

tween the radical anions and cations of TMBZ also takes place. The free enthalpy changes can be calculated as the differences of the standard redox potentials of solvated electrons and of the formation of radical cations. Table V lists these values including the free enthalpy change of the electron transfer reaction between the radical cations and anions of TMBZ ($\text{TMBZ}^{\cdot+} + \text{TMBZ}^{\cdot-} \rightarrow 2\text{TMBZ}$) and the singlet energies. Energetically, all of the systems described above are fairly "energy sufficient" for the direct production of the excited singlet state.

As shown in Figure 11, however, there are additional emission bands in the eel spectra whose peak positions are located in the region $2.0\text{--}2.2 \mu^{-1}$. At present, the origin of these additional lower energy bands cannot be explained by the above preliminary experiments. There are several interpretations for these bands. One of them is that the lower wavenumber bands are due to the formation of excimers. To check the above possibility we tried to measure the fluorescence of relatively high concentrations of TPAA solutions using a normal photoexcitation technique. Unfortunately, no additional band in the lower wavenumber region could be observed until the concentration of TPAA was 15 mM. The other possibility is that the additional band is caused by decomposition products of the radical anions. Although the reduction behavior of the above compounds is not clear at present, the oxidation peak of solvated electrons is diminished in the case of TPAA and DMPA as shown in Figure 10. Details will be published elsewhere.

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Kinetics of the Protolysis of Cryptands in Basic Aqueous Solution

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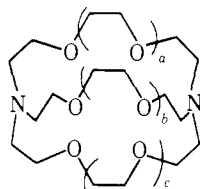
Abstract: The kinetics of the proton transfer reaction between hydroxide ions and the monoprotated cryptands 2,1,1, 2,2,1, 2,2,2, and 2,2,2B have been investigated in aqueous solution, using the pressure-jump technique. Except for 2,2,1, the observed relaxation times for the cryptands are consistent with a simple rate-determining proton transfer step. The observed rate constants for the proton transfer to hydroxide are relatively low, varying from $1.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for 2,1,1 to $1.0 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for 2,2,2 (25 °C). The results for 2,2,1, however, require the postulation of a more complex reaction path. These relatively slow rates, together with the results for the 2,2,1 system, suggest that conformational changes within the ligands, associated with the inversion of the nitrogens, may play an important role in determining the overall kinetics of the reactions.

Introduction

A variety of macrocyclic ligands synthesized in recent years, such as the polyethers (crown ethers)² and macrobicyclic ligands of the type 1–4 (cryptands, Cry),³ display strong cation selectivity, comparable to that of naturally occurring metabolites such as nonactin and valinomycin.⁴ This has resulted in

a number of kinetic^{5–9} and thermodynamic studies^{10–13} of their ion binding properties.

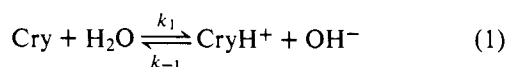
In aqueous solution, cryptands, in addition to their ability to form strong complexes with metal ions, may exist as monoprotated and diprotated derivatives because of the two basic nitrogen atoms. This then provides the opportunity for



1. $a = b = c = 0$ 1,1,1
2. $a = b = 0; c = 1$ 2,1,1
3. $a = 0; b = c = 1$ 2,2,1
4. $a = b = c = 1$ 2,2,2

kinetic studies of the removal of protons from within the cavity of the ligands. The protonated 1,1,1 cryptand is known to give up its protons very reluctantly, the doubly protonated form reacting only slowly with 5 M KOH.¹⁴ Kinetic studies of the protolysis of the larger cryptands have, however, not been reported.

In the present paper, we report the results of a pressure-jump study of the kinetics of the equilibria



with Cry = 2,1,1, 2,2,1, 2,2,2, and 2,2,2B, the latter having a benzene ring fused to the central $-\text{CH}_2\text{CH}_2-$ group of one of the bridges. The dissociation constants corresponding to equilibria 1 for each of the cryptands have also been determined from conductivity measurements on solutions of the cryptands.

Experimental Section

The cryptands 2,1,1, 2,2,1, 2,2,2, and 2,2,2B were commercial samples (Merck) used without further purification. The purity has been tested in the course of pK_a determinations. Kinetic measurements were made with a pressure-jump apparatus, described earlier,¹⁵ together with associated facilities for automatic data collection and processing.^{16,17} Conductivity measurements were made with a Wayne Kerr Autobalance Universal Bridge B 642, using a conventional dip conductivity cell with platinized platinum electrodes (WTW LT1/A).

