Kinetic Studies on Conformational Change of Cryptand 221 and Formation of Copper(II) Cryptate 221 in Dimethyl Sulfoxide, *N,N*-Dimethylformamide, and Acetonitrile

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Abstract: Ultrasonic absorption spectra of cryptand 221 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane) have been measured over the frequency range from 5 to 290 MHz at various concentrations and temperatures in dimethyl sulfoxide, *N,N*-dimethylformamide, and acetonitrile. A single relaxation process has been observed and interpreted by the conformational equilibrium between two configurations of the cryptand: (i,o) $\rightleftharpoons$ (i,i), where (i,o) is the isomer with the lone electron pairs of the two nitrogens residing one inside and one outside with respect to the molecular cavity and (i,i) is the isomer with both lone electron pairs residing inside. Thermodynamic and kinetic parameters for the conformational change are estimated. (i,i) is the dominant conformation in the solvent under investigation. We have also studied the kinetics of the complexation of copper(II) ion with 221 and the dissociation of the copper(II) cryptate in the three solvents by the high-pressure stopped-flow technique. Rate constants and activation parameters for complexation are obtained. The complexation process of the cryptand is interpreted by the Eigen–Winkler mechanism, where both the desolvation of the metal ion and the rearrangement of the cryptand for encirclement of the metal ion may play a role in the activation process. The fact that the activation volumes for formation of the cryptate are almost 0 cm^3 mol^{-1} (−1.6 ± 1.5 cm^3 mol^{-1} in Me$_2$SO and −0.4 ± 0.6 cm^3 mol^{-1} in DMF) supports the proposed mechanism.

Introduction

Understanding the interactions between macrocyclic ligands and metal ions requires the study of structural and mechanistic factors governing the reactions. Of particular interest are the kinetic origins of the selectivity of the macrocyclic ligands and also the mechanisms by which the solvent molecules associated with the metal ions are substituted through complexation. Extensive thermodynamic and kinetic data have already been collected concerning interactions between macrocyclic ligands and cations, especially alkali and alkaline-earth metal ions.[1] The formation rates of cryptates of alkali and alkaline-earth metal cations have generally been estimated by combining observed rates of the corresponding dissociation with independently measured stability constants because the reaction is too fast to be followed directly.[2-9] On the other hand, much less is known about cryptate complexes of transition-metal and heavy-metal cations, especially their kinetic properties. Moreover, there are scarce data for formation rates measured directly.[10-13]

Two main mechanisms for complexation of a macrocyclic ligand C have been proposed: The first is the so-called Chock mechanism,[14] envisaging a rapid conformational change of C followed by the reaction of one of the conformers of C with the cation. The rate-determining step is the complexation step, isomeric transformation of the ligand being relatively fast. The second is the so-called Eigen–Winkler mechanism,[15] which assumes the formation of the encounter complex, followed by a desolvation–ligand rearrangement step to form the final product. In this mechanism, the rate-determining step results from superposition of the desolvation of the metal ion and the rearrangement of the ligand. Some available data were at least qualitatively amenable to interpretation by both mechanisms.[16a] One of our purposes in this work is to throw more light on the mechanistic aspect concerning complex formation of macrocyclic ligands.

Ultrasonic absorption data for cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) in several solvents have already been interpreted by the conformational changes involving three conformations of 222;[16b,17] i.e., each bridgehead may be turned either inward or outward with respect to the molecular cavity, leading to the three forms endo–endo (i,i), endo–exo (i,o), and exo–exo (o,o).[18] It has been concluded that the isomeric rearrangement of the cryptand does not appear to be the rate-determining step for the complexation reaction.[16b] In this work, we selected cryptand 221 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane) and copper(II) ion. Since the (o,o) conformer of 221 does not seem to exist judging from the CPK model, the situation in the case of 221 would be simpler in comparison with that of 222. Copper(II) ion was chosen as one of the transition-metal ions because its solvent exchange is known to be very fast.[19-22] Furthermore, the interaction of copper(II) ion with the donor nitrogen atom in amines is expected to cause the change in visible absorption spectra. Dimethyl sulfoxide (Me$_2$SO), *N,N*-dimethylformamide (DMF), and acetonitrile as aprotic solvents were used because of their very different basicities.[23]

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First, we have investigated the kinetics of conformational changes of cryptand 221 in Me_2SO, DMF, and CH_3CN by using the ultrasonic absorption method. Second, we have followed the formation of copper(II) cryptate 221 by using a high-pressure stopped-flow apparatus with spectrophotometric detection. The mechanism of complexation of cryptand 221 has been proposed on the basis of activation parameters. This seems to be the first report on the high-pressure study on the formation of cryptates, although a report on the dissociation of cryptates at high pressure is available.[24]

Experimental Section

Materials. Cryptand 221, purchased from Merck (Kryptofix 221), was used without further purification. Solvents such as Me_2SO, DMF, and CH_3CN were dried and purified by the previously described methods.[25,26] The water content of the solvents, determined by the Karl-Fischer method, was less than 5×10^{-3} mol dm^{-3}. Solvated copper(II) perchlorates $[Cu(Me_2SO)_4](ClO_4)_2$, $[Cu(DMF)_4](ClO_4)_2$, and $[Cu(C-H_3CN)_4](ClO_4)_2$ were prepared by the similar reference method.[27,28] Elemental analysis for Cu, N, C, and H with agreement to within 0.3% supported the composition having four solvent molecules. Dichloroacetic acid (DCA or Hdca) was purified by vacuum distillation. Triethylamine (Et_3N; Wakojunyaku, Osaka) was distilled twice after each reflux over potassium hydroxide and sodium wire. Triethylenediamine (TEDA = 1,4-diazabicyclo[2.2.2]octane; Wakojunyaku) was recrystallized from acetone and then purified by sublimation. Solvents and solutions were prepared fresh and used within 24 h after preparation. Sample solutions were prepared in a drybox with dry nitrogen gas flow.
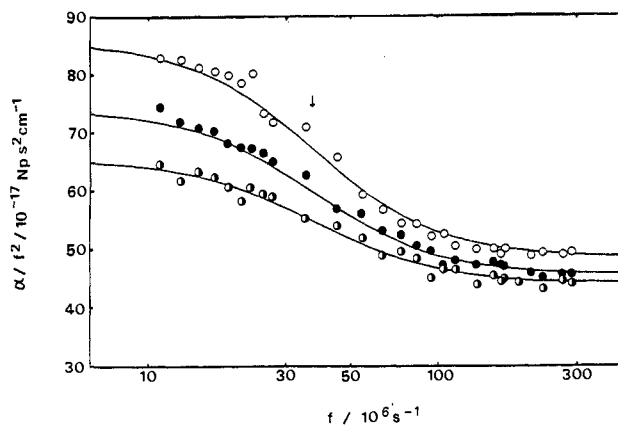
Measurements. Three different concentrations of 221 ranging from 0.1 to 0.2 mol kg^{-1} were supplied for the measurement of the sound absorption. Measurements of sound absorption by an ultrasonic pulse method have been carried out on an ultrasonic apparatus, which consists of a pulse modulator/receiver (Model 6600; Matec Corp., R1), an absorption cell, an attenuation recorder, and a synchroscope. The pulse modulator/receiver is equipped with a Matec 756-, 760-, or 765-V rf plug-in unit. The measurable frequency range is from 5 to 290 MHz.

