Solvents of Low Nucleophilicity. IX. Inductive and Participation Effects in Carbonium Ion Reactions in Acetic, Formic, and Trifluoroacetic Acid[1]

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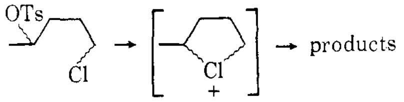
Abstract: Rates of solvolysis of ω-chloro- and ω-fluoro-substituted 2-alkyl tosylates were determined in acetic, formic, and trifluoroacetic acid for tosylates having four to seven carbon atoms in the aliphatic chain. The magnitude of rate-decreasing inductive influences upon the rates of reaction diminished as the solvent was varied according to the order trifluoroacetic acid > formic acid > acetic acid. The magnitude of superimposed rate-increasing effects of 1,4-chlorine (and possibly 1,4-fluorine) participation varied with solvent in qualitatively the same order, as did the per cent of over-all retention of configuration in solvolysis of 5-chloro-2-hexyl tosylates. Slow attenuation of substituent effects with distance occurred in formic as well as trifluoroacetic acid. These studies serve to relate previous studies of carbonium reactions in trifluoroacetic acid to the extensively reported studies of similar reactions in other hydroxylic solvents. A qualitative theory of the origin of inductive and participation effects is proposed to account for the quantitatively different responses of inductive and participation effects to a change of solvent or reaction type.

Although the study of "carbonium ion" reactions is being vigorously pursued in many laboratories, important basic information concerning the effect of inductive substituents[2] in these reactions has not been available.[3] We have now substantially filled this gap by a study of chloro- and fluoro-substituted aliphatic tosylate solvolyses in acetic, formic, and trifluoroacetic acid.

The special purpose of the present study, however, was to determine whether carbonium ion reactions in general exhibit several interesting phenomena previously discovered in our laboratories during studies of cationic additions of trifluoroacetic acid to double and triple bonds. We especially wanted to obtain further evidence for and to explore the scope of 1,4-halogen participation, as exemplified in eq 1 for the hypothetical chlorine-assisted solvolysis of 5-chloro-2-pentyl tosylate.



(1)

Prior to the present study this type of participation had been observed only in trifluoroacetic acid and only for cationic solvent addition reactions, as evidenced by moderate rate enhancements in additions to haloalkenes[4] and by predominant 1,4-chlorine shift in the addition of trifluoroacetic acid to 5-chloro-1-pentyne.[5] We were prompted to include ω-fluoroalkyl tosylates in the present study because of the novel possibility of obtaining evidence for fluorine participation, which had not been previously postulated.[6]

In a previous study apparently surprising inductive effects of substituents located as far as ten carbon atoms from the reaction center were observed in addition reactions of alkenes.[4b] In the present study we are interested in examining solvolyses (as compared to addition reactions) for such effects and in studying the solvent dependence of the attenuation of the inductive effect with distance. Such studies not only would reveal the relationship between our own studies of carbonium ion reactions in trifluoroacetic acid and the many studies in the literature involving other solvents, but might also have implications in regard to the origin of substituent effects.

Description and Results

Among the characteristics used in appropriate instances to detect neighboring group participation are (1) rearrangements,[7] (2) rate acceleration, and (3) stereochemical effects. Whereas our previous studies of 1,4-halogen participation in addition reactions have involved instances of the first two characteristics, the tosylate solvolysis study reported here involved the latter two. In view of the controversial and subjective nature of evidence based on reaction rates it seems appropriate initially to describe the stereochemical results of the solvolysis of the separate diastereomeric 5-chloro-2-hexyl tosylates. In these solvolyses the formation of products with net retention of configuration may be taken to indicate 1,4-chlorine participation,

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[1] This work was supported in part by grants from the Petroleum Research Fund of the American Chemical Society (790-A4) and from the National Science Foundation (GP 2917).

[2] The term "inductive effect" is used here in its original sense to mean (for unconjugated systems) the total electrical effect. Separation into a "true inductive effect" and a "field effect" is not attempted although the implications of our work in regard to the origin of substituent effects are discussed.

[3] Solvolysis of *cis*-2-substituted cyclohexyl tosylates in acetic acid have been reinterpreted: (a) A. Streitwieser, Jr., *Chem. Rev.*, 56 571 (1956); (b) *J. Am. Chem. Soc.*, 78, 4935 (1956). Acetolyses of 4-substituted cyclohexyl tosylates have been carried out: (c) H. Kwart and T. Takeshita, *ibid.*, 86, 1161 (1964); (d) D. S. Noyce, B. N. Bastian, and R. N. Monson, *Tetrahedron Letters*, 863 (1962). Recently the relation of the role of inductive substituents to the question of the existence or nonexistence of bridged ions has been discussed: (e) P. G. Gassman and J. I. Marshall, *J. Am. Chem. Soc.*, 87, 4648 (1965); 88, 2822 (1966).

[4] (a) P. E. Peterson and G. Allen, *ibid.*, **85**, 3608 (1963); (b) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *ibid.*, **87**, 5163 (1965); (c) P. E. Peterson and E. V. P. Tao, *ibid.*, **86**, 4503 (1964).

[5] P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

[6] For a preliminary report see P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1283 (1967).

[7] 1,4-Halogen shifts, for example.

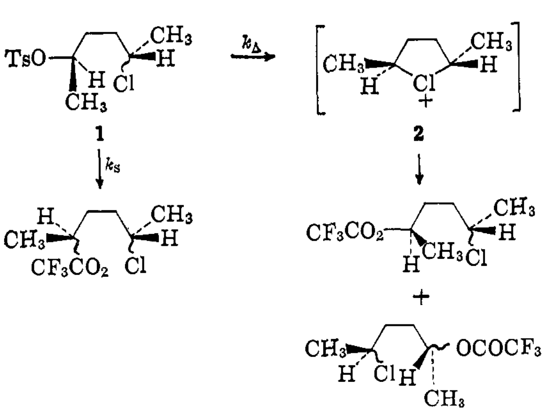
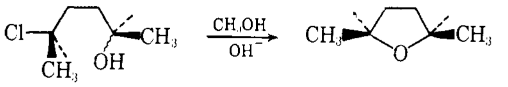


Figure 1. Possible solvolysis paths for *erythro*-5-chloro-2-hexyl tosylate.

as postulated in the classic type of scheme shown in Figure 1.

The key to the preparation of the required diastereomeric 5-chloro-2-hexyl tosylates was the separation of a mixture of the corresponding trifluoroacetates by distillation through a high-speed Teflon spinning-band column. Both conventional spinning-band distillation and preparative gas chromatography earlier failed to give the desired separation. The configuration of the separated isomers was assigned by hydrolysis to the alcohols and cyclization, on a micro scale, of one of the isomers to the corresponding 2,5-dimethyltetrahydrofuran (eq 2), whose gas chromatographic retention time was shown to be identical with that of one of the two known isomers, both of which were available for comparison.



(2)

threo-5-chloro-2-hexanol *cis*-2,5-dimethyltetrahydrofuran

Solvolysis of the tosylates obtained from the separate alcohols gave the corresponding esters of inverted or retained configuration, which fortunately could be analyzed by capillary column gas chromatography in each case. The results are shown in Table I.

Table I. Per Cent Retention of Configuration in the Solvolysis of 5-Chloro-2-hexyl Tosylates

Diastereomer	CF_3CO_2H	HCO_2H	CH_3CO_2H
erythro[a]	92[a]	61[a]	29[a]
threo[b]	89[b]	49[b]	22[b]

[a] Result obtained from tosylate prepared from alcohol containing less than 1% of the *threo* isomer. [b] Corrected for the presence of 9.1% of *erythro* isomer in the acohol from which the tosylate was prepared.

