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The Reactions of Mobile Electrons in the Frozen Solution of Ethylene Glycol-Water at 77°K

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The yield of trapped electrons produced in ethylene glycol-water glass at 77°K increased linearly with the gamma dose up to 1.5×10^{20} eV/g, and the *G* value was estimated to be 2.8 ± 0.2. The relative reaction rates of mobile electrons with various inorganic ions at 77°K were determined by competition kinetics. The observed relative reaction rates with simple inorganic ions corresponded to those of hydrated electrons obtained at room temperature. For complex ions, however, the reactivities of the mobile electrons were larger than those of hydrated electrons. The reaction products, such as bromine dioxide, Cr(V) species, and the pentacyano Co(II) ion, all of which are unstable at room temperature, could be detected by optical and ESR spectroscopies at 77°K.

A large number of rate constants for the reaction of the hydrated electron, e_{aq}^-, with solutes have been determined by competition kinetics and pulse-radiolysis techniques.[1] For the mobile electron, e_m^-, produced in acidic or alkaline ices at 77°K, some investigators[2-4] have determined the relative rates of reaction with metal cations and oxyanions. The results observed have shown that the relative reactivity of e_m^- with a solute is quantitatively similar to that of e_{aq}^- with the same solute. Based on these correlations, Kevan has postulated e_m^- as a mobile solvated electron in ice.[2] This preposition also implies that the structure of e_m^- at the time of reaction is similar to that of e_{aq}^-.

Dainton and his co-workers[4,5] have demonstrated that, in 5.4 M sulfuric acid at 77°K, an e_m^- can reduce solutes such as transition metal cations and nitrous oxide. The reaction products of lower valency states are trapped in the matrix; they have been studied by both optical and ESR spectroscopies. However, it is difficult to study the reactivity of e_m^- with solutes which are subject to decomposition in concentrated acid or alkaline solutions.

In the present paper, a study on the rate of the reaction of e_m^- with electron scavengers such as simple inorganic and complex ions was made by employing a neutral solution of an ethylene glycol-water mixture as the solvent matrix. The trapped electron, e_t^-, produced in this matrix by gamma irradiation is indefinitely stable in dark at 77°K and has an absorption band in the visible region which can be readily photobleached by exposure to the visible light. It is well-known[6,7] that the *G* value of the e_t^- produced at 77°K is comparatively high and reaches its maximum in the region of 50—65 vol% ethylene glycol, which is suitable for quantitative investigations of the reactivity of e_m^-. The products resulting from the e_m^- reactions could also detected by optical and ESR spectroscopies. In some cases, the results were correlated with the data obtained by pulse-radiolysis and flash photolysis.

Experimental

Sample Preparation. Water was distilled three times, and ethylene glycol from the Kanto Kagaku Co., Ltd., was fractionally distilled. All of the other chemicals were of analytical reagent grade and were used without further purification. As the solvent matrix, 67 vol% ethylene glycol diluted with pure water was used. Each sample contained 10^{-3}—5×10^{-2}M metal sulphate or potassium salt as an electron scavenger. The solution was degassed and made into the glassy state by the freeze-pump-thaw technique at 77°K.

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[1] M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

[2] L. Kevan, *J. Amer. Chem. Soc.*, **89**, 4238 (1967).

[3] L. Kevan, P. N. Moorthy, and J. J. Weiss, *ibid.*, **86**, 771 (1964); L. T. Bugaenko and O. S. Povolotskaya, *Khim. Vys. Energ.*, **1**, 480 (1967); B. G. Ershov and A. K. Pikaev, *Radiation Res. Rev.*, **2**, 62 (1968).

[4] D. M. Brown and F. S. Dainton, *Trans. Faraday Soc.*, **62**, 1139 (1966).

[5] F. S. Dainton and F. T. Jones, *ibid.*, **61**, 1681 (1965).

[6] H. Hase, *J. Phys. Soc. Jap.*, **24**, 589 (1968).

[7] I. E. Makarov, B. G. Ershov, and A. K. Pikaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2170 (1969).

The cells for the spectrophotometric measurement were made of quartz with rectangular cross-sections and with overall dimensions of $0.10\times1.2\times3.5$ cm. For the ESR study, Spectrosil tubings of 0.45 cm i.d. were used.

