g. of cycloheximide acetate, m.p. 145–146.3°. One recrystallization from isopropyl alcohol raised the melting point to 147–148°, undepressed on admixture with authentic cycloheximide acetate, m.p. 147–148°.[24] Identity was further shown by comparison of infrared spectra. The 0.65 g. of acetate corresponded to a 35% recovery of cycloheximide.

When the pyrolysis, on 2.0 g. of cycloheximide, was carried out at 177–178° (bath temperature) for 75 min. there was obtained a small amount of volatile ketone from which was obtained (+)-2,4-dimethylcyclohexanone semicarbazone (10 mg.), identified by melting point, mixture melting point and infrared spectrum.

Epimerization of (+)-2,4-Dimethylcyclohexanone.—A solution of 2.10 g. of (+)-2,4-dimethylcyclohexanone ($[\alpha]^{24}\text{D}$ +64.8°, *c* 6, EtOH) in 30 ml. of 0.09 *N* potassium hydroxide in absolute methanol was maintained at 26° for 20 min., and then at −10° for 90 min. The solution was dissolved in 50 ml. of cold 10% brine, and the resulting solution was extracted twice with 25 ml. of chilled petroleum ether (b.p. 35–40°), and the combined extracts were washed twice with 25 ml. of cold 10% brine, six times with cold water, and finally with brine again. The extracts were then dried over magnesium sulfate, and removal of the solvent, followed by distillation afforded 1.65 g. (79%) of (−)-2,4-dimethylcyclohexanone, b.p. 67° (17 mm.), 176.3° (766 mm.),[25] $n^{22}\text{D}$ 1.4437, $[\alpha]^{24}\text{D}$ +4.6° (*c* 6.6, EtOH), infrared spectrum identical with that obtained from authentic (−)-2,4-dimethylcyclohexanone by the alkaline degradation of cycloheximide. In addition, both the semicarbazone and thiosemicarbazone (crude) of the epimerized ketone proved to be identical with the same derivatives (purified) of authentic (−)-2,4-dimethylcyclohexanone, by comparison of melting points, mixture melting points, infrared spectra and optical rotations.

Vapor Phase Chromatography.[27]—Chromatography was carried out using a Perkin–Elmer column R (Ucon polyglycol LB-550-X), 6 ft. × 4 mm. column, 120°, helium inlet pressure 20 p.s.i. The ketone from alkaline degradation ($[\alpha]^{24}\text{D}$ +4.3°, EtOH) exhibited two typical peaks corresponding to 89.5% of pure (−)-2,4-dimethylcyclohexanone, and to 10.5% pure (+)-2,4-dimethylcyclohexanone. Ketone from thermal degradation ($[\alpha]^{24}\text{D}$ +64.8°) was shown to consist of 7.2% of pure (−)-2,4-dimethylcyclohexanone, and 92.8% of pure (+)-2,4-dimethylcyclohexanone. Mixtures of the foregoing ketones having rotations of +43.6° and +24.0° were shown to consist of 35.2% and 63.4%, respectively, of pure (−)-2,4-dimethylcyclohexanone. A plot of the preceding optical rotations as a function of composition of the epimers, as determined by vapor phase chromatography, afforded a straight line having intercepts at −3.2 and at +70.0 (optical rotations in ethanol). Typical retention times for pure (−)-2,4-dimethylcyclohexanone and for pure (+)-2,4-dimethylcyclohexanone were 25.0 and 27.9 minutes, respectively. The following experiment ruled out epimerization on the column. A sample of (−)-2,4-dimethylcyclohexanone ($[\alpha]^{24}\text{D}$ +4.3°, EtOH) was injected and allowed to stand on the column at 120° for 1 hour with no helium flow. When the gas flow was resumed the results obtained were identical (within 1%) with those obtained using the standard conditions described above.

Acknowledgment.—Many thanks to Doctors W. T. Sumerford, S. J. Dykstra, C. W. Waller, T. Stevens and R. T. Arnold for helpful discussions, and to Dr. R. F. Feldkamp for encouragement.

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[27] I am indebted to Mr. William Stevenson for his skillful development of a suitable method.

[Contribution from the Department of Chemistry, University of California, Berkeley, Calif.]

