The Dynamical Behavior of the Sodium Cation in Some Crown Ether-Na^+-$TCNE^-$ Ternary Complexes as Studied by ESR

Hiroyuki KOHAMA, Mayumi YOSHINAGA, and Kazuhiko ISHIZU*

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790

(Received April 25, 1980)

Synopsis. ESR observations were performed for the ternary complexes formed with Na^+-$TCNE^-$ and 5*O*-crown ethers. The temperature dependence of the observed Na hyperfine line width was analyzed by applying Bloch's two-jump model, and the thermodynamical parameters of the complex formation were determined. The stability of the ternary complexes were found to be much affected by the substitution of either the fused benzene ring or the 2,2′-biphenyldiyl group, which acts as a steric restriction during the optimum metal binding to the flexible crown ring.

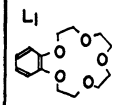
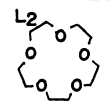
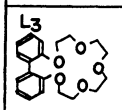
Usually, the alkali metal salts of tetracyanoethylene (M–TCNE) are insoluble in nonpolar solvents. In the presence of crown ether (CR), however, these salts can be solubilized by the complex formation between the alkali metal cation and the crown ether. Based on the ESR observation of the TCNE–crown ether complexes, Eastman *et al.*[1] previously suggested that the ternary complex, CR–M^+–$TCNE^-$, can be formed in these solutions, but the details of the dynamical behavior of alkali metal cations are not well known in these complexes. In this paper, the ESR measurements were applied to the ternary complexes composed of TCNE and 5*O*-crown ether solubilized in a nonpolar solvent. From the analysis of the temperature dependent line width alterations detected in the Na hyperfine splitting, the thermodynamical parameters of the complex formation were determined. The thermodynamical behavior of the metal cation, which will undergo a thermal vibration in the double minimum electric potential involving TCNE and crown ethers, was discussed with the aid of Bloch's equations for the two-jump processes.

Experimental

The 5*O*-crown ethers shown in Table 1 and NaTCNE were prepared according to the methods described in previous works.[2,3] Pure benzo-15-crown-5 was obtained by recrystallization in hexane; mp 80—82 °C (uncorrected). Elementary analysis: Calcd for $C_{14}H_{20}O_5$: C, 62.69; H, 7.46. Found: C, 62.48; H, 7.46%. 5,8,11,14-Pentaoxa-1,2,3,4-dibenzo-1,3-cycloheptadecadiene was purified by recrystallization using a benzene–hexane mixture (1 : 1); mp 107—109 °C (uncorrected). Elementary analysis: Calcd for $C_{20}H_{24}O_5$: C, 69.77; H, 6.98. Found: C, 69.62; H, 7.07%. 15-Crown-5 purchased from Aldrich Chemicals were used without further purification. The sample was made according to the following procedure: 2 mg of NaTCNE and an excess of CR were placed in the quartz sample tube and the desired amount of the purified solvent was brought into the cell in vacuum.

ESR spectra were measured with a JES-ME-3X spectrometer. The ESR splitting were determined by using $(KSO_3)NO$ ($a^N = 1.305 \pm 0.003$ mT) as a standard.

Table 1 Thermodynamical Parameters of CR–Na^+–$TCNE^-$ Complexes

	Toluene	o-Xylene	m-Xylene
L1 	ΔH −14.6	−13.0	−17.6
	ΔS 62.8	50.6	71.6
L2 	ΔH −26.4	−26.0	−27.2
	ΔS 98.4	99.6	100.0
L3 	ΔH −9.2	−22.2	−15.9
	ΔS 40.6	93.8	70.3

ΔH: K J/mol ΔS: J/mol deg

Results and Discussion

The ESR spectra were measured in the temperature range from −50 to 50 °C. The alkali metal hyperfine

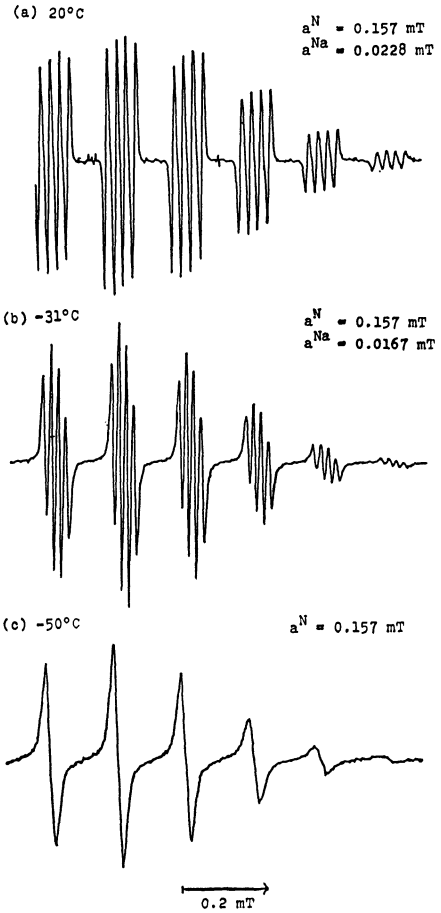


Fig. 1. The higher field halves of ESR spectra of benzo-15-crown-5–Na^+–$TCNE^-$ complex recorded in toluene solution.

line revealed a typical line width variation due to the rapid exchange between the two different paramagnetic species. The observed hyperfine structure measured at room temperature exhibits well resolved hyperfine lines composed of nine lines due to the equivalent four nitrogens ($a^{N}=0.157$ mT), which further split into the Na hyperfine lines ($a^{Na}=0.023$ mT) with equal line intensity [Fig. 1(a)].

