[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

A Quantitative Study of the Acidity of Certain Hydrocarbons[1,2]

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Mixtures of ethylbenzene-d_α with two other alkylaromatic hydrocarbons were heated at 150° with potassium metal in sealed ampoules for varying time periods, and the relative rates at which deuterium was transferred to the α-carbon of the two non-deuterated hydrocarbons was measured. The relative first-order rates were: cumene, 1.87; *sec*-butylbenzene, 1.00; 2-phenylpentane, 0.90; 3-phenylpentane, 0.23; 2-methyl-3-phenylbutane, 0.24; 2,2-dimethyl-3-phenylbutane, 0.14. The amount of potassium affected the absolute but not the relative exchange rates. Cumene-d_α as a deuterium source decreased α-deuteration and increased ring deuteration. Phenylcyclopropane polymerized under the exchange conditions, and diphenylmethane did not exchange with ethylbenzene-d_α. The mechanism of the exchange is discussed; the relative exchange rates are believed to be a measure of the acidities of the α-hydrogens.

Introduction

The pioneering work of Conant and Wheland[4] was the first attempt to assign pK_a values to a number of extremely weak organic acids, including hydrocarbons.[5] The position of the equilibrium RH + R'K $\rightleftarrows$ RK + R'H was determined either by observation of the color or carbonation and analysis of the resulting carboxylic acid mixture.[6] McEwen[7] extended the study to include a greater number of acids and improved the method quantitatively by using colorimetric, spectroscopic or polarimetric methods to determine the position of equilibrium.[8] Kleene and Wheland,[9] using the carbonation method, examined some monoalkylbenzenes and established the order of decreasing acidity to be phenylcyclopentane > cumene > phenylcyclohexane.

A rather different approach to acidities of very weak acids has been used by Shatenshtein[10] and by Bryce-Smith,[11] who measured rates rather than equilibria. Shatenshtein pointed out the close parallel between the exchange rate constants for a number of weak acids in ND_3 containing potassium amide and the ionization constants reported by Conant and Wheland[4] and McEwen.[7] Furthermore, "acidities" of different hydrogens in the same molecule were compared. For example, the exchange rates of methyl *vs.* ring hydrogens in toluene were 2×10^{-3} and 4×10^{-5} sec.$^{-1}$, respectively (0.05 N KND_2 in ND_3, 25°).[12] Somewhat similar results were described by Hall, Piccolini and Roberts,[13] who used deuterated benzene derivatives with KNH_2 in liquid NH_3.

Bryce-Smith,[11] in a metallation study, mainly with ethylpotassium, found metallation at the α-position in toluene, ethylbenzene and isopropylbenzene to be 100, 50 and 13%, respectively, of the total substitution. Isotopic rate effects established proton removal to be involved in the rate-determining step.[14] The rate of metallation was said to be proportional to the acidity of the hydrogen being displaced ("protophilic substitution"). As measured this way, the *m*- and *p*-hydrogens of cumene are more acidic than the α-hydrogen (although with toluene, the reverse is true[12]). Finally, the acidity of toluene was demonstrated in the most classic sense by the reported liberation of hydrogen gas on treatment with cesium metal.[15]

It is apparent from the above discussion that although the relative acidities of a wide variety of hydrocarbons have been established, precise quantitative data are lacking. Previous investigations, especially equilibria studies were limited in the main to hydrocarbons with relatively large acidity differences, in part due to the lack of sensitive methods. The present study was initiated with the hope of remedying this situation; although it was successful only in a very limited sense in meeting this goal, the results seem to be of some interest and are reported here.

It was observed[16] that the α-hydrogens of alkylaromatics exchange at measurable rates in the presence of reactive alkali metals, metal hydrides and other bases. For example, ethylbenzene-d_α, when refluxed over potassium metal, disproportionated to ethylbenzene-$d_{\alpha,\alpha}$ and ordinary ethylbenzene.

$$2C_6H_5CHDCH_3 \overset{K}{\rightleftarrows} C_6H_5CD_2CH_3 + C_6H_5CH_2CH_3$$

Presumably an organometallic compound, C_6H_5-$C^-HCH_3\ K^+$, was produced in small quantity, the anionic portion of which abstracted a proton (or deuteron) from the α-carbon of another hydrocarbon molecule. If the carbanionic species could select between two sources of α-protons, presumably it would obtain the proton from the most acidic

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] Presented before the symposium on "Carbanion Reactions and Processes of Hydrocarbons," Petroleum Division of the American Chemical Society, Atlantic City, N. J., September, 1959.