Acidity of Hydrocarbons. I. Kinetics of Exchange of Toluene-α-*d* with Lithium Cyclohexylamide[1]

By A. Streitwieser, Jr.,[2] D. E. Van Sickle[3a] and W. C. Langworthy[3b]

Received June 21, 1961

The kinetics of the proton exchange reaction between toluene-α-*d* and lithium cyclohexylamide in cyclohexylamine have been studied at 50°. The reaction is first order each in toluene-α-*d* and in monomeric lithium cyclohexylamide. Free ions are apparently not involved to a significant extent in the concentration range studied. Lithium cyclohexylamide appears to be in equilibrium with relatively inert dimers, trimers, etc.

Introduction

This paper introduces an extensive investigation of the relative acidities of hydrocarbon derivatives through the study of the rates and equilibria of proton exchange reactions. Compared to the numerous and detailed studies of carbonium ion stabilities, surprisingly little has been done with hydrocarbon anions. However, many hydrocarbons are so weakly acidic that the meaning of the term, acidity, must be questioned. Ideally, for use in the theory of organic chemistry, we would like to know the relative energetics of the gas phase reaction

$$\text{RH} \longrightarrow \text{R}^- + \text{H}^+$$

Such values are derivable from the bond dissociation energies, the ionization potential of hydrogen atom and the electron affinity of the alkyl radical. The first two are known or accessible numbers; the last is exceedingly difficult to measure.

We are forced to rely instead on quantities that may be expected to parallel variations in the gas phase energetics, such as the relative equilibrium constants for the metal exchange reaction

$$\text{RH} + \text{R'M} \rightleftarrows \text{RM} + \text{R'H}$$

in which the metal is chosen to be such that the R–M bond has substantial ionic character.

This approach was developed by Conant and Wheland[4] and culminated in the work of McEwen[5] who proposed a rough set of *pK* values for a number of hydrocarbons. These values, important as they are in the theory of organic chemistry, are now a quarter of a century old, and have come down to us without significant further study or elaboration.

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[2] Alfred P. Sloan fellow.

[3] (a) Shell Development Co. fellow, 1957–1958; (b) National Science Foundation Co-operative fellow, 1959–1960.

[4] J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).

[5] W. K. McEwen, *ibid.*, **58**, 1124 (1936).

More recent metalation studies have been still more qualitative in nature and have not always distinguished between rate- and equilibrium-controlled metalations. Such studies have yielded tables of relative orders of "acidity" for additional hydrocarbons.

A further approach is through the relative rates of proton exchange reactions, the underlying assumption being that the rate of exchange will parallel the equilibrium acidity. This approach is not without its dangers (for example, the rates of formation of anions from various nitroalkanes do not parallel the equilibrium acidities[6]) but could be of value if used with circumspection (for example, rates of exchange parallel equilibrium acidities for carbonyl compounds over a wide range).[6] This general approach has been studied extensively by Shatenshtein, *et al.*,[7] who used primarily a potassium amide–liquid ammonia system. Their important results have led to relative measures of acidity for a variety of compounds and will be discussed in reference to our work throughout this series of papers. However, much of their work relates to the *introduction* of deuterium into hydrocarbons from deuterated solvent; many of the derived rate constants show poor reproducibility.

Our initial study has concerned the *removal* of deuterium from specifically labeled hydrocarbons using lithium cyclohexylamide in cyclohexylamine. We wished to use an organic amine as the solvent rather than liquid ammonia because of its more convenient properties; cyclohexylamine was chosen because of the several readily available amines studied it alone would dissolve the corresponding lithium amide.

Preliminary studies showed that reproducible kinetics could be obtained only by using rigorously purified and dried compounds and vacuum line techniques. Lithium cyclohexylamide was prepared on a vacuum line from the reaction of ethyllithium or butyllithium with cyclohexylamine, and toluene-α-d was distilled into the resulting solution. In the original procedure (A) the mixture was transferred on the vacuum line to tubes which were sealed and thermostated; at intervals, a tube was removed for the recovery of toluene. In the modified procedure (B) the mixture was contained in a flask under nitrogen pressure. At intervals, aliquots of the solution were removed by a capillary sidearm.

The aliquots were treated with dilute hydrochloric acid and extracted with carbon tetrachloride. The amount of deuterium lost from the toluene-α–d was determined by the infrared spectrum. The base present was determined by one of several titration methods. These procedures gave reproducible results and were applied to a number of hydrocarbons. The details of the method, applied to toluene-α–d, are reported in the Experimental section.

