Kinetics in Antimony Pentafluoride–Sulfur Dioxide Solution. Rate of Reaction of Tetramethylenechloronium Ions with Aliphatic Carboxylic Acids

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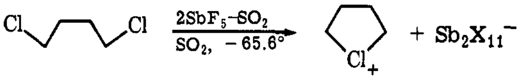
Abstract: The rates of the alkylation of various halogenated acetic acids and acetic acid by tetramethylenechloronium ion have been measured in SbF_5–SO_2 solution at $-65.6 \pm 0.1°$. A competing fast reaction of the nucleophile with SbF_5–SO_2 and/or $Sb_2X_{11}^-$ attenuates the reactivity of a portion of the CH_3CO_2H to a negligible value. A possible explanation of the observed rates, which exhibit half-order dependence upon the CH_3CO_2H concentration and first-order dependence upon the chloronium ion concentration, is that a prior equilibrium exists between dimer and monomer acetic acids in SO_2 and that the monomer present in low concentration is the species alkylated. The activation parameters $\Delta H^{\ddagger}$ (kcal/mol) and $\Delta S^{\ddagger}$ (eu) for the acids are CH_3CO_2H, 12.9, −2.1; HCO_2H, 14.0, 4.9; $ClCH_2CO_2H$, 13.8, −2.4. A ρ_I of −2.39 has been determined for the reaction. When 3-chlorotetramethylenechloronium ion was used in the alkylation of CH_3CO_2H and CF_3CO_2H, the electronegative substituent enhanced the leaving group ability of RCl^+.

Solvolysis reactions of sulfonates, halides, sulfonium salts, and other compounds having suitable leaving groups have been the subject of a vast number of studies over the past few decades including, particularly, kinetic studies of substrate structure–reactivity relationships and solvent effects. More recently Olah and coworkers (see subsequent references) have made available a large number of carbonium, halonium, and oxonium ions, frequently in the form of species stable in SbF_5–SO_2 solutions at low temperature. Many of the stable ions display the ability to alkylate oxygen containing functional groups (*e.g.*, the OH group in methanol). These alkylation reactions are themselves typical solvolysis reactions or reactions which exhibit some features which also characterize solvolysis reactions. However, essentially no kinetic studies of the reactions of Olah type ions have appeared. Indeed the "quenching" reactions of stable ions in solvents often appear to be "instantaneous" as a consequence of their high reactivity. Nevertheless, the prospect of opening up a large new group of compounds (Olah-type ions) to studies of solvolytic type reactions has prompted us to make a special effort to bring such reactions under kinetic control. Halonium ions were attractive substrates for our first endeavors in this direction, described in the present paper.

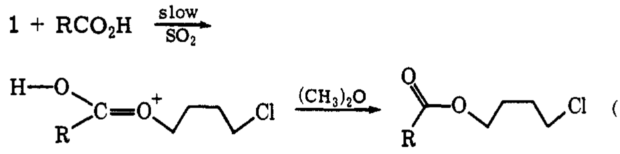
Various halonium ions,[2] including tetramethylenehalonium ions,[3] have recently been prepared as stable species in SbF_5–SO_2 or related solvents. In the present study, the tetramethylenechloronium ion **1** prepared according to the still incompletely specified[4] equation (1) was utilized as the reactive alkylating agent. It seemed possible that the group, RCl^+, contained within the five-membered ring, would be the most reactive leaving group yet found, making the measurement of its reactivity particularly challenging. Acetic acid and various halogenated acetic acids were chosen as the solvent-like nucleophiles (eq 2). It was envisioned that low temperatures would be employed to decrease the reaction rates, but that the most important decrease would come from using relatively dilute solutions of the reactants in the "inert diluent" SO_2, since the half-life increases with dilution for reactions of greater than first order. As we shall see, these strategems succeeded, although nucleophiles better than acetic acid were too reactive to measure at the concentration levels which we used. In addition to the reactions mentioned above, the alkylation of CH_3CO_2H and CF_3CO_2H by the 3-chlorotetramethylenechloronium ion **3** was studied in order to probe the effect of a β chlorine substituent on the reaction. In addition to the kinetic studies described below, various preparative reactions described in the Experimental Section served further to characterize the reaction of eq 2.



