Contribution from the Radiation Laboratory and the Department of Chemistry, University of California]

Some Exchange Experiments Involving Hexacyanoferrate(II) and Hexacyanoferrate(III) Ions[1]

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Exchange reactions involving the following pairs of ions have been investigated using radioactive iron: hexacyanoferrate(II) and hexacyanoferrate (III) ions, iron(III) and hexacyanoferrate(III) ions, iron(III) and hexacyanoferrate(II) ions, iron(II) and hexacyanoferrate(II) ions, and iron (II) and hexacyanoferrate(III) ions. The exchange of activity between hexacyanoferrate(II) and hexacyanoferrate(III) ions can be accomplished by an oxidation–reduction reaction involving only the transfer of an electron. The other reactions investigated require the exchange of an atom between molecules.

Most of these exchange reactions were previously investigated by Kennedy, Ruben and Seaborg, who also studied the exchange between iron (II) and iron(III) ions. The results of this earlier investigation were referred to in a review article by Seaborg,[3] but the details of the work have not been published. The experiments reported here will confirm the absence of any detectable exchange in the case of the atomic interchanges studied. However, complete and rapid exchange was observed in the case of the hexacyanoferrate (II)–hexacyanoferrate(III) ion pair, whereas Kennedy, *et al.*, detected no exchange in this case.

Experimental

The radioactive iron employed as tracer was a mixture of the beta-emitting $^{59}_{26}$Fe of forty-seven day half-life[4] and the four year $^{55}_{26}$Fe which decays by orbital electron capture.[5] These isotopes were prepared by bombardment of an iron plate with 22 Mev. deuterons obtained from the 60 inch cyclotron of the University of California.

A sample of potassium hexacyanoferrate(II) containing radioactive iron was synthesized by addition of a solution of active iron(II) chloride to a saturated solution of potassium cyanide. The product was purified by crystallization from ethanol–water mixtures. Active potassium hexacyanoferrate(III) was synthesized by oxidation of active potassium hexacyanoferrate(II) with chlorine and purified by crystallization from ethanol–water mixtures.

Hexacyanoferrate(II)-Hexacyanoferrate(III) Exchange.—Equal volumes of 0.2 *M* solutions of active potassium hexacyanoferrate(II) and inactive potassium hexacyanoferrate(III) were mixed and samples taken from this mixture at intervals of from one minute to five days after mixing. The *p*H of this mixture was 8.1 as measured with a Beckman *p*H meter. A solution of cerium(III) nitrate was added to the samples immediately after removal from the mixture, which resulted in the selective precipitation of the hexacyanoferrate(II) ion as $KCeFe(CN)_6$.[6] This precipitate was separated by centrifugation, washed, slurried onto platinum plates and the radioactivity measured with a bell-type Geiger tube having a 3 mg./sq. cm. mica window. The supernatant solution and washings were combined, evaporated on platinum plates and also counted. Of the activity recovered in these two fractions, an average of 56% was found in the hexacyanoferrate(II) precipitate and the remainder in the hexacyanoferrate(III) supernatant solution. The range of values observed in six determinations over a five-day interval was 53 to 60%. From 87 to 94% of the initial activity was recovered in each experiment.

The experiment was then repeated, starting with active potassium hexacyanoferrate(III) and inactive potassium hexacyanoferrate(II). Practically identical results were obtained with an average of 58% of the total recovered activity being found in the potassium cerium(III) hexacyanoferrate(II) precipitate. The *p*H of the exchange mixture in this case was 7.3.

The exchange between 0.1 *M* solutions of hexacyanoferrate(II) and hexacyanoferrate(III) ions was also studied in 1.0 *M* hydrochloric acid and in 0.05 *M* sodium hydroxide solutions, and the exchange between 0.009 *M* solutions of hexacyanoferrate(II) and hexacyanoferrate (III) ions was studied in neutral solution. In all of these cases complete exchange was observed within one minute after the time of mixing.

Cerium(III) ion was chosen to effect the separation of hexacyanoferrate(II) and hexacyanoferrate(III) ions after experiments had shown iron(III) ion to be unsatisfactory for this purpose. The addition of iron(III) ion to a mixture of hexacyanoferrate(II) and hexacyanoferrate(III) ions resulted in the precipitation of more than 75% of the radioactivity regardless of whether this activity was added in the form of hexacyanoferrate(II) or hexacyanoferrate(III) ion. Because cerium was employed in its more stable oxidation state and because essentially identical results were obtained in approaching the equilibrium from both directions it can be assumed that the presence of cerium does not induce an exchange.

