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THE EQUILIBRIUM AND KINETIC ACIDITIES OF ISOMERIC CARBORANE METHINES*

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SUMMARY

The equilibrium and kinetic acidities of the methines of isomeric carboranes and of some of their derivaties in several solvents have been determined. Calculated pK_a values were successfully correlated with Streitwieser's hydrocarbon acidity scale. The kinetics and activation parameters of hydrogen isotopic exchange have been measured. The absence of a deuterium-tritium kinetic isotope effect has been shown. The rate constants of reversible metallation of 1-alkyl-*o*-carboranes have been determined.

INTRODUCTION

Conant and Wheland were the first[1] to quantitatively determine hydrocarbon acidities while studying reaction equilibria in the competitive metallation of hydrocarbons in ether. McEven[2] carried out analogous measurements in benzene and constructed a pK_a scale for hydrocarbons, assuming the pK_a of methanol to be 16. Subsequently[3] it was proposed to determine the acidities of hydrocarbons by measuring the kinetics of their hydrogen isotope exchange with liquid ammonia. It was shown thereby that a correlation exists between the kinetic acidities of hydrocarbons and their equilibrium acidities as determined by McEven. However, further kinetic measurements of acidities of CH-acids (see reviews[4-8]), have revealed among other facts, that such a direct correlation between kinetic and equilibrium acidities does not always exist. Considerable attention is now being given to the differentiating effect of solvents on the strength of CH-acids[9].

It was of interest to obtain information on the equilibrium and kinetic CH-acidities of compounds with structures much different from those of hydrocarbons. As such could serve carboranes whose molecules according to X-ray data[10] have almost regular icosahedral structure with the two carbon atoms in *ortho-*, *meta-* or *para-*postion (*o-*, *m-* and *p-*carboranes). These electron deficient structures with an

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* Throughout this paper the following nomenclature is used: *o*-carborane = 1,2-dicarbadodecaborane (12); *m*-carborane = 1,7-dicarbadodecaborane (12) and *p*-carborane = 1,12-dicarbadodecaborane (12).

unusual valence state of the carbon atoms are of quasi-aromatic character. The CH-hydrogen atoms can be readily substituted by a metal[11-14], *i.e.* these compounds behave similar to CH-acids.

We determined the metallation equilibrium constants of the isomeric carboranes and of some of their derivatives[15-17] and measured the kinetics of deuterium and tritium exchange in these compounds[15,17-19]. Data have also been obtained on the kinetics of metallation of alkyl-*o*-carboranes[16] and on the deuterium-tritium kinetic isotope effect in the exchange reactions of carboranes[19]. The results are discussed below.

RESULTS AND DISCUSSION

Equilibria of the metallation reactions

The equilibrium concentration constants of carborane metallation by organoalkali metal compounds were determined by the method analogous to that of Streitwieser[20].

The first experiments on carborane metallation which were carried out in 1,2-dimethoxyethane (DME) using alkylaromatic potassium compounds, displayed a rapid decrease in optical density of the solution followed by further gradual decline due to some unknown side reaction especially marked in *o*-carboranes. The side reaction was practically eliminated in DME by the use of lithium instead of potassium or by using diethyl ether (Et_2O) as solvent*.

In calculating the equilibrium acidities (pK_a's) of the carboranes it was assumed that the pK_a's of the reference hydrocarbons in ethereal solution are the same as those in cyclohexylamine (CHA) found by Streitwieser. Hence the pK_a values of the carboranes in ether are of a somewhat conditional nature. However, we were able to refer these values directly to the Streitwieser's hydrocarbon acidity scale by determining the equilibrium metallation constants of *p*-carborane not only in DME, but also in CHA since the carbanions of this compound are relatively stable in the latter solvent. The equilibrium position was determined for both the forward and reverse directions. The results are shown in Table 1.

Equilibrium acidities of *p*-carborane determined in CHA with two indicators are practically the same ($pK_a = 31.0 \pm 0.1$). This value found directly from the Streitwieser's scale shows that *p*-carborane is similar to triphenylmethane in acidity.

It should be noted that since the pK_a's of both *o*-carborane and its substituted derivatives (excepted 9,10-dichloro-*o*-carborane) are referred to fluorene, these values can serve for comparative assessment of their strengths as CH-acids. The same is true for *m*-carborane and its derivatives.

