trophilic catalysis without pH limitations.

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References and Notes

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The Role of Reversible Hydrogen Abstraction in the Mechanism of the Bromination of Cyclohexane. A Comparison of the Differences between the Liquid and Vapor Phase Reactions

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Abstract: The role of reversible hydrogen abstraction in the bromination of cyclohexane has been investigated by a study of the kinetics of the bromination of perdeuteriocyclohexane in the presence of large amounts of hydrogen bromide and molecular bromine. By a determination of the relative rate constants for transfer of the radical with the two transfer agents, bromine (k_2) and hydrogen bromide (k_{-1}), a ratio of rate constants k_2/k_{-1} could be obtained. In solution at 30° k_2/k_{-1} varied depending upon the concentration of molecular bromine and hydrogen bromide, while in the vapor phase, 20–28°, $(k_2/k_{-1}) = 2.81 \pm 0.06$ at all concentrations. The change in the ratio of transfer rates in solution and their difference from the vapor phase value is attributed to a complex formation between hydrogen bromide and molecular bromine, the complex acting as a transfer agent at a faster rate (k'_{-1}) than hydrogen bromide itself. The ratio of transfer rates for the solution reaction of bromine relative to HBr_3, k_2/k'_{-1}, is approximated, $(k_2/k_{-1})^{vp}/(k'_{-1}/k_{-1}) = 0.13$, and found to be in good agreement with the values obtained at high bromine concentration. Cage return of the radical with hydrogen bromide as a kinetically masked process in the bromination reaction is also discussed.

The effect of reversible hydrogen abstraction on the kinetics of bromination of alkanes and substituted alkanes with a number of brominating agents (e.g., bromine,[2] *N*-bromosuccinimide,[2] bromotrichloromethane[3]) has been a topic of considerable concern. For any understanding of the details of the mechanism of bromination, it is necessary to know the relative rates of transfer of alkyl radicals with bromine and hydrogen bromide. As the reaction appeared to be more complicated than previously reported,[4] a comparison of the kinetics of the liquid and vapor phase brominations of perdeuteriocyclohexane has been undertaken.

In the simplest mechanism involving reversible abstraction, the alkyl radicals generated by abstraction of a hydrogen atom from an alkane by bromine atoms have two fates: transfer with molecular bromine to give substitution product, or transfer with hydrogen bromide to regenerate the substrate.

$$RH + Br\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\cdot + HBr \xrightarrow[k_2]{Br_2} RBr + Br\cdot \quad (1)$$

The importance of the reversal reaction relative to product formation is related to the ratio k_2/k_{-1}. This ratio may be

Table I. Photobromination of Perdeuteriocyclohexane with Excess Bromine and Hydrogen Bromide

		Concentration (mol/l.) × 10^{5a}										
Reaction	Temp, °C	$[C_6D_{12}]^0$	$[C_6D_{11}H]^0$	$[Br_2]^0$	$[HBr]^0$	$[C_6D_{12}]^f$	$[C_6D_{11}H]^f$	$[C_6D_{11}Br]$	$[C_6D_{10}Br_2]$	Material balance,[b] %	% Reaction	$k_2/k_{-1}{}^c$
1[d]	24.0	21.0	1.41	35.6	150	9.29	8.00	2.94	1.54	97.2	18.9	2.74
2[d]	28.0	24.0	1.62	38.8	283	16.6	6.17	1.50	0.26	95.7	7.2	2.88
3[d]	20.0	23.6	1.58	37.7	36.2	21.3	2.11	1.48	0.00	99.1	5.9	2.72
4[e]	20.2	102.1	6.87	155	160	97.9	7.73	2.32	0.00	99.0	2.1	2.80
5[e]	22.2	103.3	6.92	176	157	89.0	9.59	7.60	0.88	97.2	7.9	2.89
6[f]	30.0	1910	142	5,210	3,770	1600	312	145	53.0	102.8 (98.1)	9.6	0.84
7[f]	30.0	1200	99.8	1,460	2,140	1190	126	18.5	1.3	100.8 (95.9)	1.7	1.13
8[f]	30.0	1970	144	5,400	3,870	1700	294	118	45.0	102.0 (98.9)	7.7	0.78
9[f]	30.0	2170	147	22,900	3,220	2110	168	52.7	0.00	100.6 (98.9)	2.3	0.36
10[f]	30.0	1370	92.9	58,900	2,370	1260	105	91.3	0.00	99.6	6.3	0.31
11	30.0	19.90		53,300	37,600	12,700		157	595	101.6 (99.6)	36.0	

