Dehydrochlorination of 4-Chlorobutyryl Cation. An Acid- and Base-Catalyzed Reaction in Superacids

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Summary: Acyl cation **2** eliminates HCl in HF–SbF$_5$ and FSO$_3$H–SbF$_5$. The rate dependence on acidity indicates that in the stronger acid HF–SbF$_5$ the reaction (first-order kinetics) is triggered by acid-catalyzed ionization of chloride with the acyl-alkyl dication as the probable intermediate. Dehydrochlorination is significantly slower in the more weakly acidic FSO$_3$H–SbF$_5$ mixtures, and its rate varies inversely with acidity, indicating assistance from a proton acceptor. After an induction period, the reaction in these acids is first-order in reactant and first-order in the product **3**, indicating that the latter assists the proton loss from the former.

Sir: Reactions that occur in superacids and have rates varying with the acid strength are known.[1] In all cases the reactions involved a second proton transfer to a carbocation as the rate-determining step and were favored by an increase in the protonating ability of the acid. We report here on a reaction exhibiting an unusual dependence on acidity.

Ionization of 4-chlorobutyryl chloride (**1**) in superacid led to the corresponding acyl cation, **2**.[2] Upon standing in a sealed tube at –10 °C for several weeks, the NMR spectrum of **2** in 4:1 FSO$_3$H–SbF$_5$ was gradually replaced by the spectrum of the 2-butenoyl (crotonyl) cation, **3** (^{13}C: δ 25.46, 83.16, 150.46, and 202.29. ^{1}H: δ 2.63 (dd, *J* = 6.82 and 1.48 Hz), 6.64 (dq, *J* = 16.39 and 1.48 Hz), and 9.15 (dq, *J* = 16.39 and 6.82 Hz),[3] both in agreement with literature values[4]). Thus, the reaction was an elimination of hydrogen chloride,[5] with the migration of the double bond to the α,β-position. The conversion was clean and also fast enough at 25–55 °C to allow the convenient measurement of reaction rates by the integration of the ^{1}H NMR spectrum.

$$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CO}^+ \rightarrow \text{MeCH=CHCO}^+ + \text{HCl}$$
$$\underset{\textbf{2}}{} \qquad \underset{\textbf{3}}{}$$

There are two general mechanisms of hydrogen halide elimination from alkyl halides.[6] The first is base-catalyzed, as in the E2 eliminations. The second is promoted by electrophiles (acids in a general sense) such as the cations of silver, mercury, and other metals,[7] or iodine,[8] which assist the departure of the leaving group. The classical E1 elimination[6b,c] also involves electrophilic attack at the leaving group, this time by the solvent[9] (anion stabilization mechanism[10]).

For the elimination occuring in superacid solution, the electrophilic attack is intuitively expected to provide the driving force. Ion **2**, however, gives a dication[11] in which one of the charged centers is a primary carbon. Hydride shift concerted with ionization can move the charge to a carbon which is secondary, but at the same time closer to the other positive charge of the acyl cation. The alternative, catalysis by a nucleophile or base, can be pictured as forming a neutral acid derivative (or a ketene)[12] which then loses a chloride ion by reaction with the Lewis acid.

The overall acid-catalyzed nature of the elimination studied by us is shown by the significantly faster rate in 1:1 HF–SbF$_5$ (half-life 1.4 h at 28 °C) than in the weaker 1:1 FSO$_3$H–SbF$_5$ solution (half-life ca. 20 h at 39 °C). It appears, then, that dehydrochlorination of **2** can be used for comparing superacidic strengths in the range of acidity from 1:1 FSO$_3$H–SbF$_5$ to 1:1 HF–SbF$_5$.[1,10b,13]

On the other hand, no conversion of **2** to **3** occurred until the substrate was lost to nonspecific decompositions at 46 °C in the much weaker superacid 16:1 CF$_3$SO$_3$H–TaF$_5$ (3.1:1 TaF$_5$ to **1**),[14] where a 3:1 equilibrium mixture of **2** and **1** was present.