Three different absorption cells were constructed in this work. One for the frequency range of 5–27 MHz is of a single-crystal-reflector type with a 3-cm-diameter cross-cut quartz crystal of 1-MHz fundamental frequency. The maximum path length of this cell is ca. 60 cm. Additional cells for 25–165 and 170–290 MHz as the frequency range are of the two-crystal type (i.e., sender/receiver type) having two cross-cut quartz crystals of fundamental frequencies 5 and 10 MHz, respectively. The sender of a 5-MHz cell consists of a 2-cm-diameter cross-cut quartz crystal, and the corresponding receiver is a 2-cm-diameter cross-cut quartz crystal bonded to a 2-in.-long fused-quartz delay rod. In the 10-MHz cell, two transducers were made up of cross-cut quartz crystals with a 2-cm diameter bonded to a 1-in.-long fused-quartz delay rod for the sender and a 2-in.-long delay rod for the receiver. The crystal used in the 1-MHz cell supplied by Kinseki Corp. (Tokyo) and the crystals used in the sender/receiver-type cells supplied by Valpey-Fisher Corp. (MA) were frequency-matched within 0.5%. They were polished flat and parallel for overtone operation. The attenuation of the ultrasonic signal was measured with a Matec Model 2470A attenuation recorder. Echoes were displayed on a synchroscope (Model SS-5321; Iwatsu Electric Corp., Tokyo).
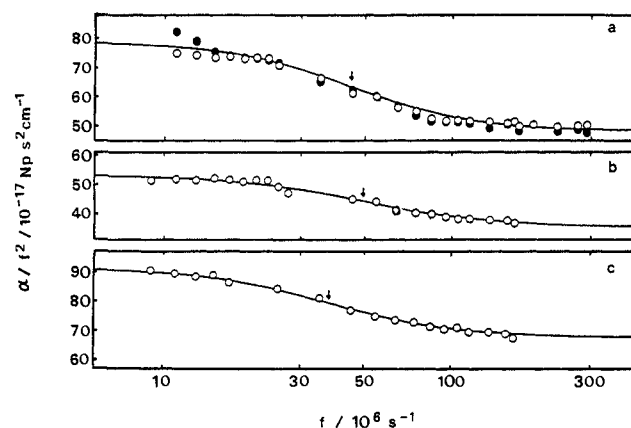
The ultrasonic absorption of 221 in three different solvents, Me_2SO, DMF, and CH_3CN, was measured for at least 15 distance settings between the transducers or the transducer and reflector as varied by a micrometer. The slope of loss of the sound intensity vs the distance was converted to an α/f^2 value. Absorption values at lower frequencies were corrected for diffraction loss. The absorption cells were thermostated to within ±0.05 °C over the temperature range 15–35 °C.

The sound velocities in each solvent at various temperatures were measured by means of the ultrasonic interferometer constructed in this work.

A stopped-flow technique with spectrophotometric detection was used for the kinetic measurements for the formation of copper(II) cryptate

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Figure 1. α/f^2 vs f, where α and f are the absorption coefficient and frequency, respectively. Ultrasonic absorption of 221 in Me_2SO at 20.0 °C and at the different concentrations of 221: 0.171 mol dm^{-3} (O), 0.136 mol dm^{-3} (●), and 0.102 mol dm^{-3} (◑). The solid curves were depicted with use of the finally obtained values given in Table III. The arrow indicates the relaxation frequency (f_r).

Figure 2. α/f^2 vs f, where α and f are the absorption coefficient and frequency, respectively. Ultrasonic absorption of 221 at 25.0 °C in the different solvents. Key: a, in Me_2SO at $C_{221} = 0.102$ mol dm^{-3}; b, in DMF at $C_{221} = 0.098$ mol dm^{-3}; c, in CH_3CN at $C_{221} = 0.096$ mol dm^{-3}. Filled circles in (a) correspond to data for the solution in the presence of 0.85 mol dm^{-3} water.

221, started by mixing a copper(II) solution and a 221 solution, and for the dissociation in Me_2SO, started by mixing a cryptate 221 solution and a dichloroacetic acid solution. In the kinetic experiments for the formation and dissociation of copper(II) cryptate 221, the total concentrations of copper(II), 221, and DCA were as follows: $C_{Cu} = 5 \times 10^{-4}$–5 $\times 10^{-3}$ mol kg^{-1}, $C_{221} = 2.3 \times 10^{-3}$–1.5 $\times 10^{-1}$ mol kg^{-1}, and $C_{DCA} = 1.7 \times 10^{-2}$–0.1 mol kg^{-1}. We used a stopped-flow spectrophotometer (Type RA 1100; Union Giken Co., Osaka) at atmospheric pressure and a high-pressure stopped-flow apparatus (Type FIT-3)[29] under high pressures up to 200 MPa. The molar absorption coefficient of the $Cu(221)^{2+}$ cryptate is 115 dm^3 mol^{-1} cm^{-1} at the maximum wavelength of 835 nm. Knowing of the visible spectra of the copper(II) complexes with 221, Et_3N, and TEDA, we followed the change in absorbance during the formation process of the $Cu(II)$ complexes by means of stopped-flow technique. The conditional first-order rate constant k_0 was evaluated by the nonlinear least-squares fitting to time–absorbance reaction curves.