[3] Petroleum Research Fund Fellow, 1956–1958.

[4] J. B. Conant and G. W. Wheland, THIS JOURNAL, **54**, 1212 (1932).

[5] For a brief discussion, see G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 347–350.

[6] Implicit is the assumption that the degree of dissociation of the potassium salts of all these weak acids is approximately the same.

[7] W. K. McEwen, THIS JOURNAL, **58**, 1124 (1936).

[8] Some of the pKa values assigned to hydrocarbons by Conant and Wheland and by McEwen were indene, 9-phenylfluorene and phenylacetylene 21, fluorene 25, diphenylbenzylmethane 31, triphenylmethane 33, 1,1-diphenylpropene 36, and cumene 37. More acidic than any of these is the remarkable triphenylmethane derivative fluoradene, reported by H. Rapoport and G. Smolinsky, *ibid.*, **80**, 2910 (1958), to have a pKa of 11 ± 0.5.

[9] R. D. Kleene and G. W. Wheland, *ibid.*, **63**, 3321 (1941).

[10] A. I. Shatenshtein, *Doklady Acad. Nauk S.S.S.R.*, **70**, 1029 (1950); *C. A.*, **44**, 5194 (1950); A. I. Shatenshtein and E. A. Israilevich, *Zhur. Fiz. Khim.*, **28**, 3 (1954); *C. A.*, **48**, 10413 (1954).

[11] D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

[12] N. M. Dykhno and A. I. Shatenshtein, *Zhur. Fiz. Khim.*, **28**, 11 (1954); *C. A.*, **48**, 10413 (1954).

[13] G. E. Hall, R. Piccolini and J. D. Roberts, THIS JOURNAL, **77**, 4540 (1955).

[14] D. Bryce-Smith, V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 2743 (1954).

[15] J. dePostis, *Compt. rend.*, **222**, 398 (1946).

[16] H. Hart, THIS JOURNAL, **78**, 2619 (1956).

source. The relative rates of deuterium exchange of two hydrocarbons might furnish, then, a method for measuring their acidities.

Alternatively, it is possible that the rate-controlling step would be metallation, proton (or deuteron) transfer to the carbanionic moiety being rapid. In this event, differences in exchange rate would still be a measure of hydrocarbon acidities, to the extent that ease of metallation depends on the acidity of the hydrogen being displaced.[11]

The relative exchange rates of the several hydrocarbons listed in the abstract were measured as described in the Experimental part. In principle, the procedure consisted in heating a mixture of an α-deuterated alkylaromatic and two non-deuterated alkylaromatics in the presence of an appropriate catalyst, withdrawing samples periodically, separating the structurally pure components and analyzing each for its deuterium content.

Experimental

Preparation of Deuterated Hydrocarbons.—The deuterated hydrocarbons were synthesized by three general methods: (A) reduction of α-chloroalkylbenzenes with lithium aluminum deuteride and lithium deuteride, (B) hydrolysis of the appropriate Grignard reagent with D_2O and (C) cleavage of α-methoxyalkylbenzenes with potassium, followed by hydrolysis with D_2O. The following deuterated hydrocarbons were synthesized (procedure in parentheses) for the preparation of analytical calibration curves (*vide infra*): ethylbenzene-d_α (A),[17] ethylbenzene-$d_{\alpha,\alpha}$ (A),[16] diphenylmethane-d_α (A), diphenylmethane-$d_{\alpha,\alpha}$ (A), cumene-d_α (C), cumene-d_p (B), *sec*-butylbenzene-d_α (C), 3-phenylpentane-d_α (C), 2-phenylpentane-d_α (C), 2-methyl-3-phenylbutane-d_α (C) and 2,2-dimethyl-3-phenylbutane-d_α (C).[18]

