of the higher extinction. The IR bands of $ClOClO_3$ generated photochemically agree excellently with those given in ref 14.

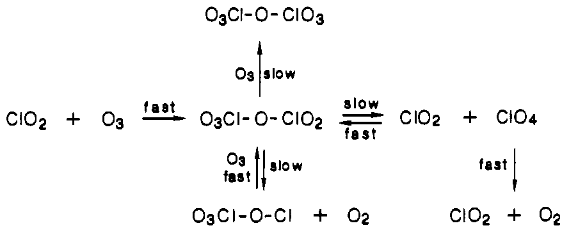
Mechanism of Formation and Decomposition of Cl_2O_6. In order to characterize the chemical behavior of Cl_2O_6 in more detail, we have followed both the formation and the decomposition in a gas cell using FTIR spectroscopy. Appropriate quantities of the reagents were allowed to stream into the evacuated cell at room temperature. Spectra were then recorded immediately.

Investigations of the formation of Cl_2O_6 from pure ClO_2 and O_3 in equimolar ratios showed that the rate of reaction was dependent on the partial pressures of both reagents and that the reaction proceeds according to the stoichiometry

$$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$$

At room temperature the reaction of 4 mbar of ClO_2 and 4 mbar of O_3 is complete in about 15 s, with 2 mbar of each reagent in about 60 s, and with 0.5 mbar of each in about 10 min. Excess of either ClO_2 or O_3 accelerates the reaction. No reaction intermediates, e.g. ClO_3 or Cl_2O_5, could be detected. Excess ClO_2 does not react with Cl_2O_6 after the reaction, but it strongly reduces the rate of decomposition. Excess O_3 inhibits the decomposition of Cl_2O_6 and also oxidizes it slowly (in 30–60 min) to Cl_2O_7. The simplest method of preparing pure gaseous Cl_2O_6 is, therefore, to mix stoichiometric quantities of ClO_2 and O_3 at 25 °C without exceeding the vapor pressure of 2 mbar for Cl_2O_6.

In contrast to its behavior in the liquid and solid states, Cl_2O_6 is very short-lived in the gas phase. Its half-life in completely dry, well-conditioned glassware is about 8 min with a starting pressure of 1 mbar at room temperature. ClO_2, $ClOClO_3$, and O_2 were detected as decomposition products. No bands of the possible radical intermediates, ClO_3 and ClO_4, could be detected in the IR spectra during the decomposition, so their partial pressures must be less than about 0.05 mbar. In the presence of traces of moisture or organic matter, $HClO_4$ was also formed. Addition of gaseous H_2, Cl_2, or Cl_2O_7 to Cl_2O_6 had no influence on the decomposition products, but the rate of decomposition was reduced slightly. These observations suggest that the decomposition is surface-catalyzed. In conclusion, the reactivity of Cl_2O_6 can be summarized by the following scheme:



Acknowledgment. Support by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. Cl_2O_6, 12442-63-6; Cl_2O, 10049-04-4; O_3, 10028-15-6; Ar, 7440-37-1; Ne, 7440-01-9; ^{35}Cl, 13981-72-1; ^{37}Cl, 13981-73-2.

Contribution from the Laboratory of Analytical Chemistry, Faculty of Science,
Nagoya University, Chikusa, Nagoya, 464-01 Japan

Kinetic Study of the Dissociation of Sodium Cryptate(2,2,1)

Koji Ishihara, Hiroko Miura, Shigenobu Funahashi, and Motoharu Tanaka*

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The rate of dissociation of sodium cryptate(2,2,1) ($NaCry^+$) has been measured at various temperatures and pressures in dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (DMF), and acetonitrile (MeCN) by using a high-pressure stopped-flow apparatus with conductometric detection. There are two reaction paths: an acid-independent path (k_{d1}), $CryNa^+ \rightarrow Cry + Na^+$, and an acid-dependent path (k_{d2}), $CryNa^+ + Hdca \rightarrow CryH^+ + Na^+ + dca^-$, where Hdca is dichloroacetic acid. Activation parameters are as follows: in Me_2SO, $k_{d1}/s^{-1} = (7.65 \pm 0.05) \times 10^{-1}$ (25 °C), $\Delta V_{d1}^{\ddagger}/cm^3\ mol^{-1} = 2.1 \pm 0.7$, $\Delta H_{d1}^{\ddagger}/kJ\ mol^{-1} = 70.4 \pm 0.8$, and $\Delta S_{d1}^{\ddagger}/J\ mol^{-1}\ K^{-1} = -11 \pm 3$; in DMF, $k_{d1}/s^{-1} = (3.37 \pm 0.03) \times 10^{-1}$ (25 °C), $k_{d2}/mol^{-1}\ kg\ s^{-1}$ (25 °C), $\Delta V_{d1}^{\ddagger}/cm^3\ mol^{-1} = 2.0 \pm 0.2$, $\Delta V_{d2}^{\ddagger}/cm^3\ mol^{-1} = -8.8 \pm 1.0$, $\Delta H_{d1}^{\ddagger}/kJ\ mol^{-1} = 73.0 \pm 0.9$, $\Delta H_{d2}^{\ddagger}/kJ\ mol^{-1} = 30 \pm 5$, $\Delta S_{d1}^{\ddagger}/J\ mol^{-1}\ K^{-1} = -9 \pm 3$, and $\Delta S_{d2}^{\ddagger}/J\ mol^{-1}\ K^{-1} = -140 \pm 20$; in MeCN, $k_{d2}/mol^{-1}\ kg\ s^{-1} = 73.5 \pm 0.5$, $\Delta V_{d2}^{\ddagger}/cm^3\ mol^{-1} = -16.0 \pm 0.8$, $\Delta H_{d2}^{\ddagger}/kJ\ mol^{-1} = 41.1 \pm 1.3$, and $\Delta S_{d2}^{\ddagger}/J\ mol^{-1}\ K^{-1} = -71 \pm 4$. The reaction volume for the formation of $NaCry^+$ in Me_2SO has also been measured dilatometrically: $\Delta V^{\circ} = 3.3 \pm 0.4\ cm^3\ mol^{-1}$. The reaction mechanism is discussed on the basis of these parameters.