(1)

1

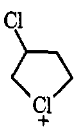
X = Cl or F



(2)

2

R = H, CH_3, $ClCH_2$, Cl_2CH, CF_3



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Kinetic Method

Antimony pentafluoride and 1,4-dichlorobutane were allowed to react in SO_2 (10 ml) for 1 day at −65° in

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[1] Postdoctoral research investigator.

[2] (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 947, 2587 (1968); (b) G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969); **92**, 718, 2562 (1970).

[3] (a) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968); (b) G. A. Olah and P. J. Szilagyi, *J. Org. Chem.*, **36**, 1121 (1971).

[4] P. E. Peterson, P. R. Clifford, and F. J. Slama, *J. Amer. Chem. Soc.*, **92**, 2840 (1970).

Table I. Per Cent Reaction of Tetramethylenechloronium Ion in Presence and Absence of Free Acetic Acid

$[SbF_5]$, M	[1,4-Dichlorobutane], M	Total $[CH_3CO_2H]$, M	Free $[CH_3CO_2H]$, M^a	Time, min	% completion
0.01344	0.00587	0.03312	0.02555	3.75	76.5
0.01406	0.00524	0.00779	0.0000	2700.0	44.2

[a] See text.

order to ensure complete formation of ion **1** in dilute solutions (10^{-2}–10^{-3} M). However, in the preparation of the more slowly formed ion **3**, the SbF_5 was dissolved in a minimum amount of SO_2, 1,2,4-trichlorobutane was added, and the reaction was allowed to proceed for 2 days (−65°). The solution was then diluted with SO_2 to the mark. All weighing and diluting operations were performed under 1 atm of dry nitrogen. The reaction of ion **1** or **3** with solutions of nucleophile (10 ml in SO_2) was carried out in a specially constructed glass mixing apparatus (Figure 1) which consisted of two chambers of *ca.* 15 ml capacity connected by an inverted U-shaped bridging tube. The SO_2 solutions were introduced into the apparatus by separate vertical tubes attached to each chamber. Samples were quenched in a weakly basic solvent, $(CH_3)_2O$, by forcing aliquots of the reacting solution into a receiving well. The entire glass assembly was thermostated utilizing a refrigerated bath.[5] The quenched samples were evaporated nearly to dryness, diluted with CS_2, and analyzed with a Hewlett-Packard Model 5750 flame ionization gas chromatograph using standard solutions of each component for calibration. The molar amounts of ester **2** (eq 2) and 4-chlorobutyl methyl ether (**4**), formed from the unreacted chloronium ion **1** in a multistep process represented by eq 3, were fitted to an assumed rate law

$$1 + (CH_3)_2O \longrightarrow$$

4

(3)

by a least-squares program coupled with a Calcomp plotter.

Results and Discussion

The first objective was the establishment of the rate law for the alkylation reaction. For this purpose, CH_3CO_2H was chosen as the nucleophile. Since 2 mol of SbF_5 was required to form the reactant chloronium ion (eq 1), and since the not fully characterized product $Sb_2X_{11}^-$ may be regarded as a loosely bonded adduct of SbX_5 and SbX_6^-, it seemed likely that a stoichiometric amount of the nucleophile, acetic acid, would be deactivated by rapid complexing with SbF_5 (or SbX_5) including that contained in the $Sb_2X_{11}^-$ ion (eq 4). According to this picture 1 mol of SbF_5 is consumed in forming chloronium ion and the additional SbF_5 deactivates an equimolar quantity of acetic acid, leaving any additional acetic acid as "free acetic acid" which is available to react with nucleophile. Specifically, at the beginning of the alkylation reaction, [free acetic acid] = [total acetic acid] − ($[SbF_5]$ − [dichlorobutane]), where terms in brackets are concentrations. The data in Table I, showing a drastic decrease in acetic acid reactivity when concentrations are adjusted to give no free acetic acid, are in agreement with this concept. The consistent interpretation of kinetic results reported below based on use of the free acetic acid concentration, as defined here, provides further evidence for our interpretation. Nmr spectra, mentioned in the next paragraph, also indicate that SbF_5 does form complexes with the carboxylic acids used in our rate studies.