The equilibrium constants of metallation (K) depend upon both the solvent and counterion. The equilibrium constants of 1-methyl-*o*-carborane (Table 1; Nos. 5–8) and those of 1-isopropyl-*o*-carborane (Nos. 11–14) decrease in the series (I): $Li, Et_2O > Li, DME \gg K, DME > K, Et_2O$.

On the other hand the basicity of fluorenyl anion as seen from the hypsochromic shift of the absorption maximum[22,23] decreases in the other series (II): $Li, DME > K, DME > K, Et_2O > Li, Et_2O$.

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* For the metallation of 1-methyl-*o*-carborane the rate of the side reaction was found to fall with decreasing cation solvating power of the solvent ($CHA > DME \approx THF >$ 1,4-dioxane $> Et_2O$), *cf.*[21].

TABLE 1

EQUILIBRIUM CONSTANTS OF METALLATION AND pK_a'S OF CARBORANES AND THEIR SUBSTITUTED DERIVATIVES

No.	Compound	Ind[a]	Sv	M[b]	K[c]	pK_a
1	9,10-Dichloro-*o*-carborane	PhFl	DME	Li	140	16.3
2	1-Phenyl-*o*-carborane	Fl	DME	K	1.4	22.6
3		EtFl	DME	K	1.3	22.7
4		Fl	Et_2O	K	0.2	23.4
5	1-Methyl-*o*-carborane	Fl	DME	K	0.45	23.1
6		Fl	Et_2O	K	0.3	23.3
7		Fl	DME	Li	6.0	22.0
8		Fl	Et_2O	Li	30	21.4
9	*o*-Carborane	Fl	DME	K	0.25	23.3
10		Fl	Et_2O	K	0.10	23.8
11	1-Isopropyl-*o*-carborane	Fl	DME	K	0.07	23.9
12		Fl	Et_2O	K	0.06	24.0
13		Fl	DME	Li	1.2	22.8
14		Fl	Et_2O	Li	3.3	22.3
15	1-Phenyl-*m*-carborane	PhX	DME	K	1.0	27.5
16	1-Methyl-*m*-carborane	PhX	DME	K	0.6	27.9
17	*m*-Carborane	PhX	DME	K	0.6	27.9
18	*p*-Carborane	BDM	DME	K	1.5	30.0
19		BDM	CHA	Cs	0.17	31.0
20		TPhM	CHA	Cs	2.5	31.1

[a] Ind = indicator compound with the known pK_a of Streitwieser[20] (between parentheses); PhFl = 9-phenylfluorene (18.5); Fl = fluorene (22.8); EtFl = 9-ethylfluorene (22.9); PhX = 9-phenylxanthene (28.5); BDM = *p*-biphenylyldiphenyl methane (30.2); TPhM = triphenylmethane (31.5). [b] M = metal. [c] K = equilibrium constant of metallation (average of 5–6 measurements.

Probably such discrepancy between series (I) and (II) implies that the change in value of the equilibrium constant is due to change in basicity of the carborane anion rather than of the fluorenyl anion.

The pK_a value of 1-isopropyl-*o*-carborane ($pK_a = 22.1$) close to that shown in Table 1 has been obtained by an other method based on the GLC analysis of the carbon dioxide reaction products of an equilibrium mixture of 1-isopropyl-*o*-carborane, fluorene and their lithium derivatives in Et_2O. A similar study was made of the equilibrium between two pairs of *o*-carboranes and their lithium derivatives in Et_2O:

$R = i\text{-}C_3H_7$; $R' = CH_3$ or CH_2Cl

Based on the values of the equilibrium constants obtained and on the above mentioned pK_a value of 1-isopropyl-*o*-carborane the pK_a's for 1-methyl- and 1-chloromethyl-*o*-carborane have been found to be 21.8 and 20.4, respectively.

Kinetics of the metallation reactions

Equilibrium of the reaction between fluorenyllithium with *o*-carboranes in

Et_2O is attained rather slowly. This permitted the measurement of both the kinetics and equilibrium of the metallation reaction in a single experiment.

Table 2 compares the mean values for the rate constants (10^3 l · mole^{-1} · sec^{-1}) of the forward (k_1) and reverse (k_{-1}) metallation reactions of 1-methyl- and 1-isopropyl-*o*-carboranes with fluorenyllithium in Et_2O and the equilibrium constants (K) measured under the same conditions.

