[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

Acidity of Hydrocarbons. II. Effect of Methyl Substituents in the Exchange Reaction of Toluene-α-*d* with Lithium Cyclohexylamide[1]

BY A. STREITWIESER, JR.,[2] AND D. E. VAN SICKLE[3]

RECEIVED JUNE 21, 1961

The rates of exchange of several deuterated hydrocarbons with lithium cyclohexylamide in cyclohexylamine at 49.9° give the following relative rates: toluene-α-*d*, 1.00; *m*-xylene-α-*d*, 0.60; *p*-xylene-α-*d*, 0.29; ethylbenzene-α-*d*, 0.116; cumene-α-*d*, 0.0079. Because of the electron-donating character of methyl substituents, these results indicate a highly carbanionic transition state and provide evidence that such exchange rates are valid measures of the relative acidities of hydrocarbons.

In the first paper of this series,[4] we presented data on the kinetics of the proton exchange reaction of toluene-α-*d* with lithium cyclohexylamide in cyclohexylamine and showed that the experimental techniques developed would give reproducible and meaningful rate constants. This system was studied with the hope that the relative rates of the exchange reaction for different deuterated hydrocarbons would reflect the relative acidities of these compounds. In this paper we test this presumption by an examination of the effect of methyl groups on the rate of exchange. Methyl groups are known to be electron-donating in general and anion-destabilizing in particular; for example, *m*- and *p*-cresol are 0.81 and 0.54, respectively, as acidic as phenol.[5] If our exchange rates are measures of acidity, we expect methyl substitution to result in lower rates; if this general pattern is followed the details may then contribute to our understanding of carbanions.

Experimental

Deuterated Hydrocarbons.—*m*-Xylene-α-*d* and *p*-xylene-α-*d* were prepared from the Grignard reagents of the corresponding halides and D_2O. In such preparations we have found that the use of a small amount of EtBr prior to the addition of the desired halide removes any residual water and gives product of high deuterium content. For example, the *m*-xylene-α-*d* prepared in this manner showed 0.96 ± 0.12 methyl deuterium in the n.m.r. (determination by Mr. R. Lawler using a Varian A60 n.m.r. instrument). *m*-Methylbenzyl chloride was prepared from *m*-xylene and sulfuryl chloride using the procedure of Kharasch and Brown.[6] *p*-Methylbenzyl bromide was Eastman Kodak Co. white label recrystallized from pentane. *m*-Xylene-α-*d* had b. 138°, $n^{25.5}_D$ 1.4941 and a C–D stretching band at 4.66 μ. *p*-Xylene-α-*d* had b. 137–138°, $n^{25.5}_D$ 1.4932, and a C–D stretching band at 4.53 μ.

Ethylbenzene-α-*d* was prepared by the reduction of α-phenethyl chloride with lithium aluminum deuteride and lithium deuteride as described by Eliel,[7,8] b. 135–136°, n^{21}_D 1.4939, C–D stretching band at 4.57 μ with small shoulders at 4.45 and 4.65 μ.

2-Methoxy-2-phenylpropane was converted to cumylpotassium according to Brown, Mighton and Senkus.[9] Treatment with D_2O gave cumene-α-*d*, b. 150–152°, $n^{25.5}_D$ 1.4882, C–D stretching band at 4.74 μ with strong shoulders at 4.60 and 4.86 μ. Extensive deuteration was established in the infrared by the virtual absence of intense bands at 7.8, 7.9, 9.6 and 10.9 μ present in cumene.

The infrared spectra were taken as carbon tetrachloride solutions on a Baird double-beam infrared spectrophotometer. In all cases, known mixtures were made up with the corresponding undeuterated hydrocarbons; Beer's law was followed for the C–D stretching intensities.

Exchange Rates.—The kinetics of the proton exchange reactions of the deuterated hydrocarbons with lithium cyclohexylamide in cyclohexylamine were conducted in the manner of procedure (A) of the preceding paper.[4] Semilog plots of $\%(D - D_e)$ generally gave excellent straight lines. An example for ethylbenzene-α-*d* is given in Fig. 1. The experimental pseudo-first order-rate constants, k_{exp}, derived from such plots are summarized in Table I.

