V. Acknowledgments

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Kinetics of Complexation of Macrocyclic Polyethers with Sodium Ions by Nuclear Magnetic Resonance Spectroscopy. II. Solvent Effects

E. Shchori, J. Jagur-Grodzinski,* and M. Shporer

Contribution from the Weizmann Institute of Science,
Rehovot, Israel. *Received January 4, 1973*

Abstract: The kinetics of complexation of sodium ions (or of its ion pairs) with dicyclohexyl-18-crown-6 (DCC) in methanol and with dibenzo-18-crown-6 (DBC) in DMF, methanol, and dimethoxyethane has been investigated using ^{23}Na nmr. The influence of substituents in the aromatic rings of DBC on the decomplexation rates was also studied. Kinetic data were derived from pulse nmr measurements of the longitudinal relaxation rates of solvated sodium in the presence of complexed species. Analysis of the results indicates that the dominant exchange mechanism involves, in all investigated systems, the decomplexation step $Na^+(X^-)$, crown $\rightleftarrows$ $Na^+(X^-)$ + crown. The energy of activation of the decomplexation of DBC and of its derivatives was found to be nearly constant (12.6 ± 1.0 kcal/mol) in all investigated solvents. The coincidence of this value with the energy of activation of a conformational rearrangement of the macrocyclic ring has been discussed. The relatively low energy of activation of decomplexation of DCC (8.3 kcal/mol) has been attributed to the flexibility of the macrocyclic ring in DCC. The values of the rate constants of complexation and of the rate constants of decomplexation at 25° were found, in all investigated systems, to be within the range of 2×10^7–3×10^8 M^{-1} sec^{-1} and of 10^4–2×10^5 sec^{-1}, respectively. The latter decrease and the former increase in the order of increasing stabilities of the complexes.

In the first part of the study,[1] the application of nmr spectroscopy of cations for the kinetic investigation of their complexation with macrocyclic polydentate ligands had been discussed. A detailed investigation of the complexation of a macrocyclic polyether dibenzo-18-crown-16 (DBC) with sodium ions in the *N,N*-dimethylformamide (DMF) solutions was described. The mechanism of the exchange reaction was elucidated and the rate constants of the decomplexation were calculated on the basis of a quantitative analysis of the line width of the ^{23}Na nmr signal at various temperatures and concentrations. The thermodynamic constants of the system were evaluated from conductometric measurements.

This work has now been extended and the complexation of DBC and of its derivatives was studied in DMF, methanol, and dimethoxyethane (DME). The kinetics and the thermodynamics of complexation of DBC with sodium ions could be thus compared in solvents characterized by different solvating power, and the effect of substituents on the complexing ability of DBC could be evaluated.

While in the previously reported study[1] relaxation rates were derived from the line width of the ^{23}Na absorption spectra, in the present investigation longitudinal relaxation rates directly determined by a pulse technique have been used for the kinetic analysis. Thus, accuracy of the results and the experimentally accessible concentration range could be greatly enhanced.

Experimental Section

Dibenzo-18-crown-6 (DBC) was prepared and purified as previously described.[1]

The two isomers of dicyclohexyl-18-crown-6 (DCC) (Aldrich, Practical) were separated chromatographically according to the procedure given by Frensdorff.[2] Isomer B [DCC (IB)], mp 65–67°, was used in our experiments.

cis-4,4′-Dinitrodibenzo-18-crown-6 (NDBC) was prepared by nitration of DBC. DBC (37 g) was dissolved in 800 ml of chloroform and 700 ml of acetic acid. Nitric acid (250 ml, 70%) was slowly added to this solution. The temperature was kept constant at 20 ± 5°. After 24 hr the reaction mixture was washed with water and aqueous Na_2CO_3. The residual light yellow solid obtained after evaporation of chloroform consisted of the two isomers of NDBC.[3] The crude product (10 g) was refluxed with 400 ml of ethylene glycol monomethyl ether, and the hot solution was filtered from the insoluble trans isomer and twice recrystallized from this solvent. The thus obtained cis isomer had a mp = 200–201°.

cis-4,4′-Diaminodibenzo-18-crown-6 (AmDBC) was prepared by reduction of the nitro derivative. Ethylene glycol monomethyl ether (300 ml) was mixed with 5.2 g of *cis*-NDBC. The reduction

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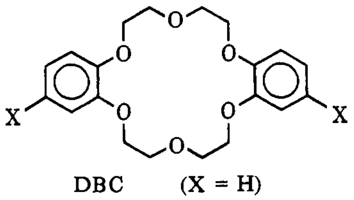
(1) E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *J. Amer. Chem. Soc.*, 93, 7133 (1971).

