

rates against these  $pK$  values in Figure 4 shows no semblance of a correlation. It seems clear that dif-

ferent factors are involved in the effect of structure on these two systems. It may be noted incidentally that the simple MO argument in eq. 2 can be applied as well to the amine basicities but the values in Table IV also do not correlate with  $\pi_{\tau,r}$ . Daudel<sup>35</sup> has shown recently that advanced MO theories provide little improvement over this simple method but that the introduction of a solvation energy term does help to explain the variations in amine basicities.

(35) R. Daudel, *Tetrahedron Suppl.*, 2, 351 (1963).

## Acidity of Hydrocarbons. XIX. Kinetics and Mechanism of Exchange of Benzene and *sec*-Butylbenzene with Cesium Cyclohexylamide<sup>1</sup>

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Contribution from the Department of Chemistry, University of California, Berkeley, California. Received July 19, 1965

Proton exchange of benzene-*t* with cesium cyclohexylamide (CsCHA) is first order each in hydrocarbon and in CsCHA ion pairs. The second-order rate constants are 3300 times faster than the comparable rate constants with lithium cyclohexylamide and the reaction has a high primary isotope effect ( $k_D/k_T = 2.5$ ). The  $\alpha$ -position of 2-phenylbutane has a  $k_T$  0.38 that of benzene-*t* and each replacement of an  $\alpha$ -hydrogen by hydrogen occurs with complete racemization. The reaction mechanism appears to be a rate-determining proton transfer to a cesium cyclohexylamide ion pair giving an organocesium as a definite intermediate which reacts with solvent by the microscopic reverse process.

### Introduction

An extensive and continuing study of hydrocarbon acidities, as determined by rates of proton exchange reactions in cyclohexylamine with lithium cyclohexylamide (LiCHA) as catalyst, has been carried out in these laboratories.<sup>3</sup> The mechanisms of the exchange reactions with LiCHA have been studied in considerable detail and the observed rate constants apparently are useful measures of relative carbanion stabilities. Benzylic,<sup>4</sup> arylmethyl,<sup>5</sup> phenylalkyl,<sup>6</sup> and aryl<sup>1b</sup> anions have been studied in this manner. However, the exchange rate of benzene-*d* or -*t* itself is inconveniently slow with LiCHA and application to still less reactive hydrocarbons would be difficult.

(1) (a) This work was supported in part by grants from the Petroleum Research Fund of the American Chemical Society; (b) paper XVIII: A. Streitwieser, Jr., and R. G. Lawler, *J. Am. Chem. Soc.*, **87**, 5388 (1965).

(2) National Science Foundation Predoctoral Cooperative Fellow, 1962-1964.

(3) See ref. 1b and preceding papers in this series.

(4) A. Streitwieser, Jr., and W. C. Langworthy, *J. Am. Chem. Soc.*, **85**, 1757 (1963).

(5) A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

(6) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 249 (1962).

In preliminary experiments<sup>7</sup> we found that cesium cyclohexylamide (CsCHA) gave exchange several orders of magnitude faster than LiCHA. These observations led to the present study of the kinetics and mechanism of exchange with CsCHA of benzene-*d,t* and 2-phenylbutane-2-*d,t*.

### Experimental Section

Benzene-*d,t* was described earlier.<sup>8</sup>

**2-Phenylbutane.** Addition of phenylmagnesium bromide to 2-butanone afforded 2-phenyl-2-butanol, b.p. 91° (8 mm.) (lit.<sup>9</sup> b.p. 97° (15 mm.)). The lithium salt of this alcohol was prepared in dry benzene with butyllithium. Addition of methyl *p*-toluenesulfonate to the benzene solution and refluxing for 2 days afforded 2-phenyl-2-methoxybutane, b.p. 84-89° (10 mm.). Cleavage with sodium-potassium alloy (78% potassium, from MSA Research Corp.) in ether and quenching with tritiated D<sub>2</sub>O afforded 2-phenylbutane-2-*d,t*, b.p. 77-78° (25 mm.).

(-)-2-Phenylbutane was prepared following Cram.<sup>10</sup>

**Kinetic Procedures.** The general procedures were patterned after those used for LiCHA with changes as noted.

**A. Preparation of Cesium Cyclohexylamide Solutions.** Metallic cesium was obtained from MSA Research Corp. in sealed ampoules. The ampoules were broken under vacuum in a reactor designed for that purpose. The cesium was then allowed to react with cyclohexylamine, which was bulb-to-bulb distilled from LiCHA into the reactor. Reaction of 1 g. of cesium with 25 ml. of cyclohexylamine at about 60° required about 1 day. A piece of platinum wire

(7) Unpublished results of W. M. Padgett, II, H. F. Koch, and R. G. Lawler.