$$Sb_2X_{11}^- + CH_3CO_2H \longrightarrow SbX_5 \cdot CH_3CO_2H + SbX_6^- \qquad (4)$$

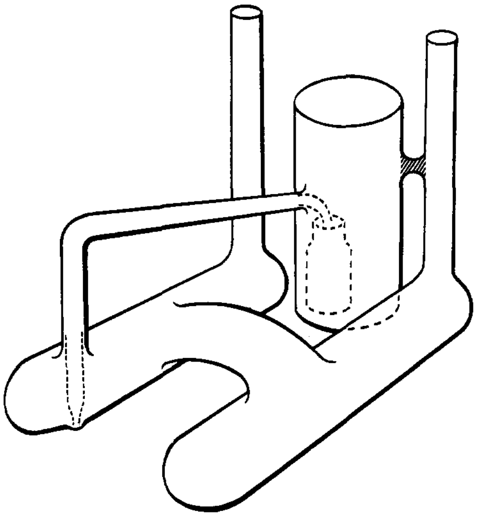
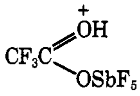


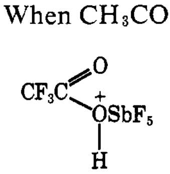
Figure 1. Diagram of glass mixing apparatus.

The complexation of *trifluoroacetic* acid by SbF_5–SO_2 was especially amenable to hydrogen nmr investigation, since any peaks observed must be derived from the OH hydrogen. Somewhat to our surprise SbF_5: CF_3CO_2H in the molar ratio 0.14:0.13 gave a singlet (in SO_2, −65°) at the unusual position, δ 2.80, presumably characteristic of the Lewis acid–base adduct having one of the formulas, **5** or **6**. When CH_3CO_2H was used



5

or



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and the molar ratio of SbF_5:CH_3CO_2H was 0.19:0.12, several peaks appeared in the region δ 2.2–2.6, with the two principal singlets at 2.48 and 2.29. These principal singlets are possibly ascribable to hydroxyl and methyl of the predominant isomer of the complexed CH_3CO_2H while the minor peaks arise from a mixture of syn and anti isomers analogous to those observed for protonated acids.[6]

Returning to consideration of the rate law, we note that an expression (eq 6) first order in **1** and in the nu-

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[5] The low-temperature circulating bath, Model LT-9, is manufactured by Neslab Instruments, Inc., Portsmouth, N. H. Long-term temperature variation was less than 0.1° at −65°, as measured with slush-bath calibrated thermocouples.

[6] M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967); G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

Table II. Experimental Conditions and Observed Rate Constants for the Reaction of Ion **1** with Acetic Acid

$[SbF_5]$, M	[1,4-Dichlorobutane], M	Free $[CH_3CO_2H]$, M[a]	Temp, °C	k_2, M^{-1} sec^{-1}	$k_{1/2} \times 10^2$, $M^{-1/2}$ sec^{-1}[b]
0.07190	0.03410	0.09640	−65.8	0.11[c]	3.15[c] (3.26)[d]
0.03758	0.01752	0.04879	−65.8	0.16[c]	3.18[c] (3.30)[d]
0.02846	0.01236	0.03284	−65.6	0.27[c]	4.41[c] (4.43)[d]
0.01410	0.00622	0.01294	−65.1	0.45[c]	4.48[c] (4.15)[d]
0.01344	0.00587	0.02555	−65.1	0.29[c]	4.31[c] (3.97)[d]
0.00760	0.00315	0.00358	−65.8	1.2[c]	5.24[c] (5.42)[d]

[a] See text. [b] The reactions were followed until 69–81% completion. [c] At temperatures tabulated. [d] At −65.6°, utilizing data from Table IV for calculation according to the absolute rate theory equation.

