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Spectroscopic Investigation of Methyl Viologen Radical Cation Included in ß-Cyclodextrin

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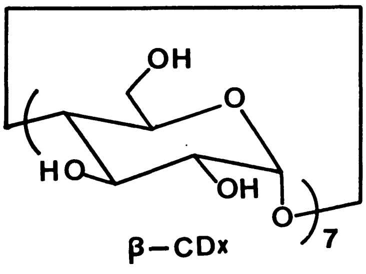
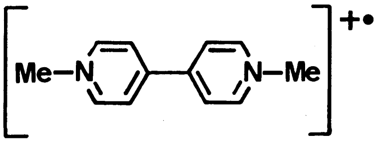
A stable ß-cyclodextrin inclusion complex with methyl viologen radical cation has been prepared in solution and in the form of polycrystalline powder, enabling us to study the ESR, electronic absorption, and induced circular dichroism spectra.

Cyclodextrins (CDxs) are known as typical hosts in inclusion phenomena. The CDx inclusion complex formation with radicals has been attempted by choosing stable nitroxide radicals as guests.$^{1)}$ Recently, we have reported stabilization of aromatic radical ions by the inclusion complex formation with CDx in aqueous environments.$^{2,3)}$ In this report, we discuss the ESR, electronic absorption, and induced circular dichroism (ICD) spectra of methyl viologen radical cation ($MV^{+\cdot}$) included in ß-CDx.

The $MV^{+\cdot}$ was prepared in aqueous ethanol by irradiation of ultraviolet light from a 250-W high-pressure mercury arc lamp after full deaeration by freeze-pump-thaw cycles. The radical cation was found to be most efficiently stabilized for a water fraction of 50%. Hereafter, discussion is restricted to the results obtained for 50% aqueous ethanol solutions, as far as the solutions are concerned. A part of the ESR spectra observed at different temperatures are shown in Fig. 1. The two spectra were recorded at each temperature in the raising and lowering courses of temperature, and both spectra were identical with each other. In the solutions without CDx, the radical cation persisted for about an hour. For the ESR spectra of radicals included in or incorporated into molecular assemblies, several kinds of transverse relaxation processes are operative. Among them, only the contribution from modulation of the anisotropic tensors by motional tumbling is associated with the nuclear spin states, giving rise to unsymmetrical ESR spectra.$^{4)}$ The others contribute equally in line width broadening to any hyperfine line. Among the four spectra in Fig. 1, the spectra at 10 and 50 °C are composed of relatively broad lines compared with those at 20 and 70 °C. The spectral envelope is evidently unsymmetrical at 10 °C. The unsymmetrical line feature at 10 °C is interpreted to reflect the inclusion-induced suppression of the