Results

(I) Kinetics of Conformational Change of Cryptand 221. The absorption coefficient α in units of sound intensity absorbed per unit length was measured as a function of frequency f at various concentrations of 221 in Me_2SO, DMF, and CH_3CN and at various temperatures (all data of α/f^2 as functions of f summarized in Table SI in the supplementary material). Some typical data in each solvent are shown in Figures 1 and 2. The dependency of α on f shows the characteristic behavior due to a single re-

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Table I. Ultrasonic Relaxation Parameters for 221 in Me_2SO, DMF, and CH_3CN

T (°C)	C_{221} (mol dm^{-3})	A^a (10^{-17} Np s^2 cm^{-1})	B^a (10^{-17} Np s^2 cm^{-1})	f_r^a (10^6 s^{-1})
		In Me_2SO		
20.0	0.102	22 $(22)^b$	44	41 $(37)^b$
	0.136	30 (30)	45	40 (37)
	0.171	39 (38)	48	39 (37)
25.0	0.102	18 (19)	42	51 (45)
	0.136	24 (25)	45	42 (45)
	0.171	29 (31)	49	40 (45)
35.0	0.102	11 (13)	41	84 (64)
	0.136	18 (17)	41	62 (64)
	0.171	24 (22)	43	55 (64)
		In DMF		
15.0	0.098	21 (21)	32	31 (34)
	0.131	26 (28)	33	49 (34)
	0.175	32 (37)	39	36 (34)
25.0	0.098	14 (13)	35	40 (49)
	0.131	18 (17)	36	54 (49)
	0.175	22 (22)	38	38 (49)
35.0	0.098	9 (8)	38	48 (69)
	0.131	10 (10)	38	56 (69)
	0.175	15 (14)	40	44 (69)
		In CH_3CN		
15.0	0.096	24 (23)	68	38 (37)
	0.128	32 (31)	69	42 (37)
	0.170	37 (41)	71	42 (37)
25.0	0.096	19 (14)	70	45 (54)
	0.128	21 (19)	70	47 (54)
	0.170	28 (25)	71	51 (54)
35.0	0.096	10 (9)	71	55 (79)
	0.128	12 (12)	71	51 (79)
	0.170	16 (16)	70	67 (79)

^{a} A, B, and f_r are the relaxation amplitude, the background absorption, and the relaxation frequency, respectively, and the relation is given by eq 1. Values for A, B, and f_r have ca. 10% deviation. ^{b} Numerical values in parentheses calculated with use of the finally obtained values given in Table III.

laxation process. The absorption due to a single relaxation is given by eq 1, where f_r, A, and B refer to the relaxation frequency, the

$$\alpha/f^2 = A/(1 + (f/f_r)^2) + B \qquad (1)$$

relaxation amplitude, and the background absorption, respectively.[30,31] In Table I are summarized the ultrasonic parameters of A, B, and f_r determined by the best fit of the experimental data for a certain concentration of 221 in each solvent at a given temperature. As seen from Table I, for three different concentrations of 221 at a given temperature the relaxation amplitudes are proportional to the total concentration of 221 (C_{221}), while the relaxation frequencies and background absorptions are roughly independent of the concentration of 221 within experimental error. There is the possibility of the single relaxation due to a reaction between the cryptand and the large amounts of solvent. The size of solvent is so large that the solvent should not be accommodated in the cavity of the cryptand, and furthermore there is no remarkable difference in the rate and parameters for the relaxation in the three solvents (vide infra) although the basicity is very different.[23] It is therefore concluded that the observed processes do not correspond to a solute–solvent interaction but rather to a molecular property of the cryptand. These findings suggest that the unimolecular transformation of 221 is the source of the relaxation phenomenon that may be described as the conformational change (2), where C_1 is the cryptand with conformation 1 and

$$C_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2 \qquad (2)$$

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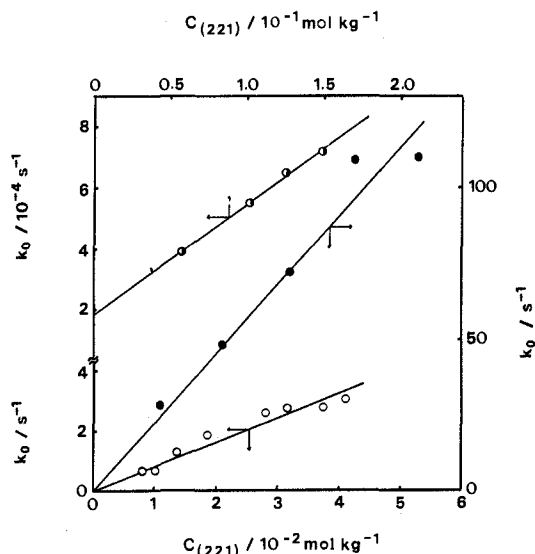
Figure 3. Dependence of the conditional first-order rate constant k_0 for formation of the copper(II) cryptate 221 on the concentration of 221 in Me_2SO (O), DMF (●), and CH_3CN (◑) at 25.0 °C. C_{Cu} (mol kg^{-1}) = 5.00×10^{-4} (Me_2SO), 5.31×10^{-4} (DMF), and 4.99×10^{-3} (CH_3CN).

k_1 and k_{-1} are first-order rate constants. The relaxation time τ and relaxation amplitude A are given by eqs 3 and 4,

$$\tau^{-1} = 2\pi f_r = k_1 + k_{-1} \qquad (3)$$

$$A = \frac{2\pi^2 \rho v}{RT}\left(\Delta V^{\circ} - \frac{\alpha_p \Delta H^{\circ}}{\rho C_p}\right)^2 \Gamma\tau \qquad (4)$$

respectively, where ρ, α_p, and C_p refer to the density, the expansion coefficient, and the heat capacity of the solution, respectively; v is the sound velocity in the solution, and ΔV° represents the volume change in this relaxation process. We have then

$$\Delta H^{\circ} = \Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger} \qquad (5)$$

$$\Gamma^{-1} = \frac{1}{[C_1]} + \frac{1}{[C_2]} = \frac{1}{C_{221}}(2 + K + K^{-1}) \qquad (6)$$

where $[C_1]$ is the concentration of 221 with conformation 1 and K is the equilibrium constant defined by $K = k_1/k_{-1}$.

