Weighed samples of the acids to be titrated were placed in the arm of the H cell and *ca.* 20 ml of dimethyl sulfoxide was added. The solutions were always less than 10^{-3} *M* in the acid. The acid solution was then titrated with standardized dimsylcesium solution. At least ten points were taken in each titration, and usually many more. The p*K*'s were calculated from each point, and were found to be constant.

In the titrations of triphenylmethane, no end points were detected. The p*K* value was approximated from the pH of the solution when the color of the anion became permanent.

In the titrations of *p*-nitrophenol, 4,5-methylenephenanthrene, and tetraethylammonium cyanide, rather poor Nernst plots were observed, showing deviations of *ca.* 10 mv over the range of 20–80% titration.

Stable Carbonium Ions. XXXVI.[1a] Protonated Aliphatic Ethers and Their Cleavage to Carbonium Ions

George A. Olah and Daniel H. O'Brien[1b]

Contribution from the Department of Chemistry, Western Reserve University, Cleveland, Ohio 44106. *Received November 25, 1966*

Abstract: A series of aliphatic ethers have been studied in HSO_3F–SbF_5–SO_2 solution. O protonation was observed at −60° by nmr spectroscopy with negligible exchange rates. At higher temperatures, cleavage to carbonium ions takes place. The kinetics of cleavage of *sec*-butyl methyl ether to trimethylcarbonium ion and protonated methanol was measured.

The proton acceptor properties of ethers have been investigated extensively[2] by infrared,[3] conductance,[4] and solubility[5] measurements. These studies indicate the existence in solution of O-protonated ethers, R_2OH^+. Kinetic measurements of cleavage of unsymmetrical ethers in sulfuric acid solution[6] indicate that fission occurs by a unimolecular mechanism to form the most stable carbonium ion.

Nuclear magnetic resonance spectroscopy offers a good possibility of directly observing protonated ethers in acidic solutions. Birchall and Gillespie[7] as well as Brouwer, Mackor, and MacLean[8] investigated protonated anisoles. No study, however, relating to protonation of aliphatic ethers has been made.

Results and Discussion

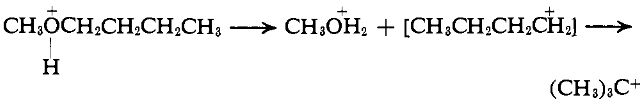
We wish now to report the direct observation of protonated primary and secondary aliphatic ethers in the extremely strong acid system, FSO_3H-SbF_5, using SO_2 as diluent.

$$R_2O \xrightarrow[-60^\circ]{FSO_3H\text{-}SbF_5,\ SO_2,} R_2OH^+\ SbF_5FSO_3^-$$

The protonated ethers give well-resolved nmr spectra showing very slow exchange rates at −60°. Protonated methyl ether (Figure 1) shows the methyl doublet at −4.49 ppm (J_{H-H} = 3.4 cps) and the OH^+ septuplet at −9.03 ppm. Protonated ethyl ether (Figure 2) shows the expected quintet for the proton on oxygen being split by the four methylene hydrogens. The methylene hydrogens give rise to an octet which can clearly be seen to be a doublet of quartets caused by the splitting of the original quartet by the proton on oxygen. The spectra of other protonated ethers studied are shown in Figures 3–7. Assignments of derived shifts and coupling constants are summarized in Table I.

The proton on oxygen in the protonated ethers (Table I) is more shielded than the previously reported proton on oxygen in protonated alcohols (−9.42 to −9.71 ppm from capillary TMS).[9] In isopropyl ether, the proton on oxygen is considerably upfield at −7.88 ppm, reflecting the greater electron-donating power of the isopropyl group compared to primary alkyl groups. The coupling constant, J_{H-H}, is also consistent with those reported for the protonated alcohols (2.9–3.7 cps).[9]

Kinetics of Cleavage. The protonated *n*-alkyl ethers are stable even at higher temperatures. *n*-Butyl methyl ether does not show any significant change, either cleavage or rapid exchange, as indicated by the nmr spectrum up to +40° in a solution of HSO_3F-SbF_5 (1:1). At this temperature, *n*-butyl methyl ether cleaves and a sharp singlet appears at −4.0 ppm. This can be attributed to the rearrangement of the *n*-propyl carbonium ion, formed in the cleavage, to trimethylcarbonium ion.



$$CH_3\underset{\displaystyle H}{\overset{+}{O}}CH_2CH_2CH_2CH_3 \longrightarrow CH_3\overset{+}{O}H_2 + [CH_3CH_2CH_2\overset{+}{C}H_2] \longrightarrow (CH_3)_3C^+$$

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[6] (a) R. L. Burwell, *Chem. Rev.* **54**, 615 (1954); (b) D. Jacques and J. A. Leisten, *J. Chem. Soc.* 4963 (1961).

