Stable Carbocations. CXXVIII.[1] Protonated Acyclic Carboxylic Acid Anhydrides and Their Cleavage to Oxocarbenium Ions. The Question of the Formyl Cation in Superacid Media

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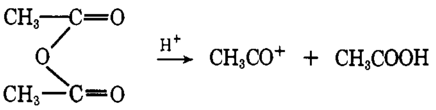
Abstract: Protonation of acyclic carboxylic acid anhydride in $FSO_3H-SbF_5-SO_2$ solution leading to the formation of intra- and intermolecularly rapidly proton exchanging protonated anhydrides was studied by pmr spectroscopy. Cleavage of acyclic carboxylic anhydrides in excess $FSO_3H-SbF_5-SO_2$ solution was found to give their corresponding protonated carboxylic acids and oxocarbenium ions. The mechanisms for the rapid proton exchange processes of protonated anhydrides and for the cleavage reaction in excess $FSO_3H-SbF_5-SO_2$ solution are discussed. Protonated acyclic carboxylic acid anhydrides were also obtained by the reaction of alkyloxocarbenium (acyl) hexafluoroantimonate salts with anhydrous aliphatic acids. Attempts to obtain the formyl cation by several routes, including one under carbon monoxide pressure, were unsuccessful. The formyl cation was not observed as a long-lived species in superacid solution because of the ease of protolytic cleavage to carbon monoxide.

A preliminary study of protonation of carboxylic anhydrides in $FSO_3H-SbF_5-SO_2$ solution leading to the formation of their corresponding protonated acids and oxocarbenium ions was reported.[2] Acid-catalyzed acylations with carboxylic acid anhydrides are considered to involve the intermediate formation of oxocarbenium ions as the reactive species.[3] Furthermore, Gillespie and Leisten showed in their cryoscopic study fourfold depression of the freezing point by acetic anhydride in sulfuric acid.[4] On the other hand, succinic anhydride was reported to be only partially protonated in sulfuric acid.[4]



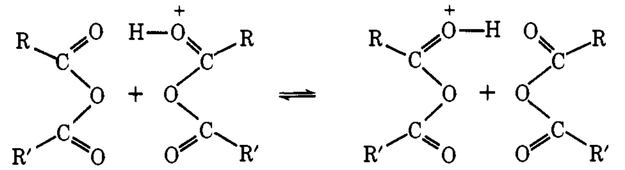
$$(CH_3-C{=}O)_2O \xrightarrow{H^+} CH_3CO^+ + CH_3COOH$$

We presently wish to report the result of protonation of acyclic carboxylic acid anhydrides and their cleavage reaction in $FSO_3H-SbF_5-SO_2$ solution.

Results and Discussion

Acyclic anhydrides (**1**) were protonated in a small amount of $FSO_3H-SbF_5-SO_2$ solution (less than 1 mol relative to acid anhydrides) at −78°. The pmr spectra of all these solutions show substantially deshielded proton absorptions (═OH$^+$) between δ 14.5 and 16.0. The pmr absorptions of the alkyl protons (R and R′) were slightly deshielded from their precursors. These results show that all the acyclic anhydrides were partially protonated and that the protonated acyclic anhydrides **2** undergo intermolecular proton exchange with their precursors **1**. The substantially deshielded exchanging proton indicates that it is associated with two oxygen atoms.

The pmr spectra of an equimolar **1** in $FSO_3H-SbF_5-SO_2$ solution show an increased intensity of the most deshielded ═OH$^+$ proton absorption, but the chemical shifts are essentially unchanged. However, the chemical shifts of the alkyl protons are now further deshielded. Peak integration shows the most deshielded proton, ═OH$^+$, is equal to one proton. Pmr spectrum of monoprotonated formic acetic anhydride in $FSO_3H-SbF_5-SO_2$ solution is shown in Figure 1. Pmr parameters of the rapid proton-exchanging monoprotonated acyclic anhydrides and their precursors are summarized in Table I.