β-CDx



$MV^{+\bullet}$

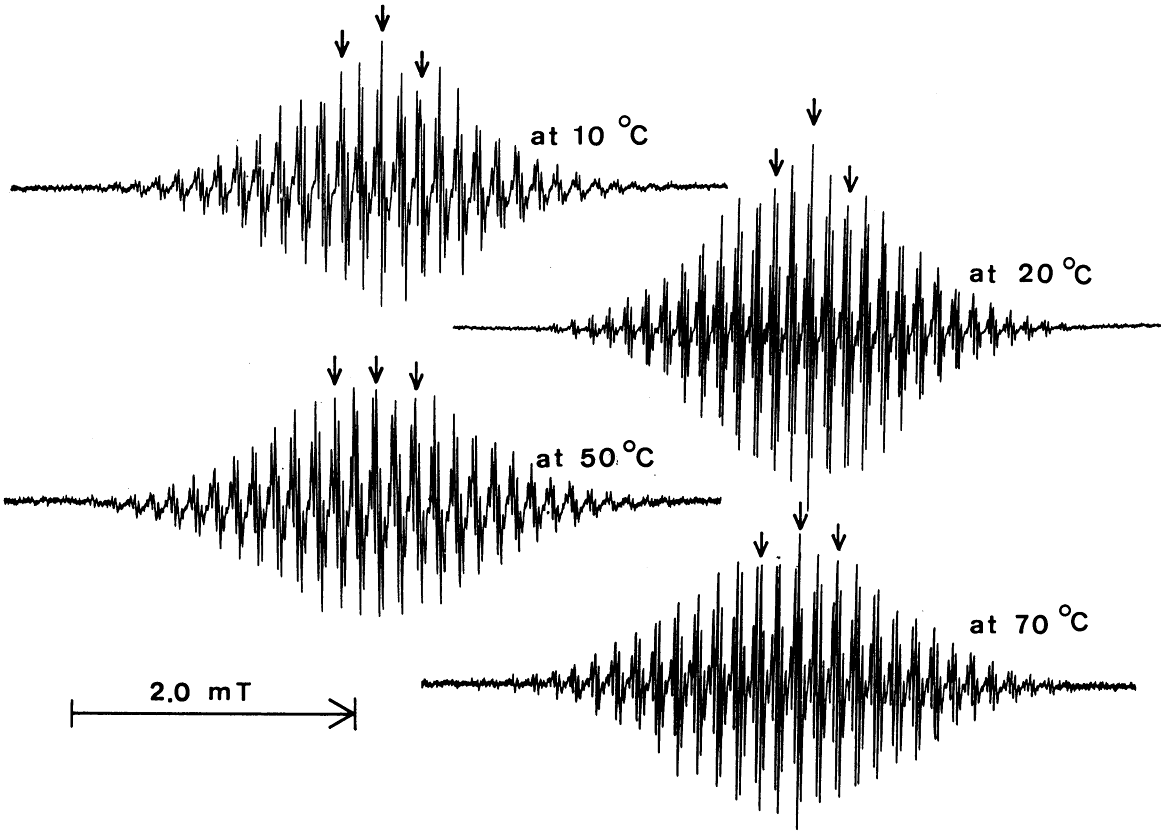


Fig. 1. ESR spectra of $MV^{+\cdot}$ included in ß-CDx observed in 50% aqueous ethanol at different temperatures. The concentrations of MV and ß-CDx were 1.0 X 10^{-3} and 1.0 X 10^{-2} mol dm^{-3}, respectively. Marked with arrows are the N(+1), N(0), and N(-1) lines from left to right; as for the line notation, see text.

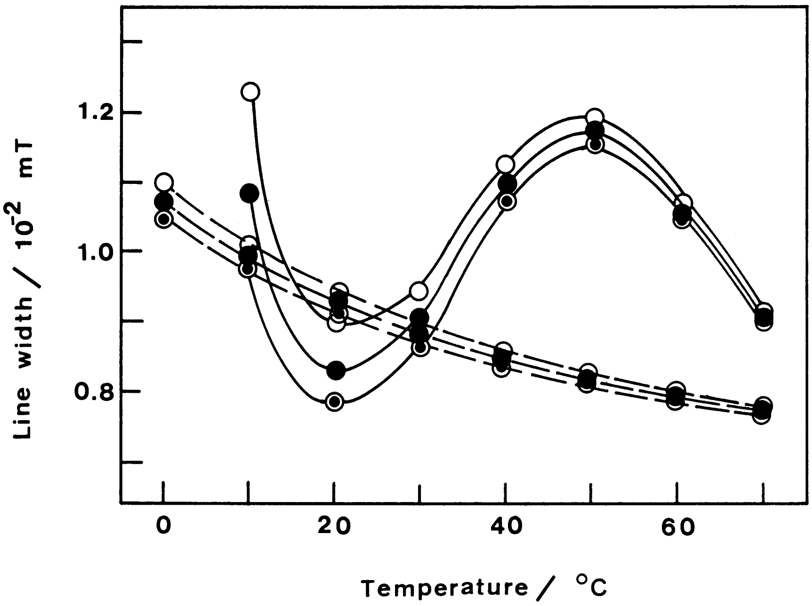


Fig. 2. Temperature variations of line widths in the ESR lines, N(+1) (●), N(0) (◉), and N(-1) (○), marked with arrows in Fig. 1, of $MV^{+\cdot}$ included in ß-CDx in 50% aqueous ethanol (full lines) and those of the inclusion-free radical cation in absolute ethanol (dashed lines). As for the notation $N(I_N)$, see text.

motional tumbling.

Figure 2 shows the variations of the N(+1) and N(0) line widths of $MV^{+\cdot}$ included in ß-CDx in 50% aqueous ethanol and those of $MV^{+\cdot}$ in absolute ethanol without ß-CDx. Here $N(I_N)$ denotes the ESR line for which the nitrogen nuclear spin quantum number is I_N, while the resultant hydrogen nuclear spin quantum number vanishes. The motional narrowing is seen to develop monotonically with increasing temperature for the inclusion-free $MV^{+\cdot}$ in absolute ethanol, whereas the temperature variation is sinuous for the included $MV^{+\cdot}$, suggesting that at least two competitive processes are involved. The decrease in line width in the included $MV^{+\cdot}$ is seen from 10 to 20 °C, which is ascribed to the increased motinal narrowing with increasing temperature. The narrower widths for the included $MV^{+\cdot}$ than those for the inclusion-free $MV^{+\cdot}$, at about 20 °C, are attributed to the inclusion-induced reduction of such perturbations as the spin-dipolar and spin-exchange interactions; the collisions with other radicals and solvated ions are effectivley diminished when the radical is included. The increase in line width observed for the included $MV^{+\cdot}$ in the 20-50 °C region may be brought about by the increased rate of chemical exchange, that is, the increased rates of the forward and reverse processes in the inclusion equilibrium. The increased chemical exchange rate decreases the transverse relaxation time, leading to line broadening. This implies that the inclusion process is accompanied with thermal activation. The existence of ß-CDx - $MV^{+\cdot}$ 2:1 complex seems to be probable, since the CDx concentration is much higher than that of $MV^{+\cdot}$ and the length of a $MV^{+\cdot}$ radical is as long as 12.7 Å, taking the van der Waals radius of a methyl group as 2.0 Å. At present, we have no direct evidence for the nonexistence of the 2:1 inclusion complex. The line width narrowing above 50 °C is an indication of the motional narrowing predominating over the broadening due to the chemical exchange.