The parameters $\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_{-1}^{\ddagger}$, $\Delta S_{-1}^{\ddagger}$, and ΔV° for the conformational change in each solvent have been estimated as the values that make the sum of squares of the residuals of the observed ultrasonic absorption ($\sum[(\alpha/f^2)_{calc} - (\alpha/f^2)_{obs}]^2$) minimum with use of the relation of eqs 1 and 3–6 and the Eyring equation ($\ln(k/T) = \ln(k_B/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$).[32] In the evaluation, we used the values of ρ, v, α_p, and C_p for pure solvent summarized in Table II. Values of the parameters obtained are given in Table III. Although we can determine the absolute value of ΔV° by an ultrasonic absorption measurement, ΔV° for this conformational change may be positive as will be discussed later.

The addition of water up to 0.85 mol dm^{-3} did not affect the ultrasonic relaxation spectra for 221 (see Figure 2a).

(II) Kinetics of Formation of $Cu(221)^{2+}$ Cryptate. The formation reaction of the copper(II) cryptate 221 was followed spectrophotometrically under the pseudo-first-order conditions with cryptand in a large excess over copper(II) ion.

$$Cu^{2+} + 221 \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Cu(221)^{2+} \qquad (7)$$
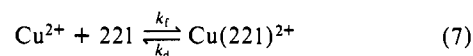
Since the pseudo-first-order plot is linear, the rate is first-order

(32) It has been confirmed that it is possible to deduce the five parameters by the present analysis. Since the relation $k_1 \geq k_{-1}$ in the present reaction system is accepted as described in the Discussion, we have $2\pi f_r = k_1$. Then k_1 is obtainable from the f_r values at three different temperatures given in Table I. The Eyring plot for the Me_2SO system gave $\Delta H_1^{\ddagger} = 24.1$ kJ mol^{-1} ($\sigma = 3.6$) and $\Delta S_1^{\ddagger} = -2$ J mol^{-1} K^{-1} ($\sigma = 12$), which agree with those given in Table III.

Table II. Sound Velocity v, Density ρ, Expansion Coefficient α_p, and Heat Capacity C_p in Me_2SO, DMF, and CH_3CN

solvent	T (°C)	v (m s^{-1})	ρ^a (g cm^{-3})	$\alpha_p^{a,b}$ (K^{-1})	$C_p^{a,b}$ (J K^{-1} mol^{-1})
Me_2SO	20.0	1504.02 ± 0.23	1.106	0.000928	153.18
	25.0	1484.77 ± 0.58	1.096		
	35.0	1453.30 ± 0.27	1.086		
DMF	15.0	1501.46 ± 0.31	0.9535	0.00100	148.36
	25.0	1458.91 ± 0.88	0.9440		
	35.0	1420.12 ± 0.09	0.9361		
CH_3CN	15.0	1320.09 ± 0.07	0.7876	0.001368	91.46
	25.0	1278.57 ± 0.23	0.7766		
	35.0	1238.92 ± 0.10	0.7659		

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Table III. Parameters[a] for the Conformational Change of 221 in Me_2SO, DMF, and CH_3CN

solvent	k_1[b]	$\Delta H_1^\ddagger$	$\Delta S_1^\ddagger$	k_{-1}[b]	$\Delta H_{-1}^\ddagger$	$\Delta S_{-1}^\ddagger$	K[b]	ΔH°	ΔS°	ΔV°
Me_2SO	2.8×10^8	25	−1	6.8×10^5	31	−30	4.1×10^2	−6	29	40
DMF	3.0×10^8	24	−2	6.4×10^5	19	−70	4.7×10^2	5	68	41
CH_3CN	3.4×10^8	25	5	1.2×10^6	23	−51	3.0×10^2	−2	56	43

[a] Units: k, s^{-1}; $\Delta H^\ddagger$ and ΔH°, kJ mol^{-1}; $\Delta S^\ddagger$ and ΔS°, J mol^{-1} K^{-1}; and ΔV°, cm^3 mol^{-1}. Values of parameters have ca. 15% deviation. [b] At 25 °C.

Table IV. Kinetic Parameters[a] for Formation and Dissociation of Cu(221)$^{2+}$ and Na(221)$^+$ [b] in Me_2SO, DMF, and CH_3CN

metal ion	formation				dissociation			
	k_f	$\Delta H_f^\ddagger$	$\Delta S_f^\ddagger$	$\Delta V_f^\ddagger$	k_d	$\Delta H_d^\ddagger$	$\Delta S_d^\ddagger$	$\Delta V_d^\ddagger$
				In Me_2SO				
Cu^{2+}	83 ± 4 37[c]	42 ± 2	−69 ± 6	−1.6 ± 1.5[e]	0.12 ± 0.01 0.11[c]	47 ± 4	−105 ± 14	1.6 ± 0.5[g]
Na^+	7.2×10^6 [d]			5.4 ± 1.1[b]	0.765 ± 0.005[b]	70.4 ± 0.8[b]	−11 ± 3[b]	2.1 ± 0.7[b]
				In DMF				
Cu^{2+}	$(2.1 ± 0.2) \times 10^3$	35 ± 4	−65 ± 14	−0.4 ± 0.6[f]				
Na^+	1.8×10^7 [d]				0.337 ± 0.003[b]	73.0 ± 0.9[b]	−9 ± 3[b]	2.0 ± 0.2[b]
				In CH_3CN				
Cu^{2+}	$(3.6 ± 0.2) \times 10^{-3}$				$(1.8 ± 0.2) \times 10^{-4}$			

[a] Units: k_f, mol^{-1} dm^3 s^{-1}; k_d, s^{-1}; $\Delta H^\ddagger$, kJ mol^{-1}; $\Delta S^\ddagger$, J mol^{-1} K^{-1}; and $\Delta V^\ddagger$, cm^3 mol^{-1}. [b] Reference 24. [c] Reference 11. [d] Reference 3. [e] 35.0 °C. [f] 25.0 °C. [g] 39.5 °C.

with respect to copper(II) ion. Therefore, the conditional first-order rate constant k_0 is given by eq 8. All values of k_0 obtained

$$k_0 = k_f C_{221} + k_d \qquad (8)$$

in Me_2SO, DMF, and CH_3CN under various conditions were listed in Tables SII–SIV, respectively. At various concentrations of 221, k_0 in each solvent was determined as shown in Figure 3. Plots of k_0 vs the total concentration of 221 lie on the straight line without an intercept for Me_2SO and DMF but with an intercept for CH_3CN. Rate constants for formation k_f can be estimated from the slope of the straight lines. In the case of CH_3CN, the reverse reaction contributes to the measurement under the present experimental conditions. Thus, we have $k_0 = k_f[221] + k_d$. The intercept in Figure 3 corresponds to the rate constant for the dissociation of Cu(221)$^{2+}$. Obtained values are tabulated in Table IV.