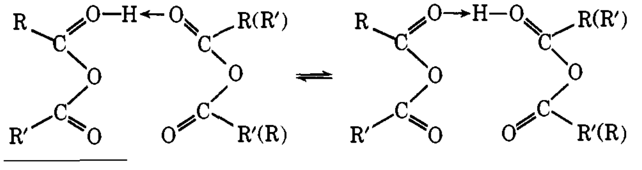


1 **2** ⇌ **2** **1**

a, R = H; R′ = CH_3
b, R = R′ = CH_3
c, R = CH_3; R′ = C_2H_5
d, R = R′ = C_2H_5
e, R = R′ = *i*-Pr
f, R = R′ = *tert*-Bu
g, R = R′ = CF_3

The most deshielded proton absorption is temperature dependent; it becomes sharper at lower temperature (−80°) indicating that the exchange process is slowed down. However, at this temperature the alkyl groups of protonated acetic anhydride (**2b**) are still equivalent and in the case of mixed anhydrides,[5] such as protonated acetic propionic anhydride (**2c**), only one ═OH$^+$ pmr signal is observed. These observations can be explained by both inter- and intramolecular proton exchange processes, such as Schemes I and II,

Scheme I



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[1] Part CXXVII: G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3544 (1972).

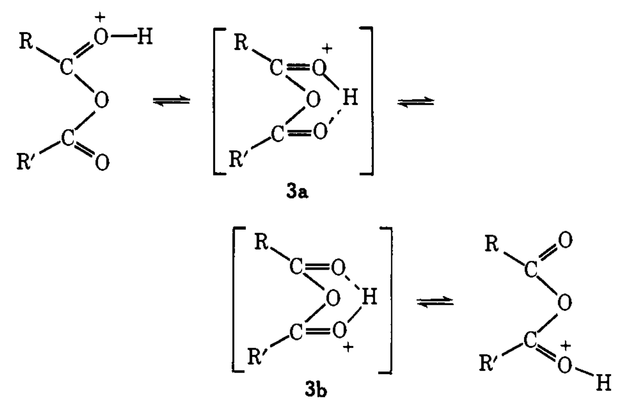
[2] G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

[3] A. G. Peto in "Friedel-Crafts and Related Reactions," Vol. III, Part 2, G. A. Olah, Ed., Wiley-Interscience, New York, N. Y., 1966.

[4] R. J. Gillespie and J. A. Leisten, *Quart. Rev., Chem. Soc.*, **8**, 40 (1954).

[5] C. D. Hurd and A. S. Roe, *J. Amer. Chem. Soc.*, **61**, 3355 (1939), and D. Stevens and A. Van Es, *Recl. Trav. Chim. Pays-Bas*, **83**, 863 (1964).

Scheme II



respectively.

The possibility of intermolecular proton exchange can be substantiated by comparing protonation of carboxylic acids, esters, and ketones under similar conditions (equal molarity of superacids and esters, acids, or ketones) which also show intermolecular proton exchange. For example, protonated acetone shows equivalent methyl groups and protonation of acetic acid shows equivalent protons on the oxygen atoms. On the other hand, intramolecular proton exchange involving chelate ring structure **3** as an intermediate is also plausible since six-membered chelate ring systems have been established experimentally in carbohydrate systems by Mester,[6] in enolized diacetoacetic esters and triketones by Forsen,[7] and in β-diketones by Reeves[8] and Burdett and Rogers.[9]

When acyclic anhydrides were protonated in 1.1-1.5 mol equiv of $FSO_3H-SbF_5-SO_2$ solution, the low-field $=OH^+$ proton was shielded (*e.g.*, from δ 15.11 to 13.88 in **2b**) while the alkyl groups (R and R') were deshielded (*e.g.*, from δ 2.50 to 3.10 in **2b**). The amounts of shielding of $=OH^+$ and of deshielding in R and R' are proportional to superacid added to the solution. Pmr integration shows the most deshielded peak corresponds to more than one proton. No FSO_3H-SbF_5 acid absorption was observed in these particular cases. This behavior indicates that an additional intermolecular proton exchange process occurs (Scheme III). The shielding of the $=OH^+$ proton can be explained by this exchange process (Scheme III) because the proton shift of FSO_3H-SbF_5 in SO_2 is around δ 12.0, always shielded from the $=OH^+$ proton. The observed shifts are the average weight of the acid and monoprotonated anhydride $=OH^+$ proton shifts.

Scheme III

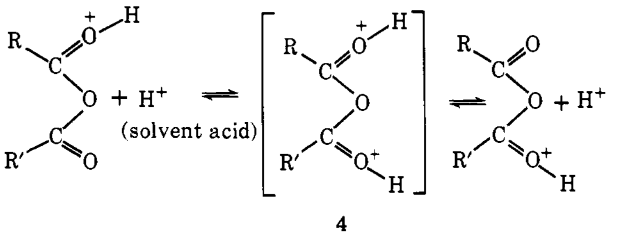
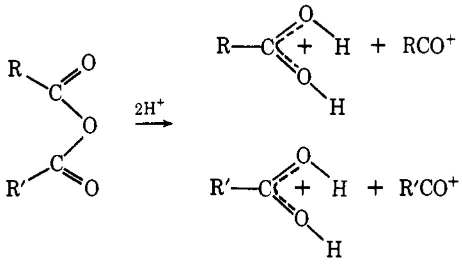


Figure 1. Pmr spectrum of monoprotonated formic acetic anhydride in $FSO_3H-SbF_5-SO_2$ at −70°.