[a] Superscript 0 refers to initial concentrations and f to final concentrations. [b] Material balances are based on hydrocarbon and bromination products accounted for. The values in parentheses are based on bromine consumed and brominated products formed. [c] Calculated using eq 6; the values for the average concentrations of Br_2 and HBr during the reactions were used. This correction is only significant when the conversion is greater than 10% (reaction 1). The values $[C_6D_{11}Br]$ of eq 6 was taken as the sum of $[C_6D_{11}Br]$ and $[C_6D_{10}Br_2]$. [d] Gas phase, 22 l. reaction bulb. [e] Gas phase, 5 l. reaction bulb. [f] Freon 113 solution, 30.0 ± 0.1°.

evaluated by determining the relative yields of brominated and protiated products in the photobromination of perdeuteriocyclohexane in the presence of excess bromine and hydrogen bromide.

$$C_6D_{12} + Br\cdot \xrightarrow{k_1} C_6D_{11}\cdot + DBr \qquad (2)$$

$$C_6D_{11}\cdot + HBr \xrightarrow{k_{-1}} C_6D_{11}H + Br\cdot \qquad (3)$$

$$C_6D_{11}\cdot + Br_2 \xrightarrow{k_2} C_6D_{11}Br + Br\cdot \qquad (4)$$

drogen bromide. The relative rates of formation of the two products are given by eq 5. If the reaction is carried out to

$$\{d[C_6D_{11}Br]/dt\}/\{d[C_6D_{11}H]/dt\} = k_2[Br_2]/k_{-1}[HBr] \qquad (5)$$

low conversion, the possibility of multiple exchange (D for D or H for H), which is not experimentally detectable, is limited, and under conditions of high concentrations of bromine and hydrogen bromide, when the concentration of these reagents is negligibly changed during the reaction, eq 5 can be evaluated to yield the desired ratio of rate constants, eq 6. The reintroduction of deuterium by transfer of

$$k_2/k_{-1} = \{[C_6D_{11}Br][HBr]\}/\{[C_6D_{11}H][Br_2]\} \qquad (6)$$

an alkyl radical with deuterium bromide will be unimportant, due to its negligible concentration relative to hydrogen bromide, and, furthermore, the operation of an unfavorable deuterium isotope effect will, likewise, limit its reincorporation.

The simplest reaction path, corresponding to eq 2-4, would be expected to occur in the vapor phase. In a degassed reaction bulb (5 or 22 l.) were placed perdeuteriocyclohexane (99.4 atom % D), bromine, and hydrogen bromide; see Table I. The reaction mixture was photolyzed with incandescent light, 100 W, at ambient temperature until the perdeuteriocyclohexane had reacted to between 2 and 19%. The contents of the bulb were collected in the absence of light, and the residual bromine and hydrogen bromide were destroyed with aqueous sodium bisulfite. An internal standard, σ-dichlorobenzene, was added, the organic material was extracted with Freon 113, dried, and analyzed by GLC. The material balance on recovered organic material was always from 100 to 96% (see Table I). The unbrominated perdeuteriocyclohexane was collected by preparative GLC and its protium content was compared, mass and NMR spectra, to that before the reaction; see Table I. Control experiments were carried out on known mixtures of cyclohexane, cyclohexyl bromide, *trans*-1,2-dibromocyclohexane, bromine, and hydrogen bromide. A mixture corresponding to the final product composition obtained in reaction 1 (see Table I) was placed in the vapor phase, reisolated, and subjected to the analytical procedure. The material balance, based on carbon, was >98.8% and for the bromination products it was >99.7%. The ratio of dibromide to monobromide was found to change slightly (~2%, dark reaction); however, the material balance was found to be quantitative within the experimental limits given. The isolated reaction mixtures showed no detectable products other than protium incorporated cyclohexane and its mono- and dibromination products. The bromination products had the same GLC retention times (10% UCON 50 LB 500X) as bromocyclohexane, *trans*-1,2-dibromocyclohexane, and 1,1-dibromocyclohexane.[2j] The mass spectral cracking patterns of these products, isolated by preparative GLC, were identical with those of the authentic unprotiated compounds, when the values for *m/e* were corrected for deuterium instead of protium.