Results

pK_a Measurements. The interpretation of the kinetic measurements (see later) required a knowledge of the dissociation constants, K_b , corresponding to equilibria 1. For the cryptands 2,1,1,¹⁰ 2,2,1,¹⁰ and 2,2,2,^{10,13} these values are available at 25 °C from previously reported pK_a values, determined using potentiometric measurements with glass electrodes. However, for the more strongly basic ligands 2,1,1 and 2,2,1, there exists the possibility of significant errors resulting from liquid junction potentials, as the concentration of (highly mobile) hydroxide ions in the test solution were not negligible compared to the electrolyte concentrations in the salt bridges used. For this reason, the required dissociation constants for all four cryptands used here have been determined by conventional conductometric techniques.¹⁸ The conductances of solutions of the ligands (resulting from CryH^+ and OH^- produced according to equilibria 1) were measured at 25 and 1.2 °C, under an atmosphere of nitrogen, with ligand concentrations between ca. 2×10^{-4} and 10^{-2} M. The required λ^0 values for OH^- were obtained from the literature,¹⁹ the conductance due to OH^- accounting for ca. 90% of the observed conductances. λ^0 values for CryH^+ were obtained from measurements on solutions CryH^+Cl^- , prepared by neutralization of the ligands with HCl (ca. 98% neutralized to avoid the presence of LH_2^{2+}). The results have been corrected to infinite dilution¹⁸ to allow for the small effects of the electrolyte concentrations ($\leq 2 \times 10^{-3}$ M) on the mobilities and activities of the ions. The results are summarized in Table I.

The agreement between the present results for 2,2,2 (pK_a

Table I. pK_a Values^a for Cryptands in Aqueous Solution

Cryptand (Cry)	Temp, °C	$\lambda^0(\text{CryH}^+)^b$	pK_b^c	pK_a
2,1,1	25	24.4	2.83	11.17
2,1,1	1.2	13.3	3.05	11.84
2,2,1	25	23.2	3.09	10.91
2,2,1	1.2	11.1	3.11	11.78
2,2,2	25	24.6	4.14	9.86
2,2,2	1.2	10.4	4.23	10.66
2,2,2B	25	24.3	4.31	9.69
2,2,2B	1.2	11.7	4.38	10.49

^a pK_a values refer to the process $\text{CryH}^+ = \text{Cry} + \text{H}^+$. ^b ± 0.5 . Values in $\text{cm}^2 \text{Int}\Omega^{-1} \text{equiv}^{-1}$. ^c ± 0.05 . $K_b = [\text{OH}^-][\text{CryH}^+]/[\text{Cry}](\text{eq 1})$.

= 9.86 at 25 °C) and the results from earlier potentiometric measurements ($pK_a = 9.60^{10}$ and 9.71^{13}) is probably within the combined experimental uncertainties. The earlier results, in addition, refer to ionic strengths of 0.05 and 0.1 M, respectively, which may also have a slight effect. However, the values reported here for 2,1,1 and 2,2,1 ($pK_a = 11.17$ and 10.91 at 25 °C) differ considerably from those previously obtained (10.64 and 10.53, respectively).¹⁰ We have checked these values using conventional potentiometric measurements with a glass electrode and a reference calomel electrode connected by a salt bridge containing 1 M Et_4NBr as bridge electrolyte. The results obtained were $pK_a = 11.0$ and 10.9 for 2,1,1 and 2,2,1, in reasonable agreement with those obtained by the conductometric method.

Rate Measurements. The kinetics of the reaction shown in eq 1 could be very conveniently followed with the pressure-jump apparatus,¹⁵⁻¹⁷ using the conductance change to monitor the reactions. If it is assumed that the proton transfer is a simple one-step process, the usual relaxation treatment leads to

$$\tau^{-1} = k_1 + k_{-1}\gamma_{\pm}^2\kappa(m_{\text{CryH}} + m_{\text{OH}}) \quad (2)$$