Experimental

Toluene-α-d was prepared by the reaction of benzylmagnesium chloride with deuterium oxide.[8] The product had typically $n^{25.5}_{\mathrm{D}}$ 1.4939 and C–D stretching band at 4.59 μ in the infrared (carbon tetrachloride solution). The product contained no detectable amount of toluene in the infrared; the spectrum was identical with that of a sample prepared by reaction of benzyl chloride with lithium aluminum deuteride and showed the complete absence of bands at 9.6, 11.2 and 12.7 μ present in toluene.

Ethyllithium.—The procedure of Talalaeva and Kocheshkave[9] was used with slight modifications.

Ethyllithium was kept as a clear benzene solution, 1.2–1.4 M, free of other salts.

Exchange Procedure (A).[10]—A known amount of a benzene solution of ethyllithium was syringed into a calibrated mixing flask while the flask was flushed with purified nitrogen. The flask was attached to the vacuum line and the benzene was removed *in vacuo*. On another part of the vacuum line, previously fractionated cyclohexylamine (Eastman Kodak Co.) was distilled *in vacuo* onto previously degassed Linde 4A molecular sieves. After drying, a small amount of cyclohexylamine was distilled into the mixing flask and frozen above the ethyllithium. After the amine had melted and reacted with the ethyllithium, the system was re-evacuated, and the remainder of the cyclohexylamine was distilled to known volume into the mixing flask. The resulting solution of lithium cyclohexylamide was clear and of a pale pink color. Any air leaks resulted in a yellow solution; when this occurred, the run was discarded. The mixture was frozen and a known weight of toluene-α-d was distilled from molecular sieves into the mixing flask *in vacuo*. After melting and thorough magnetic stirring, 5-ml. aliquots of the solution were pumped with purified nitrogen into six previously degassed tubes which were sealed and placed in a thermostat.

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(10) Further details of the apparatus and technique may he found in the Ph.D. Dissertation of Dale E. Van Sickle, University of California, 1959.

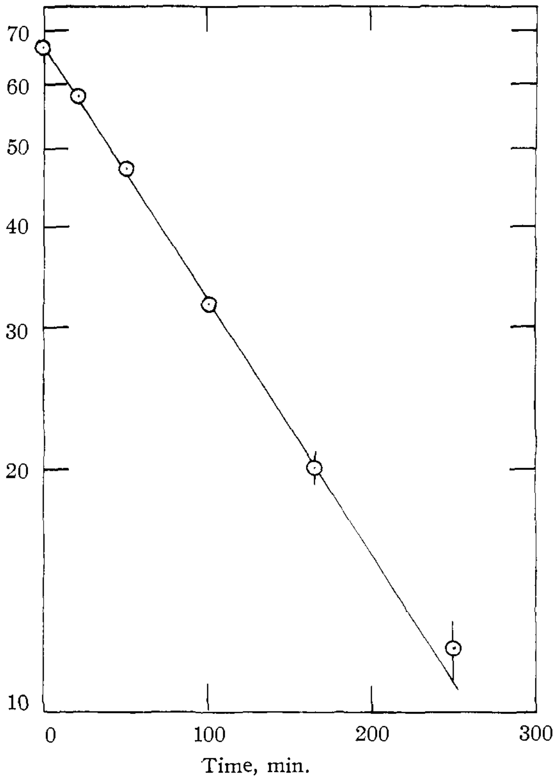

Fig. 1.—A typical kinetic run (run 11 in Table I); for exchange of toluene-α-*d* with lithium cyclohexylamide.

The solution remaining in the mixing flask was titrated for base content: A 5-cc. aliquot mixed with 1 cc. of water was titrated potentiometrically with constant boiling hydrochloric acid using a Gilmont microburet. A Beckman model G *p*H meter was used with a Beckman "blue glass" high alkaline-sensitive glass electrode and a platinum thimble electrode. Purified nitrogen was allowed to bubble through the titration mixture during titration. At least two titrations were normally carried out for each run. The volume of titrant was typically about 0.060 ml. with an estimated precision of about 2%. The base concentration determined by this procedure generally agreed well with the amount of ethyllithium used. In an alternative procedure, which was used generally with later runs, an aliquot of the mixture was added to water and the solution was evaporated to dryness in the absence of air. Titration of the residual lithium hydroxide gave results which agreed within 5% with the results of the potentiometric method.