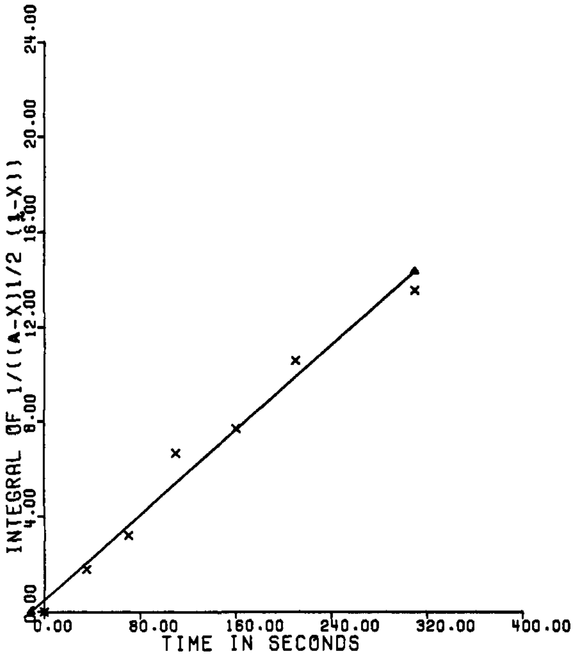

Figure 2. Rate plot for alkylation of acetic acid by ion **1**: SbF_5 (0.01410 M), HOAc (0.01294 M), 1,4-dichlorobutane (0.00622 M), $T = -65.1°$, $K = 0.04480634\ M^{-1/2}\,\mathrm{sec}^{-1}$.

$$\frac{-\mathrm{d}N}{\mathrm{d}t} = k_2[1][N] \qquad (5)$$

cleophile N (free acetic acid) might be anticipated (eq 5). However, the data were better accommodated

$$\frac{-\mathrm{d}N}{\mathrm{d}t} = k_{1/2}[1][N]^{1/2} \qquad (6)$$

by eq 6 where the dependence is first order in **1** and half order in nucleophile.[7] In Table II, the fit of the data to the integrated forms of eq 5 (column 5 of Table II) and eq 6 (last column) is illustrated. The integrated form[8] of eq 6 is shown below (eq 7), where [N] and [**1**] are the

$$\frac{1}{([N]-[1])^{1/2}} \times \ln\left[\frac{(([N]-x)^{1/2}+([N]-[1])^{1/2}) \times (([N]-[1])^{1/2}-[N]^{1/2})}{(([N]-[1])^{1/2}-([N]-x)^{1/2}) \times ([N]^{1/2}+([N]-[1])^{1/2})}\right] = kt \qquad (7)$$

initial concentrations of nucleophile and ion and x is the number of moles per liter reacted, respectively. It is noteworthy that $k_{1/2}$ (Table II) varies by less than a factor of two when the product of initial concentrations varies by approximately a factor of 300. A typical rate plot is shown in Figure 2. The half order in CH_3CO_2H would result from a prior equilibrium between dimer and monomer (eq 8) provided the dimer dissociation

$$(CH_3CO_2H)_2 \underset{SO_2}{\overset{K_d}{\rightleftarrows}} 2CH_3CO_2H \qquad (8)$$

constant (K_d) in SO_2 is sufficiently small ($\leq 10^{-4}$ M) and provided the monomer is the species alkylated. The approximate limit $K_d \leq 10^{-4}$ M is reasonable, based on the K_d values from the literature listed in Table III.

