Cyclic Halonium Ions with Five-Membered Rings

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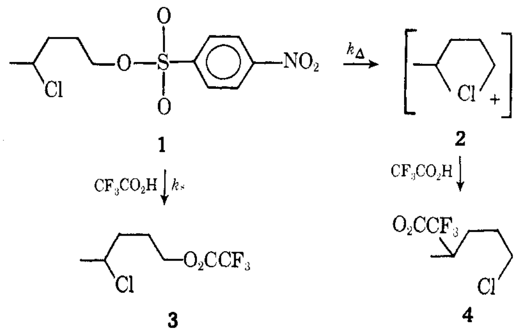
The reaction of the primary *p*-nitrobenzenesulfonate **1** in trifluoroacetic acid may be considered to proceed *via* two competing paths having rate constants designated k_Δ and k_s, respectively (Scheme I). Recent work in our laboratories[1] indicates that reaction *via* the path having rate constant k_Δ strongly predominates over the alternative path, the ratio k_Δ/k_s being approximately 760. The intermediacy of the five-membered ring halonium ion **2** in the "k_Δ reaction" is strongly implied by the structure, **4**, of the isolated reaction product, which is seen to be the result of a 1,4 halogen shift. This example of neighboring group participation by the somewhat remote neighbor chlorine is representative of the relatively recently discovered reactions proceeding *via* five-membered-ring halonium ions, to be examined in this Account. The preparation of the ions as stable species observable by nmr in SO_2–SbF_5 solutions[2] also will be described.

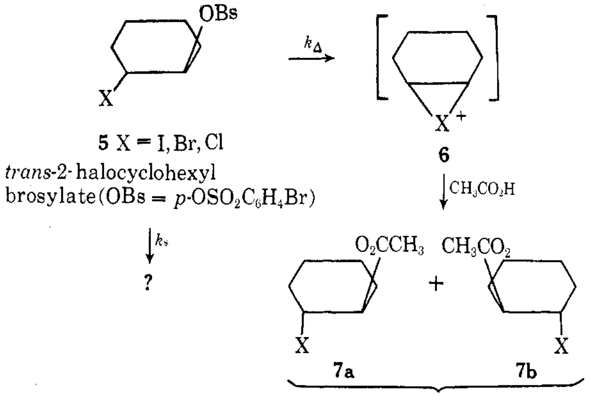
Scheme I
Competing Paths for Trifluoroacetolysis of 4-Chloro-1-pentyl Nosylate



The concept, employed in Scheme I, that competing paths, one involving neighboring group participation, occur in a substantial number of reactions has been a fruitful one.[3,4] An analysis comparable to that in Scheme I was used in 1948 by Winstein, Grunwald, and Ingraham in adducing evidence for three-membered-ring halonium ion intermediates in the acetolysis (reaction in acetic acid) of *trans*-2-halocyclohexyl brosylates (Scheme II, X = I, Br, and possibly Cl).[5] The label k_Δ which they applied to the rate constant for the path involving participation was coined to signify that this additional path could lead to an increased total rate constant, k_T, for disappearance of reactant.

It should be noted that in 1948 the nonparticipation reaction was assumed to involve the formation of a planar carbonium ion in the rate-determining step.[5a] The associated rate constant was designated by the symbol k_c. More recent studies[6] make it clear that transition states for the solvolysis of secondary as well as primary substrates exhibit considerable bond formation to solvent, which results, ultimately in the formation of the product of Walden inversion.[7] The designation k_s has been used for the rate constant of this solvent-assisted process (as in Scheme II). Both the k_s and the k_Δ reactions may, in a broad sense, be considered in most instances to be "carbonium ion reactions," since in the respective transition states of the rate-determining steps a partial positive charge may appear on the carbon atom bearing the leaving group (OBs in Scheme II).

Scheme II
Example of a Solvolysis Reaction Thought to Involve a Halonium Ion Intermediate



The earliest postulation of a halonium ion intermediate in a reaction seems to have been made by Roberts and Kimball, in their now familiar rationalization of the trans addition of bromine to alkenes.[8] The general form of their postulate is illustrated (Scheme III) by some recent examples of addition reactions in which

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[1] (a) P. E. Peterson and J. F. Coffey, *J. Amer. Chem. Soc.*, **93**, 5208 (1971); (b) P. E. Peterson and J. F. Coffey, *Tetrahedron Lett.*, 3131 (1968).

[2] For a review, see G. A. Olah, *Science*, **168**, 1298 (1970).

[3] For a review, see B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 21 (1964).

[4] A striking example of recent progress is the apparently precise determination of the extent of phenyl participation in the previously controversial solvolysis of 3-phenyl-2-butyl tosylate: H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5245 (1970).