By analogy with earlier studies of alkenes,[4b] rate-decreasing inductive effects and rate-increasing participation effects might be expected to influence the rates of substituted tosylate solvolyses. The separation of these effects based on "attenuation plots" (*cf.* Discussion section) required the preparation of homologous series of ω-chloro- and ω-fluoro-2-alkyl tosylates. The apparent simplicity of this task was deceptive, but various satisfactory approaches were ultimately developed, of which a representative is shown in Figure 2.

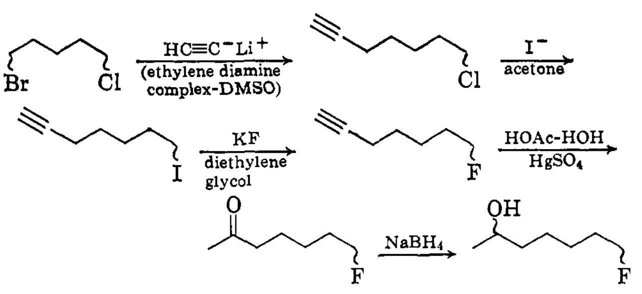
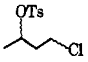
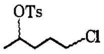
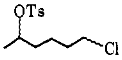
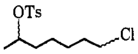
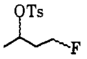
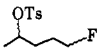
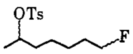
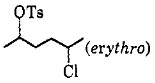
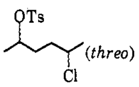
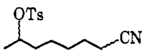
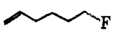
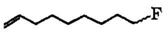


Figure 2. Synthesis of 7-fluoro-2-heptanol.

First-order rates of solvolysis of the tosylates prepared from the corresponding alcohols were measured in three solvents by previously reported methods.[8] The results are given in Table II, along with rates of addition of trifluoroacetic acid to three fluoroalkenes which we determined for purposes of comparison.

Table II. Rate Constants for Solvolysis of Tosylates and Additions to Alkenes

	$k \times 10^7$, sec^{-1}		
Compound	Trifluoroacetic acid[a]	Formic acid[b]	Acetic acid[c]
	4.44	4.27	24.6
	1790	156	284
	443	197	339
	607	236	427
	4.88	8.06	29.1
	215	106	177
	743	345	395
	5300	257	300
	3520	171	
	374	224	354
	661[d]	...	...
	1310[d]	...	...
	7940[d]		

[a] For solvolysis at 25.0° of solutions 0.05 *M* in tosylate and 0.125 *M* in sodium trifluoroacetate. [b] For solvolysis at 25.0° of solutions 0.1 *M* in tosylate. [c] For solvolysis at 70.0° of solutions 0.1 *M* in tosylate and 0.11 *M* in sodium acetate. [d] For reaction at 60.0° in the presence of 0.125 *M* sodium trifluoroacetate.

Discussion

Preliminary Deductions from Stereochemical Results. The observed high percentages of trifluoroacetolysis

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[8] P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.*, 87, 5169 (1965).

products of both *erythro*- and *threo*-5-chloro-2-hexyl tosylate showing net retention of configuration (Table I) constitute the first evidence for 1,4-chlorine participation in solvolytic substitution reactions (as compared with addition reactions). The ring opening of the chloronium ion **2**, Figure 1, provides the first stereochemical information concerning the properties of the chloronium ion as a leaving group, as well as the first demonstration that the weakly nucleophilic solvent trifluoroacetic acid–sodium trifluoroacetate may react to give predominant Walden inversion. Since it is now known that the solvolysis of secondary tosylates in acetic acid proceeds with a high percentage of inversion,[9] the 29 and 22%, respectively, of acetolysis products of the above-mentioned tosylates having retained configurations very probably are indicative that halogen participation occured to some extent in these acetolyses. According to the same criterion, formolyses are intermediate among the three solvolytic reactions studied (trifluoroacetolysis, formolysis, and acetolysis) in the amount of halogen participation which occurs, as evidenced especially by the predominant (61%) retention observed in the products derived the *erythro* tosylate.

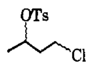
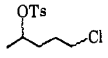
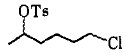
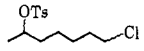
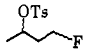
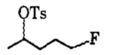
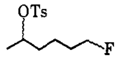
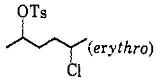
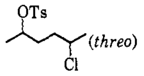
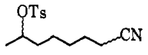
At this point, having briefly discussed stereochemical evidence that 1,4-chlorine participation occurs in the more commonly used carbonium ion solvents, as well as in trifluoroacetic acid where it was first observed, we turn to an analysis of our evidence for such participation derived from rates of reaction.

Influence of Inductive and Participation Effects upon Rates. By analogy with the reactions of the corresponding substituted alkenes[3b] the solvolyses of 4-halo-2-butyl and 7-halo-2-heptyl tosylates may be expected not to be influenced by substituent participation. Accordingly, values of k_H/k_X, the ratios of the rate constants for solvolysis of the unsubstituted and substituted tosylates, respectively, serve as direct measures of the rate-retarding inductive effect. In Table III those ratios are given for the various tosylates which we studied.

Examination of the butyl tosylate k_H/k_X ratios given in Table III makes it immediately apparent that the observed inductive effects show a striking solvent dependence, the magnitudes of the effect varying in the order trifluoroacetic acid > formic acid ≫ acetic acid. To the best of our knowledge there is no indication in the literature of this type of marked difference between the latter two commonly used "carbonium ion solvents." It is pertinent that in his defense of phenyl participation Cram[10] recently assumed the inductive influence of the phenyl group to be the same for reactions in acetic and formic acid.

We attribute the observed relatively small inductive effects in acetic acid to marked nucleophilic character of this solvent. Other criteria likewise indicate that acetolyses of secondary tosylates, far from being limiting,[11] show marked SN2 character. These are the formation of inverted product[9] and the formation of markedly smaller amounts of rearranged products characteristic of cationic reactions, including hydrogen-shifted products,[12] carbon-shifted products,[13] and halogen-shifted products,[14] compared to reactions in trifluoroacetic acid.

Table III. Values of k_H/k_X for Tosylate Solvolyses

Tosylate	Solvent CF_3CO_2H	 HCO_2H	 CH_3CO_2H
	329	129	18.7
	1.06	3.43	1.69
	4.32	2.76	1.42
	3.88	2.32	1.13
	299	68.2	16.5
	8.83	5.04	2.71
	3.35	1.58	1.22
	0.362	2.11	1.60
	0.545	3.18	...
	7.03	2.44	1.29

It may be argued that solvolyses in acetic acid are still limiting in the rate-determining step, and that the solvent variation of inductive effects might reflect differing amounts of bond breaking in the transition states. The known insensitivity of (for example) acetolysis rates to added sodium acetate[15] perhaps provides the strongest argument against nucleophilic solvent participation in the absence of acetate ions. The argument is not compelling, however, since the ratio of the nucleophilicities of acetate (actually acetate hydrogen bonded to acetic acid) to that of acetic acid may well be lower than the comparable ratio (*e.g.*, that of CH_3O^- and CH_3OH) characteristic of a more nucleophilic solvent. Furthermore, for reactions that are not limiting but do have some SN1 character the sensitivity to this ratio must be smaller than that shown by "purer" SN2 reactions. At some point in the SN2–SN1 spectrum the effect of added negative ions derived from the solvent would, accordingly, become negligible.

The literature contains few if any comparisons of inductive effects in cationic reactions where formally identical cations are generated by different methods. In this connection it is instructive to compare k_H/k_X values in trifluoroacetic acid for solvolysis of 4-chloro-2-butyl tosylate (329) and 7-chloro-2-heptyl tosylate (3.88) with the values (421 and 5.00, respectively) found for addition of trifluoroacetic acid to the corresponding chloro-substituted alkenes.[4b] Inductive effects clearly

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(9) (a) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, *J. Am. Chem. Soc.*, **87**, 3682 (1965); (b) *cf.* H. Weiner and R. Sneen, *ibid.*, **87**, 287 (1965).