The water effect on the rate was checked by the addition of some amount of water (see Figure 4). As apparent from Figure 4, the presence of more than 10^{-1} mol dm^{-3} of water accelerates the rate. This is the case for the other systems (data given in the supplementary material). Since the content of water in our reaction systems is less than 5×10^{-3} mol kg^{-1}, the contribution of water is negligible under the present experimental conditions.
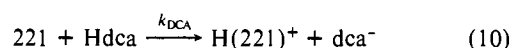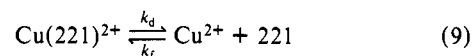
In Figure 5 are shown the Eyring plots, and in Figure 6 is given the pressure dependence of k_f according to ln $k = -\Delta V^\ddagger P/RT$. The activation parameters for formation of copper(II) cryptate 221 are summarized in Table IV. We have carried out the additional experiment: We tried to follow the complexation reaction of Cu^{2+} with 1,4-diazabicyclo[2.2.2]octane and triethylamine in Me_2SO by the stopped-flow technique. Judging from the dead time of the stopped-flow technique used, the second-order rate constant for this reaction is much larger than 10^4 mol^{-1} dm^3 s^{-1}.

(III) Kinetics of Dissociation of Cu(221)$^{2+}$ Cryptate. The conditional first-order rate constants (k_0) with respect to Cu(221)$^{2+}$
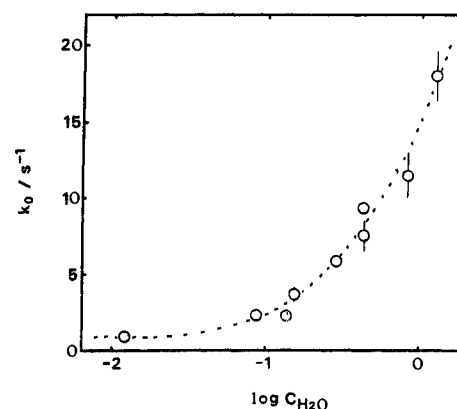
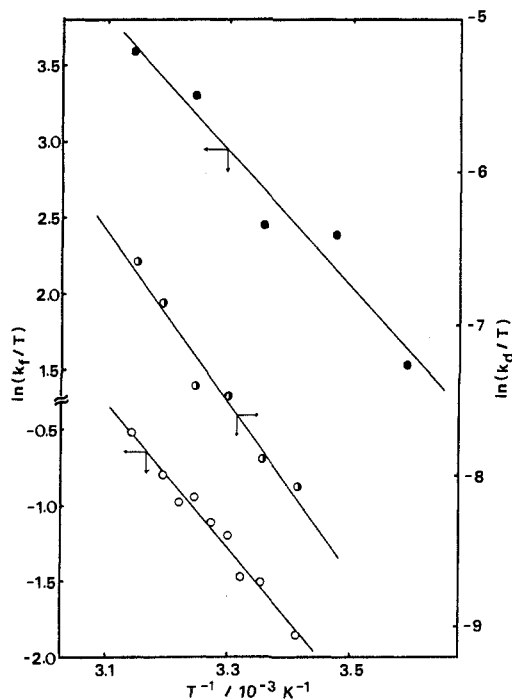
Figure 4. Effect of water addition on the formation of the copper(II) cryptate 221 in Me_2SO at 25 °C. $C_{221} = 1.86 \times 10^{-2}$ mol kg^{-1} and $C_{Cu} = 1.17 \times 10^{-3}$ mol kg^{-1}.

were determined as a function of the concentration of dichloroacetic acid or water, temperature, or pressure (Table SVa–d). The dissociation of Cu(221)$^{2+}$ by dichloroacetic acid is expressed by eqs 9 and 10. Since the stability constant of the cryptate is large

$$Cu(221)^{2+} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} Cu^{2+} + 221 \qquad (9)$$

$$221 + Hdca \xrightarrow{k_{DCA}} H(221)^+ + dca^- \qquad (10)$$

and the protonation reaction of the free cryptand is very fast, the steady-state approximation is applicable to the concentration of the free cryptand ([221]). Thus, we obtain eq 11. Then k_0 is

$$-d[Cu(221)^{2+}]/dt =$$
$$k_{DCA} k_d [Hdca][Cu(221)^{2+}]/(k_f[Cu^{2+}] + k_{DCA}[Hdca]) \qquad (11)$$

Cryptand 221 and Copper(II) Cryptate 221

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Figure 5. Temperature dependence of the formation rate constant k_f and the dissociation rate constant k_d of the copper(II) cryptate 221. For formation in Me$_2$SO (O), C_{221} = 1.82 × 10^{-2} mol kg^{-1} and C_{Cu} = 1.28 × 10^{-3} mol kg^{-1}. For dissociation in Me$_2$SO (◐), C_{221} = 2.26 × 10^{-3} mol kg^{-1}, C_{Cu} = 2.86 × 10^{-3} mol kg^{-1}, and C_{DCA} = 5.80 × 10^{-2} mol kg^{-1}. For formation in DMF (●), C_{221} = 3.21 × 10^{-2} mol kg^{-1} and C_{Cu} = 6.18 × 10^{-4} mol kg^{-1}.
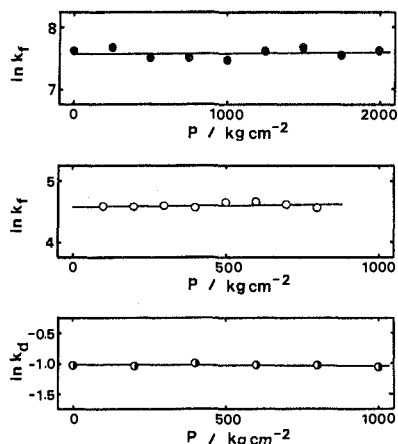
Figure 6. Pressure dependence of the formation rate constant k_f and the dissociation rate constant k_d of the copper(II) cryptate 221. For formation in Me$_2$SO at 35.0 °C (O), C_{221} = 4.04 × 10^{-2} mol kg^{-1} and C_{Cu} = 1.63 × 10^{-3} mol kg^{-1}. For dissociation in Me$_2$SO at 39.5 °C (◐), C_{221} = 2.99 × 10^{-3} mol kg^{-1}, C_{Cu} = 2.42 × 10^{-3} mol kg^{-1}, and C_{DCA} = 4.75 × 10^{-2} mol kg^{-1}. For formation in DMF at 25.0 °C (●), C_{221} = 2.99 × 10^{-2} mol kg^{-1} and C_{Cu} = 2.57 × 10^{-3} mol kg^{-1}.

expressed by eq 12. Since values of k_0 are independent of the total concentration of DCA (C_{DCA} (see Table SVa)), k_0 should be equal to k_d under the present conditions.[24] Temperature and pressure

$$k_0 = k_{DCA}k_d[Hdca]/(k_f[Cu^{2+}] + k_{DCA}[Hdca]) \quad (12)$$

dependences of k_d are given in Figures 5 and 6, respectively. Activation parameters are summarized in Table IV. There is almost no effect of water addition on the dissociation rate (Table SVb).