Cumene-d_α.—Procedure C appears to be general for making α-deuterated alkylbenzenes, and the experimental details will be given for this typical example.[19] α-Phenylisopropylpotassium was prepared according to Ziegler[22] from 14.8 g. (0.38 g. atom) of potassium and 30.0 g. (0.20 mole) of 2-methoxy-2-phenylpropane in heptane. To this was added with stirring (argon atmosphere, 30 minutes) a solution of 8.2 g. (0.45 mole) of deuterium oxide (Stuart Oxygen Co., San Francisco, Calif.) in 75 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride). The mixture was stirred overnight, 20 ml. of water was added, the organic layer and extracts dried (calcium chloride) and distilled, giving 13.1 g. (57%) of cumene-d_α, $n^{20}\mathrm{D}$ 1.4903. Mass spectrometric analysis[23] showed 83.6%-d_1, 17.4%-d_0, no β-deuterium. This material contained $<2\%$ ring deuterium.

Analytical Procedure.—Because a mass spectrometer was not available for routine analyses, the deuterium content of the various hydrocarbons, after being subjected to exchange conditions, was determined from the intensity of the C–D stretching frequency in the infrared, using a Perkin-Elmer model 21 spectrophotometer with 0.515-mm. sodium chloride cells. Calibration curves were prepared correlating deuterium content with C–D stretching intensity in the region of 4.7 μ. Samples of known deuterium content were prepared by diluting mass spectranalyzed deuterated samples with ordinary hydrocarbon. The solvent was purified carbon tetrachloride,[24] the usual volume ratio of hydrocarbon/carbon tetrachloride being 1/1.4. Under the kinetic exchange conditions, a hydrocarbon seldom gained more than 15 atom % D, so that calibration curves were limited to this region. The logarithm of the optical density plotted against percentage deuterium gave straight lines; it was possible to estimate the deuterium content of an unknown sample ± 0.2 absolute per cent.

Separation Procedure.—Small amounts (about 1 ml.) of a three-component hydrocarbon mixture were used in the kinetic experiments, and it was necessary to separate such mixtures prior to the infrared deuterium analysis of each component. A Perkin–Elmer model 154 Vapor Fractometer was adapted for sampling and used for this purpose. Columns with type A (didecyl phthalate) or type O (silicone) were used. Experiments with test mixtures showed that separations and recovery were essentially quantitative. The hydrocarbons, collected in spiral traps, were diluted with carbon tetrachloride in a standard manner before infrared analysis.

Exchange Procedure.—Ampoules were carefully dried and flushed with argon several times, to remove air and moisture. For each kinetic run, a stock solution containing the proper ratio of hydrocarbon components was prepared. Identical volumes (1.00–1.50 ml.) of stock solution, measured with a pipet calibrated to 0.01 ml., were placed in each ampoule and a previously weighed amount of catalyst (usually 0.200 g. of potassium) added. The sealed tubes were clamped to the arm of a model BB Burrell "wrist-action" shaker (Burrell Corporation, Pittsburgh, Pa.) extending into an oil-bath (usually at 150 ± 0.5°). At the end of the designated time, ampoules were cooled in an ice-bath to quench the reaction. The contents (usually deep-red, due to organometallic) were washed two times with 1 ml. of distilled water, dried (Drierite) and set in tubes stoppered with rubber serum bottle caps, ready for injection into the Vapor Fractometer for separation and analysis (*vide supra*).

Exchange Conditions. (A) **Catalyst.**—A highly reactive catalyst was sought, to permit kinetic measurements at relatively low temperatures. High surface sodium (HSS) and potassium (HSP) on a charcoal support[25] allowed exchange as low as 65°, but unfortunately neither of these catalysts was very discriminating. Appreciable ring as well as side-chain deuteration occurred, as shown by the appearance of strong bands at 4.40 μ (the aliphatic C–D band appears near 4.68 μ; see Fig. 1).

Potassium metal at 150° was a more satisfactory catalyst, in the sense that side-chain exchange predominated (see Fig. 3). Furthermore, being a liquid at exchange temperature, a fresh catalyst surface was constantly exposed to the hydrocarbons; the disadvantage was the high temperature, which demanded a sealed ampoule technique. At temperatures below 150°, exchange was too slow for convenience; above 150°, the rate increased but exchange was less specific.

