

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

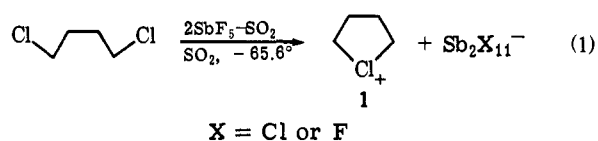
Paul E. Peterson\* and Francis J. Waller<sup>1</sup>

Contribution from the Department of Chemistry, St. Louis University, St. Louis, Missouri 63156. Received December 11, 1971

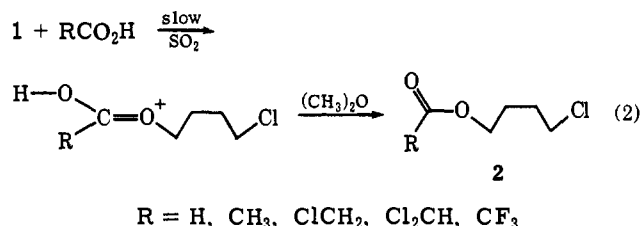
**Abstract:** The rates of the alkylation of various halogenated acetic acids and acetic acid by tetramethylenechloronium ion have been measured in  $\text{SbF}_5\text{-SO}_2$  solution at  $-65.6 \pm 0.1^\circ$ . A competing fast reaction of the nucleophile with  $\text{SbF}_5\text{-SO}_2$  and/or  $\text{Sb}_2\text{X}_{11}^-$  attenuates the reactivity of a portion of the  $\text{CH}_3\text{CO}_2\text{H}$  to a negligible value. A possible explanation of the observed rates, which exhibit half-order dependence upon the  $\text{CH}_3\text{CO}_2\text{H}$  concentration and first-order dependence upon the chloronium ion concentration, is that a prior equilibrium exists between dimer and monomer acetic acids in  $\text{SO}_2$  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  $\text{CH}_3\text{CO}_2\text{H}$ , 12.9,  $-2.1$ ;  $\text{HCO}_2\text{H}$ , 14.0, 4.9;  $\text{ClCH}_2\text{CO}_2\text{H}$ , 13.8,  $-2.4$ . A  $\rho_1$  of  $-2.39$  has been determined for the reaction. When 3-chlorotetramethylenechloronium ion was used in the alkylation of  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CF}_3\text{CO}_2\text{H}$ , the electronegative substituent enhanced the leaving group ability of  $\text{RCl}^+$ .

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  $\text{SbF}_5\text{-SO}_2$  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.

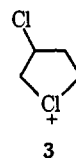
Various halonium ions,<sup>2</sup> including tetramethylenehalonium ions,<sup>3</sup> have recently been prepared as stable species in  $\text{SbF}_5\text{-SO}_2$  or related solvents. In the present study, the tetramethylenechloronium ion **1** prepared according to the still incompletely specified<sup>4</sup> equation (1) was utilized as the reactive alkylating agent. It seemed possible that the group,  $\text{RCl}^+$ , 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”  $\text{SO}_2$ , 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  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CF}_3\text{CO}_2\text{H}$  by the 3-chlorotetramethylenechloronium ion **3** was studied in



order to probe the effect of a  $\beta$  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.

## Kinetic Method

Antimony pentafluoride and 1,4-dichlorobutane were allowed to react in  $\text{SO}_2$  (10 ml) for 1 day at  $-65^\circ$  in

\* Address correspondence to this author at: Department of Chemistry, University of South Carolina, Columbia, S. C. 29208.

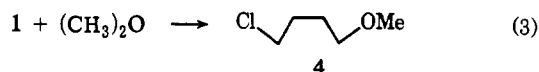
(1) Postdoctoral research investigator.  
(2) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 947, 2587 (1968); (b) G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969); **92**, 718, 2562 (1970).  
(3) (a) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 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 Tetramethylechloronium Ion in Presence and Absence of Free Acetic Acid

[SbF <sub>5</sub> ], <i>M</i>	[1,4-Dichlorobutane], <i>M</i>	Total [CH <sub>3</sub> CO <sub>2</sub> H], <i>M</i>	Free [CH <sub>3</sub> CO <sub>2</sub> H], <i>M</i> <sup>a</sup>	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

<sup>a</sup> See text.