Discussion

Mechanism of Conformational Change of Cryptand 221. Petrucci et al. have studied the equilibrium of the conformational change of 222 in some solvents and detected two relaxation

processes in protic solvents and one in aprotic solvents.[16,17] It has been pointed out that since the (i,i) conformation of 222 seems the most flexible of the three conformations, the equilibrium (i,i) ⇌ (i,o) would be faster than (i,o) ⇌ (o,o) and that the (o,o) conformation has a tendency to be stabilized in protic solvents by hydrogen bonding with the solvent proton. They concluded that the process in the aprotic solvents is attributed to the conformational equilibrium (i,o) ⇌ (i,i), judging from the similarity of the relaxation frequency in the aprotic solvents to the upper one in the protic solvents. Furthermore, the conformation of cryptands and bicyclic diamines of various sizes has been extensively studied by means of X-ray diffraction,[33-35] IR spectroscopy,[35-38] conformational analysis by a semiempirical CNDO2 calculation,[39] and NMR spectroscopy.[40,41] As a result, (i,i) would be the most stable of the three conformations in most cases except for the case of bicyclic compounds with very small size. According to the considerations on the CPK molecular model, we can build up the three conformations of 222 while we could not construct the (o,o) conformation of 221 because of the strong strain, although both (i,o) and (i,i) of 221 could be made.

The conformation (i,i) tends to have a larger value in the distance between the two nitrogen atoms,[39] regarded as a measure of the intrinsic volume of the molecule. Additionally, hydrogen bonding between a lone electron pair directed away from the cavity of (i,o) and a hydrogen atom of the solvent molecules may cause a decrease in volume. Thus, the partial molal volume of (i,o) might be smaller in comparison with (i,i). From these results, we can conclude that the ultrasonic relaxation observed results from the conformational change (i,o) ⇌ (i,i) of 221 and that (i,i) is more stable than (i,o), which would be smaller in size than (i,i). Therefore in the present system, C_1 and C_2 in eq 2 correspond to (i,o) and (i,i), respectively, ΔV^o may be positive, and K should be larger than unity. So the main conformation of 221 is (i,i) in all solvents used.

The large positive change in entropy ($\Delta S^o = \Delta S_1^{\ddagger} - \Delta S_{-1}^{\ddagger}$) for the conformational change from (i,o) to (i,i) supports that the (i,i) conformation of 221 is more flexible than (i,o). There is no remarkable difference in rate for the conformational change in the three aprotic solvents under investigation. The mechanism of the conformational change would be that the bridgehead nitrogen atom is in the sp^2 state in the transition state, followed by the inversion of a lone electron pair of the nitrogen atom. In general, the energy barrier necessary for the inversion of the nitrogen atom is 21–33 kJ mol^{-1}, which corresponds to the rate of $>10^3$ s^{-1}.[42-44] These figures are comparable in order of magnitude to our results.

Mechanism of Formation and Dissociation of Cu(221)$^{2+}$ Cryptate. The mechanism now generally accepted for metal complex formation reactions of solvated metal ions with "normal" ligands is as follows: The metal ion M^{n+} and the ligand L diffuse together rapidly to form an outer-sphere complex, and a coordinated solvent on the metal ion interchanges with the incoming

(33) (a) Metz, B.; Moras, D.; Weiss, R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 423–429; (b) Ott, N. L.; Barnes, C. L.; Taylor, R. W.; van der Helm, D. *Acta Crystallogr.* **1982**, *B38*, 2277–2280.

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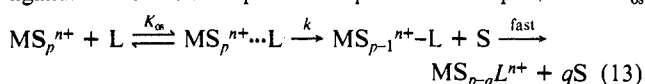(40) Dietrich, B.; Lehn, J.-M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, 2885–2888.

(41) Schmidt, E.; Tremillon, J.-M.; Kintzinger, J.-P.; Popov, A. I. *J. Am. Chem. Soc.* **1983**, *105*, 7563–7566.

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(44) Lehn, J.-M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311–377.

ligand. The reaction sequence is expressed as in eq 13, where K_{os}

$$MS_p^{n+} + L \underset{K_{os}}{\rightleftharpoons} MS_p^{n+}\cdots L \xrightarrow{k} MS_{p-1}^{n+}-L + S \xrightarrow{fast}$$
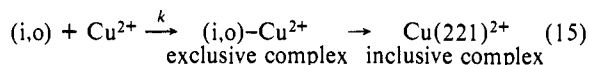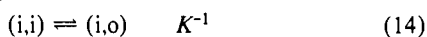$$MS_{p-q}L^{n+} + qS \quad (13)$$

is the equilibrium constant for the outer-sphere association, $MS_p^{n+}\cdots L$ is the outer-sphere complex, and k is the first-order rate constant for the interchange of solvent S with incoming ligand L. Therefore, the observed second-order rate constant k_f is equal to the product of K_{os} and k, and k values roughly correspond to those of the solvent exchange rate on the metal ion. Here, a "normal" ligand means that the ligand has a donor atom that can enter into the inner coordination sphere of the metal ion without deformation prior to a rate-determining step and steric hindrance for penetration of the ligand.

