References and Notes

(1) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).
(2) G. Richards, *Int. J. Mass Spec. Ion Phys.* **2**, 149 (1969).
(3) The topic of Koopmans' theorem breakdown in small molecules has received attention from several authors. See M. Okuda and N. Jonathan, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 19 (1974); A. Potts and T. Williams, *ibid.*, **3**, 3 (1974); L. Cedarbaum, *Chem. Phys. Lett.*, **25**, 562 (1974); L. Cedarbaum, *J. Phys. B*, **8**, 290 (1975); L. Cedarbaum, W. Doncke, and W. von Niessen, *Chem. Phys. Lett.*, **34**, 60 (1975); M. Morrell, R. Parr, and M. Levy, *J. Chem. Phys.*, **62**, 549 (1975); R. DeKock, *Chem. Phys. Lett.*, **27**, 297 (1974); T. Chen, W. Smith, and J. Simons, *ibid.*, **26**, 296 (1974), and references therein.
(4) T. Koenig, R. Wielesek, W. Snell, and T. Balle, *J. Am. Chem. Soc.*, **97**, 3225 (1975).
(5) J. Pearson, H. Six, D. Williams, and M. Levy, *J. Am. Chem. Soc.*, **93**, 5034 (1971).
(6) D. Longone and H. Chow, *J. Am. Chem. Soc.*, **92**, 994 (1970).
(7) W. Simpson and C. W. Looney, *J. Am. Chem. Soc.*, **76**, 6285, 6793 (1954).
(8) T. Koenig and H. Longmaid, *J. Org. Chem.*, **39**, 560 (1974); R. Wielesek and T. Koenig, *Tetrahedron Lett.*, 2429 (1974).
(9) J. A. Pople, D. Beveridge, and P. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
(10) The overlap between bands makes accurate area ratios impossible to determine. The ratio of areas of the first three bands is crudely estimated as 1:0.85:0.50.
(11) Michl and co-workers have given the CI coefficients for these two a_{1g} configurations as 0.88 and 0.36. C. Flynn and J. Michl, *J. Am. Chem. Soc.*, **96**, 3280 (1974). See ref 13.
(12) Configuration interaction as it applies to the excited states of doublets is discussed by Salem, "Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, Reading, Mass., 1966, pp 435–443.
(13) The published wave function of Michl[11] gives an unrealistically large contribution from $\Psi(1b_{3u}{}^2 1b_{2g}{}^2 1b_{1g}{}^2 2b_{2g}{}^2)$ to the closed shell ground state because of the assumption of benzene ring geometry. His wave function implies $\Psi_{2B_{2g}} \simeq 0.32\chi_{m-2,m} - 0.95\chi_{m,m+1}$ assuming positive interaction constants in the CI matrix.[14]
(14) Professor Michl has informed us of the results of a new CI treatment of **1** using polyene geometry. This wave function and the approximate intensity ratio found here gives $\Psi_{2B_{2g}} \simeq 0.55\chi_{m-2,m} - 0.84\chi_{m,m+1}$. The change in the wave functions with geometry is in the expected direction although the estimated character of $\chi_{m,m+1}$ suggests it may have a lower configurational energy than that of (Koopmans' theorem configuration) $\chi_{m-2,m}$.
(15) National Science Foundation Undergraduate Research Participant, 1975.

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The Acid Catalyzed Dissociation of Metal Cryptate Complexes

Sir:

The ability of synthetic macrobicyclic ligands, such as those of the type **1–3** (cryptands) described by Lehn and co-workers,[1] to form stable complexes with alkali and alkaline earth cations has resulted in many studies of their chemical properties. However, although a considerable amount of thermodynamic data on the metal complexes (cryptates) exists,[2-4] very few kinetic data are available, despite the potential information on the mechanism of complex formation that could come from such studies. This presumably results, at least in part, from the lack of significant visible or ultraviolet (>250 nm) spectral changes associated with complex formation, and also from the difficulty of avoiding effects from competitive protonation of
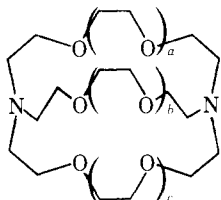
1, $a = 1$; $b = c = 0$ (2,1,1)
2, $a = b = 1$; $c = 0$ (2,2,1)
3, $a = b = c = 1$ (2,2,2)

Table I. Reaction of HCl with K(2,2,2)$^+$ Cryptate.

