

which is interpreted to be a decrease in extinction coefficient of the cation. The sharp decrease in optical density from 40 to 30% H_2SO_4 is regarded as the true shift in equilibrium from BH^+ to B. Supporting this viewpoint are the rates of decomposition which

maximize at 35% acid (Table IV), the point at which c_B/c_{BH^+} equal unity, as required for a bimolecular decomposition path.³

Acknowledgment.—The innumerable discussions with Dr. Herman G. Richey, Jr., are gratefully acknowledged.

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Ionization Rates of Weak Acids. I. Base-Catalyzed Proton Exchange between Toluene and Tritiated Dimethyl Sulfoxide

BY J. E. HOFMANN, RENE J. MULLER,¹ AND A. SCHRIESHEIM

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The base-catalyzed hydrogen isotope exchange between toluene and tritiated dimethyl sulfoxide has been carried out using potassium *t*-butoxide at temperatures ranging from 23.5 to 80°. The reaction is first order in isotope concentration and proceeds by ionization, followed by abstraction of tritium from the solvent. The reaction shows marked similarities to olefin double bond isomerization carried out in the same media and is being introduced as a simple technique for measuring the rate of ionization of very weak acids.

Introduction

The discovery that dimethyl sulfoxide exchanges protons with weakly acidic hydrocarbons under the influence of potassium *t*-butoxide² has opened a new area for the study of hydrocarbon acidity. Isotopic proton exchange has been used for a number of years for the measurement of hydrocarbon acidity,³ but except for a few cases^{4,5} this technique has been limited to substrates of $\text{p}K_a < 30$. The use of tritiated dimethyl sulfoxide and potassium *t*-butoxide in conjunction with a radio-assaying gas chromatograph now makes possible the measurement of the relative acidity of hydrocarbons of $\text{p}K_a \sim 40$.

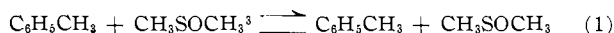
The first paper in this series gives the results for the exchange between toluene and tritiated dimethyl

sulfoxide and the following paper reports the results for exchange with a number of polyalkylbenzenes.

Results

The results of all the kinetic experiments are shown in Table I. The reported first-order rate constant is the slope of the line obtained from equation 4. From these and subsequent experiments,⁶ the precision of a single kinetic determination was found to be about $\pm 10\%$.

From the data shown in Fig. 1, it is clear that, over the temperature range studied, the exchange of toluene with tritiated dimethyl sulfoxide (eq. 1) is first order according to the general equation for isotope exchange^{7,8}



(eq. 2). If, as in the present work, dimethyl sulfoxide

$$\text{rate} = R = \frac{(T)(D)}{\alpha(T) + \beta(D)} \frac{1}{t} \ln \left(1 - \frac{X_t}{X_\infty} \right) \quad (2)$$

T = concentration of toluene

D = concentration of dimethyl sulfoxide

α = kinetic isotope effect in forward direction

β = kinetic isotope effect in reverse direction

X_t = specific activity of toluene at time (t), per reactive hydrogen

X_∞ = specific activity of toluene at equilibrium, per reactive hydrogen

is in large excess, eq. 2 reduces to

$$R = \frac{(T)}{\beta t} \ln \left(1 - \frac{X_t}{X_\infty} \right) \quad (3)$$

which can be rearranged to give

$$\ln \left(1 - \frac{X_t}{X_\infty} \right) = \frac{R\beta}{(T)} (t) \quad (4)$$

A plot of $\ln \left(1 - \frac{X_t}{X_\infty} \right)$ vs. time should then give a straight line.

No attempt has been made to measure the isotope effect β but the ratio of α to β was determined by two independent methods. First, the distribution of tritium at equilibrium was determined and second, the rate of the reverse reaction was measured by exchanging tritiated toluene with unlabeled dimethyl sulfoxide. The ratio α/β for K_{eq} is 1.49 and that for k_t/k_r

(6) For part 11, see J. E. Hofmann, R. J. Muller, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 3002 (1963).

(7) G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 315-317.

