CHEMISTRY AND SPECTROSCOPY IN STRONGLY ACIDIC SOLUTIONS. Part IX [1]

Configurational preference in protonated carboxylic acids. Kinetics of reversible alkyl oxocarbonium ion formation

BY

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   Protonation of aliphatic carboxylic acids RCOOH in HF-BF$_3$ solution at low temperature leads to dihydroxycarbonium ions. The configurations as regards the groups R and H at the partly double C$\rlap{=}{-}$O bonds depend on the steric requirements of group R: In the case of R=CH$_3$, CH$_2$Cl, CH$_3$CH$_2$ and (CH$_3$)$_2$CH both a *cis*- and a *trans*-configuration, and in the case of R=(CH$_3$)$_3$C two *trans*-configurations probably exist.
   The rate constants of the dehydration of the protonated acids to acyl cations that takes place at higher temperatures proved to vary only slightly for R=CH$_3$, CH$_3$CH$_2$, (CH$_3$)$_2$CH and (CH$_3$)$_3$C. In agreement with previous work on protonated formic acid the rates were found to be much lower in HF-BF$_3$ than in sulfuric acid solution (as estimated from *Deno*'s results), possibly due to a difference in molecularity of the reaction.
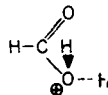
I. Introduction

   In a previous publication [2] we have shown that two different protonated species are formed when formic acid is dissolved in HF$-$BF$_3$. The structures of these ions can probably be represented by I and II, although an alkoxy-oxygen protonated structure III instead of structure II cannot be excluded
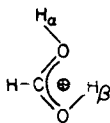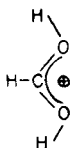
| I | II | III |

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[1] Part VIII, *H. Hogeveen*, Rec. Trav. Chim., in press.
[2] *H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor* and *C. MacLean*, Chem. Comm. **1966**, 898; Rec. Trav. Chim. **86**, 687 (1967).

on the basis of the experimental data. Additional information, which makes this possibility highly unlikely, has now been obtained by measuring the NMR spectra of some other protonated aliphatic carboxylic acids at low temperature.

Deno et al.[3] have measured the equilibria

$$RCOOH + H^{\oplus} \rightleftarrows RCOOH_2^{\oplus} \rightleftarrows RCO^{\oplus} + H_2O$$

in sulfuric acid solutions. The individual rate constants for methyl oxo-carbonium ion formation and hydration were recently determined by us together with the activation parameters for the former reaction[4]. The kinetic investigation has now been extended to some other aliphatic carboxylic acids in order to evaluate the substituent effect on these processes.

II. Results and discussion

A. *Configurational preference in protonated carboxylic acids*

The chemical shifts and coupling constants of the protonated carboxylic acids at low temperature are given in Table I.

Table I

Chemical shifts[a] and coupling constants for some protonated
carboxylic acids at about −75 °C

Compound	COOH₂		CH₃	CH₂	CH
$CH_3COOH_2^{\oplus b}$	12.95	13.57	2.87		
$CH_2ClCOOH_2^{\oplus}$	13.70	13.90		4.90	
$CH_3CH_2COOH_2^{\oplus b}$	12.96	13.21	1.47[c]	3.14[d]	
$(CH_3)_2CHCOOH_2^{\oplus}$	12.95	13.25	1.55[e]		3.20[f]
$(CH_3)_3CCOOH_2^{\oplus}$	13.00		1.57		

[a] Chemical shifts in ppm from TMS (tetramethylammonium chloride was used as internal reference, $\delta_{TMS} = -3.20$ for the reference ion);
[b] These species were observed by T. *Birchall* and R. J. *Gillespie* in HFSO₃ − SbF₅ solutions (Can. J. Chem. **43** (1965) 1045);
[c] Triplet (J = 7.0 c/s);
[d] Quartet (J = 7.0 c/s);
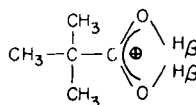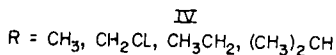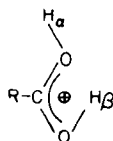[e] Doublet (J = 6.9 c/s);
[f] Septet (J = 6.9 c/s).

