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Acidity of Hydrocarbons. III. Primary Isotope Effects in the Proton Exchange of Toluene and Ethylbenzene with Lithium Cyclohexylamide[1]

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Primary isotope effects were determined for the proton exchange reactions of toluene-α-*d* and -α-*t* and of ethylbenzene-α-*d* and -α-*t* with lithium cyclohexylamide in cyclohexylamine. The k_D/k_T values average 3.0 ± 0.2, a rather high value that corresponds to $k_H/k_D \cong 12$. This high isotope effect is shown to rule out a one-step mechanism for the exchange and to implicate relatively stable intermediates of the carbanion type.

In the first paper of this series,[4] we showed that the exchange reaction between toluene-α-*d* and lithium cyclohexylamide in cyclohexylamine is a second-order process between the hydrocarbon and monomeric lithium cyclohexylamide. In the second paper[5] the rate-retarding effect of methyl substituents was taken to indicate the development of substantial negative charge on the benzylic carbon at the transition state. Such a process suggests that the rate-determining step involves breaking of the C–D bond, a not unexpected result, but one that is readily checked by the primary isotope effect.

The reaction examined is a net replacement of D by H; the replacement of H by H is undetected in this system. Hence, we cannot measure directly a k_H/k_D isotope effect. Fortunately, nature has blessed us with three isotopes of hydrogen and we can determine a deuterium–tritium isotope effect. A mixture of toluene-α-*d* and toluene-α-*t* was prepared by treating benzylmagnesium chloride with tritium-enriched D_2O. Ethylbenzene-α-*t* was prepared by reduction of acetophenone with tritium-enriched sodium borohydride. The resulting alcohol was mixed with 1-phenylethanol-1-*d* and both were converted to the hydrocarbon *via* the chloride. The exchange rates were determined as in previous examples, except that both loss of deuterium and tritium from the hydrocarbon were followed simultaneously within each run; loss of deuterium was followed by the infrared spectrum of the hydrocarbon and loss of tritium was followed by scintillation counting of aliquots of the hydrocarbon. The results of three runs are summarized in Table I.

TABLE I

PRIMARY ISOTOPE EFFECTS ON EXCHANGE RATES AT 49.9°

RD + RT, R	Concn. of hydrocarbon, mole/l.	Formal concn. of $LiNHC_6H_{11}$ c, mole/l.	10^5 $k_{D\text{exp}}$, sec.$^{-1}$	10^5 $k_{T\text{exp}}$, sec.$^{-1}$	k_D/k_T[a]	k_H/k_D eq. 1
$C_6H_5CH_2$–	0.77	0.059	9.9	3.47	2.8	10
$C_6H_5CH_2$–	.76	.050	10.5	3.30	3.2	14
$C_6H_5CH(CH_3)$–	.69	.095	1.26	0.424	3.0	12

[a] Estimated error is ±0.3.

Experimental

Ethylbenzene-α-*t* + Ethylbenzene-α-*d*.—To a solution of 5.7 mg. of sodium borohydride in 13.3 ml. of isopropyl alcohol was added 2 mg. of tritium-enriched sodium borohydride (New England Nuclear Corp., activity 1 mc./mg.). To this solution was added 1.5 g. of acetophenone in 5 ml. of isopropyl alcohol. After the solution was warmed to 70° and allowed to stand at room temperature for 36 hours, the isopropyl alcohol was evacuated and the residue was digested on the steam-bath for 24 hours with 10 ml. of 10% aqueous sodium hydroxide.

Meanwhile, 24 g. (0.2 mole) of acetophenone was reduced with 2.0 g. of lithium aluminum deuteride in the usual way. The resulting ether solution of 1-phenylethanol-1-*d* was added to the tritiated product and the resulting mixture was washed, dried and distilled to yield 21.7 g. (85% yield) of a mixture of 1-phenylethanol-1-*d* and 1-phenylethanol-1-*t*, b. 74° (4 mm.), having a specific activity of 25,300 c./mg. min.

The alcohol was converted to the chloride by dissolving 10 g. in 50 ml. of chloroform and adding this solution to a mixture of 40 ml. of pyridine and 7.0 g. of hydrogen chloride. After cooling to −20°, 11 g. of phosphorus oxychloride was added with stirring. The mixture was washed, dried and distilled to give 7.0 g. (61%) of the deuterated and tritiated α-phenethyl chloride, b. 50–51° (3 mm.).

