Communications to the Editor

Stable Carbonium Ions. XXXIX.[1] Formation of Alkylcarbonium Ions *via* Hydride Ion Abstraction from Alkanes in Fluorosulfonic Acid–Antimony Pentafluoride Solution. Isolation of Some Crystalline Alkylcarbonium Ion Salts

Sir:

We have previously reported the generation of stable alkylcarbonium ions from alkyl halides in SbF_5 and SbF_5–SO_2 solutions[2] and from alcohols in FSO_3H–SbF_5 solution.[3] We wish now to report our observations relating to the generation of alkylcarbonium ions from alkanes *via* hydride (methide) ion abstraction with the extremely strong acid FSO_3H–SbF_5.

$$R_3CH \xrightarrow{FSO_3H-SbF_5} R_3C^+SbF_5FSO_3^- + H_2$$

n-Butane and isobutane both form exclusively the *t*-butyl cation I (sharp singlet at −4.50 ppm). The *t*-butyl cation is, in our experience, the most stable alkylcarbonium ion. When generated in FSO_3H–SbF_5 solution *via* the hydride ion abstraction the solutions of I are unchanged even after having been heated to 150°. All other investigated alkylcarbonium ions were observed to convert to ion I at higher temperatures through various fragmentation (and isomerization) pathways.

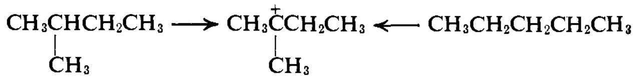
$$(CH_3)_3CH \longrightarrow \underset{\text{I}}{(CH_3)_3C^+} \longleftarrow CH_3CH_2CH_2CH_3$$

n-Pentane and isopentane are ionized in FSO_3H–SbF_5 to the *t*-amyl cation (II). At −30° the pmr spectrum (see Table I) shows a methyl triplet at −4.42 ppm (with the large long-range coupling, $^4J_{H-H}$ = 5.0 Hz, through the sp^2 hybridized carbonium ion carbon atom), methylene multiplet at −4.75 ppm, and methyl triplet at −2.17 ppm ($^3J_{H-H}$ = 5.6 Hz).

Table I. Nmr Data of Alkylcarbonium Ions in FSO_3H–SbF_5 Solution

Ion	Temp, °C	δ, ppm (J_{H-H}, Hz)[a] α-CH_3	β-CH_3	α-CH_2	β-CH_2
I	100	−4.50 s			
II	−30	−4.42 tr (5.0)	−2.17 tr (5.6)	−4.75 m	
	90		−3.60 m	−4.75 m	
III	40	−4.40 q (4.8)	−2.20 tr (4.8)	−4.70 m	
IV	40	−4.30 tr (4.8)	−1.83 tr (4.8)	−4.70 m	−2.72 m
V	80	−3.32 d (4.2)			

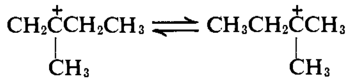
[a] From TMS in a capillary centered in the nmr tube; s, singlet, d, doublet, tr, triplet, q, quintuplet, and m, multiplet.



$$\underset{CH_3}{CH_3\overset{|}{C}HCH_2CH_3} \longrightarrow \underset{CH_3}{CH_3\overset{+}{C}CH_2CH_3} \longleftarrow CH_3CH_2CH_2CH_2CH_3$$

II

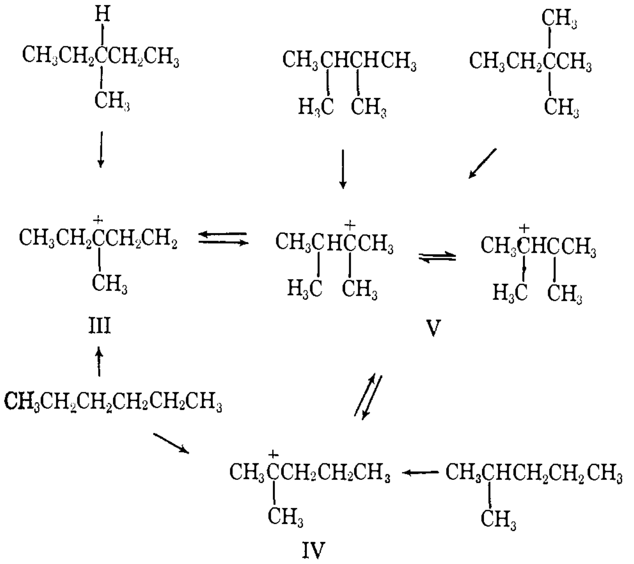
With increasing temperature the methyl peaks start to coalesce until they collapse at 90° to give a single broad peak at −3.60 ppm. The position of the board methylene peak is unchanged, with the fine structure lost. The observed temperature dependence of the spectrum of II indicates equilibration at elevated temperatures.