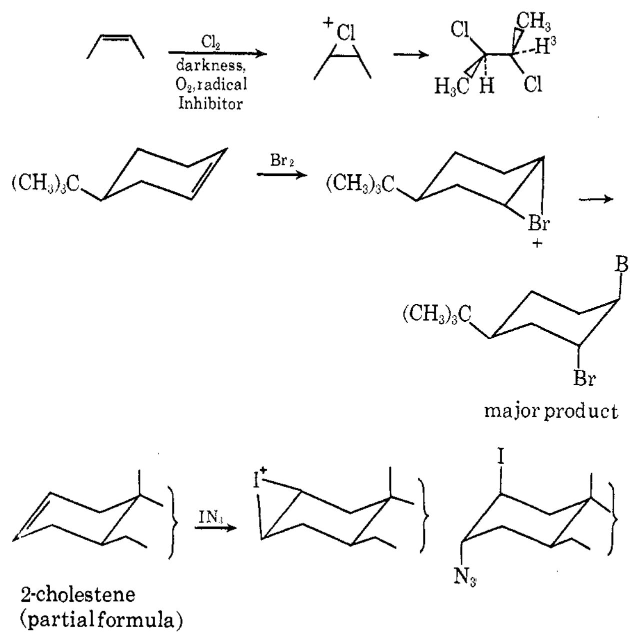
[5] (a) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948); (b) E. Grunwald, *ibid.*, **73**, 5458 (1951).

[6] P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970), and accompanying papers.

[7] A. Streitwieser, Jr., T. O. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965).

[8] I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).

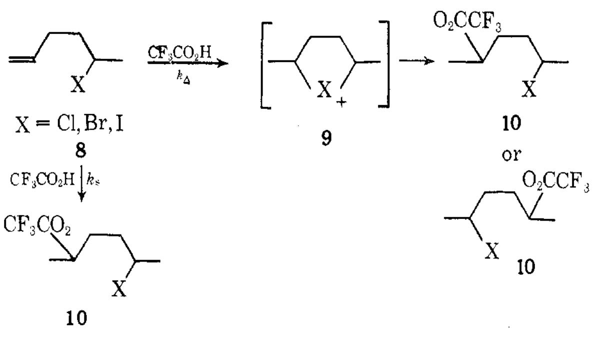
Scheme III
Examples of Addition Reactions Thought to Involve Halonium Ion Intermediates



chloronium, bromonium, and iodonium ion intermediates are thought to open with Walden inversion to give overall trans additions to alkenes.[9]

Additions to Alkenes. In our research group 1,4 halogen participation and the concomitant five-membered-ring halonium ions were first invoked[10] to explain the rates of reaction of 5-chloro-, 5-bromo-, and 5-iodo-1-hexene with trifluoroacetic acid (Scheme IV). It is interesting to note that the inference of halogen participation was made on the basis of rate evidence which a number of chemists might have regarded as an overinterpretation of small rate differences. Allen's data[10a] are given in Table I.

Scheme IV
Competing Paths in the Addition of Trifluoroacetic Acid to 5-Halo-1-hexenes



We argued that the reaction of 5-halo-1-hexenes would have been retarded to a greater extent than was observed (3.35- to 4.13-fold) owing to the inductive effect of halogen if a second reaction, 1,4 halogen participation, had not contributed to the overall rate.

Table I
Relative Rates of Reaction of 5-Substituted-1-hexenes with Trifluoroacetic Acid

Substituent, X	k_H/k_X, 60°
H	1
Cl	4.13
Br	3.35
I	3.50
O_2CCH_3	32.6
O_2CCF_3	167

However, solvent-induced modification of the electronegativity of some substituents, owing to hydrogen bonding of trifluoroacetic acid to the substituent, prevented a quantitative assessment of the extent of neighboring group participation using the Hammett–Taft substituent effect equation, $\log k_X/k_H = \rho\sigma_I$. The closely similar behavior of the various halogens was puzzling, as we shall see later.

The symmetrical halonium ion **9** should, in the absence of complications, react to give a product, **10**, which is 50% halogen shifted. An alkene corresponding to **8**, X = Cl, but having a deuterium label on the carbon bearing chlorine, reacted to give a product showing the presence of 40% CH_3CHCl groups, in addition to 60% CH_3CDCl groups.[11] This result suggested that reaction occurred predominantly *via* ion **9**.

Determinations of the rates of reaction of a large number of substituted alkenes, $CH_2{=}CH(CH_2)_{n-2}X$, permitted us to give a more firmly based interpretation of the rates of reaction of substituted alkenes, including a quantitative separation of overall rate constants into the presumed components, k_Δ and k_s, for those cases where the substituent, X, participates. We assumed[12] that the rate-retarding inductive free energy effect of a substituent upon the normal addition would fall off by a constant factor, ϵ, per methylene group—a rule of thumb long used by chemists.[13,14] Alkenes having nonparticipating substituents (cyano, trifluoroacetoxy, and acetoxy) obeyed this rule extraordinarily well, as seen in the linear graphical representation of the appropriate function[14] of the data (Figure 1), which we have termed an attenuation plot.[15] Deviations from the rule shown by 5-chloro-1-pentene (Figure 2) and the similar methoxy compound permitted evaluation of the additional contribution to the rate constant, k_Δ, arising from 1,4-chlorine (or methoxyl) participation. The k_Δ/k_s values

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[9] For a review, see R. C. Fahey, *Top. Stereochem.*, **3,** 237 (1968).

