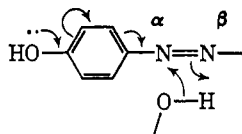


change systematically with changing substituents, and suggests a progressive change in mechanism. The more electrophilic substrates, **5** and **6**, probably undergo reduction by electron transfer from H_2Q with added assistance by concerted proton transfer from external acid. The less electrophilic, but more basic substrate, **2**, may react through a four-centered transition state in which the hydrogen from the reducing agent is transferred to the relatively basic β nitrogen, while electrons are being simultaneously transferred to the α nitrogen. Such a mechanism would account for the deuterium isotope effect being less than the maximum for a linear



transfer of a proton along the reaction coordinate, since the effect would arise largely from the difference in zero-point energy for a bending, rather than a stretching, vibration. It is also possible that the progressive change in structure of the azobenzenes leads to a change from attack by H_2Q at the α - to the β -azo nitrogen. The changes in the activation parameters can be interpreted in terms of a progressive change in the activated complex proceeding from **6** to **2** from one involving considerable orientation at a highly electron-deficient site where ΔH^\ddagger for electron transfer is low, to one requiring little orientation but a high ΔH^\ddagger for electron transfer, and finally to still another requiring consid-

erable orientation at an electron-rich site but where ΔH^\ddagger is again low. Thus, in the case under study, where the oxidizing agent is both an electrophile and weak base and the reducing agent is a nucleophile and a weak acid, the nucleophile-electrophile interaction can become entangled with the acid-base interaction. A similar suggestion was advanced by Brown and Subba Rao to explain the fact that azobenzene is not reduced by borohydride ion, a Lewis base, but is readily reduced by diborane, a Lewis acid.¹⁷

Most of the other results that are not obscured by uncertainty regarding mechanism are interpretable in terms of the electrophile-nucleophile model for the oxidant-reductant interaction. Lowering the electron density at the reaction site in the azobenzene by protonation and by substituents, and increasing the electron density on the reactive functional group of the hydroquinone by ionization both facilitate electron transfer. The combined effect of protonation and two powerful electron-withdrawing substituents in **6** leads to a rate that is nearly diffusion controlled (Table II). The observed effect of substituents on the acid-catalyzed reduction rates shows remarkable parallelism with substituent effects in nucleophilic condensations with carbonyl compounds.¹⁸

Acknowledgment. We wish to thank Dr. S. G. Smith for helpful discussions of this work.

(17) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

(18) (a) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964); (b) R. L. Reeves in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, pp 567-619.

Acidity in Nonaqueous Solvents. IV. Hydrocarbon Acids in Dimethyl Sulfoxide^{1,2}

Calvin D. Ritchie and Ronald E. Uschold

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received November 29, 1966

Abstract: By use of the glass electrode, we have measured the acidities of a number of weak acids in dimethyl sulfoxide solution relative to a standard state in the same solvent. The glass electrode is found to respond reversibly to changes of hydrogen ion activity over a range of 25 powers of ten. Surprisingly, for many of the hydrocarbon acids, the absolute values of the determined pK 's are identical with those determined by acidity function techniques. The factors contributing to this behavior are discussed.

The acidities of hydrocarbon acids have been of interest to organic chemists in connection with a number of problems.³ Both kinetic and equilibrium measurements have been used to estimate acidities of very weak acids, and a single scale covering an ex-

tremely wide range of acidities has recently been proposed.³ Rather large discrepancies in the proposed scale, however, have been noted in a study of the acidity of hydrocarbons in dimethyl sulfoxide solution utilizing acidity function techniques.⁴ Part of the discrepancy undoubtedly arises from the fact that measurements in a variety of solvents have been used in establishment of the single scale. A second contributing factor to the noted discrepancies is the complicating effect of ion pairing on some of the measurements which were made in solvents of extremely low dielectric constant.⁵

(1) For previous papers in this series, see: C. D. Ritchie and P. D. Heffley, *J. Am. Chem. Soc.*, **87**, 5402 (1965); C. D. Ritchie and G. H. Megerle, *ibid.*, **89**, 1447 (1967); **89**, 1452 (1967).

(2) This work was supported by Grant No. GP 2635 from the National Science Foundation, and by Grant No. GM 12832 from the Public Health Service.

(3) For an excellent discussion of the use and establishment of the acidities of a number of hydrocarbon acids, see: D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(4) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).

(5) A. Streitwieser, *Progr. Phys. Org. Chem.*, **3**, 44 (1965); see also ref 3, p 44.