According to the X-ray analysis, copper(II) ion in water has the distorted octahedral structure due to the Jahn–Teller effect.[19a] The axial–equatorial interconversion of the copper(II) ion and the solvent exchange at the copper(II) ion in water and methanol are very fast.[19b] We expect similar structural and kinetic aspects of the copper(II) ion in the other solvents. Rates for solvent exchange at copper(II) ion in Me_2SO and DMF have not yet been reported, but rate constants k_{ex} (s^{-1}) in water, acetonitrile, acetic acid, and methanol are available: $k_{ex} = 5 \times 10^9$ s^{-1} (25 °C) in H_2O,[19b] $>3.7 \times 10^8$ s^{-1} (25 °C) in CH_3CN,[20] 1×10^7 s^{-1} (−25 °C) in acetic acid,[45] and 3.1×10^7 s^{-1} (25 °C) in CH_3OH.[21] It should be noted that rate constants for formation of the Cu(221) cryptate (see Table IV) are extremely small in comparison with those for solvent exchange at the copper(II) ion.

It is possible to envisage an "external" complex in which the metal ion is entirely outside the cavity and interacting with only one of nitrogen atoms of the cryptand because the copper(II) ion should strongly interact with the nitrogen atom. However, this is not the case for alkali and alkaline-earth metal cations.

We have measured the complex formation in Me_2SO of Cu^{2+} with Et_3N and TEDA, where the lone electron pairs of nitrogens of TEDA are restricted to be outward.[36] Since the complexation reactions proceeded within the dead time of the stopped-flow technique, the rate should be much faster than 10^4 mol^{-1} dm^3 s^{-1}. On the other hand if the (i,o) form of 221 could exist predominantly, the external (i,o)–Cu^{2+} complex would be formed immediately by mixing under the present experimental conditions because (i,o) is a "normal" ligand such as TEDA. In fact, we did not observe such an absorbance jump due to the formation of an external complex. These findings strongly support that the predominant conformation is not (i,o) but (i,i), as already described above.

Existence of two forms of 221 seems to give some support to Chock's mechanism. Assuming the Chock mechanism,[14] we present the following scheme:

$$(i,i) \rightleftharpoons (i,o) \qquad K^{-1} \qquad (14)$$

$$(i,o) + Cu^{2+} \xrightarrow{k} \underset{\text{exclusive complex}}{(i,o)-Cu^{2+}} \rightarrow \underset{\text{inclusive complex}}{Cu(221)^{2+}} \quad (15)$$

Then we expect the following mechanism: A "normal" ligand (i,o) reacts with Cu^{2+} to give the intermediate (i,o)–Cu^{2+} in which the copper(II) ion is not involved in the cavity. The exclusive (i,o)–Cu^{2+} complex changes to the final product, i.e., the inclusive complex $Cu(221)^{2+}$. Assuming this scheme, the observed second-order rate constant k_f is given by the product of the equilibrium constant for reaction 14 and the second-order rate constant for formation of the exclusive complex: $k_f = K^{-1}k$. Generally, k is nearly equal to the second-order rate constant k_{ex} for solvent exchange on the copper(II) ion. Thus, the observed volume of activation $\Delta V_f^{\ddagger}$ is assumed to be the sum of the reaction volume for reaction 14 and the activation volume $\Delta V_{ex}^{\ddagger}$ for the solvent exchange. Since in the solvent under investigation the reaction volume for reaction 14 is ca. −40 cm^3 mol^{-1} and $\Delta V_f^{\ddagger}$ is almost 0 cm^3 mol^{-1} (see Tables III and IV), values of the activation

volume for the solvent exchange could be ca. 40 cm^3 mol^{-1}. That is not reasonable, judging from the available $\Delta V_{ex}^{\ddagger}$ value (+8.3 cm^3 mol^{-1} in methanol).[21] This discrepancy indicates that the Chock mechanism may be ruled out. Furthermore, if the inversion process of exclusive (i,o)–Cu^{2+} to inclusive $Cu(221)^{2+}$ would be rate-limiting, the reactivity trend could be explained. But in contrast to the inversion of a lone electron pair on the nitrogen atom of cryptand 221, it is impossible that the exclusive form converts to the inclusive form without breaking of the Cu–N bond. Interestingly, the rate for conformational change is almost the same in the three solvents, while the cryptate formation of Cu^{2+} is very different in rate in different solvents.

According to the Eigen–Winkler mechanism,[15] the formation of the cryptate is expressed as

$$221 + Cu^{2+} \underset{K_{os}}{\rightleftharpoons} 221\cdots Cu^{2+} \rightarrow Cu(221)^{2+}$$
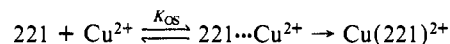
where the formation of an encounter complex $221\cdots Cu^{2+}$ is diffusion-controlled. The Eigen–Winkler mechanism may be depicted as a series of steps where both desolvation of the metal ion and rearrangement of the cryptand for accepting the metal ion play a role in the activation process. After the outer-sphere complex is formed, the first step involves the partial rearrangement of the cryptand and the partial desolvation of the metal ion and the subsequent step leads to the encirclement of the metal ion with much more desolvation. Prior to the rate-determining step, there are a series of equilibria depending on the relative energy of the desolvation vs that for cryptand rearrangement. The Eigen–Winkler *multistep* mechanism is capable of interpreting the complexation process of cryptands.

An interesting difference between the behaviors of sodium(I) cryptates and those of copper(II) cryptates may be seen from the comparisons with activation parameters (see Table IV). Rate constants for complexation of both Na^+ and Cu^{2+} with normal ligands are ca. 10^8 mol^{-1} dm^3 s^{-1}, comparable to the solvent exchange rates. However, the formation rate of copper(II) cryptate is much lower than that of sodium(I) cryptate in both Me_2SO and DMF. This is due to much stronger solvation of Cu^{2+} in comparison with that of Na^+.[11] The slowness of the Cu(II) ion should be attributed to higher energies needed for dissociation of two or more coordinated solvent molecules. On the other hand, dissociation rates of the cryptates of Na^+ and Cu^{2+} in Me_2SO are of the same order. Therefore, the stability constant of the $Cu(221)^{2+}$ complex is smaller than that of the $Na(221)^+$ complex; $K_{Cu(221)} = 336$ mol^{-1} dm^3 estimated from k_f/k_d, and $K_{Na(221)} = 9.6 \times 10^6$ mol^{-1} dm^3.[3,4] Moreover, as pointed out by Cox et al., the cryptate formation rates for alkali and alkaline-earth metal cations are not very sensitive to solvent variation.[3,4,11] However, the rates for copper(II) cryptate formation are very different in each solvent. The simplest interpretation for such different reactivities is that interactions between cations and the binding sites of the ligand and solvent are mainly electrostatic for Na^+ and nonelectrostatic for Cu^{2+} in nature (the strong specific Cu^{2+}–cryptand interaction (especially Cu^{2+}–N)). In the copper(II) cryptate formation via the Eigen–Winkler multistep mechanism, solvent molecules in the inner coordination sphere of the copper(II) ion have to be replaced stepwise by binding sites of the cryptand in one or more of the several intermediate steps. The degree of such a replacement should be dependent on properties of solvent, and the bulkiness of solvent molecules should also affect the solvation of the intermediate due to the steric rigidity of the ligand.

