1100 © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 1100—1104 (1985) [Vol. 58, No. 4

Decomposition of Crystalline Potassium Hexacyanoferrate(II) Trihydrate by Incident Energetic Argon Ions†

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(Received November 9, 1984)

Ar^+ ions in the energy range of 0.4 to 2 MeV was found to induce a chemical reaction in solid potassium hexacyanoferrate(II) trihydrate giving rise to Fe^{3+}-ion clusters which have been evidenced by EPR observations. γ-Irradiations at high doses ($>10^9$ rad) followed by heating (>150 °C) were found to induce the same reaction. Irradiations with γ-rays, protons, or low-energy (<40 keV) Ar^+ ions alone did not induce this reaction, nor did a thermal activation. A possible mechanism for this reaction is discussed mainly from a qualitative point of view on the basis of experimental observations and results of atomic collision physics. It is concluded that the reaction is caused by a highly inelastic excitation of iron(II) in the complex which is accompanied with a simultaneous momentum transfer.

Radiation chemical reactions in matter due to energetic ion passage, and different from those due to γ-irradiations, are generally interpreted in terms of an LET (linear rate of energy transfer per unit length) effect.[1,2] An LET value itself for an energetic ion traversing a given medium increases with decreasing ion velocity and different LET radiations generally produce different spatial distributions of the initial products of radiolysis.[1,2]

On the other hand, recent results in atomic collision physics,[3–5] suggest that slow-moving particle collisions (in the energy range of 10 to 1000 keV) may result in such primary processes as inner shell or multiple excitations of an atom or molecule, which would involve an energy transfer per event much larger than outer-shell or single excitations. Thus, low-energy particle collisions may induce chemical reactions different from those induced by γ- and UV-irradiations. The importance of these highly inelastic processes in chemical or biological effectiveness was pointed out a long time ago,[6,7] and the processes themselves have been studied rather extensively[3–5] since then, but their chemical or biological consequences remain unexploited except for a few cases.[5,7,8] Atomic displacements in a collision cascade zone may also be important for possible chemical reactions in a material bombarded with energetic ions.[7]

In this paper we report that Ar^+ ions of a certain energy range induce a chemical reaction in solid cyanide complexes giving rise to Fe^{3+}-ion clusters, which have been evidenced by EPR observations. γ-Irradiations at doses higher than 10^9 rad (1 rad$=10^{-2}$ J kg^{-1}) followed by heating (>150°C) were found to induce the same reaction. Irradiations with γ-rays, protons, or helium ions alone did not induce this reaction, nor did a thermal activation. It seems that the reaction is caused through electronic excitations of the iron(II) in the complex which are accompanied by a simultaneous momentum transfer.

Experimental

Sample Preparation. Single crystals of potassium hexacyanoferrate(II) trihydrate (Koso Chemicals Co., Inc.) were grown from aqueous solutions. In some cases powders were pressed into disks of the diameter of 1 cm.

For comparison of the EPR spectra of the irradiated sample, some EPR spectra of solid solutions of aluminum oxide containing various amount of iron(III) were recorded. These solid solutions were prepared from aqueous solutions of $KAl(SO_4)_2 \cdot 12H_2O$ containing varing concentrations of iron(III) sulfate, reacted with NH_3+NH_4Cl to form precipitate, and then fired in a crucible for 20 min at 1000°C.

Irradiations. The samples to be irradiated were mounted onto the sample holder by means of clamps or with the aid of adhesives and were irradiated at ambient temperatures in vacuum (*ca.* 10^{-5} Pa) with energetic ion beams or γ-rays.

i) Van de Graaf accelerator: Ar^+ ions in the energy range of 0.4 to 2 MeV were from a Van de Graaf accelerator equipped with PIG- and RF-type ion sources. Other ions like H^+, N^+, and O^+ were also used in the present study.

ii) Low-energy ion accelerator: Ions with lower energies were from a small accelerator[9] which has been constructed in our laboratory. The Ar^+ ions were extracted from a Duoplasma-type source operated at a pressure of 20 to 50 Pa and further accelerated to a desired energy (10—100 keV), focussed by an electrostatic lens system, and analyzed electromagnetically before impinging on the target.

iii) Beam intensity: The intensity of the beam was from 0.1 to 10 μA depending on the ion used, and typically $\approx 10^{12}$ ions s^{-1} through an aperture of 0.4 cm^2.

iv) γ-Irradiation: γ-Irradiations were performed with a 4.5 kCi ^{60}Co source in aerated conditions. Irradiations were also done in vacuum for analysis of the evolved gases.