[7] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964).

[8] D. M. Brouwer, E. L. Mackor, and C. MacLean *Rec. Trav. Chim.*, **85**, 114 (1966).

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Table I. Nmr Chemical Shifts and Coupling Constants of Protonated Ethers at −60° in HSO_3F–SbF_5–SO_2 (ppm)[a]

Ether	H_1	H_2	H_3	H_4	OH^+	J_{H-HO^+}, cps
$(\overset{1}{CH_3})_2O$	−4.49 (2)				−9.03 (7)	3.4
$(\overset{2}{CH_3}\overset{1}{CH_2})_2O$	−4.73 (8)	−1.53 (3)			−8.61 (5)	3.6
$(\overset{3}{CH_3}\overset{2}{CH_2}\overset{1}{CH_2})_2O$	−4.63 (6)	−1.90 (6)	−0.92 (3)		−8.60 (5)	3.8
$((\overset{2}{CH_3})_2\overset{1}{CH})_2O$	−5.18 (m)	−1.55 (2)			−7.88 (3)	4.1
$(\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2})_2O$	−4.52 (6)	∼−1.60 (m)	∼−1.60 (m)	∼−0.90 (m)	−8.56 (5)	3.8
$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1a}{CH_2}O\overset{1b}{CH_3}$	a, −4.73 (6) b, −4.37 (2)	∼−1.66 (m)	∼−1.66 (m)	−0.90 (3)	−8.86 (6)	3.7
$\overset{3}{CH_3}\overset{2a}{CH_2}\underset{\underset{2b}{CH_2}}{\overset{1a}{CH}}O\overset{1b}{CH_3}$	a, −4.96 (m) b, −4.30 (2)	a, −1.97 (m) b, −1.61 (2)	−0.97 (3)		−8.47 (5)	3.8

[a] From external capillary of TMS; figures in parenthesis represent multiplicity of peaks; m = multiplet.

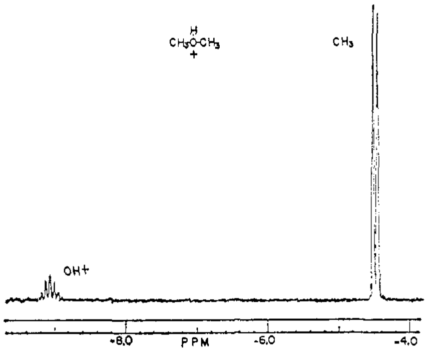
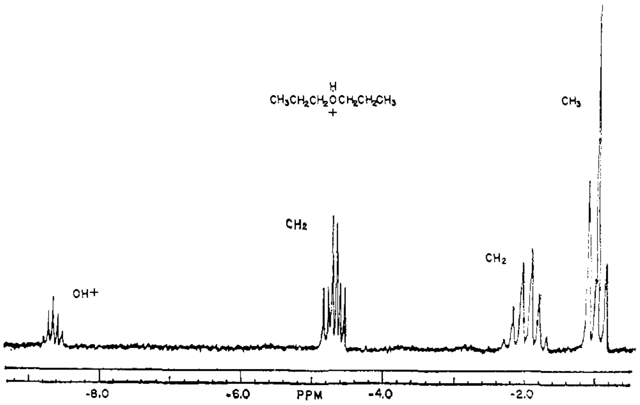


Figure 1.



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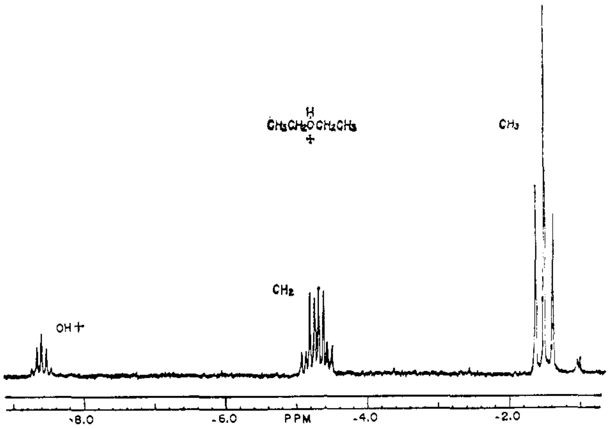


Figure 2.