(10) D. J. Cram, *ibid.*, **86**, 3767 (1964).

(11) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 64.

(12) P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 5834 (1960).

(13) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **82**, 4299 (1960).

(14) As inferred from the present study, by comparison with reactions cited herein known to proceed with halogen shift (*cf.* ref 4c and 5).

(15) W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962).

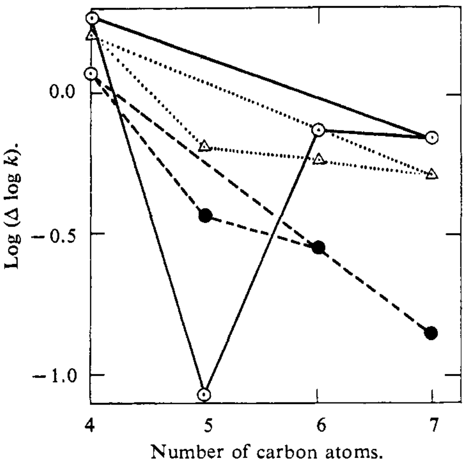


Figure 3. Attenuation plot of ω-chloro-2-alkyl tosylate solvolysis data. Solvent: trifluoroacetic acid, ○; formic acid, Δ; acetic acid, ●. In addition to the correlation line connecting points for butyl and heptyl tosylates, all points for a common solvent have been connected to aid in visualizing deviations from linearity ascribable to participation.

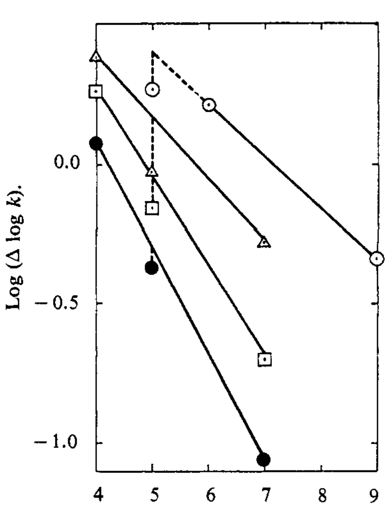


Figure 4. Attenuation plot for ω-fluoro-2-alkyl tosylate solvolysis data. Solvent: trifluoroacetic acid, Δ; formic acid, □; acetic acid, ○. The upper plot (●) is for addition of trifluoroacetic acid to ω-fluoro-1-alkenes. The scale has been changed, compared to Figure 3, to accommodate the point for 9-fluoro-1-nonene.

are very similar in the two series for both butyl and heptyl compounds. Accordingly the attenuation of the substituent effect with increasing chain length is likewise similar; for these solvolyses, as found previously for addition reactions,[4b] remarkably little attenuation per methylene group is observed. For reasons to be discussed it is perhaps surprising that a similar observation is seen to be applicable in the case of formic acid solvolyses. Appreciable effects of remote substituents upon reaction rates are, therefore, not anomalies which are limited to reactions in trifluoroacetic acid.

The close analogy between reactions of tosylates and alkenes in trifluoroacetic acid suggests that "attenuation plots," used previously for alkene data,[4b] should provide an appropriate visual comparison of the attenuation of inductive effects with distance in solvolyses and that the attenuation method should permit a quantitative separation of inductive and participation effects. Such plots of log ($\log k_H - \log k_X$) *vs.* the number of carbon atoms in the aliphatic chains are shown in Figures 3 and 4 for the ω-chloro-2-alkyl tosylate and ω-fluoro-2-alkyl tosylate solvolysis data, respectively. Also included in Figure 4 is a plot of our rate data for addition of trifluoroacetic acid to ω-fluoro-1-alkenes. These plots are based on the assumption that $\log k_H - \log k_X \equiv \Delta \log k$ falls off by a constant factor per methylene group. Accordingly

$$\Delta \log k_n = \epsilon^{n-m}(\Delta \log k_m) \qquad (3)$$

where n, m = numbers of carbon atoms in the aliphatic chain of the tosylates whose inductive effects are compared. Taking the logarithm of both sides

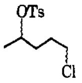
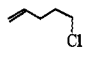
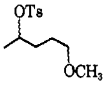
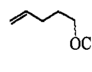
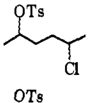
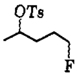
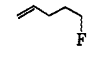
$$\begin{array}{lcccccc} \log (\Delta \log k_n) & = & (\log \epsilon) & (n - m) & + & \log (\Delta \log k_m) & (4) \\ cf. \quad y & = & m & x & + & b & \end{array}$$

Instead of the variable $n - m$ we may use the number of carbon atoms in the chain as the abscissa in a plot of eq 4, since the latter number will differ from $n - m$ by a constant.

For the alkenes studied previously, linearity of plots based on eq 4, indicative of attenuation of the inductive effect by a constant factor, ϵ, per methylene group, was *demonstrated* for 19 substituted alkenes encompassing data for three "purely inductive" substituents. In the present study the butyl and heptyl tosylates are assumed to define a similar line having slope log ϵ.

Again by analogy with the earlier study, deviations of points from the line are postulated to provide an indication of the amount of halogen participation in pentyl and hexyl tosylates. A quantitative analysis may be made from the assumption that the rate constants for normal solvolysis, k_s, lie on the line. Since the total rate, k_X, is the measured rate, the relationship $k_X = k_s + k_\Delta$ defines a separation of k_Δ and k_s. The derived values of k_Δ/k_s are given in Table IV, along

Table IV. k_Δ/k_s Values for Paired Alkenes and Tosylates (Trifluoroacetic Acid)

Tosylate	k_Δ/k_s	Alkene	k_Δ/k_s
	33		8.6[a,b]
	166[c]		5.1[a]
	99,65[d]		11[e]
	2.4		~1.3

[a] The unassisted rate was estimated from k_H/k_X for the substituted butene and an attenuation factor of 0.65. [b] This value differs slightly from the previously used value of 7.5 derived from an earlier attenuation plot. [c] The unassisted rate was estimated using the ratio $\sigma_{CH_3O}/\sigma_{Cl} = 0.922$, derived from rates of addition of trifluoroacetic acid to methoxybutenes. From this ratio and k_H/k_X for 4-chloro-2-butyl tosylate the k_H/k_X value for 4-methoxyl-2-butyl tosylate was derived, to which an attenuation factor of 0.62 was applied. [d] Values are for the two diastereomers. [e] Previously,[4c] a k_Δ/k_s value of 7.5, applicable to 5-chloro-1-pentene, was used also for 5-chloro-1-hexene. The presently used value is based on the assumption that the unassisted rate for 5-chloro-1-hexene is subject to the same inductive effect as the unassisted rate for 5-chloro-1-pentene.

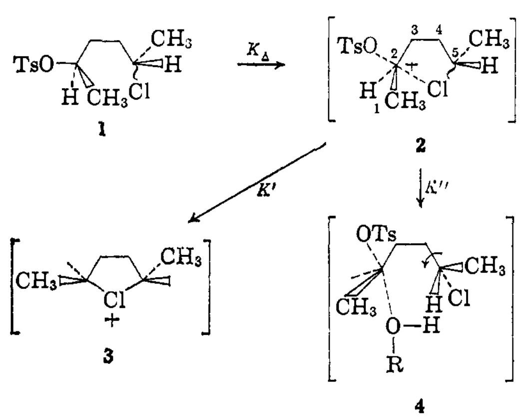


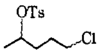
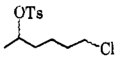
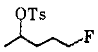
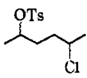
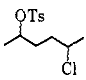
Figure 5. Scheme for chlorine participation.

with some old and new estimates of k_Δ/k_s for addition of trifluoroacetic acid to alkenes.

