Et to $\mathrm{Pr^i}$ until it is virtually nonexistent for t-butyl halides. (ii) Strongly ionising solvents which stabilise incipient charges facilitate mechanism S_N1 more than S_N2. (iii) Electron-releasing substituents which are able to delocalise positive charge, favour mechanism S_N1 more than mechanism S_N2.

Before discussing Table 1 in more detail we must take into account that the ratios need not be absolutely precise, since most of the rate constants were obtained in various laboratories using slightly different solvent grades. The values are accurate enough, however, to show a discernible pattern; this is all the more satisfactory because individual rates for the series of alkyl bromides and toluene-*p*-sulphonates appear to be quite erratic and are difficult to interpret. An important feature of Table 1 is the steady increase of the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios from methyl to 2-pentyl, suggesting progressively increasing charge separation in the transition state. The ratio for the phenethyl system, in particular, is strikingly high when compared with other primary alkyl derivatives and the explanation for this should lie in the structure of the transition state. For the formolysis of phenethyl toluene-*p*-sulphonate a nucleophilic participation of the neighbouring phenyl group has been deduced by Winstein and Heck [4] from a consideration of relative rates and entropies of activation. This has been supported by other workers [5,17,18] and confirmatory evidence is now provided by the comparatively large $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratio, indicating an enhanced charge dispersal over the quasi-cation in the transition state.

In this context, it is attractive to discuss the ratios for the isobutyl and neopentyl systems, as well; these ratios are both greater than one would expect from an extrapolation

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* Although we only know the ratio for t-butyl in solvent acetonitrile ($k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ = 1670 at 50°), we may safely conclude that by the very properties of t-butyl toluene-*p*-sulphonate, this ratio must be high in all solvents.

[11] R. E. Robertson, R. L. Heppolette, and J. M. W. Scott, *Canad. J. Chem.*, 1959, **37**, 803.
[12] R. E. Robertson, *Suomen Kem.*, 1960, **33**, *A*, 63.
[13] R. E. Robertson, *Canad. J. Chem.*, 1953, **31**, 589.
[14] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700.
[15] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1602.
[16] E. D. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.
[17] C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Canad. J. Chem.*, 1957, **35**, 1417.
[18] (*a*) W. H. Saunders and R. Glaser, *J. Amer. Chem. Soc.*, 1960, **82**, 3586; (*b*) D. J. Cram, *ibid.*, 1964, **86**, 3767.

of the values for the first three members of the series. Rearrangements in solvolytic reactions of neopentyl derivatives is familiar.[19] Similarly, isobutyl derivatives may rearrange [20] and, interestingly, even n-propyl toluene-*p*-sulphonate forms 2·8% isopropyl acetate in boiling acetic acid.[21]

Although rearrangement does not prove the existence of a " non-classical " transition state, rate comparisons,[3] and now the k_{OTs}/k_{Br} ratio, indicate a weak neighbouring-group assistance in the formolysis of neopentyl toluene-*p*-sulphonate. Even the formolysis of isobutyl toluene-*p*-sulphonate appears to be mildly assisted by an alkyl and hydride shift, as tentatively suggested by Winstein and Marshall.[3]

It is interesting that for most alkyl derivatives the ratios parallel the rates of the unimolecular gas-phase elimination of the alkyl bromides (Table 1); this gives striking support to the proposed analogy between S_N1 and $E1$ reactions in solution and unimolecular dehydrohalogenations in the gas-phase.[22]