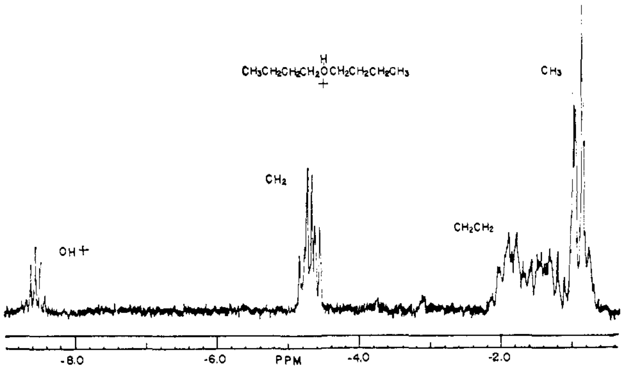
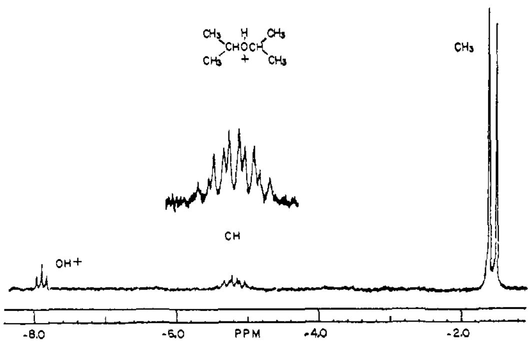


Figure 4.

However, ethers in which one of the groups is secondary begin to show appreciable cleavage at −30°. Protonated *sec*-butyl methyl ether cleaves cleanly at −30° to protonated methanol and trimethylcarbonium ion. The nmr spectrum (Figures 7–9) clearly shows the appearance of a quartet at −9.2 ppm for the protons on oxygen of protonated methanol and a triplet at −4.3 ppm for the methyl group of protonated methanol.[9] Trimethylcarbonium ion appears as a sharp singlet at −4.0 ppm.

Ethers in which one of the groups is tertiary cleave rapidly even at −70°. *t*-Butyl methyl ether gave a spectrum for protonated methanol and trimethylcarbonium ion at −70° even when measured less than 2 min after sample preparation.

It was found possible to measure the kinetics of cleavage of protonated *sec*-butyl methyl ether by fol-



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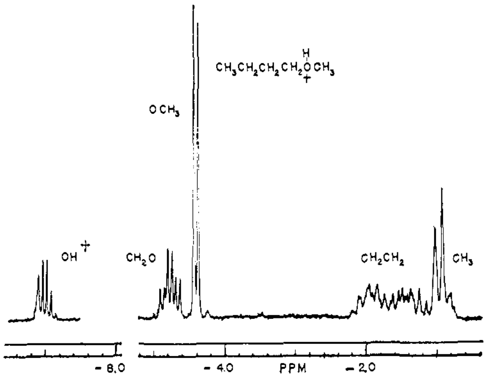


Figure 6.

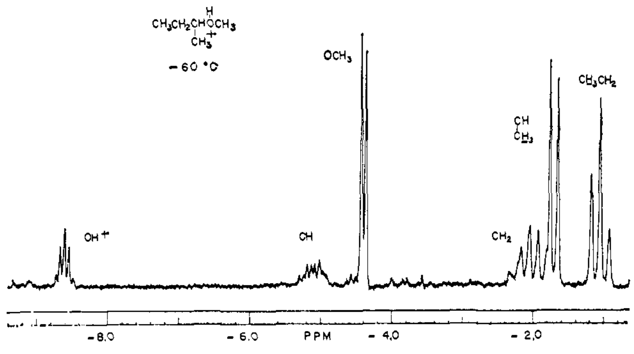


Figure 7.

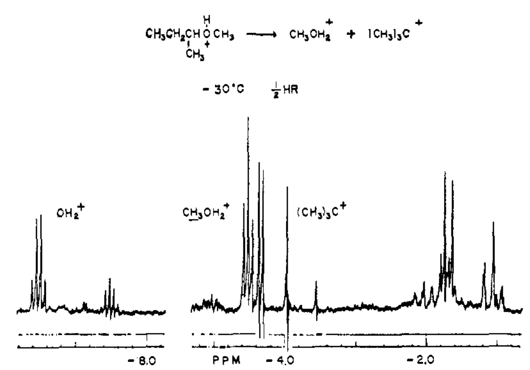


Figure 8.

