Solvent Effects on Optical and ESR Spectra of One-Electron Reduced Species of Cobalt(III) and Manganese(III) Tetraphenylporphyrins Produced by γ-Radiolysis at 77 K

Mikio HOSHINO,* Shiro KONISHI, and Masashi IMAMURA
Solar Energy Research Group, The Institute of Physical and Chemical Research, Wako, Saitama 351

(Received October 31, 1983)

One-electron reduction by γ-ray irradiation of cobalt(III) and manganese(III) tetraphenylporphyrins (ClCo(III)TPP, ClMn(III)TPP, and IMn(III)TPP) in ethanol and MTHF(2-methyltetrahydrofuran) solutions at 77 K results in the reduction of the central metals of these porphyrins. From the optical and ESR measurements, the reduced species are found to retain the axial anion, Cl^- or I^-, in MTHF but not in ethanol. The absorption spectroscopic studies of these porphyrins in ethanol solutions indicate that the axial halide ion is displaced by an ethanol molecule prior to γ-ray irradiation.

Reduced and oxidized porphyrins generated chemically and electrochemically have been subjected to numerous spectroscopic studies because of their importance as key intermediates in biological reactions.[1] In particular, optical absorption and ESR spectroscopic studies provide useful information on thir electronic structures and chemical properties. However, chemical reduction and oxidation and electrolysis techniques are unable to be applied to observation of unstable reduced and oxidized species in fluid solutions.

Radiation chemical techniques have been successfully applied to the detection of one-electron oxidation and reduction products of inorganic compounds,[2–7] metalloporphyrins,[8,9] and biologically important substances.[10,11] Recently we have systematically carried out optical and ESR measurements of one-electron reduced and oxidized products of metalloporphyrins and cobaloximes formed by γ-radiolysis of rigid solutions at 77 K.[12–19] Since molecules are immobilized in the low-temperature rigid solutions, the reduced or oxidized species are trapped as stable products and are subjected to the conventional spectroscopic measuremens.

In previous papers[12,16] we have shown that ClCo(III)TPP and ClMn(III)TPP in a less-polar solvent, MTHF, are reduced upon γ-ray irradiation at 77 K to from $Cl^-\cdots$Co(II)TPP and $Cl^-\cdots$Mn(II)TPP in which the anion Cl^- is confined in the axial position. These results imply that ClCo(III)TPP and ClMn(III)TPP hardly undergo ionic dissociation in MTHF.

In a preliminary experiment, we found that the absorption spectra of ClCo(III)TPP, ClMn(III)TPP, and IMn(III)TPP in ethanol solutions distinctly differ from those in MTHF solutions. The purpose of the present study is to investigate the one-electron reduced species of ClCo(III)TPP, ClMn(III)TPP, and IMn(III)TPP, produced by γ-ray irradiation at 77 K in a polar solvent, ethanol. The optical absorption and ESR spectra of the reduced species in ethanol are presented for the comparison with those in MTHF.

Experimental

Metalloporphyrins, ClCo(III)TPP, ClMn(III)TPP, and IMn(III)TPP, were prepared according to literature[20,21] and purified by column chromatography on Sephadex LH 20. 2-Methyltetrahydrofuran was purified by fractional distillation and stored on Na–K alloy to remove traces of water. Ethanol was used as supplied.

Optical absorption and ESR spectra were recorded on a Cary 14 spectrophotometer and a JEOL JES FE-3AX X-band spectrometer, respectively.

High-purity quartz cells having an optical pathlength of 0.1 mm were used for optical measurements. Two Kinds of ESR tubes were used: one is made of high-purity quartz and the other, specially prepared glass in which no hydrogen atoms are formed upon γ-ray irradiation at 77 K. A 1.2 kCi ^{60}Co source was used for γ-ray irradiation at a dose rate of *ca.* 53 kr min^{-1}.

Sample solutions containing 10^{-3} M (1 M=1 mol dm^{-3}) porphyrins were degassed and frozen in a Dewar vessel before γ-ray irradiation. A broad absorption due to trapped electrons formed by irradiation was eliminated by photobleaching before optical measurements of the reduced species. For the study of chemical reactions occurring in the irradiated solutions at elevated temperatures, the sample cells and tubes were warmed slightly by withdrawing them from liquid nitrogen for suitable time.

