to H (eq 2, 3). This band appears only in the spectra of the adducts of [IrCl(CO)(Ph$_3$P)$_2$]. On the other hand, all the adducts of HCl (**2**, **3**, **6**, **7**, **10**, **11**) show a common property in the other ν_{IrCl} near 312 cm^{-1}, and this is compatible with the suggestion that the reacting halide (of HX) is found *trans* to CO in the adduct (eq 3, 4).[23]

The studies reported here are being extended to include observations on potential isomerization of the initial products (Table I) and formation of the HX adducts homogeneously in solution. We are also examining the structures of other types of adducts of [IrY(CO)(Ph$_3$P)$_2$], *e.g.*, with organic and metallic halides, and these will be described in subsequent communications.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (Grant No. HE-09678) of the U. S. Public Health Service, for partial support of this research. The author thanks Mr. S. L. Lindenberger for experimental assistance.

[23] In *trans*-[IrCl(CO)(Ph$_3$P)$_2$] and *trans*-[RhCl(CO)(Ph$_3$P)$_2$], the ν_{MCl} 's are found at 321 and 315 cm^{-1}, respectively.

[24] Address inquiries to this location.

L. Vaska

Department of Chemistry, Clarkson College of Technology
Potsdam, New York 13676,[24] *and Mellon Institute*
Pittsburgh, Pennsylvania 15213

Received August 11, 1966

Stable Carbonium Ions. XXVIII.[1] Protonated Aliphatic Alcohols

Sir:

We reported in previous work[2,3] that tertiary and certain secondary alcohols such as *t*-butyl alcohol, *t*-amyl alcohol, 1-adamantanol, 2-*exo*-norborneol, and miscellaneous phenylethyl alcohols ionize to stable carbonium ions in the extremely strong acid FSO$_3$H–SbF$_5$, generally diluted with SO$_2$. It was also found that less reactive secondary phenylethyl and phenylpropyl alcohols such as 3-phenyl-2-butanol and 1-phenyl-1-*p*-tolyl-2-propanol are only protonated in the same acid system, and at −60° (using SO$_2$ as diluent) the protonated alcohol shows extremely slow exchange rates allowing the observation of well-resolved nmr spectra.[3]

To our knowledge, with the exception of the observation of MacLean and Mackor[4] who found that the exchange of ethyl alcohol in HF–BF$_3$ can be slowed down at −70°,[5] no observation relating to other protonated aliphatic primary and secondary alcohols was known.[6]

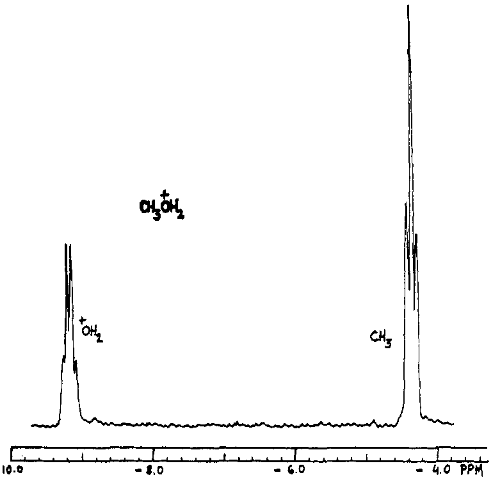

Figure 1.

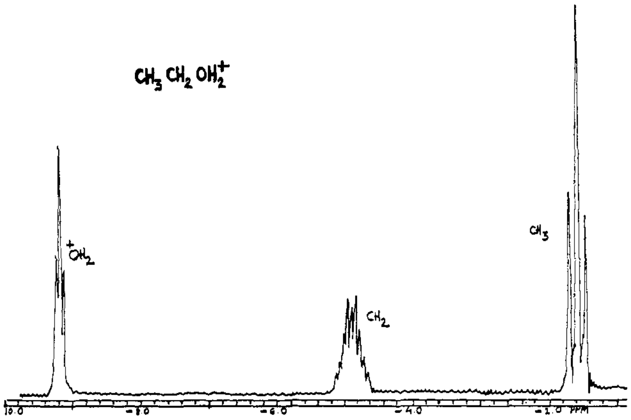

Figure 2.

