the loss of some delocalization energy at the transition state.

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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 $\mathrm{p}K_a$ of 19.7 in DMSO, and that 4,5-methylenephenanthrene has a $\mathrm{p}K_a$ 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,

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

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

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. 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 $k_{-1}(\mathrm{PH}) > k_{-2}(\mathrm{FH})$). 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.

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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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[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).