Since the dibrominated material must have arisen, regardless of mechanism, from the monobrominated substitution product, the extent of monobromination was calculated as the sum of the mono- and dibromination products. This assumption must indeed be correct since reactions producing dibromide (reactions 1, 2, 5, Table I) and reactions not yielding dibromide (reactions 3 and 4, Table I) gave within the experimental error the same average relative rate constants. The variation in the amount of dibrominated material obtained in the various reactions does not appear to arise from a competition having a constant ratio of rates for the abstraction from substrate and monobrominated substrate. This variation may be rationalized on the basis of a combination of the relative rates of reversal with hydrogen bromide and/or the occurrence of a dark reaction of monobrominated material, in the condensed phase, with the high concentration of bromine and hydrogen bromide[2k] (i.e., for the vapor phase reaction the material is in the liquid phase prior to isolation). As was discussed above, however, the production of dibrominated products, regardless of mechanism, will not effect the relative rate data reported.

The relative rates of transfer were calculated using eq 6, and for the vapor phase reactions, at various ratios of bromine to hydrogen bromide, $k_2/k_{-1} = 2.81 \pm 0.06$. The difficulty in controlling the temperature of the large vessels (22 and 5 l.) used to carry out the vapor phase reactions was worrysome; however, since the kinetic values obtained were relative rates, which both increase with increasing temperature, and the average of five determinations (reactions 1-5) did not deviate by more than ±2% over the 8° range (20-28°), it was justified to assume that the values obtained in these reactions were relatively insensitive to temperature at this temperature range.

In order to relate the ratio of rate constants obtained for the deuterated substrate to that of the nondeuterated substrate, the assumption is made that the ratio of transfer rates, k_2/k_{-1}, will be the same for the deuterated and protiated radicals.

When Freon 113 solutions of perdeuteriocyclexane, hydrogen bromide, bromine, and Freon 112 (internal standard) were allowed to react, 30°, in a similar manner (see Table I), the observed value for k_2/k_{-1} was found to be variable, and unlike the vapor phase reactions, dependent upon the relative concentration of bromine and hydrogen bromide. One reaction run in solution (reaction 11, Table I) was photolyzed to 36% conversion. The material balance obtained for the reaction mixture based on bromine (99.6%) or on initial cyclohexane and recovered products (101.6%) gives assurance that the bromination products were not preferentially lost in the reactions run to low conversion.

A detailed scheme which would be consistent with the liquid phase reactions must necessarily consider the involvement of geminate radical molecule transfer reactions as well as the transfer of radicals which are free of the solvent cage.

$$C_6D_{12} + Br\cdot \rightleftharpoons (C_6D_{11}\cdot + DBr) \longrightarrow C_6D_{11}\cdot \longrightarrow \text{products}$$

Cage return of deuterium is likely to be competitive with diffusion from the cage; however, the observation of this process is masked in these experiments, since only protium incorporation can be detected. This reaction is undoubtedly operative in the bromination of nondeuterated substrates where hydrogen bromide is the transfer agent, and in structurally unsymmetric radicals and substituted alkanes, where different isomeric radicals will have different rates of reversal compared to diffusion, the process may account for isomer product distributions which are different than those which reflect the kinetic distribution of radicals formed by abstraction. The importance of cage reversal, however, can only be determined by a comparison of the kinetics of these reactions in the liquid and vapor phase.