Introduction

Cryptands as well as crown ethers form unusually stable complexes with metal cations, especially with alkali- and alkaline-earth-metal cations, which play an important role biologically. Thus, metal cryptates have been the subject of extensive study in the past two decades.

Kinetics for the formation and dissociation of cryptates has been fairly extensively studied, although more attention has been drawn to the thermodynamics of metal cryptates than to their kinetics.[1-11] However, no data of activation volumes for these reactions have been reported, partly because of little change in visible or ultraviolet spectra associated with formation of alkali- or alkaline-earth-metal cryptates and partly because of the lack of means to follow these reactions under high pressure.

We have developed a high-pressure stopped-flow apparatus with conductometric detection to follow such fast reactions under high pressure with no color change.

In this work, dissociation reaction 1 of sodium cryptate(2,2,1) has been followed conductometrically at various pressures up to 200 MPa with Me_2SO, DMF, and MeCN as solvents. Dichloroacetic acid (Hdca) was used as a scavenger for the dissociated cryptate. We selected these three solvents because of their very different basicities. This is apparently the first report both

$$NaCry^+ + Hdca \rightarrow Na^+ + CryH^+ + dca^- \qquad (1)$$

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(1) Cox, B. G.; Schneider, H. *J. Am. Chem. Soc.* **1977**, *99*, 2809.
(2) Henco, Von K.; Tummler, B.; Maass, G. *Angew. Chem.* **1977**, *89*, 567.
(3) Loyola, V. M.; Pizer, R.; Wilkins, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7185.
(4) Cox, B. G.; Schneider, H.; Stroka, J. *J. Am. Chem. Soc.* **1978**, *100*, 4746.
(5) Cox, B. G.; Schneider, H. *J. Am. Chem. Soc.* **1980**, *102*, 3628.
(6) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1054.
(7) Cox, B. G.; Van Truong, Ng.; Garcia-Rosas, J.; Schneider, H. *J. Phys. Chem.* **1984**, *88*, 996.
(8) Kitano, H.; Hasegawa, J.; Iwai, S.; Okubo, T. *J. Phys. Chem.* **1986**, *90*, 6281.
(9) Cox, B. G.; Stroka, J.; Schneider, H. *Inorg. Chim. Acta* **1987**, *128*, 207.
(10) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. *Coordination Chemistry of Macrocyclic Compounds*; Plenum: New York, 1979; p 145.
(11) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271.

0020-1669/88/1327-1706$01.50/0

Table I. Kinetic Parameters for Dissociation of Sodium Cryptate(2,2,1) at 25 °C

solvent	k_{d1}, s^{-1}	ΔV_{d1}^{*}, cm^3 mol^{-1}	ΔH_{d1}^{*}, kJ mol^{-1}	ΔS_{d1}^{*}, J mol^{-1} K^{-1}	k_{d2}, M^{-1} s^{-1}	ΔV_{d2}^{*}, cm^3 mol^{-1}	ΔH_{d2}^{*}, kJ mol^{-1}	ΔS_{d2}^{*}, J mol^{-1} K^{-1}
Me_2SO	(7.65 ± 0.05) × 10^{-1}	2.1 ± 0.7[a]	70.4 ± 0.8	−11 ± 3				
DMF	(3.37 ± 0.03) × 10^{-1}	2.0 ± 0.2	73.0 ± 0.9	−9 ± 3	1.53 ± 0.08	−8.8 ± 1.0	30 ± 5	−140 ± 20
MeCN					73.5 ± 0.5	−16.0 ± 0.8	41.1 ± 1.3	−71 ± 4

[a] At 40 °C.