Results

Absorption Spectra. Figure 1 shows the absorption spectra of ClCo(III)TPP in ethanol solution before and after γ-ray irradiation at 77 K. The absorption

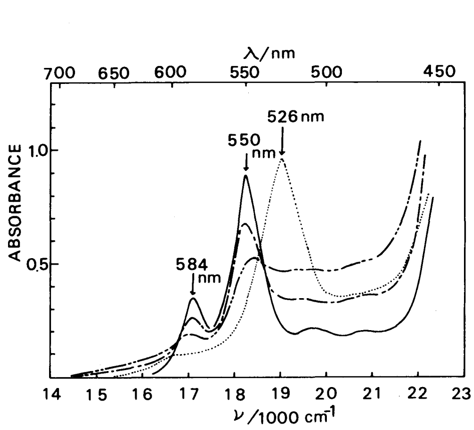


Fig. 1. Absorption spectra of ClCo(III)TPP in ethanol solution at 77K before γ-ray irradiation (——), after γ-ray irradiation for 60 min (—-—) and 150 min (——--——), and after once warming the irradiated solution for 2.0 min (……).

peaks of ClCo(III)TPP are located at 550 and 584 nm. Except for band narrowing, the spectrum at 77 K is in good accord with that measured at room temperature. Upon γ-ray irradiation the intensities of these peaks decrease and a broad absorption appears over the wavelength region from 450 to 700 nm; the spectral change shows isosbestic points at 595 and 537 nm. The spectrum measured after irradiation for 150 min still indicates the presence of ClCo(III)TPP. Warming of the irradiated solution for 2 min gives the spectrum at 77 K shown by a dotted line in Fig. 1. Since the spectrum is the same as that of authentic Co(II)TPP in ethanol solution at 77 K, the broad absorption in 450—700 nm observed after irradiation is considered to be due to the one-electron reduced species of ClCo(III)TPP, which is transformed to Co(II)TPP at elevated temperatures. The absorption spectrum of the warmed solution shows the absence of ClCo(III)TPP, indicating that the remaining ClCo(III)TPP is reduced by solvent radicals formed upon γ-ray irradiation at 77 K.

An MTHF solution of ClCo(III)TPP at 77 K gives absorption peaks at 557 and 598 nm. The spectrum measured after γ-ray irradiation for 50 min shows the formation of a reduced species having an absorption peak at 513 nm. The reduced species changed to Co(III)TPP after warming the irradiated solution to room temperature.[12] It is noted that the reduced species of ClCo(III)TPP in MTHF exhibits a clear absorption peak at 513 nm, while that in ethanol, a broad band in the Q band region.

Figure 2 shows the absorption spectra of IMn(III)-TPP in MTHF measured before and after γ-ray irradiation at 77 K. The spectrum of IMn(III)TPP at 77 K closely resembles that at room temperature; the peak maxima are located at 550, 568, 602, and 646 nm in the Q band region. After γ-ray irradiation for 30 min the solution gives a new spectrum at 77 K. Since the spectrum measured at 77 K after once warming the irradiated solution for 1.0 min was identical with that of Mn(II)TPP prepared chemically, the new band is ascribed to the one-electron reduced species of IMn-(III)TPP, which is transformend to Mn(II)TPP at elevated temperatures.

Figure 3 shows the absorption spectra of IMn(III)-TPP in ethanol solution before and after γ-ray irradiation at 77 K. No marked differences were observed between the two spectra of IMn(III)TPP at room temperature and 77 K. The location of the major absorption peaks in ethanol solution is fairly different from that in MTHF solution. γ-Ray irradiation of the solution gives rise to a new spectrum having major absorption peaks at 570 and 607 nm. The spectrum measured after once warming the irradiated solution shows the absorption maxima at 568 and 606 nm at 77 K, indicating the formation of Mn(II)TPP.

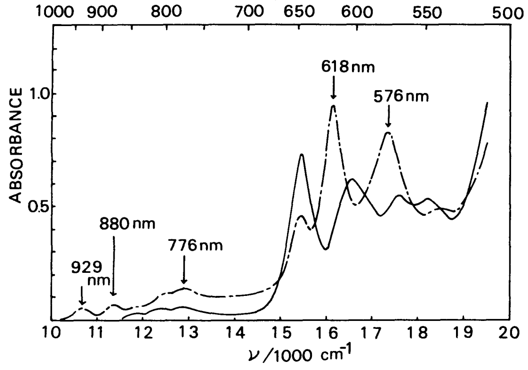


Fig. 2. Absorption spectra of IMn(III)TPP in MTHF solution at 77 K before (——) and after γ-ray irradiation for 30 min (— - —).