Table III. Summary of Dissociation Constants (K_d) of Acetic Acid and Halogenated Acetic Acids in Various Solvents

Acid	Solvent	Temp, °C	$K_d \times 10^4$, M
CH_3CO_2H[a]	Cyclohexane	25	0.47
CH_3CO_2H[b]	Benzene	30	2.4
HCO_2H[b]	Heptane	30	0.08
HCO_2H[b]	Benzene	30	7.1
$ClCH_2CO_2H$[c]	Benzene	30	8.8
Cl_2CHCO_2H[a]	Cyclohexane	25	6.6
CF_3CO_2H[a]	Cyclohexane	25	31

[a] F. Thyrior and D. Decroocq, *C. R. Acad. Sci.*, **260** (10) (Group 7), 2797 (1965). [b] H. A. Pohl, M. E. Hobbs, and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941). [c] A. A. Maryott, M. E. Hobbs, and P. M. Gross, *J. Amer. Chem. Soc.*, **71**, 1671 (1949).

Rate constants based on the integrated eq 7 also were determined for the alkylation of $ClCH_2CO_2H$, Cl_2CHCO_2H, CF_3CO_2H, and HCO_2H although the rate law was not investigated in these instances. The rate constants and the activation parameters for the alkylation of CH_3CO_2H, $ClCH_2CO_2H$, and HCO_2H are given in Table IV. With CF_3CO_2H as the nucleophile, the decrease in alkylation rate is so great that relatively concentrated solutions do not react immediately, as shown in appropriate nmr experiments. In Figure 3 the 100-MHz nmr spectrum of a partly reacted solution 0.1 M in chloronium ion **1** and 0.39 M in free CF_3CO_2H is shown. After 8.6 hr the reaction had gone only to 28% completion. The complete disappearance of ion **1** was verified at a later time.

In Figure 4 the logarithms of the rate constants for the alkylation reaction are plotted as a function of the pK_a value of the acids[9a] CH_3CO_2H, $ClCH_2CO_2H$, Cl_2-

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[7] The concentration of **1** was varied from 10^{-2} to 10^{-3} M. We tentatively assume that ion pair association does not complicate the kinetic picture. For a discussion of ion pairing in SO_2 see N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963).

[8] "Handbook of Chemistry and Physics," 43rd ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962, p 258.

[9] (a) G. Kortum, W. Vazel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths, London, 1961; (b) A. K. Covington, J. G. Freeman, and T. H. Tilley, *J. Phys. Chem.*, **74**, 3773 (1970).

Table IV. Experimental Conditions for the Determination of the Rate Constants of Ion **1** with Acetic and Halogenated Acetic Acids

Nucleophile	$[SbF_5]$, M	[1,4-Dichlorobutane], M	[Free acid], M	Temp, °C	$K_{3/2}$, $M^{-1/2}$ sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
CH_3CO_2H	0.01400	0.00622	0.01294	−65.1	4.5×10^{-2}	12.9	−2.1
	0.00982	0.00331	0.00890	−70.1	2.0×10^{-2}		
$ClCH_2CO_2H$	0.00832	0.00350	0.02592	−55.1	2.2×10^{-2}	13.8	−2.4
	0.00791	0.00323	0.01979	−65.1	4.6×10^{-3}		
Cl_2CHCO_2H	0.01238	0.00571	0.02516	−65.5	2.3×10^{-4}		
CF_3CO_2H	0.01542	0.00240	0.04264	−65.7	8.7×10^{-6}		
HCO_2H	0.00894	0.00288	0.00416	−65.7	5.6×10^{-2}	14.0	4.9
	0.01344	0.00610	0.02438	−71.1	2.2×10^{-2}		

[a] The reaction was followed until 82–88, 39, 36, and 62–80% completion, respectively, for $ClCH_2CO_2H$, Cl_2CHCO_2H, CF_3CO_2H, and HCO_2H.