The chloride (5 g.) was reduced with excess lithium aluminum hydride in tetrahydrofuran in the usual way. An additional 2.0 g. of ethylbenzene-α-*d* was added as a carrier; the final product was 3.5 g. of ethylbenzene-α-*d* and ethylbenzene-α-*t*, b. 135–136°, having 14,400 c./mg. min.

Toluene-α-*d* and Toluene-α-*t*.—Benzylmagnesium chloride was prepared from 126.5 g. (1 mole) of benzyl chloride and 24.3 g. of magnesium after first preparing a small amount of ethylmagnesium bromide in the same solution to remove residual water. To this solution was added 0.50 ml. of water prepared by diluting 0.10 ml. of tritiated water of activity 0.1 mc./mg. (New England Nuclear Corp.) to 15 ml. After allowing the tritiated water to react thoroughly, excess D_2O was added. Distillation of the product through a small column gave 56 g. (60%), b. 109.6–110°. Infrared analysis showed that the product was about 90% monodeuterated; its specific activity was 440 c./mg. min.

Kinetic Measurements.—The reactions with lithium cyclohexylamide in cyclohexylamine were carried out as described previously.[4] Procedure (A) was used for ethylbenzene; procedure (B) for toluene. The hydrocarbon was isolated from aliquots by extracting with ether and distilling. Toluene so isolated was 98–99% pure by v.p.c. analysis, the contaminant being ether. The infrared deuterium analyses and the liquid scintillation tritium counts were corrected appropriately. No such corrections were applied in the ethylbenzene experiment.

Scintillation counting was performed using a toluene-diphenyloxazole counting solution in conjunction with liquid scintillation counter facilities kindly furnished by the University of California Lawrence Radiation Laboratory.[6] Samples to be analyzed were chilled to *ca.* −30° before counting in order to increase reproducibility.

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[2] Alfred P. Sloan Fellow.

[3] (a) National Science Foundation Coöperative Predoctoral Fellow, 1959–1960; (b) 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] A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 249 (1962).

[6] Details of the counter are published in E. M. Baker and E. Vogelsberg, UCRL 3240, Dec., 1955, p. 28. We are indebted to Irving Whittemore for technical assistance.

The experimental rate constants were determined by plotting the measures of isotope content minus the infinity values against time on semi-log paper. Straight lines were obtained, the slopes of which were used to derive the rate constants in Table I. This procedure is more accurate for data such as ours than calculating the instantaneous rate constants. However, as an example, one run with toluene is given in Table II. Because our isotope effects are measured in competition reactions, the comparisons may be made using the k_{exp} values; it is unnecessary to use corrected rate constants.[4]

TABLE II

EXCHANGE OF TOLUENE-α-d AND -α-t

Temperature = 49.9°, formal lithium cyclohexylamide concn. = 0.050 M, toluene concn. = 0.76 M

Time, min.	Tritium counts	k_T,[a] min.$^{-1}$	C–D intensity[b]	k_D,[a] min.$^{-1}$	k_D/k_T
0	40210		0.408		
70	35430	2.05	.293	5.9	2.9
120	33140	1.83	.223	6.0	3.3
200	28600	1.96	.147	6.4	3.3
290	23970	2.08	.115	5.8	2.8
2500	4300		.047		

[a] Calculated as $k = \frac{2.303}{t} \log \frac{y_0 - y_\infty}{y_0 - y}$. [b] log I_0/I for C–D stretching band.

The isotope contents of hydrocarbon at infinity provide measures of the isotope effect in the equilibrium distribution constant.[4] In the example in Table II these quantities are 0.107 for tritium and 0.115 for deuterium. In the other toluene run, these ratios are 0.112 and 0.112, respectively. The equality of these numbers within experimental error provides evidence for the absence of a substantial isotope effect in the exchange equilibrium.

