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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[10] A. I. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 313.

[11] J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.*, 54, 2088 (1932).

Communications to the Editor

Hydrocarbon–Carbanion Proton Exchange Reactions in Dimethyl Sulfoxide

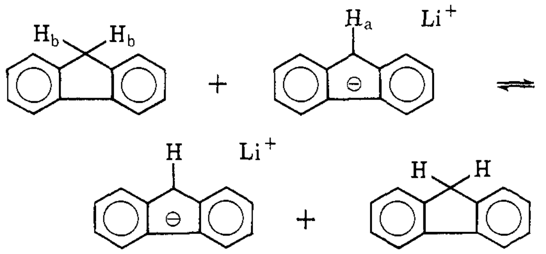
Sir:

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.

lifetime, τ, of species must be 5 min > τ > 0.1 sec. It is possible to measure the rate of this reaction by making use of nuclear magnetic double resonance.[8] Sweeping rapidly and repeatedly (0.7-sec scan) through the resonance of H_a under conditions of slow passage, one observes a signal of reproducible amplitude. Then, applying a strong radiofrequency field at the resonance frequency of H_b while continuing to sweep through H_a, one observes partial saturation of H_a (see Figure 1). Thus, protons H_b achieve a saturation condition and are converted chemically to H_a before relaxation is complete. By making use of the rate of decay of the resonance of H_a, a pseudo-first-order rate constant can be obtained. This technique is based on that of Forsén and Hoffman,[8] but it has been modified in that the proton we observe remains associated with the same molecule and changes chemical environment by virtue of another proton's being transferred. Under the conditions of our experiments, the mean lifetime of protons H_a is *ca.* 3 sec—corresponding to a bimolecular rate constant $k_2 = 0.5\ M^{-1}\ \text{sec}^{-1}$ (DMSO, 38°) assuming the reaction to be first order in anion and hydrocarbon. It is also significant that no proton exchange involving DMSO itself occurs under these conditions. Thus, the rate of proton exchange between DMSO and its conjugate base is suppressed, and protons from fluorene are exchanged with those from DMSO about 10^5 times more slowly than with other molecules of fluorene.

The rates measured by this technique are reproducible and must be correct to within at least an order of magnitude. However, the rate constant has been computed by assuming that all of the base is present as one reactive species. If free ions or various types of ion pairs are present and react at different rates, then the observed rate constant is a composite one. At the concentrations of these experiments (0.3 *M*), such effects may be important.[9,10] The observed rate constant will then be smaller than the true value, but the significance of the faster rate in DMSO remains unchanged.

Base-catalyzed reactions often occur more rapidly in DMSO than in other solvents, particularly protic solvents.[11] In the case of alkoxide ion catalyzed reactions, one suggested cause of the increased rates is associated with the increased thermodynamic basicity of alkoxide ions relative to carbanions when the solvent is changed to DMSO. The H_- function in DMSO–methanol mixtures correlates linearly with the log of rate constants for proton removal from 2-methyl-3-phenylpropionitrile with a slope of 0.87.[12] This is analogous to a Brønsted plot with a slope of close to unity, suggesting that, at the transition state, the proton has, largely, been transferred to the alcohol. One might also have expected this by applying the reasoning of Hammond's postulate, since the reaction is so endothermic.[13] The mechanism proposed[12] has the proton *completely* transferred at the transition state for other reasons as well. One then expects that, because the transition state looks like the reaction products, the effect of solvent on the transition state will resemble its effect on the products. Then, $\Delta\Delta G^{\neq} \approx \Delta\Delta G^\circ$ for the solvent change. Such reasoning is not applicable to the identity reaction (2). First, the transition state is different from reactants and products; second, $\Delta G^\circ = 0$ irrespective of solvent. Thus, DMSO can provide an additional enhancement of rates which depends on *relative* stabilization of transition states of intermediate structure and is not related to thermodynamic changes for the over-all reaction.