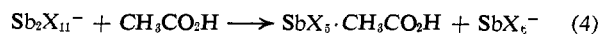
order to ensure complete formation of ion 1 in dilute solutions ( $10^{-2}$ – $10^{-3}$  *M*). However, in the preparation of the more slowly formed ion 3, the SbF<sub>5</sub> was dissolved in a minimum amount of SO<sub>2</sub>, 1,2,4-trichlorobutane was added, and the reaction was allowed to proceed for 2 days ( $-65^{\circ}$ ). The solution was then diluted with SO<sub>2</sub> 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<sub>2</sub>) 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<sub>2</sub> solutions were introduced into the apparatus by separate vertical tubes attached to each chamber. Samples were quenched in a weakly basic solvent, (CH<sub>3</sub>)<sub>2</sub>O, by forcing aliquots of the reacting solution into a receiving well. The entire glass assembly was thermostated utilizing a refrigerated bath.<sup>5</sup> The quenched samples were evaporated nearly to dryness, diluted with CS<sub>2</sub>, 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



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<sub>3</sub>CO<sub>2</sub>H was chosen as the nucleophile. Since 2 mol of SbF<sub>5</sub> was required to form the reactant chloronium ion (eq 1), and since the not fully characterized product Sb<sub>2</sub>X<sub>11</sub><sup>-</sup> may be regarded as a loosely bonded adduct of SbX<sub>5</sub> and SbX<sub>6</sub><sup>-</sup>, it seemed likely that a stoichiometric amount of the nucleophile, acetic acid, would be deactivated by rapid complexing with SbF<sub>5</sub> (or SbX<sub>5</sub>) including that contained in the Sb<sub>2</sub>X<sub>11</sub><sup>-</sup> ion (eq 4). Ac-



ording to this picture 1 mol of SbF<sub>5</sub> is consumed in forming chloronium ion and the additional SbF<sub>5</sub> 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<sub>5</sub>] - [dichlorobutane]), where terms in brackets are concentrations. The data in

(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  $-65^{\circ}$ , as measured with slush-bath calibrated thermocouples.

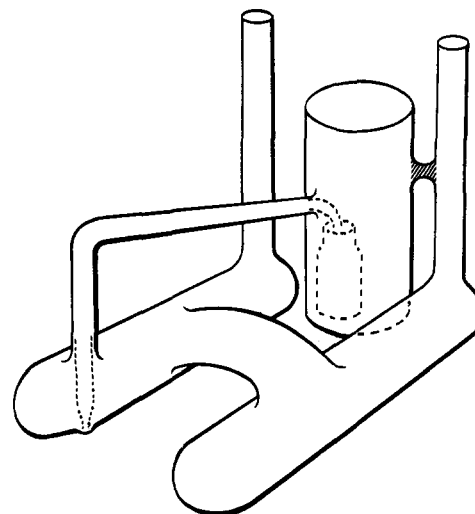
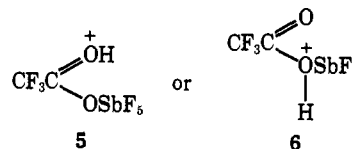


Figure 1. Diagram of glass mixing apparatus.

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<sub>5</sub> does form complexes with the carboxylic acids used in our rate studies.

The complexation of trifluoroacetic acid by SbF<sub>5</sub>-SO<sub>2</sub> was especially amenable to hydrogen nmr investigation, since any peaks observed must be derived from the OH hydrogen. Somewhat to our surprise SbF<sub>5</sub>:CF<sub>3</sub>CO<sub>2</sub>H in the molar ratio 0.14:0.13 gave a singlet (in SO<sub>2</sub>,  $-65^{\circ}$ ) at the unusual position,  $\delta$  2.80, presumably characteristic of the Lewis acid-base adduct having one of the formulas, 5 or 6. When CH<sub>3</sub>CO<sub>2</sub>H was used



and the molar ratio of SbF<sub>5</sub>:CH<sub>3</sub>CO<sub>2</sub>H was 0.19:0.12, several peaks appeared in the region  $\delta$  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<sub>3</sub>CO<sub>2</sub>H while the minor peaks arise from a mixture of syn and anti isomers analogous to those observed for protonated acids.<sup>6</sup>