[10] (a) P. E. Peterson and G. Allen, *J. Amer. Chem. Soc.*, **85,** 3608 (1963). (b) The idea for such participation had, as we shall mention later, been considered in Winstein's research group and in a few scattered references.

[11] P. E. Peterson and E. V. P. Tao, *ibid.*, **86,** 4503 (1964).

[12] P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. W. Thompson, *ibid.*, **87,** 5163 (1965).

[13] *Cf.* G. E. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p 204.

[14] We assume $\log k_H - \log k_X \equiv \Delta \log k$ falls off by a constant factor, ϵ, per methylene group (k_H and k_X are rate constants for reactions of substituted and unsubstituted compounds, respectively). Then

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

where n, m = numbers of carbon atoms in the aliphatic chains being compared. This leads to

$$\log \Delta \log k_n = (\log \epsilon)(n - m) + \log \Delta \log k_m$$

$$Cf. \quad y \quad = \quad m \quad x \quad + \quad b$$

[15] For an earlier use of this approach see H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82,** 508 (1963).

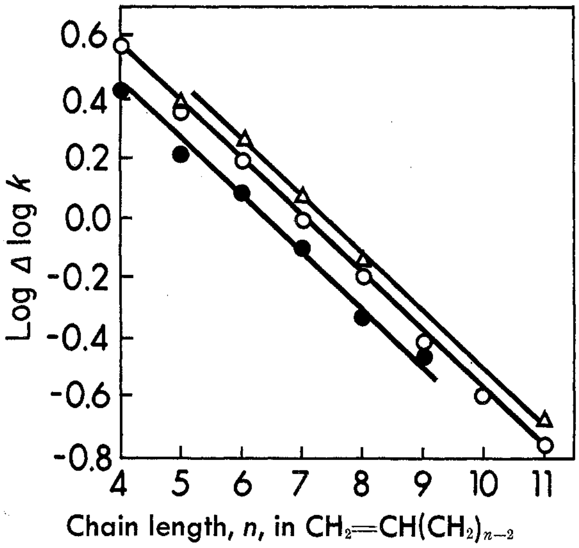


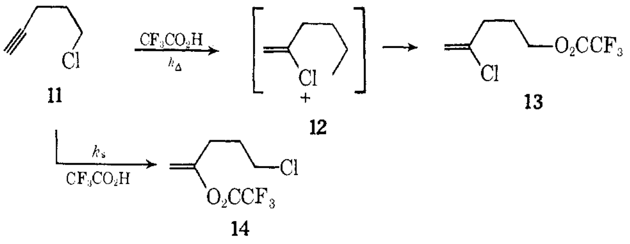
Figure 1. Plot of rate data for addition of trifluoroacetic acid to alkenes having cyano (Δ), trifluoroacetoxy (○), and acetoxy (●) substituents, based on the assumption that the substiutent effect changes by a constant factor per methylene group. Slopes of the lines shown here and in Figure 6 correspond to an attenuation factor, ϵ, of 0.65. (*Cf.* ref 14.)

obtained in this way for 1,4 chlorine and 1,4 methoxyl participation were 7.5 and 6.1, respectively.

That substituents up to 11 carbon atoms from the reaction site could exert effects discernible above the "noise level" of presumably random, unpredictable influences upon reaction rates was somewhat surprising, but the remarkable linearity of the plots of Figure 1 gave assurance that the effects observed were real and regular. At the time of our study it was a bit unsatisfying that 5-chloro-1-pentene, $CH_2{=}CH(CH_2)_3Cl$, did not react with concomitant halogen shift. That this result is a consequence of the direction of ring opening of the intermediate chloronium ion has now been confirmed by its independent generation (Scheme I). Alkynes, encouragingly, *did undergo halogen shifts*, as outlined below.

Additions to Alkynes. The observation[16] of 1,4 chlorine shift in the reaction of 5-chloro-1-pentyne with trifluoroacetic acid (Scheme V) predated the already mentioned[11] evidence of a chlorine shift in a deuterium-labeled alkene. Subsequent work substantiated the original inference made by Duddey, then a graduate student, that the major product of reaction was the vinyl halide **13**, and showed that both rates and products were reasonably accounted for according to Scheme V.[16b,17] Later in this review the amounts of halogen-shifted products for a number of alkynes are compared with those expected from analysis of the reaction rates. In the absence of sufficient data to make attenuation plots, the Hammett–Taft equation, log $k_H/k_X = \rho\sigma_I$, was used to estimate k_s despite the previously mentioned lack of a reliable basis for establishing σ_I values.