(8) Paper XVII: A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *J. Am. Chem. Soc.*, **87**, 5383 (1965).

(9) K. T. Serijan and P. H. Wise, *ibid.*, **74**, 365 (1952).

(10) D. J. Cram, *ibid.*, **74**, 2137 (1952).

was usually used to catalyze the reaction. Hydrogen gas pressure was relieved at intervals. Stock solutions so prepared were yellow-green in color and contained a white precipitate. After the white precipitate had settled, an aliquot of the stock solution was pressured into one side of a bifurcated reactor for carrying out type B<sup>1b,8</sup> kinetics.

A modified procedure for obtaining metallic cesium involved the pyrolysis *in vacuo* of cesium azide (Eastman White Label) with subsequent distillation of the cesium metal as formed. Two distillations were found to be necessary to remove the last traces of nonvolatile material formed during the pyrolysis. The pyrolysis section and the distillation section were sealed off from the body of the reactor before cyclohexylamine was distilled in. Thus, the cyclohexylamine had contact only with the doubly distilled cesium. In some runs singly distilled cesium was used but gave high rate constants—the catalyst appeared to be in excess of that titrated. Results from this and other studies<sup>11,12</sup> showed that doubly and triply distilled cesium gave results in agreement with those using the MSA ampoules.

**B. Exchange Procedures.** Exchange reactions were run in a fashion similar to that employed for the relatively fast reactions (half-lives on the order of minutes) with LiCHA.<sup>4</sup> With a solution of cesium cyclohexylamide on one side of the bifurcated reactor,<sup>4</sup> the hydrocarbon or hydrocarbons to be exchanged were bulb-to-bulb distilled from thoroughly outgassed molecular sieves into the other side of the reactor. Cyclohexylamine was similarly distilled into the reactor from a storage flask containing lithium cyclohexylamide as drying agent. The reactor was maintained under a pressure of about 2 atm. of purified nitrogen or argon. After equilibration in a constant temperature bath at  $25.00 \pm 0.02^\circ$ , the two sides were mixed thoroughly, and aliquots were ejected at intervals through a side arm and stopcock into a small amount of water. Aliquots were partitioned between either spectral grade cyclohexane or spectral grade isooctane and dilute HCl; the hydrocarbon layer was dried over magnesium sulfate and saved for analysis.

In some of the runs as indicated in the tables the nitrogen or argon was "purified" by passing through benzophenone ketyl in tetraglyme. It was found subsequently that traces of tetraglyme were carried over with the gas and produced rate constants that were not consistent with the amounts of base titrated. The absolute rates in these cases are not meaningful, but relative rates of hydrocarbon mixtures run together are still satisfactory.

**C. Base Titration.** It proved difficult to obtain solutions of cesium cyclohexylamide uncontaminated by basic materials which were inactive as exchange catalysts. Accordingly, the active base titration described earlier,<sup>13</sup> involving quenching of the solution with bromobenzene and titration of the liberated bromide ion, was used. In much of the present work, bromobenzene was dried over outgassed molecular sieves and distilled into ampoules, which were then sealed off.

(11) Paper XX: A. Streitwieser, Jr., R. A. Caldwell, R. G. Lawler, and G. R. Ziegler, *J. Am. Chem. Soc.*, **87**, 5399 (1965).

(12) G. R. Ziegler, unpublished results.

(13) A. Streitwieser, Jr., R. A. Caldwell, M. R. Granger, and P. M. Loughton, *J. Phys. Chem.*, **68**, 2916 (1964).

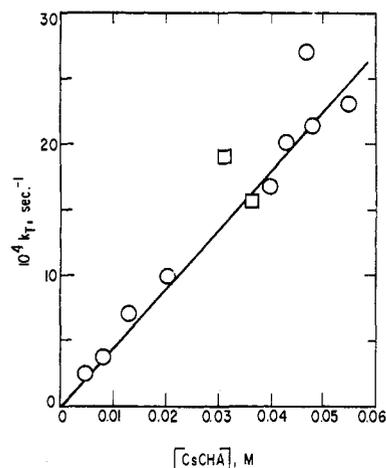


Figure 1. The plot of pseudo-first-order rate constants for benzene-*t* vs. CsCHA concentration shows that the exchange reaction is first order in CsCHA. Squares are tritio-deprotonation rates.

These ampoules could be placed inside an appropriately constructed reactor and broken at the end of a run; it was thus possible to quench the solution in an inert atmosphere.