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

(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 <sub>5</sub> ], M	[1,4-Dichlorobutane], M	Free [CH <sub>3</sub> CO <sub>2</sub> H], M <sup>a</sup>	Temp, °C	k <sub>2</sub> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>1/2</sub> × 10 <sup>2</sup> , M <sup>-1/2</sup> sec <sup>-1</sup> <sup>b</sup>
0.07190	0.03410	0.09640	-65.8	0.11 <sup>c</sup>	3.15 <sup>c</sup> (3.26) <sup>d</sup>
0.03758	0.01752	0.04879	-65.8	0.16 <sup>c</sup>	3.18 <sup>c</sup> (3.30) <sup>d</sup>
0.02846	0.01236	0.03284	-65.6	0.27 <sup>c</sup>	4.41 <sup>c</sup> (4.43) <sup>d</sup>
0.01410	0.00622	0.01294	-65.1	0.45 <sup>c</sup>	4.48 <sup>c</sup> (4.15) <sup>d</sup>
0.01344	0.00587	0.02555	-65.1	0.29 <sup>c</sup>	4.31 <sup>c</sup> (3.97) <sup>d</sup>
0.00760	0.00315	0.00358	-65.8	1.2 <sup>c</sup>	5.24 <sup>c</sup> (5.42) <sup>d</sup>

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

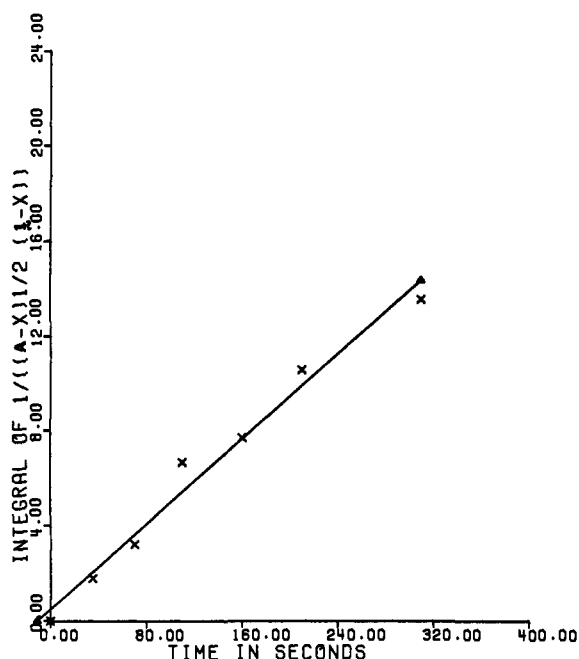


Figure 2. Rate plot for alkylation of acetic acid by ion 1: SbF<sub>5</sub> (0.01410 M), HOAc (0.01294 M), 1,4-dichlorobutane (0.00622 M), T = -65.1°, K = 0.04480634 M<sup>-1/2</sup> sec<sup>-1</sup>.

$$\frac{-dN}{dt} = k_2[1][N] \quad (5)$$

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

$$\frac{-dN}{dt} = k_{1/2}[1][N]^{1/2} \quad (6)$$

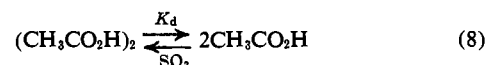
by eq 6 where the dependence is first order in 1 and half order in nucleophile.<sup>7</sup> In Table II, the fit of the data to the integrated forms of eq 5 (column 5 of Table II) and eq 6 (last column) is illustrated. The integrated form<sup>8</sup> of eq 6 is shown below (eq 7), where [N] and [1] are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

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

(7) The concentration of 1 was varied from 10<sup>-3</sup> to 10<sup>-5</sup> M. We tentatively assume that ion pair association does not complicate the kinetic picture. For a discussion of ion pairing in SO<sub>2</sub> see N. N. Lichtin, *Prog. Phys. Org. Chem.*, **1**, 75 (1963).

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

initial concentrations of nucleophile and ion and x is the number of moles per liter reacted, respectively. It is noteworthy that k<sub>1/2</sub> (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<sub>3</sub>CO<sub>2</sub>H would result from a prior equilibrium between dimer and monomer (eq 8) provided the dimer dissociation



constant (K<sub>d</sub>) in SO<sub>2</sub> is sufficiently small (≤ 10<sup>-4</sup> M) and provided the monomer is the species alkylated. The approximate limit K<sub>d</sub> ≤ 10<sup>-4</sup> M is reasonable, based on the K<sub>d</sub> values from the literature listed in Table III.