In eq 2 m_{CryH} and m_{OH} refer to the concentrations of CryH^+ and OH^- , respectively, k_1 and k_{-1} are the forward and reverse rate constants, referred to infinite dilution, γ_{\pm} is the ionic activity coefficient, again referred to infinite dilution in water and $\kappa = (1 + d \ln \gamma_{\pm} / d \ln m)$ when no inert electrolyte is added. In the concentration range used the contribution of κ is of negligible importance. In the special case of solutions being prepared by dissolving a known amount, C_0 , of the ligand in solution, it can be readily shown that eq 5 follows from eq 3 and 4

$$\tau^{-1} = k_1 + 2x\gamma_{\pm}^2k_{-1} \quad (3)$$

$$K_b = \frac{x^2\gamma_{\pm}^2}{C_0 - x} = \frac{k_1}{k_{-1}} \quad (4)$$

$$\tau^{-2} = k_1^2 + 4C_0\gamma_{\pm}^2k_1k_{-1} \quad (5)$$

in which x refers to the concentration of OH^- and CryH^+ produced by hydrolysis of Cry according to eq 1. The particular conditions under which the relaxation experiments were carried out and the method of treatment of the data are discussed separately below for each of the cryptands. In all cases the required activity coefficients were calculated from the Davies equation²⁰

$$-\log \gamma_{\pm} = \frac{AI^{1/2}}{1 + I^{1/2}} - 0.3AI \quad (6)$$

where A is the Debye-Hückel function and I is the ionic strength.

2,1,1. Two series of relaxation experiments were carried out in the temperature range 5–25 °C. In the first series, the re-

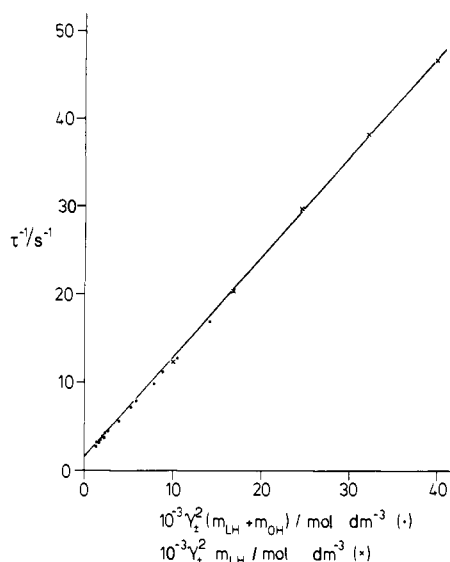


Figure 1. Linear dependence of the reciprocal relaxation time for the first protonation step of $L = 2,1,1$ on concentration at 25 °C.

Table II. Concentration Dependence of the Relaxation Times for Cryptand 2,1,1 in Water at 25 °C

$10^3 C_0,^a$ mol dm ⁻³	$10^3 x,^b$ mol dm ⁻³	γ_{\pm}^2	τ^-, s^{-1}^c	τ^{-1}, s^{-1} (calcd) ^d
49.7	8.57	0.824	16.95	16.8
27.8	6.14	0.846	12.8	12.8
20.5	5.13	0.857	11.2	11.1
16.7	4.54	0.865	9.89	10.1
10.0	3.33	0.881	7.88	7.93
8.20	2.95	0.888	7.25	7.25
5.00	2.15	0.902	5.65	5.78
3.20	1.60	0.914	4.72	4.75
2.78	1.46	0.918	4.47	4.48
2.40	1.32	0.922	4.17	4.21
2.05	1.18	0.926	3.88	3.96
2.01	1.16	0.926	3.94	3.91
1.64	1.00	0.931	3.54	3.60
1.39	0.883	0.935	3.15	3.37
1.20	0.796	0.938	3.39	3.20
1.03	0.706	0.941	2.76	3.03

^a Total cryptand concentration. ^b Calculated from eq 4 with $K_b = 1.47 \times 10^{-3} \text{ mol dm}^{-3}$. ^c Experimental values. ^d Calculated from eq 3 with $k_1 = 1.59 \text{ s}^{-1}$ and $k_{-1} = 1.08 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

laxation times were measured for solutions prepared by dissolving varying amounts of the cryptand (ca. 10^{-3} to 5×10^{-2} M) in water. In principle, these results could be used in conjunction with eq 5 to determine both k_1 and k_{-1} , and hence K_b ($= k_1/k_{-1}$). In practice, however, the intercept of the plots of τ^{-2} vs. C_0 were too small to be accurately determined. An alternative approach is to use an iterative procedure based on eq 3. Thus, a value of K_b is assumed and used to calculate values of x and γ_{\pm} for various total ligand concentrations. Then values of k_1 and k_{-1} (and hence a new value of K_b) may be obtained from a plot of τ^{-1} vs. $2x\gamma_{\pm}^2$, the procedure being repeated until internally consistent results are obtained. Again, however, it was difficult to obtain accurate values for k_1 , and hence reliable values of K_b , because of the relatively small intercept in the plots of τ^{-1} against $2x\gamma_{\pm}^2$. The results are, however, entirely consistent with the experimentally measured values of K_b . This may be seen from, for example, the detailed results for 2,1,1 at 25 °C shown in Table II. Here the values of x and γ_{\pm} have been calculated using the experimentally measured K_b ($1.47 \times 10^{-3} \text{ mol dm}^{-3}$). The results plotted according to eq 3 give

