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A Re-investigation of the Conformational Interconversion in the 1,2,3,6,7,8-Hexahydropyrene Anion Radical by ENDOR

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Synopsis. The ENDOR spectra of the 1,2,3,6,7,8-hexahydropyrene anion radical were measured at −94—−60 °C. Based on the computer simulation of the temperature-dependent ENDOR spectra, the thermodynamic constants of the conformational interconversion of the anion radical were determined and compared with those previously obtained by ESR spectroscopy.

Magnetic resonance spectroscopy has been used as one of the most effective techniques for the investigation of chemical-dynamic processes. Many papers have been reported on the ESR investigation of the conformational intercoversion of radical molecules. Iwaizumi *et al.*[1] and de Boer *et al.*[2] have reported on the line-width-alternation effect on the ESR spectra of the anion radical of 1,2,3,6,7,8-hexahydropyrene (HP) (Fig. 1); they attributed the effect to the conformational interconversion of the $HP^{\overline{\cdot}}$ molecule between a chair form and a boat form. Claridge *et al.*[3] and Pijpers *et al.*[4] made more detailed kinetic studies and obtained the thermodynamic constants of the conformational interconversion through a computer simulation of the ESR spectra, depending on the temperature. However, appreciably different thermodynamic parameters were reported by the two groups (see Table 1). Both groups measured the ESR spectra of $HP^{\overline{\cdot}}$ in the same solvent, but they used different counter ions in their experiments; *i.e.*, Claridge *et al.* treated $HP^{\overline{\cdot}}$ in 1,2-dimethoxyethane (DME) with the sodium ion, while Pijpers *et al.* treated $HP^{\overline{\cdot}}$ in DME with the potassium ion. In our experiment, however, no differences in the ESR spectra could be found between those two solvent and counter-ion systems to give such different thermodynamic constants. In the present work, we attempted a reexamination of the conformational interconversion of $HP^{\overline{\cdot}}$ by means of ENDOR spectroscopy. Shain has also examined $HP^{\overline{\cdot}}$ by the use of ENDOR, but he could not observe the ENDOR spectra at various temperatures.[5]

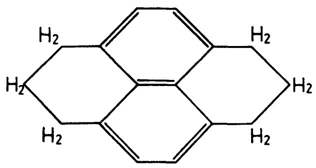

Fig. 1. 1,2,3,6,7,8-Hexahydropyrene, HP.

The magnitude of ENDOR enhancement depends on all the possible transition rates in the spin system; it changes with the temperature and with the viscosity of the solvents, and in some cases the observation of the ENDOR spectra is limited to a narrow temperature region. In Shain's experiment, where DME was used as the solvent, the observation of the ENDOR spectra was possible only in the vicinity of the freezing point of the solution (up to about 10 °C above the freezing point). In the present work, we used bis(2-methoxyethyl) ether (diglyme), with a higher viscosity than DME, and DME as the solvents. The latter was used for the measurements at temperatures below the freezing point of the former.

Results and Discussion

The ENDOR spectra were recorded with a JEOL ES-EDX-1 ENDOR spectrometer. By the use of diglyme, the ENDOR spectra could be observed up to about −60 °C. Over the temperature range used (−60 — −94 °C), the line widths, positions, and shapes of the ENDOR signals due to the β and γ protons change with the temperature; the signals due to the β protons broaden, and the separation between the two lines attributable to the axial and equatorial ones becomes smaller with an increase in the temperature, representing that the dynamic process of the β protons is in the slow-rate region, $\Delta\omega_{\beta_0}\tau \ll 1$, while the two ENDOR lines attributable to the axial and equatorial γ protons observed at the low temperatures collapse into a single line with an increase in the temperature, representing that the dynamic process of the γ protons ranges from the slow- to the fast-rate region, $\Delta\omega_{\gamma_0}\tau \gg 1$—$\Delta\omega_{\gamma_0}\tau \ll 1$. Here, τ is the mean lifetime of each conformation, and $\Delta\omega_{\beta_0}$ and $\Delta\omega_{\gamma_0}$ are $2\pi|(a_{\beta\mathrm{ax}}-a_{\beta\mathrm{eq}})/2|$ and $2\pi|(a_{\gamma\mathrm{ax}}-a_{\gamma\mathrm{eq}})/2|$ respectively, the hyperfine coupling constants for the axial and equatorial β and γ protons, $a_{\beta\mathrm{ax}}$, $a_{\beta\mathrm{eq}}$, $a_{\gamma\mathrm{ax}}$, and $a_{\gamma\mathrm{eq}}$, being measured in Hz. We obtained τ values as a function of the temperature, based on the computer simulation of the line shape, for the β- and γ-proton ENDOR lines. It is known that the line-shape for ordinary ENDOR lines of radicals should be a saturated Lorentzian.[6] In the present case, however, we ignored such an effect and simply assumed that the line-shape for the ENDOR signals under the dynamic process are expressed by the

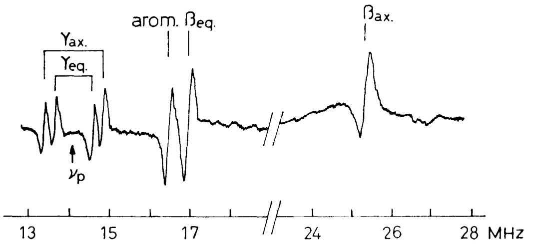

Fig. 2. ENDOR spectrum of $HP^{\overline{\cdot}}$ in DME with K^+ at −94 °C. ν_p is free proton frequency and β_{ax}, β_{eq}, γ_{ax}, γ_{eq}, and arom. indicate the signals due to the axial and equatorial β and γ protons and aromatic protons, respectively.