The amount of catalyst affected the absolute, but not the relative exchange rates, as demonstrated by the following experiments. Ampoules containing 1.200 ml. of stock solution made up in the proportions 3.680 ml. of ethylbenzene-d_α, 4.200 ml. of cumene and 4.680 ml. of *sec*-butylbenzene were heated at 150° with either 0.100 g. or 0.200 g. of potassium for varying times and the first-order exchange rate constants determined. The ratio of these rate constants (k 0.100 g./k 0.200 g.) was 0.747 for cumene and 0.749 for *sec*-butylbenzene.

(B) **Deuterium Source.**—*sec*-Butylbenzene and 2-methyl-3-phenylbutane were allowed to compete, at identical temperatures over equal amounts of the same catalyst, for the deuterium in ethylbenzene-d_α and cumene-d_α. More ring deuteration occurred with the latter than with the former; furthermore, side-chain deuteration proceeded 30–50% farther with ethylbenzene-d_α than with cumene-d_α (see

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(17) E. L. Eliel, THIS JOURNAL, **71**, 3970 (1949).

(18) For details of these syntheses and infrared spectra of the deuterated hydrocarbons, see Richard E. Crocker, Ph.D. Thesis, Michigan State University, 1959.

(19) This procedure is described in some detail because while this work was in progress a paper appeared[20] describing a rather similar approach to cumene-d_α which, however, gave an appreciable quantity of ring-deuterated product. Careful examination of the infrared spectrum of our cumene-d_α and comparison with spectra of mixtures containing known amounts of cumene-d_α, as well as with the spectrum of authentic cumene-d_α prepared by alkylation of benzene with 2-bromopropane-d_2 (we are indebted to Professor A. Streitwieser, Jr., for this material), showed no ring deuteration in the product obtained from procedure C; n.m.r. spectra and oxidation to benzoic acid confirmed the absence of ring deuterium. For a possible explanation of the difference between our results and those of Russell, see ref. 21.

(20) G. A. Russell, THIS JOURNAL, **79**, 3871 (1957).

(21) G. A. Russell, *ibid.*, **81**, 2017 (1959).

(22) K. Ziegler and H. Dislich, *Ber.*, **90**, 1107 (1957).

(23) We are indebted to Mr. Seymour Meyerson, Standard Oil Co. (Indiana) for all the mass spectrometric analyses connected with this work.

(24) L. F. Fieser, "Experiments in Organic Chemistry," D. C Heath and Co., Boston, Mass., 1955, p. 283.

(25) "High Surface Sodium on Inert Solids," U. S. Industrial Chemicals Co., Bulletin, 1953, p. 8.

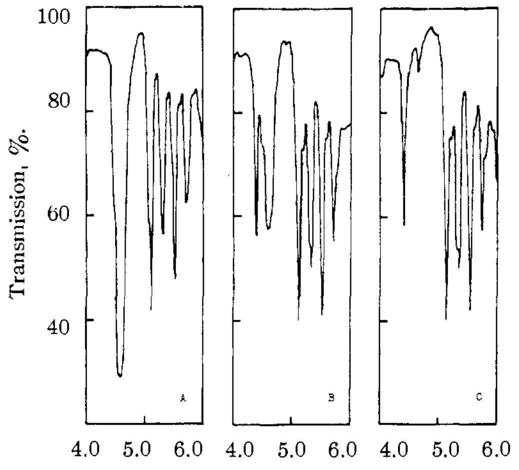

Fig. 1.—Infrared curves show extensive ring exchange with high surface sodium: A, ethylbenzene-d_α; B, recovered ethylbenzene-d after exchange with ordinary cumene at 100° for 6 hours over HSS; C, recovered cumene from the same experiment. The intense bands at 4.40 μ are due to aromatic C–D stretching.