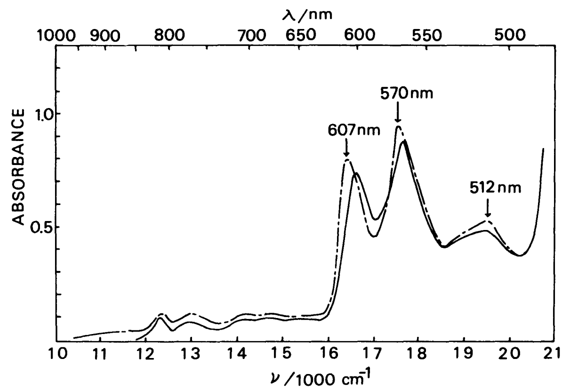


Fig. 3. Absorption spectra of IMn (III)TPP in ethanol solution at 77K before (——) and after γ-ray irradiation for 30 min (— - —).

The absorption spectrum of ClMn(III)TPP in MTHF solution markedly differs from that of IMn-(III)TPP in MTHF, probably due to the effects of the different axial ions, Cl^- and I^-. Contrary to the MTHF solutions, ethanol solutions of ClMn(III)TPP and IMn(III)TPP give the same absorption spectrum. This result is interpreted by assuming that both ClMn-(III)TPP and IMn(III)TPP undergo ionic dissociation in ethanol solutions to from a common species, $Mn(III)TPP^+(EtOH)_2$, in which the axial positions are occupied by two ethanol molecules.[22,23]

ESR Spectra of γ-Irradiated Solutions. Figure 4A shows the ESR spectrum obsérved for ethanol solution of ClCo(III)TPP γ-irradiated at 77 K. The hyperfine structure of a cobalt atom (I=7/2) appearing in the parallel component reveals that the central metal, Co(III), in ClCo(III)TPP is reduced to Co(II). The ESR parameters determined for the reduced species are $g_{/\!/}=2.010\pm0.005$, $A_{/\!/}=105\pm5\times10^{-4}\ \mathrm{cm}^{-1}$, $g_\perp\simeq2.45$, and $A_\perp\simeq57\times10^{-4}\ \mathrm{cm}^{-1}$. Figure 4B shows the ESR spectrum measured at 77 K after warming the irradiated solution for 1.0 min. This spectrum is identical with that of authentic Co(II)TPP which is expected to have a structure of $Co(II)TPP(EtOH)_2$ in ethanol solution at 77 K. The ESR parameters are $g_{/\!/}=2.024\pm0.005$, $A_{/\!/}=99\pm5\times10^{-4}\ \mathrm{cm}^{-1}$, $g_\perp\simeq2.45$, and $A_\perp\simeq57\times10^{-4}\ \mathrm{cm}^{-1}$.

Figure 5A shows the ESR spectrum observed for the γ-irradiated MTHF solution of IMn(III)TPP at 77 K. The spectrum shows well-resolved six hyperfine lines due to ^{55}Mn (I=5/2) at the g=6 region in addition to an intense signal from solvent radicals at g=2.0. The absence of the hyperfine coupling due to the iodine

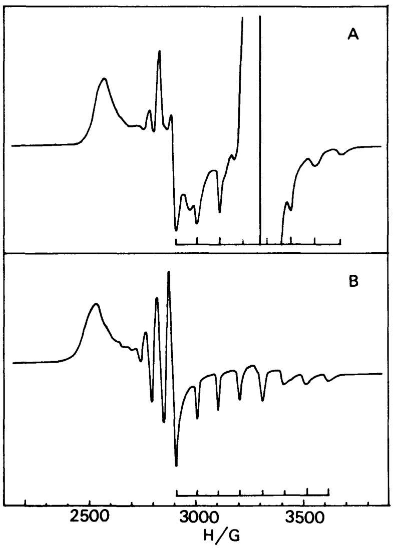


Fig. 4. ESR spectra of ClCo(III)TPP solution in ethanol measured at 77K after 20 min γ-irradiation (A), followed by 2.0 min warming of the irradiated solution (B).