EPR Measurement. EPR spectra of irradiated samples were obtained with a JP-1 X-band (9.5 GHz) spectrometer (Japan Electron Optics Co., Ltd.) with a modulation of 100 kHz using a polycrystalline DPPH as a magnetic field marker and Mn^{2+} in MgO as a reference for the magnetic field strength.

The signal intensity of the absorption was measured by using an approximation $h \cdot \Delta H_m^2$, where h is the peak-to-peak height and ΔH_m the peak-to-peak linewidth of the first derivative of the spectrum, respectively.

Secondary Ion Mass Spectrometry. Secondary ions emitted from the surface of the sample during ion bombardment were mass analyzed with a quadrupole mass filter (MSQ-300, Ulvac Co., Tokyo). Bombardment were performed through an aperture of 2 mmϕ. Current densities were adjusted to 0.1 μA cm^{-2} for the convenience of getting relative yields of the emitted ions due to different kind of bombarding ions with

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[†] Chemical Reactions Induced by Energetic Particles. I.

different energies.

Results

EPR Measurements. Potassium hexacyanoferrate(II) trihydrate, a low spin Fe(II) complex, is a diamagnetic compound and shows no EPR signals. On exposure to a beam of 1.8 MeV Ar^{2+} or 450 keV Ar^+ ion the bombarded (010) surface of a single crystal of the sample was decomposed to give EPR-absorption spectra. In Fig. 1 are shown some of the spectra thus obtained.

The signal intensities of the central absorption at g=2.0 as a function of irradiation time are shown in Fig. 2, together with the values of the linewidth. As may be seen in Fig. 2, the signal grows linearly with irradiation time up to 2—3 min and then levels off. The linewidths are also dependent on irradiation time, ranging from 140 at the beginning to 300 G in cases of 1.8 MeV Ar^{2+} bombardment, and from 100 to 150 G in cases of 450 keV Ar^+ bombardment.

It should be noted that (i) these spectra were obtained at 300 K and stable for several months at room temperature, (ii) the central absorption at g=2.0 with a large width has a Lorentzian shape, and (iii) the ratio of the signal intensities taken at 300 and 77 K, I_{300}/I_{77}, for this absorption is remarkably large compared with the corresponding ratio for the absorption lines of Mn^{2+} in MgO.

Irradiations of the sample with 40 or 20 keV Ar^+ ions at the beam intensity of 0.3 and 10 μA cm^{-2} produced no remarkable EPR signal and, only after prolonged irradiations over 10 min at the intensity of 10 μA cm^{-2}, yielded the spectra which are shown in Fig. 3 (a) and (b). Besides the distinct line at the lower field, the central portion of the spectrum became gradually with irradiation time like that which would be obtained from the sample pre-heated at temperatures higher than 200 °C.

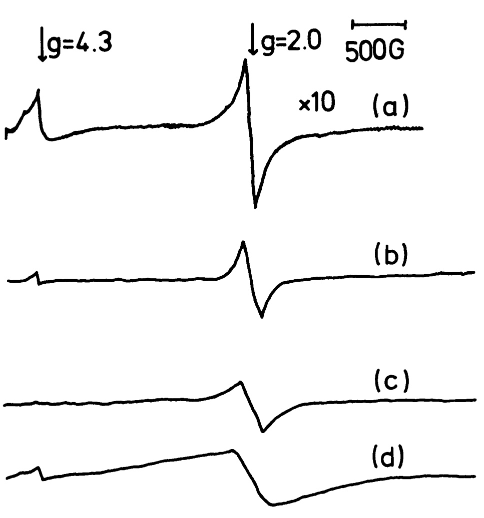

Fig. 1. EPR spectra of 1.8 MeV Ar^{2+}-irradiated (010) surface of $K_4[Fe(CN)_6]\cdot 3H_2O$. Current density: 0.75 μA cm^{-2}; irradiation time: (a) 10 s, (b) 1 min, (c) 5 min, and (d) 15 min.