(8) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press, New York, N. Y., 1960.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR PROTON EXCHANGE IN TOLUENE AT DIFFERENT TEMPERATURES

Expt. ^a	Temp., °C.	Toluene concn., moles/l.	Base concn., moles/l.	First-order slope, sec. ⁻¹
1	23.5	0.35	0.56	1.7×10^{-4}
2	30.0	.35	.56	2.7×10^{-4}
3	55.0	.35	.56	2.9×10^{-3}
4	80.0	.35	.56	2.2×10^{-2}
5	30.0	.125	.56	3.2×10^{-4}
6	30.0	.250	.56	3.2×10^{-4}
7	30.0	.375	.48	3.3×10^{-4}
8	30.0	.375	.32	3.1×10^{-4}
9	30.0	.375	.16	1.7×10^{-4}
10	30.0	.375	.08	9.1×10^{-5}
11	30.0	.375	.56	3.0×10^{-4}
12 ^b	55.0	.375	.56	2.0×10^{-3}

^a Experiments 1-4 employed a stock solution of 0.56 M KO*t*-Bu in DMSO which was shown in subsequent work⁶ to exhibit, at standard conditions of 30.0° and 0.56 M base, an average first-order slope for 15 experiments of 2.80×10^{-4} sec.⁻¹. Experiments 5-11 employed a similar stock base-solvent solution whose average first-order slope for 6 determinations was 3.16×10^{-4} sec.⁻¹. ^b This experiment was performed using unlabeled dimethyl sulfoxide and toluene having an initial specific activity in the methyl group of 0.0225 mc./mmole.

(1) Summer employee of Esso Research & Engineering Co. (1962).

(2) A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961).

(3) (a) E. A. Halevi and F. A. Long, *ibid.*, **83**, 2809 (1961); (b) R. G. Pearson and J. M. Mills, *ibid.*, **72**, 1692 (1950); (c) R. E. Dessy, Y. Okuzumi, and A. Chev, Petroleum Division, American Chemical Society, Preprints, Vol. 7, No. 1, 1962, p. 239.

(4) (a) A. Streitwieser, Jr., *et al.*, *J. Am. Chem. Soc.*, **84**, 244 (1962); (b) **84**, 249 (1962); (c) **84**, 254 (1962).

(5) (a) A. I. Shatenshtein, *et al.*, *Tetrahedron*, **18**, 95 (1962); (b) *Dokl. Akad. Nauk SSSR*, **79**, 479 (1951).

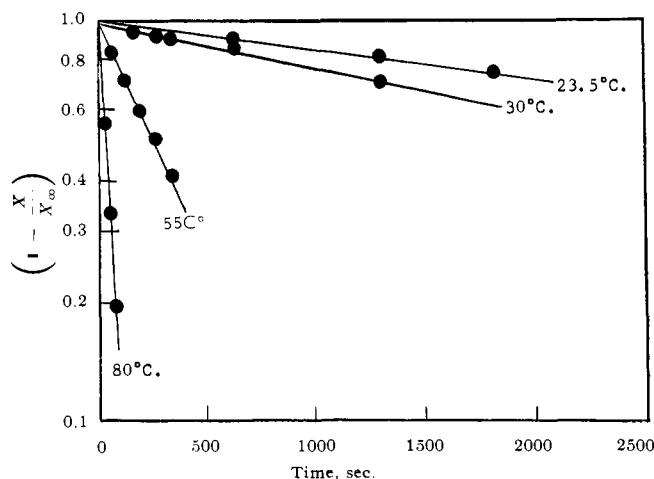


Fig. 1.—First-order behavior of proton-exchange reaction.