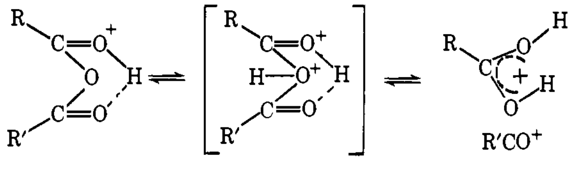
The deshielding of R and R' in **2** is probably also due to the involvement of diprotonated acyclic anhydride **4**.

When acyclic anhydrides were protonated in a large excess of superacid solution, we obtained the corresponding cleavage products, protonated carboxylic acids and oxocarbenium ions. Cleavage of symmetrical anhydrides gives a single protonated acid and the corresponding oxocarbenium ion. In the case of unsymmetrical, mixed anhydrides, both protonated acids and oxocarbenium ions are formed.



As both carbonyl oxygens are associated with the proton in the protonated acyclic anhydrides **3** and **4** or in the rapid intra- and intermolecular proton exchanging processes (Schemes I-III), the second protonation may not be on the remaining lone pair of the already coordinated carbonyl oxygens, but ether oxygen. Charge-charge repulsion destabilizes the diprotonated species and causes cleavage (Schemes IV and V).

Scheme IV



Scheme IV shows diprotonation to occur in the monoprotonated chelate form **3** and Scheme V shows the second protolytic attack on the ether oxygen of a monoprotonated anhydride which is associated with another protonated anhydride. The cleavage reactions of acyclic anhydrides in superacids thus are similar to those of esters in superacids.[10]

In comparison, the alkyl groups (R and R') of rapidly proton-exchanging monoprotonated acyclic anhydrides are less deshielded than those of their corresponding protonated acids or of oxocarbenium ions. For exam-

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[6] L. Mester, A. Stephen, and J. Parello, *Tetrahedron Lett.*, 4119 (1968).

[7] S. Forsen and M. Nilsson, *Acta Chem. Scand.*, **14**, 1333 (1960); 13, 1383 (1959).

[8] L. D. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

[9] J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

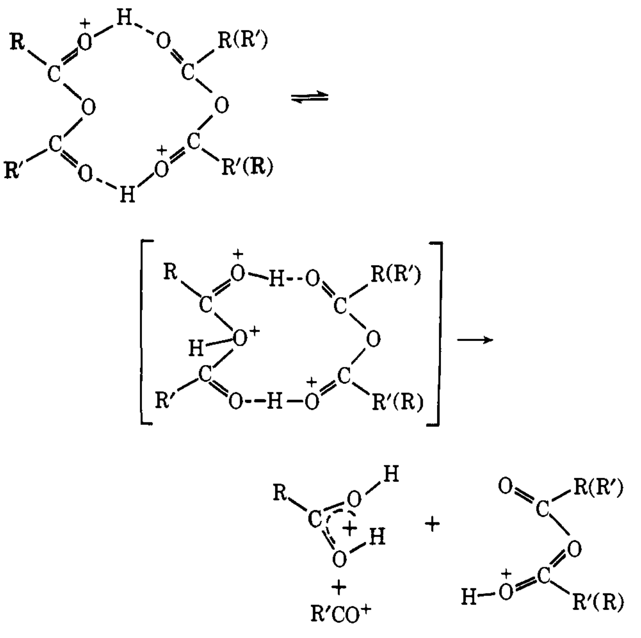
[10] G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

Table I. Pmr Parameters of Protonated and Parent Carboxylic Acid Anhydrides RCOOOCR′[a]