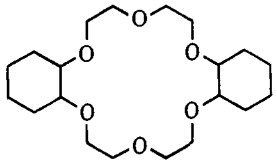
(2) H. K. Frensdorff, *ibid.*, 93, 4684 (1971).

(3) W. M. Feigenbaum and R. H. Michel, *J. Polym. Sci., Part A-1*, 9, 817 (1971).

was started upon addition of 0.6 g of 10% Pd/C catalyst followed by the addition of 30 ml of hydrazine hydrate. After 30 min of reflux the reaction mixture was filtered and evaporated. The pure product obtained after recrystallization from ethanol had mp 177–178°.



DBC (X = H)
NDBC (X = NO_2)
AmDBC (X = NH_2)



DCC

Methanol (Frutarom, analytical grade) was distilled from sodium methoxide.

DMF (Fluka, Puriss) was dried over molecular sieves 4A (BDH). It had a specific conductance of (0.5–0.8) × 10^{-6} ohm^{-1} cm^{-1}.

Dimethoxyethane (DME) was refluxed over potassium metal and fractionated with a 3-ft Vigreux column. It had a specific conductance of (0.5–2.0) × 10^{-9} ohm^{-1} cm^{-1}.

Sodium thiocyanate (Baker, reagent grade), sodium tetraphenylboron ($NaBPh_4$) (Fluka, Puriss), and lithium thiocyanate (Fluka, Practical) were dried under high vacuum (10^{-4} mm) at 90°.

All solutions were prepared at 25°. Changes in volume were taken into account in the calculation of the molar concentrations at other temperatures.

Bruker pulsed nmr spectrometer B-KR 322S was used for T_1 measurements at 15.8 MHz. The following procedure was adopted. Pairs of pulses, 180 and 90°, were applied, and the free induction decay following the 90° pulse was time averaged, using a Hewlett-Packard Signal Analyzer 5480. In order to allow for a nearly complete decay of the fast component of magnetization of the complexed species, the intensity of the decaying signal, following the 90° pulse, was measured after a time lag of 200–600 μsec. Values of T_1 were calculated from semilog plots of the measured intensities as a function of the time interval separating the 180 and the 90° pulse.

This pulse technique which involves the time averaging is much more convenient and accurate than the technique based on line-width measurements. It also enables much better resolution of the signal. Thus, DME solutions, in which relaxation rates of the complexed and solvated sodium differ only by a factor of 9, could be accurately analyzed.

Samples (1 ml) contained within 10-mm o.d. thin wall glass tubes were used in the experiments. The temperature was controlled with a Bruker B-ST 100/700 temperature control unit and was monitored using a thermocouple, housed in a thin capillary, inserted into the solution.

Kinetic Measurements. It was previously shown (*cf.* ref 1) that the lifetime (τ_A) of a solvated sodium ion in the presence of a macrocyclic ligand, competing with the solvent for its solvation, may be calculated from the relaxation rate of ^{23}Na nuclei ($1/T_2$) in such an environment and from the relaxation rate ($1/T_{2A}$) in the absence of the ligand. Since the dominant mechanism of the ^{23}Na relaxation in such diamagnetic systems is the modulation of the quadrupole interaction *via* molecular tumbling, the values of the longitudinal and the transversal relaxation rates should be identical in the extreme narrowing limit. This has been shown to be the case for both solvated and complexed sodium.[1] In the absence of a chemical shift between the two species, the effect of chemical exchange is also expected to be the same on both relaxation times T_1 and T_2. Comparison of $1/T_2$ derived from the line width of the nmr absorption spectra in DMF with those of $1/T_1$ determined directly by the pulse technique shows that this is indeed the case (see Figure 1).