Owing to the difficulty of preparing cesium cyclohexylamide solutions of known concentrations, only indirect checks on the stoichiometry of the reaction between cesium cyclohexylamide and bromobenzene were possible. Titration with standard acid affords a maximum value for the cesium cyclohexylamide concentration, whereas titration with bromobenzene gives at worst a minimum value. We use the rate constant for tritio-benzene exchange as another monitor of the active base concentration to compare runs which give the same rate constant but in which total base was titrated in one and active base was titrated in the other. We find that total base titrations are in general 30–80% higher than active base titrations in this comparison, but that some experiments, in which only small amounts of inactive base must have been present, give total base titers which agree with active base titers. Such agreement, taken together with the smooth plot in Figure 1 and the reproducibility of the active base titer for a given rate constant, lends strong credence to our assumption of 1:1 stoichiometry. Nevertheless, as indicated above, in some of the runs impurities were present which catalyzed exchange but did not titrate by the bromobenzene method. These runs are labeled in the tables of results to follow.

**D. Analysis of Kinetic Points.** In general, more than one labeled hydrocarbon was present in a given run. A gas chromatograph-proportional flow counter<sup>5</sup> was used for tritium analysis; either Carbowax 20 M or Vytan was found to be satisfactory for all of the separations used in this research.

Deuterium analyses were performed by isolation of hydrocarbon samples *via* preparative gas chromatography and subsequent examination of the C–D stretching intensity in the neat hydrocarbon using a Perkin-Elmer 0.1-mm. microcell. Under these analysis conditions Beer's law was found to hold for the compounds studied. Care was taken to collect the entire peak in order to avoid isotopic fractionation on the g.c. Rate constants for deuterium exchange obtained for mixtures

**Table I.** Exchange of Benzene-*d,t* with CsCHA at 25°

Run no.	[CsCHA], <sup>a</sup> mole/l.	10 <sup>4</sup> k <sub>D</sub> , sec. <sup>-1</sup>	10 <sup>4</sup> k <sub>T</sub> , sec. <sup>-1</sup>	k <sub>D</sub> /k <sub>T</sub>	10 <sup>2</sup> k <sub>2</sub> <sup>T</sup> , l. mole <sup>-1</sup> sec. <sup>-1</sup>
10	(0.023) <sup>b</sup>	32.1 ± 1.1	12.0 ± 0.9	2.67 ± 0.22	
11 <sup>c</sup>	(0.020) <sup>b</sup>		9.8 ± 0.3		
13 <sup>c,d</sup>	(0.032)		8.1 ± 0.9		
14 <sup>e</sup>	0.048 (0.051)		21.2 ± 1.0		4.4
15 <sup>e</sup>	0.043 (0.050)		20.3 ± 1.1		4.7
16 <sup>d</sup>	(0.019)	24.7 ± 1.3	10.8 ± 0.7	2.29 ± 0.21	
19	0.047		27.4 ± 0.4		5.9
20	0.055 (0.105)		24.2 ± 0.1		4.4
21	0.0047		2.78 ± 0.08		6.0
22	0.013		7.50 ± 0.25		5.8
23 <sup>c,d</sup>	0.020		10.4 ± 0.1		5.2
24 <sup>d</sup>	0.0079		3.62 ± 0.08		4.6
25 <sup>e</sup>	0.013 <sup>e</sup>		3.49 ± 0.10		
27 <sup>d,t</sup>	0.0145 <sup>e</sup>		10.0 ± 0.5 <sup>f</sup>		
28 <sup>d,t</sup>	0.0076 <sup>e</sup>		5.45 ± 0.11		
32 <sup>e</sup>	0.0098 <sup>e,g</sup>		9.03 ± 0.22		
42 <sup>h</sup>	0.040		17.0		

<sup>a</sup> Cesium was obtained from MSA Corp. or doubly distilled from pyrolysis of CsN<sub>3</sub> unless otherwise noted. Numbers in parentheses are total base content by acid titration; otherwise, results of the bromobenzene reaction are cited. <sup>b</sup> Fisher Chemical Co., once distilled. <sup>c</sup> These runs also contained toluene-*o,m*, or *p-t* or cumene-*α-t* and are discussed in ref. 11. <sup>d</sup> These runs contained 2-phenylbutane; cf. Table III. <sup>e</sup> Benzophenone ketyl used to "purify" pressurizing inert gas; k<sub>2</sub> values are not valid. <sup>f</sup> At 49.9°. <sup>g</sup> CsN<sub>3</sub> pyrolysis product once distilled. <sup>h</sup> Run contained propene-2-*t* to be published later.

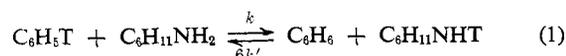
by the method above agreed with the results of experiments with the individual deuterated hydrocarbons, in which g.c. separation was not necessary.

Polarimetric analyses were carried out directly on the hydrocarbon extract from each aliquot in a 1-dm. tube. The concentration of optically active hydrocarbon was obtained via g.c. analysis with an internal standard.

