well with the inductive substituent constants." They concluded that 2-naphthyl β-D-glucuronide (XXVII), as well as other glucuronides, hydrolyze by specific acid catalyzed mechanisms only.

In conclusion it may be stated that of the 15 compounds in Table IV, all of the ketals (from this study)

and most acetals hydrolyze by specific acid catalysis. Only the acetals XXV and XXVI may hydrolyze in the low-acid region by carboxyl group participation.

Stable Carbonium Ions. XLI.[1a] Protonated Aliphatic Alcohols and Their Cleavage to Carbonium Ions

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Abstract: A series of aliphatic alcohols have been studied in HSO_3F–SbF_5–SO_2 solution. O-Protonation was observed by nmr spectroscopy with negligible exchange rates at temperatures ranging from -60 to $+60°$. The protonated alcohols cleave at higher temperatures to carbonium ions. The kinetics of cleavage of protonated 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol have been measured by nmr spectroscopy, and the mechanism of the reaction is discussed.

W e reported in a previous short preliminary communication[2] that normal and secondary aliphatic alcohols can be protonated in the strong acid system FSO_3H–SbF_5–SO_2 and can be observed at $-60°$ with slow exchange rates. We wish now to report in detail the observation of protonated aliphatic alcohols at temperatures up to $+60°$ and their cleavage to carbonium ions.

Results and Discussion

The following aliphatic alcohols were protonated in FSO_3H–SbF_5–SO_2 solution at $-60°$: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-amyl, isoamyl, neopentyl, n-hexyl, and neohexyl alcohol.

The protonated aliphatic alcohols give well-resolved nmr spectra at $-60°$.

$$ROH \xrightarrow[-60°]{FSO_3H-SbF_5-SO_2} R\overset{+}{O}H_2$$
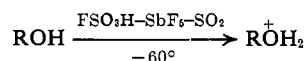
The protons on oxygen are shifted downfield approximately to -9.3 ppm from external TMS capillary. Figures 1–12 show the nmr spectra at $-60°$. Assignments of chemical shifts and coupling constants are summarized in Table I.

Protonated Methyl Alcohol. $CH_3OH_2^+$ (Figure 1) shows the methyl triplet at 4.7 ppm and the OH_2^+ quadruplet at -9.4 ppm, $J_{H-H} = 3.6$ cps.

Protonated Ethyl Alcohol. $CH_3CH_2OH_2^+$ (Figure 2) shows the methyl triplet at -1.9 ppm ($J_{H-H} = 7.1$ cps) and the OH_2^+ triplet at -9.3 ppm ($J_{H-H} = 3.6$ cps).

The methylene signal is the expected nine-line pattern at -4.9 ppm as the coupling with the CH_3 group is about twice that with OH_2^+.

Protonated n-Propyl Alcohol. $CH_3CH_2CH_2OH_2^+$ (Figure 3) shows the methyl triplet at -0.8 ppm ($J_{H-H} = 7.2$ cps), the C_2 methylene multiplet (six lines) at -1.8 ppm, the C_1 methylene multiplet (seven lines) at -4.7 ppm, and the OH_2^+ triplet at -9.4 ppm ($J_{HH} = 3.5$ cps).

Protonated Isopropyl Alcohol. $(CH_3)_2CHOH_2^+$ (Figure 4) shows the methyl doublet at -1.7 ppm ($J_{HH} = 7.0$ cps), the OH_2^+ doublet at -9.1 ppm ($J_{HH} = 3.0$ cps), and the methine proton multiplet at -5.5 ppm.

Protonated n-Butyl Alcohol. $CH_3CH_2CH_2CH_2OH_2^+$ (Figure 5) shows the methyl triplet at -1.1 ppm ($J_{HH} = 7.0$ cps), methylene multiplets (C_2, C_3) between -1.2 and -2.1 ppm, the C_1 multiplet (seven lines) at -5.0 ppm, and the OH_2^+ triplet at -9.4 ppm ($J_{HH} = 3.5$ cps).

Protonated Isobutyl Alcohol. $(CH_3)_2CHCH_2OH_2^+$ (Figure 6) shows the methyl doublet at -1.1 ppm ($J_{HH} = 7.0$ cps), the methine proton multiplet at -2.3 ppm, the methylene multiplet (five lines) at -4.7 ppm, and the OH_2^+ triplet at -9.4 ppm ($J_{HH} = 3.6$ cps).

