The Fate of Recoil-^{59}Fe in an Iron Double Complex Specifically Enriched with ^{59}Fe

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The trisbipyridyliron(II) cation and ferricyanide form a crystalline precipitate with the formula $[Fe(bipy)_3]_3[Fe(CN)_6]_2,1—3H_2O$. Samples of this complex, separately enriched with ^{58}Fe in each complex ion, were used to study the chemical effects of the $^{58}Fe(n,\gamma)^{59}Fe$ reaction. The initial distribution of ^{59}Fe-activity as well as the thermal annealing pattern are nearly the same for the two samples. This indicates that nearly all bonds to the recoiling ^{59}Fe are broken, and that the ultimate chemical form of the ^{59}Fe depends more upon the properties of the lattice than upon its original chemical state.

COMPOUNDS containing the same element in different chemical states offer interesting possibilities for studying the chemical effects of nuclear transformations. In 1962 Saito *et al.*[1] used this approach in comparative studies of the $^{59}Co(n,\gamma)^{60}Co$ reaction in $[Co(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Fe(CN)_6]$. Recently [2] we have shown that such an investigation can be carried out using only one compound, soluble Prussian blue, which was specifically enriched in ^{58}Fe in either the cation or the complex anion; this permitted a comparison between the chemical effects of the $^{58}Fe(n,\gamma)^{59}Fe$ reaction taking place in two different species in the same lattice. The results suggested that it would be profitable to extend the studies to a related compound in which the cation is also complexed.

It has been observed [3,4] that the complex $Fe(bipy)_3^{2+}$ forms a crystalline precipitate with $Fe(CN)_6^{3-}$; we have determined [5] its composition to be $[Fe(bipy)_3]_3[Fe(CN)_6]_2,1—3H_2O$ and found that it is suited for hot-atom studies, since there is no iron exchange between the two complexes, either in the solid or in solution. On the other hand its thermal decomposition at *ca.* 100 °C could be a drawback in annealing studies.

Recoil effects in compounds containing $Fe(bipy)_3^{2+}$ have not been investigated before, but several studies have concerned the related cobalt complex.[6-8] It appears that most of the ^{60}Co recoils out of the parent complex and is predominantly stabilized as Co^{2+}; subsequently, upon annealing, it enters the bipyridyl complex through ' thermal ' or ' solid-state ' exchange.[9] The chemical effects of $^{58}Fe(n,\gamma)^{59}Fe$ in hexacyanides have been studied in a few cases.[10-12] High retentions were observed, but our experiments with Prussian blue [2] suggested that this may result from immediate recombination and/or annealing. In fact it appears that most ^{59}Fe atoms recoil out of the complex and can be found as free iron ions. If the recoil-^{59}Fe always breaks its original chemical bonds, the only difference between the situation in the two differently enriched complexes is a rather different distribution of fragments at the recoil sites. Therefore a comparison between the resulting distributions of ^{59}Fe activity might show whether annealing leads to recombination of fragments only from the parent complex ion or that other components of the lattice are involved.

EXPERIMENTAL AND RESULTS

Enriched compounds for neutron activation, *i.e.*, $[^{58}Fe(bipy)_3]_3[^{56}Fe(CN)_6]_2$, $[^{56}Fe(bipy)_3]_3[^{58}Fe(CN)_6]_2$, $[^{58}Fe(bipy)_3]SO_4$, and $K_4{}^{58}Fe(CN)_6,3H_2O$ were prepared as described.[2,5] The iron isotopes were supplied from Oak Ridge National Laboratory, U.S.A., in the form of Fe_2O_3. ' ^{56}Fe ' contains less than 0·01% ^{58}Fe and was used directly, whereas ' ^{58}Fe ' was diluted with natural iron to contain *ca.* 13% ^{58}Fe. ^{59}Fe-Labelled compounds for identification and control experiments were prepared by similar procedures. The ^{59}Fe was supplied by the Isotope Division at Risø in the form of $FeCl_3$. For all experiments samples of a few mg were sealed in evacuated silica ampoules.