As part of our continuing studies of solvent effects on acidities,¹ and in order to provide more extensive data on hydrocarbon acids in a single solvent where ion pairing is unlikely, we have measured the acidities of a number of weak acids in dilute dimethyl sulfoxide solution. The titration technique which has been developed in this study should prove extremely useful in extending the measurements to more compounds. Essentially, the technique, using the glass electrode, eliminates the bothersome problem of finding overlapping indicators.

Kolthoff and Reddy⁶ have previously used the glass electrode in dimethyl sulfoxide solution to measure pK 's up to *ca.* 12. In the present study, we report data which indicate that the glass electrode functions reversibly up to a pH of *ca.* 28.

Results

The Glass Electrode in Dimethyl Sulfoxide. The apparatus used in the pK measurements consisted of a thermostated H cell assembly similar to that described by Kolthoff.⁶ The glass electrode was immersed in the solution to be titrated in one arm of the assembly. This arm was connected to the reference electrode arm by a salt bridge filled with 0.10 *M* tetraethylammonium perchlorate in dimethyl sulfoxide. Contact was made through a fine-porosity, glass frit. The reference electrode consisted of a silver billet electrode immersed in a 5.0×10^{-2} *M* solution of silver perchlorate in dimethyl sulfoxide. The emf of the system was measured with a Beckman research pH meter, Model 1019, operated on the millivolt scale.

The electrode system was shown to respond reversibly to hydrogen ion concentrations in titrations of pure dimethyl sulfoxide with a standardized solution of *p*-toluenesulfonic acid. Plots of concentration of acid *vs.* millivolts showed the theoretical, 59-mv slope within ± 1 mv over a range of acid concentrations from 10^{-4} to 10^{-2} *M*. Further verification of the reversibility of the electrode system was obtained from plots of $\log P/(1 - P)$ *vs.* millivolts in titrations of various acids with dimethylsulcesium solutions,⁷ where *P* is the fraction of acid titrated. The plots generally showed the theoretical slope within $\pm 10\%$ (see Experimental Section). Standardization of the electrode with dilute solutions of *p*-toluenesulfonic acid and subsequent potentiometric titration of acetic acid with dimethylsulcesium gave a pK of 11.6, in excellent agreement with the value of 11.4 reported by Kolthoff.⁶

In early measurements, a commercial electrode was used, but it was found that in high pH solutions the response of the electrode became extremely slow. Replacing the aqueous internals of the electrode with a dimethyl sulfoxide solution containing silver perchlorate and *p*-toluenesulfonic acid resulted in an electrode which showed greatly improved response. In solutions of pH above about 10, stable readings required approximately 15 min. In very high pH, the response was slower, but much faster than with the unmodified electrode. We have recently found that replacement of the aqueous internal solution of the commercial electrode with triply distilled mercury gives an electrode with

similar characteristics to that with the nonaqueous internals. Because of the ease of preparation, the mercury internals are preferred.

All of the glass electrodes tested were found to be sensitive to the presence of sodium or potassium ions in high pH solutions. Cesium ions, however, caused no trouble, and we have observed no indication of variations of either junction potentials or glass electrode response on change in cesium ion concentration.

It is interesting that the use of *p*-toluenesulfonic acid monohydrate seems to produce no difficulties in the measurements. In the low pH regions, this statement is based on the fact that calibration of the electrode with *p*-toluenesulfonic acid monohydrate and subsequent determination of the pK of acetic acid give the correct value as mentioned above. In the high pH region, we have found that titration of a solution of *p*-toluenesulfonic acid monohydrate with dimethylsulcesium gives a single sharp end point corresponding to 1 mole of acid titrated per mole of dimethyl sulfoxide. On the basis of these observations, we suggest that water in dimethyl sulfoxide is a very weak base and a very weak acid. This weakly basic character of water compared to dimethyl sulfoxide is not at all surprising since acidity function techniques have shown that dimethyl sulfoxide is approximately 1.8 pK units more basic than is water.⁸ The weakly acidic character of water compared to dimethyl sulfoxide at first sight may seem surprising, but is consistent with previous observations that alkoxides in dimethyl sulfoxide solution are at least comparable in basicity to trityl anion.^{3,4,9}

pK Measurements. For all acids except hydrazoic acid and hydrocyanic acid, the pK 's were determined by potentiometric titration of the acid with a standardized solution of cesium dimethylsulcesium. The acid concentrations were always below 10^{-3} *M*, and the solutions were maintained under an atmosphere of purified argon throughout the titrations. The pK 's of hydrocyanic and hydrazoic acids were determined by titration of tetraethylammonium cyanide¹⁰ and sodium azide, respectively, with *p*-toluenesulfonic acid.