The lower value of the observed ratio of k_2/k_{-1} in solution compared to the vapor phase value appears to be fundamental to brominations in solution. It may be caused by either a smaller rate constant for bromine atom transfer or a larger rate constant for hydrogen atom transfer in solution. The latter seems to be more likely, since any species which complexes with the transfer agent would tend to lower the bond strength of the transfer agent. An attractive proposal, to explain why cyclohexyl radicals in solution transfer with "hydrogen bromide" faster than with bromine, is that the transfer agent is a complex of hydrogen bromide and molecular bromine, and that the rate constant for this process, k'_{-1}, is larger than that for transfer with hydrogen bromide.

$$HBr + Br_2 \rightleftharpoons HBr_3 \tag{7}$$

$$C_6D_{11}\cdot + HBr_3 \xrightarrow{k'_{-1}} C_6D_{11}H + Br_3\cdot \tag{8}$$

Complexes of the type HX_3 are well established for bromine,[5] chlorine,[6] and iodine,[7,5] and the equilibrium constant for the latter complex has been estimated to be between 25 and 400 l./mol (CCl_4, 25°).[8]

If one includes eq 7 and 8 in the mechanism used to derive the relative rate of transfer of cyclohexyl radicals, expression 5 becomes eq 9.

$$\{d[RBr]/dt\}/\{d[RH]/dt\} = \frac{k_2([Br_2]^0 - [HBr_3])}{k_{-t}([HBr]^0 - [HBr_3]) + k'_{-1}[HBr_3]} \tag{9}$$

Integration and rearrangement of eq 9 gives eq 10. Using the expression for the equilibrium constant (eq 11) and the

$$\frac{[RBr]k_{-t}}{[RH]k_2} = \frac{[Br_2]^0 - [HBr_3]}{[HBr]^0 - [HBr_3] + (k'_{-t}/k_{-1})[HBr_3]} \tag{10}$$

$$K = [HBr_3]/\{[Br_2]^0 - [HBr_3]\}\{[HBr]^0 - [HBr_3]\} \tag{11}$$

vapor phase result for k_2/k_{-1}, 2.81, eq 10 can be evaluated to give k'_{-1}/k_{-1}, if a value for K could be determined independently. The equilibrium constant (eq 11) was determined, using standard techniques,[9] from the concentration dependence of the downfield shift of the NMR signal for the hydrogen bromide proton (maximum Δ 31.3 Hz, Freon 113, 32.8°) when different amounts of molecular bromine were added (see Table II). K was found to be 2.8 ± 0.3 (32.8°) by this method. Using this value of K, a value for k'_{-1}/k_{-1} of 21.8 ± 6.7 could be obtained using all of the solution data (reactions 6-10).

Inherent in the NMR method for the calculation of the maximum chemical shift is the assumption that the chemical shift of complexes of higher order in bromine than HBr_3 have approximately the same chemical shift as HBr_3.[10]

$$HBr_3 + Br_2 \rightleftharpoons HBr_5 \overset{Br_2}{\rightleftharpoons} HBr_7 \rightleftharpoons \text{etc},$$

This seems to be a valid assumption (see Table II), since, when the value of K was computed by iterative treatment of the data, using only the values for $[Br_2]/[HBr] \leq 5$, the computed K was found to be 2.8 ± 0.3 and the maximum shift computed Δ, 32.2, was in good agreement with that calculated using all the values reported in Table II.