Neutron activations were made at solid CO_2 temperature in the thermal column of the Danish reactor DR 2 for 5·8 h (thermal neutron flux: 4×10^{12} neutrons cm^{-2} s^{-1}; cadmium ratio, measured with a cobalt detector, 81; dose rate of ionizing radiation: 0·8 Mrads h^{-1}). γ-Irradiations, likewise at solid CO_2 temperature, were carried out in the ^{60}Co-facility at the agricultural department at Risø (dose rate: 0·6 Mrads h^{-1}). The radioactive samples were thermally annealed in dry ice, in a deep freezer, in a refrigerator, and in a thermostatted water bath. They were dissolved (1 mg/ml) in solutions containing 25% dimethyl sulphoxide and 5×10^{-4}M-ethylenediamine tetra-acetic acid (edta). The dimethyl sulphoxide enabled higher concentrations of solute to be obtained.

Analyses were performed by high-voltage electrophoresis (voltage gradient: 3000 V/80 cm; paper: Whatman 3MM, washed in edta and hydrochloric acid; temperature: *ca.* 1 °C; separation time: 45 min; electrolyte: 0·025M-HOAc–0·025M-NaOAc, pH = 4·5). After drying the strips were cut into pieces of 1 cm, which were counted on a sample changer equipped with a well-type scintillation detector and a single-channel analyser set to span the 1·10

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and 1·29 MeV photons from ^{59}Fe. The electrophorograms (Figure 1) showed six fractions, denoted a—f. By means of ^{59}Fe-labelled complexes and colour reactions the three major fractions were identified as (a) $Fe(bipy)_3^{2+}$; (c) $Fe(edta)^-$; and (f) $Fe(CN)_6^{3-}$. The e-fraction is probably $Fe(CN)_5H_2O^{2-}$ and/or $Fe(CN)_5H_2O^{3-}$.

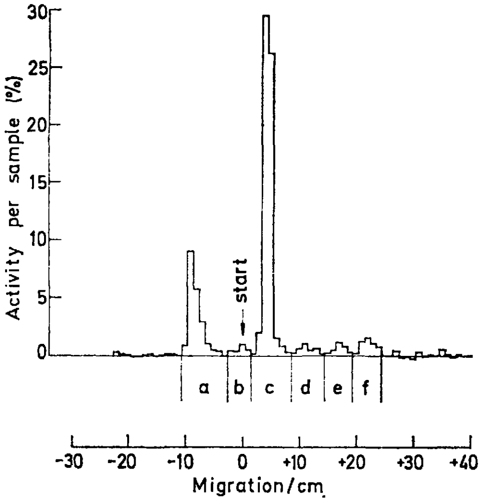

FIGURE 1 Electrophorograms of neutron-activated $[^{56}Fe(bipy)_3]_3$-$[^{58}Fe(CN)_6]_2$. The radioactive fractions were identified as: a, $^{59}Fe(bipy)_3^{2+}$; c, $Fe(edta)^-$; and f, $^{59}Fe(CN)_6^{3-}$. The identities of the peaks b, d, and e are discussed in the text

In order to identify the minor fractions b and d, samples containing only one of the complexes were neutron-activated and analysed. In experiments with $[^{58}Fe(bipy)_3]SO_4$ all ^{59}Fe-activity was found only in the a and c fractions, whereas in experiments with $K_4{}^{58}Fe(CN)_6,3H_2O$ activity was found only in the b, d, e, and f fractions. Thus b and d may be different iron cyano-complexes; if mixed ligand complexes are formed, it must be with insignificantly low yields.