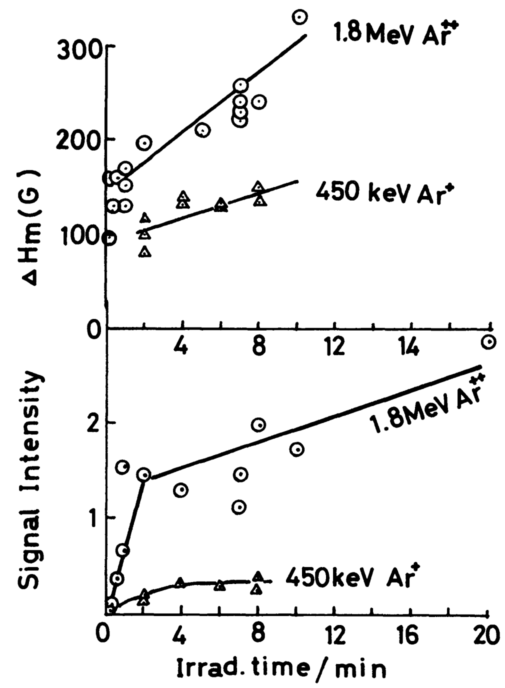

Fig. 2. Irradiation time dependence of signal intensity and linewidth ΔH_m of EPR spectrum of Fe^{3+} clusters formed in 1.8 MeV Ar^{2+}- and 450 keV Ar^+-ion bombarded (010) surface of $K_4[Fe(CN)_6]\cdot 3H_2O$. Ion current density: 0.75 μA cm^{-2}.

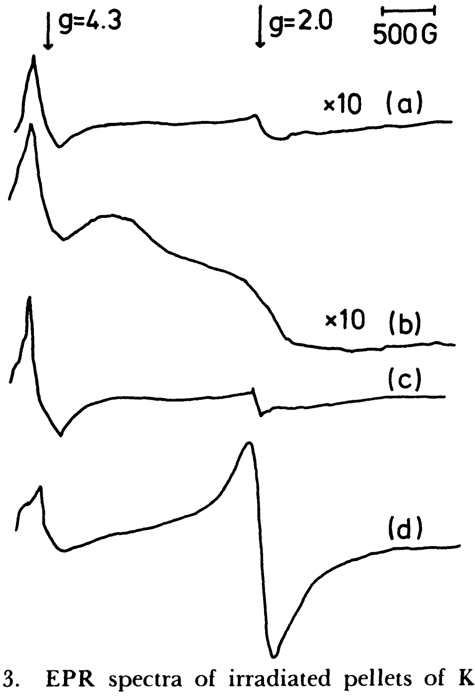

Fig. 3. EPR spectra of irradiated pellets of $K_4[Fe(CN)_6]\cdot 3H_2O$.
(a) 40 keV Ar^+-bombarded at 10 μA cm^{-2} for 10 min,
(b) 40 keV Ar^+-bombarded at 10 μA cm^{-2} for 30 min,
(c) 1.45 MeV H^+-bombarded at 1.5 μA cm^{-2} for 10 min, (d) ^{60}Co-γ irradiated at 4×10^9 rad followed by heating at 150 °C for 30 min.

Irradiations with 0.4 or 1.6 MeV H^+ ions were also performed at the intensity of 0.6 μA cm^{-2} with the results of Fig. 3 (c), similar to those obtained in the 20

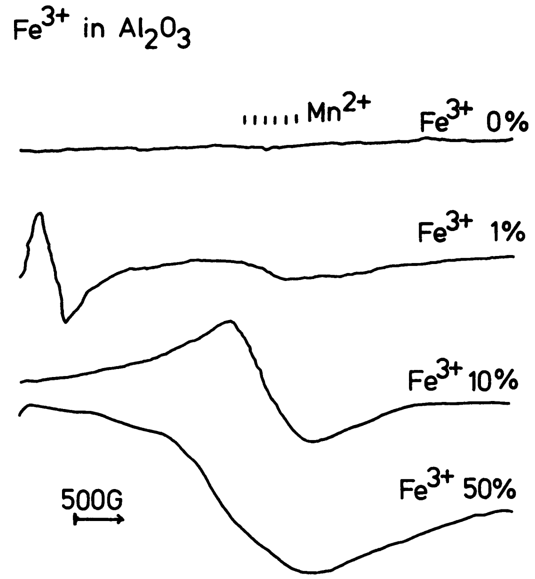

Fig. 4. EPR spectra of solid solutions of iron(III) oxide in aluminum oxide. The concentration of Fe^{3+} (*vs.* Al^{3+}): (a) 0, (b) 1, (c) 10, (d) 50%.