TABLE I

PROTON EXCHANGE RATES OF DEUTERATED HYDROCARBONS WITH LITHIUM CYCLOHEXYLAMIDE IN CYCLOHEXYLAMINE AT 49.9°

Hydrocarbon	Concn. of hydrocarbon, *a*, mole/l.	Formal concn. of lithium cyclohexylamide, *c*, mole/l.	10^5 k_{exp}, sec.$^{-1}$	10^5 k, sec.$^{-1}$	10^3 k_2, l./m.-sec.
m-Xylene-α-*d*	0.48	0.044	6.7	5.2	4.0
m-Xylene-α-*d*	.48	.056	7.4	5.7	4.0
p-Xylene-α-*d*	.49	.057	3.35	2.57	1.79
p-Xylene-α-*d*	.48	.042	3.2	2.46	1.90
Ethylbenzene-α-*d*	.47	.062	1.21	1.17	0.80
Ethylbenzene-α-*d*	.48	.067	1.29	1.18	.78
Ethylbenzene-α-*d*	.69	.055	1.26	1.12	.79
Ethylbenzene-α-*d*	.71	.049	1.20	1.07	.79
Cumene-α-*d*	.47	.061	0.080	0.078	.053

Discussion

The kinetics of each of the present exchanges is pseudo-first order. As in the comparable reaction with toluene-α-*d* studied in the preceding paper, the rate constants obtained from plots of the experimental data, k_{exp}, must be corrected for the back reaction and for the increasing probability during reaction that a reacting system can encounter a deuterium in solvent and end with no net reaction. These complications were treated in the same manner as with toluene-α-*d* by a correction factor (eq. 8 in ref. 4). The *k*'s so derived are the true pseudo-first-order rate constants for the forward reaction and are summarized in Table I.

The kinetics of the exchange of toluene-α-*d* with lithium cyclohexylamide in cyclohexylamine was interpreted with a scheme in which the reactive catalyst, monomeric lithium cyclohexylamide, is in equilibrium with relatively inert dimer, trimer and

---

[1] This work was supported by The United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-105. Reproduction in whole or in part is permitted for any purpose of The United States Government. This paper was presented in part at the Sixteenth National Organic Symposium of the American Chemical Society, Seattle, Wash., June, 1959.

[2] Alfred P. Sloan Fellow.

[3] Shell Development Co. Fellow, 1957–1958.

[4] A. Streitwieser, Jr., D. E. Van Sickle and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962).

[5] E. F. G. Herington and W. Knyaston, *Trans. Faraday Soc.*, **53**, 138 (1957).

[6] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).

[7] E. L. Eliel, *ibid.*, **71**, 3970 (1949).

[8] We are indebted to Mr. Gilbert Burton for this preparation.

[9] W. G. Brown, C. J. Mighton and N. Senkus, *J. Org. Chem.*, **3**, 62 (1939).

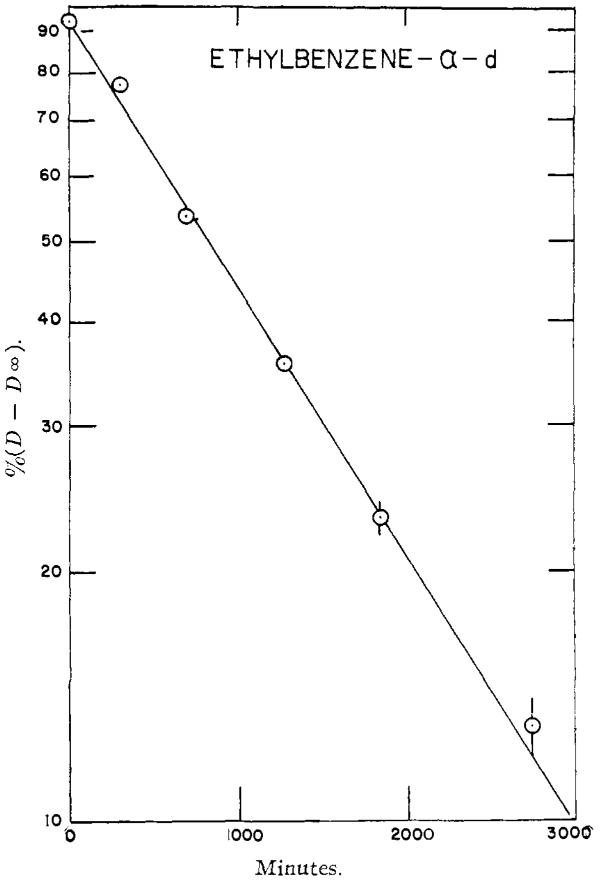

Fig. 1.—Typical kinetic run with [$C_6H_5CHDCH_3$] = 0.5 *M*, *c* = 0.063 *M*.