It is of immediate interest to compare values of k_Δ/k_s for the two types of reactions, since few if any comparisons of this type have been made in the literature. The solvolyses, which, as we have noted, show slightly smaller inductive effects compared to the corresponding addition reactions, are seen to show notably larger participation effects. Since both types of effects might have been expected to reflect similarly the electron deficiencies in the transition states, the observation of nonparallel inductive and participation effects offers an important clue to the nature of both effects. A working hypothesis which rationalizes this observation is discussed later. Here we note only that the consistent pattern observed in Table IV not only provides an interesting indication that "participation tendency" is an independent reaction parameter, but also tends to show that the attenuation plot treatment provides meaningful results and does not represent a gross overinterpretation of the data.

Turning to the solvent influence upon participation, we note that the values of k_Δ/k_s obtained in the way outlined above and given in Table V provide satisfying independent support for the participation order $CF_3CO_2H > HCO_2H > CH_3CO_2H$ which was deduced also from our stereochemical results. Quantitatively, however, the rates uniformly lead to markedly higher estimates of the proportion of reaction proceeding with participation. Reasons could be advanced for not trusting either set of results, but our considered analysis leads us, instead, to propose a mechanistic scheme which can accommodate both sets of data. The elaboration (Figure 5) of the chloronium ion forming step from Figure 1 appears to accomplish the desired result and, more importantly, to lead to additional insight into previously studied participation reactions.

Table V. Values of k_Δ/k_s for Tosylate Solvolyses in Acid Solvents

Tosylate	k_Δ/k_s CF_3CO_2H	 HCO_2H	 CH_3CO_2H
	33	3.6	0.7
	1.1	0.7	0.0
	2.4	0.5	0.2
 (*erythro*)	99	6.7	0.8
 (*threo*)	65	4.1	. . .

In Figure 5 the assisted ionization step is pictured as giving the unsymmetrical ion **2**, solvated by TsO^- and by a weak interaction with Cl. The predominant product-determining step, **2** → **3**, involves the capture of chlorine by the cationic carbon to give the chloronium ion **3**. Alternatively, however, displacement of solvating R–Cl by solvent to give **4** or a similar species leads to some inverted product among the products derived from the anchimerically assisted path. The formation of racemized tosylate prior to solvolysis would also fill the need based on our stereochemical results for a source, in addition to that of normal solvolysis, of inverted product. Such prior racemization, however, should be favored by ion-pairing solvents (trifluoroacetic and acetic acid) whereas experimentally the formolyses also appear to exhibit greater anchimeric assistance than would be predicted from stereochemical results.

More importantly the proposed scheme resolves a long-standing dilemma in our studies—the failure of the transition states for participation to reflect the expected stability of the halonium or oxonium ion intermediates. The order of stability of these ions should depend on the hetero atom or group according to the sequence $F \ll Cl \ll Br \ll I \ll OCH_3$, whereas we have observed the participating tendency $F \leq Cl \cong Br \cong I \leq OCH_3$.[4a,5] It becomes easy to accept the latter stability order of ions analogous to **2**, however, if we regard the weak C····X–R interaction as somewhat analogous to a hydrogen-bonding interaction of type H····X–R, where the stability order is $F \gg Cl > Br > I$.[16] The analogy with hydrogen bonding suggests that fluorine participation which is proposed for the first time in this paper and in the preliminary report of our fluorotosylate solvolyses[6,17] might actually be expected to be more favorable than participation of other halogens in the case of weak participation. The failure to observe this result is not as detrimental to the proposed participation mechanism as it might seem to be, however. Examination of models shows that fluorine alone among the halogens has such a short C–F bond distance that it fails to reach within covalent bonding distance of the incipient cationic carbon in an ion analogous to **2** (Figure 5).

The scheme of Figure 5 further suggests a reason for the previously puzzling contrast between the observed order for 1,2-halogen participation ($I \gg Br \gg Cl$)[3b,18] with that for 1,4 participation. The inductive effect of a 1,2-neighboring halogen essentially precludes weak participation to give intermediates of type **5**, Figure 6,

[16] R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3321 (1962). Inspection of the ΔH and ΔS values given in this reference for hydrogen bonding of phenol to heptyl halides shows only slight differences among the halogens, with the exception of fluorine.

[17] *Cf.* G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 3313 (1966).

[18] For recent references see C. A. Clarke and D. L. H. Williams, *J. Chem. Soc., B*, 1126 (1966).

which are analogous to **2**, since **5** is essentially still a carbonium ion whose inductive destabilization would be similar to that in *cis*-2-halocyclohexyl brosylate acetolyses where the rates are decelerated by a factor of ~10,000.[3b] The transition state is forced toward a halonium ion structure resembling **6**, in which the transition state does exhibit the stability order characteristic of halonium ions. 1,2-Neighboring methoxyl is not so effective a participator as might be expected from the relatively high stability of oxonium ions because its inductive effect is also small, leading to a transition state nearer to **5** in which carbon bears more of the charge. Superimposed on these effects is the strong statistical preference for the formation of three-membered rings in comparison with five-membered rings.

A somewhat related point may be made regarding the stability order of the chloronium ion **2**, Figure 1, in which the methyl groups are *trans* on the five-membered ring and its diastereomer in which the methyl groups are *cis*. By analogy with the 2,5-dimethylfurans the *cis* isomer, which may have pseudo-equatorial methyl groups, might be expected to be more stable.[19] This stability order is not reflected in the rates of solvolysis, however, since the *erythro* tosylate which leads to *trans* methyl groups in the chloronium ion reacts *via* a path involving chlorine participation faster than the *threo* tosylate reacts. Examination of models shows that the transition-state stability will depend on different, not readily predicted, steric factors if there is only weak participation in the transition state. Perhaps significantly, *erythro*-5-methoxy-2-hexyl tosylate, where a large rate acceleration is indicative of oxonium ion character in the transition state, is less reactive than the *threo* isomer.[20]

Influence of the Solvent upon the Attenuation of Inductive Effects. The slopes of the lines which are defined by purely inductive (nonparticipating) substituents in the attenuation plots of Figures 4 and 5 have the value log ϵ, where ϵ is the attenuation factor of the inductive effect per methylene group.[4b] The calculated ϵ values corresponding to the plots shown in Figures 3 and 4 are given in Table VI, along with values of the dielectric constants of the solvents, and other quantities which vary with solvent, to be discussed. The ϵ values for acetolyses are subject to large errors because the observed inductive effects were small, but it is clear that no apparent correlation of ϵ with the solvent dielectric constant is found.

In the Westheimer–Kirkwood formulation inductive influences are attributed to electrostatic interactions of centers separated by a molecular cavity of dielectric constant 2 and by surrounding solvent having its own bulk dielectric constant.[21] The resulting effective dielectric constant is close to 2 for nearby electrostatic centers and approaches that of the solvent for long, thin molecules, leading (subject to numerous qualifications) to the prediction that inductive effects will be attenuated rapidly with distance in solvents with high dielectric constant (formic acid, water) compared to those with low dielectric constants (trifluoroacetic acid, acetic acid). Despite the many duly noted pitfalls which attend the use of the theory, prominent among which is the flexibility of aliphatic molecules, the rapid attenuation of substituent effects upon ω-substituted aliphatic acid ionization constants compared to the decreased attenuation observed by measurement of ionization constants for 4-substituted bicyclo[2.2.2]-octane-1-carboxylic acids has been taken[22] as evidence that substituent effects arise from electrostatic influences as pictured by Westheimer and Kirkwood.

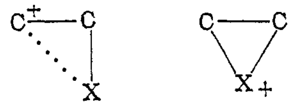


Figure 6. 1,2-Halogen participation.