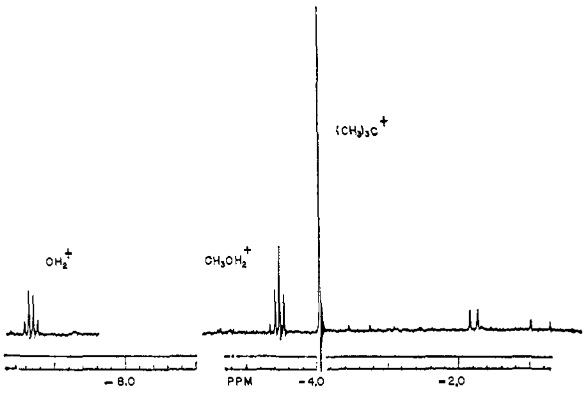


Figure 9.

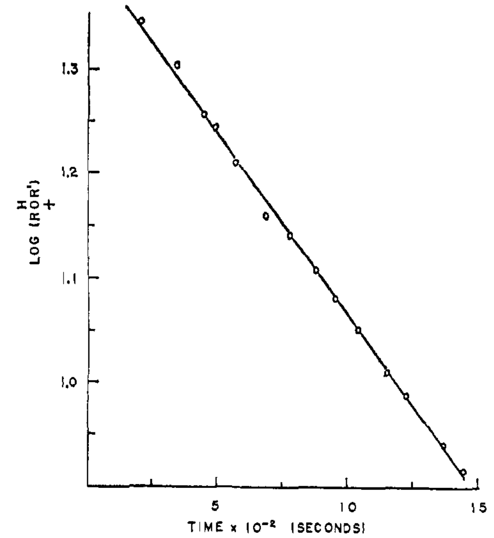
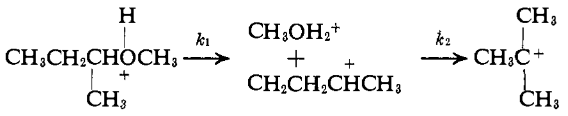


Figure 10.

lowing the disappearance of the methoxy doublet in the nmr spectrum with simultaneous formation of protonated methanol and trimethylcarbonium ion. Kinetic data are summarized in Table II. The cleavage shows pseudo-first-order kinetics (Figure 10). This indicates that the rate-determining step is the formation of methylethylcarbonium ion followed by rapid rearrangement to the more stable trimethylcarbonium ion ($k_1 << k_2$).



$$CH_3CH_2\underset{CH_3}{CH}\overset{H}{\underset{+}{O}}CH_3 \xrightarrow{k_1} \begin{matrix} CH_3OH_2^+ \\ + \\ CH_2CH_2\overset{+}{C}HCH_3 \end{matrix} \xrightarrow{k_2} CH_3\overset{CH_3}{\underset{CH_3}{C^+}}$$

This agrees well with the mechanism proposed by Jacques and Leisten[6b] for ether cleavage in sulfuric acid based on cryoscopic data.

Table II. Kinetics of Cleavage of $CH_3CH_2\underset{CH_3}{CH}\overset{H}{\underset{+}{O}}CH_3$

Temp, °C	k, sec^{-1} × 10^4
−29.0	3.64
	3.68
	5.11
	Av 4.14 ± 0.64
−17.5	10.9
	8.22
	7.57
	9.65
	Av 9.08 ± 1.2
E_a = 8.5 ± 3 kcal	

In a subsequent paper of this series we will report the related protonation of esters in FSO_3H-SbF_5 solution and investigation by nmr spectroscopy of the kinetics of ester cleavage.

Experimental Section

Materials. Dialkyl ethers were reagent grade and were used without further purification.

n-Butyl ether and *sec*-butyl methyl ether were prepared from sodium butylate and *n*-butyl iodide or sodium *sec*-butylate and methyl iodide.[10] Alcohol in the product ethers was removed by reaction with sodium. The ethers were twice distilled from sodium. The fractions between 59 and 60° for *sec*-butyl methyl ether and between 69 and 70° for *n*-butyl ether were used.

t-Butyl methyl ether was prepared from 15% aqueous sulfuric acid, methanol, and *t*-butyl alcohol according to the method of Norris and Rigby.[11] The product was purified by distillation from sodium. The fraction between 53 and 55° was used.

Antimony pentafluoride and fluorosulfonic acid were obtained from the Allied Chemical Co. and purified as described previously. Sulfur dioxide (anhydrous grade, Matheson) was used without further purification.