higher aggregates.[4] The kinetic development gives the actual concentration of monomeric lithium cyclohexylamide from the formal concentration, *c*, and allows the calculation of second-order rate constants, k_2 (eq. 16 in ref. 4). We assume the correctness of this treatment and summarize the corresponding k_2-values in Table I for the present set of compounds. The discussion that follows is actually not dependent on this assumption since all of the present kinetics were done at similar catalyst concentrations. Nevertheless, we find that the k_2-values so derived are highly reproducible.

The relative rates of the present set of hydrocarbons are compared with toluene-α-*d* in Table II. The effect of methyl substituents is clearly to retard the reaction, as expected if negative charge is developed at the benzylic position at the transition state. A methyl group is more rate-retarding in the *p*-position than in the *m*-position, indicating substantial transmission of negative charge in the ring. The three points, H, *m*-methyl and *p*-methyl, give an excellent Hammett $\sigma\rho$-line with ρ = 3.2, a rather large value substantially in excess of that given by phenol dissociations in water, 2.11,[10] and indicates further the carbanionic character of the transition state.

The closer proximity of a methyl group at the reacting center would be expected to exert a considerably greater electronic effect than at the *p*-position. Yet, ethylbenzene-α-*d* is hardly less than half as reactive as *p*-xylene-α-*d*. Certainly, most, if not all, of this diminished reactivity must be associated with the increased effectiveness of the electron-donating power of the attached methyl group in ethylbenzene-α-*d;* we are left, then, with rather little rate-retardation to be ascribed to any steric hindrance to approach of the attacking catalyst at a secondary rather than a primary hydrogen. We must conclude that methyl groups attached to the reactive center provide no effective steric hindrance in the reaction; the relatively low reaction rate of cumene-α-*d* with two methyls at the reacting center must then also be largely electronic in origin. Similarly, the small magnitude of any remaining effect means that steric inhibition of resonance cannot be a matter of large importance.

TABLE II

RD, R	$10^3 k_2$, l./m.-sec.	Relative rate	Rel. rate RH + KND_2 10° (ref. 11)
$C_6H_5CH_2$	6.7[a]	1.00	1.0
m-$CH_3C_6H_4CH_2$	4.0	0.60	
p-$CH_3C_6H_4CH_2$	1.85	.29	
$C_6H_5CH(CH_3)$	0.79	.116	0.1
$C_6H_5C(CH_3)_2$	0.053	.0079	0.03

[a] Reference 4.

It is of value to compare these results with those of Shatenshtein and Izraelevich[11] who examined the rate of introduction of deuterium into several hydrocarbons with potassium deuterioamide in liquid ND_3. Their relative rates for toluene, ethylbenzene and cumene are summarized in Table II; these values have rather large probable errors but compare qualitatively with our results. This comparison gains added significance from Shatenshtein's investigation of comparable exchange reactions of far more acidic hydrocarbons (e.g., fluorene, triphenylmethane, etc.) in liquid ND_3 without added catalyst.[12] The rates of such exchanges were found to correlate well with the *pK* values assigned by McEwen[13] to these hydrocarbons.

We conclude that the exchange rates with lithium cyclohexylamide in cyclohexylamine provide meaningful measures of hydrocarbon acidities. We are currently applying the method to a variety of additional compounds and hope to report on these studies in subsequent publications.

---

[10] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[11] A. I. Shatenshtein and E. A. Izraelevich, *Zhur. Fiz. Khim.*, **32**, 2711 (1958).

[12] A. I. Shatenshtein, *Doklady Akad. Nauk S.S.S.R.*, **70**, 1029 (1950); *cf.* also A. I. Shatenshtein and E. A. Yakovleva, *Zhur. Obsch. Khim.*, **28**, 1713 (1958).

[13] W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).