Since the electrode system used in the measurements was standardized in *ca.* 10^{-3} *M* *p*-toluenesulfonic acid solution, the pK values determined are referred to a standard state of *ca.* 10^{-3} *M* in dimethyl sulfoxide solution. No correction for ionic strength effects was made since the precision of the data did not warrant the small corrections involved. The pK values obtained at 25.0° are reported in Table I.

The precision obtained in duplicate determinations was usually ± 0.2 pK unit. The sensitivity of many of the compounds to traces of oxygen and other impurities is probably responsible for this relatively poor precision. Unless otherwise stated in the table, we estimate that the accuracy of the values is ± 0.3 pK unit.

Most of the previous measurements on these compounds are not directly comparable with the present results, since they utilize different standard-state defini-

(8) E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 283 (1963).

(9) In our laboratories, we have observed that *t*-butoxide is comparable in basicity to dimethylsulcesium. We suggest that hydroxide ion may prove to be a great deal more basic than dimethylsulcesium anion.

(10) We gratefully acknowledge the gift of a generous sample of tetraethylammonium cyanide from Drs. S. Andreades and O. Webster, Du Pont Central Research Laboratories, Wilmington, Del.

(6) I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, 1, 189 (1962).

(7) Dimethylsulcesium is the cesium salt of the conjugate base of dimethyl sulfoxide. See: E. J. Corey and M. Chaykofsky, *J. Am. Chem. Soc.*, 84, 866 (1962).

Table I. pK of Acids in Dimethyl Sulfoxide Solution at 25.0°^a

Acid	pK	Lit. pK^b	Ref ^b
Hydrazoic acid	7.9	...	
<i>p</i> -Nitrophenol	10.4	9.9	11
Acetic acid	11.6	11.4	6
Benzoylacetone	12.1	9.6 (H ₂ O)	3
Tris(<i>p</i> -nitrophenyl)-methane	12.2	13.8 ^c	<i>e</i>
Hydrocyanic acid	12.9	...	
2,4-Dinitroaniline	14.8	14.7 ^d	4
<i>p</i> -Nitrophenyl-diphenylmethane	15.5 (?) ^e	15.8 ^e	<i>e</i>
Nitromethane	15.9	10.2 (H ₂ O)	3
9-Methylfluorene	19.7	...	
4,5-Methylene-phenanthrene	20.0	<19.5 ^d	4
		22.6 (C ₆ H ₁₀ NH ₂)	5
Fluorene	20.5	20.5 ^d	4
		22.8 (C ₆ H ₁₀ NH ₂)	5
Triphenylmethane	28 (±0.5) ^f	27.2 ^d	4
		31.5 (C ₆ H ₁₀ NH ₂)	5

^a Standard state in dimethyl sulfoxide solution. ^b The reference numbers refer to footnote numbers in the text. ^c Values calculated from the reported stabilities of the anions relative to triphenyl methane, $pK = 27.2$. ^d These values were determined by acidity function techniques in dimethyl sulfoxide solution, and therefore have standard state of aqueous solution. ^e Although our value is in good agreement with that reported by Taft [L. D. McKeever and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 4544 (1966)], we have some doubts about this value. Good end points were not obtained in the titrations, and the spectrum of the anion is not exactly what we would expect. The elemental analysis of the hydrocarbon, however, agrees perfectly with the theoretical. ^f An end point was not observed in this titration. The pK was approximated by the pH of the solution when the anion color became permanent.

tions. The pK values for *p*-nitrophenol and acetic acid, however, have been determined relative to a standard state in dimethyl sulfoxide. Our value of 11.6 for acetic acid is in excellent agreement with the value of 11.4 reported by Kolthoff.⁶ The value of 10.4 for *p*-nitrophenol is just within the combined experimental errors of the value of 9.9 reported by Parker.¹¹

The most convincing argument for the accuracy of the present data, and for the astoundingly precise operation of the glass electrode over the entire pH region studied, is found in a comparison of the present data with that obtained by Steiner.⁴ The three compounds, 2,4-dinitroaniline, fluorene, and triphenylmethane, were studied by Steiner, and his results are shown in the table. Although the absolute values of the pK 's are defined relative to different standard states, and therefore the agreement of the absolute values is unexpected, the near perfect agreement of the differences in pK between the three compounds leaves little doubt as to the validity of our method.