To our surprise, however, the elimination was faster in 4:1 FSO$_3$H–SbF$_5$ (half-life 15 h at 39 °C) than in 1:1 FSO$_3$H–SbF$_5$,[15] even though the former is a weaker acid than the latter.[1] The same ordering of rates was observed when the temperature or substrate concentration was varied.

These results indicate that two mechanisms are operating in the dehydrochlorination of **2**. In the very strong superacid HF–SbF$_5$, an acid-catalyzed ionization occurs, forming the dication as an intermediate. In the weaker acids, ionization is still acid-catalyzed, but a base-catalyzed (or nucleophile-catalyzed) process operates at the same time, assisting with the proton loss from the substrate. Formation of the dication is thus avoided in superacid solutions of the strength of the FSO$_3$H–SbF$_5$ mixtures.

The proton loss accompanying chloride ionization was confirmed by an experiment of conversion of **2** in FSO$_3$D–SbF$_5$.[16] Both the carbon-13 and the deuterium NMR spectra[3] indicated that deuterium was incorporated in the methyl group of **3**, which means that 3-butenoic acid (**4**)

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(3) The NMR spectra were recorded at 90 and 250.1 MHz for protium, 22.5 MHz for carbon-13, and 38.4 MHz for deuterium.

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(5) For analogous HCl elimination converting a 3-chloroalkyl cation to an alkenyl cation, see: Fărcaşiu, D. *J. Chem. Soc., Chem. Commun.* **1977**, 394. Fărcaşiu, D. *J. Am. Chem. Soc.*, **1978**, *100*, 1015.

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(11) Reviews on carbodications: (a) Surya-Prakash, G. K.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390. (b) Pagni, R. M. *Tetrahedron* **1984**, *21*, 4161.

(12) Ogata, Y.; Harada, T.; Sugimoto, T. *Can. J. Chem.* **1977**, *55*, 1268.

(13) (a) Fărcaşiu, D. *Acc. Chem. Res.*, **1982**, *15*, 46. (b) Fărcaşiu, D.; Marino, G.; Miller, G.; Kastrup, R. V. *J. Am. Chem. Soc.* **1989**, *111*, 7210.

(14) Increasing the TaF$_5$:**2** ratio to 7.8 still did not result in any conversion of **2** to **3**.

(15) Even though the superacids were procured from a reputable source and were freshly opened, their composition was checked by fluorine NMR.

(16) The composite was prepared from commercially available components, in a 1:1 molar ratio. The acid strength was lower, however, than that of the 1:1 nondeuterated acid, because deuteriofluorosulfuric acid is sold with KF added as stabilizer.

is formed by elimination, and rearranges to **3** in a fast step:

$$F_5Sb + ClCH_2CH_2CH_2CO^+ + B \rightarrow H_2C\!\!=\!\!CHCH_2CO^+$$
$$\underset{\textbf{2}}{} \underset{\textbf{4}}{}$$

$$\textbf{4} \xrightarrow{\text{+D}^+;\ \text{–H}^+} DCH_2CH\!\!=\!\!CHCO^+$$
$$\phantom{\textbf{4} \xrightarrow{\text{+D}^+;\ \text{–H}^+}} \underset{\textbf{3-4d}}{}$$
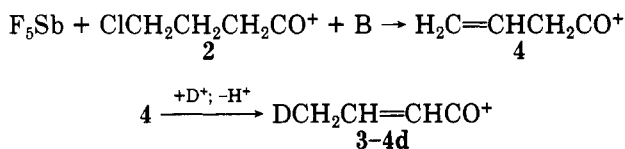
Under the same conditions, no deuterium incorporation was observed in a sample of **3** prepared from crotonyl chloride.

A clue as to the nature of the base B was offered by a careful kinetic study of the conversion. Thus, the reaction in fluoroantimonic acid followed clean first-order kinetics ($k_1 = 8.96 \times 10^{-4}$ s^{-1} at 50 °C,[17] $\Delta H^* = 15.4$, $\Delta S^* = -24.9$[18]).