After the tubes in the thermostat had been allowed to come to thermal equilibrium, one was removed to provide the initial point. The contents were diluted with ice and hydrochloric acid and the mixture was extracted with carbon tetrachloride to give a 10 mole per cent. solution of the hydrocarbon. Other tubes were removed from the thermostat at intervals and handled in the same way.

Exchange Procedure (B).—The reaction mixture was prepared as in (A) except that commercially available butyllithium in heptane was frequently used in place of ethyllithium in benzene. The mixture was prepared in a cylindrical flask attached to the vacuum line by stopcock and standard taper joint. A capillary sidearm, attached at the bottom of the vessel, ran up the outside and was closed by a stopcock. After the mixture was prepared, pre-purified nitrogen was admitted at −80°, the stopcock was closed and the entire flask was removed and thermostated. At 50° the nitrogen pressure in the flask was about 2 atmospheres. Aliquots of the solution were ejected at intervals by opening the stopcock on the capillary sidearm.

Kinetic Behavior.—The infrared spectra of the dried carbon tetrachloride solutions were taken as 1-mm. films on a Baird model AB2 infrared spectrometer at "slow" speed with the "2X" slit program. Intensities with this procedure were reproducible to a fraction of a per cent. The intensity of the C–D band was compared to a calibration curve (Beer's law is obeyed). Since the actual concentrations in the carbon tetrachloride varied somewhat, the intensities were normalized by using a band at 5.1 μ which is identical in toluene and in toluene-α-*d*. All samples in a given run were analyzed at the same time.

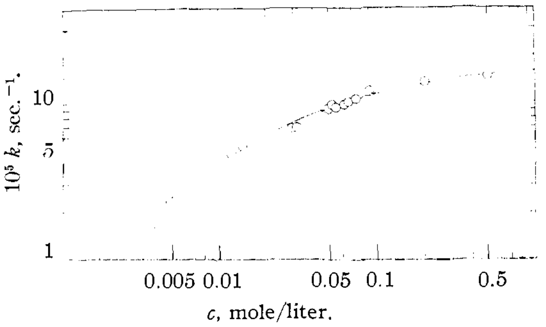

Fig. 2.—Effect of formal concentration of lithium cyclohexylamide, *c*, on pseudo-first-order rate constants, *k*. Curve is the theoretical curve from eq. 16 with $k_2 = 6.70 \times 10^{-3}$ l./m.-sec. and $K_1 = 35$.

A semi-log plot against time of the deuterium content minus the infinity value gave, generally, an excellent straight line indicating pseudo-first-order behavior. An example for a typical run is given in Fig. 1. Similar plots were constructed for each run. The best straight line was fitted visually to the points with due note taken that a constant error in the extent of reaction, x, becomes an increasing error in log $(x - x_e)$. This effect for an assumed error of 0.01 in x is shown in Fig. 1. A careful analysis shows that this procedure is clearly superior to the usual least squares treatment. The resulting pseudo-first-order rate constants, k_{exp}, are summarized in Table I. The results in this table show that reproducibility is generally no worse than about 5%; the results of four different workers are included.

Rate Expression.—The reaction studied may be given as eq. 1. Experimentally, because the catalyst

$$C_6H_5CH_2D + C_6H_{11}NH_2 \underset{k'}{\overset{k}{\rightleftarrows}} C_6H_5CH_3 + C_6H_{11}NHD \tag{1}$$

remains unchanged, the kinetics is pseudo-first order within a given run to at least 90% reaction. The experimental first order constants, k_{exp}, so obtained must be corrected for the back reaction. Furthermore, even the forward rate must be corrected, since, as the deuterium content of the solvent builds up, there is an increasing probability that the deuterium removed will be replaced by another deuterium. Although the proton pool of solvent is in large excess over the deuterium, the relative amount of the deuterium used is by no means negligible. Hence, for the general case in eq. 2, the "first order" rate system must be expressed as eq. 3. This expression assumes that the single

$$RH_{n-1}D + R'NH_2 \underset{k'}{\overset{k}{\rightleftarrows}} RH_n + R'NHD \tag{2}$$

$$\frac{d[RH_n]}{dt} = k[RH_{n-1}D]\,\frac{2[R'NH_2] + [R'NHD]}{2[R'NH_2]_0} - nk'\,[RH_n]\,\frac{[R'NHD]}{2[R'NH_2]_0} \tag{3}$$

hydrogen in monodeuterated amine is as available as the two hydrogens in undeuterated amine. With the further assumption that dideuterated species may be neglected, stoichiometry gives eq. 4. At equilibrium, the derivative equals zero