Table VI. Solvent Dependence of ϵ and Other Quantities

Quantity	Solvent CF_3CO_2H	 HCO_2H	 CH_2CO_2H
ϵ,ω-Chlorotosylates	0.62[a]	0.56	0.35
ϵ,ω-Fluorotosylates	0.60[a]	0.48	0.4
Dielectric constant[b]	8.42 (20°)	57.9 (20°)	6.15 (20°)
ρ_I^R (alkyl)[c]	−15.7	−7.79	−5.72
1,2-H shift, %[d]	22	6	2
Elimination, %[d]	86	20	13
ρ_I^X (butyl)[e]	−5.36	−4.49	−2.71
ρ_I^X (heptyl)[f]	−1.25	−0.78	−0.11

[a] This value may be compared with the ϵ value 0.65 for addition of trifluoroacetic acid to various substituted alkenes[4b] and 0.67, calculated from the data in Table II for 6-fluoro-1-hexene and 9-fluoro-1-nonene. [b] For reference see A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1640 (1959), footnote 10. [c] The ρ_I^R values[8] correspond to substitution of hydrogen in isopropyl tosylate with alkyl groups, *e.g.*, methyl, ethyl, etc. [d] For 2-hexyl tosylate solvolysis, reported in ref 12. [e] For 4-chloro-2-butyl tosylate solvolysis, reported in Table III, calculated from the equation log $(k_H/k_X) = \rho_I^R\sigma_I$; $\sigma_I = 0.47$. [f] For 7-chloro-2-heptyl tosylate solvolysis, Table III.

The failure of our ϵ values to correlate with solvent dielectric constant of course does not rule out the Kirkwood–Westheimer theory as a basis for the origin of substitutent effects in our systems, but it does show that the theory does not in general have useful predictive value for aliphatic systems, and by implication, for comparison of aliphatic systems with others. In a sense our results show that carbonium ions in trifluoroacetic acid and formic acid cannot "see the solvent." The result is reminiscent of the observation that σ_I values derived from *meta*-substituted fluorobenzene nmr frequencies are solvent independent (unless the solvent, in effect, changes the substituent by hydrogen bonding).[23] In the next section we use alkyl group substituent effects as a basis for developing a modified hypothesis of the origin of substituent effects and the associated ϵ values in carbonium ion reactions.

The Origin of Inductive Effects of Alkyl and Nonalkyl Groups. Alkyl group inductive effects have always posed a problem, since σ values derived originally from substituted acetate ester hydrolysis data show alkyl groups to be electron releasing, compared to hydrogen,

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(19) M. Lj. Mihailović, R. I. Mamuzić, Lj. Zigić-Manuzić, J. Bošnjak, and Ž. Cekovic, *Tetrahedron*, 23, 215 (1967).

(20) S. Winstein, E. Allred, R. Heck, and R. Glick, *ibid.*, 3, 1 (1958).

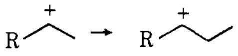
(21) F. H. Westheimer and J. G. Kirkwood, *J. Chem. Phys.*, 6, 513 (1938).

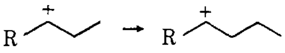
(22) J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953).

(23) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709 (1963).

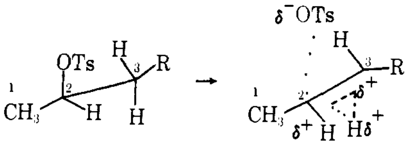
whereas other reactions have shown no effect or a slightly inverse effect.[24] It has been noted that attenuation factors for the σ^* values of alkyl groups (presumably derived originally from ester hydrolysis data) are anomalous,[25] but the physical origin of these anomalies has remained obscure, as has their possible variation with reaction type. In this connection, examination of previously reported data for alkyl tosylate solvolyses in trifluoroacetic acid and other acids[8] is particularly revealing in comparison with the results of the present study.

If the solvolysis rates are taken as a measure of carbonium ion stability, the earlier study[8] shows that the replacement sequence shown below is accompanied by stabilizing effects in units of log k of 0.77, 0.72, 0.66, and 0.73 (average = 0.719) for trifluoroacetolysis where R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, and $CH_3CH_2CH_2CH_2$, respectively. The replacement shown below is attended by Δ log k values 0.11, 0.05 and 0.12 (average = 0.093), where R = CH_2, CH_3CH_2, and $CH_3CH_2CH_2$, respectively.[8] The average attenuation factor for replacement of hydrogen by methyl at the two positions indicated (0.093/0.719) is only 0.13, strikingly different from the value of 0.62 found in the present study for replacement of hydrogen by chlorine. Examination of the previously reported formolysis and acetolysis data[8] shows that the alkyl group effect is even more sharply attenuated, ϵ being, in fact, indistinguishable from zero for the replacement sequence mentioned above. Kwart and Takeshita[3c] and others (*cf*, ref 24) have previously emphasized the absence of evidence for electron-releasing effects of remote alkyl groups. The comparison of the attenuation of alkyl and nonalkyl group inductive effects, made here, again serves to emphasize that there is "something different" about alkyl group inductive effects.





A recent deuterium isotope effect study has led to the postulate of unsymmetrical hydrogen participation (viewed as an extreme manifestation of the type of electronic interaction also associated with hyperconjugation) in the solvolysis of *cis*-4-*t*-butylcyclohexyl brosylate in aqueous ethanol.[26a] Furthermore, nonequivalent axial β-hydrogen isotope effects in the solvolysis of *trans*-4-*t*-butylcyclohexyl brosylate led to the postulation of a twist-boat transition state[26b] involving some hydrogen participation. A similar postulate was made in regard to cyclohexyl tosylate solvolysis.[26c] In our view, these studies, in connection with our observation of rapid attenuation of alkyl group inductive effects with distance, compared to other inductive effects, suggests that alkyl group effects are actually effects upon hyperconjugation. Thus the change from R = H to R = CH_3 in 7 exerts a stabilizing influence on the transition state **8**. The precise nature of the stabilizing influence cannot be specified, since there is no way to evaluate such factors as the relative importance of carbon (*vs.* hydrogen) hyperconjugation, or the amount of release of steric strain during the change **7** → **8**, etc. Since overlap of the partially vacant C_2 p orbital with the C_3–H bond would leave C_3 somewhat electron deficient, the stabilizing effect attending the change from R = H to R = CH_3 is perhaps best pictured as similar to (but much smaller than) the effect of making the same change in a carbonium ion (*i.e.*, a change from a primary to a secondary carbonium ion). Whatever the origin of the alkyl group effect, the effect is clearly additive on a free-energy scale when a second replacement of H by CH_3 is made at C_1 in **7**, as may be seen from the linearity of the Hammett–Taft plot for alkyl tosylates, given in ref 8. This result can of course be accommodated if simultaneous overlap of the C_2 p orbital with a participating C_1–H bond and a C_3–H bond is envisioned. The results of Shiner and Jewett,[26a,b] which seemed to indicate participation by only one neighboring hydrogen, can be accommodated by the suggestion that simultaneous bridging by two neighboring hydrogens in the transition state does not occur in cyclohexyl tosylate solvolyses as a consequence of the strain associated with the fusion of two "three-membered" rings to the cyclohexyl ring.