Nuclear Magnetic Resonance Spectra. A Varian Associates Model A-56-60A nmr spectrometer with a variable-temperature probe was used for all spectra. The spectra of O-protonated ethers were observed using a 1:1 solution of HSO_3F-SbF_5 diluted with SO_2 at $-60°$. Samples were prepared by diluting the 1:1 acid solution with approximately an equal volume of SO_2 at $-76°$. The ether, diluted with SO_2 at $-76°$, was then added slowly with agitation to the acid solution to give approximately a 5% by weight solution. The acid was always in large excess compared to the protonated ether as indicated by strong acid peak at about -10.4 ppm. No significant shifts in the spectra of O-protonated ethers (Table I) were noted with either temperature or small variations of concentration. An external capillary of TMS was used as reference.

In the kinetic experiments, the temperature was calibrated against the shift between the OH quartet and methyl doublet of methanol before and after each run. The temperature is believed to be precise to ±1.5°. Samples were prepared by diluting the 1:1 acid solution with approximately an equal volume of SO_2 at $-76°$. The *sec*-butyl methyl ether was cooled to $-76°$ and slowly added with agitation neat to the acid to give an initial concentration of ether of 5–7% by weight. Reproducible pseudo-first-order kinetics were observed by following the disappearance of the sharp methoxy doublet of the protonated ether (Figure 10). The sum of the peak height of this doublet was used as a measure of the relative concentration of ether.

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

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Communications to the Editor

Hydrocarbon–Carbanion Proton Exchange Reactions in Dimethyl Sulfoxide

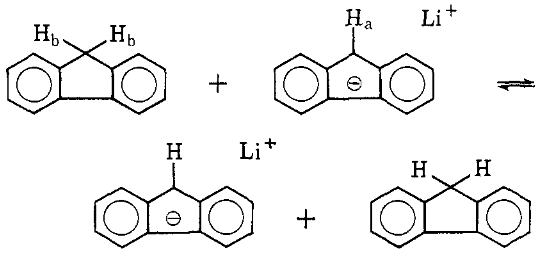
Sir:

Proton-transfer reactions between hydrocarbons and carbanions have long been used to achieve equilibria such as (1),[1-3] but the reaction itself has not been studied

$$AH + B^-M^+ \rightleftharpoons A^-M^+ + BH \qquad (1)$$

in any detail. In particular, rates of such reactions have not been measured for the case where B is similar to or identical with A. The positions of such equilibria have been determined spectrophotometrically as well as by quenching reactions with carbon dioxide or deuterium oxide. Consequently, the rates at which such equilibria are set up are important in relative acidity measurements, since if the rate of (1) is comparable to the quenching rate, spurious results will be obtained.[4]

As part of a general investigation of proton-transfer reactions, we have previously determined the rate of reaction 2 in ethyl ether and found this rate to be quite slow, with a rate constant $k_2 = 1.9 \times 10^{-5}\ M^{-1}\ sec^{-1}$ (25°, ethyl ether).[5]



(2)

Since we have also shown the rate of proton exchange between dimethyl sulfoxide (DMSO) and its conjugate base (eq 3) to be very fast ($k_3 = 7\ M^{-1}\ sec^{-1}$, DMSO,

$$(CH_3)_2SO + CH_3SOCH_2^-Li^+ \rightleftharpoons CH_3SOCH_2^-Li^+ + (CH_3)_2SO \qquad (3)$$

25°),[6] it was of great importance to determine the rate of (2) in DMSO in order to assess the relative effects of solvent and molecular structure on the rates. In this communication we report a study of the rate of this reaction, making use of an important novel technique.

The reaction of fluorenyllithium with fluorene in DMSO is too rapid to be followed by conventional techniques, but since the nmr is that of a normal superposition of anion and hydrocarbon the rate is too slow to be studied by line broadening.[7] Thus, the mean

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[1] J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).

[2] A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, 87, 384 (1965); A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *ibid.*, **89**, 59 (1967); A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, **89**, 63 (1967).

[3] See also E. C. Steiner and J. M. Gilbert, *ibid.*, 87, 382 (1965).

[4] C. D. Ritchie and R. Uschold, *ibid.*, **86**, 4488 (1964).

[5] J. I. Brauman and D. F. McMillen, unpublished results.

[6] J. I. Brauman and N. J. Nelson, *J. Am. Chem. Soc.*, **88**, 2332 (1966).

[7] Solutions were prepared with a vacuum line. DMSO was dried over Molecular Sieves Type 4-A and contained less than 10 ppm of water. The solutions were *ca.* 0.3 *M* each in anion and hydrocarbon. Spectra were taken with Varian HR-100 and A-60 spectrometers.