Protonated sec-Butyl Alcohol. $CH_3C(OH_2^+)HCH_2CH_3$ (Figure 7) shows one methyl triplet at -0.9 ppm ($J_{HH} = 7.5$ cps), the methyl group nearest to the oxygen as a doublet at -2.6 ppm ($J_{HH} = 6.4$ cps), the methylene multiplet at -1.9 ppm, the methine proton multiplet at -5.4 ppm, and the OH_2^+ doublet at -9.1 ppm ($J_{HH} = 3.0$ cps).

Protonated n-Amyl Alcohol. $CH_3(CH_2)_4OH_2^+$ (Figure 8) shows the methyl triplet at -0.9 ppm, the methylene (C_2 to C_4) multiplets between -1.1 and -2.3 ppm, the C_1 methylene multiplet (seven lines) at -4.9 ppm, and the OH_2^+ triplet at -9.3 ppm ($J_{HH} = 3.4$ cps).

(1) (a) Part XL: G. A. Olah, D. H. O'Brien, and C. U. Pittman Jr., *J. Am. Chem. Soc.*, **89**, 2996 (1967); (b) NATO Postdoctoral Research Investigator, 1966–1967; (c) National Science Foundation Postdoctoral Investigator, 1965–1966.
(2) G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966).

Table I. Nmr Shifts and Coupling Contents of Protonated Alcohols[a] at −60° in HSO_3F–SbF_5–SO_2

Alcohol	OH_2	H_1	H_2	H_3	H_4	H_5	H_6	J_{HOH}, cps
1 CH_3OH	−9.4(q)[b]	−4.7(t)						3.6
2 1 CH_3CH_2OH	−9.3(t)	−4.9(m)	−1.9(t)					3.6
3 2 1 $CH_3CH_2CH_2OH$	−9.4(t)	−4.7(m)	−1.8(m)	−0.8(t)				3.5
2 1 CH_3CHCH_3 | OH	−9.1(d)	−5.5(m)	−1.7(d)					3.0
4 3 2 1 $CH_3CH_2CH_2CH_2OH$	−9.4(t)	−5.0(m)	~2.0(m)	~1.4(m)	−1.1(t)			3.5
3 2 1 $\frac{CH_3}{CH_3}$>$CHCH_2OH$	−9.4(t)	−4.7(m)	−2.3(m)	−1.1(d)				3.6
4 3 1 2 $CH_3CH_2CHOHCH_3$	−9.1(d)	−5.4(m)	−1.6(d)	−1.9(m)	−0.9(t)			3.0
5 4 3 2 1 $CH_3CH_2CH_2CH_2CH_2OH$	−9.3(t)	−4.9(m)	−2.3(m)→ −1.1 (H_2–H_4)			−0.9		3.4
4 3 2 1 $\frac{CH_3}{CH_3}$>$CHCH_2CH_2OH$	−9.4(t)	−4.3(m)	~1.8(m) (H_2–H_3)		−0.9(d)			3.6
2 1 $(CH_3)_3CCH_2OH$	−9.5(t)	−4.5(t)	−1.0(s)					3.7
6 5 4 3 2 1 $CH_3CH_2CH_2CH_2CH_2CH_2OH$	−9.2(t)	−4.8(m)	−2.8(m) to −0.8 (H_2–H_6)					3.5
3 2 1 $(CH_3)_3CCH_2CH_2OH$	−9.3(t)	−4.9(m)	−1.9(t)	−0.8(s)				3.5

[a] From TMS external capillary. [b] Multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet.

Protonated Isoamyl Alcohol. $(CH_3)_2CHCH_2$-$CH_2OH_2^+$ (Figure 9) shows the methyl doublet (J_{HH} = 6.2 cps) at −0.9 ppm, the C_2 methylene multiplet and the methine proton multiplet at −1.8 ppm, the C_1 methylene multiplet at −4.9 ppm (seven lines), and the OH_2^+ triplet at −9.4 ppm (J_{HH} = 3.5 cps).

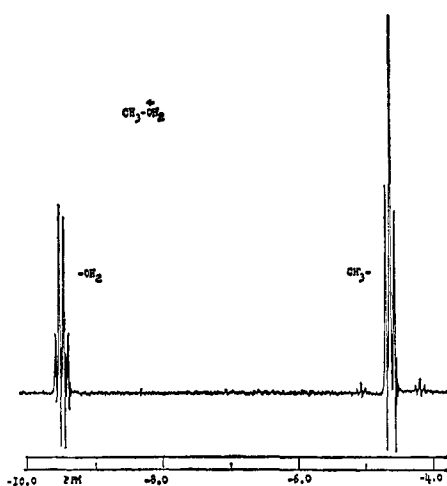appears at −4.8 ppm and the OH_2^+ triplet at −9.2 ppm (J_{HH} = 3.5 cps).