Table III. Summary of Dissociation Constants (K<sub>d</sub>) of Acetic Acid and Halogenated Acetic Acids in Various Solvents

Acid	Solvent	Temp, °C	K <sub>d</sub> × 10 <sup>4</sup> , M
CH <sub>3</sub> CO <sub>2</sub> H <sup>a</sup>	Cyclohexane	25	0.47
CH <sub>3</sub> CO <sub>2</sub> H <sup>b</sup>	Benzene	30	2.4
HCO <sub>2</sub> H <sup>b</sup>	Heptane	30	0.08
HCO <sub>2</sub> H <sup>b</sup>	Benzene	30	7.1
ClCH <sub>2</sub> CO <sub>2</sub> H <sup>c</sup>	Benzene	30	8.8
Cl <sub>2</sub> CHCO <sub>2</sub> H <sup>a</sup>	Cyclohexane	25	6.6
CF <sub>3</sub> CO <sub>2</sub> H <sup>a</sup>	Cyclohexane	25	31

<sup>a</sup> F. Thyrior and D. Decroocq, *C. R. Acad. Sci.*, **260** (10) (Group 7), 2797 (1965). <sup>b</sup> H. A. Pohl, M. E. Hobbs, and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941). <sup>c</sup> 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<sub>2</sub>CO<sub>2</sub>H, Cl<sub>2</sub>CHCO<sub>2</sub>H, CF<sub>3</sub>CO<sub>2</sub>H, and HCO<sub>2</sub>H although the rate law was not investigated in these instances. The rate constants and the activation parameters for the alkylation of CH<sub>3</sub>CO<sub>2</sub>H, ClCH<sub>2</sub>CO<sub>2</sub>H, and HCO<sub>2</sub>H are given in Table IV. With CF<sub>3</sub>CO<sub>2</sub>H 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<sub>3</sub>CO<sub>2</sub>H 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<sub>a</sub> value of the acids<sup>9a</sup> CH<sub>3</sub>CO<sub>2</sub>H, ClCH<sub>2</sub>CO<sub>2</sub>H, Cl<sub>2</sub>

(9) (a) G. Kortum, W. Vazel, and K. Andrussov, "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 <sub>5</sub> ], M	[1,4-Dichlorobutane], M	[Free acid], M	Temp, °C	$K_{2/2}$ , M <sup>-1/2</sup> sec <sup>-1</sup>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
CH <sub>3</sub> CO <sub>2</sub> H	0.01400	0.00622	0.01294	-65.1	$4.5 \times 10^{-2}$	12.9	-2.1
ClCH <sub>2</sub> CO <sub>2</sub> H	0.00982	0.00331	0.00890	-70.1	$2.0 \times 10^{-2}$	13.8	-2.4
Cl <sub>2</sub> CHCO <sub>2</sub> H	0.00832	0.00350	0.02592	-55.1	$2.2 \times 10^{-2}$	13.8	-2.4
	0.00791	0.00323	0.01979	-65.1	$4.6 \times 10^{-3}$		
	0.01238	0.00571	0.02516	-65.5	$2.3 \times 10^{-4}$		
CF <sub>3</sub> CO <sub>2</sub> H	0.01542	0.00240	0.04264	-65.7	$8.7 \times 10^{-6}$		
HCO <sub>2</sub> H	0.00894	0.00288	0.00416	-65.7	$5.6 \times 10^{-2}$	14.0	4.9
	0.01344	0.00610	0.02438	-71.1	$2.2 \times 10^{-2}$		

<sup>a</sup> The reaction was followed until 82–88, 39, 36, and 62–80% completion, respectively, for ClCH<sub>2</sub>CO<sub>2</sub>H, Cl<sub>2</sub>CHCO<sub>2</sub>H, CF<sub>3</sub>CO<sub>2</sub>H, and HCO<sub>2</sub>H.