Table III. Protolysis of Cryptand 2,1,1 in Water (eq 1)

Temp, °C	$10^4 K_b$	$k_1,^a \text{ s}^{-1}$	$10^{-2} k_{-1},^a$ mol ⁻¹ dm ³ s ⁻¹	$10^{-2} k_{-1},^b$ mol ⁻¹ dm ³ s ⁻¹
25	14.7 ^c	1.59	10.8	11.3
20	13.3 ^d	1.11	8.34	8.60
15	12.0 ^d	0.756	6.30	6.73
10	10.8 ^d	0.512	4.74	5.10
5.15	9.71 ^d	0.359	3.70	3.83
1.20	8.89 ^c			

^a Determined using eq 3 (see text). ^b Determined from measurement in buffers using eq 7 (see text). ^c From Table I. ^d Interpolated from results in Table I.

values of $k_1 = 1.59 \text{ s}^{-1}$ and $k_{-1} = 1.08 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Values of τ^{-1} calculated from eq 3 using the above values for k_1 and k_{-1} have been included in the table, and may be compared with the experimentally measured values over the range of ligand concentrations used.

As an independent check on the values obtained above, a second series of experiments was carried out, in which relaxation times were measured in buffers prepared by half neutralizing the cryptand (i.e., $[\text{Cry}] = [\text{CryH}^+]$) by the addition of HClO_4 . Measurements were carried out in the concentration range $[\text{Cry}] = 0.9[\text{CryH}^+] = \text{ca. } 1 \times 10^{-2}$ to $6 \times 10^{-2} \text{ M}$ with the total ionic strength maintained at 0.06 M by the addition of Et_4NBr . Under these conditions, $[\text{OH}^-]$ is constant (and low, being $\leq 10\% [\text{CryH}^+]$). Equation 2 then gives

$$\tau^{-1} = k_1' + k_{-1}\gamma_{\pm}^2 m_{\text{CryH}} \quad (7)$$

in which $k_1' = k_1 + k_{-1}\gamma_{\pm}^2 m_{\text{OH}^-}$ (in practice small compared with $k_{-1}\gamma_{\pm}^2 m_{\text{CryH}}$). From a plot of τ^{-1} vs. m_{CryH} , a value of $k_{-1} = 1.13 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 25 °C was obtained. This may be compared with the value of $k_1 = 1.08 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ obtained via the measured stability constant, as described above. The results from both series of measurements at 25 °C are shown in Figure 1. The rate of reaction between CryH^+ and OH^- has also been directly measured using stopped-flow with conductivity detection and found to agree within experimental error with those obtained from the relaxation measurements.

The combined results for cryptand 2,1,1 are summarized in Table III. Detailed results, from which the various k_1 and k_{-1} were obtained, are given in the microfilm edition²⁷ (Table 2a).

2,2,1. The relaxation times were measured for solutions containing only dissolved cryptand, with cryptand concentrations varying between ca. 5×10^{-4} and 10^{-1} M (10^{-2} M at temperatures above 10 °C). It was not possible to carry out measurements using buffers, as described for 2,1,1, as the relaxation times in such solutions were too short for the pressure-jump technique (τ (min) ca. 50–100 μs). This means that for 2,2,1 (and cryptands 2,2,2 and 2,2,2B) we were unable to independently vary the concentrations of CryH^+ and OH^- . The results for this cryptand were, however, found to be incompatible with eq 2–5, which were derived on the assumption that only a simple rate-determining proton transfer step was involved in equilibrium 1. This may be illustrated by the results listed in Table IV and shown in Figure 2, obtained at 10 °C. In Figure 2 a plot of τ^{-2} vs. $\gamma_{\pm}^2 C_0$ according to eq 5 is shown, and it can be seen that the plot is distinctly curved. The initial slope and intercept give values of k_1 and k_{-1} corresponding to $K_b = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$, compared with the measured value of $K_b = 7.9 \times 10^{-4} \text{ mol dm}^{-3}$. Attempts to fit the results to eq 3 as described for cryptand 2,1,1 were also unsuccessful. Detailed results at other temperatures are given in the microfilm edition²⁷ (Table 4a).