*E. Kinetic Expressions.* Several runs involved the exchange of more than one hydrocarbon. The associated complications have been discussed previously.<sup>5,8</sup> Perrin's program<sup>8</sup> was used to derive those rate constants for which standard deviations are assigned. Kinetic expressions for the case in which only one hydrocarbon is present have been derived previously for both deuterium<sup>14</sup> and tritium<sup>5</sup> exchange.

## Results and Discussion

*Kinetic Order in CsCHA.* In the exchange of tritio-benzene with cyclohexylamine catalyzed by CsCHA,



the reverse reaction must be considered because the proton pool in the solvent is not infinite compared to the substrate. The kinetic treatment has been derived before.<sup>5</sup> We assume that  $k = k'$  in eq. 1; that is, that the distribution of tritium between benzene and cyclohexylamine is statistical at equilibrium. This assumption appears to be valid (*vide infra*) although even a substantial isotope effect could be tolerated since  $k'$  is used only as a small correction factor to the observed rate. For benzene-*t* run by itself a plot of  $\log(x - x_\infty)$ , where  $x$  is the specific tritium activity, vs.  $t$  gives a straight line whose slope is used to derive  $k$ .<sup>5</sup> In eq.

$$\ln \frac{x_0 - x_\infty}{x - x_\infty} = \left(1 + \frac{na}{2bK}\right)kt \quad (2)$$

2,  $n$  is the number of exchangeable hydrogens,  $a$  is the

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

**Table II.** Exchange of Benzene with Cyclohexylamine-*t* and CsCHA

Run no. <sup>a</sup>	Temp., °C.	[CsCHA], <sup>b</sup> mole/l.	10 <sup>4</sup> k <sub>T</sub> , sec. <sup>-1</sup>	10 <sup>2</sup> k <sub>2</sub> <sup>T</sup> , l. mole <sup>-1</sup> sec. <sup>-1</sup>
34	25.0	0.0083 <sup>c,d</sup>	6.75	
35	25.0	0.0056 <sup>c,d</sup>	1.66	
36	48.3	0.055 <sup>d</sup>	215	
37	49.8	0.066 <sup>d</sup>	275	
38	25	0.033 <sup>d</sup>	25.0	
39	25	(0.0063) <sup>d,e</sup>	16.0	
40	25	0.036	15.7	4.3
41	25	0.031	19.2	6.2

<sup>a</sup> Mixtures with one or more of the following hydrocarbons were used; norbornene, norbornadiene, cyclohexane, cyclopropane, and cyclobutane. These results will be discussed in subsequent papers. [CsCHA] determined by bromobenzene method. <sup>b</sup> Doubly distilled cesium from pyrolysis of CsN<sub>3</sub> unless noted otherwise. <sup>c</sup> Benzophenone ketyl used to treat the pressurizing gas; k<sub>2</sub> values are not valid. <sup>d</sup> Pyrolysis cesium was singly distilled; k<sub>2</sub> values are not valid. <sup>e</sup> [CsCHA] apparently in error.

concentration of hydrocarbon, usually 0.1–0.3 M,  $b$  is the concentration of cyclohexylamine, and  $K$  is the distribution constant which is taken as unity. Experimentally, first-order dependence was verified up to 90% reaction. In the many runs which contained two or more hydrocarbons, Perrin's program<sup>8</sup> was used for extracting the rate constants. The results for protodeuteration and detritiation of benzene-*d,t* are summarized in Table I. In some runs, ordinary benzene was used with tritiated cyclohexylamine. These results are summarized in Table II and show that  $k'$  in eq. 1 is close to  $k$ . Perrin's program is not applicable to tritiodetritiation and these rate constants were determined graphically.

Because of aggregation of LiCHA ion pairs,<sup>13,14</sup> in exchange reactions catalyzed by LiCHA a log-log plot of the pseudo-first-order rate constant vs. the LiCHA concentration is a curve tending towards zero slope at high LiCHA concentrations. A similar plot of the benzene results with CsCHA gives a straight line with a

slope close to unity; the reaction is of first order in CsCHA. This fact is also demonstrated by the approximate constancy of the second-order rate constants in Tables I and II,  $k_2^T = 5.0 \pm 0.6 \times 10^{-2}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. A better method is the plot of  $k_T$  vs. [CsCHA] given in Figure 1. Nine points have been used to define a straight line through the origin with  $k_2^T = 4.5 \times 10^{-2}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. There is some suggestion of a higher slope near the origin, curving downwards slightly at higher concentrations, a phenomenon that could be attributed to a salt effect, but the accuracy of the CsCHA assays do not justify such elaboration at this time. Because of the problems in determining the CsCHA concentration, two or more hydrocarbons were exchanged together in most runs in order to obtain relative rates directly.