Scheme V
Competing Paths in the Reaction of Trifluoroacetic Acid with 5-Chloro-1-pentyne



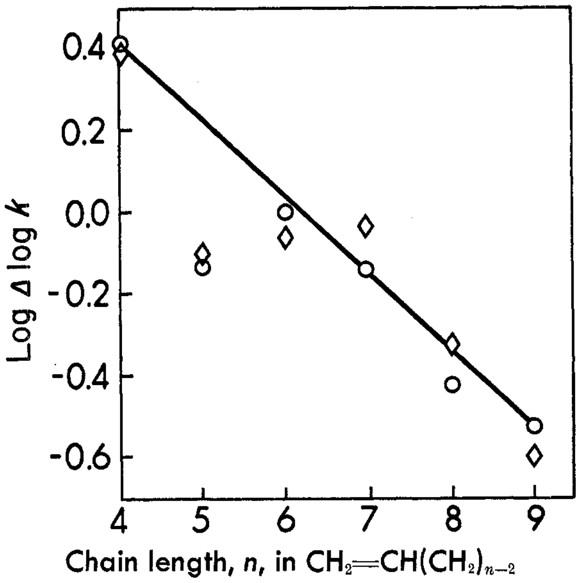


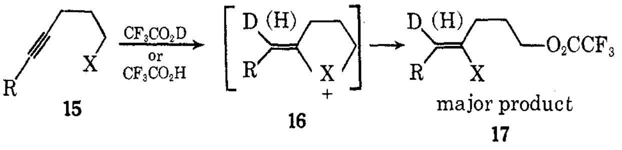
Figure 2. Plot of rate data for addition of trifluoroacetic acid to alkenes having methoxy (□) and chloro (○) substituents, based on the assumption that the substituent effect changes by a constant factor per methylene group.

Table II
Per Cent Cis Isomer in the Predominantly Trans Vinyl Halides from Halogen Shift Reactions of Alkynes 15, Scheme VI

Reactant	Cis product, %
5-Chloro-1-pentyne	8
5-Bromo-1-pentyne	8
5-Iodo-1-pentyne	5
6-Chloro-2-hexyne	9.6
6-Iodo-2-hexyne	16.6

The use of deuterated trifluoroacetic acid solvent or alkynes bearing a terminal alkyl group permitted the stereochemistry of the addition to the triple bond during the halogen shift reaction to be determined. Predominant anti addition of D (or H) and X was found (*cf.* Scheme VI and Table II). The reasons for the

Scheme VI
Stereochemical Course of Alkyne Reactions (R = H or CH_3)



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(16) (a) P. E. Peterson and J. Duddey, *J. Amer. Chem. Soc.*, **85**, 2865 (1963); (b) P. E. Peterson and J. Duddey, *ibid.*, **88**, 4990 (1966).

(17) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *ibid.*, **92**, 2834 (1970).

stereochemical results remain speculative since the stereochemistry of such additions is presently unpredictable.[9]

The reasonable success in predicting the per cent of halogen shift from reaction rates suggested that the halonium ions **16** and similar ones do *not* open at the vinyl carbon. A few years later we were able to provide solid support to previous somewhat vague notions of the unreactivity of vinyl compounds by synthesizing the first simple, secondary, aliphatic vinyl sulfonates and determining[18] the relative rates of reaction in 50% methanol, shown in Scheme VII. Almost simultaneously, a number of workers independently reported related work in the area of vinyl reactivity.[19]

Scheme VII

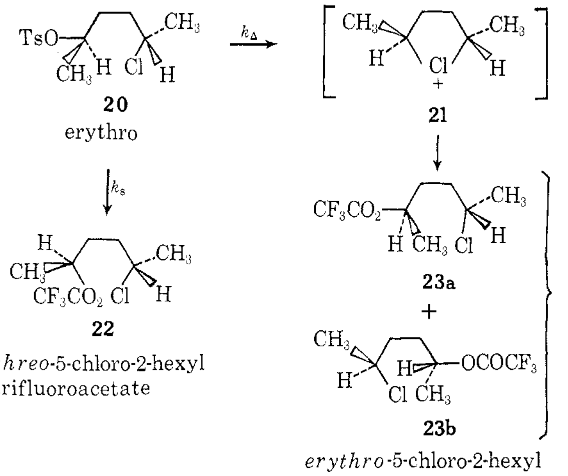
Reactivity of Vinyl and Saturated Secondary Tosylates
(OTs = p-$OSO_2C_6H_4CH_3$)

18 relative $k = 1$ **19** relative $k = 8.8 \times 10^{-7}$

Sulfonate Solvolyses. Sulfonate solvolyses have been employed much more extensively than the reactions of alkenes and alkynes in the demonstration of neighboring group participation, including the previously mentioned early studies of 1,2 halogen participation in the cyclohexane series (*cf.* Scheme II). Using tosylate (p-toluenesulfonate) substrates designed for 1,4 chlorine participation we were able to obtain[20] a third kind of evidence for such participation, supplementing the studies of rate effects and halogen shifts, described above. Specifically we determined the stereochemical course of solvolysis of *erythro*-5-chloro-2-hexyl tosylate (**20**, Scheme VIII) and of the threo isomer. The results for reaction in several solvents are given in Table III.