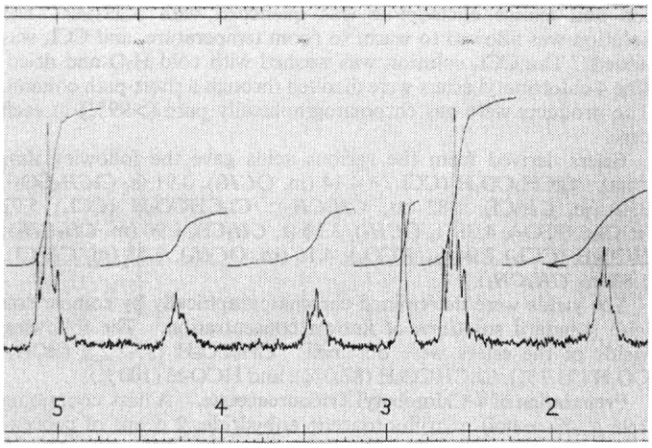
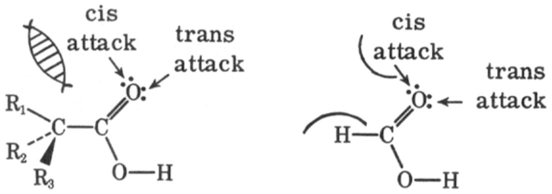


Figure 3. Nmr spectrum (100-Hz offset) of the reaction of the tetramethylenechloronium ion (SO_2, −60°) with CF_3CO_2H: molar concentration, SbF_5:1,4-dichlorobutane:free CF_3CO_2H, 22:0.11:0.39. Peaks of unreacted halonium ion appear at δ 5.06 and 2.57. The singlet at δ 2.87 is assigned the shielded hydroxyl proton of CF_3CO_2H–SbF_5.

$CHCO_2H$, HCO_2H, and CF_3CO_2H.[9b] It is seen that an approximate linear free-energy relationship exists, although a plot involving the unavailable pK_a values for the protonated acids would be more appropriate. The point for HCO_2H lies appreciably off of the line drawn through the points for the remaining four acids. However, it seems likely that formic acid is unique in offering two alkylation sites, whereas steric hindrance prevents cis attack (Chart I) in the other acids.

Chart I. Alkylation of Acetic Acids and Formic Acid



Division of the formic acid rate constant by two, as suggested by this argument, causes the formic acid rate to correlate fairly well (open triangle, Figure 4).

The electronic effect of the substituents on the alkylation rate of acetic acid and substituted acetic acids is reflected by the linearity of the plot (Figure 5) of the logarithm relative rates (Table V) against the sum of the substituent constants,[10] σ_I. The ρ_I value (Figure 5) is −2.39.

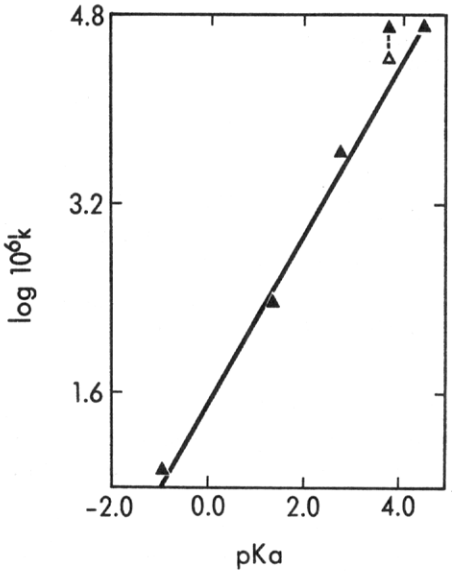


Figure 4. Dependence of log 10^6k for alkylation on the pK_a of the nucleophiles CF_3CO_2H, Cl_2CHCO_2H, $ClCH_2CO_2H$, HCO_2H, and CH_3CO_2H (lower left to upper right, respectively). The open triangle shows the corrected k (see text) for alkylation of HCO_2H.