Table IV. Concentration Dependence of the Relaxation Times for Cryptand 2,2,1 in Water at 10 °C

$10^3 C_0,^a$ mol dm ⁻³	$10^3 x,^b$ mol dm ⁻³	γ_{\pm}^2	$10^{-3} \tau^{-1},$ s ⁻¹	$10^{-6} \tau^{-2},$ s ⁻²
106.8	9.66	0.820	16.1	260
60.8	7.09	0.841	13.5	182
30.4	4.83	0.864	10.7	114
10.4	2.62	0.896	6.89	47.5
8.40	2.31	0.902	6.31	39.8
6.20	1.92	0.909	5.63	31.7
4.15	1.51	0.919	4.76	22.7
2.07	0.965	0.934	3.98	15.8
1.40	0.742	0.941	3.22	10.4
0.732 ^c	0.468	0.953	2.83	8.0
0.418 ^c	0.305	0.962	2.36	5.6

^a Total cryptand concentration. ^b Calculated from eq (4) with $K_b = 7.87 \times 10^{-4}$ mol dm⁻³. ^c 8×10^{-4} M Bu₄NBr added to reduce the pressure-jump cell resistance.

Table V. Concentration Dependence of the Relaxation Times for Cryptand 2,2,2 in Water at 10 °C

$10^3 C_0,^a$ mol dm ⁻³	$10^3 x,^b$ mol dm ⁻³	γ_{\pm}^2	$10^{-3} \tau^{-1},^c$ s ⁻¹	$10^{-3} \tau^{-1},$ s ⁻¹ (calcd) ^d
9.89	0.787	0.940	6.24	6.33
5.93	0.600	0.947	4.95	4.92
3.95 ^d	0.492	0.913	3.93	3.94
1.98 ^d	0.338	0.916	3.02	2.79
0.989 ^d	0.230	0.918	1.94	1.99
0.593 ^d	0.171	0.920	1.32	1.55

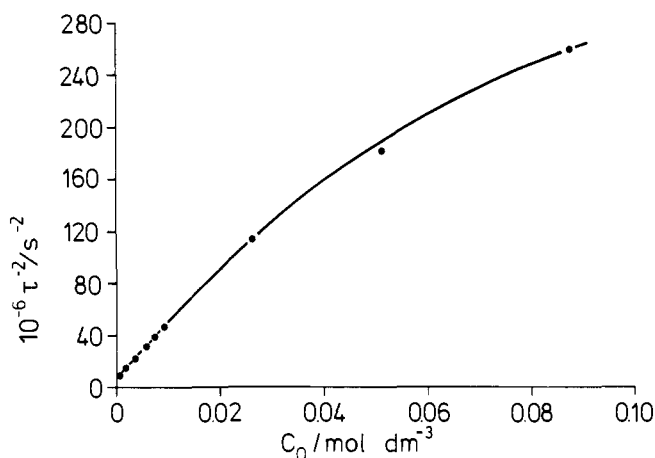
^a Total cryptand concentration. ^b Calculated from eq 4 with $K_b = 6.39 \times 10^{-5}$ mol dm⁻³. ^c Experimental values. ^d Calculated from eq 3 with $k_1 = 2.62 \times 10^2$ s⁻¹, $k_{-1} = 4.10 \times 10^6$ mol⁻¹ dm³ s⁻¹. ^e 1.3×10^{-3} M Bu₄NBr added to reduce the pressure-jump cell resistance.

2,2,2. Relaxation times were measured in the temperature range 5–20 °C for solutions containing only dissolved cryptand. Cryptand concentrations were in the range 5×10^{-4} to 10^{-2} M. The reactions were too fast to allow measurements in buffers containing higher concentrations of the protonated cryptand. The results could be fitted to eq 3 using the measured K_b to calculate $2x\gamma_{\pm}$, as described for cryptand 2,1,1. Again, however, it was not possible to independently determine K_b from the kinetic results alone, because of the very small and uncertain intercepts obtained in plots of the data according to eq 3 or 5. Results at 10 °C are given in Table V, and the combined results at the various temperatures are summarized in Table VI. Detailed results at temperatures of 5.15, 10, 15, and 20 °C are given in the microfilm edition²⁷ (Table 5a).