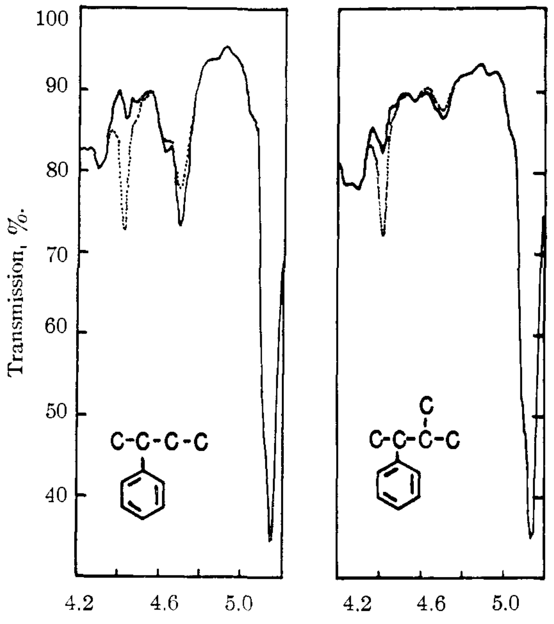

Fig. 2.—Infrared spectra illustrate the dependence of exchange on the deuterium source. *sec*-Butylbenzene and 2-methyl-3-phenylbutane were allowed to compete for the deuterium in ethylbenzene-d_α (solid line) and cumene-d_α (dotted line) under identical conditions. Exchanges with cumene showed more ring (4.40 μ) and less side-chain (4.68 μ) deuteration.

Fig. 2). Accordingly, ethylbenzene-d_α was used as the source of exchangeable deuterium in the kinetic experiments.

Results

It was first necessary to demonstrate that no rearrangements or other side reactions accompanied the deuterium exchange. In a "blank" run, a mixture of ethylbenzene, *sec*-butylbenzene and 2,2-dimethyl-3-phenylbutane was heated with potassium metal under conditions analogous to those used in the kinetic experiments (150°, 10 hours). The three hydrocarbons were not affected by this treatment (no change in infrared spectra of the separated components), although appreciable deuterium transfer from ethylbenzene-d_α to the other two hydrocarbons occurred under identical experimental conditions. Furthermore, after many of the exchange experiments, complete infrared spectra were determined on the separated products; in no case was there any change in the spectrum that could not be explained simply as a result of substitution of deuterium for hydrogen (*i.e.*, no skeletal rearrangements were apparent).

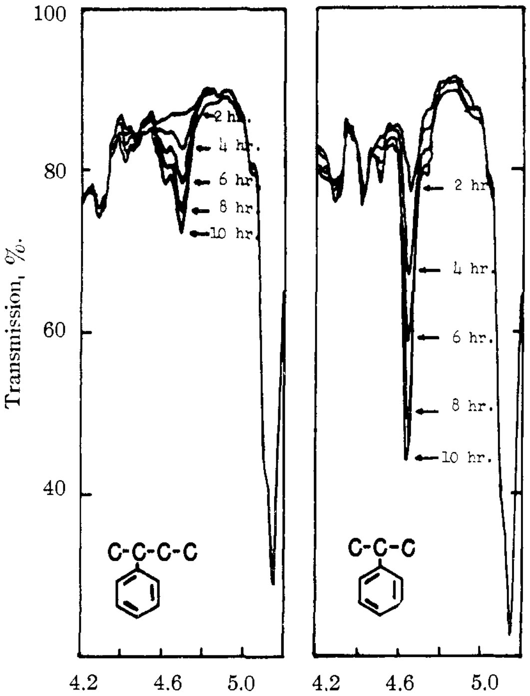

Fig. 3.—Aliphatic C–D stretching region of the infrared, showing progressive increase in side-chain exchange with time (the data are in Table I). The nearly complete lack of ring deuteration over potassium metal is to be noted (*cf.* Fig. 1).

The rates were followed by the increasing intensity of the aliphatic C–D band at about 4.68 μ; all exchange rates, then, correspond only to exchange at the α-carbon of the side-chain. Aromatic ring deuteration which, although minor, accompanied the side-chain deuteration, did not interfere, for the aromatic C–D band occurs at 4.40 μ.