TABLE 2

RATE CONSTANTS OF FORWARD AND REVERSE REACTIONS OF METALLATION AND EQUILIBRIUM CONSTANTS

Compound	k_1	k_{-1}	K
1-Methyl-*o*-carborane	31	1.0	30
1-Isopropyl-*o*-carborane	5.3	1.7	3.3

It can be seen from Table 2 that a correlation exists between the k and K values, characterizing the kinetic and equilibrium acidities in the metallation reaction.

Judging from the k_{-1} values, the anion basicities of alkyl-*o*-carboranes differ less than one might have expected from the acidities of their conjugate CH-acids. This is probably because of the interaction between cation and carbanion, resulting in a lower protophilicity of the latter. The kinetic acidity studies in metallation reactions of the kinetic isotope effect are still in progress (*cf.* ref. 24).

Kinetics of deuterium and tritium exchange

In order to compare the kinetic CH-acidities of isomeric carboranes and of some of their substituted derivatives, we determined the rate constants of hydrogen isotope exhange with liquid ammonia, ethanol and t-butanol (catalyzed by the corresponding alcoholates). Table 3 compares the rate constants of the deuterium and tritium exchange in the indene (In) and fluorene methylenes. The rate constants were calculated by the first order equation (sec^{-1}).

Table 3 presents the activation parameters of the exchange reactions. Due to the experimental difficulties arising at the lower temperatures, the rate constants and activation parameters are less accurate for the *ortho*-isomer and its substituted derivatives than for the *meta*-isomer.

Comparison of the data (Table 3, Nos. 5 and 14, 9 and 19) shows that the isotopic exchange reaction in both liquid ammonia and ethanol in the presence of alcoholate is 10^4 times faster in the case of *ortho*- than of *meta*-isomer. In turn the kinetic acidity of the *meta*-isomer exceeds that of the *para*-isomer (see Table 3, Nos. 16 and 35, 18 and 36).

The free energy of activation ($\Delta F^{\neq}$) of the exchange reaction is approximately 6 kcal/mole lower for *o*-carborane compared with *m*-carborane (Table 4).

It is noteworthy that the enthalpies and entropies of activation of the carborane exchange reactions are considerably higher in ethanol than in ammonia solution. Activation parameters of the *m*-carborane reaction in tert-butanol approach those for liquid ammonia solution.

Table 5 compares the values of $10^4 \cdot k$ (sec^{-1}) for the deuterium exchange of fluorene and *m*-carborane with three solvents.

TABLE 3

RATE CONSTANTS OF DEUTERIUM AND TRITIUM EXCHANGE

No[a]	Compound[b]	Solvent[c]	Temp. (°C)	k[d] (sec^{-1})
1	*o*-Carborane	NH_3(D)	−78	1.5×10^{-4}
2			−60	5.6×10^{-4}
3			−50	1.4×10^{-3}
4			−30	(5×10^{-3})
5			25	(6×10^{-2})
6		EtOH(D)	−50	1.5×10^{-5}
7			−30	4.1×10^{-4}
8			−20	1.4×10^{-3}
9			25	(2×10^{-1})
10*	*o*-Carborane (D)	EtOH	−30	4.2×10^{-4}
11*	*o*-Carborane (T)		−30	3.9×10^{-4}
12	1-Methyl-*o*-carborane	NH_3(D)	−30	4.8×10^{-3}
13		EtOH(D)	−30	2×10^{-4}
14	*m*-Carborane	NH_3(D)	25	3.0×10^{-6}
15			40	5.4×10^{-6}
16			50	9.0×10^{-6}
17*	*m*-Carborane(D)	NH_3	25	3.1×10^{-6}
18			120	1.0×10^{-4}
19		EtOH	25	1.8×10^{-5}
20*			25	3.7×10^{-5}
21			40	1.4×10^{-4}
22			50	6.0×10^{-4}
23*		t-BuOH	25	1.6×10^{-4}
24*			30	2.6×10^{-4}
25*	*m*-Carborane(T)	NH_3	25	3.0×10^{-6}
26*		EtOH	25	3.7×10^{-5}
27*		t-BuOH	25	1.7×10^{-4}
28*			30	2.5×10^{-4}
29*			39.5	4.7×10^{-4}
30	1-Methyl-*m*-carborane	NH_3(D)	25	4.5×10^{-6}
31	1-Methyl-*m*-carborane(D)	EtOH	25	3.1×10^{-5}
32	1-Phenyl-*m*-carborane	NH_3(D)	25	1.9×10^{-5}
33			50	5.3×10^{-5}
34	1-Phenyl-*m*-carborane(D)	EtOH	25	7.9×10^{-5}
35	*p*-Carborane	NH_3(D)	50	8.5×10^{-7}
36			120	4.2×10^{-6}
37[e]	Indene(D)	NH_3	25	1.4×10^{-3}
38		EtOH	25	1.7×10^{-4}
39[e]	Fluorene(D)	NH_3	25	1.6×10^{-4}
40		EtOH	25	2.2×10^{-5}
41*			25	4.3×10^{-5}
42*		t-BuOH	25	3.3×10^{-5}
43*[e]	Fluorene(T)	NH_3	25	8.3×10^{-5}
44*		EtOH	25	1.9×10^{-5}
45		t-BuOH	25	1.6×10^{-5}