We wished to obtain the activation parameters for the exchange of benzene, but, unfortunately, all of the runs at higher temperature in this study have suspect CsCHA concentrations. Our best approach is to compare those exchange reactions in which the CsCHA was prepared from once-distilled cesium from the pyrolysis of cesium azide. Runs 32, 34, and 38 plus other runs of Ziegler<sup>15</sup> indicate that exchange rates with this procedure are high by ~75%. If this correction is applied to runs 36 and 37, we calculate  $\Delta H^* \cong 13$  kcal./mole and  $\Delta S^* \cong -22$  e.u. These results are unlikely to be much in error especially since they compare with Ziegler's values for toluene-2-*t*,  $\Delta H^* = 15$  kcal./mole and  $\Delta S^* = -17$  e.u. For comparison, Shatenshtein and Izrailevich<sup>16</sup> report  $\Delta H^* = 15$  kcal./mole,  $\Delta S^* = -19$  e.u. for exchange of benzene-*d* with potassium amide in liquid ammonia, and Lawler<sup>8</sup> finds  $\Delta H^* = 12$  kcal./mole,  $\Delta S^* = -37$  e.u. for exchange of naphthalene-2-*d* with LiCHA. The CsCHA and KNH<sub>2</sub> exchange systems are similar in having  $\Delta S^*$  values that are normal for second-order reactions, and much less negative than the LiCHA reactions in which additional solvation of the lithium cation appears to be required at the transition state.

Monomeric CsCHA ion pairs are the active catalysts in this system. Some limited conductivity studies were made with the results in Table III.<sup>17</sup> The results are

Table III. Conductivity of CsCHA at 25 ± 1°

[CsCHA], <i>M</i>	$L^s$ , mho/ohm	$\Lambda_s$ , mho cm. <sup>2</sup> /equiv.
0.036	$1.3 \times 10^{-7}$	$3.6 \times 10^{-4}$
0.022	$0.84 \times 10^{-8}$	$4.0 \times 10^{-4}$

approximate but agree with independent work of Schwager<sup>18</sup> who found  $\Lambda_c = 3 \times 10^{-4}$  for [CsCHA] = 0.02 *M* at 49.5°. If CsCHA were completely ionized in cyclohexylamine the expected  $\Lambda_c$  would be about 30–40, or ~10<sup>5</sup> greater than observed. If the free

(15) G. R. Ziegler, unpublished results.

(16) A. I. Shatenshtein and E. A. Izrailevich, *Zh. Fiz. Khim.*, **28**, 3 (1954).

(17) The apparatus and technique used are described in A. Streitwieser, Jr., W. M. Padgett, II, and I. Schwager, *J. Phys. Chem.*, **68**, 2922 (1964). The bromobenzene assay method was used with CsCHA.

(18) I. Schwager, unpublished results.

ions in equilibrium were the active catalytic agent, the kinetics would be half-order in [CsCHA]; the observed first-order dependence is conclusive evidence for reaction *via* monomeric ion pairs. Aggregation of LiCHA was associated with the loss of solvent molecules required to solvate lithium cations in the monomeric ion pair.<sup>13</sup> The larger cesium cation probably is not solvated appreciably and this type of mechanism is not operative. The absence of solvation requirements also explains the normal  $\Delta S^*$  for exchange with this reagent.

The second-order rate constant for reaction of benzene-*t* with LiCHA at 25° may be estimated as  $1.4 \times 10^{-5}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. This estimate comes from the known  $k_2^T$  at 50° and the activation energy for exchange of naphthalene- $\beta$ -*d*.<sup>8</sup> From the ratio of second-order rate constants, CsCHA is 3300 more active than monomeric LiCHA. Because of the aggregation of LiCHA, the experimental rate constants show greater differences which vary with the base concentration. At 0.05 *M*, a common concentration in many of our studies, the ratio of experimental pseudo-first-order rate constants is 35,000. This large rate difference allows the study with CsCHA of exchange rates of hydrocarbons too slow for satisfactory measurement with LiCHA. The large rate differences appear to be explicable in terms of cation solvation. The small lithium cation requires extensive solvation; in LiCHA ion pair this role is partially filled by cyclohexylamide ion, and the close proximity of the two ions presents a substantial coulombic attraction. The larger cesium cation has a more diffuse charge and has much lower solvation requirements. The distance to cyclohexylamide ion in the ion pair is greater and the coulombic attraction is less; hence, cyclohexylamide ion is "freer" and has a more concentrated negative charge available for function as a base.