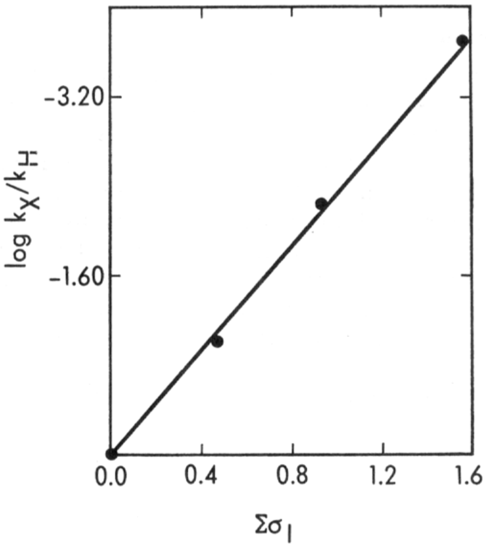


Figure 5. Log k_X/k_H for alkylation of CH_3CO_2H, ClH_2CO_2H, Cl_2CHCO_2H, and CF_3CO_2H (lower left to upper right, respectively) plotted against $\Sigma\sigma_I$.

In order to study the effect of a β-halogen substituent in the chloronium ring upon the alkylation rate, the 3-

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(10) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

Table V. Summary of Rate Constants for the Reaction of Tetramethylenechloronium Ion **1** with Nucleophiles at −65.6 ± 0.1°

Nucleophiles	$k_{3/2}$, $M^{-1/2}$ sec^{-1}	k_{rel}[a]
HCO_2H	5.6×10^{-2}	1.37
CH_3CO_2H	4.1×10^{-2}	1.00
$ClCH_2CO_2H$	4.2×10^{-3}	1.02×10^{-1}
Cl_2CHCO_2H	2.3×10^{-4}	5.6×10^{-3}
CF_3CO_2H	8.7×10^{-6}	2.1×10^{-4}

[a] The rate constants are relative to that of CH_3CO_2H.

chlorotetramethylchloronium ion **3**[11] was studied. In Table VI, rate constants are given for the reaction of **3** with CH_3CO_2H and CF_3CO_2H. The effect of the β-chlorine substituent is to increase the rate constants by factors of ~3.3 and 4.6, respectively. Other work[11] demonstrates that the chlorine substituent in ion **3** causes reaction to occur almost exclusively at C-4, the more remote site from the substituent, presumably owing to steric and inductive factors. Accordingly, the actual rate enhancements at C-4 are approximately given by the factors 6.6 and 9.2, obtained by multiplying the above mentioned ratios by two to correct for the two sites of reaction of tetramethylenechloronium ion.

Table VI. Summary of Rate Constants from the Reaction of 2-Chlorotetramethylenechloronium Ion **3** with Nucleophiles at −65.8 ± 0.1°

Nucleophile	[SbF_5], *M*	[1,2,4-Trichlorobutane], *M*	[Free acid], *M*	$k_{3/2}$, $M^{-1/2}$ sec^{-1} [a]
CH_3CO_2H	0.01165	0.00462	0.01043	13.5×10^{-2}
CF_3CO_2H	0.01389	0.00487	0.02023	40.2×10^{-6}

[a] The reactions were followed until 93 and 48% completion, respectively, for CH_3CO_2H and CF_3CO_2H.

Conclusion

The goal of bringing the fast reactions of chloronium ions under kinetic control appears to have been satisfactorily attained. The kinetic effects of substantial variation in the nucleophile structure and one variation in the ion structure have been assessed. These results are in accord with expectations, suggesting that further work will not result in substantial modification of the picture presented here. Accordingly, it is attractive to consider using our rate constants as a basis for a nucleophilicity scale for carboxylic acids. We hope to expand this suggestion in a future paper.[12] On the other hand, the observation of approximate half-order dependence of rate upon nucleophile concentration and the concomitant proposal that monomer carboxylic acid is much more reactive than dimer must be regarded as tentative, in view of the many unfamiliar features of the system at hand. However, if the observation and the rationalization of the result should stand the test of time, the investigation of the nucleophilicity of monomeric nucleophiles could become an attractive research area having implications for all solvolytic reactions.