For the neutral hydrolysis of alkyl halides and benzenesulphonates, Robertson's precise data [11,12] (cf. Table 2) are available. On comparison with the ratios of Table 1, there are two important differences. (i) The ratios for the hydrolysis are *smaller*, although they refer to benzenesulphonates (which react faster than toluene-*p*-sulphonates) and to a lower temperature (which usually leads to higher ratios, since the activation energy of toluene-*p*-sulphonates is normally smaller than that of bromides). (ii) Within the primary series, ratios decrease, and for neopentyl in particular, $k_{OTs}/k_{Br} = 4$ which is, so far, the lowest value observed for an S_N1 reaction. Concerning (i), the much smaller ratios for hydrolysis seem reasonable since it is known that water is a more nucleophilic solvent than formic acid.[8,23] Concerning (ii), a similar decrease along the β-methylated series may be observed for S_N2 displacements by ethoxide ion,[24] but this will be considered in more detail in a future Paper. The trend of these ratios can be reconciled with the positive shift in entropy of activation on passing along the series of alkyl benzenesulphonates.[11] This shift has been explained by a decreasing reorganisation of solvent in the transition state,[11] together with the change-over from mechanism S_N2 to S_N1, resulting in decreasing covalent participation of water in the activation process.[25]

Interestingly, the ratio for the neopentyl hydrolysis (and even formolysis) is small when compared with that of fast S_N1 (and $E1$) reactions,[1] suggesting a weakly ionic transition state for the former reaction. Confirmatory evidence can be adduced as follows. For an S_N1 (and $E1$) reaction, in which a non-polar molecule reacts by way of an ionic transition state, the Hughes–Ingold solvent theory predicts[2] that rates will increase with a change to a more polar solvent. As a corollary, a more ionic transition state will be influenced more strongly by a solvent change than a less ionic one. This we observe (cf. Table 4), since the solvolysis of t-butyl bromide does not only have the higher k_{H_2O}/k_{HCO_2H} ratio, but is also much more sensitive to a change from leaving bromide group to toluene-*p*-sulphonate.

These results may be generalised and it is suggested that, in good approximation, *the faster an* S_N1 (*and* E1) *reaction, the more ionic its transition state.*

We shall now consider this rule for various changes which speed unimolecular ionisation.

(1) *Change in the alkyl group.* The preceding Paper shows that the ratio k_{OTs}/k_{Br} increases with increasing ionisation tendency of the substrate, becoming very large

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[19] F. C. Whitmore, E. L. Whittle, and A. H. Popkin, *J. Amer. Chem. Soc.*, 1939, **61**, 1586; I. Dostrovsky and E. D. Hughes, *J.*, 1946, 166.

[20] Y. Pocker in " Molecular Rearrangements," ed. P. de Mayo, Wiley, New York and London, 1963, p. 1.

[21] R. Huisgen and C. Rüchardt, *Annalen*, 1956, **601**, 1.

[22] (*a*) A. Maccoll in " Theoretical Organic Chemistry " (Kekulé Symposium), Butterworths, London, 1959, p. 230; (*b*) H. M. R. Hoffmann and A. Maccoll, *J. Amer. Chem. Soc.*, 1965, **87**, 3774.

[23] R. E. Robertson and J. M. W. Scott, *J.*, 1961, 1596.

[24] H. M. R. Hoffmann, unpublished results.

[25] G. Kohnstam, " The Transition State," *Chem. Soc. Spec. Publ.*, 1962, No. 16, p. 190.

TABLE 4

Solvolyses of t-butyl bromide and neopentyl toluene-*p*-sulphonate in water and formic acid

		$k_1 \times 10^5$ (sec.$^{-1}$)			
	Temp.	H_2O	HCO_2H	k_{H_2O}/k_{HCO_2H}	k_{OTs}/k_{Br},H_2O
NeopentylOTs	50°	0·39 [a]	0·107 [b]	3·7	4
Bu^{t}Br	25	77,000 [c]	958 [c]	80	>4000 [d]

[a] From ref. 12, assuming $k_{OTs}/k_{OSO_2Ph} = 0{\cdot}7$. [b] Extrapolated from data in ref. 3. [c] Ref. 15. [d] Estimated from data in ref. 1.

(>4000) for fast solvolyses. Another manifestation of this point is shown by the experimental difficulty in preparing toluene-*p*-sulphonates attached to mesomerically stabilised alkyl groups. For primary and secondary alkyl derivatives, unimolecular ionisations are usually difficult to observe in solution; hence the k_{OTs}/k_{Br} ratios obtained for formolyses (Table 1) probably represent an upper limit to the actual ratios which could be considerably smaller. For gas-phase heterolyses, k_{Br}/k_{Cl} ratios are available (Table 5). Although these ratios are considerably less sensitive to a structural change than k_{OTs}/k_{Br} ratios, they again show a gradation,[*] which we attribute to the increasingly ionic character of the transition state as these eliminations become faster.