TABLE I

KINETICS OF EXCHANGE OF TOLUENE-α-*d* WITH LITHIUM CYCLOHEXYLAMIDE AT 50 ± 0.1°

Run	Method[a]	a = [toluene-α-*d*], mole/l.	b = [cyclohexylamine], mole/l.	Q (eq. 7)	c,[b] mole/l.	$10^5 k_{exp}$, sec.$^{-1}$ [c]	$10^5 k$, sec.$^{-1}$ (eq. 8)	$10^3 k_2$, l./m. sec. (eq. 16)
1	B	0.46	8.05	18.3	0.0038	1.72	1.52	(5.00)
2	B	.49	8.02	18.3	.0049	2.68	2.35	6.09
3	B	.48	8.03	18.3	.012	5.45	4.78	6.92
4	B	.48	8.03	18.3	.014	6.15	5.39	7.10
5[d]	B	.45	8.06	18.3	.029	7.83	6.92	6.17
6	A	.49	8.02	18.3	.031	8.00	7.01	6.05
7	B	.48	8.03	18.3	.049	10.4	9.13	6.60
8	B	.25	8.24	17.7	.052	10.5	9.75	7.00
9	A	.25	8.24	17.7	.055	10.1	9.40	6.62
10	B	.49	8.02	18.3	.062	11.1	9.75	6.63
11	A	.49	8.02	18.3	.066	11.6	10.2	6.79
12	A	.49	8.02	18.3	.074	12.1	10.6	6.84
13	A	.56	7.96	18.5	.090	14.1	12.1	7.39
14	A	.49	8.02	18.3	.20	15.5	13.5	6.89
15[e]	B	.49	8.02	18.3	.50	17.0	14.9	6.64
16	A	1.04	7.52	19.6	.060	10.8	8.3	(5.8)
17	A	1.04	7.52	19.6	.060	10.8	8.3	(5.8)
18	A	1.04	7.52	19.6	.060	10.5	8.0	(5.5)
19[f]	A	0.49	8.02	18.3	.059	8.4	7.3	(5.0)
								6.70 ±0.29[g]

[a] See Experimental. [b] Formal concentration of lithium cyclohexylamide. [c] Calcd. from the slope of log $(x - x_e)$ *vs.* time. [d] Experiment by R. G. Lawler. [e] Experiment by W. M. Padgett. [f] This run included 0.048 *M* lithium perchlorate. [g] Average does not include values in parentheses.

$a = [\mathrm{RH}_{n-1}\mathrm{D}]_0$
$b = [\mathrm{R'NH_2}]_0$
$K = k/k'$
$x = [\mathrm{RH}_{n-1}\mathrm{D}]/a$ = fraction of deuterium in hydrocarbon
$[\mathrm{RH}_n] = [\mathrm{R'NHD}] = a(1 - x)$
$[\mathrm{R'NH_2}] = b - a(1 - x)$

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k}{2b}[2b - a(1 - x)]x - \frac{na}{K}(1 - x)^2 \qquad (4)$$

and we solve for K in terms of the equilibrium value of x, x_e. Since the rate constants were defined per hydrogen, K is a distribution constant and should equal unity if there is no isotope effect for the net reaction. In this way, K is given by eq. 5.[11]

$$K = \frac{na(1 - x_e)^2}{x_e[2b - a(1 - x_e)]} \qquad (5)$$

The values of K for several hydrocarbons with n ranging from 2 to 6 are summarized in Table II. Since the error in x_e is about 0.01, the K-values are indistinguishable from unity; there is no important isotope effect in this equilibrium. Several runs at lower hydrocarbon concentrations have much larger relative errors but still give K-values of 0.7-1.4. Further evidence for the absence of an isotope effect in the equilibrium appears in runs in which deuterated and tritiated toluenes were exchanged together. In these cases, the percentage of original tritium remaining in the hydrocarbon at equilibrium was equal within experimental error to the corresponding figure for deuterium (paper III). For related equilibria in deuterated ammonia, Shatenshtein, *et al.*,[7h,f] found distribution constants a few per cent. lower than unity.