Discussion

For hydrogen transfer reactions, Swain, *et al.*,[7] have shown how the hydrogen, deuterium and tritium rates are interrelated. Their derivation made use only of the usual assumptions in the theoretical treatment of hydrogen isotope effects, namely, neglect of anharmonicity, the assumption of relatively high vibration frequencies and the assumption that the entire isotope effect lies in zero point energy differences. Their result, which is transposed for our purposes into eq. 1, was tested and found to be correct for two widely different isotope effect magnitudes.

$$k_H/k_D = (k_D/k_T)^{2.26} \qquad (1)$$

Melander[8] has given an equivalent derivation and has considered a further extreme case in which not only the stretching frequency of the hydrogen being transferred contributes to the reaction coördinate but the bending frequencies also become very small. For this case, we have eq. 2.

$$\frac{k_H}{k_D} = \left(1.11\,\frac{k_D}{k_T}\right)^{2.26} \qquad (2)$$

With the aid of these interrelationships, our experimental k_D/k_T ratios may be converted to k_H/k_D values for comparison with related isotope effects. For our average value of $k_D/k_T = 3.0 \pm 0.2$, eq. 1 gives $k_H/k_D = 12 \pm 2$ (Table I); eq. 2 yields k_H/k_D = 13–18. Although these equations are only approximations, they are not unreasonable approximations; our isotope effects are certainly relatively large, and probably not much smaller than 10. This effect may be compared with certain "theoretical maximums" for primary hydrogen isotope effects. With the usual assumptions of neglect of anharmonicity, and the changes in other vibration frequencies, etc., the loss of a C–H stretching mode has a maximum isotope effect $k_H/k_D \cong 7$, whereas the loss of the two C–H bending frequencies as well gives a theoretical maximum of $k_H/k_D \cong 13$ at 50°.[9] These maxima are, themselves, approximations, but our isotope effect is clearly large by comparison.[10]

Isotope effects for two comparable reactions have been reported. In the metalation of toluene-α-d with ethylpotassium, Bryce-Smith, Gold and Satchell[11] found $k_H/k_D = 5$. More recently, Shatenshtein, *et al.*,[12] found the exchange of fluorene in liquid ammonia with no catalyst to have $k_D/k_T = 2.0$, a value that corresponds to $k_H/k_D \cong 5$.

In exchange reactions between benzylic hydrogens and lithium cyclohexylamide, the primary isotope effect shows that the motion of the abstracted hydrogen is an important part of the reaction mode. We may examine further aspects of the reaction mechanism; in particular, let us examine the one-step mechanisms, for which Fig. 1 is a possible but not unique transition state. Regardless of stereochemical and other structural details, all such mechanisms have in common the concerted motion of two hydrogens, that from the hydrocarbon to lithium cyclohexylamide and another from either solvent or lithium cyclohexylamide to the hydrocarbon. The fact that the over-all equilibrium in this reaction shows no significant isotope effect (the distribution constant for deuterium between hydrocarbon and cyclohexylamine is unity)[4] means that the isotope effect for the reverse reaction (putting deuterium into the hydrocarbon) must be the same as that for the forward reaction (removing deuterium from the hydrocarbon). Hence, in the one-step mechanism the motions of both hydrogens are important in the reaction mode. *To get an isotope effect that approaches the theoretical maximum with any such mechanism, both hydrogens would have to be isotopically substituted.* Isotopic substitution of only one hydrogen would give a substantially smaller isotope effect than that actually observed.

The argument is sufficiently illustrated by the following simplified example in which we put the entire isotope effect into the loss of zero point energy of one stretching mode that is approximated as the reaction mode, all other vibrations being neglected. The two virtually uncoupled C–H and N–H stretching modes of the reactants pass over into *sym*- and *antisym*-stretching modes of the transition state. The *antisym*-mode corresponds to the reaction mode and vanishes. The zero-

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(7) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958).

(8) L. Melander, "Isotope Effects on Reaction Rates," The Roland Press Co., New York, N. Y., 1960, p. 23.

(9) Reference 8, Table 2-1.

(10) We should note that our high isotope effect cannot be attributed to tunneling. The effect was measured with deuterium and tritium whose heavier masses lead to less tunneling. The extrapolation to k_H/k_D assumes the absence of tunneling; if tunneling is significant, k_H will be higher than calculated and k_H/k_D will be still larger than our extrapolated values.