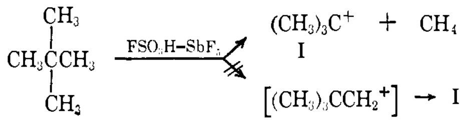
$$\underset{CH_3}{CH_2\overset{+}{C}CH_2CH_3} \rightleftharpoons \underset{CH_3}{CH_3CH_2\overset{+}{C}CH_3}$$

It is significant, however, that in FSO_3H–SbF_5 solution this is observed only at substantially higher temperatures than in SbF_5 or SbF_5–SO_2 solution.[2] At 150° the rate of decomposition of II to I is still slow. These observations seem to indicate remarkable stabilization of alkylcarbonium ions in the highly acidic solvent, involving in all probability solvation of tight ion pairs.

n-Hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane all show in FSO_3H–SbF_5 solution at room temperature a spectrum (Figure 1) consisting of all three isomeric tertiary hexyl cations: the methyldiethylcarbonium ion (III), the dimethyl-*n*-propylcarbonium ion (IV), and the dimethylisopropylcarbonium ion (V). On heating, ions III and IV are increasingly converted into ion V, which seems to be the most stable hexyl cation. The spectrum of ion V consists of a single doublet at −3.32 ppm (J_{H-H} = 4.2 Hz), indicating a rapid 1,2-hydrogen shift which cannot be frozen out even at the lowest temperatures attainable in the used acid solvent system. The *t*-hexyl cations convert to the *t*-butyl cation (I) above 80°.



Neopentane (2,2-dimethylpropane) forms ion I and not II. This observation indicates that the extremely strong acid FSO_3H–SbF_5 is capable of extracting a methide ion from a tertiary position (methane evolved in the reaction was identified by mass spectroscopy) in preference to abstraction of hydride ion from a primary position (which would lead to the neopentyl cation



$$\underset{CH_3}{\overset{CH_3}{CH_3CCH_3}} \xrightarrow{FSO_3H-SbF_5} \begin{cases} (CH_3)_3C^+ + CH_4 \\ [(CH_3)_3CCH_2^+] \rightarrow \text{II} \end{cases}$$

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[1] Part XXXVIII: G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, in press.

[2] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

[3] G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965).

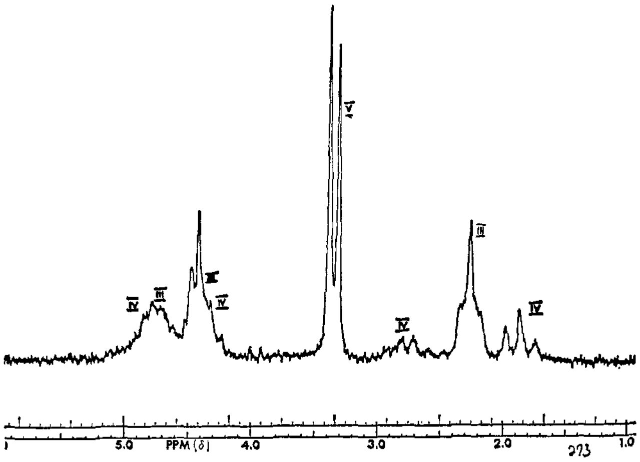

Figure 1. Nmr spectrum of *t*-hexyl cations in FSO_3H-SbF_5 solutions.

known to rearrange extremely rapidly to ion II). Alkanes with more than seven carbon atoms in FSO_3H-SbF_5 solution at room or more elevated temperature all convert to ion I. Investigated examples are: *n*-heptane, 2,2,3-trimethylbutane, 3-ethylpentane, 2,4-dimethylpentane, 2-methylhexane, 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, 2,2,3-trimethylpentane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, and hexadecane. Even paraffin wax and polyethylene gave ion I. Obviously complex isomerization and fragmentation processes in the strong acid solution lead ultimately to the very stable *t*-butyl cation (I).

Methane does not ionize under the reaction conditions. Ethane gives a mixture of 90% I and 10% V through some dimerization and trimerization pathway. Propane forms also I and V, the amount of the latter decreasing with increasing acid strength.