Upon lowering the temperature, the magnitude of the alkali metal hyperfine splitting begins to decrease slightly. In addition, the line width corresponding to the alkali metal magnetic quantum number for $M_z=\pm 3/2$ increases in comparison with that for $M_z=\pm 1/2$ [Fig. 1(b)].

At -50 °C, the alkali metal splitting which had decreased by lowering the temperature merges into a single line [Fig. 1(c)].

We assume that the alkali metal cation undergoes a thermal vibration in two different electric potential minima, V_A and V_B which can be defined to CR and $TCNE^-$ respectively. At a lower temperature, a stronger ionic interaction can be expected between the Na^+ and CR, than occurs between Na^+ and $TCNE^-$; that is, $V_A<V_B$, where the alkali metal cation can be so closely accessible to the minimum potential of the CR as to reduce the magnitude of a^{Na}. At room temperature or above, the thermal activation moves the metal cation away from the CR potential; thus the contribution of the V_B could be enhanced, and the larger a^{Na} value was observed.

The equilibrium constant, K, at any temperature T is given by

$$K=\frac{a(T)-a_A}{a_B-a(T)},\quad \underset{A}{CR\text{–}Na^+\cdots TCNE^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{B}{CR\cdots Na^+\text{–}TCNE^-}$$

where a_A and a_B are the a^{Na} values of two different ion pairs at the energy minimum for V_A and V_B; $a_A=0$ mT, $a_B=0.0257$ mT, $a(T)$ is the Na splitting measured at the temperature T.

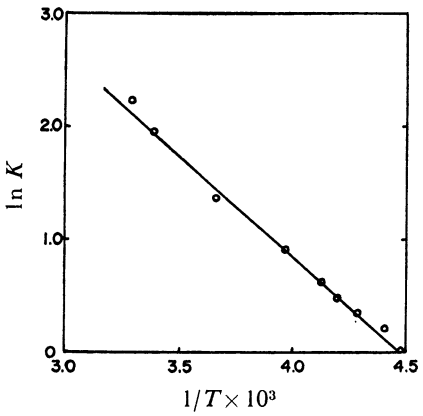


Fig. 2. Plot of ln K *vs.* $1/T$ for benzo-15-carown-5–Na^+–$TCNE^-$ complex in toluene.

The plots for ln K *vs.* $1/T$ gave an excellent straight line over the observed temperature range, as shown in Fig. 2. The value of ΔH and ΔS were calculated from the least-squares fits of the plots; $\Delta H=-14.6$ K J/mol, $\Delta S=62.8$ J/mol deg, respectively.

The rate constants k_1 and k_{-1} were also estimated by using the following equation:[4]

$$k_1=(2.03\times 10^7)\frac{K^2(a_B-a_A)^2(M_z^2-M_{z'}^2)}{(1+K)^3[(I_{M_{z'}}/I_{M_z})^{1/2}-1)\Delta H_{M_{z'}}}\ (s^{-1})$$

$$k_{-1}=\frac{k_1}{K}\ (s^{-1})$$

where I_{Mz} and $I_{Mz'}$ denote the line intensity corresponding to the alkali metal magnetic quantum number ($M_z=\pm 3/2$, $M_{z'}=\pm 1/2$), and $\Delta H_{Mz'}$ is the line width for Mz' peak. The linear plots are obtained between the logarithm of the rate constants ($\ln k_1$, $\ln k_{-1}$) and $1/T$.

The activation energy E_1 and E_{-1} thus estimated are 25.1 and 11.3 K J/mol for the TCNE–15-crown-5 complex. In order to obtain the more detailed view of these ternary complexes, the thermodynamical parameters (ΔH and ΔS) were obtained for several crown ethers, which have different steric factors upon incorporation of the alkali metal cation.

From the inspection of the thermodynamical parameters ΔH and ΔS measured in the different solvents (Table 1), some important features are found concerning the alkali metal complex formation of crown ethers containing five chelating oxygens, L_1, L_2, and L_3. No important difference in the thermodynamical parameters can be recognized by changing the solvent in each complex. This means that ternary complexes are essentially tight ion pairs. The largest values of both ΔH and ΔS are obtained for the L_2 complexes everywhere, while the ΔH values as well as the ΔS values are considerably reduced for the L_2 and L_3 complexes. This will be probably due to the fact that the planar fused benzene ring or sterically hindered 2,2′-biphenyldiyl groups act as restrictions toward any conformational change in the crown ring during the optimum binding of the alkali metal cation.

References

1) M. P. Eastman, D. A. Ramlrez, C. D. Jaeger, and M. T. Watts, *J. Phys. Chem.*, **80**, 182 (1976).
2) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
3) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).
4) K. S. Chem, S. W. Mao, K. Nakamura, and N. Hirota, *J. Am. Chem. Soc.*, **93**, 6004 (1971).