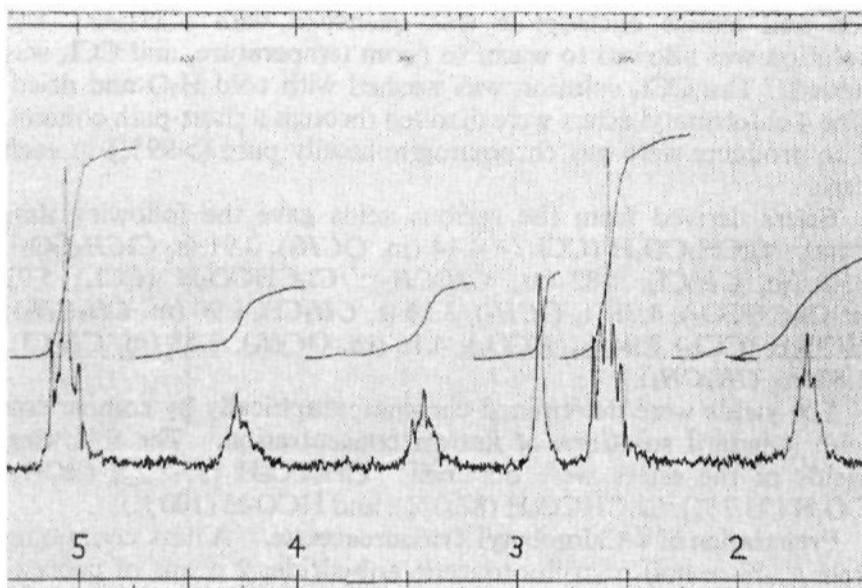
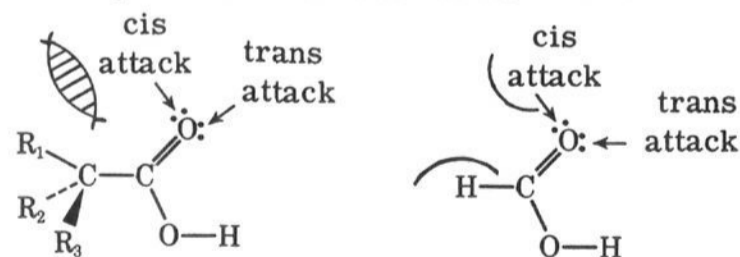


Figure 3. Nmr spectrum (100-Hz offset) of the reaction of the tetramethylechloronium ion (SO<sub>2</sub>, -60°) with CF<sub>3</sub>CO<sub>2</sub>H: molar concentration, SbF<sub>5</sub>:1,4-dichlorobutane:free CF<sub>3</sub>CO<sub>2</sub>H, 22:0.11:0.39. Peaks of unreacted halonium ion appear at  $\delta$  5.06 and 2.57. The singlet at  $\delta$  2.87 is assigned the shielded hydroxyl proton of CF<sub>3</sub>CO<sub>2</sub>H-SbF<sub>5</sub>.

CHCO<sub>2</sub>H, HCO<sub>2</sub>H, and CF<sub>3</sub>CO<sub>2</sub>H.<sup>9b</sup> It is seen that an approximate linear free-energy relationship exists, although a plot involving the unavailable pK<sub>a</sub> values for the protonated acids would be more appropriate. The point for HCO<sub>2</sub>H 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,<sup>10</sup>  $\Sigma\sigma_I$ . The  $\rho_I$  value (Figure 5) is -2.39.

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

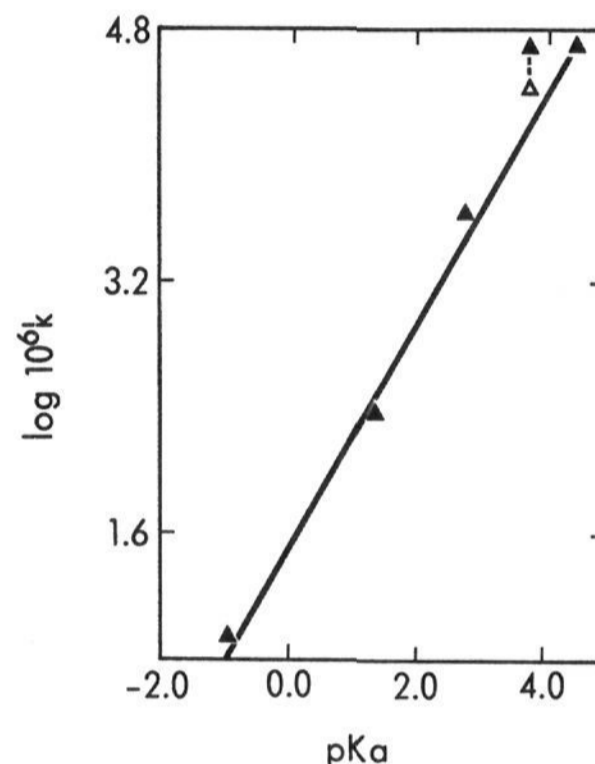


Figure 4. Dependence of  $\log 10^6k$  for alkylation on the pK<sub>a</sub> of the nucleophiles CF<sub>3</sub>CO<sub>2</sub>H, Cl<sub>2</sub>CHCO<sub>2</sub>H, ClCH<sub>2</sub>CO<sub>2</sub>H, HCO<sub>2</sub>H, and CH<sub>3</sub>CO<sub>2</sub>H (lower left to upper right, respectively). The open triangle shows the corrected  $k$  (see text) for alkylation of HCO<sub>2</sub>H.