The reaction in the fluorosulfuric acid based composites, however, showed an induction period, after which the reaction exhibited second-order kinetics overall, first-order in **2** and first-order in the reaction product **3** ($k_2 = 1.23 \times 10^{-4}$ L mol^{-1} s^{-1} at 50 °C,[17] $\Delta H^* = 16.0$, $\Delta S^* = -27.1$, and $k_2 = 1.94 \times 10^{-4}$ at 50 °C, $\Delta H^* = 16.6$, $\Delta S^* = -25.2$, for the 1:1 and 4:1 acid, respectively).

When **2** and **3** were prepared in the same solution from the corresponding acid chlorides at low temperature, and conversion of **2** was followed, no induction period was observed. It appears, therefore, that **3** is assisting the proton loss from **2**.

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(17) Calculated from data at other temperatures.
(18) ΔH^* and ΔS^* values are in kcal/mol and cal/mol deg, respectively (1 cal = 4.184 J).

Deamination of *n*-Octylamine in Aqueous Solution: The Substitution/Elimination Ratio Is Not Altered by a Change of 10^8 in Hydroxide Ion Concentration

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Summary: Two different pathways for breakdown of the *n*-octyldiazonium ion appear to account for the several products obtained from the reactions of *n*-octylamine with both aqueous nitrous acid at low pH and with nitroprusside ion under alkaline conditions.

Sir: Deaminations of primary aliphatic amines by nitrous acid are known to yield a variety of products reflecting solvolysis, elimination, and rearrangement of the intervening carbonium ions. The idea that such reactions involve unusually reactive or "hot" carbonium ions came about as a result of observations that the products in such cases usually differed from those obtained from solvolyses of corresponding alkyl halides, tosylates, etc., that are thought to involve the same carbonium ion intermediates.[1–5] As compared to the latter, deaminations of amines tend to give a greater proportion of elimination and rearranged products. The amount of rearrangement and elimination is greatest in polar, protic solvents due, presumably, to the greater stabilization of those intermediates by those solvents.

In 1971, Maltz and co-workers[6] described the use of sodium nitroprusside to bring about the deamination of primary aliphatic amines. Unlike the reaction with nitrous acid, that with sodium nitroprusside proceeds most readily under alkaline conditions. This study was conducted to determine the extent to which solvent composition, particularly pH, might be used to influence the nature of the products obtained upon the deamination of an amine. The absence of a single predictable product in good yield has limited the use of nitrous acid as a means to effect the deamination of amines for most synthetic and analytical purposes.

A relatively large number of products can be identified following the reaction of *n*-octylamine with either nitrous acid or sodium nitroprusside. Yields of the six major products of its reaction with nitrous acid varied with pH

as shown in Figure 1. The reaction was most rapid at approximately pH 3.5–4, and the main product under those conditions was 1-octyl nitrite. The formation of both 1- and 2-octyl nitrites at low pH in the presence of excess nitrite appears to reflect the initial formation of 1- and 2-octanol and their subsequent equilibrium as follows:[7]

$$ROH + NO_2^- + H^+ \rightleftharpoons RONO + H_2O \qquad (1)$$
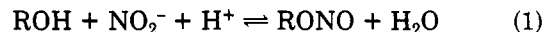
although direct formation of small amounts of these compounds according to eq 2 cannot be precluded. In the

$$RN\!\!=\!\!N^+ + NO_2^- \rightarrow RONO + N_2 \qquad (2)$$

presence of chloride ion, for example, an analogous reaction as follows:

$$RN\!\!=\!\!N^+ + Cl^- \rightarrow RCl + N_2 \qquad (3)$$

gives rise to significant amounts of 1- and 2-chlorooctane, with the former becoming the principal product (i.e. ∼53% of the total) in 5 M sodium chloride (Table I).

In contrast to the reaction with nitrous acid, that with sodium nitroprusside proceeds optimally under alkaline conditions. Thus, as shown in Table I, yields were greatest at high pH, in accord with a kinetic dependence on the unprotonated amine.[8] Under such conditions, no alkyl nitrites and, in the absence of added chloride ion, no alkyl chlorides were observed. Aldehydic products, as detected following reactions under similar conditions by Maltz et

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