[a] Experiments from which the data are employed for calculating the kinetic isotope effect are marked with asterisks. [b] An isotope chemical symbol shown in parentheses near the formula means that the heavy hydrogen isotope (D or T) participates in a CH bond or hydroxy group of the solvent. [c] Formulae of EtOH and t-BuOH conventionally denote solutions of C_2H_5ONa (0.05 *N*) in ethanol and t-C_4H_9OLi (0.13 *N*) in t-butanol. [d] Rate constants between parentheses were estimated from the activation energies of Table 4. [e] Data of No. 37 are taken from ref. 25 and those of Nos. 39 and 43 from ref. 26.

TABLE 4

ACTIVATION PARAMETERS OF HYDROGEN ISOTOPIC EXCHANGE OF *o*- AND *m*-CARBORANES

Parameter	*Ortho*-Isomer		*Meta*-Isomer		
	NH_3	EtOH+EtONa (0.05 *N*)	NH_3	t-BuOH + t-BuOLi (0.13 *N*)	EtOH + EtONa (0.05 *N*)
E^a	6.8	16.5	8.6	12.6	27
log A	3.8	11.5	0.8	5.3	15.5
$\Delta H^{\neq a}$	6.2	15.9	8.0	12.0	26.4
$\Delta S^{\neq b}$	−42	−8	−57	−36	10
$\Delta F^{\neq a}$	18.7	18.3	25.0	22.7	24.1

[a] in kcal/mole. [b] in e.u.

TABLE 5

THE $k_D \times 10^4$ (SEC^{-1}) VALUES OF DEUTERIUM EXCHANGE OF FLUORENE AND *m*-CARBORANE (AT 25°)

Compound	$k_D \times 10^4$ (sec^{-1})			
	NH_3	EtOH + EtONa (0.05 *N*)	t-BuOH + t-BuOLi (0.13 *N*)	t-BuOH + t-BuONa (0.13 *N*)
Fluorene (D)	1.6	0.43	0.33	10
m-Carborane (D)	0.03	0.37	1.7	90
$(k_{Fl}/k_{m-carborane})$	50	1.2	0.21	0.11

The ratio of the rate constants of exchange of fluorene and *m*-carborane varies considerably with the solvent and even depends on the catalyst counterion. At 25° in liquid ammonia the rate of deuterium exchange of the fluorene methylene is 50 times that of the *m*-carborane methine whereas in tert-butanol in the presence of sodium tert-butylate (0.13 *N*) it is 9 times slower, *i.e.* a differentiation effect with respect to the kinetic acidity is observed.

The deuterium-tritium kinetic isotope effect

Table 6 shows the ratios of the rate constants of exchange of deuterium and tritium (k_D/k_T) for *m*-carborane and fluorene with three solvents. Values of k_D/k_T for the first compound are taken from Table 3 (Nos. 17 and 25, 20 and 26, 23 and 27). For the second compound data on the reaction with NH_3 are presented in ref. 26 (Nos. 39, 43). For the reaction with EtOH+EtONa (0.05 *N*) the constants are in Nos. 41 and 44, and for that with BuOH+t-BuOLi (0.13 *N*) in Nos. 42 and 45.