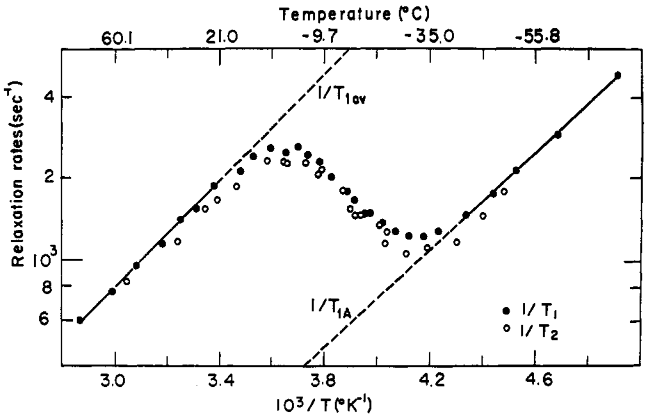


Figure 1. Semilog plots of $1/T_1$ and $1/T_2$ for ^{23}Na *vs.* the reciprocal absolute temperature for a solution containing 0.57 *M* NaSCN and 0.2 *M* DBC in DMF. T_2 was determined from the line width at 8.1 MHz; T_1 was determined by the pulse method at 15.8 MHz.

Though eq 7 given in ref 1 was derived for the limiting case of a negligible chemical shift between the exchanging species, the validity of an analogous equation based on the values of $1/T_1$ is not restricted by such a condition. (For the detailed analysis of the decay of magnetization in pulse experiments, see ref 4.) Substitution of the transverse relaxation rates used in eq 7 of ref 1 by longitudinal relaxation rates yields

$$1/\tau_A = \frac{(1/T_{1B} - 1/T_1)(1/T_1 - 1/T_{1A})P_B}{(1/T_{1av} - 1/T_1)} \tag{1}$$

where

$$1/T_{1av} = P_A/T_{1A} + P_B/T_{1B} \tag{1a}$$

and P_A and P_B are molar fractions of the solvated and complexed sodium ions, respectively.

$1/T_{1av}$ is equal to $1/T_1$ at the high-temperature range, when $1/\tau_A \gg 1/T_1$. Extrapolation of $1/T_{1av}$ (*cf.* Figure 1) to lower temperatures yields values used in eq 1 for the calculation of $1/\tau_A$ in the temperature range amenable to the kinetic interpretation, at which the rate of exchange and values of $1/T_1$ are of the same order of magnitude. Values of $1/T_{1B}$ are calculated from eq 1a. The fraction (P_B) of the sodium ions complexed with the ligand can be calculated from the initial concentrations of the reagents if the equilibrium constant of complexation is known. In the investigated systems, $P_B \simeq [\text{crown}]_0/[\text{Na}^+]_0$.

Determinations of $1/T_1$ were carried out for 0.1–1.0 *M* solutions of NaSCN in methanol in the presence of DBC and DCC and for 0.5 *M* $NaBPh_4$ solutions of DBC in dimethoxyethane. Experiments with the cis isomers AmDBC and NDBC were conducted in 0.29–0.93 solutions of NaSCN in DMF. Some runs were performed at a constant ionic strength of $I \simeq 1$ maintained by the addition of LiSCN.

Typical values of $1/T_1$, $1/T_{1A}$, and $1/T_{1B}$ at −13° are given in Table I. At this temperature, $1/\tau_A$, and $1/T_1$ are of the same order of magnitude for all investigated systems, the only exception being the DCC solution in methanol, for which a fast exchange still prevails at −13°. As may be seen from the ratio T_{1A}/T_{1B} (*cf.*

Table I. The Observed Relaxation Rates of ^{23}Na and the Extrapolated Values of Relaxation Rates for Solvated and Complexed Species at −13°[a]

	DMF			Methanol		DME
	DBC[b]	NDBC	AmDBC	DBC	DCC[c]	DBC
$1/T_1$ (sec^{-1})	1700	3100	2500	470	1230	1100
$1/T_{1A}$ (sec^{-1})	300	365	290	93	98	550
$1/T_{1B}$ (sec^{-1})	7850	16300	12500	5000	2220	4900
T_{1A}/T_{1B}	26	45	43	54	23	9

[a] 0.29 *M* NaSCN + 0.1 *M* polyether in DMF and methanol. 0.46 *M* $NaBPh_4$ + 0.24 *M* DBC in dimethoxyethane. [b] From line-width measurements.[1] [c] A 0.15 *M* solution of DCC was used in this experiment.

