ENDOR Studies of the Complexation Reaction between Spin-Labeled Crown Ether and Alkali Metal Salts

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Synopsis. A new crown ether spin-labeled by the phenoxyl radical moiety was prepared. Intramolecular odd-π electron delocalization was investigated by means of ENDOR spectroscopy. On the basis of ENDOR spectrometric titration, the equilibrium constant for Na^+-labeled crown-ether-complex formation was evaluated to be $pK_{Na^+}=3.5$ in 2-propanol at −30 °C.

The spin-labeling technique has been applied to obtain information about the molecular structures of both labeled crown ether and its metal complexes. For example, the molecular structure of 2:1 sandwich type complexes of labeled crown ethers were characterized on the basis of detailed analyses of the triplet ESR spectra.[1-3] In addition, the dihedral angles of the vibrating crown methylene protons were estimated by means of temperature-dependent ENDOR measurements.[4] In the previous studies, however, the details of the metal-complexation reaction between these labeled crown ethers and metal cations have not been fully compiled. Here, a stable spin-labeled crown ether bearing the phenoxyl radical moiety (CR-O·) was newly prepared and isolated as pure crystals in order to obtain an improved view of the host-guest chemistry relating to this crown ether. The conformational change in the benzylic methylene protons upon metal chelation was investigated in detail by ENDOR. In addition, the equilibrium constants of alkali metal complex formation were also estimated.

Experimental

The spin labeled crown ether CR-O· (Fig. 1) was synthesized by the usual procedures,[3,5] (Found: C, 69.99, H, 8.79%. Calcd for $C_{31}H_{46}O_7$: C, 70.16; H, 8.79%. Mp 135—136 °C). The purity of the CR-O· was estimated to be above 98% by means of magnetic susceptibility measurements at 25 °C. The ENDOR spectra were recorded by a JEOL ES EDX-1 spectrometer in the temperature range from −50 to +10 °C in dry 2-propanol. All the measurements were performed at the Advanced Instrumental Center for Chemical Analysis, Ehime University.

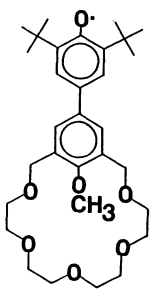

Fig. 1. The molecular structure of the phenoxyl radical crown ether CR-O·.

Results and Discussion

Figure 2 shows the higher half frequency field of the ENDOR spectra observed for metal free CR-O· (1.0 m M†) in 2-propanol. The ENDOR fine structures were safely assigned with reference to the results of previous report[6] as summarized in Table 1. The benzylic methylene protons, H_1 and H_2, revealed a nonequivalence in the magnitude of proton hfcc at −30 °C (Fig. 2-3), as has already been noted for other spin-labeled crown ethers.[4] On raising the temperature, the distance between these two lines began to decrease, finally they collapsed together into a single

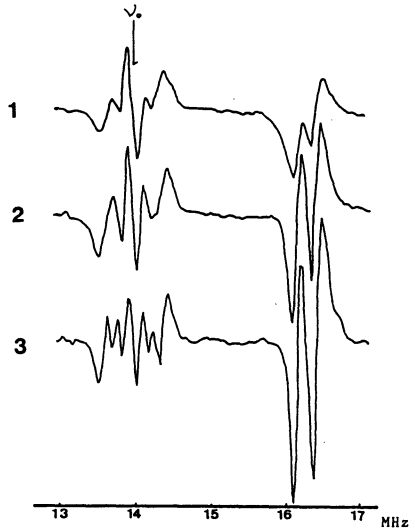

Fig. 2. The higher frequency half of ENDOR spectra observed in the absence of alkaline metal salts at (1) +10 °C, (2) −20 °C, and (3) −30 °C.

Table 1. Observed Proton Hyperfine Coupling Constants (hfcc in mT) of CR-O· and Its Alkaline Metal Complexes

Position	CR-O· 10 °C	CR-O· −30 °C	Na^+-CR-O· −30 °C	K^+-CR-O· −30 °C
2	0.0107	0.0076	0.0086	0.0080
3	0.1610	0.1601	0.1682	0.1704
4	0.0270	0.0290	0.0482	0.0392
H_1,H_2	0.0268	0.0167 0.0293	0.0482	0.0394

† 1 M=1 mol dm^{-3}.

line above +10 °C (Fig. 2-1). Based on the proton hfcc of the benzylic methylene protons H_1 and H_2 at the maximum separation, the equilibrium dihedral angles were estimated to be 55 ° and 61 ° in terms of the McConnell-Heller equation,[7] as illustrated in Fig. 3. A restricted movement, as demonstrated in the benzylic methylene protons, may be attributed to a steric repulsion occurring between the crown ether chain and the methoxyl group. The activation energy for the vibrating benzylic methylene protons were evaluated to be 14 kJ mol^{-1} after Gutowsky and Holm's treatment.[8]

The ENDOR spectra were measured in the presence of a ten-fold molar equivalent of alkali metal salts: Li^+-, Na^+- and K^+ClO_4. No important ENDOR spectral change was detected, even after the mixing of $LiClO_4$ with the CR-O· (Fig. 4-1), indicating that no complex formation occurs between $LiClO_4$ and the radical crown ether. On the other hand, both Na^+ and K^+ salts showed a drastic variation upon the ENDOR fine structure recorded at −30 °C, as shown in Fig. 4-2 and -3. A nonequivalence in the benzylic-methylene-proton splitting disappeared in the temperature range from −30 °C to +10 °C upon the addition of Na^+ and K^+ salts. This implies that the thermal motion occurring in the benzylic-methylene protons is tightly locked by metal chelation in the crown ether cavity. Interestingly, the ENDOR signal of the metal-free CR-O· was again recorded, after the addition of a 20 molar excess of 18-CR-6, which had a pronounced affinity for Na^+ and K^+ ions. These findings, therefore, indicate that marked conformational changes in the crown ether moiety take place upon the complex formation with Na^+ and K^+ ions.