R	R′	Solvent system (temp, °C)	δ R	δ R′	δ =OH+[b]
H	CH_3	SO_2 (−80)	8.90 (s)	2.11 (s)	
		$FSO_3H-SbF_5-SO_2ClF$ (−85)	9.01 (s)	2.21 (s)	15.74 (s)
CH_3	CH_3	SO_2 (−75)	1.95 (s)	1.95 (s)	
		$FSO_3H-SbF_5-SO_2ClF$ (−65)	2.50 (s)	2.50 (s)	15.11 (s)
CH_3	CH_3CH_2	SO_2 (−60)	1.90 (s)	0.80 (CH_3, t, J = 7 Hz) 2.35 (CH_2, q, J = 7 Hz)	
		$FSO_3H-SbF_5-SO_2ClF$ (−60)	2.54 (s)	1.21 (CH_3, t, J = 7 Hz) 2.90 (CH_3, q, J = 7 Hz)	14.64 (s)
CH_3CH_2	CH_3CH_2	SO_2 (−60)	0.87 (CH_3, t, J = 7.5 Hz) 2.31 (CH_2, q, J = 7.5 Hz)	0.87 (CH_3, t, J = 7.5 Hz) 2.31 (CH_2, q, J = 7.5 Hz)	
		$FSO_3H-SbF_5-SO_2ClF$ (−75)	0.98 (CH_3, t, J = 7 Hz) 2.55 (CH_2, q, J = 7 Hz)	0.98 (CH_3, t, J = 7 Hz) 2.55 (CH_2, q, J = 7 Hz)	15.03 (s)
$(CH_3)_2CH$	$(CH_3)_2CH$	SO_2 (−70)	0.94 (CH_3, d, J = 7 Hz) 2.50 (CH, hep, J = 7 Hz)	0.94 (CH_3, d, J = 7 Hz) 2.50 (CH, hep, J = 7 Hz)	
		$FSO_3H-SbF_5-SO_2ClF$ (−60)	1.45 (CH_3, d, J = 7 Hz) 2.40 (CH, hep, J = 7 Hz)	1.45 (CH_3, d, J = 7 Hz) 2.40 (CH, hep, J = 7 Hz)	14.17 (s)
$(CH_3)_3C$	$(CH_3)_3C$	SO_2ClF (−60)	1.32 (s)	1.32 (s)	
		$FSO_3H-SbF_5-SO_2ClF$ (−70)	1.70 (s)	1.70 (s)	12.80 (s)

[a] Proton chemical shifts are referred to external (capillary) TMS. Abbreviation: s = singlet, d = doublet, t = triplet, q = quartet, and hep = heptet. [b] Rapidly exchanging (see text).

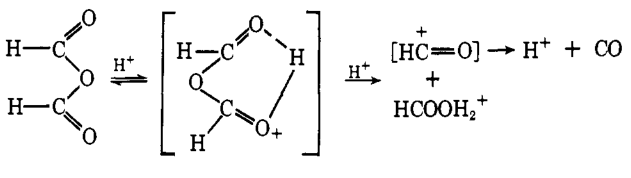
Scheme V



ple, the methyl proton shift in rapidly proton exchanging monoprotonated acetic anhydride (δ 2.50) is less deshielded than that of protonated acetic acid (δ 2.93) or of the acetyl cation (δ 4.11). This is reasonable since the charge can be better delocalized in protonated acetic anhydride than in protonated acetic acid. However, in the case when more than 1 mol equiv of $FSO_3H-SbF_5-SO_2$ solution was used to protonate acid anhydrides (as observed before cleavage occurs), the alkyl proton shifts are somewhat similar to those of their corresponding protonated acids.

There are two acid anhydrides, formic and trifluoroacetic anhydride, which show somewhat different chemical behavior toward $FSO_3H-SbF_5-SO_2$ solution.

Formic anhydride[11] decomposes immediately upon attempted protonation and the only species observed is protonated formic acid. The protolytic cleavage of formic anhydride must first give formic acid and the formyl cation. The latter, however, decomposes spontaneously to carbon monoxide, the evolution of which is observed. Evolution of some carbon monoxide is also observed upon protonation of acetic formic anhydride with excess $FSO_3H-SbF_5-SO_2$ solution. However, the rapidly proton exchanging monoprotonated acetic formic anhydride is more stable and can be observed at lower temperature, −85°. Excess superacid cleaves



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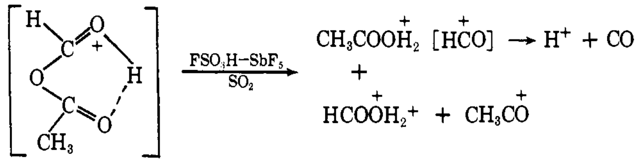
[11] Formic anhydride was first obtained in the reaction of formyl fluoride with metal formates (see G. A. Olah and S. J. Kuhn in "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Wiley-Interscience, New York, N. Y., 1964, p 1243, and references given therein). Formic anhydride was prepared in pure form by Stevens and Van Es,[6] and by I. Muramatsu, M. Itoi, M. Tsuji, and A. Hagitani, *Bull. Chem. Soc. Jap.*, 37, 756 (1964).