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(4) (a) D. E. Woessner, *J. Chem. Phys.*, 35, 41 (1961); (b) D. E. Woessner and J. R. Zimmerman, *J. Phys. Chem.*, 67, 1590 (1963).

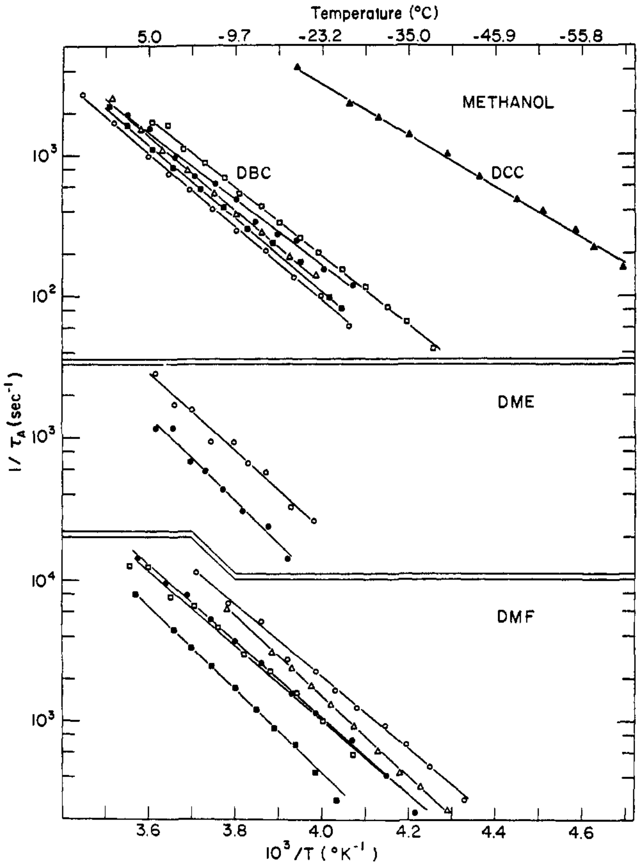

Figure 2. Arrhenius plots of $1/\tau_A$. Methanol: (□) $[NaSCN]_0$ = 0.29 *M*, $[DBC]_0$ = 0.1 *M*; (●) $[NaSCN]_0$ = 0.145 *M*, [LiSCN] = 0.82 *M*, $[DBC]_0$ = 0.06 *M*; (○) $[NaSCN]_0$ = 0.32 *M*, [LiSCN] = 0.68 *M*, $[DBC]_0$ = 0.1 *M*; (△) $[NaSCN]_0$ = 0.58 *M*, [LiSCN] = 0.42 *M*, $[DBC]_0$ = 0.2 *M*; (■) $[NaSCN]_0$ = 1.00 *M*, $[DBC]_0$ = 0.3 *M*; (▲) $[NaSCN]_0$ = 0.28 *M*, $[DCC]_0$ = 0.15 *M*. DME: (●) $[NaBPh_4]_0$ = 0.48 *M*, $[DBC]_0$ = 0.15 *M*; (○) $[NaBPh_4]_0$ = 0.46 *M*, $[DBC]_0$ = 0.24 *M*. DMF: (○) $[NaSCN]_0$ = 0.29 *M*, $[NDBC]_0$ = 0.1 *M*; (●) $[NaSCN]_0$ = 0.29 *M*, [LiSCN] = 0.67 *M*, $[NDBC]_0$ = 0.1 *M*; (□) $[NaSCN]_0$ = 0.55 *M*, [LiSCN] = 0.37 *M*, $[NDBC]_0$ = 0.2 *M*; (■) $[NaSCN]_0$ = 0.93 *M*, $[NDBC]_0$ = 0.2 *M*; (△) $[NaSCN]_0$ = 0.29 *M*, $[AmDBC]_0$ = 0.1 *M*.