The CsCHA–cyclohexylamine system has an exchange reactivity somewhat greater than but similar to that of KNH<sub>2</sub>–liquid ammonia. The rate of exchange of benzene-*d* with CsCHA is 27 times that of benzene with KND<sub>2</sub> in ND<sub>3</sub> at 25°. It is interesting that our system with CsCHA ion pairs is actually *more reactive* than the KNH<sub>2</sub>–NH<sub>3</sub> system in which the catalytic species appears to be the free amide ion,<sup>16</sup> perhaps because amide ion in ammonia is encumbered by hydrogen bonds to solvent.

*2-Phenylbutane.* Included in this study are some exchange rates with 2-phenylbutane-2-*d,t* as summarized in Table IV. The  $\alpha$ -position of 2-phenylbutane is 0.38 as fast as benzene at 25°, 0.46 as fast at 50°. This exchange for 2-phenylbutane has  $\Delta H^* = 1.4$  kcal./mole higher and  $\Delta S^* = 1.2$  e.u. more positive than reaction with benzene.

The primary reason for including 2-phenylbutane in this study was to determine the stereochemistry of the exchange reaction. Racemization,  $k_\alpha$ , is 13 times faster than tritium exchange of benzene. This relative  $k_\alpha$  needs to be compared with the relative  $k_H$  for specification of the stereochemistry. From the primary isotope effect,  $k_D/k_T = 2.7 \pm 0.3$  (*vide infra*),  $k_D/k_{C_6H_5T} = 1.0 \pm 0.2$ , and from the relationships between  $k_T$ ,  $k_D$ , and  $k_H$ ,<sup>19,20</sup>  $k_H/k_{C_6H_5T} = 10 \pm 3$ ; thus  $k_\alpha/k_H = 1.3$

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

(20) A. Streitwieser, Jr., W. C. Langworthy, and D. E. Van Sickle, *ibid.*, **84**, 251 (1962).

**Table IV.** Exchange Rates of 2-Phenylbutane-2-*d,t* with CsCHA at 25°

Run no. <sup>a</sup>	[CsCHA], <sup>b</sup> mole/l.	10 <sup>4</sup> k <sub>T</sub> , sec. <sup>-1</sup>	k <sub>T</sub> /k <sub>C<sub>6</sub>H<sub>5</sub>T</sub>	10 <sup>4</sup> k <sub>D</sub> , sec. <sup>-1</sup>	k <sub>D</sub> /k <sub>T</sub>
13	(0.032)	2.9 ± 0.2	0.36	6.6 ± 0.2	2.3 ± 0.2
16	(0.019)	4.05 ± 0.13	0.38	12.5 ± 0.4	3.1 ± 0.1
18	(0.034)	0.84 ± 0.06		2.45 ± 0.02	2.9 ± 0.2
23	0.020	4.01 ± 0.16	0.39	10.4	2.6
24	0.0079	(48) <sup>c</sup>	(13.3) <sup>e</sup>		
26	0.0044	(15.3) <sup>c</sup>	(12.8) <sup>d</sup>		
27 <sup>e,f</sup>	0.0145	4.64 ± 0.24	0.46		
28 <sup>e,f</sup>	0.0076	2.52 ± 0.07	0.46		
43 <sup>g</sup>	0.051	8.92			

<sup>a</sup> Hydrocarbon mixture contained labeled benzene and/or toluene and/or cumene. <sup>b</sup> Concentration by bromobenzene assay except for values in parentheses which are for acid titration. MSA cesium or doubly distilled pyrolysis product of CsN<sub>3</sub> was used. <sup>c</sup> Rate of racemization (k<sub>α</sub>), of optically active 2-phenylbutane. <sup>d</sup> Run contained cumene- $\alpha$ -*t*; relative rate toward benzene-*t* derived from relative rates in ref. 11. <sup>e</sup> Pressurizing gas was treated with benzophenone ketyl in tetraglyme. <sup>f</sup> At 49.9°. <sup>g</sup> Run contained propene-2-*t*.

± 0.3. If Melander's treatment<sup>21</sup> of the relations between k<sub>H</sub>, k<sub>D</sub>, and k<sub>T</sub> is applied, k<sub>H</sub>/k<sub>C<sub>6</sub>H<sub>5</sub>T</sub> becomes 12 ± 3 and k<sub>α</sub>/k<sub>H</sub> = 1.1 ± 0.3. It seems clear that the exchange reaction is one largely of racemization; the slight amount of net inversion suggested by the experimental results is probably an artifact of the approximations required in this type of analysis and is less than the experimental uncertainty.

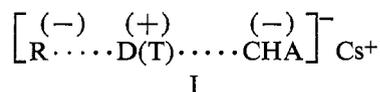
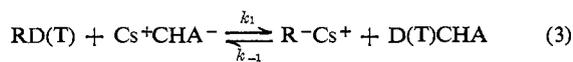
**Primary Isotope Effects.** Primary isotope effects in proton-exchange reactions have assumed an enhanced significance in view of the generality of Cram's internal return hypothesis for carbanion reactions.<sup>22</sup> Convenient measures of the primary isotope effects are the k<sub>D</sub>/k<sub>T</sub> values and are summarized in Table V. Both systems give comparatively large effects. The extrapolated<sup>19,20</sup> k<sub>H</sub>/k<sub>D</sub> values are about the maximum normally expected.