2,2,2B. The experimental conditions used were essentially the same as for 2,2,2, and the kinetic behavior very similar. The relaxation times could again be fitted to eq 3, with an internally consistent set of k_1 , k_{-1} , and K_b (using measured K_b values). The reactions were studied over the temperature range 0–20 °C. Detailed results at 0 °C are given in Table VII, and the combined results at the various temperatures are summarized in Table VIII. Results at 5, 10, 15, and 20 °C are given in the microfilm edition²⁷ (Table 6a).

Discussion

The systems studied here are potentially rather complex because of the conformational changes, associated with nitrogen inversion, that may occur in both the unprotonated and monoprotated forms. Thus the observed basicity constants refer to a rapidly interconverting mixture of the three unprotonated forms (Scheme I) and the four monoprotated forms (o^+, o, o^+, i, i^+). The magnitude and concentration de-

**Figure 2.** Plot of τ^{-2} vs. stoichiometric concentration of 2,2,1 in aqueous solutions at 10 °C.**Table VI.** Protolysis of Cryptand 2,2,2 in Water (eq 1)

Temp, °C	$10^5 K_b$	$10^{-2} k_1,^a$ s ⁻¹	$10^{-6} k_{-1},^a$ mol ⁻¹ dm ³ s ⁻¹
25	7.32 ^b		
20	7.01 ^c	5.15	7.35
15	6.70 ^c	3.83	5.72
10	6.39 ^c	2.62	4.10
5.15	6.11 ^c	1.93	3.15
1.20	5.87 ^b		

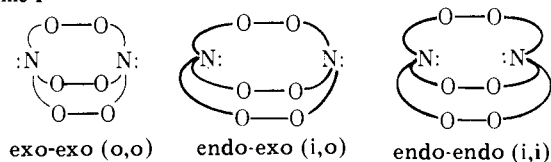
^a Determined using eq 3 (see text). ^b From Table 1. ^c Interpolated from results in Table 1.

Table VII. Concentration Dependence of the Relaxation Times for Cryptand 2,2,2B in Water at 0 °C

$10^3 C_0,^a$ mol dm ⁻³	$10^3 x,^b$ mol dm ⁻³	γ_{\pm}^2	$10^{-3} \tau^{-1},^c$ s ⁻¹	$10^{-3} \tau^{-1},$ s ⁻¹ (calcd) ^d
19.9	0.915	0.936	2.46	2.49
15.9	0.815	0.940	2.18	2.23
13.5	0.749	0.942	2.08	2.06
11.9	0.701	0.944	1.82	1.94
7.96	0.568	0.949	1.65	1.59
5.17	0.452	0.954	1.31	1.28

^a Total ligand concentration. ^b Calculated from eq 4 with $K_b = 4.13 \times 10^{-5}$ mol dm⁻³. ^c Experimental values. ^d Calculated from eq 3 with $k_1 = 59$ s⁻¹ and $k_{-1} = 1.42 \times 10^6$ mol⁻¹ dm³ s⁻¹.

Scheme I



pendence of the observed relaxation times for solutions of the cryptands, however, may be used to distinguish between a number of possible reaction paths and, in addition, to give an indication of the most stable forms of the protonated and free ligands.

It was shown in the Results section that for the cryptands 2,1,1, 2,2,2, and 2,2,2B, the reciprocal relaxation times, τ^{-1} , showed a simple linear dependence upon the concentrations of the hydroxide and CryH⁺ ions. The results are, moreover, quantitatively consistent with the simple equilibria shown in

Table VIII. Protolysis of Cryptand 2,2,2B in Water (eq 1)

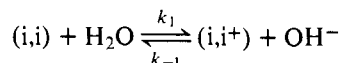
Temp, °C	$10^5 K_b$	$10^{-1} k_1,^a$ s ⁻¹	$10^{-6} k_{-1},^a$ mol ⁻¹ dm ³ s ⁻¹
25	4.86 ^b		
20	4.72 ^c	23.9	5.06
15	4.57 ^c	17.1	3.75
10	4.44 ^c	11.8	2.66
5	4.28 ^c	8.8	2.06
0	4.13 ^b	5.9	1.42

^a Determined using eq 3 (see text). ^b From Table I. ^c Interpolated from results in Table I.

eq 1. The kinetic and activation parameters, at 25 °C, obtained for these three systems are summarized in Table IX.