$T/°C$	$10^3[2,2,2]/$ mol dm^{-3}	$10^3[KNO_3]/$ mol dm^{-3}	$10^3[HCl]/$ mol dm^{-3}	k_e/s^{-1} ^{a}
10.0	0.109	1.06	2.40	1.2$_7$
10.0	0.0272	0.265	0.47	1.2$_4$
17.9	0.109	1.06	2.40	3.2$_8$
17.9	0.109	1.06	1.15	3.1$_6$
17.9	0.109	2.12	1.15	3.1$_3$
17.9	0.109	0.53	1.15	3.1$_7$
17.9	0.109	4.24	1.15	3.1$_6$
17.9	0.0272	0.265	0.60	3.2$_9$
17.9	0.0272	0.265	0.29	3.3$_1$
24.5	0.109	1.06	2.40	7.1$_6$
24.5	0.0272	0.265	0.60	7.2$_1$
30.4	0.109	1.06	2.40	15.$_0$
30.4	0.0272	0.265	0.60	16.$_0$

^{a} Each value represents an average of at least three determinations. k_e values ±4%.

the strongly basic nitrogen centers. With the exception of a stopped flow study of the kinetics of formation of Ca cryptates,[5] existing rate data have come from NMR line broadening techniques,[6-8] and in the most comprehensive study,[6] are limited to measurements on (2,2,2) cryptates at the coalescence temperature.

We wish to report results of a method of apparent general applicability to the measurement of dissociation rates of metal cryptates in aqueous solution, involving the observation of conductance changes following the addition of excess acid to the cryptates. We have also found in the course of these studies, that in many cases the dissociation rates are *acid catalyzed*, and the significance of this is discussed.

When excess acid is added to a solution containing a metal cryptate (MCry^{n+}), the overall reaction is as shown in eq 1.

$$MCry^{n+} + 2H^+ \xrightarrow{k_e} CryH_2{}^{2+} + M^{n+} \qquad (1)$$

However, if the reaction proceeds via the free cryptand, as in eq 2 and 3,[9]

$$MCry^{n+} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} M^{n+} + Cry \qquad (2)$$

$$Cry + H^+ \xrightarrow{k} CryH^+ \qquad (3)$$
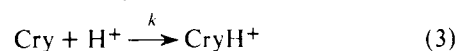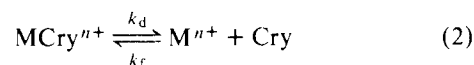
it can be readily shown that, provided the rate of protonation of the cryptand is significantly greater than the rate of formation of the metal cryptate, the observed rate law is given by eq 4;

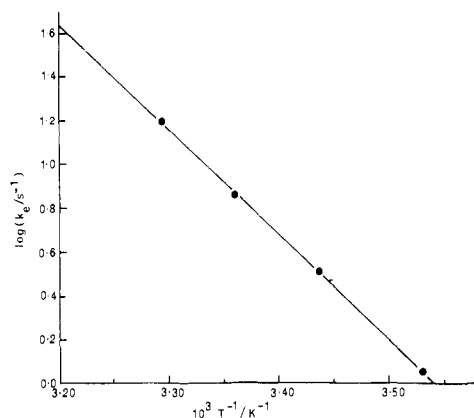$$-d\frac{[MCry^{n+}]}{dt} = k_d[MCry^{n+}] \qquad (4)$$

i.e., the observed rate constant corresponds to the rate constant for the dissociation of the cryptate. Under these conditions, the observed rate constant should be independent of both the acid and metal ion concentrations. The reactions can be conveniently followed by observing the rate of change of conductance (the observed decrease in conductance resulting primarily from the loss of H$^+$) either using conventional techniques for slow reactions, or stopped-flow with conductance detection for rapid reactions. Any competitive protonation of the cryptand prior to the addition of the acid used to initiate the reaction has no effect on the observed kinetics (other than to reduce the amplitude of the conductance change occurring during the reaction). The formation rates can of course be readily obtained from the dissociation rates via the stability constants.