**Table V.** Primary Isotope Effects with CsCHA

	k <sub>D</sub> /k <sub>T</sub> , 25°	k <sub>H</sub> /k <sub>D</sub> <sup>a</sup>
Benzene- <i>d,t</i>	2.5 ± 0.2	8.0 ± 1.4
2-Phenylbutane- 2- <i>d,t</i>	2.7 ± 0.3	9.4 ± 2.4

<sup>a</sup> Estimated from Swain's equation, ref. 19 and 20.

**Mechanism.** The mechanism appears clearly to be a straightforward reaction of a highly ionic CsCHA ion pair with the C-H bond to yield the cesium salt of a carbanion and cyclohexylamine. The high isotope

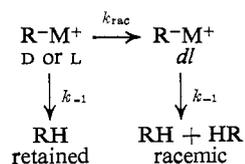


effects mean that Cram's internal return mechanism is not operative and that the rate constants measured pertain to the forward reaction as shown. The high isotope effects also suggest that the transition state (I) is symmetrical in the sense that the force constants of the central C···H and N···H bonds are about the

same.<sup>23</sup> Note that the isotope effect, k<sub>D</sub>/k<sub>T</sub>, for the  $\alpha$ -position of *sec*-butylbenzene with CsCHA, 2.7 ± 0.3, is essentially the same as that for the  $\alpha$ -position of toluene with LiCHA, 2.8 ± 0.2,<sup>18,20</sup> whereas the value for benzene with CsCHA, 2.5, greatly exceeds that with LiCHA, 1.5.<sup>8</sup> In the latter case it was suggested that the transition state has some of the covalent C-Li bond character of the phenyllithium intermediate formed. Phenylcesium is probably a completely ionic salt-like material and no significant covalent bonding is expected in the transition state. The isotope effect for this reaction is thus comparable to the other reactions with cyclohexylamide salts in which completely ionic bonding character is apparently the rule.

The noninvolvement of the internal return mechanism means that the organocesium intermediate is sufficiently stable to allow the now-labeled cyclohexylamine to diffuse away; reaction with the original isotope must be negligible compared to reaction with another solvent proton.

The stereochemistry of the CsCHA exchange contrasts markedly with that found for LiCHA and optically active ethylbenzene- $\alpha$ -*d*: ~82% net retention of configuration.<sup>24</sup> We consider the following addition to the mechanism in eq. 3.



For the case where M<sup>+</sup> is Li<sup>+</sup> the distance between the ions in the ion pair is short and the work required to separate the ions sufficiently to permit rotation and racemization is such that k<sub>-1</sub> > k<sub>rac</sub> and the result is partial net retention. For the case where M<sup>+</sup> is Cs<sup>+</sup>, the cation is now large and the electrostatic attraction to the carbanion is sufficiently weak that k<sub>rac</sub> ≫ k<sub>-1</sub> and the result is predominant racemization. Alternatively, it is quite likely that the Li<sup>+</sup> is highly solvated and is effectively larger than the unsolvated Cs<sup>+</sup>; in this event we interpret the results to mean that proton donation from a solvating CHA molecule is faster than ion-pair rotation.

It is of interest to compare our results with the ex-

(21) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, p. 23.  
(22) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961); cf. also ref. 1b, 5, and J. E. Hofmann, A. Schriesheim, and R. E. Nickols, *Tetrahedron Letters*, 1745 (1965).

(23) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); however, cf. A. V. Willi and M. Wolfsberg, *Chem. Ind. (London)*, 2097 (1964).  
(24) A. Streitwieser, Jr., D. E. Van Sickle, and L. Reif, *J. Am. Chem. Soc.*, **84**, 258 (1962).

tensive data of Cram and co-workers on the stereochemical capabilities of carbanions. Few data from Cram's work are available for amine solvents. However, data in *N*-methylaniline and ethylenediamine suggest that amines are retention solvents.<sup>25</sup> From data in *t*-butyl alcohol, a retention solvent, it appears that more racemization occurs with sodium and potassium carbanides than with lithium carbanides,<sup>26</sup> although high retention occurs with all three cations. The available data in amine solvents<sup>25</sup> indicate that stereoselectivity is less for amines than for *t*-butyl alcohol; hence, cesium salts in amine solvents should exhibit the least stereoselectivity of any of the systems mentioned above.