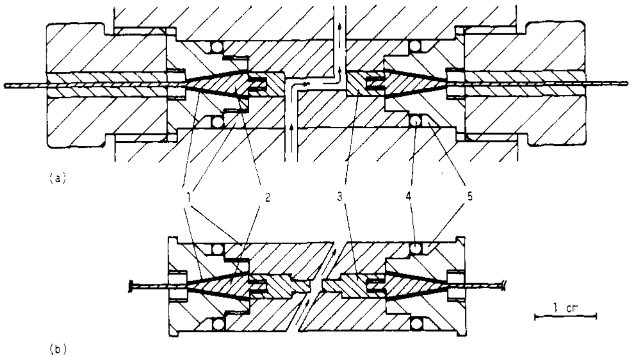

Figure 1. Platinum electrodes used in high-pressure stopped-flow apparatus FIT-3C. Interelectrode distance: 10 mm (a); 2 mm (b). Components: (1) Daiflon; (2) phosphor bronze; (3) platinum; (4) O-ring; (5) Teflon ring.

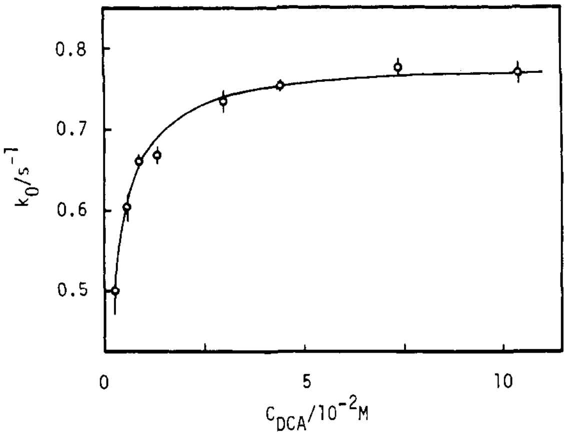

Figure 2. Acid concentration dependence of k_0 in Me_2SO at 25 °C. $C_{Cry} = 1.5 \times 10^{-5}$ M; $C_{NaClO_4} = 3.1 \times 10^{-4}$ M.

on a high-pressure stopped-flow apparatus with conductometric detection and on the high-pressure study of the reaction of cryptates.

Experimental Section

Materials. Commercially available cryptand(2,2,1) (Merck, Kryptofix 221: 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-[8.8.5]tricosane) was used without further purification. Sodium perchlorate was prepared as described previously[12] and dried at 110 °C for several days. Chemical grade dichloroacetic acid (DCA, Hdca) was purified by vacuum distillation. Dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (DMF), and acetonitrile (MeCN) were distilled twice, as described previously.[13,14] Sample solutions were prepared in a drybox with nitrogen gas flow.

Apparatus. A high-pressure stopped-flow apparatus with spectrophotometric detection (FIT-3)[13,15] was modified in order to construct an apparatus with electric conductance detection (FIT-3C). A pair of sapphire windows for spectrophotometric measurement was replaced by a pair of platinum electrodes for conductometric measurement and their holder. As depicted in Figure 1, two types of cells were made. One has a 10-mm interelectrode distance with a cell constant of ca. 20 cm^{-1} at ambient pressure, and the other has a 2-mm distance with a constant of ca. 7 cm^{-1}. The interelectrode distance of both cells increased with increasing pressure; the same is true for the cell constants because Daiflon (1 in Figure 1), which was used as both an insulator and a pressure-sealing material, is shrinkable by pressure. For an electric conductance detection system we used an electric conductance bridge (362B, a type of admittance linear bridge, Fusoseisakusho, Kanagawa, Japan) that has very fast response time (microsecond), a sine wave oscillator (361B, Fusoseisakusho), and a computer processing system developed in our laboratory. Under our experimental conditions, i.e., pseudo-first-order conditions, the increase in conductance with time was exactly single exponential.

Measurements. Reaction 1 was started by mixing a solution of sodium cryptate(2,2,1) in the presence of excess sodium perchlorate and a solution of dichloroacetic acid. The increase in electric conductance with reaction time was followed by the apparatus (FIT-3C) at various temperatures and pressures up to 200 MPa. The noise level was extremely low as compared to the signal. At any pressure the first-order plots were excellently linear, at least up to 90% reaction completion. To check the conductometric detection device, we compared the rate constant obtained by spectrophotometry with that obtained by conductometry in the reaction of the beryllium ion with 4-isopropyltropolone. The conductometric data compare very favorably with the spectrophotometric ones. In the kinetic experiments, the total concentrations of cryptand(2,2,1), sodium perchlorate, and dichloroacetic acid are as follows: with Me_2SO as a solvent, $C_{Cry} = 1.5 \times 10^{-5}$–$4.8 \times 10^{-5}$ M (M = mol dm^{-3}), $C_{Na^+} = 3.1 \times 10^{-4}$–$9.8 \times 10^{-4}$ M, and $C_{DCA} = 3.0 \times 10^{-3}$–0.10 M; in MeCN, $C_{Cry} = 1.6 \times 10^{-5}$ M, $C_{Na^+} = 2.6 \times 10^{-4}$, and $C_{DCA} = 3.0 \times 10^{-3}$–$7.5 \times 10^{-2}$ M; in DMF, $C_{Cry} = 1.6 \times 10^{-5}$ M, $C_{Na^+} = 3.2 \times 10^{-4}$ M, and $C_{DCA} = 6.0 \times 10^{-3}$–$5.0 \times 10^{-2}$ M. Molar concentration units were converted to molal units (m = mol kg^{-1}) when necessary.