7 8

Since a number of explanations for the rapid attenuation of alkyl group effects could doubtless be adduced, corroborative evidence for the hyperconjugative origin of such effects is clearly desirable. The solvent effect upon the magnitude of the alkyl group inductive effect would appear to provide such evidence, in comparison with the solvent effect upon the per cent of 1,2-hydrogen shift and the per cent of elimination in a typical tosylate solvolysis, since the latter two quantities may well be indicative of the extent of hyperconjugative interactions in the transition states for solvolyses. These comparisons are made in Table VI, where the alkyl group ρ_I values are designated by the symbol ρ_I^R to distinguish them from ρ_I^X values, which are defined as those values derived from reactions of tosylates having electronegative substituents. Examination of Table VI shows that the three quantities thought to be indicative of hyperconjugative interactions (including alkyl group "inductive" effects) do in fact decrease in magnitude according to the solvent sequence, trifluoroacetic acid $\gg$ formic acid > acetic acid, as expected if they have a common origin. By contrast the magnitudes of nonalkyl group inductive effects, based on chloro-substituted tosylate solvolysis rates, may be seen (Table VI) to exhibit a somewhat different solvent dependence (trifluoroacetic acid > formic acid $\gg$ acetic acid), suggesting their different origin.

If we may proceed on the assumption that there is at least tentative experimental support for hyperconjugative charge delocalization effects in solvolyses, it becomes important to examine the possible consequences in regard to nonalkyl group inductive effects.

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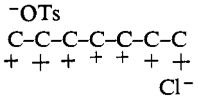
(24) For references see H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, 86, 5186 (1964).

(25) See C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 346 (1964).

(26) (a) V. J. Shiner, Jr., and J. G. Jewett, *J. Am. Chem. Soc.*, 87, 1382 (1965); (b) *ibid.*, 87, 1383 (1967); (c) W. H. Saunders, Jr., and K. T. Finley, *ibid.*, 87, 1384 (1965).

We note that in an ω-chlorotosylate (taken as a typical example) hyperconjugation delocalizes some of the carbonium ion charge toward the chlorine substituent. Since dipole moment studies suggest that substituent dipoles are delocalized to an extent of about 10% (*e.g.*, CH_3Br, 1.80 D.; C_2H_5Br, 2.06 D.[27]) we may schematically picture the transition state for 7-chloro-2-heptyl tosylate as follows.



$$\begin{array}{l} {}^{-}\text{OTs} \\ \text{C–C–C–C–C–C–C} \\ +\ +\ +\ +\ +\ +\ + \\ \qquad\qquad\quad \text{Cl}^{-} \end{array}$$

According to this picture a considerable portion of the interaction between the substituent and the reaction site results from interactions of charges located (as a consequence of delocalization) nearer the middle of the molecule than the carbons bearing the substituent and the reactive tosylate group.

Since the delocalized charges are relatively deep inside the hydrocarbon cavity their interaction as revealed by ϵ values is expected to be relatively insensitive to the dielectric constant of the solvent, in agreement with experiment. The observed entirely equivalent effect of the geometrically diverse substituents, Cl, C≡N, $OCOCH_3$, and $OCOCF_3$, at sites four to ten carbon atoms from the reaction center[3b] is likewise well accommodated if interaction takes place in the middle of the molecule. It is otherwise difficult to understand why there is no evidence for reversed substituent effects in aliphatic reactivity.[28]

Finally, we note that the solvent dependence of ϵ values (Table VI) is predictable on the basis of the picture we have outlined. As the substituent is moved farther from the reaction site in a series of ω-substituted tosylates, increased delocalization moves the carbonium ion charge closer to the substituent, causing the interaction between the substituent and the reaction site to decrease only slowly with distance. The effect is expected to be most pronounced in trifluoroacetic acid, less in formic acid, and least in acetic acid, in agreement with the observed trend in ϵ values. This result is encouraging, since we have noted that the traditional approach to substituent effects, involving solvent dielectric constants, fails to predict this trend.

The origin of substituent effects, as envisioned above, represents a middle ground between the field-effect origin championed by Dewar's school[29] and the "path" approach, for which there seem to be no champions among modern chemists. In the hyperconjugative approach the path does assume a key role, delocalization owing to orbital overlap in the bonded chain, but the magnitude of the delocalized charge decreases rapidly with distance and is in no sense identified with ϵ, in contrast with the assumptions which seem to characterize earlier path approaches. An electrostatic origin of inductive effects is retained in the hyperconjugation approach, but with emphasis on the pronounced influence exerted by even a moderate amount of charge delocalization.

Halogen Participation Effects. If a number of reaction parameters, discussed above in connection with Table VI, have their origin in weak hydrogen participation, 1,4-halogen participation might be expected to exhibit a similar solvent dependence. This expectation is realized as may be seen by comparison of data in Tables V and VI.

Turning our attention from solvent variation to the variation of reaction type, we recall that tosylate solvolyses showed greater participation effects, but slightly decreased inductive effects (of electronegative substituents), compared to additions of trifluoroacetic acid to alkenes. Since both inductive and participation effects might be expected to reflect the extent of electron deficiency in the cationic transition states, the observed results are, perhaps, unexpected. They can perhaps be accommodated, however, if it is postulated that tosylates substituted with electron-attracting inductive substituents are influenced by *ground-state destabilization* owing to dipole–dipole interactions which resembles that in the cationic transition state, but is smaller.[30] Substituted alkenes, of course, would exhibit less dipole–dipole destabilization in the ground state. Accordingly tosylates, compared to alkenes, may show a slightly smaller net *change* in interaction between the substituent and the reaction site upon going from the ground state to the transition state, but still have a larger interaction in the transition state, corresponding to a more fully developed positive charge at the cationic carbon.

The halogen participation tendency may reflect this property of the transition state, such participation being pictured as absent in the ground state which has undergone no rehybridization at the reaction site. Participation tendency may accordingly be regarded as a reaction parameter analogous in some ways to the reaction parameter ρ_I^X, but differing from ρ_I^X in that it is not subject to ground-state effects. Participation tendency, viewed in this way, measures the need of a transition state of a particular reaction type (*e.g.*, tosylate solvolysis) to be solvated (that is, bonded to an entering group).

Conclusion

A comprehensive qualitative picture of the way in which inductive and participation effects in cationic reactions vary as a function of solvent and reaction type has been outlined. Inductive effects have been postulated to arise to an important extent from interactions of hyperconjugatively delocalized charges.[31] This concept and others which have been outlined have potential significance outside the area of carbonium ion reactions. The ideas presented seem to correlate results which were previously not understood and to have definitive predictive capacity which should lead to interesting experimental tests.

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[27] S. Weiss, *J. Phys. Chem.*, 70, 3146 (1966).

[28] For an example which may be influenced by π-system delocalization as well as by internal hydrogen bonding see R. Golden and L. M. Stock, *J. Am. Chem. Soc.*, **88**, 5928 (1966).

[29] For references see M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966).

[30] For an example of ground-state effects see H. C. Goering and L. L. Sims, *ibid.*, **79**, 6720 (1957).

[31] In connection with this postulate a referee has commented on our lack of real evidence and upon difficulties associated with flexible molecules. Compared to the earlier version of our paper we believe that additional comparisons now made in Table VI, in connection with ref 26, provide a more compelling case. We (P. E. P. and D. M. C.) will shortly report data which indicate that the solvent variation of inductive effects in rigid steroidal tosylates closely parallels the data for aliphatic systems, suggesting that flexibility is not a major consideration in the present study.

Experimental Section

Rates. Rates of formolyses and trifluoroacetolyses were determined as described previously for solvolysis of unsubstituted 2-alkyl tosylates.[8] The previously reported formula for determination of the rate constant for trifluoroacetolysis contains a typographical error. The correct equation is $k = 2.303\Delta \log [A - A_\infty]/\Delta t$. Rate constants for trifluoroacetolysis are strongly dependent on the value chosen for A_∞ and must be regarded as uncertain by ±5–10%. Acetolyses were followed by the usual method involving perchloric acid in acetic acid as the titrant and brom phenol blue as an indicator. Further details are given in the footnotes of Table II.

Tosylates and Alcohols. Tosylates were prepared from the alcohols by the usual procedure.[32] The alcohols and intermediates in their preparation, described below, gave satisfactory nmr and infrared spectra. Distillations were performed on spinning-band columns.