Protonated Neohexyl Alcohol. $(CH_3)_3CCH_2CH_2OH_2^+$ (Figure 13) shows the methyl singlet at −0.8 ppm, the C_2 methylene triplet at −1.9 ppm (J_{HH} = 8.2 cps), the C_1 methylene multiplet at −4.9 ppm, and the OH_2^+ triplet at −9.3 ppm (J_{HH} = 3.5 cps).

Figure 1.

Figure 2.

Protonated Neopentyl Alcohol. $(CH_3)_3CCH_2OH_2^+$ (Figure 10) shows the methyl singlet at −1.0 ppm, the C_1 methylene triplet at −4.5 ppm, and the OH_2^+ triplet at −9.5 ppm (J_{HH} = 3.8 cps).

Protonated n-Hexyl Alcohol. $CH_3(CH_2)_5OH_2^+$ (Figures 11 and 12) shows the methyl and the methylene (C_2 to C_4) lines as complex multiplets between −2.8 and −0.8 ppm. The C_1 methylene multiplet (seven lines)
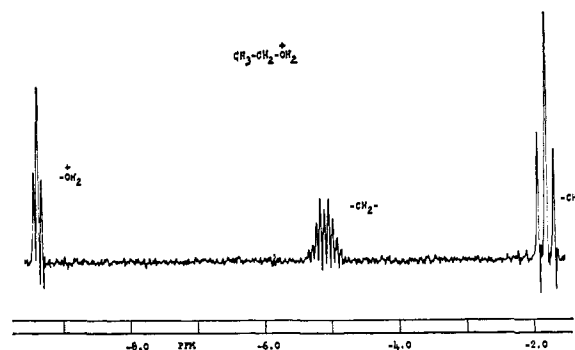
The OH_2^+ protons of the normal alcohols appear at a lower field (−9.3 to 9.5 ppm) than their homologs of the secondary alcohols (−9.1 ppm). This is due to a different charge distribution as confirmed by the C_1 protons appearing at higher field with the normal alcohols (−5.0 to 4.7 ppm) than for the C_1 methine proton of the secondary alcohol (−5.4 and 5.5 ppm).