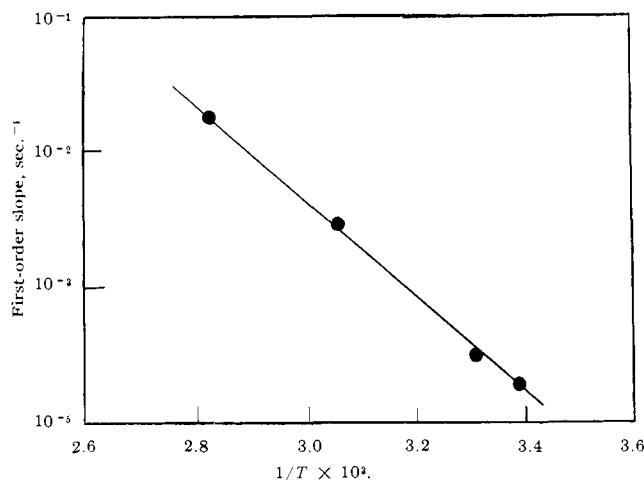


Fig. 2.—Temperature dependence of rate constant.

is 1.45, the two values being well within experimental error.

An Arrhenius plot of the temperature dependence of the rate constant is shown in Fig. 2. The activation parameters for the exchange reaction are given in Table II and compared with values obtained by Schriesheim and Rowe⁹ for the base-catalyzed isomerization of 2-methyl-1-pentene to 2-methyl-2-pentene in dimethyl sulfoxide. The entropy and enthalpy of activation were calculated from a machine least squares program and the deviation indicates the maximum and minimum slopes that could be drawn through the points.

TABLE II

ACTIVATION PARAMETERS FOR ISOTOPE EXCHANGE AND OLEFIN ISOMERIZATION

	Isotope exchange	Isom. of 2-methyl-1-pentene ^a
E_a , kcal.	18.2 ± 0.4	22.0
ΔH^\ddagger , kcal.	$17.6 \pm .3$	21.4
ΔS^\ddagger , e.u.	$-16.6 \pm .9$	-16.7

^a See ref. 9.

The effects of base and toluene concentration on the first-order slope are shown in Fig. 3 and 4, respectively. Above 0.3 *M*, the reaction is independent of base concentration but below 0.3 *M*, it approaches something close to first order.¹⁰ The same general type of behavior has been noted for other base-catalyzed re-

(9) A. Schriesheim and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3160 (1962).

(10) No attempt was made to extend this to lower base concentrations with the present techniques because trace impurities begin to contribute significantly to unreliability.

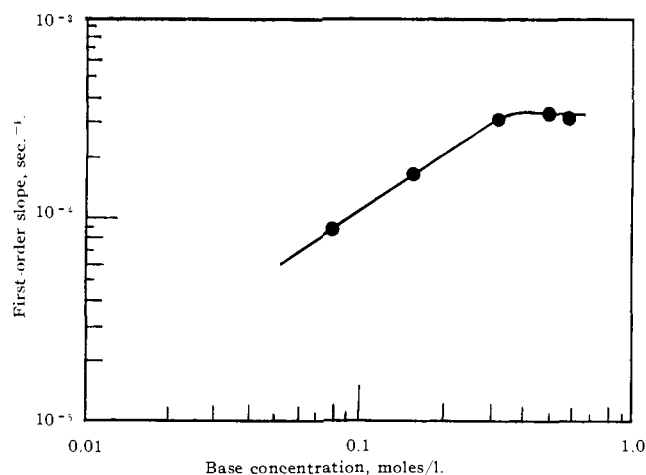


Fig. 3.—Effect of base concentration on rate of proton exchange.

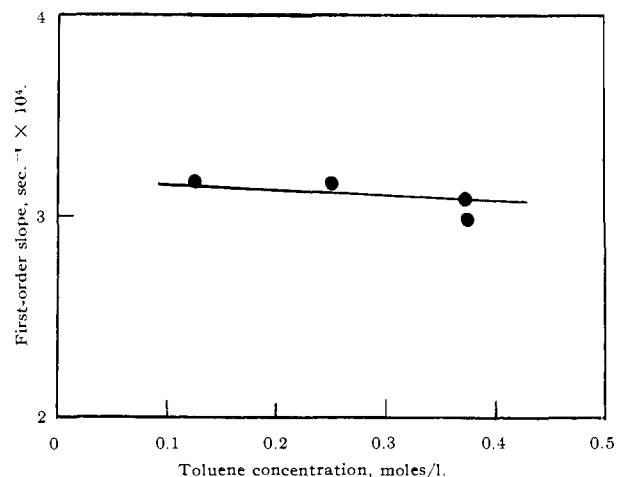


Fig. 4.—Effect of toluene concentration on rate of proton exchange.

actions in dimethyl sulfoxide.^{3a,9} Varying the toluene concentration had essentially no effect on the first-order slope up to 0.4 *M*.