The observation of two low-field signals of equal intensity in RCOOH₂⊕ with R=CH₃, CH₂Cl, CH₃CH₂ and (CH₃)₂CH is consistent with a planar configuration of the ions as shown in IV.

[3] *N. C. Deno, C. U. Pittman* Jr. and *M. J. Wisotsky*, J. Am. Chem. Soc. **86**, 4370 (1964).
[4] *H. Hogeveen*, Rec. Trav. Chim. **86**, 289 (1967).

$$
\begin{array}{c}
H_\alpha \\
\backslash \\
O \\
/ \\
R-C \overset{\oplus}{\big(} \; H\beta \\
\backslash \;/ \\
O
\end{array}
\qquad\qquad
\begin{array}{c}
CH_3 \quad O \\
| \qquad /\backslash \\
CH_3-C-C\overset{\oplus}{\big(} \; H\beta \\
| \qquad \backslash\; / \; H\beta \\
CH_3 \quad O
\end{array}
$$

$$\text{IV} \qquad\qquad\qquad\qquad \text{V}$$

$$R = CH_3, \; CH_2Cl, \; CH_3CH_2, \; (CH_3)_2CH$$

The signals of the non-equivalent O-protons in IV can be identified by comparing them with those in protonated formic acid [2]. With the aid of the coupling constants it was established that protons H_α and H_β in structure I absorb at 14.16 and 13.82 ppm, respectively. We assume therefore that also in structure IV the lower-field signal is due to H_α and the other to H_β. Protonated pivalic acid, however, gives only one low-field signal (intensity ratio of O−H and C−H signals 1 : 5.0 (exp.), 1 : 4.5 (theor.)), which indicates a structure with identical O-protons. On the basis of its chemical shift structure V is proposed with the two hydrogens in *trans*-position in relation to the tertiary butyl group. The ion will be forced into this configuration by the steric requirements of the bulky group $(CH_3)_3C$.

The effects of the R group on the configuration(s) of the protonated aliphatic carboxylic acids $RCOOH_2^\oplus$ appear to be of a steric rather than of an electronic nature. The values for the Taft's steric substituent constants E_s [5a] are H (1.24), CH_3 (0.00), CH_3CH_2 (−0.07), CH_2Cl (−0.24), $(CH_3)_2CH$ (−0.47), $(CH_3)_3C$ (−1.54), whilst those for the polar substituent constants σ^* [5b] are H (0.49), CH_3 (0.00), CH_3CH_2 (−0.10), CH_2Cl (1.05), $(CH_3)_2CH$ (−0.19), $(CH_3)_3C$ (−0.30). In $HCOOH_2^\oplus$ the non-bonding repulsion between C-hydrogen and the O-hydrogens is so small that besides species (I) also species (II) occurs. Increasing the size of R (E_s range from 0.00 to −0.47) results in the presence of structure IV only, while the very large steric effect of $R=(CH_3)_3C$ makes configuration V the only observable species in protonated pivalic acid.

The general correlation of our results with steric effects also provides an argument against structure III for the species having equal oxygen-bound hydrogens, since it cannot be understood that only for R=H a species of type III would be observed.

B. *Kinetics of formation and hydration of alkyl oxocarbonium ions*

   Formation of alkyl oxocarbonium ions

   As mentioned in the Introduction equilibria of the type

⁵ *R. W. Taft* Jr., in Steric Effects in Organic Chemistry, John Wiley and Sons, Inc., N.Y., 1956; a) p. 598; b) p. 619.