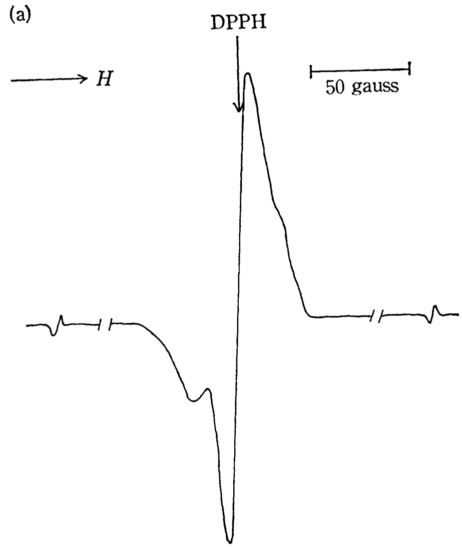
Irradiation and Measurement. Gamma irradiations by a ^{60}Co source were carried out in the dark at 77°K. The dose rate was 4.0×10^{18} eV g^{-1} hr^{-1} except where otherwise described.

The optical absorption spectra were obtained with a Shimadzu QV-50-type spectrophotometer by the use of a Dewar flask with quartz windows. The yield of e_t^- was determined from the decrease in the optical density at 530 nm after the photobleaching procedure. The photobleaching of e_t^- was performed with a 400-W tungsten lamp whose UV light of wavelengths shorter than 350 nm was cut off with a Toshiba color filter.

The ESR spectra were scanned on an X-band ESR spectrometer (Japan Electron Optics Laboratory Co., Ltd., JEP-1) operating at ~9.3 kMc/s and employing 100 kc/s magnetic-field modulation and phase-sensitive detection. The gamma-irradiated samples were first transferred into a quartz Dewar flask of the temperature of liquid nitrogen. Then the vessel was placed inside the cavity of ESR spectrometer equipped with a dry N_2 gas-flow system. The *g*-factors were determined by employing nitrogen oxide radicals trapped in 0.6M $NaNO_3$ ice as a standard. Its isotropic splitting constant was taken to be 54.7 *G*, with a *g*-factor of 2.001.[8]

Results and Discussion

Yield of e_t^- in the Ethylene Glycol-Water Mixture. After gamma irradiation in the dark at 77°K, ethylene glycol-water glass developed a deep blue color. The color readily decayed, however, upon exposure to the visible light ($\lambda>350$ nm). The optical absorption spectra were essentially identical with those of e_t^- reported by Ershov *et al.*[9]



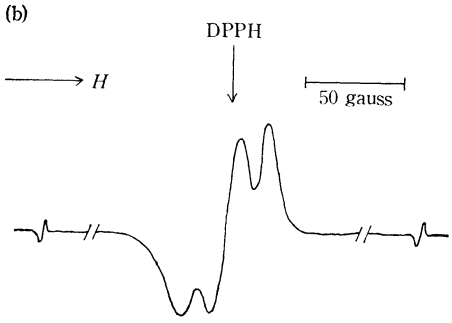


Fig. 1. ESR spectra of ethylene glycol-water glasses irradiated with gamma rays to a dose of 5.0×10^{18} eV/g at 77°K.
(a) before photobleaching, (b) after photobleaching