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

(12) F. S. Yakushin, Y. G. Dubinskii, E. A. Yakovleva and A. I. Shatenshtein, *Russ. J. Phys. Chem.*, **33**, 647 (1959).

point energy change is then given as

$$\Delta E^0 = \frac{1}{2}\,h\,(\nu^{\ddagger}_{\text{sym}} - \nu_{\text{C-H}} - \nu_{\text{N-H}}) \qquad (3)$$

For simplicity, we take all of these frequencies to be the same and equal to 3000 cm.$^{-1}$ and approximate the changes on isotope substitution to be due to the changes in reduced masses assuming that all other atoms in the molecules are infinitely heavy compared to hydrogen. We have, then

$$\Delta E^0(\text{H,H}) = -\frac{1}{2}\,h\nu_{\text{C-H}} = -4.32 \text{ kcal./mole}$$

$$\Delta E^0(\text{H,D}) = -\frac{1}{2}\,h\left(-\frac{\sqrt{3}}{2} + \frac{2+\sqrt{2}}{2}\right)\nu_{\text{C-H}} = -3.65 \text{ kcal./mole}$$

$$\Delta E^0(\text{D,D}) = -\frac{1}{2}\,h\left(-\frac{1}{\sqrt{2}} + \frac{2}{\sqrt{2}}\right)\nu_{\text{C-H}} = -3.05 \text{ kcal./mole}$$

Replacement of a single hydrogen by deuterium increases the activation energy by 0.67 kcal./mole compared to the 1.27 kcal./mole increase caused by replacement of both hydrogens. This 1.27 kcal./mole increase is exactly that given by a comparable treatment for the effect of deuterium substitution on loss of zero point energy of a single C–H stretching vibration.

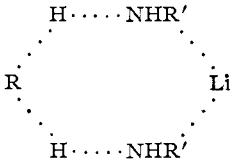

Fig. 1.—Possible transition state for a one-step mechanism of proton exchange between RH and LiNHR' in R'NH$_2$.

Consequently, the present experimental results enable us to eliminate all one-step or concerted mechanisms. At least one discrete intermediate must be implicated in the exchange reaction. At this point, the only reasonable such intermediate or intermediates are of the carbanion or alkyllithium type.

It is important now to determine to what extent the kinetics of a reaction involving an intermediate are consistent with the kinetic formulation of the exchange reaction developed in Paper I.[4] The reaction may now be written as eq. 4:

$$\text{RH}_{n-1}\text{D} \underset{k_{-\text{D}}}{\overset{k_{\text{D}}}{\rightleftharpoons}} \text{I} \underset{k_{\text{H}}}{\overset{k_{-\text{H}}}{\rightleftharpoons}} \text{RH}_n \qquad (4)$$

We again must consider the increasing content of deuterium in solvent by writing

$$-\frac{\mathrm{d}[\text{RH}_{n-1}\text{D}]}{\mathrm{d}t} = k_{\text{D}}[\text{RH}_{n-1}\text{D}] - k_{-\text{D}}[\text{I}]\rho \qquad (5)$$

in which ρ is the proportion of deuterium in solvent; *e.g.*, $\rho = [\text{R'NHD}]/[\text{R'NH}_2]_0$. By this formulation of the reaction with solvent in terms of the relative proportions of hydrogen and deuterium in solvent, all of the rate constants remain pseudo-first-order constants.

Application of the steady state procedure gives eq. 6 as the expression for [I].

$$[\text{I}] = \frac{k_{\text{D}}[\text{RH}_{n-1}\text{D}] + nk_{\text{H}}[\text{RH}_n]}{k_{-\text{D}}\rho + k_{-\text{H}}(1-\rho)} \qquad (6)$$

which may be substituted into eq. 5. To derive the equilibrium distribution, we set eq. 5 equal to zero; using the same symbols as in Paper I[4] gives eq. 7 in which $k_{\text{D}}k_{-\text{H}}/k_{-\text{D}}k_{\text{H}}$ is now identified as the same distribution constant, K, derived previously.[4]

$$\frac{k_{\text{D}}k_{-\text{H}}}{k_{-\text{D}}k_{\text{H}}} = \frac{na(1-x_{\text{e}})^2}{x_{\text{e}}[2b - a(1-x_{\text{e}})]} = K \qquad (7)$$