The fact that the electrode is standardized at pH 3 and measures pH 11.6 for acetic acid buffer in agreement with Kolthoff's value, and then pH up to 20 for fluorene in agreement with Steiner's measurements, shows clearly that the glass electrode is accurately following the activity of hydrogen ion over a range of at least 20 powers of ten.

In several cases, the relative pK values reported have been qualitatively checked by spectrophotometric or visual observations. A solution of 4,5-methylene-phenanthryl anion was prepared by titration of the

(11) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **88**, 1911 (1966).

hydrocarbon with potassium *t*-butoxide. This solution was mixed with a solution of 9-methylfluorene, and the spectrum of the 9-methylfluorenyl anion was observed. The reverse reaction could not be observed. In fact, we have now studied the rate of the reaction between the 4,5-methylene-phenanthryl anion and 9-methylfluorene and have reported the results in a separate paper.¹² The relative acidity of hydrocyanic acid and tris(*p*-nitrophenyl)methane was verified by observation of the characteristic color of the carbanion on mixing a solution of cyanide ion with a solution of the hydrocarbon.

Discussion

The most striking feature of the data in Table I is the identity of the pK values determined by the present method and by the acidity function technique⁴ for 2,4-dinitroaniline, fluorene, and triphenylmethane. The values determined by the acidity function technique are relative to a standard state in aqueous solution, whereas our values are relative to a standard state in dimethyl sulfoxide solution. The pK values in different standard states are related through the "degenerate activity coefficients," defined by Grunwald,¹³ through

$$pK_{H_2O} = pK_{DMSO} + \log \gamma'_{HA} - \log \gamma'_{A^-} - \log \gamma'_{H^+} \quad (1)$$

eq 1, where γ'_{HA} is the degenerate activity coefficient of the acid, γ'_{A^-} that of the conjugate base, and γ'_{H^+} that of the proton, and where $-RT \ln \gamma'_S$ is defined as the free energy of transfer of 1 mole of S from dimethyl sulfoxide solution to aqueous solution.

Thus, the equivalence of the pK values determined relative to the different standard states requires that eq 2 be satisfied.

$$\log \gamma'_{HA} - \log \gamma'_{A^-} - \log \gamma'_{H^+} = 0 \quad (2)$$

It seems most unlikely that each term in eq 2 is individually equal to zero. Electrostatic effects, alone, should make both γ'_{H^+} and γ'_{A^-} greater than unity since the dielectric constant of dimethyl sulfoxide is much less than that of water. To a first approximation, the electrostatic effect should be the same on both terms.

Since the solubility of organic compounds is greater in dimethyl sulfoxide than in water, we should expect that γ'_{HA} is less than unity. If we ascribe the greater solubility to a lower internal pressure in dimethyl sulfoxide, however, we would expect the same effect on γ'_{A^-} , and therefore no effect on the difference in pK is expected from this source.

Counterbalancing the electrostatic effect, the greater basicity of dimethyl sulfoxide than water⁸ would decrease γ'_{H^+} . From the reported difference in the basicity of water and dimethyl sulfoxide of 1.8 pK units, and the relative concentration of water in water and dimethyl sulfoxide in dimethyl sulfoxide, we estimate that the difference in solvent basicity should cause a change of -1.2 pK units in going from water to dimethyl sulfoxide. This value is remarkably close

(12) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1730 (1967).

(13) E. Grunwald and B. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).

to the difference of -1.1 pK units found by Kolthoff⁶ for di-*n*-butylammonium ion in the two solvents.

The magnitude of the electrostatic effect is difficult to evaluate since the proper radius to be used for the proton is difficult to determine. It seems unlikely, however, that the effect would be small enough to just balance the solvent basicity effect estimated above. We therefore believe that some other effect must be operative.

A comparison of the change in pK of acetic acid with the change for fluorene can be made in the same fashion as recently made by Grunwald¹⁴ for the comparison of acetic acid and picric acid in terms of dispersion interactions. The intensely colored anions of 2,4-dinitroaniline, fluorene, and triphenylmethane would be expected to have strong dispersive interactions with solvent. Since dimethyl sulfoxide is more polarizable than is water, this anion-stabilizing interaction will result in a decrease in γ'_{A-} . The situation here is quite similar to that in the reactions of highly colored carbonium ions which we have recently discussed.¹⁵ This type of effect is consistent with the present data in that the equivalence in pK in water and dimethyl sulfoxide does not extend to other acids such as nitromethane or benzoylacetone whose conjugate bases are not intensely colored.