$$RCOOH + H^\oplus \rightleftarrows RCOOH_2^\oplus \underset{k_2}{\overset{k_1}{\rightleftarrows}} RCO^\oplus + H_2O$$
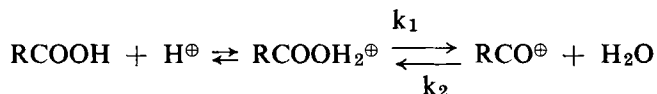
have been determined by *Deno* et al. [3] in sulfuric acid solutions. Individual rate constants could not be determined, the reaction in these systems being so fast that the signals of the group R in $RCOOH$, $RCOOH_2^\oplus$ and $RCO^\oplus$ had already coalesced. Previously [2], we determined the second-order rate constant of the deprotonation of protonated formic acid by fluoride anions to be diffusion-controlled. In the case of protonated acetic acid — which remains nearly completely protonated in this system — the rate constants of acetyl cation formation and its hydration could be estimated in $HF-BF_3$ solution [4], since both the methyl absorption of $CH_3COOH_2^\oplus$ and of $CH_3CO^\oplus$ appear as sharp signals in the NMR spectrum. The same holds for the other protonated carboxylic acids and acyl cations. The absorptions of the latter are summarized in Table II.

Table II

Chemical shifts and coupling constants of the NMR signals of some acyl cations in HF-BF₃ solution

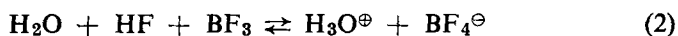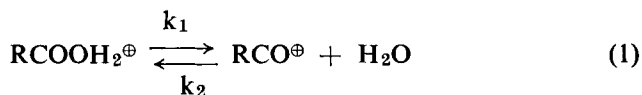| Compound	CH₃	CH₂	CH
$CH_3CO^\oplus$	3.93		
$CH_3CH_2CO^\oplus$	1.93[a]	4.19[b]	
$(CH_3)_2CHCO^\oplus$	2.00[c]		4.34[d]
$(CH_3)_3CCO^\oplus$	2.05		

[a] Triplet (J = 7.0 c/s);
[b] Quartet (J = 7.0 c/s);
[c] Doublet (J = 6.9 c/s);
[d] Septet (J = 6.9 c/s).

The reaction scheme thought to be involved is:

$$RCOOH_2^\oplus \underset{k_2}{\overset{k_1}{\rightleftarrows}} RCO^\oplus + H_2O \qquad (1)$$

$$H_2O + HF + BF_3 \rightleftarrows H_3O^\oplus + BF_4^\ominus \qquad (2)$$

The rate constants of acyl ion formation were obtained with the equation

$$\ln \frac{ax_e + x(a - x_e)}{(x_e - x)a} = \frac{2a - x_e}{x_e} k_1 \cdot t,$$

where a is the initial concentration of $RCOOH_2^\oplus$, x is the conversion at

time t and x_e is the equilibrium conversion [6]. This equation holds whether or not the reaction product H_2O is protonated. The rate of the hydration reaction is of course strongly dependent on the degree of protonation of H_2O (See further on).

The rate constants are given in Table III.

Table III

First-order rate constants of acyl cation formation
in HF-BF$_3$ solution at -26 °C

Compound	$10^4 \cdot k_1(s^{-1})$
$CH_3CO^{\oplus}$	1.5
$CH_3CH_2CO^{\oplus}$	2.8
$(CH_3)_2CHCO^{\oplus}$	3.7
$(CH_3)_3CCO^{\oplus}$	3.1

There proves to be a small substituent influence on the unimolecular decomposition of the protonated acids (Table III). Since contributions to the differences in rate are probably both of a steric and an electronic nature and only a small number of acids have been investigated, an analysis of the data in terms of a linear free energy relation does not seem to be warranted.