Table I), the substitution in the aromatic ring further disturbs the symmetry of the electric field around the sodium ion in the complex. Low values of $1/T_{1A}$ in methanol make measurements in this solvent more accurate and permit a considerable extension of the experimentally available concentration range.

Arrhenius plots of values of $1/\tau_A$ calculated from eq 1 yield apparent energies of activation of decomplexation for the investigated systems (see Figure 2 and Table II).

Surprisingly enough, a change of solvent does not seem to affect significantly the apparent energy of activation of the decomplexation of the sodium-DBC complex. The energy of activation of decomplexation of the DCC complex seems to be, however, lower than for DBC and its derivatives.

Discussion

The basicity of four oxygens in the macrocyclic ring of DBC may be affected by introduction of electron-withdrawing or electron-donating substituents into its aromatic rings. Thus, the complexing power of DBC should be, in principle, affected by such substituents. The strongly electrophilic NO_2 group seems to exert, indeed, such influence. Comparison of the respective equilibrium constants of complexation of sodium ions, in DMF at 25° (see Table III), reveals that the dinitro derivative NDBC is five times less effective than the unsubstituted DBC. The rate of removal of sodium from the complex is even more strongly affected by the substituent. On the other hand, the complexing powers of DBC and of its diamino derivate AmDBC are nearly identical in DMF. The enthalpy of the complexation is also unaffected by this strongly electron-donating substituent, while the rate of decomplexation is even faster for AmDBC than for DBC. Such anomalous behavior may, perhaps, be attributed to conformational changes in the macrocyclic ring due to hydrogen-bonding interactions involving the two amino groups.

Table II. Apparent Activation Energies of Decomplexation and Reciprocal Mean Lifetimes of Sodium Ions at −13°

	$[Na^+]_0$,[a] *M*	$[crown]_0$, *M*	$1/\tau_A$ (−13°), sec^{-1}	E_{app}, kcal/mol
DBC in DMF	0.57	0.20	1800[b]	12.0
			1950[c]	12.7
DBC in methanol	0.098	0.04	550	12.4
	0.29	0.10	450	11.2
	0.15[d]	0.06	375	10.8
	0.32[d]	0.10	230	12.0
	0.58[d]	0.20	300	12.1
	1.00	0.30	278	11.75
DBC in DME	0.48	0.15	255	13.8
	0.46	0.242	585	12.8
NDBC in DMF	0.29	0.10	5000	11.75
	0.29[d]	0.10	2700	12.5
	0.55[d]	0.20	2500	12.1
	0.93	0.20	1190	13.6
AmDBC in DMF	0.29	0.10	4000	13.1
DCC in methanol	0.28	0.15	6000[e]	8.3

[a] SCN as a counteranion in methanol and DMF. BPh_4^- as a counteranion in DME. [b] From line-width measurements.[1] [c] From T_1 measurements. [d] Solutions maintained at a constant ionic strength of about 1 *M* by addition of LiSCN. [e] Extrapolated value.

The effect of solvent on the equilibrium constants of complexation is very pronounced. The macrocyclic ring replaces solvent molecules in the solvation shell of the ion, and the solvent must be regarded as a reagent participating in the reaction. The values reported in the literature[5-7] of the thermodynamic parameters of complexation of sodium ions with DCC with DBC and with its derivatives in DMF, methanol, DME, and THF are summarized in Table III. Contrary to the large difference in the stability of the DBC complexes in various solvents, the energy of activation of their decomplexation seems to be insensitive to the nature of the solvent medium. Two mechanisms may, in principle, contribute to the overall exchange detected by ^{23}Na nmr

$$A + B^* \overset{k_1}{\rightleftharpoons} {}^*A + B \qquad (I)$$

$$A + \text{crown} \underset{k_{-2}'}{\overset{k_2}{\rightleftharpoons}} B + n(\text{solvent}) \qquad (II)$$

where A and B denote solvated sodium and complex, respectively.

Accordingly, the general expression for the mean lifetime of solvated species $1/\tau_A = k_1[B] + k_{-2}'[\text{solvent}]^n \cdot [B]/[A]$ may be used to test the mechanism of the exchange on the basis of the dependence of $1/\tau_A$ on the

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(5) H. K. Frensdorff, *J. Amer. Chem. Soc.*, 93, 600 (1971).