Results

In Dimethyl Sulfoxide. Reaction 1 was followed under pseudo-first-order conditions with dichloroacetic acid in a large excess over sodium cryptate(2,2,1). The pseudo-first-order plot was excellently linear. Thus, the rate should be first order in $NaCry^+$. Therefore, the rate law is given by eq 2, where k_0 is the conditional

$$-d[NaCry^+]/dt = k_0[NaCry^+] \tag{2}$$

first-order rate constant. At various concentrations of DCA, k_0 was determined as shown in Figure 2. The plot of k_0 vs the total concentration of DCA (C_{DCA}) levels off with increasing C_{DCA}. This implies that the dissociation of $NaCry^+$ by dichloroacetic acid is expressed by Scheme I, as already shown by Cox et al.[6]

Scheme I

$$\mathrm{NaCry^+} \underset{k_{f1}}{\overset{k_{d1}}{\rightleftharpoons}} \mathrm{Na^+ + Cry}$$

$$\mathrm{Cry + Hdca} \xrightarrow{k_{DCA}} \mathrm{CryH^+ + dca^-}$$

The stability constant of the complex is very large,[6] and the protonation reaction of the free cryptand is very fast.[6] Therefore, we can safely apply the stationary-state approximation to the concentration of the free cryptand, [Cry]. The dissociation rate law is given by eq 3. Then k_0 is expressed by eq 4. The plot

$$-d[NaCry^+]/dt = k_{DCA}k_{d1}[Hdca][NaCry^+]/(k_{f1}[Na^+] + k_{DCA}[Hdca]) \tag{3}$$

$$k_0 = k_{DCA}k_{d1}[Hdca]/(k_{f1}[Na^+] + k_{DCA}[Hdca]) \tag{4}$$

should level off with increasing C_{DCA}, provided that the concentration of sodium ion is kept low. This was in fact corroborated, as is apparent from Figure 2. The reciprocal of k_0 is given in eq 5. Therefore, the dissociation rate constant k_{d1} should be obtained

$$1/k_0 = k_{f1}[Na^+]/k_{d1}k_{DCA}[Hdca] + 1/k_{d1} \tag{5}$$

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(12) Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 2070 and references therein.

(13) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 2564.

(14) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1986**, *25*, 2898.

(15) Ishihara, K.; Funahashi, S.; Tanaka, M. *Rev. Sci. Instrum.* **1982**, *53*, 1231.

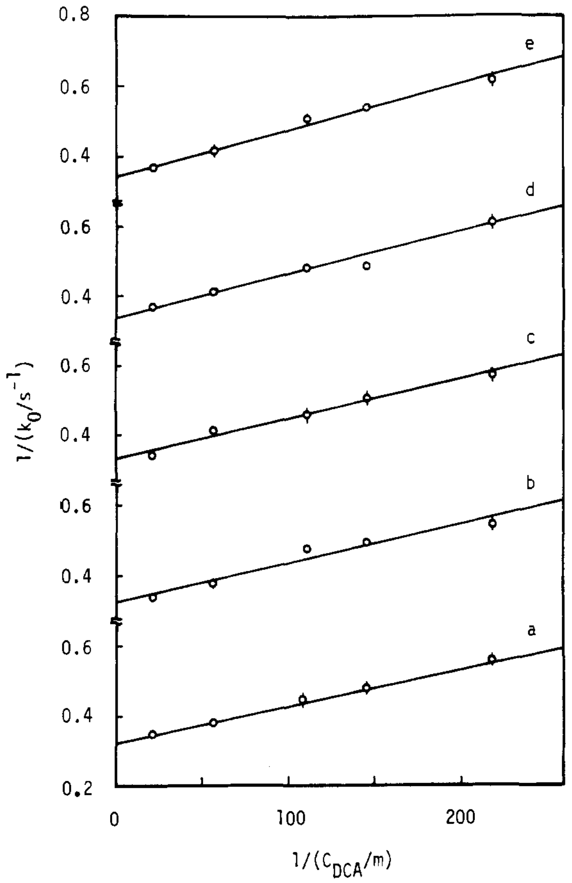

Figure 3. Plot of $1/k_0$ vs $1/[Hdca]$ in Me_2SO at 40 °C and at various pressures. P/MPa = 0.1 (a), 20 (b), 39 (c), 59 (d), 78 (e); $C_{Cry} = 4.4 \times 10^{-5}$ *m*; $C_{NaClO_4} = 9.0 \times 10^{-4}$ *m*.

from the intercepts of the plots of k_0^{-1} either against $[Na^+]$ at constant [Hdca] or against $[Hdca]^{-1}$ at constant $[Na^+]$. Both reciprocal plots were in fact nicely linear. The latter plot was used to estimate the values of k_{d1} at various pressures (Figure 3) and temperatures (Figure S1 and Table SII in supplementary material). The activation parameters are summarized in Table I.