The most notable features of these results are the relatively slow rates and high activation enthalpies for proton transfer from CryH⁺ to OH⁻, particularly for 2,1,1. These are between three and seven orders of magnitude slower than those observed for recombination reactions between hydroxide ions and protonated aliphatic amines.²¹ Such results effectively rule out any significant participation of exo (o) forms of the free ligand and o⁺ forms of the protonated ligands. The rates are too slow to be attributable to a single relaxation process involving o \rightleftharpoons o⁺, and it can be readily shown that the presence of such equilibria, in rapid equilibrium with slower relaxations involving i \rightleftharpoons i⁺, would lead to a complex nonlinear dependence of τ^{-1} upon the concentrations of OH⁻ and CryH⁺.

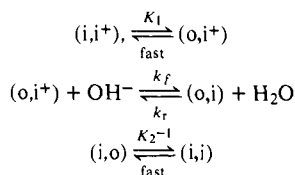
The simplest scheme consistent with the observed results is then that shown in the equation



involving direct transfer of the proton from (i,i⁺) to OH⁻. The relatively slow rate of the proton transfer could arise from the presence of internal H bonds involving the second nitrogen atom. Also in the present system, shielding of the proton by the bridging -CH₂CH₂O- groups may hinder the interaction, either direct or indirect via H bonding, between OH⁻ and the proton. More detailed discussions of factors that may give rise to slow proton transfers from nitrogen have been given by Eigen et al.²¹ and more recently by Kresge.²²

An alternative scheme, involving inversion of the free nitrogen atom prior to proton transfer, is shown in Scheme II.

Scheme II



The usual relaxation treatment applied to Scheme II leads to eq 8-10. If K_1 and K_2 are small (i.e., (i,i) and (i,i⁺) are the predominant forms as discussed above), $m_{i,i^+} = m_{CryH}$, and the equations are also clearly consistent with the observed re-

sults. Such a scheme may be particularly relevant to 2,1,1 (and also 1,1,1¹⁴), which has the smallest cavity within the ligand, and so presumably might be very unreactive in the i,i⁺ form. Depending upon the magnitudes of K_1 and K_2 , this scheme could account for very slow rates of reaction. Again in Scheme II the o,o configuration of the cryptand has been omitted for the reasons stated above.

$$\tau^{-1} = k_1 + k_{-1} (m_{OH^-} + m_{i,i^+}) \quad (8)$$

where

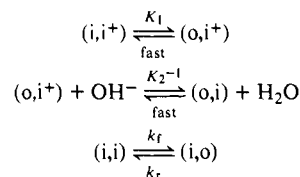
$$k_1 = k_r K_2 / (1 + K_2) \quad (9)$$

and

$$k_{-1} = k_f K_1 / (1 + K_1) \quad (10)$$

The results for 2,2,1, however, could not be fitted to a simple scheme involving a rate-determining proton transfer step. A plot of τ^{-1} against $(m_{OH^-} + m_{CryH})$, for example, is not linear, the values leveling off at higher m_{OH^-} , m_{CryH} . Such behavior is typical of systems in which a rapid protolytic equilibrium precedes a slower rate-determining reaction.²³ This could be accommodated within Scheme II, if the conformational change (i,i) \rightleftharpoons (i,o) were rate determining, as shown in Scheme III.

Scheme III



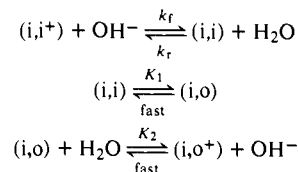
Again, assuming (i,i⁺) and (i,i) to be the predominant forms present, this scheme leads to the equation

$$\tau^{-1} = k_f + \frac{k_r (m_{CryH} + m_{OH^-})}{K_2 / K_1 + (m_{CryH} + m_{OH^-})} \quad (11)$$

The equation predicts that when $(m_{CryH} + m_{OH^-}) \ll K_2 / K_1$, τ^{-1} will be linearly related to $(m_{CryH} + m_{OH^-})$, but approaches a maximum value of $\tau^{-1} = k_f + k_r$ at high $(m_{CryH} + m_{OH^-})$. It is possible to fit the observed results to eq 11 but it is difficult to assess the significance of the values of k_f , k_r , and K_2 / K_1 so obtained, because of the relatively limited range of values of $(m_{CryH} + m_{OH^-})$ for which τ could be measured (see Results section).

Another chemically reasonable possibility is that rapid protolytic equilibria involving o⁺ forms may be involved, as shown, for example, in Scheme IV.