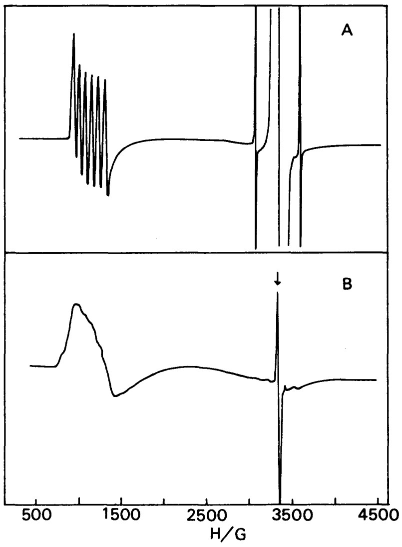


Fig. 5. ESR spectra IMn(III)TPP solution in MTHF measured at 77K after 20 min γ-irradiation (A), followed by 2.0 min warming of the irradiated solution (B). An arrow in B indicates the signal from color centers in quartz tube.

atom implies that the I–Mn bond in IMnTPP is dissociated by the dissociative electron attachment. Figure 5B shows the ESR spectrum measured for the γ-irradiated solution at 77 K after once warming it to remove signals due to solvent radicals. The low-field signal at g=6 becomes broad and the high field signals becomes observable by warming the irradiated sample. The ESR spectrum is the same as that of authentic Mn(II)TPP in MTHF solution at 77 K.

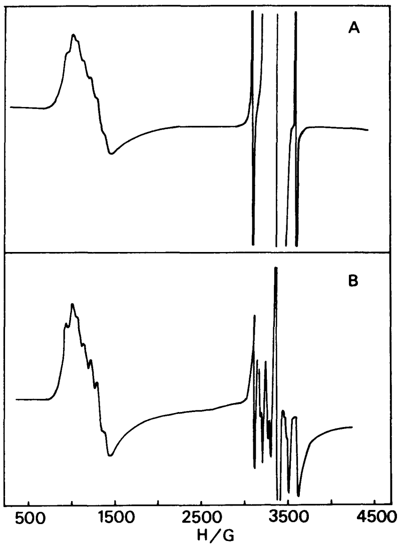


Fig. 6. ESR spectra of IMn(III)TPP solution in ethanol measured at 77K after 20 min γ-irradiation (A), followed by 2.0 min warming of the irradiated solution.

Figure 6A shows the ESR spectrum of a γ-irradiated ethanol solution of IMn(III)TPP at 77 K. The spectrum shows less-resolved six hyperfine lines at g=6. When the irradiated solution is warmed for 1.0 min and recooled to 77 K, the signal intensity at g=6 slightly decreases and a new signal due to unidentified manganese(II) species appears at $g \simeq 2$. The line shape of the low-field signals is invariant even after warming the irradiated solution. These results are in good accord with those obtained for the γ-irradiated Mn(III)TPP solution in deuterated methanol at 77 K.[9)]

A γ-irradiated ethanol solution of ClMn(III)TPP gives the same ESR spectra, both before and after warming, as those shown in Fig. 6A and 6B. This result implies that the common species is produced from the ethanol solutions of ClMn(III)TPP and IMn(III)TPP upon γ-ray irradiation. Taking account of the optical measurements, Mn(III)TPP$^+$(EtOH)$_2$ is considered to be a precursor of the reduced species in the ethanol solutions.

Discussion

Formation of One-electron Reduced Species by γ-Ray Irradiation. Solid ethanol solutions exposed to γ-rays at 77 K release mobile electrons (e_m^-) according to:

$$CH_3CH_2OH \longrightarrow CH_3CH_2OH^+ + e_m^-$$

The ethanol cation radical, $CH_3CH_2OH^+$, undergoes ion-molecular reaction with a parent ethanol molecule to form a 2-hydroxyethyl or ethoxyl radical and a protonated ethanol.[13)] The mobile electrons are either trapped in the solution or captured by solute molecules (S) if any to form trapped electrons (e_t) or solute anions (S^-), respectively:

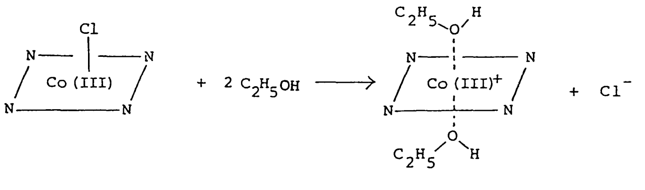
$$e_m^- \longrightarrow e_t^-$$

$$e_m^- + S \longrightarrow S^-.$$

The similar processes take place in MTHF solution, too. γ-Irradiation of metalloporphyrin solutions in ethanol or MTHF at 77 K, therefore, produces one-electron reduced metalloporphyrins along with e_t^- and radicals originated from ethanol or MTHF molecules. The absorption spectra of one-electron reduced metalloporhyrins in ethanol are measured after photobleaching of e$_t$ which has a broad absorption band centered around 530 nm.[25,26]

Identification of One-electron Reduced Species at 77 K. The one-electron reduced product of ClCo(III)TPP in MTHF at 77 K has a structure of a constrained complex in which the anion, Cl$^-$, is confined in the axial position of Co(II)TPP.[12] The ESR spectrum of the constrained complex is characteristically different from that of authentic Co(II)TPP in MTHF solution at 77 K. The ESR parameters of the constrained complex are qualitatively interpreted by assuming that A$^2_1$ state of Co(II)TPP is mixed with the higher excited states[27] such as E^4 by electrostatic interaction due to the axial anion.

The one-electron reduced species of ClCo(III)TPP in ethanol solution at 77 K, on the other hand, does not form the constrained complex. The fact that the ESR parameters of the one-electron reduced species in ethanol considerably resemble those of authentic Co(II)TPP suggests that Cl$^-$ is located far from the cobalt atom in Co(II)TPP. The paperelectrophoresis studies revealed that ClCo(III)TPP in alcohol solution is dissociated as[28]



Consequently ClCo(III)TPP in ethanol solution at 77 K is regarded as having a form of Co(III)TPP$^+$(EtOH)$_2$. When the ethanol solution is exposed to γ-rays, Co(III)TPP$^+$(EtOH)$_2$ is reduced by a mobile electron to form Co(II)TPP(EtOH)$'_2$ which is transformed to Co(II)TPP(EtOH)$_2$ by warming the irradiated solution. Since Co(III)TPP$^+$(EtOH)$_2$ may accept a mobile electon without accompanying displacement of axial ethanol molecules owing to high viscosity of the solvent at 77 K, the distance, $\mathrm{Co{-}O}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{C_2H_5}\end{smallmatrix}$, in Co(III)TPP$^+$(EtOH)$'_2$ is expected to be almost the same as that in Co(III)TPP$^+$(EtOH)$_2$. Taking account of the electrostatic interaction between a positively charged Co(III) atom and an oxygen atom of axial ethanol, the Co–O distance in Co(III)TPP$^+$(EtOH)$_2$ is reasonably assumed to be shorter than that in Co(II)TPP(EtOH)$_2$. We therefore conclude that the Co–O distance in Co(II)TPP(EtOH)$'_2$ is shorter than that in Co(II)TPP(EtOH)$_2$. The transformation of CO(II)TPP(EtOH)$'_2$ to Co(II)TPP(EtOH)$_2$ by warming presumably results in a small displacement of axial ethanol molecules and, therefore, in the absorption and ESR spectral change of the one-electron reduced product of ClCo(III)TPP in ethanol at elevated temperatures.

The ESR spectrum observed for the γ-irradiated ethanol solutions of IMn(III)TPP at 77 K shows six hyperfine lines due to ^{55}Mn at g=6, indicating the formation of high-spin Mn(II)TPP which has a d^5-electron configuration. For MTHF solution, the structure of the reduced species is concluded to be I$^-$···Mn(II)TPP on the basis of the previous ESR studies on one-electron reduced species of ClMn(II)-TPP and BrMn(III)TPP; the two species give well-resolved ESR spectrum at g=6 owing to the effects of the axial anions.[16] Warmig the irradiated IMn(III)-TPP solution gives the same ESR spectrum at 77 K as that for chemically prepared Mn(II)TPP. This result indicates that liberation of I$^-$ from I$^-$··· Mn(II)TPP occurs by warming. The one-electron reduced species of IMn(III)TPP in ethanol solution, on the other hand, gives less resolved ESR spectrum at g=6, which is in good accord with that of chemically prepared Mn(II)TPP. We concluded that axial anion I$^-$ is located far from the central Mn atom in the ethanol solution.