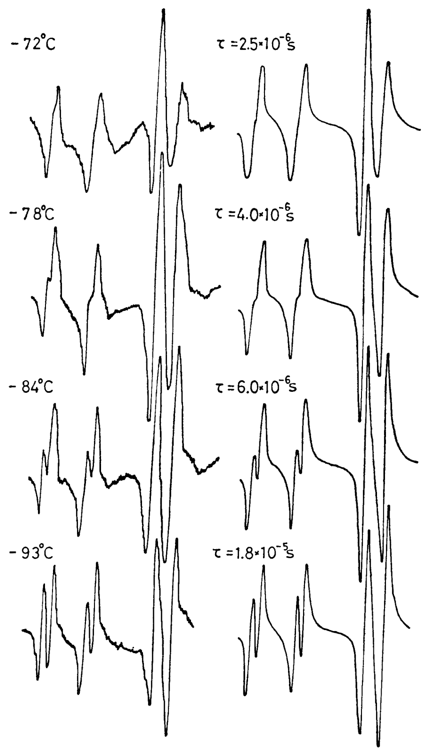

Fig. 3. Temperature dependence of the ENDOR spectra and the computer simulations. The spectrum at −93 °C was observed from HP$^{\cdot-}$ in DME with K$^+$ and the others from HP$^{\cdot-}$ in diglyme with K$^+$.

Table 1. Thermodynamic parameters for conformational interconversion of HP$^{\cdot-}$

	This work (by ENDOR)	Claridge *et al.* (by ESR)	Pijpers *et al.* (by ESR)
E_{act}/kJ mol^{-1}	29.9 ± 2.6	26.8 ± 2.5	41.8 ± 1.7
k_0/s	$2.51 \times 10^{13 \pm 0.8}$	$3.16 \times 10^{13 \pm 0.8}$	$2.5 \times 10^{14} \pm 5\%$
$\Delta H^{\pm}$/kJ mol^{-1}	28.3 ± 2.6[a]		39.7 ± 1.7[b]
ΔS/J mol^{-1} K^{-1}	7.6 ± 3.7[a]		21.8 ± 0.4[b]
ΔG/kJ mol^{-1}	26.9 ± 3.2[a]		33.9 ± 2.1[b]

a) At 190 K. b) At 273 K.

modified Bloch equation.7) The line shapes were calculated by using the four-jump model8) and using the $a_{\beta\mathrm{ax}}$, $a_{\beta\mathrm{eq}}$, $a_{\gamma\mathrm{ax}}$, and $a_{\gamma\mathrm{eq}}$ values obtained from the spectrum at the lowest temperature in the experiment. For the evaluation of τ, we also applied the following equations for the β-proton ENDOR signals:

$$1/T_2'(\mathrm{ENDOR}) = k'$$

$$\Delta\omega = (\Delta\omega_{\beta_0}^2 - 8k'^2)^{1/2}$$

where $1/T_2'$ (ENDOR) is an additional line-broadening in the ENDOR signals, $\Delta\omega$ is the observed separation between the ENDOR lines due to the axial and equatorial β protons, and $k' = 1/2\tau$.9) Figure 3 shows the temperature dependence of the ENDOR signals in the 14—17 MHz region, and the computer simulations of the spectra, the ENDOR signals due to the aromatic protons being expressed as having the same intensity over the present temperature range. The Arrehnius plot is shown in Fig. 4. The thermodynamic constants thus obtained are listed in Table 1. It may be seen that the obtained thermodynamic constants are in rather good agreement with Claridge *et al.*'s values, and that the activation energy, E_{act}, obtained in the present work for HP$^{\cdot-}$ is smaller than the value reported by Pijpers *et al.* Pijpers *et al.* have indicated that the E_{act} for HP$^{\cdot-}$ is larger than that for HP$^{\cdot+}$; *i.e.*, the E_{act} for HP$^{\cdot-}$ is 41.8 kJ mol^{-1}, while the E_{act} for HP$^{\cdot+}$ is 14.6 kJ mol^{-1}.4) However, such a large difference in the E_{act} between the anion and the cation radicals seemed quite surprising, though in our ESR studies of the conformational interconversion of 4,5,9,10-tetrahydropyrene ion radicals, too, a larger activation energy has been observed for the anion radical.10) The E_{act} value obtained in the present work indicates that the difference between the E_{act} for the anion and the corresponding cation radical may be rather smaller than that reported by Pijpers *et al.* It may also be noted that the E_{act} for HP$^{\cdot-}$ is smaller than that for the intercoversion between a chair and a boat form of the neutral cyclohexane molecule, 42.3 kJ mol^{-1}.11)

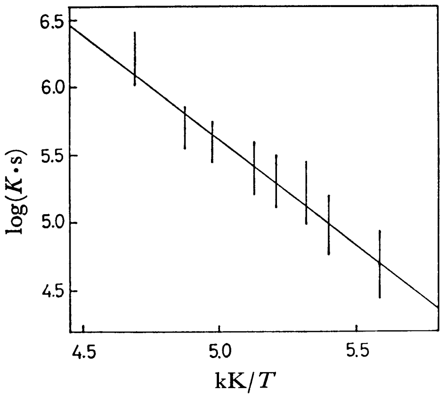

Fig. 4. The Arrehnius plot of the rate constant for the interconversion process of HP$^{\cdot-}$.

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