That only benzylic hydrogens enter the exchange reaction has been demonstrated by several experiments. Equilibration of fully deuterated toluene with unlabeled dimethyl sulfoxide resulted in the formation of methyl C-H bonds exclusively. In addition, benzene showed no measurable exchange with tritiated DMSO after 100 hr. at 55°¹¹ and *t*-butyl benzene showed no measurable exchange after 334 hr. at 30°.

Discussion

From the rate expression given in eq. 4 it is apparent that the first-order slope is equivalent to $R\beta/(T)$. Since the slope is independent of hydrocarbon concentration and base concentration above 0.3 *M*, the rate, *R*, must be first order in toluene and zero order in base (eq. 5 and 6). The general mechanism of isotope exchange undoubtedly involves the removal of a proton

$$R = k(T) \quad (5)$$

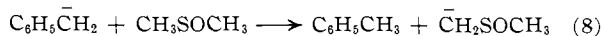
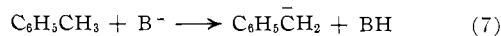
$$\text{slope} = R\beta/(T) = k\beta \quad (6)$$

from toluene (eq. 7) followed by abstraction of tritium from the solvent¹² (eq. 8). Toluene is by far the

(11) It has recently been determined that benzene does undergo exchange at 80°. However, the first-order rate constant is approximately one-millionth that of toluene and thus will have no noticeable effect on the rate constants measured for benzylic hydrogens.

(12) The postulation of a methylsulfinyl carbanion is certainly not without precedent: E. J. Corey and M. Chykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); G. A. Russell, E. G. Janzen, H. Becker, and F. J. Smentowski, *ibid.*, **84**, 2652 (1962).

least acidic of all species present and it is reasonable to



assume that the rate-determining step is the initial abstraction of a proton. The rate expression would then be given by

$$R = k_i(T)(\text{B}^-) \quad (9)$$

where k_i = rate constant for ionization.

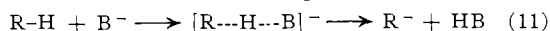
This expression is essentially equivalent to eq. 5 except for the base concentration. It has been proposed that rates become independent of base because of agglomeration.^{3a,9} Such a condition provides a constant concentration of active catalytic species even though the bulk concentration of base is changed. For these reasons, the first-order slope is, therefore, a direct measure of the rate constant for ionization (eq. 10).

$$\text{slope} = k_i/\beta \quad (10)$$

For the comparison of rates of toluene exchange at different conditions, the value of the isotope effect, β , will be essentially constant and the comparison will be related directly to the rate constants for ionization. Future work will be aimed primarily at comparing the ionization rate of toluene with other similar hydrocarbons where the ratio of β values can again be assumed to be close to unity.

The existence of an equilibrium isotope effect between toluene and dimethyl sulfoxide will not have a significant effect on the measurement of relative ionization rates. Essentially, this means a slightly higher kinetic isotope effect for the abstraction of a proton from toluene as compared to dimethyl sulfoxide. However, as previously discussed, comparisons will be made among similar compounds where all effects should be about equivalent. The isotope effect itself most likely arises because of a stronger C-H bond in the methyl group of toluene as compared to dimethyl sulfoxide, but it is not the purpose of this work to give a rigorous explanation for this observation.

The similar activation parameters for base-catalyzed olefin isomerization and isotope exchange are not unusual in view of the similarity of the proposed transition states. In both cases the rate-determining step is the initial ionization. The fraction of the initial complex that becomes free enough to abstract a proton



from the solvent or another hydrocarbon molecule has not been rigorously determined, but indications from olefin isomerization work are that the fraction is

fairly small.¹³ For exchange with alkyl aromatics there is, of course, no way of detecting how much complex is formed for each exchange measured.