Scheme VIII

Possible Solvolysis Paths for *erythro*-5-Chloro-2-hexyl Tosylate



20 erythro

21

22 *threo*-5-chloro-2-hexyl trifluoroacetate

23a + **23b** *erythro*-5-chloro-2-hexyl trifluoroacetate

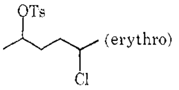
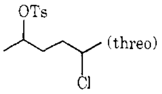
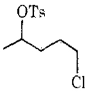
Table III

Per Cent Retention of Configuration in the Solvolysis of 5-Chloro-2-hexyl Tosylates in the Solvents Listed

Diastereomer	CF_3CO_2H	HCO_2H	CH_3CO_2H
Erythro	92	61	29
Threo	89	49	22

Table IV

Estimates of k_Δ/k_s for Tosylate Solvolyses, Based on Analysis of Rate Data

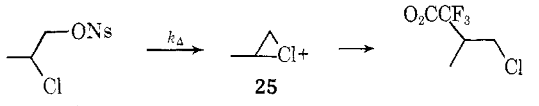
Tosylate	k_Δ/k_s for reaction in CF_3CO_2H	HCO_2H	CH_3CO_2H
 OTs Cl (erythro)	99	6.7	0.8
 OTs Cl (threo)	65	4.1	
 OTs Cl	33	3.6	0.7

Based on the assumption[7,8] that inversion (not racemization) would occur in the solvolysis without participation, as shown for the k_s path of Scheme VIII, and on the well-supported[8] presumption that 1,4 halogen participation should give net retention of configuration resulting from two inversions (Scheme VIII), the values in Table III represent direct measures of the per cent of reaction proceeding *via* the k_Δ path. That the assumptions may be imperfect is indicated by the considerably higher estimates for the extent of participation in the form of k_Δ/k_s values derived from analysis of reaction rates, using the attenuation plot approach mentioned earlier (Table IV).

The characteristic solvent effect (Tables III and IV) presumably reflects the slowing of the k_s reaction in the solvents of lower nucleophilicity relative to k_Δ, which is insensitive to solvent nucleophilicity. Presumably because of this effect trifluoroacetic acid as a solvent is dramatically effective in promoting halogen participation. The culmination of efforts to produce clear-cut instances of 1,4 halogen participation has come in recent studies of the trifluoroacetolysis of primary sulfonate-secondary halides. In this system 1,4 shifts were "quantitative," as mentioned in the introduction (Scheme I).[1] Notably, the 1,2 shift of Cl (Scheme IX) also was "quantitative," in contrast with the result for *trans*-2-chlorocyclohexyl brosylate solvolysis,[5] in which chlorine participation was not definitely discernible.

Scheme IX

Main Path for the Trifluoroacetolysis of 2-Chloro-1-propyl Nosylate (ONs = p-$OSO_2C_6H_4NO_2$)



24 **25** **26**, ~99%

Six-membered rings were formed less readily, but halogen-shifted products **28** and **29** predominated

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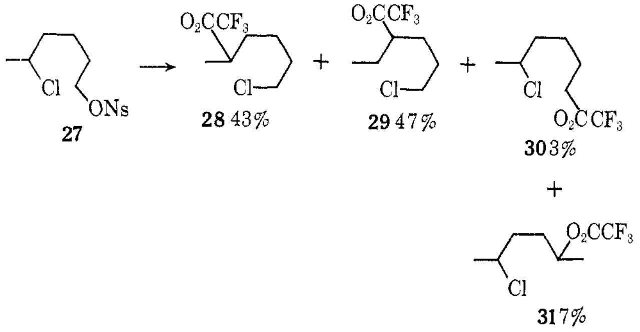
(18) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **91**, 6194 (1969).

(19) For a review see M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970).

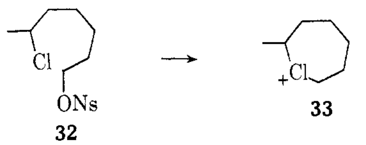
(20) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, **89**, 5902 (1967).