(6) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, 174, 459 (1971).

(7) E. Shchori and J. Jagur-Grodzinski, *Isr. J. Chem.*, in press.

Table III. Thermodynamic and Kinetic Parameters for Complexes of Sodium Ions (or Ion Pairs) in DMF, Methanol, Dimethoxyethane and THF

Crown	Solvent	$K^{25°}$, M^{-1}	ΔH, kcal/mol	ΔS, eu	E_a, kcal/mol	$k_{-2}^{-13°}$,[a] sec^{-1}	$k_{-2}^{25°}$, sec^{-1}	$k_2^{25°}$, M^{-1} sec^{-1}
DBC[b]	DMF	600	−6.0	−7	12.6	4800	1×10^5	6×10^7
NDBC	DMF	115[c]			12.5	9200	2.0×10^5	2.3×10^7
AmDBC	DMF	615[c]	−6.0[c]	−7	13.1	7600	1.9×10^5	1.2×10^8
DBC	Methanol	23000[d]			11.7	800	1.4×10^4	3.2×10^8
DCC (IB)	Methanol	4800[d]	−5.6[e]	−2	8.3		5.2×10^4	2.6×10^8
DBC	DME							
	free ions	5000[c]	−3.9[c]	+3.9				
	ion pairs	4500[c]	−3.4[c]	+5.4	13.3	540[f]	1.5×10^4[f]	6.5×10^7 [f]
MeDBC[g]	THF	$>2 \times 10^7$			12.5			

[a] For ionic strength $I = 0.3$. [b] From ref 1. [c] From ref 7. [d] From ref 5. [e] From ref 6. [f] Determined for 0.5 M $NaBPh_4$ solution. We estimate that in dilute solutions values of k_{-2} and k_2 are about 30% higher. [g] From ref 9.

concentrations of the reagents. Slopes and intercepts of plots of $1/\tau_A[B]$ *vs.* $1/[A]$ should yield values of $k_{-2} \equiv k_{-2}'[\text{solvent}]^n$ and k_1, respectively, if the activity of the solvent during such experiments is kept constant. This is achieved, by maintaining a constant ionic strength in the system, by addition of an inert salt.[1]

As may be seen from such plots, shown in Figure 3, the contribution of mechanism II to the overall exchange is predominant in all investigated systems. Taking into account the experimental accuracy, an upper limit may be set for the value of k_1^{DBC} in methanol at −13° as 250 M^{-1} sec^{-1} and for k_1^{DBC} in DME at −13° as 500 M^{-1} sec^{-1}. Obviously, the lifetime of solvated sodium is not significantly affected by the direct exchange mechanism I. Analogous behavior has recently been reported by Haynes,[8] who studied the exchange reaction between the macrocyclic nonactine and its potassium ion complex in a chloroform–methanol solvent mixture. Arrhenius plots of $1/\tau_A$ shown in Figure 2 yield, therefore, the energy of activation, E_a, of the decomplexation step. A value of E_a = 8.3 kcal/mol is thus derived for DCC in methanol. For all investigated complexes of DBC and its derivatives the experimentally determined values of E_a are constant within ±1 kcal, the average value being 12.6 kcal/mol. Interestingly enough, a nearly identical value of E_a = 12.5 kcal/mol was also reported[9] for the dimethyl-DBC, fluorenylsodium system in THF. Truter pointed out[10] that E_a = 12 kcal coincides with the activation energy required in a ring system for four trans to gauche conformational changes and that, according to her crystallographic studies, conformations of the uncomplexed DBC and of the DBC complexed with sodium differ by four dihedral angles.[11] Though the observed apparent constancy of E_a for DBC and its derivatives in the investigated solvents may be purely accidental, nevertheless one may consider the possibility that the energy barrier for the removal of sodium from DBC and its derivatives is, indeed, independent from the environment and is determined by the energy required for a conformation rearrangement of the complex.[12]