As mentioned earlier, the dehydration of protonated acids is much slower in $HF-BF_3$ than in sulfuric acid solution. From *Deno*'s work [3] a lower limit for the pseudo first-order rate constant of dehydration of protonated acetic acid in $H_2SO_4-SO_3$ solution can be estimated. From the significant broadening of the signal (due to collapse of the methyl signals from $CH_3COOH_2^{\oplus}$ and $CH_3CO^{\oplus}$) a value of 10^3-$10^4 s^{-1}$ can be obtained with the aid of the rapid exchange approximation formula [7]. In $HF-BF_3$ a value of 0.25 s^{-1} is calculated [4] at the same temperature (35°). As suggested previously [2], this difference might be due to a different molecularity of the dehydration process in the two systems. In $HF-BF_3$ solutions a unimolecular reaction is thought to occur, whereas in $H_2SO_4-SO_3$ solutions an H_2SO_4 molecule may be involved:
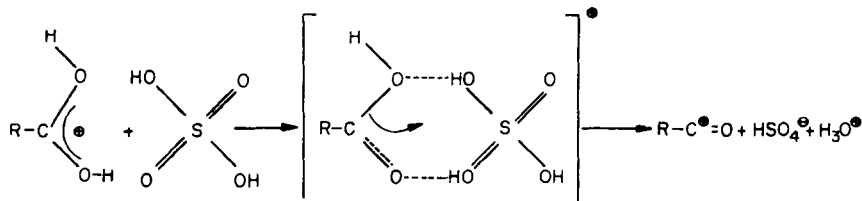
[6] *A. A. Frost* and *R. G. Pearson*, Kinetics and Mechanism, John Wiley and Sons, Inc., N.Y., 1953, p. 173.

[7] *J. W. Emsley, J. Feeney* and *L. H. Sutcliffe*, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 1, Pergamon Press, Oxford 1965, p. 481.

Hydration of alkyl oxocarbonium ions

The second-order rate constant k_2 of the hydration of alkyl oxocarbonium ions (I) can be calculated from the equilibrium equation

$$K_1 = \frac{k_1}{k_2} = \frac{[RCO^{\oplus}] \cdot [H_2O]}{[RCOOH_2^{\oplus}]} \qquad (3)$$

The concentration of unprotonated water in (3) is eliminated by means of the expression for the equilibrium constant for (2):

$$K_2 = \frac{[H_3O^{\oplus}] [BF_4^{\ominus}]}{[H_2O] [HF] [BF_3]} . \qquad (4)$$

Substitution of (4) in (3) affords

$$k_2 = \frac{k_1 \cdot K_2 \cdot [RCOOH_2^{\oplus}] [HF] [BF_3]}{[RCO^{\oplus}] [H_3O^{\oplus}] [BF_4^{\ominus}]} \qquad (5)$$

in which k_1 is known (calculated with the aid of the Arrhenius equation [4]), K_2 can be calculated from *MacLean* and *Mackor*'s data [8], the equilibrium ratio $[RCOOH_2^{\oplus}] / [RCO^{\oplus}]$ is determined from the peak heights of the NMR signals, $[HF] \approx 50$ mole $\cdot$ l^{-1} and
$[BF_4^{\ominus}] \approx [RCOOH_2^{\oplus}] + [RCO^{\oplus}] + [H_3O^{\oplus}]$. As the $[BF_3]$ at $-80°$ (the temperature of preparation of the samples) is not known and consequently neither the $[BF_3]$ at the temperatures of the kinetic measurements in the closed sample tubes, we also carried out some experiments in which protonated acetic acid was slowly heated from $-80°$ to $0°$ under about 1 atm BF_3 pressure. At $0°$ the sample tubes were closed and subsequently the ratio $[CH_3COOH_2^{\oplus}] / [CH_3CO^{\oplus}]$ was measured. At $0°$ and a known BF_3 pressure, the $[BF_3]$ in solution can be calculated [9] and then with equation (5) also k_2. Its value is estimated to be 2.10^3 l $\cdot$ mole^{-1}s^{-1} at $0°$ for the hydration of methyl oxocarbonium ion. Recently, some rate constants for the reaction of p-substituted trityl cations with water have been reported [10].