Scheme X

Products of Trifluoroacetolysis of 5-Chloro-1-hexyl Nosylate

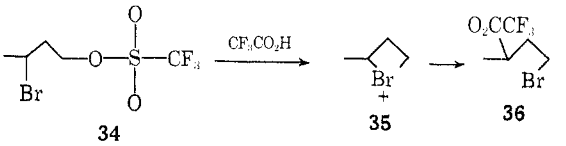


(Scheme X) in the reaction of the appropriate nosylate **27**. We note that **29** has also undergone a hydrogen shift. Even 6-chloro-1-heptyl nosylate (**32**) formed 17% of primary chlorides, presumably *via* the seven-membered-ring chloronium ion **33** (eq 1).[1] We found



(1)

that 3-chloro-1-butyl nosylate, which might form a four-membered halonium ion ring, was too unreactive for convenient study. The corresponding trifluoromethanesulfonate reacted at a convenient rate but gave no more than 6.6% chlorine shift. On the other hand, the corresponding bromide **34** reacted to give 46% of **36**, the product of 1,3 halogen shift (eq 2),[21a] presumably indicating that the four-membered-ring ion **35** was an intermediate in the reaction.[21b]



(2)

The extent to which various primary nosylate–secondary halides solvolyzed in trifluoroacetic acid *via* intermediate halonium ions is indicated in Table V where the results of the separation of rate constants into k_Δ and k_s (using the attenuation plot method described above for alkenes) are given and compared with the per cents of halogen shift. Other rate data for sulfonates are summarized in a subsequent section of this review.

Cyclopropanes, Epoxides, and Oxonium Salts. Other reactions which have now been shown to proceed at least to some extent *via* five-membered-ring halonium ion intermediates include the ring opening in trifluoroacetic acid of the cyclopropane **37**[22] and epoxides **38** and **39**[23] and the trifluoroacetolysis of *in situ* generated oxonium salt, **40** (Scheme XI).[24]

Table V

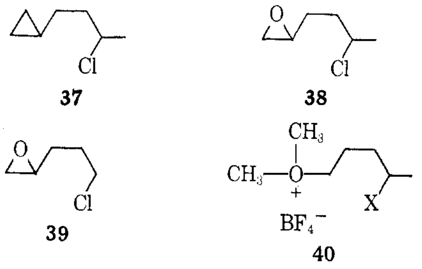
Measures of Halogen Participation in Primary Nosylate Trifluoroacetolyses

Nosylate	k_Δ/k_s	$100k_\Delta/(k_\Delta + k_s)$	Halogen shift, %
2-Chloro-1-propyl	2000	99.95	99 ± 1
3-Chloro-1-butyl[a]	≤7.1[b]		≤6.6
4-Chloro-1-pentyl	760	99.87	99.5
5-Chloro-1-hexyl	7.1	88	90
6-Chloro-1-heptyl	0.20		17
4-Chloro-1-butyl	170	99.6	~50[c]

[a] Data for 3-chloro-1-butyl trifluoromethanesulfonate. [b] Distribution between k_s and k_Δ calculation from product data rather than from attenuation plot. [c] Data for deuterium-labeled nosylate.

Scheme XI

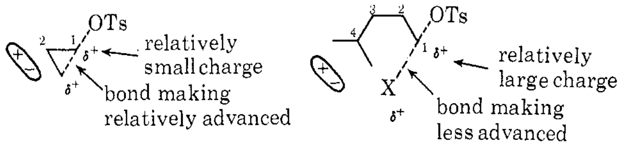
Reactants Which Give Halonium Ion Intermediates upon Trifluoroacetolysis



Variation of the Halogen. Since there is good evidence from inductive effects that nucleophilic solvents (including weakly nucleophilic trifluoroacetic acid) only partially "neutralize" the carbonium ion charge in nonparticipation (k_s) processes,[20] it is attractive to assume that nucleophilic participating groups, including halogen, likewise react *via* transition states having some charge on the potential cationic carbon, C-1, and some on the participating group (*cf.* Scheme XII). We hypothesize that this balance of charge distribution may change as the ring size varies, as shown in Scheme XII.

Scheme XII

Presumed Charge Distribution in Transition States Leading to Three- and Five-Membered-Ring Halonium Ions



The three-membered ring is pictured having the charge shifted toward halogen, since the dipole of the nonreacting C–X σ bond (shown inside the oval) would strongly destabilize a charge on C-1. Accordingly we postulate that three-membered-ring transition states exhibit the stability order I ≫ Br ≫ Cl presumed to be typical of highly charged halogen. We presume that the weaker C···X bond in the five-membered ring (which may be viewed as more of an electrostatic interaction between C-1 and the C–X dipole) has the stability order I ≧ Br ≧ Cl (I somewhat better than or equal to Br, etc.). Although "weak," the C···X bond is strong enough, in conjunction with entropy factors, to allow the k_Δ process to compete with nucleophilic solvation in the k_s

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[21] (a) P. E. Peterson and W. Boron, *J. Amer. Chem. Soc.*, **93**, 4076 (1971). (b) Another instance has been found by C. E. Reincke and J. R. McCarthy, *ibid.*, **92**, 6376 (1970).