(2) *Change to a better leaving group.* The large effect on rates of the change from RBr to ROTs in fast solvolyses is only a special example which demonstrates the greater charge-development in the transition state of the faster reaction. Similarly, for elimination reactions a change from chloride to bromide and iodide as leaving group is usually paralleled by an increase in Saytzeff product, an example being the gas-phase heterolysis of the s-butyl halides.[22a] Observations such as these have generally been rationalised by the increasing carbonium-ion (or *E*1) character of the transition state.[26] Finally, for the elimination of the 2-benzyl-2-halogeno-4,4-dimethyl-1-tetralones 100% Saytzeff product is obtained [27] and the ratio $k_{Br}/k_{Cl} > 1000$, indicating a remarkable sensitivity to a change in leaving halide group. In all cases, a better leaving group should result in a more ionic transition state.

TABLE 5

Relative rates of dehydrobromination and k_{Br}/k_{Cl} ratios for gas-phase heterolyses [a] at 100°

	Et	Pr^i	Bu^s	Cyclohexyl	Cyclopentyl	Bu^t
Relative rates, RBr 100°	1	$5{\cdot}5 \times 10^3$	$2{\cdot}63 \times 10^4$	$4{\cdot}17 \times 10^4$	$2{\cdot}24 \times 10^5$	$3{\cdot}23 \times 10^7$
k_{Br}/k_{Cl}	38	117	102	105	115	195

[a] All data from ref. 22.

(3) *Change of medium.* The most drastic medium change that can be effected is transfer of the reaction from solution into the gas-phase. For such a change rates decrease sharply, *i.e.*, activation energies increase, often by some 20 kcal./mole.[22a] It has been shown recently by other arguments that the transition state of a heterolysis in the gas-phase is also considerably less ionic than in solution.[22b] Other examples of the increase

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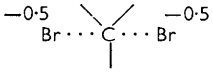
[*] Attention is drawn to the apparent anomaly for Pr^n, Bu^n, and Bu^i; using presently available data (quoted in ref. 22) we calculate k_{Br}/k_{Cl} ratios of 295, 309, and 316, respectively. However, since it is difficult to inhibit completely a free-radical chain for these three primary alkyl bromides (R. A. Ross, private communication), these ratios might well have to be revised.

[26] (*a*) C. K. Ingold, *Proc. Chem. Soc.*, 1962, 225; (*b*) J .F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225.

[27] D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Amer. Chem. Soc.*, 1964, **86**, 1553; discussed in ref. 1.

of the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratio with increasing solvent polarity can be found in this and in the preceding Paper. Although it is realised that a change of medium does not only affect the solvation of the transition state, but also that of the initial state,[28] it is predicted that, overall, a more polar solvent (which, in general, increases rates as demanded by the Hughes–Ingold solvent theory; see above) should also favour a more polar transition state. Altogether, it is evident that the first-formed carbonium-ion intermediate of an S_N1 reaction is a good *electronic* model for the preceding transition state. This view is also in accord with a proposal made by Ingold [29] who suggested that, in general, states (*i.e.*, transition states and intermediates) of *energetic* resemblance on the same reaction co-ordinate should be associated with *electronic* resemblance.*

A preliminary correlation of electron-transfer with the value of $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ can be made, and a good starting-point is provided by a symmetrical substitution whose transition state



involves a transfer of half an electron (by the principle of microscopic reversibility). $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios for bromide ion as the attacking nucleophile have been determined; thus, for the displacement on n-butyl and 1-phenylethyl derivatives in acetone, $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ is *ca.* 0·5 and 4, respectively.[1] Both ratios refer to a half-transferred electron in the displacement of bromide ion; the extent of charge-development in the attack on ROTs is unknown, but larger in the latter reaction. Hence, strictly speaking, the ratio $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ will indicate the electron-transfer value in between that for the substitution on RBr and ROTs.