The polycrystalline powder of the $MV^{+\cdot}$ included in ß-CDx was prepared as follows; the 50% aqueous ethanol solution containing 1.0×10^{-3} mol dm^{-3} of MV and 1.0×10^{-2} mol dm^{-3} of ß-CDx was slowly cooled with liquid nitrogen, and the solvent was removed by vacuum suction without heating. The fine polycrystalline sample thus obtained was dried at 40 °C under vacuum, and then the sample tube was sealed off. The sample was irradiated with ultraviolet light, and turned blue, indicating formation of $MV^{+\cdot}$. The blue color never faded even in a year. The polycrystalline powder sample of $MV^{+\cdot}$ included in ß-CDx gave a single broad line ESR spectrum, and the spectral intensity and feature remained unchanged in a year. It is remarkable that the inclusion of ß-CDx serves to stabilize the radical cation even in the polycrystalline state and at ambient temperature; ethanol might serve as space regulator in the ß-CDx cavity.

The electronic absorption and ICD spectra are shown in Fig. 3. Since neither MV nor ß-CDx shows any absorption below 30000 cm^{-1}, the absorption bands in Fig. 3 can be ascribed to the $MV^{+\cdot}$. The spectrum is very similar to that observed for N,N'-dihydro-4,4'-bipyridyl radical cation included in ß-CDx,2) confirming the present assignments of the electronic absorption bands. On the basis of the Kirkwood-Tinoco coupled oscillator model, the ICD sign of a band in the guest molecule determines the polarization direction of the corresponding electronic transition; as for an axially included guest, the positive and negative signs refer to the polarization directions parallel and perpendicular, respectively, to the moleuclar axis of ß-CDx.$^{5)}$ Thus, the two absorption bands at 16530 and 25190 cm^{-1}, both being positive in ICD sign, are interpreted to be polarized along the long molecular axis of MV$^{+\cdot}$. A molecular orbital calculation shows that the two absorption bands are polarized along the long molecular axis, and hence the axial inclusion is also confirmed theoretically, just as in the case of the N,N'-dihyro-4,4'-bipyridyl radical cation included in ß-CDx.$^{2)}$ The sign variation at about 15000 cm^{-1} is intepreted due to complicated vibronic interaction. The rather low resolution of the ICD spectrum of this work prevents us from going into detailed analysis of the vibronic interaction. At low temperatures, the absorption spectrum observed in absolute ethanol exhibited additional bands, to be attributed to the dimer, at 12550, 19420, and 28000 cm^{-1}, with the isosbestic points appearing at 13890, 18250, and 23800 cm^{-1}, accompanying the blue-to-red color change of the solution as well as the decrease in ESR intensity indicating formation of diamagnetic species such as singlet dimers. Even at room temperature, when the MV$^{+\cdot}$ concentration was sufficiently high, the ESR signal faded away. As for the included MV$^{+\cdot}$ in 50% aqueous ethanol solution, no indication of dimer formation was found either with decreasing temperature or with increasing radical concentration.

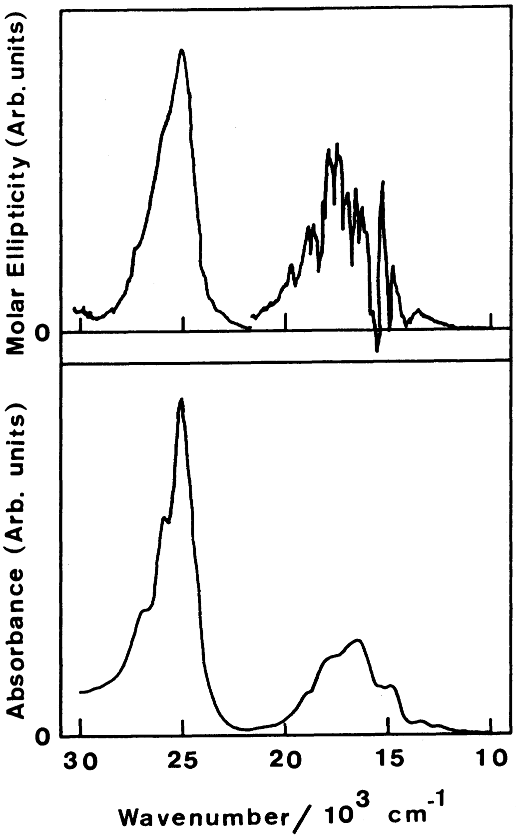


Fig. 3. ICD.(upper) and electronic absorption (lower) spectra of MV$^{+\cdot}$ included in ß-CDx observed in 50% aqueous ethanol at room temperature.

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