We wish now to report the observations that in FSO$_3$H–SbF$_5$–SO$_2$ solvent system not only primary alcohols such as methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, but also secondary alcohols such as 2-propanol can be observed at −60° as the protonated alcohols, with very slow exchange rates.

$$ROH \xrightarrow[-60°]{FSO_3H\text{–}SbF_5\text{–}SO_2} ROH_2{}^+SbF_5FSO_3{}^-$$

Protonated methanol, CH$_3$OH$_2$$^+$, shows the methyl triplet at −4.35 ppm and the $^+OH_2$ quadruplet at −9.2 ppm, $J_{\text{H-H}}$ = 3.7 cps (Figure 1). Protonated ethanol, CH$_3$CH$_2$OH$_2$$^+$, shows the methyl triplet at −1.6 ppm ($J_{\text{H-H}}$ = 7.3 cps) and the $^+OH_2$ triplet at −9.2 ppm ($J_{\text{H-H}}$ = 3.6 cps). The methylene signal is the expected nine-line pattern at −4.86 ppm (Figure 2) as the coupling with the CH$_3$ group is about twice that with $^+OH_2$.

Protonated 1-propanol shows the methyl triplet at −0.92 ppm ($J_{\text{H-H}}$ = 7.2 cps), the C$_2$ methylene multiplet at −1.73 ppm, the C$_1$ methylene multiplet (seven lines) at −4.63 ppm, and the $^+OH_2$ triplet ($J_{\text{H-H}}$ = 3.6 cps) at −8.98 ppm (Figure 3). Protonated 2-propanol shows the methyl doublet at −1.5 ppm ($J_{\text{H-H}}$ = 6.3 cps), the $^+OH_2$ doublet at −8.92 ppm ($J_{\text{H-H}}$ = 2.9 cps), and the methine proton multiplet at −5.2 ppm (Figure 4).

[1] Part XXVII: G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 4442 (1966).

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

[3] G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *ibid.*, in press.

[4] C. MacLean and E. L. Mackor, *Discussions Faraday Soc.*, **34**, 165 (1962).

[5] T. Birchall and R. F. Gillespie (*Can. J. Chem.*, **43**, 1045 (1965)) in FSO$_3$H solution at low temperature also observed protonated ethyl alcohol but were unable to observe any fine structure of the $^+OH_2$ peak or coupling with the methylene protons.

[6] M. Brookhart, A. Diaz, and S. Winstein (*J. Am. Chem. Soc.*, **88**, 3136 (1966)), after completion of the work reported in this communication, mentioned the observation of protonated methyl alcohol, without, however, giving details.

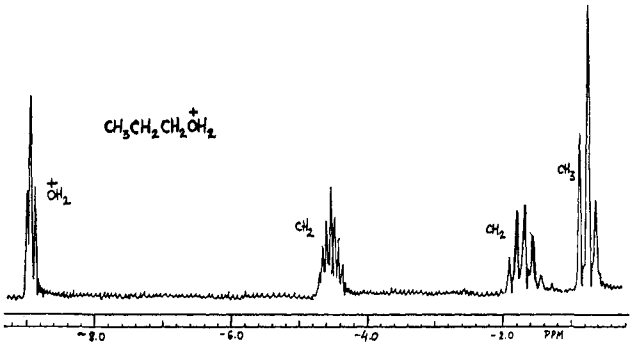

Figure 3.

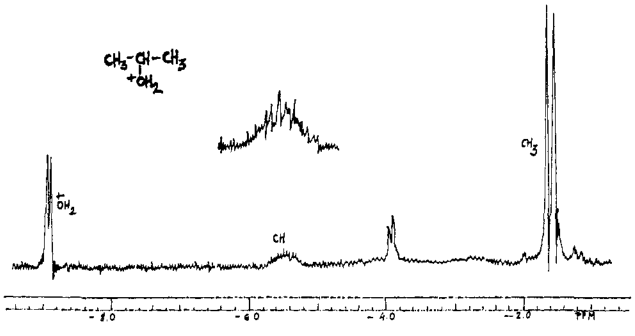

Figure 4.

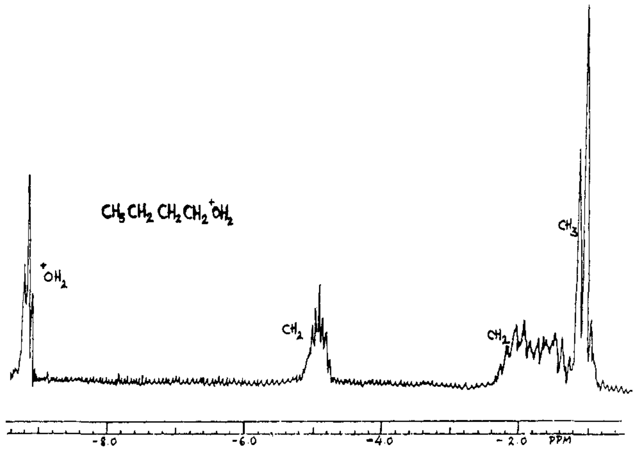

Figure 5.