Since the ratio of 0·5 (for n-butyl) is close to the lower end of the scale it is very likely that this ratio corresponds to a less than half-transferred electron from carbon to toluene-*p*-sulphonate.† 1-Phenylethyl toluene-*p*-sulphonate, on the other hand, should have a relatively high polarity, even in the ground state, since it usually reacts (and decomposes) much more quickly than 1-phenylethyl bromide.[1] Hence, a ratio $k_{\mathrm{OTs}}/k_{\mathrm{Br}} = 4$ probably indicates a more than half-transferred electron.

In the region of high ratios electron-transfer should be virtually complete in the transition state of the ionisations of ROTs. For the corresponding reactions of RBr, charge development will be smaller, but a lower limit is provided by the work of Clarke and Taft,[30] who estimated that the aqueous hydrolysis of t-butyl chloride (which, at 25°, reacts 26 times more slowly than t-butyl bromide [1]) involves an electron-transfer of *ca.* 0·8 electronic units. Thus, it would appear that the intermediate value of electron-transfer given by the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratio is not too far out from the true values of either displacement, and one might hope that with a few more calibration points a firm correlation between $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios and electron transfer can be established.

Limitations of the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ *ratio.* In order to discuss limitations, it is necessary to consider the free-energy changes that control this ratio. A solvolysis can be dissected into three steps [11,31] (the symbols having the same meaning as before [1]):

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* From a hypothesis of Streitwieser [29a] one would expect that the faster an S_N1 reaction, the closer to tetrahedral the structure of the transition state. To the extent that electronic and structural reorganisation parallel each other, this hypothesis and our rule are in conflict.

† In the region below unit, $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ cannot vary greatly with reaction conditions, *i.e.*, the smallest possible ratio is zero; a secondary standard, such as the $k_{\mathrm{OTs}}/k_{\mathrm{Cl}}$ ratio, is more sensitive, as can be seen, *e.g.*, from the data in Table 1 of the preceding Paper.

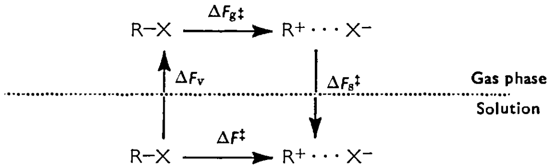
[28] E. M. Arnett, W. G. Bentrude, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 2048; for references to contributions from other workers, cf. E. M. Arnett *et al.*, *ibid.*, p. 1541.

[29] C. K. Ingold, "The Transition State," *Chem. Soc. Spec. Publ.* No. 16, p. 118; ref. 2, various applications in chs. 10 and 12.

[29a] A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York and London, 1962, pp. 67, 175.

[30] G. A. Clarke and R. W. Taft, *J. Amer. Chem. Soc.*, 1962, **84**, 2295.

[31] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.



Scheme. Free-energy cycle for solvolyses

$$\Delta F^{\ddagger} = \Delta F_v + \Delta F_g{}^{\ddagger} + \Delta F_s{}^{\ddagger} \tag{2}$$

$$\Delta F_{Br}{}^{\ddagger} - \Delta F_{OTs}{}^{\ddagger} = \Delta\Delta F_v + \Delta\Delta F_g{}^{\ddagger} + \Delta\,\Delta F_s{}^{\ddagger} \tag{3}$$

$$\Delta F_{Br}{}^{\ddagger} - \Delta F_{OTs}{}^{\ddagger} = 2{\cdot}303\boldsymbol{R}T \log\,(k_{OTs}/k_{Br}) \tag{4}$$

Limitations of the ratio as a mechanistic criterion arise from contributions of $\Delta\Delta F_v$ and $\Delta\Delta F_s{}^{\ddagger}$ to the left-hand side of equations (3) and (4).