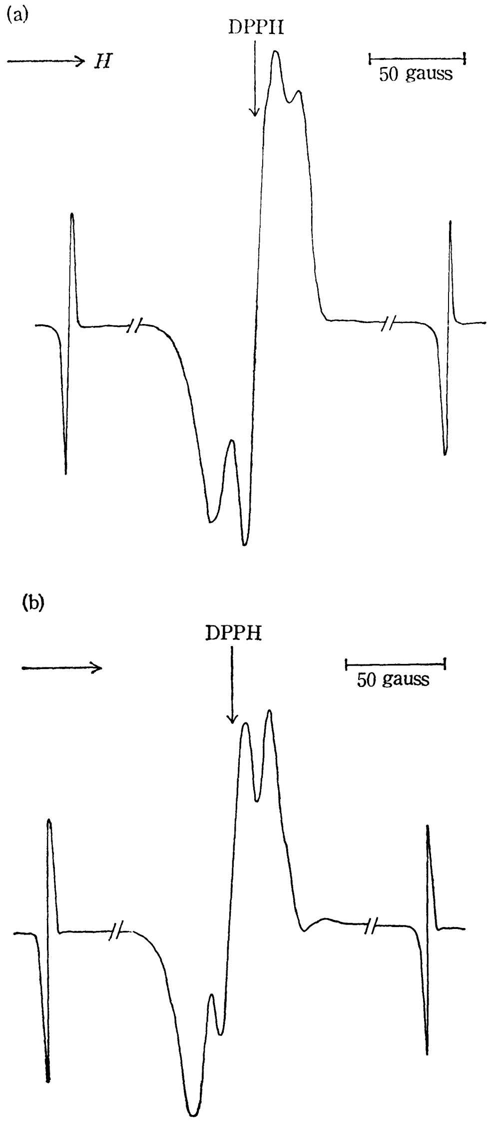


Fig. 2. ESR spectra of ethylene glycol-water glasses irradiated with gamma rays to a dose of 7.3×10^{20} eV/g at 77°K.
(a) before photobleaching, (b) after photobleaching

A signal due to e_t^- was also detected by ESR measurement, together with those of hydrogen atoms and some different organic radicals. One of the spectra observed at 77°K is displayed in Fig. 1(a). Besides an H-atom doublet with a splitting of 510 *G*, a signal attributable to e_t^- superimposed by those of the organic

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[8] L. Kevan, *J. Phys. Chem.*, **68**, 2590 (1964).

[9] B. G. Ershov, I. E. Makarov, and A. K. Pikaev, *Khim. Vys. Energ.*, **1**, 404 (1967).

radicals was observed in the central part of the spectrum. The line shape was changed by the photobleaching of e_t^- with the visible light, and the signals due to the organic radicals which have been assigned to the $HOCH_2CH_2\dot{O}$ and $HOCH_2\dot{C}HOH$ radicals[7] clearly appeared, as is shown in Fig. 1(b). For the samples irradiated with gamma doses higher than about 1.5×10^{20} eV/g, a decrease in the ratio of the signal intensity of e_t^- to that of hydrogen atoms was observed. The central part of the spectrum was also changed, as may be seen in Fig. 2.

The yield of e_t^- in the ethylene glycol-water glass increases linearly up to a dose of about 1.5×10^{20} eV/g. Assuming that the extinction coefficient of e_t^- produced in the matrix at 77°K is identical with that of e_t^- in the irradiated alkaline glass, 1.37×10^4 $\text{M}^{-1}\,\text{cm}^{-1}$ at 530 nm,[10] the G value of e_t^- can be estimated to be 2.8±0.2. It is noteworthy that this value agrees well with the maximum G value of e_t^- produced in the alkaline glasses (3.0 in 10 M KOH glass[10]). The yield of e_t^- reaches its maximum at *ca.* 1×10^{21} eV/g and then decreases, while those of the hydrogen atoms and organic radicals increase with the absorbed dose, as is shown in Fig. 3. Such a dose dependence of e_t^- is identical with the observations for the 10 M NaOH frozen solutions irradiated with gamma rays of doses higher than *ca.* 2.5×10^{20} eV/g.[11] The characteristics observed may arise from di-electron formation and the disappearance due to the recombination reaction of e_t^- with the positive-ion radicals.

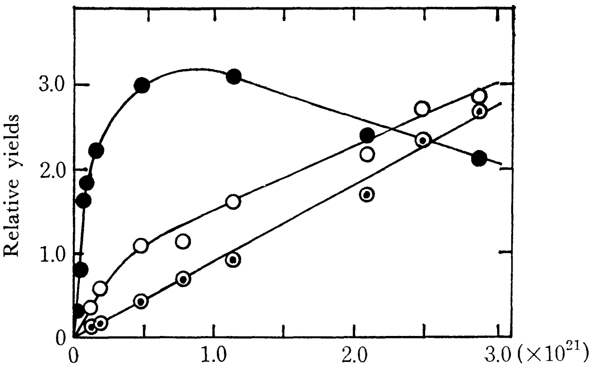

Fig. 3. Relative yields *vs.* absorbed energy of gamma irradiation. In the region of the dose higher than 1.1×10^{21} eV/g, the samples were irradiated at the dose rate of 2.4×10^{19} eV/ghr.
●: trapped electron, ○: organic radicals
⊙: trapped hydrogen atom