Table 1. EPR g factors and linewidths, and the relative yields of Fe^{3+} clusters from ion-bombarded $K_4[Fe(CN)_6]\cdot 3H_2O$.

Ion	Energy	$g(H//b)$[a]	$g(H\perp b)$[a]	ΔH_m	Relative yields
Ar^{2+}	1.8 MeV	1.98	2.03	140-300 G[b]	2.9
Ar^+	450 keV	1.99	2.02	100-150 G	0.23
Ar^+	20—40 keV	—	—	—	0
H^+	0.4—1.6 MeV	—	—	—	0

a) H=magnetic field; b=axis of irradiation beam. b) $G=10^{-4}$ T.

or 40 keV Ar^+-ion case.

γ-Irradiations at room temperature of the powder sample at doses below 10^9 rad were found to produce a line at g=4.3 alone and no other signals near at g=2.0. Further irradiations of the sample with γ-rays up to 10^{10} rad produced a single absorption line at g=2.06 of the linewidth ≈5 G at room temperature. This spectrum remained unchanged when treated at temperatures below 100 °C for an hour or so. When treated at higher temperatures, however, it disappeared to produce a strong absorption at g=2.0 with a large width as is shown in Fig. 3(d).

EPR spectra of solid solutions of aluminum oxide containing various amount of Fe^{3+} are shown in Fig. 4. Main features of the spectrum are as follows: (i) The sample of the low iron concentrations (≈1% with respect to Al) reveals an EPR absorption due to isolated Fe^{3+} ions at g=4.3, and (ii) at higher iron concentrations this spectrum is replaced by a Lorentzian signal which behaves as the absorption at g=2.0 in Fig. 1 and which has been attributed by Gesumundo *et al.*[10—12] to clusters of Fe^{3+} ions coupled by a strong exchange interaction.

Anisotropic Nature of the Line at g=2.0. The crystal type of potassium hexacyanoferrate(II) trihydrate is monoclinic, pseudo-tetragonal with lattice constants $a=c=9.3$ Å, $b=16.8$ Å, $\beta=90°$, four molecules in unit cell and space group C_{2h}^6.[13] The crystals grow in flat rectangular plates parallel to the ac plane, thus having well developed (010) faces. Energetic ions were bombarded onto a (010) plane. The EPR-absorption line at g=2.0 thus obtained was found to have an anisotropy of g factor. When the applied magnetic field is parallel to the direction of the incident beam, hereafter, denoted by b, g factor, $g(H//b)$, is around 1.98—1.99 and when the field is in the (010) plane, g factor, $g(H\perp b)$, is 2.02—2.03. The results are included in Table 1. We have verified that this anisotropic feature of the g factor is due to the direction of the Ar^+ beam and not to crystallographic anisotropy by having examined various factors which might be responsible for this anisotropy, *e.g.*, changes in the direction of the Ar^+ beam and the sizes and geometries of the sample to be bombarded, employment of the disk sample made from powders and as well as possible effects of the orientation of the specimen in the EPR cavity.

It must be noted that the absorption at g=2.0 appearing in the sample which has been γ-irradiated at doses higher than 10^9 rad and then heated at 100—200 °C shows no anisotropy of g factor.