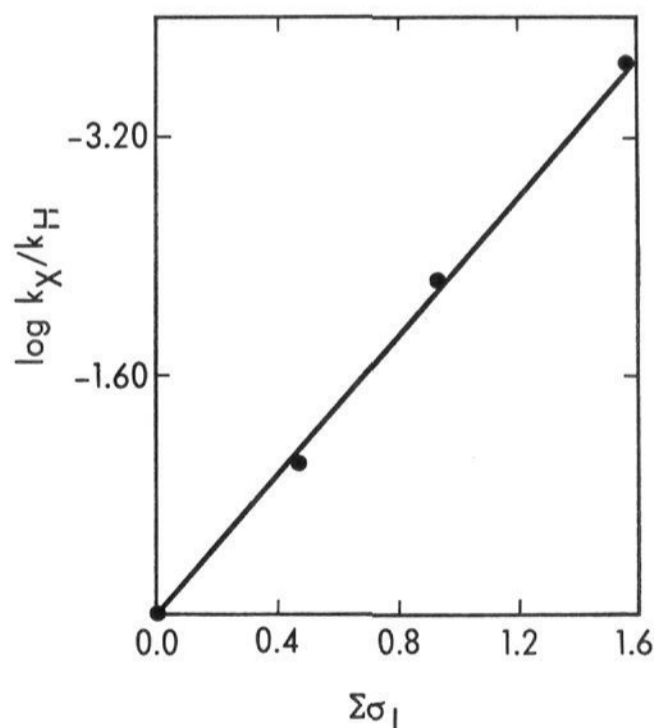


Figure 5.  $\log k_X/k_H$  for alkylation of CH<sub>3</sub>CO<sub>2</sub>H, ClH<sub>2</sub>CO<sub>2</sub>H, Cl<sub>2</sub>CHCO<sub>2</sub>H, and CF<sub>3</sub>CO<sub>2</sub>H (lower left to upper right, respectively) plotted against  $\Sigma\sigma_I$ .

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

**Table V.** Summary of Rate Constants for the Reaction of Tetramethylenchloronium Ion 1 with Nucleophiles at  $-65.6 \pm 0.1^\circ$ 

Nucleophiles	$k_{s/2}, M^{-1/2} \text{ sec}^{-1}$	$k_{rel}^a$
HCO <sub>2</sub> H	$5.6 \times 10^{-2}$	1.37
CH <sub>3</sub> CO <sub>2</sub> H	$4.1 \times 10^{-2}$	1.00
ClCH <sub>2</sub> CO <sub>2</sub> H	$4.2 \times 10^{-3}$	$1.02 \times 10^{-1}$
Cl <sub>2</sub> CHCO <sub>2</sub> H	$2.3 \times 10^{-4}$	$5.6 \times 10^{-3}$
CF <sub>3</sub> CO <sub>2</sub> H	$8.7 \times 10^{-6}$	$2.1 \times 10^{-4}$

<sup>a</sup> The rate constants are relative to that of CH<sub>3</sub>CO<sub>2</sub>H.

chlorotetramethylchloronium ion 3<sup>11</sup> was studied. In Table VI, rate constants are given for the reaction of 3

**Table VI.** Summary of Rate Constants from the Reaction of 2-Chlorotetramethylenchloronium Ion 3 with Nucleophiles at  $-65.8 \pm 0.1^\circ$ 

Nucleophile	[SbF <sub>5</sub> ], M	[1,2,4-Tri- chloro- butane], M	[Free acid], M	$k_{s/2}, M^{-1/2}$ $\text{sec}^{-1}{}^a$
CH <sub>3</sub> CO <sub>2</sub> H	0.01165	0.00462	0.01043	$13.5 \times 10^{-2}$
CF <sub>3</sub> CO <sub>2</sub> H	0.01389	0.00487	0.02023	$40.2 \times 10^{-6}$

<sup>a</sup> The reactions were followed until 93 and 48% completion, respectively, for CH<sub>3</sub>CO<sub>2</sub>H and CF<sub>3</sub>CO<sub>2</sub>H.

with CH<sub>3</sub>CO<sub>2</sub>H and CF<sub>3</sub>CO<sub>2</sub>H. The effect of the β-chlorine substituent is to increase the rate constants by factors of ~3.3 and 4.6, respectively. Other work<sup>11</sup> 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 tetramethylenchloronium ion.