In the transition state for the solvolysis of a neutral substrate, charge is created. This is in contrast to reaction (1), and, as a result, transition-state solvation differences (expressed by $\Delta\Delta F_s{}^{\ddagger}$) may now enter more markedly. Usually, the solvolysis of ROTs involves a more ionic transition state than that of RBr, so that an increase in $\Delta\Delta F_s{}^{\ddagger}$ should be linked with an increase in $\Delta\Delta F_g{}^{\ddagger}$. Exceptions, however, may occur in Wagner–Meerwein rearrangements, whose transition states involve dispersed charges; stabilisation through charge dispersal has to be bought at the price of a decrease in solvation energy of the transition-state complex.[32] As a consequence, the (in general more ionic) complex arising from ROTs will be desolvated more strongly, *i.e.*, $\Delta\Delta F_s{}^{\ddagger}$ decreases, and we should observe k_{OTs}/k_{Br} ratios that are *smaller* than expected from the contribution of $\Delta\Delta F_g{}^{\ddagger}$. One example is provided by the solvolysis of neophyl derivatives ($PhCMe_2CH_2X$), studied by Winstein and his co-workers (cf. Table 6). All these reactions are limiting S_N1; the ionisation is assisted by the neighbouring aryl group to the extent that rearrangement is essentially complete. If we accept that " fast " S_N1 reactions generally have a more ionic transition state than " slow " ones as suggested above, it follows that the formolysis of *p*-methoxyneophyl toluene-*p*-sulphonate involves the greatest spread of charge over the quasi-cation (or the strongest assistance by the migrating anisyl group) within the solvent series considered. Accordingly, one might expect the highest k_{OTs}/k_{Br} ratio for the formolysis and likewise, the highest *p*-methoxyneophyl/neophyl ratio. However, the opposite is observed; both ratios, which show similar trends (acetic acid, discussed below, being a notable exception), would imply that the ionisation of neophyl toluene-*p*-sulphonate is least assisted in formic acid. The k_{OTs}/k_{Br} ratio has even dropped below 24, the value for methyl in formic acid (Table 1). Clearly this cannot be meaningful and

TABLE 6

Relative rates of solvolysis of *p*-methoxyneophyl toluene-*p*-sulphonate. Comparison with neophyl toluene-*p*-sulphonate and k_{OTs}/k_{Br} ratios for the neophyl system [a]

Solvent	Y + 3	Rel. rate of *p*-MeOneoph/ OTs at 75°	$k_{p\text{-MeOneoph OTs}}/k_{\text{neoph OTs}}$ [b]	k_{OTs}/k_{Br} [b] (R = neophyl)
H_2O	6·49	39	—	—
HCO_2H	5·05	153	52	14 [c]
80% EtOH–H_2O	3·00	1·85	97	22
AcOH	1·36	1·00	118	163
MeOH	1·91	0·947	135	35·8
EtOH	0·97	0·370	165	106

[a] All data taken from refs. 33 and 34. [b] At 50°. [c] At 25°.

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[32] S. F. Mason, *J.*, 1958, 808.

[33] S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, 1961, **83**, 618.

[34] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1608.

it is suggested that the reason lies in the increasing influence of $\Delta\Delta F_s^{\ddagger}$ on the ratio. In contrast, it appears that differential desolvation in the formolysis of the less developed phenethyl, neopentyl, and isobutyl quasi-cations does not affect the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratio markedly (Table 1).

The *hydrolysis* of *p*-methoxyneophyl toluene-*p*-sulphonate appears to be an even more extreme example: from the Y-value of water one would expect this to be the fastest reaction; yet it appears that the quasi-cation of the transition state is now so strongly desolvated that the rate even falls below that of formolysis. Hence, this hydrolysis might still involve the greatest charge-development in the transition state and so provide an exception to the rule that the faster S_N1 reaction has the more ionic transition state.*

For the solvolyses of neopentyl derivatives, similar, although less pronounced trends may be noted. Thus, although the hydrolysis of neopentyl toluene-*p*-sulphonate is now *ca.* 3·7 times faster than the formolysis (Table 4), suggesting the more ionic transition state for the former reaction, the ratio ($k_{\mathrm{OTs}}/k_{\mathrm{Br}} = 4$ for water) is far below that for the formolysis ($k_{\mathrm{OTs}}/k_{\mathrm{Br}} = 90$), again, it would appear, owing to the adverse contribution of $\Delta\Delta F_s^{\ddagger}$ to the ratio for the hydrolysis.