Secondary Ion Mass Spectrometry. When crystals of potassium hexacyanoferrate(II) trihydrate were bombarded with energetic ions, various secondary ions were emitted from the bombarded surface. Positive secondary ions were mainly composed of H^+, C^+, O^+, K^+, and Fe^+. Such ions as C^{2+}, N^+, K_2^+, and probably K_2O^+ and KFe^+ in small yields were also included. Negative secondary ions were H^-, C^-, CH^-, O^-, and a small amount of OH^-, C_2^-, and KO^-. Effects of the kinetic energy of bombarding particle were examined in the case of Ar^+ ion in the energy range of 10 keV to 1.8 MeV. The yields of emitted ions were nearly unchanged when the energy of the bombarding Ar^+ ion varied from 1.8 MeV down to 70 keV, though increased as the Ar^+-ion energy decreased to 10—30 keV. In Fig. 5 are shown the results of changing the bombarding ion while the bombarding energy and the beam intensity were maintained at 450 keV and 0.3 μA cm^{-2}, respectively.

Gas Analysis. The gas evolved by the irradiation of the complex with ^{60}Co-γ rays at the dose of 3× 10^7 rad was submitted to mass analysis. While the main peaks in the mass spectrum were due to the water molecule, other peaks at mass number of 14 (N_2^{2+}), 28 (N_2^++CO^+), and 44 (CO_2^+) were remarkably significant, indicating that the ligand CN^- had been decomposed by γ-irradiation.

Discussion

When potassium hexacyanoferrate(II) trihydrate are subjected to ionizing radiations, *e.g.*, γ-rays or high-energy charged particles, many electronic processes will

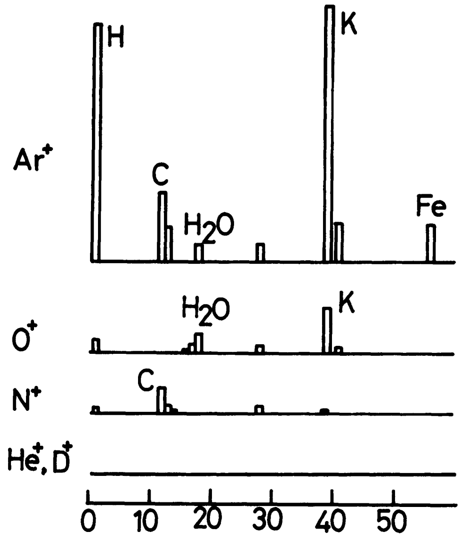

Fig. 5. Emitted positive ion spectrum from $K_4Fe(CN)_6] \cdot 3H_2O$ bombarded by various ions. Bombarding energy: 450 keV, Ion current density: 0.3 μA cm^{-2}.

occur. Among them only those processes which require a relatively small energy transfer per event have been studied from the viewpoint of chemical consequence of the initial process, the electronic transitions between d orbitals of Fe which induce the dissociation of the metal(Fe)–ligand(CN) bond and the electron transfer from metal(Fe) to ligand(CN) which results in oxidation of the Fe.[14] The oscillator strength for these electronic processes amounts only to 0.6.[15] The chemical consequence of the many other processes including inner shell and multiple excitations with a big energy transfer per event remain unstudied. In cases of the energetic particle penetrating a solid, the energy is also deposited into atomic motion, thus giving rise to a collision cascade or a thermal spike. A chemical effectiveness of the atomic motion is not clear for the present moment.[7,16,17]

Comparing the EPR spectra of Figs. 1 and 3 with those of Fig. 4, it is suggested that the spectrum at g= 4.3 observed in the irradiated sample can be attributed to the isolated Fe^{3+} ions and that the strong absorption at g=2.0 to Fe^{3+}-ion clusters. The EPR spectrum of Fe^{3+}-ion clusters have been studied by many workers[10–12,18,19] and it is known that their linewidth depends on two features, the dipole–dipole interaction which produces a broadening of the line and the exchange interaction which produces a narrowing.[10,18]

γ-Irradiations. It is expected that a single and isolated electronic excitation of the complex will be annealed at the ambient temperature without any effect of radiations, since the electronic system relaxes quickly while the atoms are still at rest.[20] The results of analyzing the evolved gas, however, indicate that γ-irradiation *does* decompose the ligand or crystalline water of the sample. Two possible processes may be assumed: (i) The electron ejected in the ionization event and having kinetic energy larger than 6 eV may be captured by H_2O molecule to form H^- and OH.[21] (ii) Ionizations of inner-shell orbital followed by the Auger process and double ionization and/or excitations of cyanides would result in the atomic displacement by Coulomb explosion mechanism.[8,22,23] In either processes the decomposition of the ligands may occur. The G value of these processes may be estimated to be 0.1.[24]

Further irradiations at doses of 10^9 rad may produce isolated Fe^{3+} ions (≈50% ligand decomposed) the d-shell electrons of which are now free from being quenched by the presence of the ligand and are responsible for an EPR signal at g=4.3.