Table I lists results obtained for the K$^+$,(2,2,2) system at various temperatures, using the stopped flow technique to

Table II. Kinetics of Complex Formation between Metal Ions and Cryptands at 25 °C

Ligand	Cation	Log K_s[a]	k_d/s^{-1}	$k_f/M^{-1} s^{-1}$ [b]	$k_{H^+}/M^{-1} s^{-1}$ [c]	k_{H^+}/k_d
2,1,1	Li$^+$	5.5	0.025[d]	8 × 10^3	21.0	850
2,1,1	Ca^{2+}	2.50	0.820[e]	2.6 × 10^2	0[f]	0[f]
2,2,1	Na$^+$	5.40	14.5	3.6 × 10^6	180	12.4
2,2,1	Ag$^+$	—	0.000 450		2.12	4700
2,2,1	Ca^{2+}	6.95	0.000 660[g]	5.9 × 10^3	0.0195	29.6
2,2,1	Sr^{2+}	7.35	0.001 47	3.3 × 10^4	0[f]	0[f]
2,2,1	Ba^{2+}	6.30	0.061 0	1.22 × 10^5	0[f]	0[f]
2,2,2	K$^+$	5.4	7.5[h]	2.0 × 10^6	0[i]	0[i]
2,2,2	Ca^{2+}	4.4	0.21[j]	5.5 × 10^3	550	2600
2,2,2	Sr^{2+}	8.0	0.000 075[k]	7.5 × 10^3	0.0213	284
2,2,2	Ba^{2+}	9.5	0.000 0175[l]	5.5 × 10^4	0.0014	80

[a] Stability constants $K_s = k_f/k_d$ from ref 2. [b] k_f obtained from $k_f = k_d K_s$. [c] Catalytic constants for acid catalyzed dissociation of complexes (eq 5). Values refer to infinite dilution in water. [d] Reference 7 gives k_d = 0.005 s^{-1} (see text). [e] Cf. k_d = 0.66 s^{-1}. ref 5b. [f] Independent of acid concentration up to 2 × 10^{-2} M. [g] Cf. k_d = 0.0025 s^{-1}, ref 5b. [h] Value at 36 °C, 29.6 s^{-1}; cf. value of 38 s^{-1} from ref 6. [i] Independent of acid concentration up to 2.5 × 10^{-3} M. [j] Cf. k_d = 0.26 s^{-1}, ref 5. [k] Cf. k_d ca. 10^{-4} s^{-1}, ref 6; k_d = 9.7 × 10^{-5} s^{-1}, ref 5b; cf. k_d ca. 10^{-5} s^{-1}, ref 6; k_d = 1.3 × 10^{-5} s^{-1}. ref 5b.

Figure 1. Temperature dependence of the rate of dissociation of K(2,2,2)$^+$ in H$_2$O.

Figure 2. Reaction between Ca(2,2,2)$^{2+}$ and HCl in H$_2$O at 25 °C. Rate constants corrected to zero ionic strength.

follow the reaction. It can be seen that the observed rate constants (k_e) are independent of the concentrations of both H$^+$ and K$^+$ over the range studied.
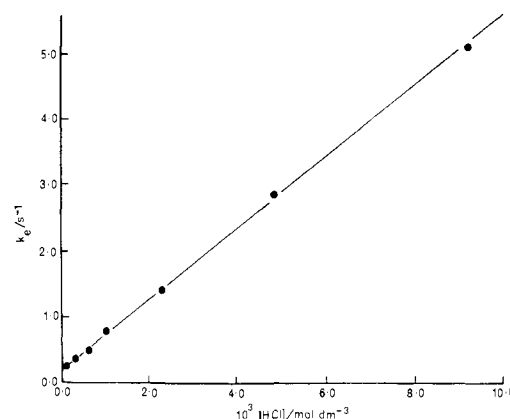
Figure 1 shows a plot of log k_e against $1/T$ (K^{-1}). Extrapolation of this plot to 309.2 K (36 °C) gives a value of k_e = 29.6 s^{-1}. This agrees satisfactorily with the value of 38 s^{-1} at 36 (±4) °C obtained by Lehn, Sauvage, and Dietrich[6] from NMR line broadening measurements, considering the uncertainty in the coalescence temperature obtained in the NMR study.