The reaction volume (ΔV°) for the formation of $NaCry^+$ was determined dilatometrically to be $\Delta V^\circ = 3.3 \pm 0.4$ cm^3 mol^{-1}.[16] With knowledge of the ΔV° value, the activation volume ($\Delta V_{f1}^{\ddagger}$) for the forward reaction and the activation volume ($\Delta V_{DCA}^{\ddagger}$) for the protonation reaction of the cryptand were estimated from the pressure dependence of the slope of the plot k_0^{-1} vs $[Hdca]^{-1}$. The obtained values are $\Delta V_{f1}^{\ddagger} = 5.4 \pm 1.1$ cm^3 mol^{-1} and $\Delta V_{DCA}^{\ddagger} = -11.1 \pm 2.6$ cm^3 mol^{-1}.

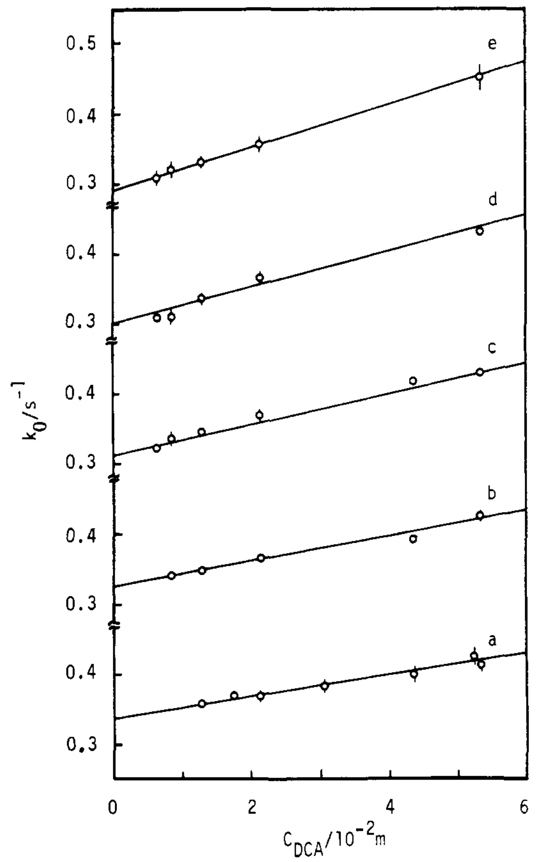

Figure 4. Acid concentration dependence of k_0 in DMF at 25 °C and at various pressures. P/MPa = 0.1 (a), 49 (b), 98 (c), 147 (d), 196 (e). $C_{Cry} = 1.7 \times 10^{-5}$ *m*; $C_{NaClO_4} = 3.3 \times 10^{-4}$ *m*.

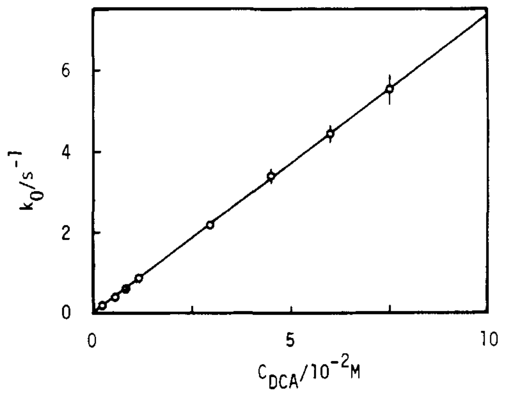

Figure 5. Acid concentration dependence of k_0 in MeCN at 25 °C. $C_{Cry} = 1.6 \times 10^{-5}$ M; $C_{NaClO_4} = 2.6 \times 10^{-4}$ M.

In *N,N*-Dimethylformamide. As shown in Figure 4, plots of k_0 vs C_{DCA} lie along the straight line with an intercept. Therefore, we should take the acid-dependent path (k_{d2} path) into consideration, as shown in Scheme II. According to Scheme II, the conditional first-order rate constant k_0 is given by eq 6. Under

$$k_0 = \frac{(k_{d1}k_{DCA} + k_{d2}k_{f1}[Na^+])[Hdca] + k_{d2}k_{DCA}[Hdca]^2}{k_{f1}[Na^+] + k_{DCA}[Hdca]} \qquad (6)$$

our experimental conditions, the first term in the denominator is negligible against the second; i.e., $k_{f1}[Na^+] \ll k_{DCA}[DCA]$, and $k_{d2}k_{f1}[Na^+]$ is much lower than $k_{d1}k_{DCA}$. Thus, eq 6 can be rewritten as eq 7.

$$k_0 = k_{d1} + k_{d2}[Hdca] \qquad (7)$$

Scheme II

$$NaCry^+ \underset{k_{f1}}{\overset{k_{d1}}{\rightleftharpoons}} Na^+ + Cry$$

$$Cry + Hdca \xrightarrow{k_{DCA}} CryH^+ + dca^-$$

$$NaCry^+ + Hdca \xrightarrow{k_{d2}} Na^+ + CryH^+ + dca^-$$

Values of k_{d1} and k_{d2} were determined at various temperatures (Figure S2 and Table SIII in supplementary material) and pressures (see Figure 4), and the activation parameters were evaluated as given in Table I.