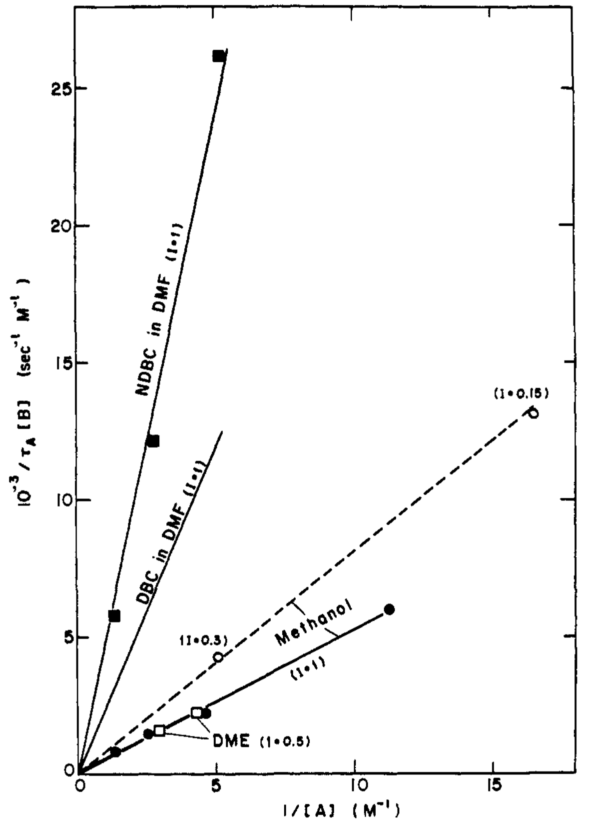

Figure 3. Plots of $1/\tau_A[B]$ *vs.* the reciprocal concentration of uncomplexed sodium salt (DBC in DMF from ref 1): (■) NDBC in DMF; (○), (●) DBC in methanol; (□) DBC in DME.

The following model may be considered to account for conformational changes leading to the removal of sodium from the DBC complex. Sodium ion is held by DBC due to electrostatic interactions with the participating dipoles, the resulting vector being zero. A conformational change, equipotential in respect to electrostatic ion dipole interactions (schematically represented in Figure 4), will disturb the equilibrium. The resulting vector A will pull the ion from its previous position and will bring it to its location in the transition state of the complex.

The difference of about 4 kcal/mol in the energy of activation of the decomplexation of the DCC and the

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[8] D. H. Haynes, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, **20**, 221 (1972).

[9] (a) K. H. Wong, G. Konizer, and J. Smid, *J. Amer. Chem. Soc.*, **92**, 666 (1970); (b) J. Smid, *Angew. Chem., Int. Ed. Engl.*, **11**, 112 (1972).

[10] M. R. Truter, private communication.

[11] (a) D. Bright and M. R. Truter, *Nature (London)*, **225**, 176 (1970); (b) D. Bright and M. R. Truter, *J. Chem. Soc. B*, 1544 (1970); (c) M. A. Bush and M. R. Truter, *ibid.*, 1440 (1971).

[12] Though conformations of the uncomplexed DBC molecules in methanol seem to depend on the environment,[13] one may expect, in the case of a complex in which all ethereal oxygens are engaged in an interaction with the complexed ion, that the energy of conformational rearrangements in the macrocyclic ring will not be affected even by strongly hydrogen-bonding solvents.

[13] P. B. Chock and Th. Funck, private communication.

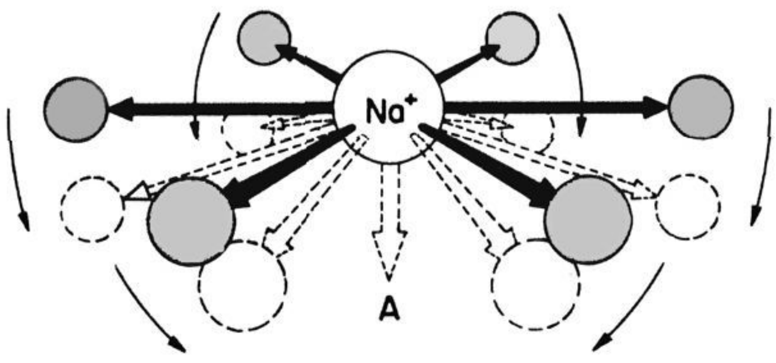

Figure 4.

DBC complexes may reflect the greater flexibility of the macrocyclic ring in DCC.