Similar measurements have been performed on a number of other systems involving the three cryptands shown above, and in all cases k_e was found to be independent of [M^{n+}]. However, in a number of systems, the rate was found to be strongly dependent upon the acid concentration, k_e having the form given in eq 5.

$$k_e = k_d + k_{H^+}[H^+] \qquad (5)$$

An example of such behavior is shown in Figure 2 where the observed rate constant for the Ca^{2+},(2,2,2) system is plotted against the acid concentration. The value of k_d (the value of k_e at zero acid concentration) = 0.21 s^{-1} may be compared with a previously quoted value[5] for the rate constant for the dissociation of Ca(2,2,2)$^{2+}$, k_d = 0.26 s^{-1}.

The results obtained to date for various cryptates at 25 °C are given in Table II. Where comparison is possible, agreement with earlier values is generally good, with the exception of the Li$^+$(2,1,1)[7] and the Ca^{2+}(2,1,1) and (2,2,1) systems.[5] The discrepancy in the Li$^+$(2,1,1) system is not surprising as the
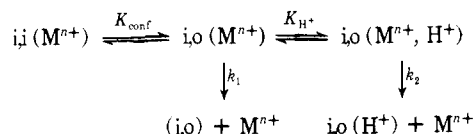
earlier value comes from the extrapolation of results from ^{7}Li NMR measurements at temperatures over 85 °C, assuming that the activation energy (21 kcal mol^{-1}) is constant over the range to 25 °C. Results obtained in the present study at temperatures between 0 and 25 °C suggest a significantly lower activation energy ($\sim$17 kcal mol^{-1}) in this region. This could readily explain the difference between the two values. We have no explanation for the differences found for Ca^{2+} with 2,1,1 and 2,2,1 cryptands. It has been previously noted[4,5] that thermodynamic properties obtained from the kinetic results[5] for the Ca^{2+},(2,1,1) and (2,2,1) differ considerably from those obtained from calorimetric studies.[3,4]

The observation of acid catalysis in the dissociation reaction may provide an important clue to the understanding of the mechanism of the dissociation reaction. The cryptates exist as an equilibrium mixture of three conformations:[6] o,o (out,out), o,i (out,in), and i,i (in,in), as shown below for the 2,2,2 complex. The i,i complex should be the most stable thermody-

o,o (M^{n+})   i,o (M^{n+})   i,i (M^{n+})
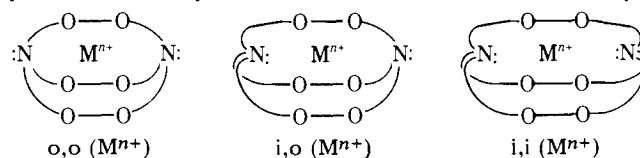
namically, and in fact, in the solid state complexes have been shown to have this conformation.[10] It is, however, difficult to see how direct dissociation from the i,i conformation could be acid catalyzed. A more reasonable mechanism is one in which

there is a preceding conformational change to give the i,o complex (or the o,o) which leaves one of the lone pairs on nitrogen free to be trapped by H^+.

$$\text{i,i} (M^{n+}) \xrightleftharpoons[\quad]{K_{conf}} \text{i,o} (M^{n+}) \xrightleftharpoons[\quad]{K_{H^+}} \text{i,o} (M^{n+}, H^+)$$

$$\downarrow k_1 \qquad\qquad \downarrow k_2$$

$$(\text{i,o}) + M^{n+} \qquad \text{i,o} (H^+) + M^{n+}$$

A possible kinetic scheme for the dissociation reaction is shown below. The scheme as written assumes that the slow steps in the process are the dissociation of the metal from the protonated and free i,o cryptates in the catalyzed and uncatalyzed paths, respectively. Under these conditions, the rate constant for the uncatalyzed dissociation would equal $k_1 K_{conf}$, which would explain the slow dissociation rates observed for the cryptates if K_{conf} is small, i.e., i,i is the dominant conformation at equilibrium. There are, however, a number of other possibilities within the same general kinetic scheme. For example, the slow step in the acid catalyzed pathway could be the protonation of the cryptate (followed by rapid dissociation of the protonated cryptate).

A further point of interest in the present results concerns the relative magnitudes of the catalyzed and uncatalyzed rates and, in particular, the fact that some of the dissociation rates are apparently independent of the acid concentration. Such a result would be obtained if the conformational change i,i (M^{n+}) to i,o (M^{n+}) were rate determining—the acid could then only affect the rates of steps subsequent to the rate determining step. A rate determining conformational change has previously been suggested to account for the observed kinetic behavior in the Ca^{2+} antamanide system.[11] Further discussion of this point will be deferred until a more systematic study of cryptates is completed. It is, however, noticeable that within the alkaline earth series, the ratio k_{H^+}/k_d increases considerably as the cryptand varies from 2,1,1 to 2,2,1 and 2,2,2, and is not smallest for the most stable cryptate, or the one having the lowest dissociation rate.