In Acetonitrile. As is apparent from Figure 5, plots of k_0 vs C_{DCA} gave a straight line without intercept. Therefore, only the acid-dependent path (the k_{d2} path given in Scheme II) should be operative. Hence, it follows that under the present experimental conditions, besides the relations mentioned above, the relation $k_{d1} \ll k_{d2}[Hdca]$ holds. Consequently, eq 7 is reduced to eq 8.

$$k_0 = k_{d2}[Hdca] \qquad (8)$$

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[16] Funahashi, S.; Sengoku, K.; Amari, T.; Tanaka, M. *J. Solution Chem.*, in press.

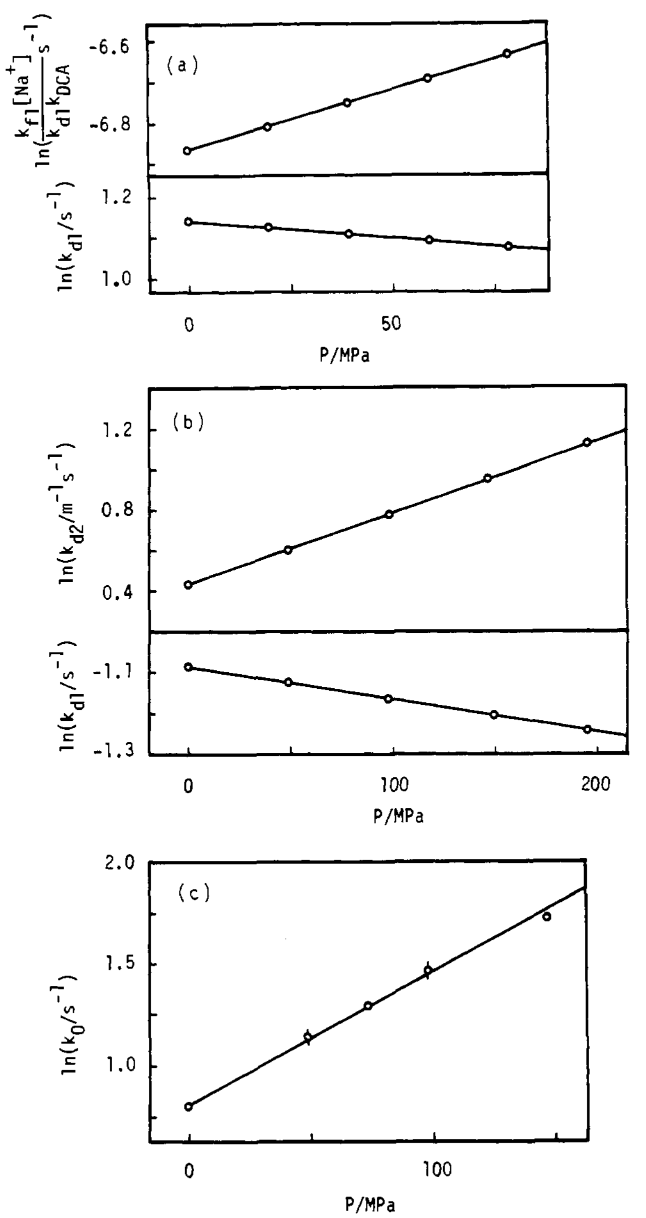

Figure 6. Pressure dependence of rate constants: (a) in Me$_2$SO at 40 °C; (b) in DMF at 25 °C; (c) in MeCN at 25 °C. $C_{\mathrm{HDca}} = 3.03 \times 10^{-2}$ M; $C_{\mathrm{Cry}} = 1.5 \times 10^{-5}$ M; $C_{\mathrm{NaClO_4}} = 3.5 \times 10^{-4}$ M.

After confirming that all activation volumes were pressure independent, we obtained kinetic parameters by means of either linear or nonlinear least-squares fitting to eq 5, 7, and 8. The pressure dependences of k_{d1} and $k_{f1}k_{d1}^{-1}k_{\mathrm{DCA}}^{-1}[\mathrm{Na}^+]$ in Me$_2$SO, of k_{d1} and k_{d2} in DMF, and of k_{d2} in MeCN are shown in Figure 6, and the obtained activation parameters are listed in Table I.

Discussion

Cox et al. have reported stability constants[17] of cryptates of metal ions and rate constants for dissociation of a variety of alkali-metal cryptates in several solvents.[6] Contrary to their findings that the rates were independent of both acid and metal ion concentrations in Me$_2$SO,[6] in the present case the dissociation rates in Me$_2$SO increased with increasing acid concentration, with the rate constants leveling off to a constant value at higher DCA concentrations in Me$_2$SO, as shown in Figure 2. However, we observed that the rate in DMF increased with increasing C_{DCA} in contrast with the reported results,[6] while their k_{d1} values in DMF and Me$_2$SO agree with ours.

According to the literature,[18,19] the order of solvent basicity is MeCN ≪ DMF < Me$_2$SO. In other words, the degree of interaction of Me$_2$SO with acids is high,[19] whereas the interaction between MeCN and acids is very weak. Judging from the pK_a value of 7.2 for dichloroacetic acid in DMF,[18] DCA is essentially undissociated in DMF under our experimental conditions. And the same is true in Me$_2$SO because DCA would have much the same pK_a in Me$_2$SO as in DMF, provided that DCA behaves just like acetic acid (pK_a of acetic acid is 11.1 in DMF and 11.4 in Me$_2$SO).[18] Moreover, it is obvious that DCA would exist as an undissociated form in MeCN.