Reaction Rates of e_m^- with Electron Scavengers. The relative reaction rates of e_m^- can be determined by a competition reaction, such as:

$$e_m^- + T \xrightarrow{k_1} e_t^- \tag{1}$$

$$e_m^- + S \xrightarrow{k_2} S^- \tag{2}$$

where T and S are the electron trap and the electron scavenger respectively. Competition kinetics applied to the e_m^- reaction in the system yields the following expression:

$$\frac{C_0(e_t^-)}{C(e_t^-)} - 1 = \frac{k_2[S]}{k_1[T]} \tag{3}$$

where $C_0(e_t^-)$ and $C(e_t^-)$ are the e_t^- concentrations in the absence and in the presence of the scavenger. Because the optical density at 530 nm, $D(e_t^-)$, is proportional to the e_t^- concentration, the relative value of k_2 is obtained from the slope of the straight line by plotting $\{D_0(e_t^-)/D(e_t^-)-1\}$ against [S].

The results for NO_3^-, $[Fe(CN)_6]^{3-}$, and $[Co(CN)_6]^{3-}$ ions, corrected for the absorption of the solvent matrix and quartz cell, are shown in Fig. 4. The ordinate values increases linearly with the scavenger concentration, and no effect on the electron-trap concentration was observed upon the addition of the electron scavenger. The relative rates for the e_m^- reactions with various inorganic ions are summarised in Table

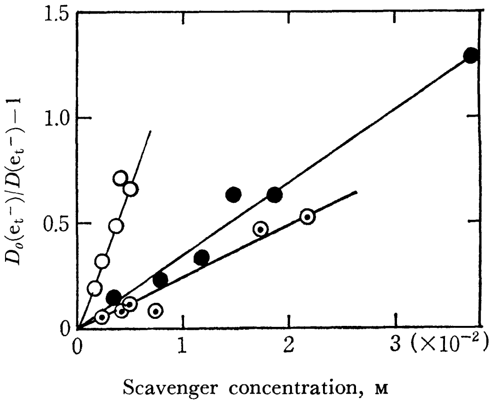

Fig. 4. Relationships between $\{D_0(e_t^-)/D(e_t^-)-1\}$ and scavenger concentration. All samples were irradiated to a gamma dose of 4.0×10^{18} eV/g at 77°K.
●: NO_3^-, ○: $[Fe(CN)_6]^{3-}$, ⊙: $[Co(CN)_6]^{3-}$

TABLE 1. RELATIVE RATES OF e_m^- AND e_{aq}^- REACTIONS WITH VARIOUS IONS

Ion(S)	Relative rates[a)]	
	$k(e_m^- + S)$ at 77°K	$k(e_{ap}^- + S)$[b)] at ∼300°K
NO_3^-	1	1
Cu^{2+}	3.6	3.0
Fe^{3+}	2.8	—
ClO_3^-	≪0.1	3.6×10^{-4}
BrO_3^-	0.2	0.19
IO_3^-	0.6	0.70
CN^-	≪0.1	$<10^{-4}$
$[Fe(CN)_6]^{3-}$	3.9	0.40
$[Fe(C_2O_4)_3]^{3-}$	2.4	—
$[Co(CN)_6]^{3-}$	0.6	0.25
$[Co(C_2O_4)_3]^{3-}$	3.1	1.1

a) All rates were normalized to NO_3^- rate=1.
b) The data were cited from the table compiled by Anbar and Neta.[1]

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[10] B. G. Ershov, O. F. Khodzhaev, and A. K. Pikaev, *Dokl. Akad. Nauk SSSR*, **179**, 911 (1968).

[11] L. Kevan, D. Renneke, and R. J. Friauf, *Solid State Commun.*, **6**, 469 (1968); H. Hase and L. Kevan, *J. Phys. Chem.*, **73**, 3290 (1969).

1; those for the e_m^- reaction obtained at pH 7.0 are also presented for comparison.