For the hydrogen exchange of *m*-carborane with the three bases the value of k_D/k_T is one, while for fluorene this ratio is almost two, *i.e.* it differs very little from the theoretical value ($k_D/k_T = 2.5$ at 25°), calculated by assuming a linear three-center structure with equivalent force constants of the hydrogen isotope-donor and acceptor bonds in the activated complex. In that case the main contribution to the value of the

TABLE 6

KINETIC ISOTOPE EFFECT (k_D/k_T) AT THE HYDROGEN EXCHANGE OF *m*-CARBORANE AND FLUORENE (AT 25°)

Compound	k_D/k_T		
	NH_3	EtOH + EtONa (0.05 *N*)	t-BuOH + t-BuOLi (0.13 *N*)
m-Carborane	1.0	1.0	0.9[a]
Fluorene	1.9	2.3	2.1

[a] At 30°, $k_D/k_T = 1.0$.

kinetic isotope effect is due to the difference in the CH (CD or CT) zero point energies[27]. Using the reported value of 3060 cm^{-1} for the CH-stretching frequency of *m*-carborane[28] one obtains a k_D/k_T of 2.6, *i.e.* the same as that for regular aromatic compounds.

The low kinetic isotope effect or its absence could be due to the fact that rupture of the CH (CD or CT) bond is not the rate determining step of the isotope exchange reaction[29] or that the difference in zero point energies of these bonds in an activated complex compensates that for the initial molecules[30,31]. In the last case there would be a large difference in pK_a of the substrate and the base-conjugated acid attacking the hydrogen (or isotope) atom of the substrate[32-34].

Let us see whether the absence of a kinetic isotope effect in the exchange reactions of *m*-carborane can be explained by the above reasons. It can not be explained by the mechanism advanced for the exchange reaction between hydrocarbons and dimethylsulfoxide catalyzed by alkaline tert-butylates which was found to have a low kinetic isotope effect[8,29,35]. According to this mechanism the reaction rate is determined by the second step involving diffusion of an alcohol molecule formed during the first step and hydrogen bonded to the carbanion. It is less probable that the second step should be rate limiting for the exchange reaction in liquid ammonia where the carbanion could be rapidly neutralized by the same solvent molecule which removes the hydrogen isotope from the solute molecule. Indeed no examples of exchange reactions in liquid ammonia have yet been reported in which k_D/k_T is equal to unity. Moreover, the value of $\Delta S^{\neq}$ should not be far from zero for exchange reactions in which diffusion is the rate limiting step as was noted by Streitwieser[36] in his study of the kinetics of hydrogen isotope exchange between polyfluorobenzenes and methanol in the presence of sodium methylate. On the other hand exchange between *m*-carborane and liquid ammonia or tert-butanol (in the latter solvent catalyzed by lithium tert-butylate) is associated with a large negative value of $\Delta S^{\neq}$ (Table 4).

On assuming the linear three-center structure for the activated complex, the change in pK_a of the base-conjugated acid affecting the symmetry of the complex for the same substrate should affect the magnitude of the kinetic isotpe effect[37]. In the *m*-carborane systems discussed the strengths of the base-conjugated acids differ substantially. But in all the cases studied the ratio $k_D/k_T = 1.0$.

A similar result is also obtained even with considerable changes in pK_a of the isomeric carborane. Thus, in the experiments with *o*-carborane (Table 3, Nos. 10,11) where the pK_a value is four units below that of *m*-carborane (23.8 and 27.9) (Table 1, Nos. 10, 17) the value of $k_D/k_T = 1.1$ at −30°.

The above discussion leads to the inference that the reason for the absence of a kinetic isotope effect in hydrogen exchange of isomeric carboranes should be sought for in deviation of the activated complex from the simple three-center structure usually postulated for this complex in protophilic hydrogen isotope exchange. Probably this is due to specificity of the carborane structure and the unusual valence state of its carbon atoms.

Comparison of the equilibrium and kinetic acidities

It is of interest to estimate the pK_a's of the isomeric carboranes from a linear plot of $\log k_{120°}$ *vs.* pK_a (Fig. 1) obtained for a series of hydrocarbons: indene, fluorene, triphenylmethane, diphenylmethane. The value of $\log k_{120°}$ for the exchange reaction between indene and liquid ammonia was determined from the reported data[25], and for those of other hydrocarbons were taken from ref. 4. Streitwieser[20] determined pK_a's in CHA, a solvent whose chemical behaviour is similar to that of ammonia.

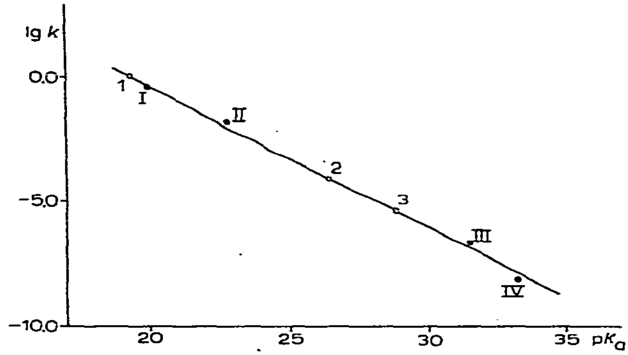

Fig. 1. I, indene; II, fluorene; III, triphenylmethane; IV, diphenylmethane; 1, *o*-carborane; 2, *m*-carborane; 3, *p*-carborane.