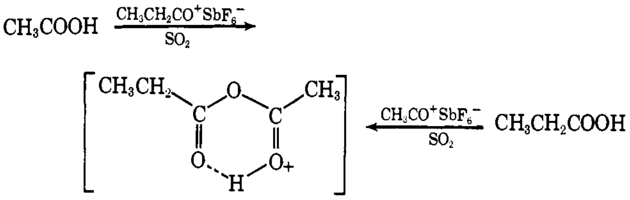
the anhydride to protonated acetic and formic acids and the acetyl cation. Again the formyl cation is not observed, as it immediately decomposes in superacid solution.



Trifluoroacetic anhydride was not protonated in either FSO_3H-SbF_5-SO_2ClF or HF-SbF_5-SO_2ClF solution at low temperature. In the case when equimolar superacid was treated with trifluoroacetic anhydride at −78°, the ^{19}F nmr spectrum of the solution shows a singlet at ϕ 76.7 which is identical with that of the parent compound in SO_2ClF solution. In the ^1H nmr spectrum, only the acid absorption (*ca.* δ 12.0) and that of the hydronium ion (*ca.* δ 10.1, caused by impurity moisture in the solvent) were observed. When an excess of FSO_3H-SbF_5-SO_2ClF or HF-SbF_5-SO_2ClF solution was treated with trifluoroacetic anhydride at −80°, protonation again was not observed. However, as the solution was allowed to warm to −50°, cleavage reaction immediately occurred. In the ^{19}F nmr spectrum, a doublet at ϕ 75.7 (J_{FF} = 6 Hz) and a quartet at 15.53 (J_{FF} = 6 Hz) were observed. These fluorine nmr data are consistent with the formation of trifluoroacetyl fluoride. In addition, a fluorine singlet at ϕ 73.7 was also observed and is identical with that of protonated trifluoroacetic acid in FSO_3H-SbF_5-SO_2ClF or HF-SbF_5-SO_3ClF solution. Furthermore, in the ^1H nmr spectrum (−80°), two equal intensity singlets at δ 14.3 and 15.0 were observed. At higher temperature (*ca.* −25°) the two peaks collapse to a singlet resonance line with an average chemical shift. Raising the temperature still further (∼0°) causes proton exchange with the solvent to become sufficiently rapid to merge the low-field OH signal with the solvent peak. This behavior is similar to that of protonated aliphatic acids.[2]

Protonation of trifluoroacetic anhydride thus was not achieved at low temperature indicating that the trifluoromethyl group is highly electron withdrawing. Cleavage reaction only occurs when an excess of superacid solvent is used and only at higher temperature. The formation of protonated trifluoroacetic acid is expected. As, however, Lidner and Hranz[12] reported the isolation of $CF_3CO^+SbF_6^+$ (from CF_3COBr and AgSbF), it is surprising that the trifluoroacetyl cation (CF_3CO^+) is unstable in the low nucleophilicity superacid medium and reacts immediately with the counteranion to form trifluoroacetyl fluoride.

An alternate and independent way to obtain monoprotonated acyclic acid anhydrides was found by the reaction of alkyloxocarbenium (acyl) hexafluoroantimonate salts with anhydrous aliphatic acids. The reaction of methyl-, ethyl-, and phenyloxocarbenium ions (as SbF_6^- salts) with formic, acetic, and propionic acids was investigated. The reaction proceeds smoothly in SO_2 solution at −60°, yielding the rapidly proton exchanging monoprotonated anhydrides. For example, the reaction of methyloxocarbenium ion with equimolar propionic acid gives an identical pmr spectrum with that of the reaction of ethyloxocarbenium ion and glacial acetic acid in SO_2.



Attempted Preparation of Formyl Cation. We attempted generating the formyl cation under a pressure of carbon monoxide, in the hope of inhibiting decomposition, in accordance with the law of mass action. Thick-walled nmr tubes fitted with a suitable pressure valve and capable of withstanding pressures of up to 50 atm were used for these experiments (for details see the Experimental Section).[13]

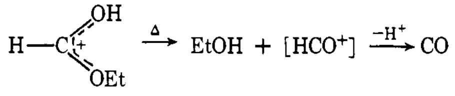
In addition to the protolytic cleavage of formic and acetic formic anhydrides, we attempted to prepare the formyl cation by the direct protonation of carbon monoxide with superacids, by the ionization of formyl fluoride[14] with antimony pentafluoride, by the cleavage of protonated formic acid and ethyl formate in superacid, as well as by cleavage in superacids of *N*-formylpiperidine, *N*,*N*-diformylpiperazine, and *N*-formylimidazole.