Scheme IV

**Table IX.** Protolysis of Cryptands in H₂O at 25 °C (eq 1)

Cryptand	$10^4 K_b,$ mol dm ⁻³	k_1, s^{-1}	$\Delta H_1^\ddagger,$ kcal mol ⁻¹	$\Delta S_1^\ddagger,$ cal K ⁻¹ mol ⁻¹	$k_{-1},$ mol ⁻¹ dm ³ s ⁻¹	$\Delta H_{-1}^\ddagger,$ kcal mol ⁻¹	$\Delta S_{-1}^\ddagger,$ cal K ⁻¹ mol ⁻¹
2,1,1	14.7	1.59	11.8	-18.2	1.08×10^3	8.4	-16.5
2,2,2	0.732	7.31×10^{2a}	10.6	-9.7	9.98×10^{6a}	9.1	4.1
2,2,2B	0.486	3.29×10^{2a}	10.6	-11.4	6.76×10^{6a}	9.6	4.8

^a Extrapolated from results at lower temperatures (0-20 °C).

This scheme leads to the equation

$$\tau^{-1} = k_r m_{\text{OH}} \left[1 + \frac{(m_{i,i^+})(1 + K_1)}{((m_{i,o^+}) + m_{\text{OH}})(1 + K_1) + K_1 K_2} \right] + \frac{k_r m_{\text{OH}}}{((m_{i,o^+}) + m_{\text{OH}})(1 + K_1) + K_1 K_2} \quad (12)$$

the most obvious feature of which is that it requires τ^{-1} to approach zero as m_{OH^-} approaches zero. This does not appear to be consistent with the observed results. Similar schemes involving two protolytic equilibria also lead to equations that were qualitatively inconsistent with the observed results.

It is perhaps surprising that 2,2,1 should behave differently to the other three cryptands. This could arise in the following manner. Both the 2,1,1 and 2,2,1 cryptands may require inversion of the free nitrogen prior to proton transfer, as shown in Schemes II and III, because of the relatively smaller cavities, leading to stronger internal H bonding, etc. However, the proton transfer from the o,i^+ form of 2,2,1 should be considerably faster than that from 2,1,1. Thus it may be faster than the subsequent conformational change $(i,o) \rightarrow (i,i)$, leading to a more complex dependence of the rate upon $m_{\text{OH}^-} + m_{\text{CryH}}$, as shown in eq 11. Further ring expansion to the 2,2,2 and 2,2,2B may enable direct proton transfer from i,i^+ to OH^- , this again resulting in a simple linear dependence of τ^{-1} upon m_{OH^-} and m_{CryH} .

A more detailed discussion of the results would require additional information about the conformational equilibria of the ligands, such as that available for the macrobicyclic ammonium ions from the NMR studies of Park, Simmons, and co-workers.²⁴ Solvent deuterium isotope effects might also provide additional information on the nature of the rate-determining step for the various ligands. The use of ultrasonic absorption techniques has also provided evidence for rapid conformational changes in biofunctional macrocyclic ligands²⁵ and crown ethers,²⁶ occurring prior to complex formation with

metal ions, and such studies on cryptands may also prove fruitful.

Supplementary Material Available: Tables of the protolysis of cryptands 2,1,1, 2,2,1, 2,2,2, and 2,2,2B in aqueous solution (4 pages). Ordering information is given on any current masthead page.

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A Study of the Vinyl Anion System. Rearrangements and Formation from H^- and Acetylene

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Abstract: As a model for nucleophilic attack on acetylenes, the formation of the vinyl anion C_2H_3^- and its rearrangements have been studied with ab initio molecular wave functions. The calculations used an extended basis set of 31 contracted Gaussian functions. The vinyl anion equilibrium structure, rearrangement transition state structures, and the $\text{H}^- + \text{HC}\equiv\text{CH}$ minimum energy reaction path were determined using the energies obtained from one-configuration self-consistent field wave functions. The relative energetics were also analyzed using well-correlated wave functions calculated from a self-consistent electron pairs (SCEP) method. Unlike the vinyl cation, the rearrangement barriers are high in energy, the lowest being 40 kcal. The activation energy of the $\text{H}^- + \text{HC}\equiv\text{CH}$ reaction is found to be 16 kcal, and the stability of the vinyl anion relative to acetylene and H^- is 26 kcal. Correlation effects are important in the reaction energetics and the minimum potential energy reaction surface indicates that the vinyl anion is formed by attachment of H^- to the first carbon it encounters.

Introduction

In recent years, many chemists have explained chemical reactivity within the paradigm of frontier molecular orbitals,

as suggested by Fukui and others.² One aspect of the frontier-orbital method which is often neglected is the direction of approach that reactants must assume, as dictated by the three-dimensional shapes of the most strongly interacting or-