Experimental

Reagents.—Baker analyzed reagent grade toluene was used as obtained from the bottle.

Potassium *t*-butoxide was obtained from Mine Safety Appliances, Inc., as the sublimed powder. Analyses showed this material to be 98.5% pure with the major impurity being potassium carbonate.

Tritiated dimethyl sulfoxide was obtained from Niche Inc. and as received had a specific activity of approximately 50 mc./g. Before use, this material was diluted 100-fold with straight DMSO that had been freshly distilled from Linde 13X Molecular Sieves. A 0.56 *M* solution of potassium *t*-butoxide in this solution was checked for catalytic activity by comparing the rate of isomerization of 2-methyl-1-pentene to 2-methyl-2-pentene with that observed for a corresponding solution of potassium *t*-butoxide in straight dimethyl sulfoxide. The rates in both solvent media agreed within experimental error.

Kinetic Procedure.—A 0.56 *M* solution of potassium *t*-butoxide in tritiated dimethyl sulfoxide was prepared in a nitrogen-blanked drybox equipped with a moisture conductivity cell. The exchange reactions were carried out using 7.0 ml. of solvent solution in small vials, capped with self-sealing neoprene stoppers in a Fisher constant temperature bath ($\pm 0.2^\circ$). After allowing sufficient time for the vial to equilibrate to bath temperatures, approximately 2.5 mmoles of toluene was injected into the solution by means of a hypodermic syringe. Aliquots were withdrawn periodically with a hypodermic syringe and injected into a small bottle containing water (to stop the reaction) and a small amount of 2,3-dimethylbutane for extraction. After shaking, the hydrocarbon phase was allowed to separate and the aqueous phase was frozen out over Dry Ice. The hydrocarbon was then analyzed on a radio-assaying gas chromatograph that has been described previously.¹⁴ A 10-ft. Dow Corning silicon oil (DC-200) column at 100° and helium pressure at 10 p.s.i.g. was employed for the chromatographic analysis. The specific activity of toluene was calculated by dividing the total counts registered (corrected for background) by the chemical peak area corrected for molar response.¹⁵ The first-order rate constants were calculated on an IBM 1620 computer, using a least squares program devised by Dr. S. Bank of this Laboratory.

The equilibrium distribution of tritium between dimethyl sulfoxide and toluene was determined by equilibrating methyl labeled toluene (obtained from New England Nuclear Corp. with a specific activity of 0.0225 mc./mmole) with unlabeled dimethyl sulfoxide. The activity of the toluene at equilibrium was measured on the radio-assaying gas chromatograph and the activity of the dimethyl sulfoxide was calculated by difference from the initial and final activities of the toluene.

Acknowledgment.—The authors wish to acknowledge helpful discussions with Professors H. C. Brown and S. J. Cristol and the Esso Research and Engineering Co. for permission to publish this work.

(13) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2115 (1963).

(14) J. E. Hofmann and A. Schriesheim, *ibid.*, **84**, 957 (1962). Note: propane was employed for the counter in place of methane.

(15) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Ionization Rates of Weak Acids. II. Base-Catalyzed Proton Exchange between Polyalkylbenzenes and Tritiated Dimethyl Sulfoxide

By J. E. HOFMANN, RENE J. MULLER,¹ AND A. SCHRIESHEIM

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The base-catalyzed hydrogen isotope exchange between polyalkylbenzenes and tritiated dimethyl sulfoxide has been carried out according to the procedures outlined in the previous paper.² It has been found that only hydrogens α to the aromatic ring undergo exchange and that ring substituents have a pronounced effect on ionization rates. Partial rate factors, defined from rate measurements with *o*-, *m*-, and *p*-xylene, have been employed to predict rate constants for benzenes containing three to six methyl groups.

Introduction

The preceding paper described the base-catalyzed proton exchange between toluene and tritiated di-

methyl sulfoxide.² The present paper gives the results for exchange with a number of polyalkylbenzenes and

(1) Summer employee of Esso Research & Engineering Co. (1962).

(2) J. E. Hofmann, R. J. Muller, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 3000 (1963).