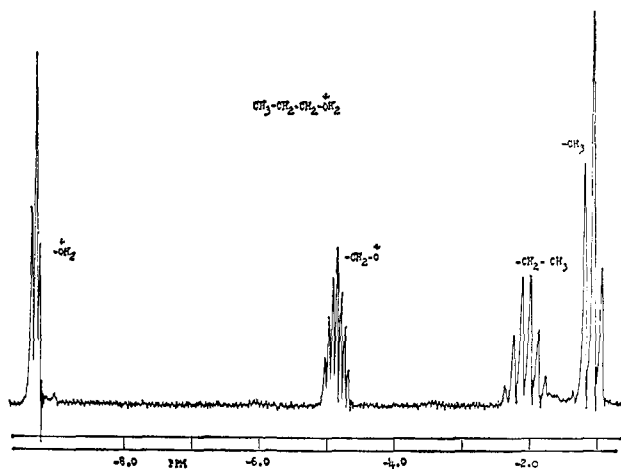Solutions of the protonated aliphatic alcohols in the strongly acidic solvent system show remarkable sta-
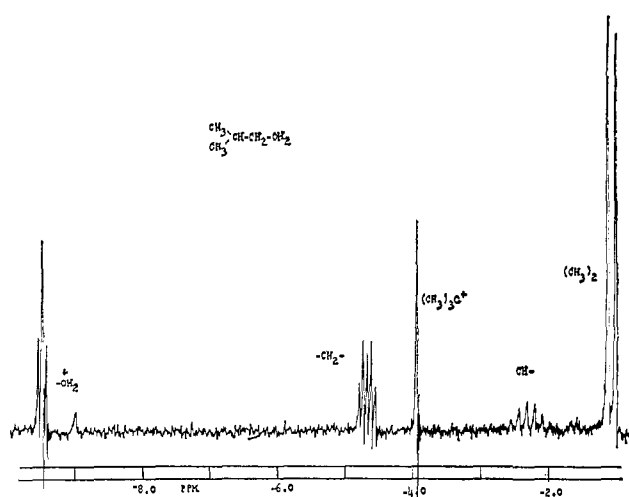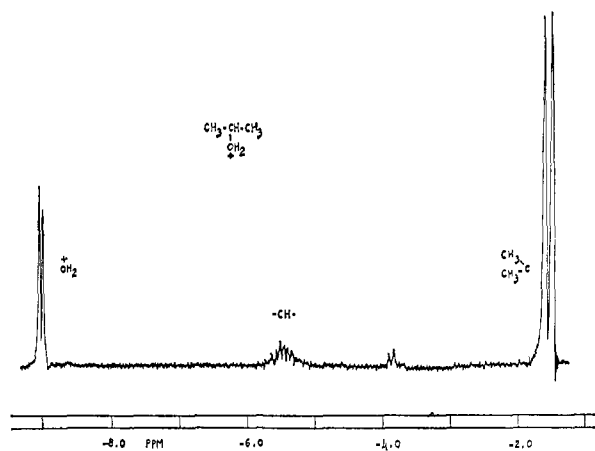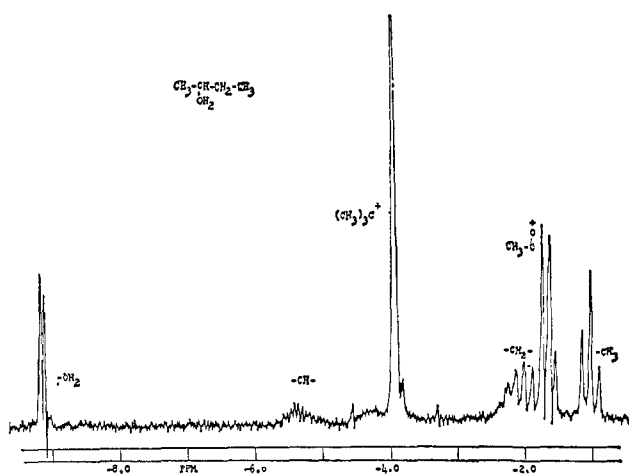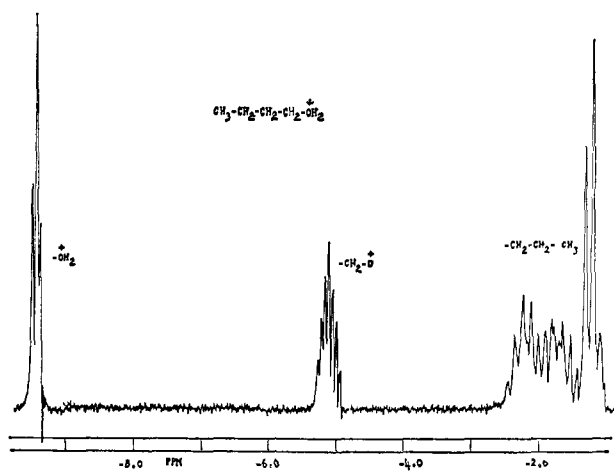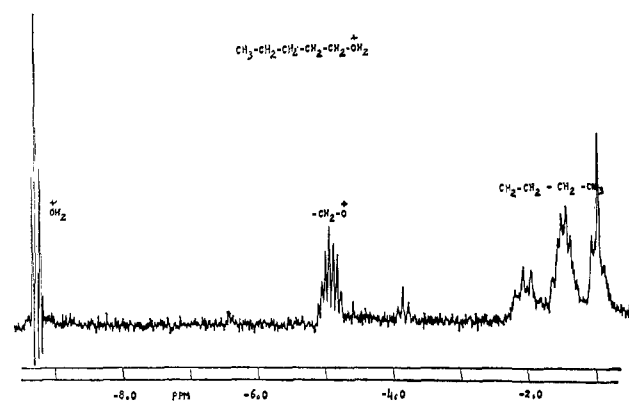
Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

bility. At higher temperatures they cleave to carbonium ions.[3]

$$\overset{+}{\text{ROH}_2} \xrightarrow[\text{SbF}_5-\text{FSO}_3\text{H}-\text{SO}_2]{\Delta} \text{R}^+ + \text{H}_3\text{O}^+$$
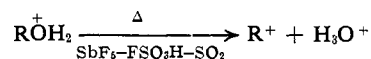
(3) The peak of variable intensity due to water is observed at −10.2 ppm. However, it has not yet been definitely established whether this resonance is due exclusively to H_3O^+ or to an intermediate hydrolysis product of the acid system, FSO_3H–SbF_5. For simplicity this peak as well as the main acid peak at −10.7 ppm were deleted from the spectra.