Several of the $\log k_{120°}$ values are rather approximate, partly owing to difficulties in rate constant measurements at low temperatures and to large extrapolation necessary for their calculation.

It has been shown above that there is no kinetic isotope effect in the hydrogen exchange reaction of *m*-carborane and liquid ammonia ($k_D/k_T = 1$). In such a case ionization of the CH bond should not be the rate limiting step of the exchange reaction which would imply deviation from the linear Brönsted relation between the ionization rate and the equilibrium ionization constants preventing the determination of pK_a values from the kinetic experiments (*cf.* ref. 9).

Despite this let us compare the graphically determined pK_a's (Fig. 1) with the values obtained from measurements of the equilibrium constants of the metallation reactions in DME:

	Ortho	*Meta*	*Para*
Isotope exchange	19.3	27.0	29.4
Metallation	23.3	27.9	30.0

It can be seen that the data obtained by both methods for *m*- and *p*-carboranes are in surprisingly good agreement whereas the pK_a's of the *ortho*-isomer differ substantially. However the results as a whole give a clear picture of the relative acidities of these peculiar CH-acids*.

Analysis of the present data shows that the electronic effect of a methyl group introduced into the quasi-aromatic carborane nucleus differs from that in protophilic substitution of hydrogen in the benzene ring. Thus the rate of exchange of the ring hydrogen of toluene and liquid ammonia (catalyzed by potassium amide) is several times below that in benzene[39]. The kinetic study in ammonia and alcohol shows the *m*-carboranes acidities to decrease in the order: 1-phenyl-*m*-carborane > 1-methyl-*m*-carborane > *m*-carborane. The determination of equilibrium constants of the metallation reaction revealed that unlike the isopropyl group not only the phenyl but also the methyl group of *o*-carborane displays a weak electron-withdrawing effect. An analogous effect of the methyl group was observed by Bowden for 9-substituted fluorenes[40]. According to his data the difference in the pK_a's of 9-methyl- and 9-isopropylfluorenes is 0.8 pK_a unit, coinciding with the difference in pK_a of the corresponding substituted *o*-carboranes (0.7–0.9 pK_a unit).

EXPERIMENTAL

Equilibrium constant determination for the metallation reaction empolying spectrophotometric method in vacuum is described elsewhere[15].

Kinetics of metallation was studied at 25–100-fold excess of carborane to that of the fluorenyllithium. The reaction course in some cases was controlled in both directions. Carborane was first added to a fluorenyllithium solution containing an excess of fluorene. This was followed by a decrease in optical density of solution (D) against the starting value (D_0) down to a constant value (D_∞) at an equilibrium position. The D_t's at certain moments between the starting point of reaction and its completion characterize kinetics of carborane metallation. After the equilibrium is attained, addition of fluorene to the reaction mixture, increases D_∞ to another constant value D'_∞ characterizing a new position of equilibrium. From the known D_0, D_∞ and D'_∞ the equilibrium constants (K) were estimated. For the determination of rate constants (k_1 and k_{-1}), log a was plotted against t, where $a=(D_0-D_\infty)/(D_t-D_\infty)$ (forward reaction), and $D'_\infty \cdot (D'_\infty - D_t)$ (back reaction). In such coordinates the tangent of slope is equal to $0.434 \times (k_1 \cdot C_c + K_{-1} \cdot C_f)$ where C_c and C_f are the carborane and fluorene concentrations.

Kinetics of the hydrogen isotope exchange reaction was measured as reported[15]. Experiments with liquid ammonia solution were carried out under elevated pressure in an installation described in ref. 41. Increased values of the rate constants in experiments Nos. 20 and 41 with respect to those in Nos. 19 and 40 are explained by a more accurate alcohol dehydration.

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* Recently the pK_a's of isomeric carboranes were determined[38] from the results of polarographic reduction of their symmetric mercury derivatives in various solvents. They were found to vary in a very wide range (for *o*-carborane from 14 to 24, for *m*-carborane from 21 to 33, and for *p*-carborane from 26 to 40).

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