TABLE II

DISTRIBUTION CONSTANTS

Hydrocarbon	n	a	b	x_e	K (eq. 5)
Toluene-α-*d*	3	0.49	8.24	0.08	0.97
m-Xylene-α-*d*[a]	6	.48	8.18	.14	.96
Ethylbenzene-α-*d*[a]	2	.70	7.94	.08	.97

[a] Runs with these compounds are described in the following paper.

Equation 4 may be solved as a second-order equation, but the solution reduces to that of a first-order equation with a modified rate constant.

$$\ln\frac{x_0 - x_e}{x - x_e} = \frac{Q}{2b}kt \qquad (6)$$

in which

$$Q = [(2b - a)^2 + 8abn/K]^{1/2} \qquad (7)$$

The left expression in eq. 6 defines k_{exp}; hence,

$$k = (2b/Q)\,k_{exp} \qquad (8)$$

The true pseudo-first-order rate constant, k, for the forward reaction must be corrected as in eq. 8 and is somewhat smaller than the experimental constant. Values for these constants are summarized in Table I.

Kinetic Order and Mechanism.—Within a given run, the reaction is first order in deuterated hydrocarbon. That this is the true kinetic order is shown by runs in which the hydrocarbon concentration has been changed. In runs 7, 8, 9, 10, 16, 17 and 18, the catalyst concentration is about the same but the toluene-α-*d* concentration varies over a fourfold range; k varies by only ±10%.

The kinetic order with respect to the catalyst concentration is particularly germane to a con-

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[11] In a system of this complexity, alternative distribution constants may be defined. The definition in eq. 5 precludes dideuteration of the hydrocarbon. Consideration of all replaceable hydrogens on the hydrocarbon as well as solvent as potential sites for deuterium leads to the alternative expression for the distribution constant,

$$\frac{a(n - x_e)(1 - x_e)}{x_e[2b - a(1 - x_e)]}.$$

This derivation, suggested to us by W. M. Padgett, gives distribution constants which are higher by a few per cent. than those defined by eq. 5 in the concentration region used by us.

sideration of reaction mechanism. If the actual catalyst is the amide ion, the equilibrium

$$\mathrm{R'NHLi} \underset{}{\overset{K'}{\rightleftarrows}} \mathrm{R'NH^-} + \mathrm{Li^+} \qquad (9)$$

will lead to half-order kinetics in the lithium cyclohexylamide concentration if K' is small, first-order kinetics if K' is large and intermediate and variable order if K' has an intermediate value. The exchange of hydrocarbons with potassium amide in liquid ammonia is of about 0.8th order in potassium amide[7f]; amide ion appears to be the active reagent in equilibrium with the weakly dissociating potassium salt. Metal amides are known to be weak electrolytes in liquid ammonia solution from conductivity studies.[12]

From a log–log plot of k *vs.* c (the formal lithium cyclohexylamide concentration), Fig. 2, we find a totally different behavior. The kinetic order in catalyst varies from close to first at low concentrations to close to zeroth at high concentrations. No mechanism based on eq. 9 can account for such behavior. Of the several further possibilities examined, one only accounts for such kinetic behavior. In this hypothesis, we assume that undissociated monomeric lithium cyclohexylamide is in equilibrium with dimers, trimers, tetramers, etc., but that *only the monomer is an active catalyst.* A kinetic expression may be derived that embodies this hypothesis.

$$\mathrm{LiNHR'} + \mathrm{LiNHR'} \overset{K_1}{\rightleftarrows} (\mathrm{LiNHR'})_2 \qquad (10)$$

$$\mathrm{LiNHR'} + (\mathrm{LiNHR'})_2 \overset{K_2}{\rightleftarrows} (\mathrm{LiNHR'})_3$$

$$\mathrm{LiNHR'} + (\mathrm{LiNHR'})_n \overset{\vdots K_n}{\rightleftarrows} (\mathrm{LiNHR'})_{n+1}$$

It is readily shown that

$$[(\mathrm{LiNHR'})_n] = [\mathrm{LiNHR'}]^n \; \pi \; K_1K_2\cdots K_{n-1} \qquad (11)$$