In the case of all inorganic ions except the complex ion, the relative values of the e_m^- rates agree with those of the e_{aq}^- rates. The correlations seem to support Kevan's postulations[2,12] that e_m^- in ice acts as a mobile solvated electron and that the entropic effects of the scavenger ions are responsible for the rate differences between the different solutes. On the other hand, the e_m^- rates for complex ions are usually larger than the e_{aq}^- rates for the corresponding ions. This finding is unexpected, and it seems that more experimental data are neccessary to give a definite explanation of the reactivity of e_m^- with complex ions.

Spectra of Reaction Products. After the photobleaching of e_t^-, the irradiated glass containing the bromate ion gave an optical absorption spectra with a tail in the UV region and a peak at 475 nm, as is shown in Fig. 5. This absorption band disappeared upon thermal annealing at *ca.* 140°K. The peak position is in good agreement with that of the transient species observed in the pulse-radiolysis experiment at room temperature;[13] therefore, it may be thought to be due to the bromine dioxide (BrO_2) which is produced in the reaction:

$$e_m^- + BrO_3^- \rightarrow BrO_2 + O^{2-} \tag{4}$$

An analogous reaction scheme was proposed for the reduction of the bromate ion with e_{aq}^- by flash photolysis.[14] In the irradiated solution containing the iodate ion, however, the clear optical spectrum of dioxide species could not be observed because it was superimposed by a tail of a stronger absorption of the iodine trioxide radical.[15]

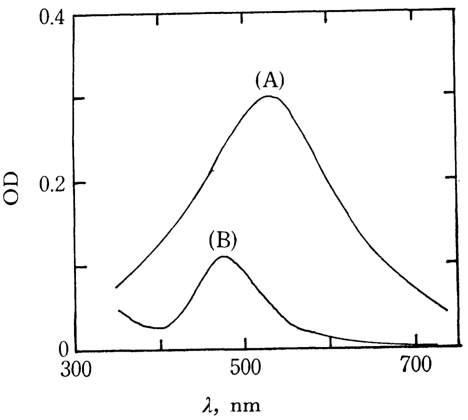

Fig. 5. Optical absorption spectra for glassy specimens irradiated gamma rays at 77°K.
(A): Ethylene glycol-water glass irradiated to a dose of 3.8×10^{18} eV/g (before photobleaching).
(B): Ethylene glycol-water glass containing 0.05 M $KBrO_3$ irradiated to a dose of 5.6×10^{19} eV/g (after photobleaching).

The extinction coefficient of the bromine dioxide observed can be determined from the optical density in Fig. 5, assuming that Eq. (3) is correct up to the solute concentration of the order of 0.05 M. Since the bromine dioxide concentration, $C(BrO_2)$, is equal to $C_o(e_t^-)-C(e_t^-)$, it can be expressed as follows:

$$C(BrO_2) = \frac{K[S]C_o(e_t^-)}{1+K[S]} \tag{5}$$

where K is $k_2/(k_1[T])$. Therefore, the extinction coefficient, $\varepsilon(BrO_2)$, is related with the reaction rate of bromate ion by the following expression:

$$\varepsilon(BrO_2) = \frac{D(BrO_2)}{C(BrO_2)\cdot l} = \frac{(1+K[S])\,D(BrO_2)}{K[S]C_o(e_t^-)\cdot l} \tag{6}$$

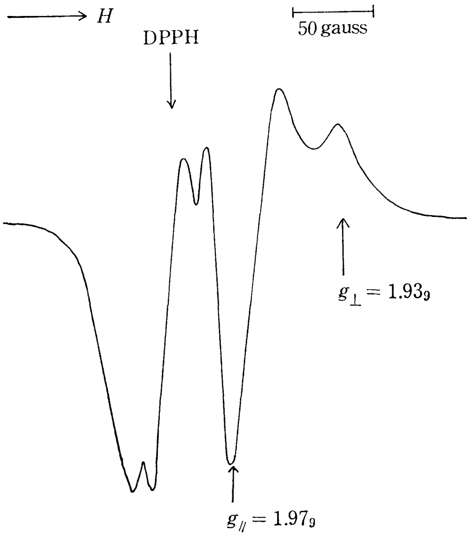

Fig. 6. ESR spectrum of 0.1 M K_2CrO_4 solution irradiated with gamma rays to a dose of 5.0×10^{19} eV/g and photobleached at 77°K.