If the samples were dissolved without the edta, very high yields (*ca.* 70%) of $^{59}Fe(bipy)_3^{2-}$ were observed with both the enriched complexes. Moreover analyses of reactor-irradiated, unannealed $^{58}Fe(bipy)_3SO_4$ yielded nearly 100% $^{59}Fe(bipy)_3^{2+}$. This suggested that $^{59}Fe(bipy)_3^{2+}$ could be formed from recoil-$^{59}Fe^{2+}$ upon dissolution of the sample. Since, however, dissolution of irradiated samples in the presence of carrier-free $^{59}Fe^{2+}$ did not give rise to formation of more $^{59}Fe(bipy)_3^{2+}$, we suppose that the recomplexing must take place during dissolution, perhaps on the surface of the dissolving crystals.

The stability constant for the $Fe(bipy)_3^{2+}$ complex is two orders of magnitude higher than that of $Fe(edta)^{2-}$ but the concentration of free bipyridyl formed in the irradiated samples must be minute. Therefore edta preferentially complexes $^{59}Fe^{2+}$ to give $Fe(edta)^{2-}$, which is readily oxidized to $Fe(edta)^-$; since Fe^{3+} is complexed immediately by edta, the recoil-$^{59}Fe^{2+}$ and $^{59}Fe^{3+}$ are therefore represented on the electrophorograms by only one peak (*cf.* Figure 1).

However, when samples of the specifically ^{59}Fe-labelled complex were dissolved in solutions containing edta, some ^{59}Fe activity was found in the edta complex owing to dissociation of $Fe(bipy)_3^{2+}$; not surprisingly $Fe(CN)_6^{3-}$ was unaffected. To find the sum of the errors introduced by the dissociation of the bipyridyl complex and possible γ-radiolysis during reactor irradiation, the following control experiment was performed: two series of samples of the specifically ^{59}Fe-labelled complexes were γ-irradiated, thermally annealed, dissolved in an aqueous solution of 25% Me_2SO and 5×10^{-4}M in edta and analysed by electrophoresis. For the $[Fe(bipy)_3]_3[^{59}Fe(CN)_6]_2$ samples, all ^{59}Fe-activity was found in the cyanide complex. For the $[^{59}Fe(bipy)_3]_3[Fe(CN)_6]_2$ samples, however, 9% of the total ^{59}Fe activity was found as the edta complex. This transfer of activity must arise mainly from breakdown of the $Fe(bipy)_3^{2+}$ since it was also observed in analyses of unirradiated samples.

In the final experiments, two series of differently enriched samples were neutron-irradiated at solid CO_2 temperature, and subsequently annealed stepwise at increasing temperatures (24 h at each temperature). The results are shown in Figure 2. Only the yields of the major fractions are plotted (standard deviation *ca.* 1%). The yields of the fractions b, d, and e were *ca.* 2% for the bipyridyl-enriched and *ca.* 2·5% for the cyanide-enriched complexes respectively. These yields did not change significantly upon annealing (standard deviation *ca.* 0·5%).

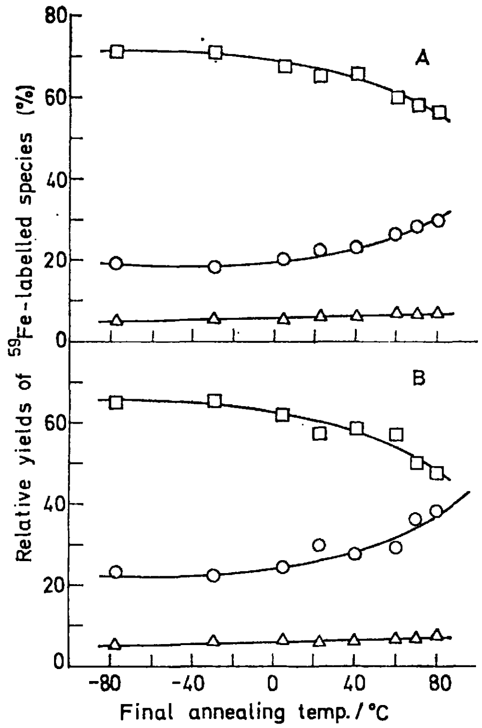

FIGURE 2 The yields of identified radioactive fractions in reactor-irradiated and stepwise annealed samples: A, $[^{58}Fe(bipy)_3]_3$-$[^{56}Fe(CN)_6]_2$; B, $[^{56}Fe(bipy)_3]_3[^{58}Fe(CN)_6]_2$; separated as shown in Figure 1. ○, $^{59}Fe(bipy)_3^{2+}$; □, $Fe(edta)^-$; △, $^{59}Fe(CN)_6^{3-}$. The yields of the fractions b, d, and e are not plotted