Typical data for an exchange (the competition between cumene and *sec*-butylbenzene for the deuterium in ethylbenzene-$d\alpha$) are given in Table I and depicted graphically in Fig. 3. The equation for initial exchange rate in competition between equimolar amounts of two hydrocarbons (RH and R'H) for the deuterium in a third (R''D) may be derived from

$$\begin{array}{c} \text{RH} \\ 100 - x \\ \\ \text{R'H} \\ 100 - y \end{array} + \text{R''D} \longrightarrow \begin{array}{c} \text{RD} \\ x \\ \\ \text{R'D} \\ y \end{array} + \text{R''H}$$

where x and y are the mole % of RD and R'D, respectively, at time t. The first-order rate constant for exchange is then given by

$$k = \frac{2.303}{t} \log \frac{100}{100 - \%D}$$

where $\%$ D is x or y. The values of k in Table I were calculated from this equation, and the linear plots of log $100/(100 - \%D)$ *vs.* t for these data are shown in Fig. 4. Table II lists the mean rate constants for the hydrocarbons studied.[26] The relative rate constants, assigning a value of 1.00 to the average rate of *sec*-butylbenzene, the common hydrocarbon in all runs, are given in Table III.

TABLE I

COMPETITION BETWEEN CUMENE AND *sec*-BUTYLBENZENE FOR THE DEUTERIUM IN ETHYLBENZENE-d_α

0.200 ± 0.004 g. K metal, 150°, 1.200 ml. of stock solution[a] per ampoule

		Cumene		*sec*-Butylbenzene	
Sample	Time, hr.	% D exchanged	$k_1 \times 10^6$, sec.$^{-1}$	% D exchanged	$k_1 \times 10^6$, sec.$^{-1}$
1	2	3.0	4.23	1.6	2.25
2[b]	2	2.5	3.51	1.9	2.67
3	4	7.0	5.04	2.6	1.83
4[b]	4	8.2	5.94	3.9	2.76
5	6	12.2	6.10	5.8	2.77
6[b]	6	11.2	5.50	4.3	2.03
7	8	15.4	5.81	7.5	2.71
8[b]	8	16.5	6.26	7.2	2.60
9	10	18.7	5.75	8.3	2.41
10[b]	10	16.8	5.11	8.2	2.38
		Av.	5.33 ± 0.68	Av.	2.44 ± 0.26

[a] Stock solution contained 3.680 ml. of 98.5% ethylbenzene-d_α, 4.200 ml. of cumene and 4.680 ml. of *sec*-butylbenzene. [b] These points were determined in a separate experiment two weeks after the odd-numbered samples.

TABLE II

ABSOLUTE DEUTERIUM EXCHANGE RATE CONSTANTS, $k_1 \times 10^6$ SEC.$^{-1}$, 150°[a]

sec-Butylbenzene k_1	Other hydrocarbon Name	k_1
2.44 ± 0.26	Cumene	5.33 ± 0.68
2.54 ± .20	3-Phenylpentane	0.658 ± .078
2.96 ± .29	2-Phenylpentane	2.57 ± .32
2.76 ± .25	2-Methyl-3-phenylbutane	0.676 ± .118
3.15 ± .43	2,2-Dimethyl-3-phenylbutane	0.390 ± .065
Av. 2.85 ± 0.28		

[a] Each ampoule in the kinetic experiments contained 0.0051 mole (0.200 g.) of potassium metal, 0.00286 mole of each non-deuterated hydrocarbon, and from 0.00285 to 0.00493 mole of ethylbenzene-d_α, a constant number of moles being used in a given run.

TABLE III

RELATIVE RATES OF DEUTERIUM EXCHANGE, 150°

Hydrocarbon	Relative rate[a]
Cumene	1.87
sec-Butylbenzene	1.00
2-Phenylpentane	0.90
3-Phenylpentane	.23
2-Methyl-3-phenylbutane	.24
2,2-Dimethyl-3-phenylbutane	.14

[a] 2.85 × 10^{-6} sec.$^{-1}$ for *sec*-butylbenzene was used as the standard.