Absolute values of the rate constants of decomplexation at $-13°$, determined for 0.3 M solutions of the sodium salt, are given in column 7 of Table III. The comparison of different systems based on such relatively diluted solutions is significant, since for the ionic strength <0.3 the apparent rate constants seem to approach their limiting values.

Extrapolation of these values based on the experimentally determined E_a and reported in the literature equilibrium constants yields values of k_{-2} and k_2 at 25°, listed in the last two columns of Table III. As one may expect, the rate constants of complexation increase with the increase in the stability of the complexes, while the rate constants of decomplexation are shifted in the opposite direction. A direct determination of the rate constant of complexation of sodium ions with DBC in methanol at 25° was attempted by Chock and Funck[13] who used the ultrasonic relaxation technique for the investigation of this system. They found $k_2^{25°} = 6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. The agreement between this value and our extrapolated value of $k_2^{25°} \approx 3.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ may be regarded as very satisfactory, especially since the two values were arrived at by completely different experimental techniques.

Acknowledgment. We thank Professor Z. Luz for helpful suggestions.

High-Pressure Mass Spectra and Gaseous Ion Chemistry of Ferrocene

Steven M. Schildcrout

Contribution from the Department of Chemistry, Youngstown State University, Youngstown, Ohio 44503. *Received August 21, 1972*

Abstract: Electron-impact mass spectra of ferrocene have been obtained at 70 eV with ion-source pressures up to 1.5×10^{-2} Torr at 400°K. Ion–neutral reactions observed are those of Fe^+ and $FeC_5H_5^+$ with ferrocene, with rate constants of $(2.6 \pm 0.5) \times 10^{-9}$ and $(2.4 \pm 0.5) \times 10^{-9}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}$, respectively, at a nominal repeller field of 4.6 V cm^{-1}. Reaction of $FeC_5H_5^+$ with ferrocene gives rise to charge transfer in competition with the formation of the stable adduct $Fe_2(C_5H_5)_3^+$. This adduct contributes up to 3% of the total ion current and is formed with a rate constant of $(3.4 \pm 1.2) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}$.

The investigation of gaseous ion–neutral reactions, or ion chemistry, has so far emphasized organic and very simple inorganic systems. The extension of this field of study to include as many classes of compounds as possible should aid the understanding of this type of reaction. An important class of compounds whose ion chemistry has been subjected to little previous study is that of transition metal complexes.[1] There appear to be no reports of measurements of rate constants for reaction of ions with a transition metal complex.

Ferrocene, or di-π-cyclopentadienyliron(II), $Fe(C_5H_5)_2$, is an appropriate choice for a study of ion–neutral reactions by mass spectrometry since it is a relatively simple complex, its bonding properties are of interest, it has an appreciable vapor pressure, and its vapor has high thermal stability. Metallocenes including ferrocene have been subjects of mass spectrometric studies, which have been recently reviewed.[2,3]

The ion $Fe_2(C_5H_5)_3^+$ at m/e 307 has been reported with an abundance of 0.06% of the total ion current in the mass spectrum of ferrocene at an ion-source pressure of 10^{-5} Torr. This ion was presumed to be a product of ion–neutral reaction and to have a "triple-decker sandwich" structure,[4] although no concrete evidence for either of these suppositions was given. It has since been suggested that it may arise in the mass spectrum by fragmentation of a small amount of neutral ferrocene dimer, rather than from ion–neutral reaction.[5]

The present work was undertaken to determine the feasibility of an ion–neutral reaction study of a transition metal complex by single-source electron-impact mass spectrometry, to determine the reactions occurring between ferrocene and its positive fragment ions and the rates of these reactions, and to

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[2] G. A. Junk and H. J. Svec in "Recent Topics in Mass Spectrometry," R. I. Reed, Ed., Gordon and Breach, New York, N. Y., 1971, p 85.

[3] M. Cais and M. S. Lupin, *Advan. Organometal. Chem.*, **8**, 211 (1970).

[4] E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **47**, 1525 (1964).

[5] R. W. Kiser in "Characterization of Organometallic Compounds," Part I, M. Tsutsui, Ed., Interscience, New York, N. Y., 1969, p 137.