Experimental Section

Preparative Reactions of Tetramethylenechloronium Ion. The solution resulting from the reaction of the tetramethylenechloronium ion and excess nucleophile was quenched with $(CH_3)_2O$. The solution was allowed to warm to room temperature, and CCl_4 was added. The CCl_4 solution was washed with cold H_2O and dried. The 4-chlorobutyl esters were distilled through a short-path column. The products were gas chromatographically pure (>99%) in each case.

Esters derived from the various acids gave the following nmr data: $ClCH_2CO_2H$ (CCl_4) δ 4.14 (m, OCH_2), 3.91 (s, $ClCH_2CO_2$), 3.49 (m, CH_2Cl), 1.82 (m, CH_2CH_2); Cl_2CHCO_2H (CCl_4) 5.92 (s, Cl_2CHCO_2), 4.31 (t, OCH_2), 3.56 (t, CH_2Cl), 1.90 (m, CH_2CH_2); HCO_2H (CCl_4) 7.94 (s, HCO_2), 4.16 (m, OCH_2), 3.53 (m, CH_2Cl), 1.83 (m, CH_2CH_2).

The yields were determined chromatographically by comparison with standard solutions of known concentration. The following yields of the esters were obtained: CH_3CO_2H (85.2%), $ClCH_2CO_2H$ (73.7%), Cl_2CHCO_2H (87.0%), and HCO_2H (100%).

Preparation of 4-Chlorobutyl Trifluoroacetate. A flask containing 4.96 g (23 mmol) of trifluoroacetic anhydride, 2 drops of concentrated H_2SO_4, and 5.0 ml of CCl_4 was cooled with an ice bath. A solution, 1.0 g (9.4 mmol) of 4-chlorobutanol in 10 ml of CCl_4, was added dropwise and the resulting mixture stirred for 0.5 hr at room temperature. Work-up consisted of separating the organic layer immediately after adding ice water, drying over molecular sieves, and removing solvent. Short-path distillation afforded pure 4-chlorobutyl trifluoroacetate (>99% by vpc): nmr (CCl_4) δ 4.33 (t, OCH_2), 3.51 (t, $ClCH_2$), 1.89 (m, CH_2CH_2).

Nmr Spectra of Monoalkylated Acids. Nmr spectra of the monoalkylated products from the reaction of a 0.1 *M* solution of tetramethylenehalonium ion and 0.12–0.39 *M* free nucleophile in SO_2 at −60° were obtained using a Varian HA-100D spectrometer. All chemical shifts in SO_2 are reported relative to external (capillary) TMS. The following characteristic absorptions were obtained for the monoalkylated products using the acids $ClCH_2CO_2H$: nmr (SO_2) δ 4.72 (t, $CH_2O{=}^{+}$), 3.39 (t, CH_2Cl), 1.79 (br peak, CH_2CH_2); Cl_2CHCO_2H (SO_2) 4.70 (t, $CH_2O{=}^{+}$), 3.39 (t, CH_2Cl), 1.79 (br peak, CH_2CH_2); CF_3CO_2H (SO_2) 4.26 (br peak, $CH_2O{=}^{+}$), 3.40 (t, CH_2Cl), 1.67 (m, CH_2CH_2).

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(11) P. E. Peterson and B. R. Bonazza, *J. Amer. Chem. Soc.*, **94**, 5017 (1972).

(12) Note Added in Proof. For a preliminary communication, see P. E. Peterson and F. J. Waller, *ibid.*, **94**, 91 (1972).