The system is mathematically tractable if we assume that all of the equilibrium constants are equal. The formal concentration of lithium cyclohexylamide, c, is then given as

$$c = [\mathrm{LiNHR'}] + 2K_1[\mathrm{LiNHR'}]^2 + \ldots + nK_1^{n-1}[\mathrm{LiNHR'}]^n + \ldots \qquad (12)$$

This infinite series has the solution[13]

$$c = [\mathrm{LiNHR'}]/(1 - K_1[\mathrm{LiNHR'}])^2 \qquad (13)$$

whence

$$[\mathrm{LiNHR'}] = (2cK_1 + 1 - \sqrt{4cK_1 + 1})/2cK_1^2 \qquad (14)$$

It may be shown, as required by the experiments, that the derivative of this expression with respect to c approaches unity for small c and zero for large c. A second-order reaction in toluene-α-d and monomeric lithium cyclohexylamide implies

$$\text{rate} = k_2[\mathrm{LiNHC_6H_{11}}][\mathrm{C_6H_5CH_2D}] = k_2[\mathrm{C_6H_5CH_2D}]\left(\frac{2cK_1 + 1 - \sqrt{4cK + 1}}{2cK_1^2}\right) \qquad (15)$$

or

$$k_2 = 2ckK_1^2/(2cK + 1 - \sqrt{4cK_1 + 1}) \qquad (16)$$

The best fit is obtained for values of K_1 close to 35 l./mole. A variation of ±5 in K_1 gives perceptible deviations from best behavior. Values of k_2 derived with this value of K_1 are recorded in Table I and are found to be relatively constant over the entire range of c.

The lowest practical concentration with the present techniques is about 0.004 M; at this concentration minute traces of water will destroy the catalyst. The runs with [toluene-α-d] = 1 M were also not included in calculating the average k_2 for these were the earliest and least accurate values, and the concentration of hydrocarbon is now sufficiently high to alter seriously the solvent. Using K_1 = 35 l./mole and $k_2 = 6.70 \times 10^{-3}$ l./mole sec., the dependence of k on c was calculated; the resulting function is shown in Fig. 2 and clearly represents the experimental points to close precision.[14]

Further evidence that amide ions are not important in this reaction was obtained by a run with added lithium perchlorate (Table I, run 19). This salt should be at least as dissociated as lithium cyclohexylamide,[15] hence should suppress ionization of the latter. Accordingly, we would expect a large rate decrease in the presence of lithium perchlorate if the amide ion were an important catalyst. The rate is diminished by only 20%, much smaller than would be expected for a mechanism involving eq. 9.

Hence, at present, it appears that the active exchange catalyst is monomeric lithium cyclohexylamide. Whether this compound has a covalent N–Li bond or whether the compound is an ion-pair presents a question which is currently under investigation. The hypothesized equilibria have further corollaries which are subject to test; the mean molecular weight is directly predictable from the foregoing treatment and is also being investigated currently.

Apparently, the higher aggregates are formed by opposing N–Li dipoles such that the basic character of a given dipole is diluted. This theme is not without precedent. In the anionic polymerization of styrene by butyllithium it has also appeared that monomeric molecular butyllithium is the active catalyst in equilibrium with relatively inert aggregates.[16]

Finally, we may inquire as to the subsequent stages of the reaction. Is the free benzyl anion or benzyllithium an intermediate in the exchange? Information about such possible reactive intermediates does not emerge from the present kinetic study, but the question is discussed further in subsequent papers of this series.

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[12] W. W. Hawes, *J. Am. Chem. Soc.*, **55**, 4422 (1933).

[13] This type of treatment has been applied independently to other systems of sets of infinite equilibria. For examples, see M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958), and A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc*,, **82**, 288 (1960).

[14] In the above model, all equilibrium constants for dissociation of polymer into monomeric lithium cyclohexylamide and the next lower aggregate are taken to be equal. An alternative model in which the equilibrium constant for dissociation is taken to be proportional to the number of monomer units in the aggregate leads to a transcendental solution, c = [LiNHR'] exp K' [LiNHR']. Reasonable agreement is obtained with the experimental results for K' = 180, but the agreement is not so good as the foregoing model.

[15] This assumption is confirmed in conductance measurements by W. M. Padgett to be published shortly.

[16] F. J. Welch, *J. Am. Chem. Soc.*, **81**, 1345 (1959).