## 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

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

this suggestion in a future paper.<sup>12</sup> 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 Tetramethylenchloronium Ion.** The solution resulting from the reaction of the tetramethylenchloronium ion and excess nucleophile was quenched with (CH<sub>3</sub>)<sub>2</sub>O. The solution was allowed to warm to room temperature, and CCl<sub>4</sub> was added. The CCl<sub>4</sub> solution was washed with cold H<sub>2</sub>O 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<sub>2</sub>CO<sub>2</sub>H (CCl<sub>4</sub>) δ 4.14 (m, OCH<sub>2</sub>), 3.91 (s, ClCH<sub>2</sub>CO<sub>2</sub>), 3.49 (m, CH<sub>2</sub>Cl), 1.82 (m, CH<sub>2</sub>CH<sub>2</sub>); Cl<sub>2</sub>CHCO<sub>2</sub>H (CCl<sub>4</sub>) 5.92 (s, Cl<sub>2</sub>CHCO<sub>2</sub>), 4.31 (t, OCH<sub>2</sub>), 3.56 (t, CH<sub>2</sub>Cl), 1.90 (m, CH<sub>2</sub>CH<sub>2</sub>); HCO<sub>2</sub>H (CCl<sub>4</sub>) 7.94 (s, HCO<sub>2</sub>), 4.16 (m, OCH<sub>2</sub>), 3.53 (m, CH<sub>2</sub>Cl), 1.83 (m, CH<sub>2</sub>CH<sub>2</sub>).

The yields were determined chromatographically by comparison with standard solutions of known concentration. The following yields of the esters were obtained: CH<sub>3</sub>CO<sub>2</sub>H (85.2%), ClCH<sub>2</sub>CO<sub>2</sub>H (73.7%), Cl<sub>2</sub>CHCO<sub>2</sub>H (87.0%), and HCO<sub>2</sub>H (100%).

**Preparation of 4-Chlorobutyl Trifluoroacetate.** A flask containing 4.96 g (23 mmol) of trifluoroacetic anhydride, 2 drops of concentrated H<sub>2</sub>SO<sub>4</sub>, and 5.0 ml of CCl<sub>4</sub> was cooled with an ice bath. A solution, 1.0 g (9.4 mmol) of 4-chlorobutanol in 10 ml of CCl<sub>4</sub>, 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<sub>4</sub>) δ 4.33 (t, OCH<sub>2</sub>), 3.51 (t, ClCH<sub>2</sub>), 1.89 (m, CH<sub>2</sub>CH<sub>2</sub>).

**Nmr Spectra of Monoalkylated Acids.** Nmr spectra of the monoalkylated products from the reaction of a 0.1 M solution of tetramethylenchloronium ion and 0.12–0.39 M free nucleophile in SO<sub>2</sub> at  $-60^\circ$  were obtained using a Varian HA-100D spectrometer. All chemical shifts in SO<sub>2</sub> are reported relative to external (capillary) TMS. The following characteristic absorptions were obtained for the monoalkylated products using the acids ClCH<sub>2</sub>CO<sub>2</sub>H: nmr (SO<sub>2</sub>) δ 4.72 (t, CH<sub>2</sub>O=+), 3.39 (t, CH<sub>2</sub>Cl), 1.79 (br peak, CH<sub>2</sub>CH<sub>2</sub>); Cl<sub>2</sub>CHCO<sub>2</sub>H (SO<sub>2</sub>) 4.70 (t, CH<sub>2</sub>O=+), 3.39 (t, CH<sub>2</sub>Cl), 1.79 (br peak, CH<sub>2</sub>CH<sub>2</sub>); CF<sub>3</sub>CO<sub>2</sub>H (SO<sub>2</sub>) 4.26 (br peak, CH<sub>2</sub>O=+), 3.40 (t, CH<sub>2</sub>Cl), 1.67 (m, CH<sub>2</sub>CH<sub>2</sub>).

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(12) NOTE ADDED IN PROOF. For a preliminary communication, see P. E. Peterson and F. J. Waller, *ibid.*, **94**, 91 (1972).