This discussion shows that care is needed when using the rate-enhancement relative to a standard compound (*e.g.*, the *p*-methoxyneophyl/neophyl ratio) as a criterion for neighbouring-group assistance. In many instances, a solvent of low polarity, *e.g.*, acetic acid, will give the most satisfactory rate enhancements. In other cases, a solvent change may introduce the additional complication of generating alternative types of ion-pairs all involving different degrees of electrostatic and/or covalent bonding[35] depending upon the solvent type.[36] It appears to the writer that the desolvation of the " non-classical " carbonium ion with its attendant rate decrease could be responsible for a good deal of current controversy in this field.

A second limitation of the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratio may arise in structurally ordered solvents, due to a marked contribution from $\Delta\Delta F_v$. ROTs as the substantially larger molecule has (at least as far as the toluene part of the molecule is concerned) a greater tendency towards " freezing "[37] its solvation shell than RBr. This is illustrated by the *positive* free-energy change[1] ($\Delta G^\circ = 10{\cdot}7$ kcal./mole) for the change:

benzene vapour (1 mole/l., hypothetical) $\longrightarrow$
solution of benzene in water (1 molal, hypothetical)

For the solvent mixtures considered in Table 7, the co-solvent appears to act mainly as a structure breaker by increasing the entropy of the solution. As a result, the influence

TABLE 7

$k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios for solvolyses in ethanol–water mixtures at 50 [a]

EtOH–H_2O (% in v/v)	Me	Et	Pr^i	Neophyl	Fluidity [c] of solvent at 50°
EtOH	16	15	73	106	78
80% EtOH	11	10	46	22	54
50% EtOH	8	5 (6) [b]	35	—	48
H_2O	12·5	11·8	73·5	—	100

[a] Table adapted from refs. 12, 13, and 33. [b] The value in parenthesis refers to a dioxan–water medium containing 60·72% dioxan by weight (ref. 38). [c] As defined by the ratio $\eta_{H_2O}/\eta_{\mathrm{solvent}}$ (cf. ref. 39).

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* Alternatively, a referee has suggested that hydrolysis should favour a path involving less delocalisation.

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of $\Delta\Delta F_v$ on the ratio decreases, *i.e.*, k_{OTs}/k_{Br} becomes smaller. The sharp decrease of the ratio for neophyl on change from ethanol to 80% ethanol should be the result of a decrease in both $\Delta\Delta F_v$ and $\Delta\Delta F_s{}^{\ddagger}$.

It is interesting that the fluidity of the solvent and the k_{OTs}/k_{Br} ratio show similar trends by going through a minimum. This suggests again that an initial-state effect is the main contributor to the variation in the ratio. Overall, it would appear that initial-state solvation can influence the absolute value of the ratio to some extent, whereas relative ratios for a series of compounds within one solvent remain unaffected.

EXPERIMENTAL

Materials.—Most of the alkyl bromides were commercial material purified by distillation. Toluene-*p*-sulphonates were prepared by standard methods. Formic acid (B.D.H., AnalaR) was used without further purification. Commercial absolute ethanol was pure by gas-chromatographic standards.

Kinetics.—The formolyses were carried out in the presence of 0·050M-pyridine (rather than sodium formate). Pyridine remained unchanged after 21 hr. at 95° in formic acid. Kinetic samples were quenched in acetic acid (40 ml.) and the excess of base was titrated with standard anhydrous perchloric acid in glacial acetic acid using Oracet Blue B as the indicator.[1] In the ethanolysis of *p*-nitrobenzyl bromide, hydrogen bromide was liberated which reacted with the solvent. Therefore, 2,6-lutidine was added (0·02M) and back-titrated, at suitable intervals, using glacial acetic acid (40 ml. per 5-ml. sample) as the solvent and standard perchloric acid in glacial acetic acid as the titrant. A blank was necessary to check the first colour change of the Oracet Blue indicator from blue to grey-blue.

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