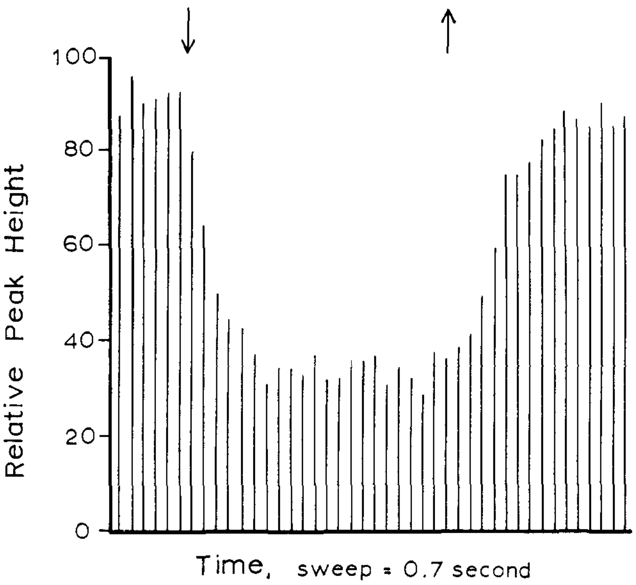

Figure 1. The decay of the nmr signal intensity of H_a on sudden saturation of H_b, and the corresponding recovery upon instantaneous removal of the saturating field. Downward arrow indicates the moment when the saturating radiofrequency field was turned on; upward arrow indicates when the saturating radiofrequency field was turned off.

DMSO is known to solvate cations effectively[14] and to promote separation in ion-paired species.[15] It may be that the rate of the reaction is enhanced because free ions or solvent-separated ion pairs are important in DMSO.[15] Neither of these species is likely to be present in ether. The effect may then be to cause less change in solvent structure and cation solvation in reaching the transition state in DMSO.[4,9] An effect of this kind can be seen readily by examining an identity reaction.

Since the nmr spectrum of a mixture of anion and hydrocarbon is a superposition of that of pure anion and pure hydrocarbon, stable hydrogen-bonded $C{-}{-}H{-}{-}C^-$ species are presumed not to be present. However, these species must have relatively large stability (at least as transition states), as evidenced by the rapid rates of proton transfer. The fact that they are not present as stable intermediates may reflect in part the added entropy of dimerizing two large molecules and

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[8] S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963); *Acta Chem. Scand.*, **17**, 1787 (1963).

[9] C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1730 (1967), have measured the rate of a similar reaction and find it to be 10^3 faster. The difference may be due, in part, to different species present at the widely different concentrations of the two experiments.

[10] Preliminary experiments indicate, however, that our rates are not suppressed by addition of a common cation.

[11] See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 1, for a good general discussion and references, and A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[12] R. Stewart and J. P. O'Donnell, *J. Am. Chem. Soc.*, **84**, 493 (1962); R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 917 (1962).

[13] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[14] J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1961).

[15] T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966).

the loss of some delocalization energy at the transition state.

Acknowledgment. We thank Professor Ritchie for informing us of his results and for helpful discussions. This work was supported, in part, by the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation.

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Proton Transfers in Dipolar Aprotic Solvents. II. Transfer from 9-Methylfluorene to 4,5-Methylenephenanthryl Anion in Dimethyl Sulfoxide Solution

Sir:

We wish to report the observation of a strikingly fast proton-transfer reaction from a hydrocarbon to a carbanion in dimethyl sulfoxide (DMSO) solution. We have found that 9-methylfluorene has a pK_a of 19.7 in DMSO, and that 4,5-methylenephenanthrene has a pK_a of 20.0 in the same solvent.[1] In view of our earlier suggestion concerning the rapidity of proton-transfer reactions in nonhydroxylic solvents,[2] it appeared of interest to measure the rate of transfer between the hydrocarbon, 9-methylfluorene, and the carbanion, 4,5-methylenephenanthryl anion, in DMSO, Certainly, if one is to find a slow proton transfer, this reaction would be expected to provide a counterexample to the previously studied cases.

A solution of 4,5-methylenephenanthryl anion in DMSO was prepared by potentiometric titration of a solution of *ca.* 5×10^{-4} *M* hydrocarbon with a solution of potassium *t*-butoxide in DMSO.[1] The solvent used was purified by the technique described in a separate paper and contained less than 5×10^{-6} *M* acidic or basic impurities and less than 10 ppm of water.