At the relative concentrations used in the solution phase reactions the possibility existed that complex formation between hydrogen bromide with itself or bromine with itself, although less favorable reactions than the complex forma-

Table II. NMR Determination of $HBr + Br_2 \rightleftharpoons HBr_3$ Equilibrium Constant (32.8°)

Spectrum	[HBr]	$[Br_2]$	δ,[b] Hz	K_T[c]	K_L[c]
1	0.0205		357.0		
2	0.0509		357.0		
3	0.0681		355.9		
4	0.0764		355.7		
5	0.0814		356.5		
6[a]	0.0955		356.1		
7	0.0963		356.0		
8	0.0925		355.3		
9	0.0981		356.4		
10	0.0716	0.0153	354.9	3.5	3.6
11	0.0675	0.0311	354.3	2.4	2.3
12	0.0475	0.0331	354.1	2.4	3.2
13	0.0727	0.0310	353.8	3.3	2.6
14	0.0338	0.0498	352.8	2.6	2.6
15	0.0253	0.0600	352.1	2.7	3.1
16	0.0793	0.0657	351.6	3.2	2.9
17	0.0746	0.1372	348.0	3.0	2.9
18	0.0723	0.1372	347.9	3.1	3.0
19	0.0742	0.1860	345.6	3.1	3.0
20	0.0655	0.1899	345.5	3.2	3.0
21	0.0630	0.3098	341.9	3.0	2.8 ± 0.3 av,
22	0.0797	0.3563	341.7	2.7	Δ 32.2
23	0.0594	0.5091	339.1	2.5	
24	0.0715	0.5730	337.4	2.8	
25	0.0900	0.7328	335.7	2.8	
26	0.0651	1.040	333.5	2.7	
27	0.0676	1.067	333.2	2.7	
28	0.0856	1.460	331.6	2.7	
29	0.0610	1.967	330.6	2.4	
30	0.0638	2.123	329.9	2.6	
31	0.0750	2.994	328.7	2.5	
32	0.0998	2.948	328.4	2.8	
				2.8 ± 0.3 av, Δ 31.3	

[a] The solution was 0.1 *M* in cyclohexane. [b] Average δ (Hz) for HBr in Freon 113 was 356.2 ± 0.4, upfield from TMS. [c] K_T is the equilibrium constant determined using the data of spectra 10–32; K_L used only the data from spectra 10–20.

tion between dissimilar species, might effect the kinetic values obtained. Examination of the hydrogen bromide concentration dependence of the NMR proton shift without bromine showed that hydrogen bromide complex formation does not affect the NMR equilibrium constants within the experimental limits reported (see Table II), and it is unlikely, therefore, that a significant complex formation is involved. No useful spectral information could be obtained on the self-complex formation of bromine in nonpolar solvents, ir, NMR (Br^{81}), or uv and for the present its possible effect is undetermined.

The observed values for the relative rates of transfer in solution were found, as would be predicted, to vary with the relative concentrations of hydrogen bromide and molecular bromine. The assumption that in the vapor phase complex formation is unimportant allows the calculation of the relative rates of transfer of the cyclohexyl radicals with bromine and with HBr_3 $k_2/k'_{-1} = (k_2/k_{-1})^{vp}/(k'_{-1}/k_{-1}) = 0.13$. At high solution concentrations of bromine relative to hydrogen bromide (i.e., high concentrations of HBr_3), reaction 10, Table I, the observed value for $(k_2/k_{-1})^{obsd}$ was 0.31, in very good agreement with the calculated value, using K and k'_{-1}/k_{-1}, of 0.20. Inherent in this calculation, which must be assumed approximate, is the assumption that at the high ratios of $[Br_2]/[HBr]$ (reaction 9) the rates of transfer from complexes of HBr_3, HBr_5, and HBr_7 are quite similar (if higher complexes are important).

It has been suggested that at high concentrations of bromine the abstracting species in solution is a complex radical $Br_3\cdot$.[11,12] If cage return of radicals is important, and if the hydrogen bromide-bromine complex is the transfer species, the likelihood of cage return is even greater than it first appears.

$$C_6H_{12} + Br_3\cdot \rightleftharpoons (C_6H_{11}\cdot + HBr_3) \longrightarrow \text{products}$$

The effect of HBr_3 and HBr transfer on the competitive rates of bromination of substrate pairs in solution as well as their effects on isomer distributions in liquid phase bromination is presently being investigated and these results will be reported in subsequent papers.