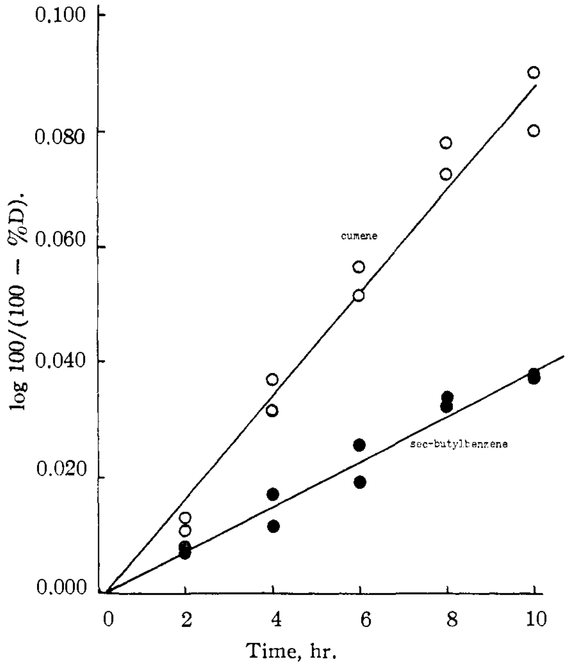

Fig. 4.—Least squares plot showing the first-order rate plots for competition between cumene and *sec*-butylbenzene for the deuterium in ethylbenzene-d_α (data derived from Table I).

It was thought of interest to compare the acidities of the α-hydrogens in cumene and phenylcyclopropane. After 10 hours with ethylbenzene-d_α over potassium at 150°, the cumene had exchanged as expected (12.9%-d_α) but the phenylcyclopropane could not be recovered; it apparently polymerized, as indicated by the loss in liquid volume and production of considerable black, tarry residue. It is possible that higher phenylcycloalkanes will be amenable to study by this technique, and some are being investigated.

Discussion

It is clear from the results summarized in Table III that in the series $C_6H_5CH(R)CH_3$ the rate of deuterium exchange at C_α is a distinct function of R, decreasing more than one order of magnitude as R is varied systematically from methyl to *t*-butyl. A similar decrease in rate (about 4-fold) was also observed for the change R′ = methyl to R′ = ethyl in $C_6H_5CH(R')CH_2CH_3$; this change is somewhat larger than the approximately 2-fold decrease for a similar change in R, but is in the same direction. It is believed that these differences in exchange rates reflect differences in the acidities of the α-hydrogens. In order to discuss them in more detail, it is necessary to consider possible steps in the exchange process.

Two steps appear likely.[27,28] These are attack by potassium metal on the hydrocarbon, forming an organoalkali compound[30]

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(26) The absolute values of these rate constants depended upon the amount of potassium metal used, decreasing with lesser amounts. The relative rates, however, were independent of the amount of catalyst (*vide supra*). In all kinetic experiments, the amount of catalyst was constant ±2 to 3%.

(27) These will be represented in a formal way, avoiding the controversy of the detailed role of the metal cation.[29] We can agree with Bryce-Smith,[11] however, that the role of the carbanion must predominate because in our experiments, where the only carbanions are of

$$\mathrm{ArCHR_1R_2 + K \longrightarrow Ar\bar{C}R_1R_2\ K^+ + H\cdot} \quad (1)$$

and proton exchange between carbanions.[27] Whether equation 1 or 2 represents the rate-determining step in the exchange process affects the order of rates to be anticipated as the structures of the hydrocarbons are systematically altered.

$$\mathrm{Ar{-}\bar{C}R_1R_2 + Ar{-}CDR_3R_4 \longrightarrow Ar{-}CDR_1R_2 + Ar{-}\bar{C}R_3R_4} \quad (2)$$

If a constant supply of carbanions were produced (*i.e.*, (1) rapid) and step 2 were rate-determining or, stated otherwise, if equal concentrations of carbanions of different basicities were produced and obliged to compete for deuterium, the least acidic hydrocarbon (most basic anion) should acquire deuterium most rapidly. Alternatively, if the reaction expressed by equation 2 were rapid and production of carbanionic species (equation 1) were rate-determining, one would expect the stablest anion (from the most acidic hydrocarbon) to be most readily produced; that hydrocarbon which was the strongest acid would then acquire deuterium most rapidly.[31] A plausible decision between these two alternatives is possible in the light of Bryce-Smith's results[11] which show that α-alkyl groups, when substituted on toluene, decrease the acidity of the α-hydrogens. We conclude that the rates of deuterium exchange correspond to the relative rates of metallation of the various hydrocarbons on the α-carbon, *i.e.*, that equation 1 is the rate-determining step.[32] The observed decreasing rates, if controlled by electronic release by R to the α-carbon, follow the inductive order for the alkyl groups. The same order might be predicted for increased steric effect of the alkyl groups, but the magnitudes of the rate differences and the gradual rate decrease (no sudden change from isopropyl to *t*-butyl) suggests electronic rather than steric control.