In all attempted cases, the formyl cation could not be observed, even at the lowest possible temperatures (−130°) and under CO pressure (50 atm).

$$H^+ + CO \rightleftharpoons [HCO^+]$$

$$FCHO + SbF_5 \rightleftharpoons [HCO^+]SbF_6^- \rightleftharpoons CO + HF + SbF_5$$

$$HCOOH_2^+ \xrightarrow{\Delta} H_2O + [HCO^+] \xrightarrow{-H^+} CO$$



$$H{-}\overset{OH}{\underset{OEt}{C^+}} \xrightarrow{\Delta} EtOH + [HCO^+] \xrightarrow{-H^+} CO$$

Treating *N*-formylpiperidine, *N*,*N*-diformylpiperazine, and 1,1-carbonyldiimidazole with superacid gave only the stable mono- and diprotonated cations **5**, **6**, and **7**, respectively. No cleavage reactions were observed, even when the solutions were allowed to warm to 0°. The pmr spectra of ions **5**, **6**, and **7** are in accordance with the protonated structures shown. On the other hand, protonation of *N*-formylimidazole in FSO_3H-SbF_5-SO_2ClF solution leads to the cleavage products protonated imidazole and carbon monoxide, again with no observation of formyl action.

Attempts to prepare the long-lived formyl cation by all methods were unsuccessful, although the ion is known to exist in the gas phase (based on mass spectrometric studies)[15] and theoretical calculations, including recent *ab initio* calculations by Ros[16] and Forsen,[17] have indicated the formyl cation as a stable species. Although the formyl cation is thought to be an intermediate in the Gattermann–Koch reaction it has never been directly observed in solution. The instability of the long-lived formyl cation in superacid media, which

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[12] E. Lidner and H. Hranz, *Chem. Ber.*, **99**, 3800 (1966).

[13] The tube is a somewhat modified version of that designed and used by Dr. H. J. Bernstein, Division of Pure Chemistry, National Research Council, Ottawa 7, Canada, whose help in providing details of this pressure tube we gratefully acknowledge.

[14] G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **82**, 2380 (1960).

[15] R. I. Reed, *Trans. Faraday Soc.*, **52**, 1195 (1956).

[16] H. B. Jansen and P. Ros, *Chem. Phys. Lett.*, **3**, 140 (1969).

[17] S. Forsen and B. Roos, *ibid.*, **6**, 128 (1970).

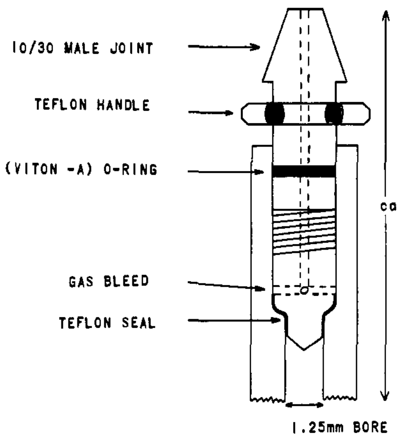
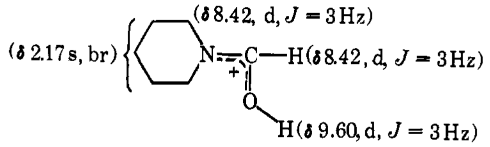


Figure 2. High-pressure nmr tube with valve.

generally provide stable ion conditions, may be caused by the oxygen lone-pair electrons undergoing a second protolytic interaction with the solvent. As the lone-pair interaction proceeds, the developing dicationic species, which is highly destabilized by charge–charge repulsion, immediately decomposes *via* proton elimination from carbon to give oxygen-protonated carbon monoxide which then exchanges rapidly with the acid solvent.



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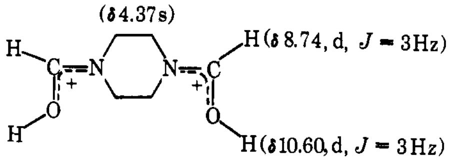

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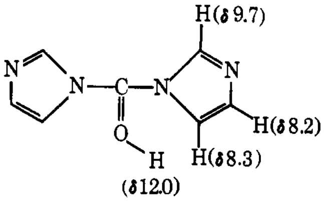

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$$\mathrm{HCO^+ + H^+ \rightleftharpoons [H\overset{+}{-}C{\equiv}O{-}{-}H^+] \longrightarrow}$$

$$\mathrm{H^+[C{\equiv}O\overset{+}{-}H] \longrightarrow H^+ + CO}$$

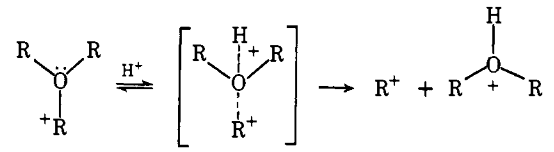
The suggestion for the protolytic instability of the formyl cation has some similarity with certain cleavage reactions of alkyloxocarbenium ions and trialkyloxonium ions in superacids.