Another manifestation of the dispersion interaction effect is probably seen in the higher acidity of 9-methylfluorene than fluorene. Grunwald¹⁴ has commented on the contribution of alkyl group substituents to the stabilization of compounds with high oscillator strengths. In the present case, the alkyl group effect is the opposite of that expected for the so-called inductive effect.¹⁶

The present data should serve as a warning against comparisons of acidities in different solvents. For example, tris(*p*-nitrophenyl)methane is a stronger acid in dimethyl sulfoxide than is nitromethane, whereas in aqueous solution the acidities are completely reversed. The same is true for acetic acid and *p*-nitrophenol. Things become even worse if we try to compare acidities of carbon acids and oxygen acids in different solvents. Steiner has reported, for example, that triphenylmethane and *t*-butyl alcohol have comparable acidities in dimethyl sulfoxide solution.^{3, 4, 9}

We believe that just as important as the data presented is the fact that the glass electrode can be used for such measurements, providing a convenient method for further measurements in nonaqueous solvents. In fact, we have already applied the glass electrode to very accurate measurements in dimethylformamide and in methanol.¹ Application of the technique in the very high pH regions reported in the present study requires a great deal of time because of slow response, but the search for overlapping indicators is probably even more time consuming. We hope that further experience in studies similar to the present one will allow the fabrication of electrodes with faster response times.

Experimental Section

Materials. Dimethyl sulfoxide was purified by a method developed by Steiner¹⁷ and previously outlined.¹⁵ Potentiometric titration of the solvent with dimethylcesium and with *p*-toluenesulfonic acid revealed less than 5×10^{-6} M acidic or basic impurities. Karl Fischer titration showed less than 10 ppm of water. The solvent was purified and stored under an atmosphere of purified argon.

Argon (99.995% purity) was passed through a train consisting of a solution of trityl anion in pyridine, concentrated sulfuric acid, and molecular sieves type 3A. Trityl anion in pyridine was prepared by the reaction of lithium aluminum hydride with benzopinacolone in pyridine solution.

Dimethylcesium solutions were prepared by treating freshly prepared cesium amide with purified dimethyl sulfoxide, followed by thorough degassing of the solutions to remove ammonia. Solutions were standardized by potentiometrically titrating a solution of *p*-toluenesulfonic acid in dimethyl sulfoxide.

Cesium amide was prepared from the reaction of liquid ammonia with cesium metal.¹⁸ A small crystal of ferrous sulfate was added to start the reaction. The ammonia was evaporated, and the amide was immediately used to prepare dimethylcesium.

All compounds titrated were commercially available with the exception of tetraethylammonium cyanide.¹⁰ Commercial materials were recrystallized before use. Fluorene was recrystallized and then sublimed under vacuum. Tetraethylammonium cyanide was recrystallized from dry acetonitrile. Toluenesulfonic acid monohydrate was used as the acid titrant.

The glass electrode used for the major part of this work was a modified Beckman Type E-2 electrode. The electrode was disassembled, and the aqueous internals were replaced with a dimethyl sulfoxide solution containing 2×10^{-2} M silver perchlorate and 6×10^{-3} M *p*-toluenesulfonic acid. A silver wire was soldered onto the platinum lead so that only the silver wire came in contact with the solution. The electrode was reassembled, sealed tightly, and stored in dimethyl sulfoxide solution for 24 hr before use. In later work, we have found that replacement of the aqueous internal solution with triply distilled mercury provides an electrode with quite similar characteristics to that with the nonaqueous internals.

An H cell apparatus was used for the pK determinations. Each arm of the H cell consisted of a container *ca.* 5 cm high and 3 cm i.d. surrounded by an outer wall to allow the circulation of thermostating liquid and fitted with a standard taper cover which held the electrode, gas inlet tube, and buret. A standard taper fitting on the side of the vessel accepted the salt bridge compartment. In use, the apparatus was completely sealed from the atmosphere and maintained under a slight positive pressure of purified argon.

Micrometer burets (Laboratory Supply Co.) were employed in the titrations and allowed accurate delivery of 0.001-ml increments of titrant.

A Beckman research pH meter, Model 1019, operated on the millivolt scale was used for all potential measurements.