4-Chloro-2-butyl Trifluoroacetate. 4-Chloro-1-butene (55.5 g, obtained from the alcohol purchased from Columbia Organic Chemicals Co.) was allowed to react at room temperature with 500 ml of trifluoroacetic acid containing 16 ml of concentrated sulfuric acid for 3 days. Removal of trifluoroacetic acid at 150 mm, followed by extraction and distillation, gave 66 g (60%) of 4-chloro-2-butyl trifluoroacetate, bp 82° (61 mm).

Anal. Calcd for $C_5H_8ClF_3O_2$: C, 35.23; H, 3.94. Found: C, 35.45; H, 4.26.

4-Fluoro-2-butanol. The known 4-chloro-2-butanol[33] was obtained in our study by hydrolysis of 4-chloro-2-butyl trifluoroacetate (120 g) upon stirring with sodium hydroxide (23.2 g) in water (500 ml) for a few minutes (until neutral). The 4-chloro-2-butanol (62.5 g) was converted to the known[34] 4-iodo-2-butanol (98 g) by refluxing 24 hr with a slight molar excess of sodium iodide in acetone. 4-Fluoro-2-butanol was prepared by dropping 4-iodo-2-butanol (96 g, 0.48 mole) into a stirred solution of anhydrous potassium fluoride (56 g, 0.96 mole) in redistilled diethylene glycol (400 ml) maintained at 100–125° (50 mm).[35] The product distilled into a cold trap as it was formed. Drying (molecular sieve 5A) and separation from 3-buten-2-ol by distillation gave 15.2 g [35%, bp 79–80° (110 mm)] of 4-fluoro-2-butanol. The nmr spectrum showed a pair of triplets arising from CH_2F centered at δ 4.47, $J_{HF} = 48$ cps.

Anal. Calcd for C_4H_8FO: C, 52.16; H, 9.85. Found: C, 51.72, 52.63; H, 9.86, 9.81.

5-Chloro-2-pentyl Trifluoroacetate. From reaction of 11.4 g of 5-chloro-1-pentene[4a] with 73 ml of trifluoroacetic acid containing 1.2 g of sodium trifluoroacetate (probably an unnecessary component) at reflux for 3.5 hr there was obtained 14.0 g (59%) of 5-chloro-2-pentyl trifluoroacetate, bp 67° (12 mm).

Anal. Calcd for $C_7H_{10}ClFO_2$: C, 38.4; H, 4.58. Found: C, 38.28; H, 4.66.

5-Chloro-2-pentanol. 5-Chloro-2-pentyl trifluoroacetate (12 g) was refluxed with a mixture of 41 g of methanol and 9.3 g of 36% hydrochloric acid for 2.3 hr. Evaporation of methanol in a rotary evaporator followed by addition of ether, washing, and drying (magnesium sulfate) gave 5.04 g (75%) of 5-chloro-2-pentanol.

Anal. Calcd for $C_5H_{11}ClO$: C, 48.9; H, 9.00. Found: C, 44.84; H, 9.30.

6-Chloro-2-hexanol. A somewhat unsatisfactory preparation was achieved as follows. A Grignard reagent was prepared from 40.4 g of 1-bromo-4-chlorobutane which had been obtained free of the dichloro- and dibromobutane contaminants by distillation on a high-speed Teflon spinning-band column. Addition of the chlorobromide to 5.73 g of magnesium in 120 ml of ether followed by reaction with 9.17 g of acetaldehyde gave 12.8 g of distilled material which was redistilled at high reflux ratio to give 6.54 g (23%) of apparently pure 5-chloro-2-hexanol, bp 58° (1.1 mm).

Anal. Calcd for $C_6H_{13}ClO$: C, 52.7; H, 9.54. Found: C, 52.90; H, 9.72.

5-Fluoro-2-pentanone. The known 5-fluoro-1-pentyne[35] was prepared in 45% yield from 5-iodo-1-pentyne[36] (125 g) by the procedure used to prepare 4-fluoro-2-butanol, except that the product was collected at atmospheric pressure. 5-Fluoro-1-pentyne (17.5 g) was added to 160 ml of a mixture of 10 g of mercuric sulfate, 10 g of concentrated sulfuric acid, and 500 g of 60% aqueous acetic acid.[37] Reaction at 65° for 10 hr gave 15.6 g (75%) of 5-fluoro-2-pentanone, bp 67–68° (64 mm).

Anal. Calcd for C_5H_9OF: C, 57.67; H, 8.64. Found: C, 57.33; H, 8.64.

5-Fluoro-2-pentanol. Reduction of 5-fluoro-2-pentanone (12.3 g) with sodium borohydride in methanol gave 10.49 g (80%) of 5-fluoro-2-pentanol, bp 55° (10 mm).

Anal. Calcd for $C_5H_{10}OF$: C, 56.58; H, 10.45. Found: C, 56.69; H, 10.45.

7-Chloro-1-heptyne. 1-Bromo-5-chloropentane (100 g) was added at ice–salt temperature to 53 g of lithium acetylide–ethylene diamine complex in dimethyl sulfoxide (225 ml). When addition was complete (30 min) the mixture was neutralized with 6 *N* hydrochloric acid and subjected to water–ether extraction. A second attempt using inverse addition gave poorer results owing to the longer addition time required. The combined yield from two preparations (22%) can be improved by rapid addition and immediate isolation. 7-Chloro-1-heptyne was separated from diyne and pentamethylene dichloride (present in the reactant) by distillation on a high-speed Teflon spinning-band column, bp 82° (45 mm).

Anal. Calcd for $C_7H_{11}Cl$: C, 64.37; H, 8.49. Found: C, 64.58; H, 8.54.

7-Fluoro-2-heptanone. 7-Chloro-1-heptyne was converted to 7-iodo-1-heptyne in 60% yield. The latter compound was converted to 7-fluoro-1-heptyne.[38] This fluoroalkyne (15.7 g) was converted to the ketone in 86% yield by the method described for 5-fluoro-2-pentanone.

Anal. Calcd for $C_7H_{13}FO$: C, 63.59; H, 9.66. Found: C, 63.23; H, 9.66.

7-Fluoro-2-heptanol. The alcohol was obtained in 80% yield from reduction of 14 g of 7-fluoro-2-heptanone, as described for 5-fluoro-2-pentanol.

Anal. Calcd for $C_7H_{15}FO$: C, 62.65; H, 11.26. Found: C, 62.76; H, 11.36.

7-Cyano-2-heptanone. Sodium cyanide (1.96 g) in dried (calcium hydride) dimethyl sulfoxide (40 ml) was allowed to react with 7-chloro-2-heptanone (3.0 g) at room temperature for 48 hr. Addition of water (300 ml) and continuous extraction with ether gave 2.1 g (76%) of 7-cyano-2-heptanone, bp 94° (0.6 mm).

Anal. Calcd for $C_8H_{13}NO$: C, 69.05; H, 9.41. Found: C, 68.77; H, 9.49.

7-Cyano-2-heptanol. Sodium borohydride reduction of the ketones described above gave 2.0 g (95%) of 7-cyano-2-heptanol, bp 93° (0.3 mm).

Anal. Calcd for $C_8H_{15}NO$: C, 68.05; H, 10.71. Found: C, 67.84; H, 10.71.

5-Chloro-2-hexyl Trifluoroacetate. The preparation from 5-chloro-1-hexene was analogous to the preparation of 5-chloro-2-pentyl trifluoroacetate.

Anal. Calcd for $C_8H_{12}O_2F_3Cl$: C, 41.30; H, 5.19. Found: C, 41.28, H, 5.17.