Conclusion

The absorpion spectra of ClCo(III)TPP and IMn(III)TPP in ethanol solutions are essentially different from those in MTHF solutions. The optical and ESR studies on their one-electron reduced species produced by γ-ray irradiation at 77 K show that these species retain axial anions in MTHF whereas not in ethanol. This fact leads to the conclusion that ClCo(III)TPP or IMn(III)TPP has already been dissociated in ethanol solutions into Co(III)TPP$^+$(EtOH)$_2$ and Cl$^-$ or Mn(III)TPP$^+$-(EtOH)$_2$ and I$^-$ prior to acceptance of an electron ejected from solvent molecules by γ-ray irradiation.

References

1) J. Faier and M. S. Davis, "The Prophyrins", ed by D. Dorphin, Academic Press: New York (1979), Vol. IV part B, p. 167.

2) M. Nakamura and S. Fujiwara, *J. Coord. Chem.*, **1**, 221 (1971).

3) H. Kawazoe, H. Hosono, J. Nishii, and T. Kanazawa, *J. Chem. Phys.*, **76**, 3429 (1982).

4) O. P. Anderson and M. C. R. Symons. *J. Chem. Soc. Commun.*, **1972**, 1020.

5) J. R. Shock and M. T. Rogers, *J. Chem. Phys.*, **62**, 2640 (1975).

6) W. C. Lin, C. A. McDowell, and D. J. Ward, *J. Chem. Phys.*, **49**, 2883 (1968).

7) M. Hoshino S. Konishi, M. Nakajima, and M. Imamura, *Bull. Chem. Soc. Jpn.*, **56**, 1233 (1983).

8) P. Neta, *J. Phys. Chem.*, **85**, 3678 (1981).

9) R. Rao and M. C. R. Symons, *J. Chem. Soc. Faraday Trans.*, **78**, 3393 (1982).

10) M. C. R. Symons and R. L. Peterson, *Biochim. Biophys. Acta*, **535**, 241 (1978).

11) L. C. Dickinson and M. C. R. Symnons, *J. Phys. Chem.*, **86**, 917 (1982).

12) S. Konishi, M. Hoshino, and M. Imamura, *Chem. Phys. Lett.*, **72**, 459 (1980).

13) S. Konishi, M. Hoshino, and M. Imamura, *J. Phys. Chem.*, **84**, 3437 (1980).

14) M. Hoshino, K. Ikehara, M. Imamura, H. Seki, and Y. Hama, *Photochem. Photobiol.*, **34**, 75 (1981).

15) M. Hoshino, S. Konishi, Y. Terai, and M. Imamura, *Inorg. Chem.*, **21**, 89 (1982).

16) S. Konishi, M. Hoshino, and M. Imamura, *J. Phys. Chem.*, **86**, 1412 (1982).

17) M. Hoshino, S. Konishi, K.Ito, and M.Imamura, *Chem. Phys. Lett.* **88**, 138 (1982).

18) S. Konishi, M. Hoshino, and M. Imamura, *J. Am. Chem. Soc.*, **104**, 2057 (1982).

19) S. Konishi, M. Hoshino, and M. Imamura *J. Phys. Chem.*, **86**, 4537 (1982).

20) T. Sakurai, K. Yamamoto, H. Naito, and M. Nakamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3042 (1976).

21) A. D. Alder, F. R. Long, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

22) L. J. Boucher, *J. Am. Chem. Soc.*, **90**, 6640 (1968).

23) L. J. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972).

24) M. Hoshino, S. Arai, M. Imamura, K. Ikehara, and Y. Hama, *J. Phys. Chem.*, **84**, 2576 (1980).

25) T. Shida and M. Imamura, *J. Phys. Chem.*, **78**, 232 (1974).

26) M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1127 (1965).

27) B. R. McGarvy, *Can. J. Chem.*, **53**, 2498 (1975).

28) K. Yamamoto, *Sci. Papers Inst. Phys. Chem. Res.*, **71**, 111 (1977).