The carbonium ions formed rearrange very rapidly to the more stable isomer which can undergo secondary reactions such as hydride abstraction, disproportionation, and polymerization at elevated temperatures.

Kinetics of Cleavage

Protonated methyl alcohol is the most stable of all investigated protonated alcohols. It can be heated up to +50° without noticeable change in its nmr spectrum.

Figure 9.
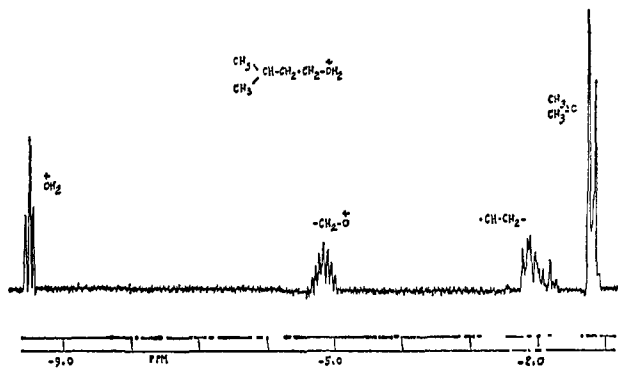

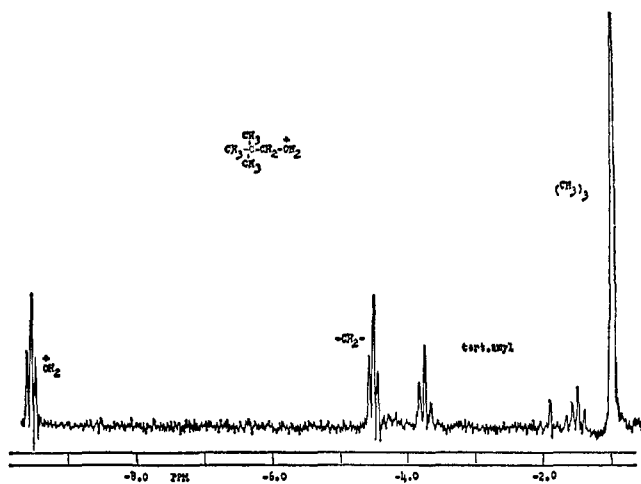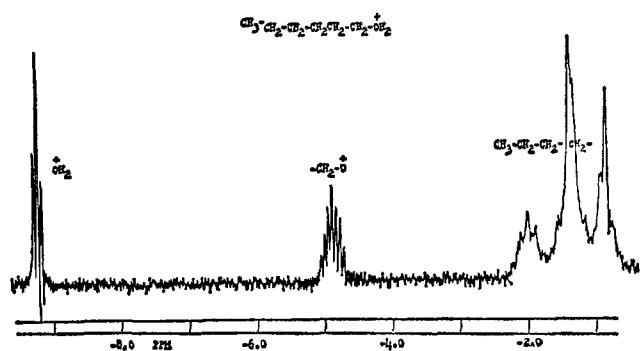Figure 12.

Figure 10.

Figure 13.

Figure 11.

Figure 14.

At +60° the lines broaden and decrease in intensity. The medium becomes viscous, then solid. The methyl cation CH_3^+ was not observed as a cleavage product.

Protonated ethyl alcohol is stable up to +30°. At higher temperatures the nmr lines show broadening and decreasing intensity with no other sharp line appearing. The medium then becomes viscous and solidifies after gas evolution. No kinetic study of cleavage was possible.