Experimental Section

Material. Perdeuteriocyclohexane (Merck Sharp & Dohme, >99 atom % D) was purified by two preparative GLC collections (20 ft × 0.25 in. 10% Carbowax 20M TPA or 10 ft × 0.25 in. 10% UCON LB 550X glass columns); GLC analysis showed it to be >99.9% pure, and mass spectral analysis showed it to contain 99.4 atom % D. Molecular bromine (McArthur Chemical Co., Reagent Grade) was washed twice with concentrated sulfuric acid and distilled from phosphorus pentoxide. Hydrogen bromide (Matheson) was passed over calcium chloride or molecular sieve 4A; for the vapour phase reactions, it was degassed twice and doubly distilled prior to being measured in a vacuum line. The Freons (Du Pont or Matheson) were distilled from P_2O_5 through a 12 in. Vigreux column. 1,1-Diphenylethylene (Aldrich) was distilled prior to use: bp 136.5–137.0° (9.6 mm), n^{20}D 1.6088 (lit.[13] bp 139° (11 mm), n^{20}D 1.6085); nmr spectroscopy and GLC analysis showed it to have no detectable impurities.

Vapor Phase Reactions. Perdeuteriocyclohexane (about 0.5 g) was carefully weighed into a Pyrex break seal, and this was degassed by the freeze–thaw method three times and finally sealed. Bromine (about 1.3 g) was similarly weighed, degassed, and sealed in a separate break seal. Hydrogen bromide was degassed and distilled in a vacuum line, measured, and distilled into a break seal. The three break seals were attached to the reaction bulb (5 or 22 l.), and the system was evacuated. The break seals were broken in the absence of light (in the order C_6D_{12}, HBr, Br_2, with 20 min intervals between each break seal) and the mixture of the three substrates was allowed to equilibrate (about 30 min), and then the bulb was photolyzed (one 100 W incandescent lamp). The contents of the bulb were condensed into a tube attached to the reaction bulb in the absence of light. The tube was opened, an internal standard was added (*o*-dichlorobenzene), and the excess bromine and hydrogen bromide were destroyed with cold (0°) sodium bisulfite. The organic substrates were extracted with Freon 113 (about 25 ml), and the Freon solution was washed with cold water and dried ($MgSO_4$). It was then analyzed by GLC (6 ft × 0.25 in. 10% UCON 50 LB 550X on Chromosorb P AW, glass column) for starting material and products. The solution was concentrated on a 24 in. Teflon spinning band column to about 4 ml, and the unreacted starting material was collected and recollected by preparative GLC (20 ft × 0.25 in. 10% Carbowax 20M TPA on Chromosorb P AW, glass column, 50°).

Liquid Phase Reactions. A Freon 113 solution of hydrogen bromide, protected from the air by a mercury seal, was allowed to equilibrate overnight at 30.0°. Aliquots of the solution were withdrawn and the concentration of hydrogen bromide was determined by iodometric titration.[14] In the absence of light, Freon 113 solutions of bromine and accurately weighed amounts of cyclohexane-d_{12} and Freon 112 were added to the hydrogen bromide solution and the concentration of bromine was determined by iodometric titration.[14]

The reaction mixture was irradiated with two 200 W incandescent lamps at 30.0 ± 0.1° until the desired amount of cyclohexane-d_{12} had reacted (10–12 hr). The bromine concentration was determined iodometrically and the excess bromine was destroyed by treating the cold solution (0°) with cold 5% aqueous sodium bisulfite. The reaction mixture was washed successively with water, 5% aqueous sodium bicarbonate, and water and dried over anhydrous sodium sulfate. The amounts of remaining cyclohexane-d_{12} and its bromination products were determined by GLC analysis (10% UCON 50 LB 550X) and the molar concentrations were obtained using standard calibration curves.