The fate of the hydride ion abstracted is not yet fully determined in the reactions. In all probability it forms molecular hydrogen by adding to a proton, part of which is observed to escape from the reaction mixture. The bulk of the nascent hydrogen, however, seems to reduce fluorosulfonic or fluoroantimonysulfonic acid.

In a typical experiment, the alkane and a tenfold (weight) excess of acid (1:1 FSO_3H-SbF_5) were vigorously stirred at room temperature until they formed a homogenous colorless mixture. The reaction is carried out with exclusion of moisture and is generally completed in 10–30 min. When using gaseous alkanes they are bubbled through the acid mixture in a slow stream.

The most surprising observation of our work is that salts of the alkyl cations I, II, and V (probably highly solvated) can be obtained and crystallized from SO_2 or SO_2ClF solutions at low temperatures (−60 to −100°). They are stable, at least to room temperature. Resolved in SO_2 they give the unchanged nmr spectra of the ions. Studies (with Professor M. Sundaralingam) on the X-ray crystallographic investigation of these alkylcarbonium ion salts are in progress.

Acknowledgment. Generous support of the work by grants of the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

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Received January 21, 1967

The Relative Sign of $J_{C^{13}-C^{13}}$

Sir:

Proton stabilization of the magnetic field in an analog frequency sweep spectrometer (Varian AFS-60) allows one to use time-averaging techniques (Varian C-1024) in the observation of C^{13} signals of relatively low intensity. This enhanced sensitivity is utilized to observe the $C^{13}-C^{13}$ splittings in an acetic acid sample which has been enriched in the carboxyl position with C^{13} to 20 atom %. Under these conditions only 0.2% of the sample molecules contains the C^{13} label in both carbon positions of acetic acid, as the 1.1% natural abundance still obtains in the methyl carbon. Figure 1 exhibits the proton-decoupled C^{13} spectrum of the carboxylic region of acetic acid. With the heteronuclear decoupler adjusted to the center of the methyl proton resonance frequency, f_0, an intense carboxyl C^{13} singlet, lowest trace, is observed for the $CH_3C^{13}O_2H$ molecules (about 20%) existing in the sample. The less intense carboxyl doublet, arising from the $C^{13}-C^{13}$ splitting in the doubly labeled species, is shown in the upper two traces for the proton decoupling frequencies f_0 −66 and +66 cps, respectively. As the directly bonded C^{13}–H coupling constant in this compound is 132 cps, these two decoupling frequencies correspond to the resonance positions of the methyl C^{13} satellites in the proton spectrum. With the magnetic field locked to the same external water sample in each instance, irradiation of the lower frequency proton line enhances the lower C^{13} line of the methyl-induced doublet. Conversely, irradiation with a frequency of f_0 +66 resulted in the higher frequency carboxyl line being enhanced (note: frequency increases to the left in Figure 1 in order to have a consistent spectral appearance with field-sweep spectra). These data indicate that the directly bonded $J_{C^{13}-C^{13}}$ has the same relative sign as the directly bonded $J_{C^{13}-H}$. As the absolute sign of directly bonded C^{13}–H couplings[1] has already been shown to be positive, it follows that the directly bonded $J_{C^{13}-C^{13}}$ should have a positive absolute sign. Furthermore, as the coupling magnitudes of Frei and Bernstein[2] are comparable with the 57.6-cps $C^{13}-C^{13}$ coupling observed here for acetic acid, it is reasonable to conclude that other directly bonded $C^{13}-C^{13}$ couplings will also be positive.

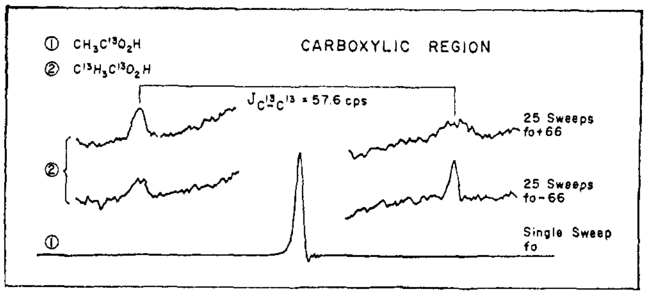

Figure 1. Carbon-13 magnetic resonance spectra of the carboxylic region of acetic acid with proton decoupling. The frequency, f_0, is the methyl proton resonance frequency for acetic acid at the magnetic field strength used in this study.

Early theoretical considerations[3] of directly bonded

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[1] A. D. Buckingham and K. A. McLauchlan, *Proc. Chem. Soc.*, 144 (1963).

[2] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

[3] M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).