[22] P. E. Peterson and G. W. Thompson, *J. Org. Chem.*, **33**, 968 (1968).

[23] P. E. Peterson, B. R. Bonazza, and J. M. Indelicato, *Tetrahedron Lett.*, 13 (1971).

[24] P. E. Peterson and F. J. Slama, *J. Amer. Chem. Soc.*, **90**, 6516 (1968).

Table VI
Halogen Dependence of k_{trans}/k_{cis} Ratios for Solvolysis of 2-Halocyclohexyl Brosylates

	k_{trans}/k_{cis}		
Halogen	CH_3CO_2H	HCO_2H	CF_3CO_2H
Cl	3.8[a]	6.8[b]	36[b]
Br	810[a]	4800[b]	10,000[b]
I	1,700,000[c,d]		

[a] Reference 5b. [b] Reference 25a. [c] Reference 5a. [a] Estimated as the k_Δ/k_c value of ref 5b.

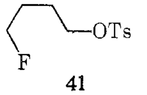
process.[6] Whether valid or not, the picture outlined correlates the striking differences noted for 1,2 participation as the halogen is changed, summarized below.

In Table VI the classic work originating in Winstein's group and extended by Grunwald[5a,b] (Scheme II) is collected with unpublished data obtained by Duddey[25a] to show that *the 1,2 participation order I ≫ Br ≫ Cl* (as reflected in the k_{trans}/k_{cis} ratio) is not an artifact of the solvent choice. 1,2 chlorine participation, not considered to be clearly established from k_{trans}/k_{cis} in acetic acid,[5b] becomes increasingly apparent in solvents of lower nucleophilicity. (Cis halogen is presumed not to participate; accordingly $k_{cis} \cong k_s$; $k_{trans} \cong k_\Delta + k_s$.)

For the newly found 1,3 participation we tentatively postulate the halogen reactivity order Br > Cl based on the 46 and 6.6% (or less) bromine and chlorine shift, mentioned above.[21a]

In the case of 1,4 participation it seems appropriate to cite some unpublished data from Glick's Ph.D. thesis[26] reporting work done in Winstein's group, along with other results, indicating a very modest extent of participation in acetic acid and showing a moderate variation among the halogens in participation tendency (Table VII). Similar comparisons of 1,4 participation in reactions of alkenes and alkynes are summarized in Table VIII.

Fluorine, surprisingly, appeared to be a weakly 1,4 participating substituent in a number of the studies of reactions of alkenes, alkynes, and tosylates which have been mentioned. However, the recently reported[17] failures of the nosylate **41** to solvolyze with rate enhancement and of the triflate **42** to react with fluorine shift raise the suspicion that previous indications of fluorine participation were mistakes! We hasten to add that further studies may yet resolve the apparently contradictory results in favor of some kind of participatory role for fluorine.



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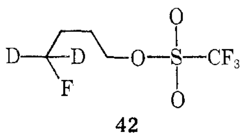


42

Stable Halonium Ions in SbF_5–SO_2. In the last six years Olah and coworkers have made an enormously important contribution to the general area of carbonium ion chemistry by showing that a large number of carbonium, halonium, and oxonium ions, many of which were known only as hypothetical intermediates in reactions, may be prepared in SbF_5–SO_2 solutions and observed by nuclear magnetic resonance.[2] Following the report of the observation in SbF_5–SO_2 of three-membered-ring halonium ions, the author spent a highly rewarding few weeks in Olah's laboratories investigating the preparation of the analogous five-membered rings. This collaborative effort resulted in the observation by nmr at low temperature of the nine ions **43**, **44**, and **45** (X = Cl, Br, I).[28] The reactions used are typified by eq 3 and 4. Other ions (**46**, **47**) have been reported from Olah's group.[29]

Table VII
Comparison of Halogens as Participating Groups in Acetolysis of 4-Halo-1-butyl Tosylates or Nosylate

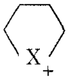
Substrate	10^5k, sec^{-1}, 99.6° $(k\Delta + k_s)^a$	$k_s(estd)^b$	$k\Delta/k_s$
4-Chloro tosylate	1.25	1.03	0.22
4-Bromo tosylate	1.73	1.03	0.70
4-Iodo tosylate	4.12	1.03	3.09
4-Chloro nosylate			0.37[c]
4-Bromo tosylate			0.79[d]

[a] Reference 26. [b] Incorporates (*cf.* ref 26) a small correction for inductive effects (for 1-butyl tosylate 10^5k was 1.53). [c] Based on per cent Cl shift; ref 1b. [d] Based on per cent shift, ref 27.