In order to evaluate the equilibrium constant for Na^+-complex formation, ENDOR spectrometric titration was carried out by changing the initial concentration ratio, R_0=[$NaClO_4$]/[CR-O·$_0$], as is shown in Fig. 5. When a two-fold excess amount of $NaClO_4$ was added to CR-O·, the observed ENDOR spectrum (Fig. 5-2) showed mixed fine structures consisting of the metal-free CR-O· and of the Na^+-CR-O· complex. The ENDOR signal intensity ascribable to Na^+ complex gradually increased, and eventually the ENDOR signals of metal free CR-O· completely disappeared at R_0=6.0 (Fig. 5-4). This ENDOR fine structure recorded during the titration from R_0=0 to 6.0 was adequately simulated by means of the computer superposition of the ENDOR fine structures of CR-O· and its Na^+ complex, as demonstrated in Fig. 5. An excellent agreement was seen between the observed spectra and those simulated, which were obtained after trial-and-error calculations by changing the mixing ratio, R'=[Na^+-CR-O·]/[CR-O·]. In

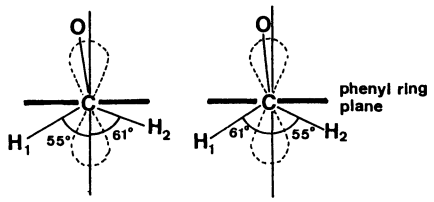

Fig. 3. The equilibrium dihedral angle of the vibrating benzylic methylene protons H_1 and H_2.

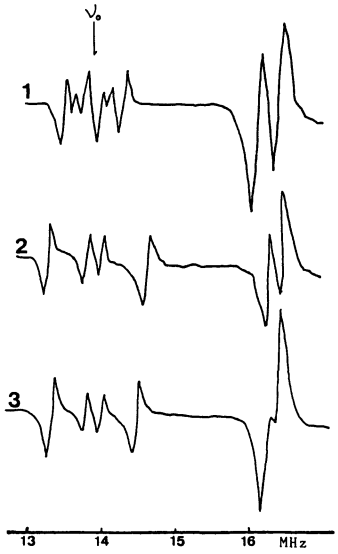

Fig. 4. ENDOR spectra observed at −30 °C in 2-propanol in the presence of ten fold excess amount of (1) $LiClO_4$, (2) $NaClO_4$, and (3) $KClO_4$.

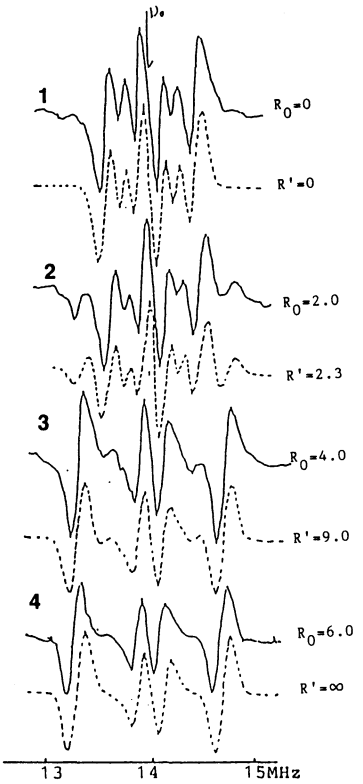

Fig. 5. ENDOR spectral changes observed (solid line) during the $NaClO_4$-titration at −30 °C and the calculated ENDOR fine structure (broken line). R_0 is initial mixing molar ratio [$NaClO_4$]/[CR-O·$_0$] and R' is the estimated molar ratio [Na^+-CR-O·]/[CR-O·] by means of computer superposition using Eq. 1.

terms of the R_0 and R' values, the equilibrium constant $pK_{Na}+$ was calculated using Eq. 1:

$$pK_{Na}+=\log(R'(1+R')/[Na^+_0]+R'[Na^+_0]-R'[CR\text{-}O\cdot_0]) \quad (1)$$

The values of $pK_{Na}+$ at −20 °C and −10 °C were also evaluated to be 3.5 and 3.3 by means of similar procedures. Based on the temperature dependence of the $pK_{Na}+$ values, the thermodynamic parameters of ΔH and ΔS were estimated to be 1.4 kJ mol^{-1} and −1.5 J mol^{-1} deg^{-1}. By a similar ENDOR titration carried out for the K^+-CR-O· system, the $pK_K{}^+$ value was estimated to be above 6.0 at −30 °C. This implies that the labeled crown ether CR-O· possesses a pronounced affinity to the K^+ ion rather than to the Na^+ ion. Further investigations to evaluate the $pK_K{}^+$ value of the K^+-CR-O· complex formation are now in progress.

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