The acetyl (methyloxocarbenium) ion and *n*-alkyloxocarbenium ions show expected stability, whereas *sec*- and *tert*-alkyloxocarbenium ions, such as the pivalyl cation (*tert*-butyloxocarbenium ion), cleave with ease due to the stability of the carbenium ion formed. Whereas we realize that the suggestion of protolytic cleavage of acyl cations is at this time speculative, as it

$$\mathrm{(CH_3)_3C\overset{+}{C}O \overset{H^+}{\rightleftharpoons} [(CH_3)_3C\overset{+}{-}{-}C{\equiv}O{-}\overset{+}{-}H] \longrightarrow}$$

$$\mathrm{(CH_3)_3C^+ + [CO\overset{+}{—}\dot{H}] \longrightarrow CO + H^+}$$

is not based on experimental observations, still a relationship with protonation of lone-pair electrons in oxonium ions can be considered. It was found in our laboratories[18] that Meerwein's trialkyloxonium ions, including the trimethyloxonium ion, which are selective heteroatom but not carbon-alkylating agents, in the presence of superacids become extremely reactive alkylating agents for aromatics; protonated dialkyl ethers are formed as by-products in the reaction. When tri-*n*-butyloxonium ion is treated with FSO_3H-SbF_5-SO_2ClF the cleaved butyl cation is directly observed as the rearranged *tert*-butyl cation.

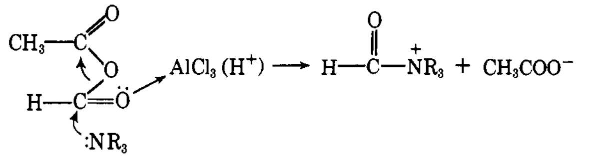


Whether protonation of ketene, $CH_2{=}C{=}O$, involves C- or O-protonation, followed by intramolecular rearrangement or a somewhat similar intermolecular process, is not possible to determine. The acetyl cation is the only observed species in superacid solution. C-Protonation would directly give the ion. However, if O-protonation would take place first, subsequent carbon protonation would yield a dication, destabilized by charge–charge repulsion, which would deprotonate to the stable acetyl cation. Attempts to observe protonated acyl (and substituted acyl) cations in superacid solution at very low temperatures were so far unsuccessful.

$$\mathrm{CH_2{=}C{=}O \overset{H^+}{\rightleftharpoons} CH_3\overset{+}{C}O \overset{H^+}{\rightleftharpoons} [H{-}{-}{-}CH_2{}^+{—}C{\equiv}O^+{-}{-}{-}H] \overset{H^+}{\rightleftharpoons}}$$

$$\mathrm{CH_2{=}C{=}\overset{+}{O}H \overset{H^+}{\rightleftharpoons} CH_2{=}C{=}O}$$

The relative instability of the formyl cation under acid-catalyzed conditions is indicated in the Friedel–Crafts formylation[14] reaction of aromatics with acetic formic anhydride. Substitution by HCO^+ would give aldehydes but the exclusive products observed are methyl ketones indicating substitution by CH_3CO^+. Acetic formic anhydride reacts with amines, however, to give exclusively formamides. The formylation of amines by acetic formic anhydride was proposed to go through the formyl cation.[5] Due, however, to the observed instability of HCO^+ in acid media, the reaction can be better considered of the SN2 type.



Experimental Section

Materials. All symmetrical anhydrides used were commercially available except formic anhydride, which was prepared according to the method of Muramatsu.[11] Assymmetrical anhydrides were prepared by the method of Hurd and Roe as used by Stevens and Van Es[5] to prepare acetic formic anhydride.

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(18) Unpublished results.

Formyl fluoride was prepared according to the method of Olah and Kuhn.[11] *N*-Formylpiperidine, *N,N*-diformylpiperazine, and 1,1′-carbonyldiimidazole were obtained from Aldrich Chemical Co. *N*-Formylimidazole was prepared according to the method of Staab and Polenski.[19]

Protonation of Carboxylic Acid Anhydrides. Protonated anhydrides were prepared by slow addition of an SO_2 solution of fluorosulfuric acid–antimony pentafluoride (1:1 *M*) to an SO_2 solution of the anhydride at −80°.