One series of experiments was performed to determine the effect of the deuterium source on the exchange rates and path. When cumene-d_α was used in place of ethylbenzene-d_α the amount of side-chain deuteration decreased and ring deuteration became important (see Fig. 2). The α-deuterium of cumene is less available for exchange than the α-deuterium of ethylbenzene.[33] This would decrease the rate of step 2, allowing for ring as well as side-chain metallation of the competing hydrocarbons.

The exchange technique cannot be applied to hydrocarbon mixtures which differ too widely in acidity. For example, when diphenylmethane was heated with ethylbenzene-d_α over potassium metal or HSS or HSP as catalysts for reaction times from 2–67 hours over temperatures from 80–175°, no deuterium was picked up by the diphenylmethane. Presumably the diphenylmethyl carbanion is not sufficiently basic to remove a proton from the α-carbon of ethylbenzene.

In summary, the relative rates of deuterium exchange in Table III appear to be related quantitatively to the acidities of the α-hydrogens in the hydrocarbons listed.[34]

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the relatively stable benzylic-type, exchange is much more selective than with ethyl potassium,[11] where the carbanion cannot be resonance-stabilized. We observe almost exclusive α-deuteration of cumene, whereas Bryce-Smith found predominant ring attack. The cations were the same.

[28] An alternative exchange process, direct displacement by hydride (or deuteride ion) $[\mathrm{D^- + Ar\text{-}CHR_2 \rightarrow Ar\text{-}CDR_2 + H^-}]$ will be neglected, for lack of evidence.

[29] See, for example, A. A. Morton and co-workers, *J. Org. Chem.*, **20**, 428, 981 (1955); THIS JOURNAL, **65**, 1339 (1943); **67**, 1620 (1945); **69**, 969 (1947); **71**, 487 (1949). See also ref. 11, 14 and D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

[30] The other product may be hydrogen gas or potassium hydride; this was not determined.

[31] As pointed out by the referee, this is of course an oversimplification since equation 2 is reversible. But in this work the deuterium source was ethylbenzene-d_α, with secondary α-hydrogens, whereas in the hydrocarbons competing for the detuerium the α-hydrogens were tertiary. The equilibrium constant for (2) was therefore at least 10 (see footnote 33) and the reverse process can be neglected in the measurement of initial rates.

[32] NOTE ADDED IN PROOF.—An alternative, more attractive, and from the present work indistinguishable mechanism is the metallation of the most acidic hydrocarbon (ethylbenzene-d_α) with subsequent competitive and selective proton transfer from the non-deuterated hydrocarbons. Tertiary carbanion formation is still rate-controlling but the base may be the secondary carbanion rather than potassium metal. We are indebted to Professor Glen Russell for calling this to our attention.

[33] Cumene is the weaker acid for electronic reasons; also, protophilic attack at the α-carbon may be sterically hindered when the α-carbon is tertiary.

[34] Shortly after this paper was submitted for publication, Professor A. Streitwieser, Jr., presented an excellent paper on "Base Catalyzed Hydrogen–Deuterium Exchange in Hydrocarbons" before the Sixteenth National Organic Chemistry Symposium in Seattle, Wash. The rate of deuterium loss from deuterated arylalkanes, studied in cyclohexylamine containing lithium cyclohexylamide, was considered to be related to the acidities of the hydrocarbons. Examples reported by Streitwieser do not permit at present a direct comparison of his results with ours, but it is pertinent that methyl substitution (alpha or on the ring) decreased the acidities of α-hydrogens markedly. The relative rates for toluene, ethylbenzene and cumene were 1.00/0.11/0.009, respectively.