Protonated n-propyl alcohol is stable up to 0°. At higher temperature it cleaves, and it was found possible to measure the kinetics of its cleavage at temperatures ranging from +5 to +25° by following the disappearance of the OH_2^+ triplet with time. The integration of OH_2^+ triplet was compared to the integration of an
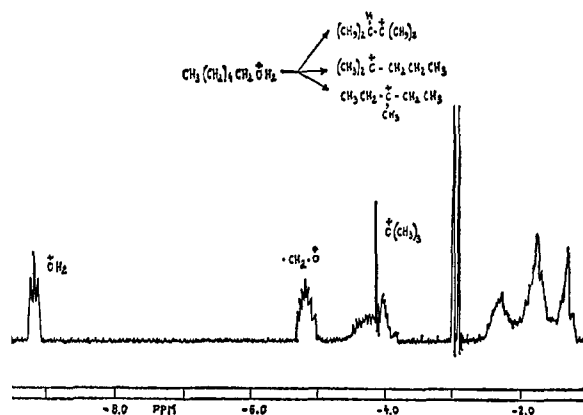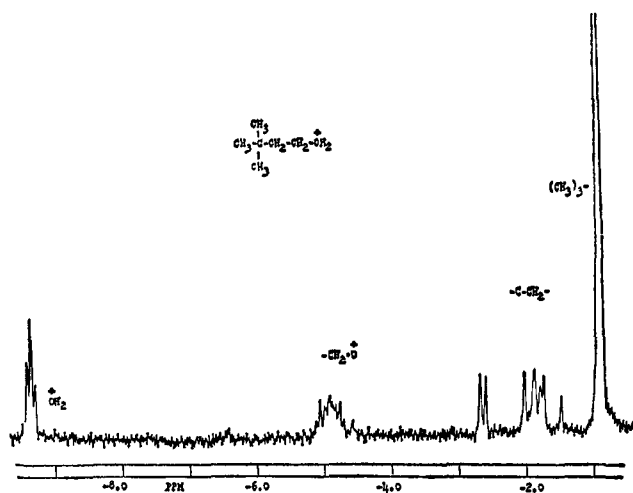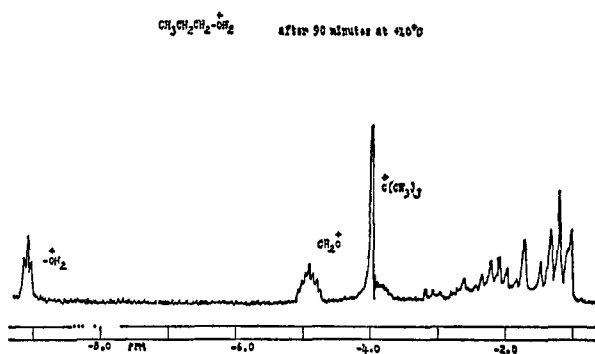
internal standard, tetramethylammonium hexafluoroantimonate, which gives a singlet at −3.1 ppm. The cleavage shows first-order kinetics with an activation energy of 19.8 kcal/mole. It was impossible to follow the kinetics by measuring the concentration of the dimethylcarbonium ion which is very unstable under the reaction conditions and undergoes secondary reactions. The nmr spectrum (Figure 14) recorded during the first half-life at +10° shows no presence of dimethylcarbonium ion but that of trimethylcarbonium ion (sharp singlet at −4 ppm) and t-hexyl cations. Kinetic data are listed in Tables II and III.

Table II. Rate of Cleavage of Protonated Normal Aliphatic Alcohols at 15°

Protonated alcohol	Rate constant $\times$ 10^{-3} min^{-1}
n-Methyl	Stable to +50°
n-Ethyl	Stable to +30°
n-Propyl	20.5
n-Butyl	48.1
n-Pentyl	68.4
n-Hexyl	91.4

Table III. Activation Energy of Cleavage of Protonated Alcohols to Carbonium Ions

Protonated alcohol	Cleavage activation energy, kcal/mole	No. of experiments
n-Propyl	19.82 ± 1.50	11
n-Butyl	19.98 ± 0.79	10
n-Pentyl	18.75 ± 0.94	8
n-Hexyl	18.63 ± 0.91	7

Protonated isopropyl alcohol is relatively unstable even at −60° and therefore it was not possible to study the kinetics of its cleavage.
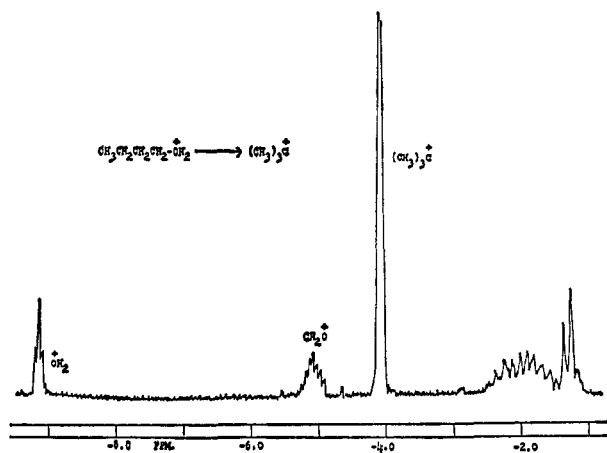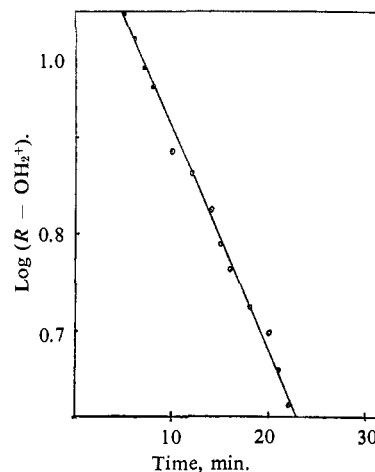

Figure 15.