Distillation of 20 g of 5-chloro-2-hexyl trifluoroacetate containing ~60% of the higher boiling, later eluted (Dow-Corning 550 silicone capillary column), *erythro* isomer on a Nester-Faust high-speed Teflon spinning-band column gave 3.4 g of material shown by gas chromatography to be ~90.9% *threo* isomer and 7 g of 99% *erythro* isomer. Distillation on an ordinary type spinning-band column at high reflux ratio failed to accomplish the separation.

Stereochemistry of 5-Chloro-2-hexyl Trifluoroacetate. The higher boiling pure diastereomer of 5-chloro-2-hexyl trifluoroacetate (10 mg) was heated for 1 hr by means of an oil bath maintained at 120° with 0.4 ml of 0.25 *M* sodium hydroxide in 50:50 methanol–water. The reaction vessel was essentially a small side-arm test tube fitted with a coldfinger condenser. The 2,5-dimethyltetrahydrofuran and some methanol collected as drops on the coldfinger and sides of the vessel. The water–sodium hydroxide solution remaining in the vessel was removed, and the distillate was washed down with a few drops of ether. The ether solution was chromatographed on a 150-ft Dow-Corning 550 silicone capillary column to give a peak corresponding to the higher boiling, later eluted, *trans*-2,5-dimethyltetrahydrofuran, expected from cyclization of *erythro*-5-chloro-2-hexanol.

An impure sample of the other diastereomer yielded a peak corresponding to *cis*-2,5-dimethyltetrahydrofuran and a small peak corresponding to the *trans* isomer arising from the contaminant.

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(32) H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, 78, 2735 (1956).

(33) N. G. Gaylord, J. H. Crowdle, W. A. Himmler, and J. H. Pepe, *ibid.*, 76, 59 (1954).

(34) T. E. Stevens and W. D. Emmons, *ibid.*, 79, 6008 (1957).

(35) The procedure is adapted from that of F. L. M. Pattison and R. E. A. Dear, *Can. J. Chem.*, 41, 2600 (1963).

(36) E. G. Eglington and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

(37) This hydration procedure is that of R. J. Thomas, K. N. Campbell, and G. F. Hennion, *J. Am. Chem. Soc.*, 60, 718 (1938).

(38) F. L. H. Pattison and J. J. Norman, *ibid.*, 79, 2311 (1957).

Commercial 2,5-dimethyltetrahydrofuran proved to be a mixture of isomers, from which a greatly enriched sample of lower boiling[19] *cis* isomer was obtained by distillation for gas chromatographic comparison.

Acknowledgment. The picture of halogen "weak participation" presented here bears marked resemblance to one which may be envisioned for phenyl participation as outlined by Professor H. C. Brown in a conversation. Samples of fluoroalkenes were furnished by Professor B. S. Rabinovitch and Professor F. L. M. Pattison. 5-Methoxy-2-pentyl tosylate was prepared and studied by Mr. R. Belloli.

α-Fluoro and α-Alkoxy Substituents as Deactivators in Carbanion Formation[1a]

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Abstract: The kinetics of the methoxide ion catalyzed deuterium exchange of the α-hydrogen atoms of several methyl esters in methanol-*d* solution have been investigated. The second-order rate constants observed for the acetate, propionate, butyrate, β-phenylpropionate, and succinate are correlated well by a Taft ρ^* value of 1.78. The β-methoxypropionate and phenylacetate are too reactive to give agreement with the Taft equation, the latter giving a carbanion stabilized by the resonance effect of the phenyl substituent. The methoxyacetate, fluoroacetate, dimethoxyacetate, and difluoroacetate are less reactive (by $10^{2.6}$-, $10^{4.7}$-, 10^{7}-, and 10^{12}-fold, respectively) than expected from the Taft equation. These deviations from the Taft equation are rationalized in terms of the differences in electronegativity between sp^3 carbon (as in the α-carbon atoms of the esters) and sp^2 carbon (as in the negative carbon atoms of the carbanions) and in terms of the stabilization associated with the attachment of several oxygen or fluorine atoms to the same sp^3 carbon atom. Literature data are quoted to show that α-fluoro and α-alkoxy substituents either decrease rate and equilibrium constants for the formation of sp^2-hybridized carbanions or they increase them to a much smaller extent than would be expected from the inductive effects of these substituents. The available data on the formation of sp^3-hybridized carbanions show that α-fluoro and α-aryloxy substituents increase the reactivity by about the amount to be expected from the inductive effect.

According to Pauling's equation[2] the energy of a carbon–halogen bond in a saturated organic halide may be expressed

$$BE_{\mathrm{sp^3C-Y}} = \frac{BE_{\mathrm{sp^3C-sp^3C}} + BE_{\mathrm{Y-Y}}}{2} + 23(X_{\mathrm{sp^3C}} - X_{\mathrm{Y}})^2 \quad (1)$$

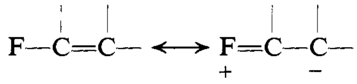
where the *BE*'s are the energies (in kcal/mole) of the bonds denoted by subscripts and the *X*'s are electronegativities. An analogous expression may be written for the energy of an sp^2 carbon–halogen bond and combination of this expression with eq 1 gives an expression for the difference in carbon–halogen bond energies for sp^3 and sp^2 carbon.

$$BE_{\mathrm{sp^2C-Y}} - BE_{\mathrm{sp^3C-Y}} = \frac{BE_{\mathrm{sp^2C-sp^2C}} - BE_{\mathrm{sp^3C-sp^3C}}}{2} + 23(X_{\mathrm{sp^2C}}{}^2 - 2X_{\mathrm{sp^2C}}X_{\mathrm{Y}} - X_{\mathrm{sp^3C}}{}^2 + 2X_{\mathrm{sp^3C}}X_{\mathrm{Y}}) \quad (2)$$

Combination of this with the corresponding expression for hydrogen yields

$$(BE_{\mathrm{sp^2C-Y}} - BE_{\mathrm{sp^3C-Y}}) - (BE_{\mathrm{sp^2C-H}} - BE_{\mathrm{sp^3C-H}}) = -46(X_{\mathrm{sp^2C}} - X_{\mathrm{sp^3C}})(X_{\mathrm{Y}} - X_{\mathrm{H}}) \quad (3)$$

According to this equation, if sp^2 carbon is more electronegative than sp^3 carbon, as has been claimed,[3] when the carbon atom to which a halogen is attached has its hybridization changed from sp^3 to sp^2, the carbon–halogen bond energy will increase less (or decrease more) than the corresponding carbon–hydrogen bond energy. The magnitude of this effect will increase with the electronegativity of the halogen. This effect has been suggested as a possible partial explanation for the deactivating effect of β-fluorine substituents (relative to β-chlorine and bromine) in E2 reactions of β-haloethyl bromides.[4] If olefin stabilities depended only on Pauling electronegativities, a fluorine substituent on a double bond would be expected to act as a destabilizer to a greater extent than any other halogen. However, from a comparison of the Hammett substituent constants for the *meta* and *para* halogens it appears that sp^2 carbon-bound fluorine is capable of resonance electron donation to a π-electron system to a greater extent than any other halogen.



$$\mathrm{F{-}C{=}C{-}} \longleftrightarrow \mathrm{\overset{+}{F}{=}C{-}\overset{-}{C}{-}}$$

Such resonance interaction should lead to a stabilization of fluoroolefins that will counteract and perhaps overwhelm the destabilization due to the electronegativity effect.

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[1] (a) Part XII in the series "Polar Effects on Rates and Equilibria." For part XI see J. Hine, *J. Am. Chem. Soc.*, 88, 5525 (1966). This work was supported in part by Research Grant GP-2002 from the National Science Foundation. Abstracted largely from the Ph.D. Thesis of L. G. Mahone, 1966. (b) Author to whom inquiries may be addressed at the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

[2] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 85–105.

[3] *Cf.* G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 128–129.

[4] J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, 78, 5002 (1956).