However, γ-irradiations up to 4×10^{10} rad did not produce an EPR signal due to Fe^{3+} clusters, indicating that the distances between Fe^{3+} ions in the γ-irradiated sample were too large to interact with each other by an exchange process. By heating at *e.g.* 150 °C, displacement of Fe^{3+} ions in the irradiated solid may occur to aproach each other within the distances smaller than 7 or 8 Å.[10] It is interesting that a g factor of an EPR absorption of the Fe^{3+} clusters thus formed is isotropic in contrast to an EPR signal of Fe^{3+} clusters formed by the Ar$^+$-ion bombardment.

Proton Irradiations. Most of the energy of fast protons (0.4—1.6 MeV) goes into electronic excitations, though energetic recoil atoms (C, N, and O) with kinetic energies of 10 keV or less may be created.[7] Thus, the action of a fast proton is essentially the same as that of γ-rays. The present results may be understood as such.

Ar$^+$-ion Bombardment. An Ar$^+$ ion in the energy range below *ca.* 40 keV loses most of its energy to create energetic recoil atoms (C, N, and O)[7] which in turn form collision cascades or thermal spikes. The results of Fig. 5 indicate that, among the various incident ions examined, the Ar$^+$ ion is most effective for the atomic displacement. Moreover, the further results showed that displacement by the energetic Ar$^+$ ion is most effective in the energy range of 10 to 30 keV.

By 40 keV Ar$^+$-ion bombardment of the complex, an EPR signal due to isolated Fe^{3+} ions alone has been observed. Further irradiations with 40 keV Ar$^+$ ions modified the spectrum to a one similar to that observed when the complex was heated at temperatures higher than 200 °C (Fig. 3; b).

At higher bombarding energies, the kinetic energy of Ar$^+$ ion goes more and more into electronic excitations.[7] Moreover, many collisions between Ar$^+$ ions and atoms in the solid will be highly inelastic due to inner-shell or multiple excitations which are pronounced in the energy range from 50 keV to 1 MeV.[3,5] As examples of this type of collisions, it should be mentioned: Collision of two Ar atoms (≈100 keV) produced a number of highly charged particles like Ar^{2+}, Ar^{4+}, and Ar^{5+}, apparently due to successive processes of autoionization and electron shake off after the deposition of some 1000 eV energy into electron cloud of two Ar atoms.[25] Probably C, N, and O atoms, and especially Fe atoms will show the same effects in the case of Ar^+ bombardment at the energy higher than 100 keV. This could lead to a violent destruction of the complex, as has been discussed by Stöcklin in the case of biological compounds.[8]

In fact, the present results at Ar^+-ion bombarding energies of 450 keV or 1.8 MeV demonstrate that an EPR absorption due to Fe^{3+} clusters was obtained even at the lowest doses examined, *i.e.* 5 s irradiation at the ion current density of $0.3\ \mu A\ cm^{-2}\ s^{-1}$ which corresponds to 10^{13} Ar^+ ions cm^{-2}. At this dose, the tracks of incident Ar^+ ions probably do not overlap each other (radius of track ≈ 3 Å). Thus, one may conclude that Fe^{3+} clusters are formed even in a single track of an incident Ar^+ ion.

It should be further noted that an EPR absorption of Fe^{3+} clusters thus formed has an anisotropic g factor which is axially symmetric with respect to the direction of the incident beam (Table 1), in remarkably contrast to that obtained by thermal decomposition of heavily γ-irradiated complex.

In cases of Ar^+-ion collisions, highly inelastic excitations of Fe may be accompanied with a simultaneous momentum transfer from the incident Ar^+ ion. This would cause a production of a Fe^{3+} cluster, the structure of which retains some axially symmetric feature with respect to the direction of an incident beam.

The authors wish to thank Mr. Chiaki Kobayashi and Mr. Susumu Kanda for their kind operation of the 2 MV Van de Graaff accelerator.

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