The reaction mixture was concentrated by distillation (24 in. Teflon spinning band column) to approximately 5 ml and dibromi-

Table III. Bromine Solvent Shift

$[C_5H_{12}]$	$[Br_2]$	Δ^a
0.0795	0.00	93.2
0.0781	0.1188	93.2
0.0779	1.0883	93.0
0.0781	2.9357	92.7

^{a}Hz, downfield from TMS, at 32.8°.

nation products were redetermined by GLC (10% UCON 50 LB 550X). The unbrominated cyclohexane-d_{12} was recovered from the concentrated reaction mixture by GLC (10% UCON 50 LB 550X). The amount of incorporation of protium into the deuteriocyclohexane was determined by both NMR and mass spectrometry.

Determination of Residual Protium in Perdeuteriocyclohexane. Accurately prepared solutions of perdeuteriocyclohexane (100-240 mg) and diphenylethylene (10-25 mg) in Freon 113 (about 0.3 ml) were analyzed by NMR spectroscopy using a Varian HR 100 spectrometer. Two spectra were run (normal and D decoupled) with the phenyl protons as lock and reference. A small amount of TMS was added, and two more spectra, normal and D decoupled, were run, with TMS as lock and reference. Each spectrum was integrated at least five times, and the average values for the integrated areas were again averaged for the four spectra. Both decoupled and undecoupled spectra gave the same integration values, within experimental error, showing the absence of any experimentally important Overhauser effects. From the relative areas of the cyclohexyl proton (τ, 8.59) and the olefinic protons of diphenylethylene (τ, 4.63), the amount of $C_6D_{11}H$ in the NMR sample could be determined. The amount of $C_6D_{10}H_2$ and other protiated cyclohexanes could not be separately determined by this method and is taken as $C_6D_{11}H$.

The residual protium was also determined by mass spectrometry, using an AEI MS9 spectrometer at 12 eV, with slow magnetic scanning to eliminate peak clipping by the galvanometers. Two samples of the predeuteriocyclohexane were scanned five times each in the molecular ion region (*m/e* 90-98). The percentage protium was calculated by the method of Biemann.[15] The results obtained by mass and NMR spectroscopy agreed within the experimental limits quoted.

Equilibrium Constant Measurements. Freon 113 (Matheson) was washed successively with water (1×), 1 *M* HCl (2×), 1 *M* NaOH (3×), and water (3×), refluxed over $CaCl_2$ overnight, distilled, and finally distilled from P_2O_5, collecting the middle fraction, bp 48.4-48.8° (685 mm). Hydrogen bromide (Matheson) was passed over $CaCl_2$, degassed, sublimed twice at −98° (methanol slush bath), and distilled. Standard solutions of bromine in Freon 113 (1% in TMS) were prepared, and aliquots were titrated iodometrically with thiosulfate. One milliliter aliquots were quantitatively transferred into 4 mm i.d. NMR tubes, and the tubes were incorporated into a vacuum line, frozen in liquid nitrogen and degassed to $<2\ \mu$. A premeasured amount of HBr was distilled into the tubes and the tubes were sealed. The tubes were allowed to equilibrate to the probe temperature, 32.8 ± 0.2°, and the NMR spectrum was obtained. All line positions were measured in hertz relative to TMS by counting the difference between the lock and sweep occillator frequencies using a Varian HA 100 spectrometer. Reproducibility of the measurement was better than 0.2 Hz.

The bromine solvent shift was determined by substituting 2,2-dimethylpropane for HBr (Table III). The results gave a straight line plot, $\Delta = -0.174[Br_2] + 93.205$, $r = 0.998$. Since the solvent shift was within the experimental error quoted for the measurements of the HBr chemical shifts, the solvent shift was not corrected for.

An iterative procedure was used to calculate the equilibrium constant K and the position of absorption of HBr_3 relative to that of HBr (Δ). Initially, Δ was assumed to be that of spectrum 32; using this value, an approximate set of values of K's was determined using all the other spectral results. The average K was used to give a new value of Δ using the data of tube 32. This new value of Δ was again used to calculate a new set of values for K, and the process was repeated until a constant average value of K was obtained. The values for K and Δ were also determined in the same manner using only the data obtained from spectra 10-20; the results are given in Table II, as K_L.

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