According to X-ray crystallographic analyses of sodium(I) and cobalt(II) cryptates 221, the metal ions are held inside the molecular cavity of the bicyclic ligand.[46,47] The cavity size of 221 has been evaluated to be ca. 1.1 Å on the basis of molecular models.[46] The radii of metal ions are 0.97 Å for Na^+ and 0.72 Å for Cu^{2+}. Cryptand 221 displays a peak selectivity for Na^+ in alkali metal ions.[48] The cage has to be opened when the metal

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(46) Mathieu, F.; Metz, B.; Moras, D.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4412–4416.
(47) Mathieu, F.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1973**, 816.

ion dissociates under the circumstances. The oxygen atoms in the bridges are able to rotate outward from the cavity, and this may form the basis of the initial interaction of the cation in the cavity with the solvent. Usually the dissociation of cryptates proceeds through two parallel paths, as already shown previously:[24] the acid-assisted path and the solvent path (i.e., acid-independent path). In Me$_2$SO, which is the most basic solvent, the solvent path prevails. Since the transition state for the dissociation reaction should be the same as for the formation reaction, it follows that the reactions would occur only through the (i,i) form. It is in the most plausible transition state **1** that one of the Cu–N bonds in
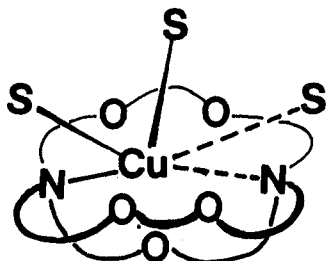
1

the intermediate, i.e., the solvated copper(II) ion binding to two nitrogens atoms of the cryptand, is dissociated by the solvent attack. Thus, the process in which the second nitrogen atom binds to the copper(II) ion to form the solvated copper(II) binding to the two nitrogen atoms is the rate-determining step for the cryptate formation.[49]

We speculate that the complex formation and dissociation occur not through the smaller 15-membered ring of the cryptand but through the larger 18-membered ring, judging from both the ring size of the cryptand and the ionic radius of the metal ion.

The small values of the activation volume imply that, in the transition state, a volume increment caused by opening the cage is almost compensated for by a volume decrement due to electrostriction. The molal volume of the transition state for copper(II) cryptate is expected to be smaller in comparison to that of sodium(I) cryptate because there is no strong interaction between the sodium ion and the two nitrogen atoms. This is consistent with the fact that ΔV_f^* for Cu^{2+} in Me$_2$SO is smaller than that for Na$^+$ (see Table IV).

In conclusion, the results of the dynamics of the conformational change (i,o) $\rightleftharpoons$ (i,i) of cryptand 221 have shown that the main conformation of 221 is (i,i) in Me$_2$SO, DMF, and CH$_3$CN. The complexation of copper(II) ion with 221 proceeds via the Eigen–Winkler mechanism. Small values of the activation volume obtained by the first high-pressure study on the cryptate formation support the proposed mechanism.

Supplementary Material Available: α/f^2 values for cryptand 221 as a function of f under various conditions (Table SI), rate constants for cryptate formation (Tables SII–SIV), and rate constants for cryptate dissociation (Table SV) (13 pages). Ordering information is given on any current masthead page.

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(49) The proposed mechanisms for the cryptate formation are restricted to the solvent studied. The mechanisms in protic solvents are probably very different due to the interaction of the protic solvent with the nitrogen atoms of cryptands.

Photochemistry of 3-Methyl- and 4-Methyl-1,2-dihydronaphthalene in Solution[1]

Robert J. Duguid and Harry Morrison*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received June 7, 1990

Abstract: Photolysis of 3-methyl-1,2-dihydronaphthalene (3-MDHN) in hexane solution with 254-nm light produces one major product, 5-methylbenzobicyclo[3.1.0]hex-2-ene (5-MBBH; $\phi = 4.7 \times 10^{-4}$). Photolysis in hexane in the presence of trifluoroacetic acid produces exclusively 2-methylene-1,2,3,4-tetrahydronaphthalene (2-MTHN). The 254-nm photolysis of 4-methyl-1,2-dihydronaphthalene (4-MDHN) in hexane produces 2-(*o*-tolyl)-1,3-butadiene (T13B; $\phi = 2.2 \times 10^{-3}$), 1-methylbenzobicyclo[3.1.0]hex-2-ene (1-MBBH; $\phi = 1.4 \times 10^{-3}$), 1-methyl-1,4-dihydronaphthalene (1-M-1,4-DHN; $\phi = 8.7 \times 10^{-3}$), 1-methyltetralin (1-MT; $\phi = 1.5 \times 10^{-3}$), and 1-methylnaphthalene (1-MN; $\phi = 2.7 \times 10^{-3}$). Triplet sensitization of 4-MDHN produces only 1-MN in small amounts, suggesting that the direct photolyses proceed via singlet chemistry. The products appear to derive from a combination of electrocyclic opening of the cyclohexadienyl ring to generate an *o*-quinodimethane intermediate, disproportionation leading to net oxidation-reduction and, in 4-MDHN, a [1.3] hydrogen shift to form 1-M-1,4-DHN. The *o*-quinodimethane intermediates further react to form benzobicyclo[3.1.0]hex-2-ene derivatives (via a photochemical [4 + 2] cycloaddition; Scheme VI) and, in the case of 4-MDHN, the 1,3-butadiene T13B (via a thermal [1,5] hydrogen shift; Scheme VII).

Some time ago we reported the photoinduced alkyl migration reaction of alkylindenes in hexane solution via a C1/C2 transposition of the indenyl five-membered ring (Scheme I).[2] More

recently, we reported[3] that the photolysis of alkylindenes in the gas phase also produces alkyl (as well as hydrogen) migration products, but deuterium and ^{13}C labeling[3,4] studies demonstrate

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(3) Suarez, M. L.; Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1989**, *111*, 6384–6391.