Protonated *n*-butyl alcohol is stable up to 0° and its cleavage could be observed between +5 and +25°. The kinetics have been measured by following the decrease of the OH$_2^+$ triplet and the increase of the trimethylcarbonium ion singlet appearing at −4.0 ppm (Figure 15). The results show first-order rate for the cleavage (Figure 16) and during the first half-life a quantitative formation of trimethylcarbonium ion.

$$CH_3(CH_2)_3\overset{+}{O}H_2 \xrightarrow{k_1} [CH_3CH_2CH_2CH_2]^+ \xrightarrow{k_2} (CH_3)_3C^+$$
$$k_1 \ll k_2$$
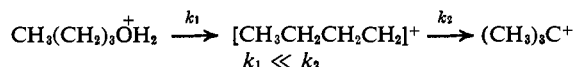
The rate-determining step is the cleavage of the protonated alcohol to the *n*-butyl cation (*n*-propylcarbonium ion). The latter rearranges very quickly to the most stable isomer (trimethylcarbonium ion), which is the only ion observed in the nmr spectra. The trimethylcarbonium ion itself undergoes under the reaction conditions slow secondary reactions which become noticeable within the experimental error only after the first

Figure 16. Cleavage of protonated 1-butanol at +20°.

half-life of the protonated alcohol. The activation energy of the cleavage of protonated 1-butanol was found to be 19.98 kcal/mole. The Arrhenius plot is shown in Figure 17.

Protonated isobutyl alcohol is relatively stable up to −30° and cleaves at higher temperature to the trimethylcarbonium ion. In Figure 6 some of this ion is already visible.

Protonated *sec*-butyl alcohol is slowly cleaved at −60° and a strong trimethylcarbonium ion singlet is already visible in the spectrum (Figure 7).

Protonated *t*-butyl alcohol could not be observed. Its cleavage at −60° is too fast. The only species observed in its acid solution is trimethylcarbonium ion.

Protonated *n*-amyl alcohol is stable up to 0° and cleaves at higher temperatures to the dimethylethylcarbonium ion (*t*-amyl cation). The kinetics of the cleavage have been measured between +5 and +25° by following the decay of the OH$_2^+$ triplet in the nmr spectra (Figure 18). Integration of suitable peaks of the dimethylethylcarbonium ion, (CH$_3$)$_2$C$^+$CH$_2$CH$_3$ (methylene multiplet at −4.5 ppm, *gem*-methyl triplet at −4.2 ppm), shows that the cleavage to the carbonium ion is quantitative during the first half-life of the protonated species. Later the *t*-amyl cation itself undergoes secondary reactions (including formation of trimethylcarbonium ion). The activation energy for the cleavage of protonated *n*-amyl alcohol was found to be 18.75 kcal/mole.

Protonated isoamyl alcohol is stable up to −30° and cleaves at higher temperatures to the *t*-amyl cation.

Protonated neopentyl alcohol is stable at −60° but cleaves above −50° to the *t*-amyl cation.

Protonated *n*-hexyl alcohol is stable up to 0°. The kinetics of its cleavage to isomeric hexyl cations has been measured between 0 and +20°. The results based on the decrease of the OH$_2^+$ peak show first-order kinetics. The cleavage forms the *n*-hexyl cation which is very unstable under these conditions and rearranges immediately to three isomeric *t*-hexyl cations:[4] the methyldiethylcarbonium ion (α-methyl triplet at −4.4 ppm, β-methyl triplet at −2.2 ppm, and methylene multiplet at −4.7 ppm), the dimethyl-*n*-propylcarbonium ion (α-methyl triplet at −4.3 ppm,

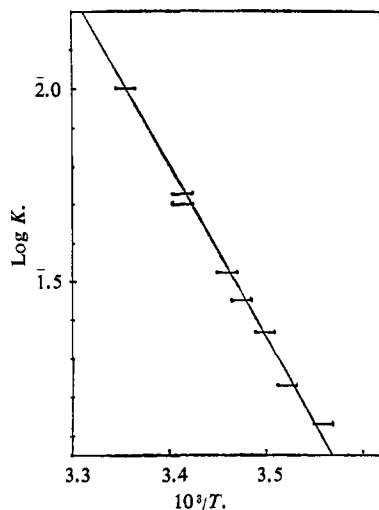(4) G. A. Olah and J. Lukas, *J. Am. Chem. Soc.* **89**, 2692 (1967).

