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IONIZATION RATES OF WEAK ACIDS III. THE ABSENCE OF A PRIMARY KINETIC ISOTOPE EFFECT IN DIMETHYL SULFOXIDE

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Recent data on the relative rates of base catalyzed isotopic proton exchange have indicated sizeable discrepancies between work at this laboratory using dimethyl sulfoxide (1) as the solvent, and comparable data obtained by Streitwieser using cyclohexylamine (2). It was postulated by ourselves (1) that this difference was due to greater charge delocalization in the more polar solvent while Streitwieser and Koch suggest that ionization may not be the true rate determining step in the alkoxide-dimethyl sulfoxide system. In order to clarify this discrepancy, work was undertaken to study the effect of solvent polarity on relative rates of exchange and to measure the kinetic isotope effect in the dimethyl sulfoxide system. The effect of polarity will be discussed in a subsequent publication. This communication describes the results of the isotope effect studies. Streitwieser has already carried out similar studies in cyclohexylamine (3) and finds the kinetic isotope effect to be quite large, $k_H/k_D = \rangle 10$, indicating that initial ionization is the rate determining step in the amine solvent.

The present work was carried out by exchanging methyl labeled toluene-d_3 with dimethyl sulfoxide and comparing the observed rate with the corresponding rate for tritium exchange. The experiments were carried out at 30°C. using a 0.6 molar solution of sublimed potassium <u>tert</u>-butoxide in dimethyl sulfoxide. The data show that the value of k_D/k_T in this system

	First Order Rate Const. @ 30°C., $sec.^{-1}$
Deuterium	9.43×10^{-5}
Tritium	1.16×10^{-4}
k_D/k_T	0.81 ± 0.1
k_H/k_D, Calc.[3]	0.62 ± 0.15

is approximately one. The data for deuterium represents an average value for all three deuteriums, but in the absence of any significant primary isotope effect there should also be no secondary isotope effect. The possibility of impurity in the deuterated toluene inhibiting the rate of exchange was also checked by carrying out the tritium exchange in an excess of the deuterated toluene. By any means of calculation the absence of a significant primary deuterium/tritium isotope effect also means that there is an absence of any significant primary hydrogen/deuterium kinetic isotope effect.

These data clearly show that the initial ionization of the C-H bond is not the rate determining step when ionization rates are measured in the alkoxide-dimethyl sulfoxide system. The important question that now arises is what, in fact, is rate controlling in dimethyl sulfoxide. Grossly, the observed rates of a number of hydrocarbons (1,4) do fall in line with the expected order of acidity. It was also found that a large kinetic isotope effect does exist for olefin isomerization (5) in the dimethyl sulfoxide-potassium tert-butoxide system ($k_H/k_D \sim 5$). A detailed interpretation of these phenomena will be discussed in a subsequent publication, but the overall conclusion is essentially the same as that originally proposed by Cram (6) for the absence of an isotope effect during racemization studies in DMSO.

This initial ionization of a hydrocarbon in the presence of an alkoxide base leads to a tight complex between the incipient carbanion and the alcohol (eq. 1). If the initial hydrocarbon is an olefin it is capable

$$RH + KOR' \rightleftharpoons \left[R^-K^+/HOR'\right] \text{ Solvated} \qquad (1)$$

of isomerizing in the complex form, thus accounting for both the isotope effect and the intramolecular nature (5,7) of the isomerization reaction. In order to undergo exchange this complex must decompose so that the carbanion is free to react with solvent (eq. 2). Qualitatively, this scheme

$$\begin{tikzcd}
\left[R^-K^+/HOR'\right]_{\text{Solv.}} \arrow[r] & \left[R^-K^+\right]_{\text{Solv.}} + HOR' \arrow[d, "CH_3SOCH_3"] \\
& RH + K^+\bar{C}H_2SOCH_3
\end{tikzcd} \qquad (2)$$

rationalizes the absence of primary isotope effect for the exchange reaction. Thus, it is not ionization (eq. 1) but complex stability and concentration that determine exchange.

Both factors depend upon the solvating power of the medium and are expected to change depending upon the nature of the base being solvated (i.e., carbon, oxygen, or nitrogen) and the stability of the incipient anion. Such changes are reflected in differences between alkoxide-alcohol-DMSO solvents and the cyclohexylamine-cyclohexylamide systems. These points will be developed in detail in a full paper.

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