Since K is found to equal unity experimentally, it follows that $k_{\text{H}}/k_{\text{D}} = k_{-\text{H}}/k_{-\text{D}}$; *i.e.*, the isotope effect for removal of hydrogen from hydrocarbon with lithium cyclohexylamide is the same as that for abstracting hydrogen from solvent with the intermediate. With the appropriate substitutions, eq. 5 now becomes

$$-\frac{\mathrm{d}[\text{RH}_{n-1}\text{D}]}{\mathrm{d}t} = k_{\text{D}}[\text{RH}_{n-1}\text{D}] - k_{\text{D}}\rho\,\frac{k_{\text{D}}[\text{RH}_{n-1}\text{D}] + nk_{\text{H}}[\text{RH}_n]}{k_{\text{D}}\rho + k_{\text{H}}(1-\rho)} \qquad (8)$$

The extreme right hand term in eq. 8 is a correction term for the back reaction and is relatively small compared to the first term ($\rho << 1$). The denominator in the last term, $k_{\text{D}}\rho + k_{\text{H}}(1-\rho) \cong k_{\text{H}}$; making this change introduces little error and makes the arithmetic far simpler. If we now let $\lambda = k_{\text{H}}/k_{\text{D}}$, eq. 8 becomes

$$-\frac{\mathrm{d}[\text{RH}_{n-1}\text{D}]}{\mathrm{d}t} = k_{\text{D}}([1-\rho\lambda][\text{RH}_{n-1}\text{D}] - n\rho[\text{RH}_n]) \qquad (9)$$

Making the substitutions as above and integrating yields the final expression for the rate constant

$$\ln\frac{x_0 - x_{\text{e}}}{x - x_{\text{e}}} = \frac{Q}{2b}\,k_{\text{D}}t \qquad (10)$$

in which $Q = \sqrt{(2b - \lambda a)^2 + 8nab}$.

This expression is identical with our original expression for the forward rate constant except for a small change in the meaning of Q. In the original derivation,[4] $Q = \sqrt{(2b-a)^2 + 8nab}$. At the concentrations normally used, the difference is only about 2%, and because of the approximation used in deriving eq. 9, we retain the original definition of Q.

This derivation shows that our rate constants as previously obtained are the rate constants for removal of deuterium to form an intermediate. This derivation and the magnitude of λ, the primary isotope effect, also mean that the intermediate is sufficiently stable to behave kinetically as a normal compound. This situation may be contrasted with that recently described by Cram, Scott and Nielsen[13] who found rather small isotope effects in proton exchange reactions of 2-octyl phenyl sulfone. Their explanation, which seems reasonable, is that the carbanion intermediate is so reactive it abstracts hydrogen from solvent faster than solvent can diffuse away. Hence, when a base removes deuterium in an isotopically substituted example, this deuterium has enhanced probability of being recovered by the sulfone. In effect, the carbanion is in equilibrium with the sulfone and the rate-determining step for isotope exchange is the diffusion away of a solvent molecule carrying the isotope. A similar situation may be responsible for the relatively small primary isotope effects observed by Hine, *et al.*,[14] in proton exchange

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[13] D. J. Cram, D. A. Scott and W. D. Nielsen, *J. Am. Chem. Soc.*, **83**, 3696 (1961).

[14] J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956); J. Hine, R. Wiesboeck and R. G. Chirardelli, *ibid.*, **83**, 1219 (1961).

reactions of polyhalo-methanes and ethanes with aqueous base.

Our relatively large isotope effect shows that we are not plagued by the phenomenon apparently observed by Cram and Hine; *i.e.*, in the present case the carbanion-type intermediate clearly reacts sufficiently slowly with solvent that diffusion of solvent is not rate-determining.

Salts in cyclohexylamine are but slightly dissociated[15]; because of its comparative stability, our intermediate is probably not a free carbanion but is probably better described as a lithium alkyl. The further question of the more detailed description of such an organometallic derivative as a covalent compound or as "tight" or "loose" ion-pair is reserved for the discussion in Paper V.[16]

[15] Conductivity experiments of W. M. Padgett to be published shortly.