Perhaps the pertinent point when comparing amines with *t*-butyl alcohol is that amines in general are less acidic than *t*-butyl alcohol, and hence are presumably

(25) D. J. Cram, J. Allinger, and A. Langemann, *Chem. Ind. (London)*, 919 (1955).

(26) D. J. Cram, F. Hauck, K. R. Kopecky, and W. D. Nielsen, *J. Am. Chem. Soc.*, **81**, 5767 (1959).

less reactive in protonating the carbanion. This implies directly a longer lifetime for the alkali metal carbanide in amine solvents, e.g.,  $k_{-1}$  for amines  $<$   $k_{-1}$  for alcohols. If the values for  $k_{rac}$  are comparable in the two types of solvents, amines are necessarily less stereoselective than alcohols.

Of particular importance is the assumption in I that the central carbon atom has much of the carbanion character expected for organocesium compounds. Relative exchange rates in this system may be expected to be useful measures of carbanion stabilities and of hydrocarbon acidities, subject to the general limitations of such rate-equilibrium correlations.<sup>27</sup>

Cesium cyclohexylamide gives exchange rates for weakly acidic hydrocarbons which are considerably greater than for any other convenient system studied. Consequently this system is now being used to study still weaker acids.

(27) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

## Acidity of Hydrocarbons. XX. Comparison of Relative Proton Exchange Rates of Hydrocarbons with Lithium Cyclohexylamide and Cesium Cyclohexylamide<sup>1</sup>

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*Contribution from the Department of Chemistry, University of California, Berkeley, California. Received July 19, 1965*

*Absolute rate constants for exchange of aryl hydrogens in toluene vary over a wide range with LiCHA or CsCHA in cyclohexylamine or with KNH<sub>2</sub> in liquid ammonia but relative rates are much the same in the different systems. There is little steric hindrance to exchange ortho to the methyl group. The relative rates of some benzylic positions are also comparable for these exchange systems. The results justify the use of such relative rates as measures of hydrocarbon acidity.*

In our studies of proton exchange rates in cyclohexylamine we have reported the use of lithium cyclohexylamide<sup>3</sup> (LiCHA) and cesium cyclohexylamide<sup>1b</sup> (CsCHA). The latter catalyst gives exchange rates  $\sim 10^4$  faster than LiCHA and allows the convenient extension of exchange kinetics to less reactive hydrocarbons.<sup>1b</sup> Since these exchange rates are being used as relative measures of acidity, it is important to compare the relative reactivities of different hydrocarbons with both catalysts. In this paper we compare such reactivities for the ring positions of toluene and mesit-

ylene and for the benzylic positions of cumene and 2-phenylbutane.

### Experimental Section

The experimental procedures follow closely those of the preceding three papers.<sup>1b,4</sup>

*Materials.* Ring-deuterated and -tritiated toluenes were prepared from the corresponding bromides by quenching the Grignard reagent with tritium-enriched D<sub>2</sub>O. The starting bromides were shown to be pure by gas chromatography (g.c.) and the products were fractionally distilled. Toluene-2-*d*(*t*), b.p. 107.8–108.8°, had a C–D band at 2262 cm<sup>-1</sup>. Toluene-3-*d*(*t*), b.p. 108.9–109.4°, had a C–D band at 2268 cm<sup>-1</sup>. Toluene-4-*d*(*t*), b.p. 108.9–109.4°, had a C–D doublet at 2264, 2287 cm<sup>-1</sup>. Other bands also serve to distinguish these isomers in the infrared: only the *ortho* has a band at 1130 cm<sup>-1</sup>; a band at 950 cm<sup>-1</sup> was present for the *ortho* and *para* but not for the *meta*. A 1670-cm<sup>-1</sup> band in the *meta* is absent in *para*. These bands show that the compounds prepared are specifically labeled to the limit of infrared analysis ( $\sim 5\%$ ).

Mesitylene-2-*t* was prepared by quenching the Grignard reagent from the bromide with tritiated water followed by fractional distillation, b.p. 162–163°.

(4) (a) A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *ibid.*, **87**, 5383 (1965); (b) A. Streitwieser, Jr., and R. G. Lawler, *ibid.*, **87**, 5388 (1965).

(1) (a) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grants No. 62-175 and 64-554, and by the Petroleum Research Fund of the American Chemical Society; (b) paper XIX: A. Streitwieser, Jr., and R. A. Caldwell, *J. Am. Chem. Soc.*, **87**, 5394 (1965).

(2) (a) National Science Foundation Predoctoral Cooperative Fellow, 1962–1964; (b) National Science Foundation Predoctoral Fellow, 1960–1963; Eastman Kodak Science Award in Chemistry, 1962–1963; (c) National Institutes of Health Predoctoral Fellow, 1964–1966.

(3) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962), and later papers in this series.