Protonated 1-butanol shows the methyl triplet at -1.02 ppm ($J_{H-H} = 6.5$ cps), methylene multiplets (C_2, C_3) between -1.2 and -2 ppm, the C_1 methylene multiplet at -4.88 ppm, and the ^+OH triplet at -9.2 ppm ($J_{H-H} = 3.2$ cps.) (Figure 5).

All spectra were obtained in 1:1 molar composition of FSO_3H-SbF_5 diluted with SO $_2$and using external TMS as reference (compared to a separate sample of TMS in chloroform; if compared to capillary reference TMS all chemical shifts should be shifted by approximately 0.5 ppm to less shielding).

The nmr spectra of secondary butyl and pentyl alcohols in FSO_3H-SbF_5 solution at $-60°$ show the tertiary trimethylcarbonium ion and dimethylethylcarbonium ion, respectively. Thus, in these cases there must be an equilibrium between the protonated alcohol and the corresponding secondary carbonium ion; the secondary ions then rearrange to the more stable tertiary carbonium ions. There is no apparent return in the thermodynamically controlled strong acid system from tertiary to secondary carbonium ion. Due to this rapid shift in equilibrium the only ions observed are the tertiary carbonium ions.

The fact that the series of protonated alcohols reported in this communication are indeed exchanging slowly was further substantiated by protonation of O-deuterated alcohols. O-Deuteriomethanol, for example, in FSO_3H-SbF_5-SO_2 solution at $-60°$ shows an nmr spectrum of CH_3ODH^+ in which the the ^+OHD peak is a quartet and the CH_3 a doublet. This is superimposed on the spectrum of some $CH_3OH_2^+$ (and probably $CH_3OD_2^+$) formed from exchange or disproportionation. J_{HD} is apparently small, causing, however, some line broadening.

We are continuing investigations, which will be reported in detail, including measurement of exchange rates by temperature-dependence studies and spin-echo investigations, as well as measurements of O_{17}-H coupling in O_{17}-labeled protonated alcohols.

Acknowledgment. Support of the work by grants of the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged

---

(7) National Science Foundation Postdoctoral Research Investigator, 1965–1966.

George A. Olah, Eli Namanworth[7]
Western Reserve University, Department of Chemistry
Cleveland, Ohio 44106

Received September 8, 1966

Stable Carbonium Ions. XXIX.[1] The Reaction of Alkyl (Acyl) Sulfinylamines and Isocyanates (Thioisocyanates) with Nitrosonium Salts. New Deaminative Formations of Carbonium (Oxocarbonium) Ions

Sir:

One of the classic methods of generating transient carbonium ions is the deamination of aliphatic amines.[2] Deamination of primary amines generally is achieved *via* diazotization of amines using different sources of nitrous acid such as alkali nitrites and alkyl nitrites[3] or stable nitrosonium salts.[4] Deamination of amides is similarly affected by nitrous acid or nitrosonium salt reactions.[5,6] In the diazotization reactions an equimolar amount of water is formed as by-product; the water interferes with the formation of carbonium ions. This is at least partially the reason that, in recently reported alkylation of aromatic hydrocarbons *via* diazotization of alkylamines,[4,7] the formation of alkylated aromatics is only a relatively minor reaction: *i.e.*, isopropylation of toluene produces a maximum of 2–4% of cymenes.

---

(1) Part XXVIII: G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966).

(2) For a recent review see R. J. Baumgarten, *J. Chem. Educ.*, **43**, 398 (1966).

(3) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961).

(4) G. A. Olah, N. A. Overchuk, and J. C. Lapierre, *J. Am. Chem. Soc.*, **87**, 5786 (1965).

(5) S. L. Bouveault, *Bull. Soc. Chim. France*, [3] **9**, 368 (1892).

(6) G. A. Olah and J. A. Olah, *J. Org. Chem.*, **30**, 2386 (1965).

(7) A. T. Jurewicz, J. H. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5790 (1965).