A final account of this work will include, in addition to results at 25 °C for a wider range of cryptates, activation parameters for the dissociation rates, to be combined with currently available enthalpies and entropies of reaction.[3,4]

References and Notes

(1) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973).
(2) J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975).
(3) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
(4) E. Kauffman, J. M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, **59**, 1099 (1976).
(5) (a) V. M. Loyola, R. G. Wilkins, and R. Pizer, *J. Am. Chem. Soc.*, **97**, 7382 (1975); (b) R. G. Wilkins, private communication.
(6) J. M. Lehn, J. P. Sauvage, and B. Dietrich, *J. Am. Chem. Soc.*, **92**, 2916 (1970).
(7) Y. M. Cohen, J. L. Dye, and A. I. Popov, *J. Phys. Chem.*, **79**, 1292 (1975).
(8) J. M. Ceraso and J. L. Dye, *J. Am. Chem. Soc.*, **95**, 4432 (1973).
(9) The cryptand is then further protonated to give $CryH_2^{2+}$. This latter step may be studied in the absence of metal ions, and has been found to be faster than all reactions reported here involving the cryptate complexes.
(10) B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 217 (1970); *Acta Crystallogr., Sect. B*, **29**, 388 (1973).
(11) W. Burgermeister, T. Wieland, and R. Winkler, *Eur. J. Biochem.*, **44**, 305 (1974).
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Macrocyclic Schiff Base Complexes Bearing Photoactive Substituent Groups. 1. The Azo Linkage

Sir:

It has long been recognized that certain organic molecules which undergo photoisomerization reactions exhibit a form of photoenergy conversion and storage.[1] In these systems a photoreaction is responsible for converting the most stable form of the compound into a thermodynamically unstable isomer. Since the isomerization of the higher energy isomer back to the more stable form is exothermic, the system has the effect of converting light energy into heat energy.

Numerous organic compounds undergo photoisomerization reactions. Azo compounds, various stilbenes, and acyclic Schiff bases and their analogues are subject to a photoisomerization about a double bond.[2] Since the separation is energy between the more stable trans and the less stable cis form is small for these compounds (3-5 kcal/mol) the energy storage capacity of the system is modest. On the other hand, for organic molecules which exhibit a photodriven bond isomerization reaction, e.g., norbornadiene and anthracene, the storage capacity can be high (~30 kcal/mol).[3] Solar energy storage systems involving bond isomerization reactions are currently being investigated as practical sources of "low grade" heat.[3,4]

Certain metalloporphyrin compounds have been successfully used as sensitizers for photoisomerization reactions.[5] However, the ability of structurally related macrocyclic Schiff base complexes to assist in photoenergy transfer and storage phenomena has not been explored. In an effort to examine the usefulness of these cyclic structures in a photoenergy storage cycle we have synthesized the macrocyclic ligand **1**, from the parent Schiff base **2**. We have found that the nickel complex

1, R₁ = H; R₂ =
2, R₁ = R₂ = H
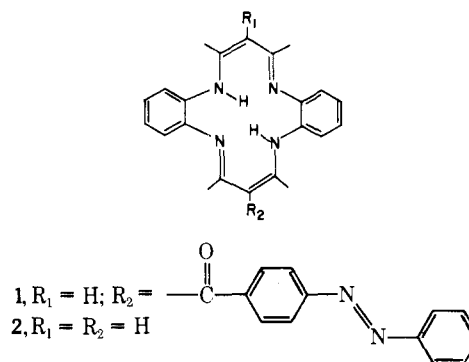
of **1**, Ni(II)-**1**, undergoes a photoisomerization about the azo linkage to give the less stable cis azo isomer. We have further demonstrated that the photogenerated cis isomer is capable of bonding to a second metallomacrocyclic complex and in so doing is catalytically reisomerized to the trans form (Scheme I). Since the reisomerization is accompanied by the release of heat, the system has the effect of converting photoenergy into heat energy.

Scheme I