[16] A. Streitwieser, Jr., D. E. Van Sickle and L. Reif, *J. Am. Chem. Soc.*, **84**, 258 (1962).

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Acidity of Hydrocarbons. IV. Secondary Deuterium Isotope Effects in Exchange Reactions of Toluene and Ethylbenzene with Lithium Cyclohexylamide[1]

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Some secondary deuterium isotope effects were studied in the exchange reactions of hydrocarbons with lithium cyclohexylamide in cyclohexylamine; $k(C_6H_5CHDCH_3)/k(C_6H_5CHDCD_3) = 1.11 \pm 0.03$, a result that is interpreted to indicate that the transition state has substantial carbanionic character. $3k(C_6H_5CH_2D)/k(C_6H_5CD_3) = 1.31$; analysis of this result suggests that the leaving deuterium and perhaps a lithium are close to the central carbon at the transition state.

Despite the several continuing controversies regarding the detailed interpretation of some secondary deuterium isotope effects, sufficient data are now available to provide useful analogies in elucidating structural and electronic influences in transition states of some reactions.[4] It was with the hope of gathering useful information about the nature of the hydrocarbon moiety of the transition state for the proton exchange reaction with lithium cyclohexylamide in cyclohexylamine that studies were undertaken of some secondary deuterium isotope effects in this reaction.

A β-deuterium isotope effect was obtained with the use of ethylbenzene-α,β,β,β-d_4. This compound was obtained by the following sequence: acetophenone was repeatedly treated with D_2O and a trace of base to exchange the α-hydrogens. Reduction with lithium aluminum hydride gave 1-phenylethanol-2,2,2-d_3, which was converted to the chloride and reduced with lithium aluminum deuteride and lithium deuteride. The resulting hydrocarbon was mixed with ethylbenzene-α-*d* and the mixture was allowed to exchange with lithium cyclohexylamide in cyclohexylamine following our usual procedure.[5] Aliquots of the hydrocarbon were isolated at intervals and the relative amounts of the various deuterated ethylbenzenes present were determined by mass spectroscopy.[6]

An α-deuterium isotope effect was obtained through the use of toluene-α,α,α-d_3. This compound was prepared by reduction of benzotrichloride with zinc and acetic acid-*d*.[7] This material was mixed with toluene-α-*d* and this mixture was also allowed to exchange with lithium cyclohexylamide following our usual procedure. Samples of toluene were isolated at intervals and analyzed by mass spectroscopy.[6]

Results and Discussion

β-Deuterium Isotope Effect.—Replacement of the α-deuterium atom in ethylbenzene-α,β,β,β-d_4 gives ethylbenzene-β,β,β-d_3. In principle, the change in either reactant or product with time could be used to give a rate constant; however, because the methyl group was not fully deuterated, enough $-d_3$ compound is converted to $-d_2$ to make more reliable the determination of the rate constant by following the disappearance of $-d_4$. For the same reason we follow the appearance of $-d_0$ rather than the disappearance of $-d_1$ for determining the rate of reaction of ethylbenzene-α-*d*.

In Fig. 1, these changes are compared graphically. The $-CD_3$ group clearly slows the rate by about 10%.

Alternately, a point by point comparison may be effected by the use of eq. 1, in which the time has been eliminated.

$$\frac{k_{CH_3}}{k_{CD_3}} = \frac{\log \dfrac{D_0{}^0 - D_0{}^e}{D_0{}^t - D_0{}^e}}{\log \dfrac{D_4{}^0 - D_4{}^e}{D_4{}^t - D_4{}^e}} \qquad (1)$$

D_n refers to the percentage of $-d_n$ component in the ethylbenzene aliquot. This procedure yields $k_{CH_3}/k_{CD_3} = 1.11 \pm 0.03$.

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[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.

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

[4] For recent reviews, see (a) L. Melander, "Isotope Effects on Reaction Rates," the Ronald Press Co., New York, N. Y., 1960, Chapt. 5; and (b) A. Streitwieser, Jr., *Ann. N. Y. Acad. Sci.*, **84**, 576 (1960).

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

[6] We are greatly indebted to Dr. David P. Stevenson of the Shell Development Co., Emeryville, Calif., for the mass spectral analyses.

[7] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956).