Attempted Preparation of the Formyl Cation. (a) An SO_2ClF solution of formyl fluoride was added to an SO_2ClF solution of antimony pentafluoride in a pressure nmr tube at −120°. The nmr tube was then pressurized with carbon monoxide, sealed, and then carefully shaken to allow mixing. (b) Protonation of carbon monoxide was attempted by pressurizing the pressure nmr tube containing an SO_2ClF solution of fluorosulfuric acid–antimony pentafluoride (1:1 *M*) at −80° with carbon monoxide. (c) Protonated formic acid was prepared by the addition of an SO_2 solution of formic acid to an SO_2 solution of fluorosulfuric acid–antimony pentafluoride (1:1 *M*) at −80°. The solution was transferred to a pressure nmr tube which was sealed under a pressure of carbon monoxide at −80°. The temperature was raised until cleavage occurred. (d) Protonated ethyl formate was prepared and treated as above. (e) Solutions of *N*-formylpiperidine, *N,N*-diformylpiperazine, and *N*-formylimidazole were made up in FSO_3H–SbF_5–SO_2ClF at −80°.

Pressure Nmr Tube. The pressure nmr tubes[13] were prepared by mounting a Fischer–Porter threaded glass needle valve on a 5 mm o.d., 3 mm i.d. thick-walled Pyrex nmr tube. The valve consists of a glass body of 1.25 mm bore and a Teflon stem which is double-sealed by a Viton-A O-ring and a machined Teflon neck. The head of the Teflon stem was machined to a 10/30 male joint and a fine gas bleed was drilled through the Teflon stem to the seal (Figure 2).

Acknowledgment. Support of our work by the National Institutes of Health and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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Platinum Hydride Addition to Geranyl and Farnesyl Methyl Ether[1]

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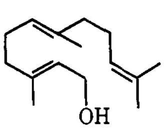
Contribution from the Department of Chemistry, The Florida State University, Tallahassee, Florida 32306. *Received October 5, 1971*

Abstract: The reaction of geranyl methyl ether with dipotassium tetrachloroplatinate(II) in aqueous ethanol afforded the σ-complex di-μ-chloro-bis(1-methoxy-3,7-dimethyl-2-octene-6σ,2π)diplatinum(II) (**7**) and 2,6-dimethyl-8-methoxy-6-octen-3-one (**9**) as major products. Proof of structure for these compounds and a study of the mechanism of the reaction are given. Similar treatment of farnesyl methyl ether gave a large number of products from which two σ complexes and an analogous ketone were isolated.

In an attempt to carry out a laboratory synthesis based on the proposed[3] enzymic conversion of farnesol (**1**) to medium ring sesquiterpenes such as germacrene B[4,5] (**2**), we were interested in preparing an olefin–transition metal π complex of general structure **3**. It was hoped that the conformational restrictions imposed by the metal on the farnesyl moiety in complex **3** would be sufficient to allow acid-catalyzed ten-membered ring cyclization to take precedence over the usually favored[6] six-membered ring formation. Consequently an investigation into the formation of such a complex was undertaken.



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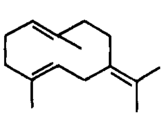

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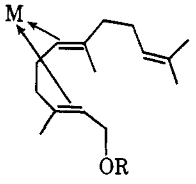

3

A number of metals such as silver, platinum, palladium, rhodium, iron, and nickel have been shown to give relatively stable π complexes with various olefinic ligands.[7] The stability of these complexes depends on several factors, including the nature of the metal, the nature of the substituents on the olefinic carbons,[8] the nature of the inorganic ligands,[9] and in the case of some diolefin–metal complexes, on the conformational rigidity of the diolefin.[9] The choice of metal to be used in complex **3** was restricted in that it had to be one that would accept an acyclic 1,5-diene as a bidentate ligand to give a stable complex, but not cause double bond isomerization. The most closely related known complexes were those of 1,5-hexadiene with platinum(II) and rhodium(I); no examples of complexes involving a more highly substituted acyclic diene could be found. The platinum complex, dichloro(1,5-hexadiene)platinum(II)[9,10] (**4**), was chosen as the best analogy on which to base the desired investigation.[11]

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(1) For a preliminary account of portions of this work, see M. A. Schwartz and T. J. Dunn, *J. Amer. Chem. Soc.*, **91**, 4007 (1969). We gratefully acknowledge the Research Corporation for partial support of this work.

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