Table VIII
Comparison of Halogens as Participating Groups in Reactions of Alkenes and Alkynes with Trifluoroacetic Acid

	$k\Delta/k_s$ for X =		
Substrate	Cl	Br	I
$CH_2{=}CH(CH_2)_2CHXCH_3$	14	14	8.1
$CH_2{=}CH(CH_2)_3X$	7.5	7.0	
$CH{\equiv}C(CH_2)_3X$	3.4,[a] 10[b]	4.3,[a] 23[b]	6.1,[a] 27[b]
$CH_3C{\equiv}C(CH_2)_3X$	5.8, 6.1	14	

[a] Based on analysis of rates. [b] Based on per cent halogen shift (probably the better value).



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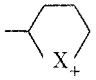

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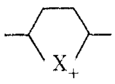
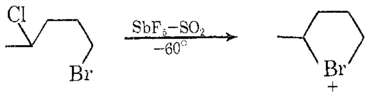
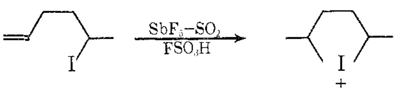


45, cis and trans mixture



cis and trans mixture

(3)



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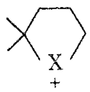

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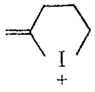

47

X = Cl, Br, I

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(25) (a) J. E. Duddey, Ph.D. Thesis, St. Louis University, 1967. (b) *Cf.* D. D. Roberts and W. Hendrickson, *J. Org. Chem.*, **34**, 2415 (1969).

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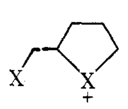
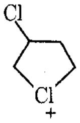
Recently we have prepared halonium ions which were halogen substituted in the side chain (**48**)[30] or in the ring (**49** and **50**).[31]



48, X = Cl, Br



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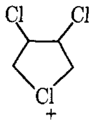
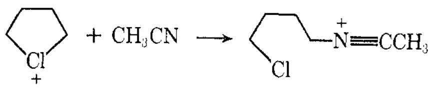


50

The nmr spectra of all ions mentioned are of interest because of the strong deshielding effect of positive halogen which leads to peaks at approximately δ 5 (methylene next to positive chlorine) and/or δ 6 (methine next to positive chlorine).

It should be mentioned that Olah and coworkers have now reported the preparation of many alkyl halonium ions, including $CH_3ClCH_3^+Sb_2F_{11}^-$ and $CH_3ICH_3^+$-SbF_6^-, as stable solids at room temperature![32] The cyclic halonium ions reviewed in this Account, accordingly, are merely the heterocyclic members of a potentially enormous class of reactive compounds. We may anticipate that rapid developments will occur in the structural elaboration of these ions and in the exploitation of their chemical properties, of which their high reactivity as alkylating agents (exemplified in the reaction of eq 5; *cf*. ref 31 and 32) has been found to be notable.



(5)

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Polycations of Group VI

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Cation formation has normally been associated with the metallic elements, but over the past few years evidence has accumulated which shows that it is a fairly common occurrence among nonmetals as well, at least insofar as polycations of the type A_m^{n+} are concerned. These polycations are important in terms of their stereochemistry and bonding and constitute a novel class of compounds of intrinsic interest. For the transition metals homonuclear groupings are well known in the "cluster" compounds which, however, have ligands attached to the metal cluster, *e.g.*, $[Mo_6Cl_8]^{4+}$. In the nonmetal cations A_m^{n+} lone pairs of electrons take the place of ligands.

It has long been known that the mercurous ion is not Hg^+, but Hg_2^{2+},[1,2] and recently it has been shown that other metallic elements form similar cations. Thus, evidence has been presented for the formation of Cd_2^{2+},[3] Zn_2^{2+},[4,5] Pb_2^{2+},[5] Mg_2^{2+},[6] Ca_2^{2+},[7] Sr_2^{2+},[8] and Ba_2^{2+} [8] on addition of the respective element to the corresponding MCl_2 melt. Various bismuth polycations have been identified, and in the process many confusing results have been rationalized. The material thought to be BiCl has been shown by an X-ray study to contain Bi_9^{5+} in addition to $BiCl_5^{2-}$ and $Bi_2Cl_8^{2-}$.[9] The Bi^+,[10] Bi_5^{3+},[10] and Bi_8^{2+} [11] ions have been identified in melts and the compounds $Bi_5(AlCl_4)_3$[12] and $Bi_8(AlCl_4)_2$[12] isolated. Recently evidence has been given for a cation containing antimony in the 1+ oxidation state.[13] Esr evidence has been presented for the formation of Ag_4^+ or Ag_4^{3+},[14] Ag_2^+,[15] and Cd_2^{3+}.[15]

There has long been evidence for positive oxidation states of iodine[16] and the I_3^+ and I_5^+ ions are now well established, although "I^+" has been shown to be I_2^+.[17]

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