After equilibrium was reached the conversion of $RCOOH_2^{\oplus}$ into $RCO^{\oplus}$ was found to be for R=CH$_3$ 40-70% (in three experiments at -26, -19 and $-13°$), R=CH$_3$CH$_2$ 65% (at $-26°$), R=(CH$_3$)$_2$CH 82% (at $-26°$) and R=(CH$_3$)$_3$C 92% (at $-26°$). Although there is a definite trend in these data, a detailed discussion is not warranted since these percentages are not absolute values but depend rather strongly (see the case of protonated acetic acid) on small casual differences in initial BF_3 pressure during sample

[8]   *C. Maclean* and *E. L. Mackor*, J. Chem. Phys. **34**, 2207 (1961).
[9]   *E. L. Mackor*, *A. Hofstra* and *J. H. van der Waals*, Trans. Far. Soc. **54**, 66 (1958).
[10] *R. A. Diffenbach*, *K. Sano* and *R. W. Taft*, J. Am. Chem. Soc. **88**, 4747 (1966).

preparation. There is only a small effect of temperature on the equilibrium position when determined in a closed system (NMR tube), as is shown in Fig. 1. The experimental points were determined by both cooling and heating the sample.
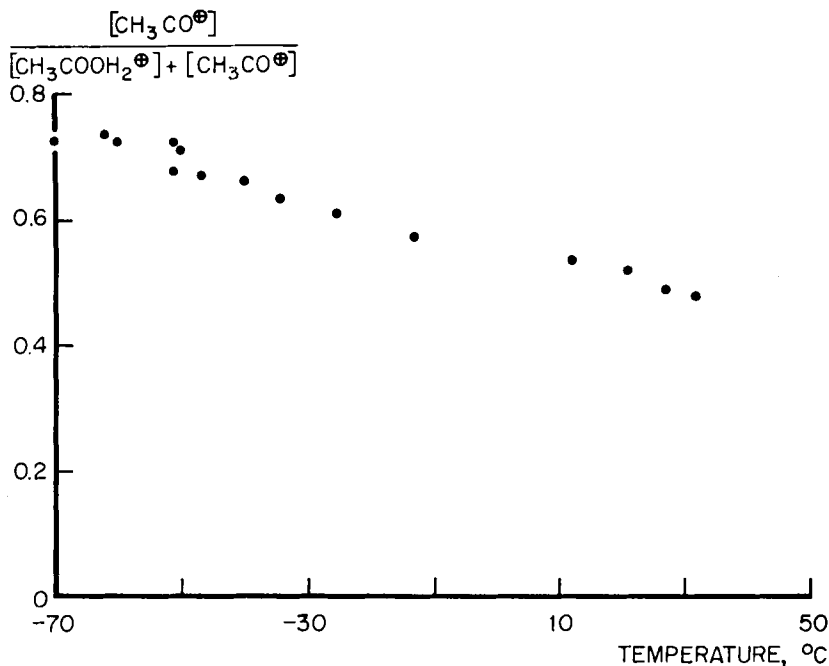

Fig. 1.   Temperature-dependence of the ratio $\dfrac{[CH_3CO^\oplus]}{[CH_3COOH_2^\oplus] + [CH_3CO^\oplus]}$ in HF-BF$_3$

solution (determined in a closed NMR sample tube).

No decomposition [11] was observed of the trimethylacetyl cation into tertiary butyl cation and carbon monoxide during the kinetic run at $-26°$.

III.   Experimental

   The samples of protonated carboxylic acids were prepared at about $-80°$ by dissolving the acids in HF solution and applying BF$_3$ pressure. The final pressure of BF$_3$ at that temperature was 1.0 atm and the concentration of the substrates 1.0 - 1.5 mole/l. The NMR spectra of the protonated acids were measured at about $-75°$. The kinetics of the alkyl oxocarbonium ion formation were determined by heating the samples rapidly to the desired temperature and transferring them to the cavity of the NMR spectrometer (Varian DP-60) where at the same temperature the conversion was followed till equilibrium by monitoring the alkyl peaks of RCOOH$_2^\oplus$ and of RCO$^\oplus$.

(Received May 30th. 1967).

[11]   *G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffitt, J. J. Bastien* and *E. B. Baker,* J. Am. Chem. Soc. **85**, 1328 (1963).