The solution of the anion was mixed with a solution of *ca.* 10^{-2} *M* 9-methylfluorene in a stop-flow apparatus,[3] and the reaction was followed either by observation of the disappearance of the absorption of the solution at 513 mμ due to the 4,5-methylenephenanthryl anion or the appearance of the absorption of the solution at 388 mμ due to the 9-methylfluorenyl anion. Rate constants calculated from the two different observations agreed within 10%. The reaction was found to be accurately second order, first order in both hydrocarbon and carbanion, and a rate constant of 1.4×10^3 M^{-1} sec^{-1} at 25.0° was obtained. A study of the reaction of 9-methylfluorene-9-*d* allowed the determination of the isotope effect on the rate. A value of $k_H/k_D = 4.2$ at 25.0° was found.

The observed reaction is most reasonably formulated as the direct proton transfer from the hydrocarbon to the carbanion. Alternative mechanisms involving indirect transfer, such as eq 1, where PH is 4,5-methylenephenanthrene, FH is 9-methylfluorene, and RH is either solvent, *t*-butyl alcohol, or water, can reasonably be ruled out on several bases.

$$P^- + RH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PH + R^- \tag{1a}$$

$$F^- + RH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FH + R^- \tag{1b}$$

If mechanism 1 were operative, second-order kinetics and a primary isotope effect would be observed only if step 1b were rate determining (*i.e.*, if $k_{-1}(PH) > k_{-2}(FH)$). This is very unlikely since (PH) is always much less than (FH) and k_{-1} is expected to be nearly equal to k_{-2}.

By methods similar to those described above, we have also observed the reaction of benzoic acid with 9-methylfluorenyl anion in DMSO solution. At a concentration of 2.9×10^{-4} *M* anion and 4.4×10^{-4} *M* benzoic acid, the reaction is complete before the solution reaches the observation chamber of the stop flow. We estimate a lower limit on the rate constant for this reaction of 10^6 M^{-1} sec^{-1}.

The rate constant observed in the present study is *ca.* 5×10^3 greater than that found by Brauman[4] for the similar reaction of proton transfer between fluorene and its lithium salt in DMSO. Several factors could reasonably be responsible for the discrepancy. At the concentrations of *ca.* 0.5 *M* used in the nmr study, ion pairing must certainly be present. If the ion pairs are less reactive than the free ions by several orders of magnitude, as is not unreasonable,[5] or if only free ions are involved in the reaction, the smaller rate constant is understandable.

In any case, the very fast proton transfers observed in DMSO provide strong evidence for the importance of solvent reorganization in drastically reducing the rates of reactions in hydroxylic solvents.

Acknowledgments. We wish to express our appreciation to Dr. Brauman for making the results of his work available to us prior to publication and for agreeing to simultaneous publication of our results. This work was supported by a grant from the Public Health Service (NIH GM-12832).

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[1] C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967).

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

[3] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, in press.

[4] J. I. Brauman, D. F. McMillen, and Y. Kanazawa, *J. Am. Chem. Soc.*, **89**, 1728 (1967).

[5] See, for example, T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307 (1966).

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γ-Deuterium Isotope Effects on the Solvolyses of Norbornyl Brosylates[1,2]

Sir:

We have measured the average kinetic isotope effects through three half-lives on the solvolysis (k_t) of *exo*-norbornyl-6-*exo*-*d* brosylate (6-*exo*-*d*-I), *exo*-norbornyl-6-*endo*-*d* brosylate (6-*endo*-*d*-I), *endo*-norbornyl-6-*exo*-*d* brosylate (6-*exo*-*d*-II), and *endo*-norbornyl-6-*endo*-*d*

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[1] This work was supported by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society.

[2] For earlier work on isotope effects in the norbornyl system, see (a) S. Borčić, V. Belanic-Lipovac, and D. E. Sunko, *Croat. Chem. Acta*, **33**, 35 (1961); (b) C. C. Lee and E. W. C. Wong, *J. Am. Chem. Soc.*, **86**, 2752 (1964); *Can. J. Chem.*, 43, 2254 (1965); *Tetrahedron*, 21, 539 (1965); (c) J. P. Schaefer and D. S. Weinberg, *Tetrahedron Letters*, 2491 (1965); (d) K. Humski, S. Borčić, and D. E. Sunko, *Croat. Chem. Acta*, 37, 3 (1965).