Figure 17. Cleavage of protonated 1-butanol, Arrhenius plot.

Figure 18.

γ-methyl triplet at −2.7 ppm, α-methylene group at −4.7, and β-methylene multiplet at −2.7 ppm), and the dimethylisopropylcarbonium ion (doublet at −3.1 ppm). The cleavage does not give a quantitative yield of hexyl cations due to the fact that the hexyl cations easily undergo secondary reactions in this medium. We observe, for example, a singlet at −4.0 ppm (tri-methylcarbonium ion) due to disproportionation of the hexyl cations.

Protonated neohexyl alcohol is stable at −60° but undergoes cleavage to carbonium ions at temperatures higher than −50°.

In FSO₃H–SbF₅–SO₂ solution at −60° all normal and secondary aliphatic alcohols could be observed as stable O-protonated species. Observation of protonated t-butyl alcohol and t-amyl alcohol have so far been unsuccessful under these conditions, due to a very fast cleavage to the corresponding tertiary carbonium ions.

The cleavage to carbonium ions shown to follow a first-order rate in the case of the normal alcohols is enhanced by branching of the chain: protonated 1-pentanol is stable up to 0°, isopentyl alcohol is stable up to −30°, and neopentyl alcohol cleaves at −50°. The stability of the protonated primary alcohols decreases also as the chain length is increased. This is shown by comparison of the rate constants of the cleavage at 15°.

The activation energies were determined from the Arrhenius equation $K = Ae^{E_a/RT}$ and by measuring the reaction rates at various temperatures between 0 and +25°. The slope of the Arrhenius plot and the experimental error were determined by the method of least squares.
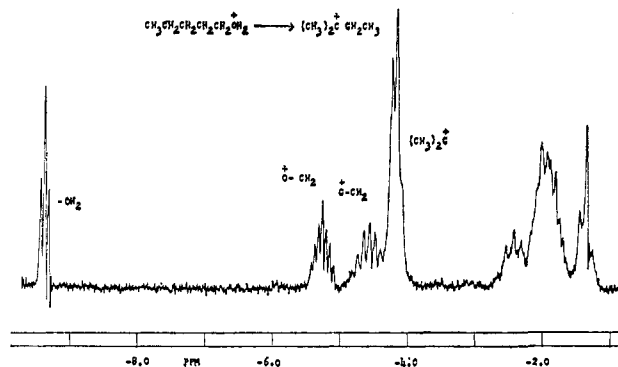
The activation energy of the cleavage seems to be almost identical for the primary protonated alcohols studied. We notice a small decrease from n-propyl to n-hexyl alcohol but this difference is within the experimental error and does not permit conclusions.

As the reaction rates are easy to determine from the slope of log $K = f$(time) (Figure 15), the main error remains the uncertainty of the temperature reading of the nmr sample during the kinetic runs.

Experimental Section

Materials. All alcohols were reagent grade materials used without further purification.

Nmr Spectra. Varian Associates Model A56-60A and A-60 nmr spectrometers with variable-temperature probes were used for all spectra. Samples of protonated alcohols were prepared by dissolving 1 ml of HSO₃F–SbF₅ (1:1 molar solution) in 2 ml of sulfur dioxide cooled to −70°. The alcohol (0.3 ml) was dissolved in 1 ml of sulfur dioxide, cooled to −70°, and added slowly to the acid mixture with vigorous agitation.

For the kinetic study, larger samples were prepared in the same manner (the molar ratio, acid mixture:alcohol 10:2). After the protonation, sulfur dioxide was pumped out under vacuum (1 mm) at −20°. All the kinetic runs were effected in neat SbF₅–FSO₃H solution.

The temperature was calibrated against the shift between the OH quartet and the methyl doublet of methanol before and after each run.

The concentration of the protonated species was measured by following the integration of the OH₂⁺ triplet compared to the integration of the singlet line of tetramethylammonium hexafluoro-antimonate, (CH₃)₄NSbF₆⁺, used as internal standard in the samples. The concentration of the carbonium ion formed was measured by the same internal standard method.