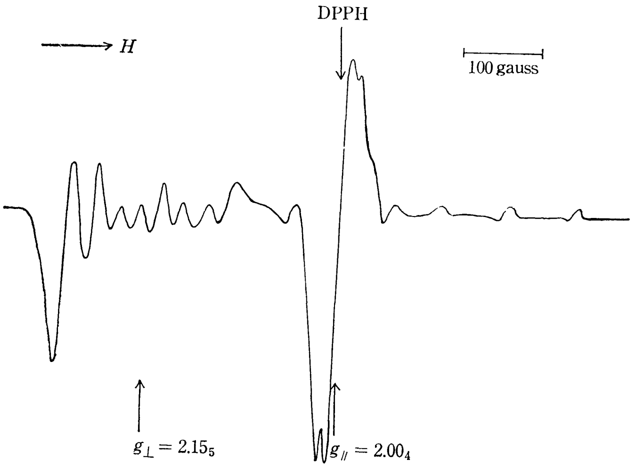

Fig. 7. ESR spectrum of 0.07 M $K_3[Co(CN)_6]$ solution irradiated with gamma rays to a dose of 5.0×10^{19} eV/g and photobleached at 77°K.

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12) L. Kevan, "Radiation Chemistry of Aqueous Systems," ed. by G. Stein, Wiley-Interscience, New York (1968); p. 64.

13) G. V. Duxton and F. S. Dainton, *Proc. Roy. Soc. A.*, **304**, 427 (1968); O. Amichai and A. Treinin, *J. Phys. Chem.*, **74**, 3670 (1970).

14) O. Amichai, G. Czapski, and A. Treinin, *Isr. J. Chem.*, **7**, 351 (1969).

15) The trioxide species might be produced in consequence of the following hole reaction:

$$M \rightsquigarrow M^+ + e_m^-$$
$$M^+ + IO_3^- \longrightarrow M + IO_3$$

where M denotes the solvent matrix.

where D is the optical density and l is the optical path. The value of K is determined to be 6.5 M^{-1} from the slope of the scavenger curve, and $C_0(e_t^-)$ is 3.2×10^{-3} M in the ethylene glycol-water glass irradiated with a dose of 5.6×10^{19} eV/g. Thus, $\varepsilon(\text{BrO}_2)$ can be estimated to be approximately $1.4\times10^3\ \text{M}^{-1}\ \text{cm}^{-1}$ at 475 nm.

In the presence of the chromate ion as an electron scavenger, an intermediate species was also detected by ESR spectroscopy. The spectrum recorded at 77°K is shown in Fig. 6. An anisotropic signal on the low g-factor side of the free-electron position, which was also observed in the 6 M sulfuric acid matrix, indicates the formation of an electron-rich center. The line shape and the principal g-factors are characteristic of the Cr(V) species formed in the frozen solutions[16] as a result of the electron capture of the chromate ion.

Figure 7 shows the ESR spectrum of a gamma-irradiated glassy specimen containing the 0.07 M hexacyano cobaltate ion. In addition to the central signals resulting from the organic radicals, the specimen gives two eight-line hyperfine patterns. The spectrum is interpreted as consisting of superimposed parallel and perpendicular absorptions; each splits into eight lines, with coupling constants of 30 and 91 G respectively, by means of ^{59}Co ($I=7/2$) nuclear interactions. The respective g-factors and the hyperfine constants are characteristic of those observed for the penta-coordinated Co(II) complex ion rather than the hexa-coordinated Co(II) complex ion in frozen solutions at 77°K by Kataoka and Kon.[17] Therefore, the spectrum obtained strongly suggests the formation of the pentacyano Co(II) ion in consequence of the reaction associated with e_m^-:

$$[\text{Co(CN)}_6]^{3-} + e_m^- \rightarrow [\text{Co(CN)}_5]^{3-} + \text{CN}^- \qquad (7)$$

The authors wish to thank Dr. Mitsuru Koike for his useful suggestions.

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[16] P. N. Moorthy and J. J. Weiss, *Advan. Chem. Ser.*, **50**, 211 (1965).

[17] N. Kataoka and H. Kon, *J. Amer. Chem. Soc.*, **90**, 2978 (1968).