The cryptates have a possibility of existing as three conformations:[20] out–out (o,o), in–out (i,o), and in–in (i,i). In the (o,o) form the lone pairs on the bridgehead-nitrogen atoms are directed away from the cavity, and this would not be expected in the metal complex appreciably.[1] The (i,i) complex, in which both lone pairs are directed inside the cavity, should be the most stable thermodynamically, and in fact, complexes have been shown to have this conformation in the solid state.[21] According to X-ray crystallographic analysis of sodium cryptate(2,2,1),[22] the sodium ion is in the midst of the cage, or cavity, of the ligand. The cage has to be opened when the sodium ion dissociates in such a circumstance. Molecular modeling shows that the oxygen atoms in the bridges can rotate outward from the cavity,[4] and this may form the basis of the initial interaction of the cation in the cavity with the solvent. The bonds between the cryptand and sodium ion are essentially electrostatic, having no intricacy as in the transition elements. It seems most likely that the complex formation and dissociation of the sodium ion occur not through the smaller 15-membered ring of the cryptand but through the larger 18-membered ring, judging from both the cavity size of the cryptand and the ionic radius of the sodium ion.

In the mechanism for dissociation of metal cryptates in water proposed by Cox and Schneider,[1] there is a preceding conformational change that gives the (i,o) complex, leaving one of the lone pairs on nitrogen free to be trapped by H$^+$. Since a hydrogen bond may cause the cryptand to open its cage without conformational change, it seems to be rather difficult to adopt the idea that dissociation proceeds through the (i,o) form. In other words, it would be much more difficult for the cryptand that contains the sodium ion in its cavity to change its conformation (i.e., from the (i,i) complex to the (i,o)) than for the cryptand without the sodium ion. Since the transition state for the forward reaction should be the same as for the backward reaction, it follows that the reactions would occur only through the (i,i) form.

If 1 mol of sodium ion dissociates perfectly, it is anticipated that the partial molar volume of the system will decrease by the partial molar volume of the sodium ion, e.g., by −4 cm^3 mol^{-1} in Me$_2$SO[23] due to electrostriction. However, the dissociation in the transition state actually would be imperfect, and it is impossible for the sodium ion in the cavity of the cryptand to be totally shielded from the environment; the cryptates behave like charged species.[24] Therefore, the volumes of activation for the acid-independent path, k_{d1}, imply that, in the transition state, each volume increment caused by opening the cage would be compensated for insufficiently by a volume decrement owing to electrostriction. On the other hand, in the case of the acid-assisted path, k_{d2}, a hydrogen bond would be formed between one of the lone pairs of the cryptand and dichloroacetic acid, and charge localization

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(17) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1384.

(18) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1911.

(19) Barrette, W. C., Jr.; Johnson, H. W., Jr.; Sawyer, D. T. *Anal. Chem.* **1984**, *56*, 1890.

(20) Lehn, J. M.; Sauvage, J. P.; Dietrich, B. *J. Am. Chem. Soc.* **1970**, *92*, 2916.

(21) Metz, B.; Moras, D.; Weiss, R. *Chem. Commum.* **1970**, 217; *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 388.

(22) Mathieu, F.; Metz, B.; Moras, D.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4412.

(23) Relative to conventional partial molal volume of H$^+$(aq) = 0: Marcus, Y. *Ion Solvation*; Wiley: New York, 1985; p 174. Millero, F. J. *Chem. Rev.* **1971**, *71*, 147.

(24) Morel-Desrosiers, N.; Morel, J.-P. *J. Am. Chem. Soc.* **1981**, *103*, 4743.

would occur in dichloroacetic acid in the transition state. An increase in electrostriction due to charge development causes a fairly large volume decrease. The electrostriction around dichloroacetate was estimated as −8 $\text{cm}^3\ \text{mol}^{-1}$ in DMF and −10 $\text{cm}^3\ \text{mol}^{-1}$ in MeCN, according to the modified Drude–Nernst expression $0.5N(2e)^2(r + r')^{-1}\epsilon^{-2}(\partial\epsilon/\partial P)_T$ with the values of $r' =$ 68 pm[25] and $(\partial\epsilon/\partial P)_T = 3.406 \times 10^{-2}\ \text{MPa}^{-1}$[26] for DMF and r' = 81 pm[25] and $(\partial\epsilon/\partial P)_T = 4.102 \times 10^{-2}\ \text{MPa}^{-1}$[27] for MeCN. Since a proton should be solvated more extensively in a basic solvent like DMF than in a less basic solvent such as MeCN, the electrostriction by a proton should be more negative in MeCN than in DMF. Then, if the partial charge separation of DCA is assumed to occur in the activated state for the acid-assisted path, the volume of activation for the dissociation of sodium cryptate may thus be interpreted qualitatively.

Activation parameters for the k_{d1} path in Me_2SO and DMF are quite similar to each other. This suggests that the dissociations proceed in much the same manner in both solvents.