DISCUSSION

Since there is a rapid electron exchange between the pairs Fe^{2+}–Fe^{3+}, $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$, and presumably also between $Fe(CN)_5H_2O^{2-}$ and $Fe(CN)_5H_2O^{3-}$ the separation used will not distinguish between these pairs. Further, if $^{59}Fe(bipy)_3^{3+}$ is formed, it is reduced in solution. Thus we cannot distinguish between different valency states of recoil-^{59}Fe, but only between different complexes. Even this distinction is complicated by secondary reactions upon dissolution. But re-formation of $^{59}Fe(bipy)_3^{2+}$ can, at least to a large extent, be quenched by complexing the $^{59}Fe^{2+}$ with edta. Since, however, edta causes dissociation of $Fe(bipy)_3^{2+}$, the yield of 'free' ^{59}Fe appears a little too high [9% of the ^{59}Fe-$(bipy)_3^{2+}$ corresponds to *ca.* 2% of the total activity]. The yield of $^{59}Fe(CN)_6^{3-}$ is not affected by edta and thus represents the content of this species in the solid sample. No information had been obtained about the formation or fate of ligand-deficient species, but it can be assumed that $Fe(CN)_5$ species are precursors of the observed aquopentacyano-complexes.

Within these limitations the results show that the chemical fate of the recoil-^{59}Fe depends little upon whether the $^{58}Fe(n,\gamma)^{59}Fe$ reaction takes place in an $^{58}Fe(bipy)_3^{2+}$ or an $^{58}Fe(CN)_6^{3-}$ complex. Thus, in agreement with our previous results,[2] nearly all chemical bonds are broken, and the fragments are separated sufficiently to avoid immediate recombination in a large proportion of the events. The yield of $^{59}Fe(bipy)_3^{2+}$ is in fact higher in $[^{56}Fe(bipy)_3]_3[^{58}Fe(CN)_6]_2$ than in $[^{58}Fe(bipy)_3]_3[^{56}Fe(CN)_6]_2$. This suggests the recoil-^{59}Fe has a reasonable probability of reaction with the neighbours nearest to the recoil site; in other words the range of the recoil-^{59}Fe may be only one or two lattice distances.

The annealing pattern is essentially the same for the two differently enriched samples. When the samples are heated, there are no significant changes in the unidentified fractions, and only a slight increase in the yield of $^{59}Fe(CN)_6^{3-}$. The main effect, however, is a transfer of ^{59}Fe from the 'free' fraction of $Fe(bipy)_3^{2+}$. This is best understood in terms of the solid-state exchange mechanism suggested for the annealing of recoil-^{60}Co in $Co(bipy)_3(ClO_4)_3$ and experimentally demonstrated by Mössbauer spectroscopy in ^{57}Co-doped sources of $Co(bipy)_3(ClO_4)_3$.[9] Essentially the same annealing pattern was observed by Saito *et al.*[1] for $[Co(NH_3)_6][Co(CN)_6]$ where the dominant reaction was a transfer of $^{60}Co^{2+}$ to $^{60}Co(NH_3)_6^{3-}$, the yield of $^{60}Co(CN)_6^{3-}$ being virtually unchanged. Clearly there must be considerable differences in the energies of activation of these 'exchange' reactions, and in this system almost all of the free cationic iron exchanges with the bipyridyl complex rather than the ferricyanide. It thus appears that the final chemical fate of ^{59}Fe-recoil atoms depends much less upon the nuclear reaction and the parent molecule than upon the chemical and physical properties of the matrix compound.

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