A Beckman Silver Billet electrode in contact with a solution of *ca.* 5×10^{-2} M silver perchlorate in dimethyl sulfoxide in one arm of the H cell served as the reference electrode.

The salt bridge of the H cell was filled with *ca.* 10^{-1} M tetraethylammonium perchlorate in dimethyl sulfoxide. The ends of the bridge were fine-porosity glass frits.

pK Measurement Technique. The electrode assembly was standardized by titration of a known volume of pure dimethyl sulfoxide with a standard solution of *p*-toluenesulfonic acid in dimethyl sulfoxide. In all cases, excellent adherence to the Nernst equation was observed, with maximum derivations of ± 1 mv over a range of 10^{-4} to 10^{-2} M acid. We do not believe that the molecule of water in the *p*-toluenesulfonic acid caused any difficulty since the electrode behavior was always found to be that expected from theory. In addition, in titrations of *p*-toluenesulfonic acid with cesium dimethyl, a single very sharp end point was always observed. It seems quite probable that hydroxide ion is a stronger base than dimethyl ion in dimethyl sulfoxide solution.^{4, 9}

(14) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).

(15) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Am. Chem. Soc.*, **89**, in press.

(16) For a discussion of the inductive effect of alkyl groups, or, rather, the absence of it, see: C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 345 (1964).

(17) E. C. Steiner and J. M. Gilbert, to be published. We wish to thank Dr. Steiner for providing us with a preprint of this paper, and for helpful discussions concerning the method of purification.

(18) We gratefully acknowledge a generous gift of cesium metal from MSA Research Co., Inc., Callery, Pa.

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 dimethylcesium solution. At least ten points were taken in each titration, and usually many more. The pK 's were calculated from each point, and were found to be constant.

In the titrations of triphenylmethane, no end points were detected. The pK 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-methylenepheneanthrene, 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

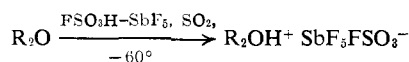
Abstract: A series of aliphatic ethers have been studied in $\text{HSO}_3\text{F-SbF}_5\text{-SO}_2$ solution. O protonation was observed at -60° by nmr spectroscopy with negligible exchange rates. At higher temperatures, cleavage to carbonium ions takes place. The kinetics of cleavage of *sec*-butyl methyl ether to trimethylcarbonium ion and protonated methanol was measured.

The proton acceptor properties of ethers have been investigated extensively² by infrared,³ conductance,⁴ and solubility⁵ measurements. These studies indicate the existence in solution of O-protonated ethers, R_2OH^+ . Kinetic measurements of cleavage of unsymmetrical ethers in sulfuric acid solution⁶ 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 Gillespie⁷ as well as Brouwer, Mackor, and MacLean⁸ 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, $\text{FSO}_3\text{H-SbF}_5$, using SO_2 as diluent.



(1) (a) Part XXV: G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 3313 (1966); (b) National Science Foundation Postdoctoral Research Investigator, 1966.

(2) W. Gerrard and E. D. Macklen, *Chem. Rev.*, **59**, 1105 (1959).

(3) (a) P. Grange, J. Lascombe, and M. L. Josien, *Spectrochim. Acta*, **16**, 981 (1960); (b) R. M. Adams and J. J. Katz, *J. Mol. Spectry.*, **1**, 306 (1957); (c) J. Arnold, J. E. Bertie, and D. J. Millen, *Proc. Chem. Soc.*, 121 (1961); (d) P. Grange and J. Lascombe, *J. Chim. Phys.*, **60**, 1119 (1963); (e) C. Quivorov and J. Neel, *Compt. Rend.*, **259**, 1845 (1964).

(4) (a) V. A. Plonikov and M. I. Kaplan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 256 (1948); *Chem. Abstr.*, **52**, 7151f (1948); (b) G. Jander and K. Kraficzky, *Z. Anorg. Allgem. Chem.*, **282**, 121 (1955).

(5) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 4999 (1964); **84**, 1680 (1962).

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

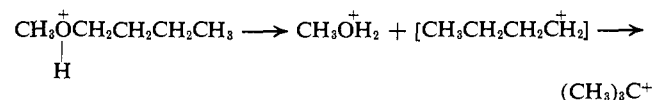
(7) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964).

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

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 ($J_{\text{H-H}} = 3.4$ 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, $J_{\text{H-H}}$, 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 $+40^\circ$ in a solution of $\text{HSO}_3\text{F-SbF}_5$ (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.



(9) G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966).