The dissociation of sodium cryptate proceeds through two parallel paths: the solvent path (i.e., acid-independent path) and the acid-assisted path. In Me_2SO, which is the most basic solvent, the solvent path prevails, while in MeCN, which is the least basic solvent, the solvent path is not appreciable and only the acid-assisted path is observed. In DMF, which is moderately basic, both the solvent path and the acid-assisted path are operative in the dissociation of the sodium cryptate.

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Supplementary Material Available: Observed rate constants at various concentrations (Tables SI and SII), temperatures (Tables SIII–SV and Figures S1 and S2), and pressures (Tables SVI–SVIII) (10 pages). Ordering information is given on any current masthead page.

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(25) Tanaka, N.; Ogata, T. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 511.
(26) Moriyoshi, T., unpublished results.
(27) Srinivasan, K. R.; Kay, R. L. *J. Solution Chem.* **1977**, *6*, 357.

Contribution from the School of Chemical Sciences,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Synthesis, Structure, and Reactivity of Organoruthenium Derivatives of Tetrathio- and Tetraselenometalates

Kevin E. Howard, Thomas B. Rauchfuss,* and Scott R. Wilson

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We describe the preparation of a series of organoruthenium tetrathiometalates and tetraselenometalates of the general formula $(RC_5H_4)_2Ru_2L_2ME_4$ (R = H, CH_3; L = PR_3, RNC, CO; M = W, Mo; E = S, Se). The compound $Cp_2Ru_2(PPh_3)_2WS_4$ (**1**) reacts with PMe_3 to give $Cp_2Ru_2(PMe_3)_2WS_4$ and with isocyanides to give $Cp_2Ru_2(RNC)_2WS_4$ (R = *t*-Bu, Me, $C_6H_5CH_2$). Only *one* of the PPh_3 ligands in **1** is substituted by an excess of carbon monoxide to give $Cp_2Ru_2(PPh_3)(CO)WS_4$. The kinetics of the ligand substitution of **1** by *t*-BuNC was examined by using ^{1}H NMR spectroscopy. The rate of the first substitution was found to be independent of [*t*-BuNC], the first-order rate constant being $5.6 \times 10^{-4}\ \text{s}^{-1}$. The rate of the first substitution was found to be approximately 4 times that of the second. All of the compounds studied undergo reversible or quasi-reversible oxidations. On the basis of the measured $E_{1/2}$ values, the donor powers of the chalcogenometalates are ranked as follows: $MoSe_4^{2-} > WSe_4^{2-} > MoS_4^{2-} > WS_4^{2-}$. The compound $Cp_2Ru_2(MeNC)_2WS_4$ crystallizes in the monoclinic space group $I2/a$ with $a = 13.840$ (13) Å, $b = 12.234$ (9) Å, $c = 14.224$ (11) Å, $\beta = 105.48$ (7)°, $V = 2321$ (3) Å^3, and $Z = 4$ and refined to $R = 0.038$ and $R_W = 0.049$. The short Ru–W distances (2.870 (2) Å) and the acute Ru–S–W angles (77° average) are indicative of metal–metal bonding. The reactivity, redox properties, and structures of these compounds are discussed in the context of the donation of t_{2g} electrons on ruthenium to tungsten.

Introduction

The tetrathiometalates have been employed as ligands for transition metals for the past 20 years.[1] Interest in these coordination compounds has expanded rapidly because of evidence or assumptions that certain thiometalate complexes are structurally related to catalytic sites in both nitrogen-fixing enzymes[2-4] and industrial hydrotreating catalysts.[5] More fundamental incentives for interest in this area follow from the electronic novelty[6,7] of these complexes vis-à-vis other dithio chelates.

Tetrathiometalate complexes are derivatives of MoS_4^{2-}, WS_4^{2-}, VS_4^{3-},[8-10] and ReS_4^{-}.[10,11] The latter two anions have been studied only recently as have tetraselenometalate complexes.[12] The majority of tetrathiometalate complexes are of the type $L_2M'(MS_4)$[13] or $M'(MS_4)_2{}^Z$[6,14,15] (many of the binary molybdenum

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(1) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *16*, 934.
(2) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455.
(3) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201.
(4) Zumft, W. G. *Eur. J. Biochem.* **1978**, *91*, 345.
(5) Pan, W.-H.; Johnston, D. C.; McKenna, S. T.; Chianelli, R. R.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *Inorg. Chim. Acta* **1985**, *97*, L17.
(6) Bowmaker, G. A.; Boyd, P. D. W.; Sorrenson, R. J.; Reed, C. A.; McDonald, J. W. *Inorg. Chem.* **1985**, *24*, 3.
(7) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K.; Zvagulis, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1065.
(8) Kovacs, J. A.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 702, 711. Carney, M. J.; Kovacs, J. A.; Zhang, Y.-P.; Papaefthymiou, G. C.; Spartalian, K.; Frankel, R. B.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 719.
(9) Halbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437.
(10) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635.
(11) Müller, A.; Krickmeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *26*, 990.
(12) Wardle, R. W. M.; Chau, C.-N.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1859.

0020-1669/88/1327-1710$01.50/0