Iron(III)-Hexacyanoferrate(III) Exchange.—A mixture 0.07 *M* in active potassium hexacyanoferrate(III) and 0.14 *M* in inactive iron(III) chloride was allowed to stand in the dark at room temperature for six days. Iron (III) hydroxide was then precipitated from the mixture by addition of 0.5 *M* sodium hydroxide. The iron(III) hydroxide precipitate was completely inactive.

Iron(III)-Hexacyanoferrate(II) Exchange.—Excess inactive iron(III) chloride solution was added to 0.05 ml. of a 0.2 *M* solution of active potassium hexacyanoferrate(II). The precipitate was separated by centrifugation, washed and allowed to stand in the dark at room temperature for six days. The precipitate was then converted to iron(III) hydroxide by addition of 0.5 *M* sodium hydroxide and the product was separated, washed and the radioactivity measured. The iron(III) hydroxide was found to be completely inactive.

Iron(II)-Hexacyanoferrate(II) and Iron(II)-Hexacyanoferrate(III) Exchange.—In similar experiments, no exchange was observed between iron(II) and hexacyanoferrate(II) ions, and none between iron(II) and hexacyanoferrate(III) ions.

Discussion

The rapid electronic exchange between hexacyanoferrate(II) and hexacyanoferrate(III) ions is not surprising since exchange has been observed in all cases in which pairs of ions differing only in electronic charge have been studied, *e. g.*, iron

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(3) Seaborg, *Chem. Rev.*, **27**, 199 (1940).

(4) Livingood and Seaborg, *Phys. Rev.*, **54**, 51 (1938).

(5) Livingood and Seaborg, *ibid.*, **55**, 1268 (1939).

(6) Banerjee, *J. Indian Chem. Soc.*, **6**, 259 (1929).

(II) and iron(III) ions,[3] lead(II) and lead(IV) acetates,[7] manganese(II) and manganese(III) (oxalate complex) ions,[8] thallium(I) and thallium (III) ions,[9] manganate and permanganate ions,[10] and mercury(I) and mercury(II) ions.[11]

Kennedy, Ruben and Seaborg studied the hexacyanoferrate(II)–hexacyanoferrate(III) equilibrium from only one direction, by mixing active hexacyanoferrate(II) and inactive hexacyanoferrate(III) ions followed by precipitation of the hexacyanoferrate(II) ion with iron(III) chloride.[12] This fact no doubt accounts for their erroneous conclusion, since it was demonstrated in the present investigation that a satisfactory separation of hexacyanoferrate(II) from hexacyanoferrate(III) could not be obtained by precipitation with iron(III) chloride.

The fact that in the present investigation slightly more than 50% of the radioactivity was precipitated with the potassium cerium(III) hexacyanoferrate(II) is clearly due to partial coprecipitation of the hexacyanoferrate(III) ion and not due to incomplete exchange, since an essentially equal excess activity was present in the precipitate regardless of whether the active iron was originally added as hexacyanoferrate(II) or hexacyanoferrate(III) ion.

The failure to observe any atomic exchange between iron(III) and hexacyanoferrate(III) ions, iron(III) and hexacyanoferrate(II) ions, iron (II) and hexacyanoferrate(III) ions and iron(II) and hexacyanoferrate(II) ions adds to our knowledge of the nature of the various compounds formed between these ions. It is now certain that the two kinds of iron atoms which enter into the formation of such compounds as iron(III) hexacyanoferrate(III), iron(II) hexacyanoferrate(II), iron(III) hexacyanoferrate(II), etc., do not occupy equivalent positions in the compound, nor do they exchange positions with each other.

The structures of substances such as $KFeFe(CN)_6$ have been the subject of X-ray analyses by Keggin and Miles.[13] The iron atoms were found to occupy the corners of a single cubic lattice, each being linked with its six neighboring iron atoms by —CN— groups extending along the edges of the cube. Potassium ions and water molecules are contained within these cubes. This structure was further elucidated by the magnetic susceptibility measurements of Davidson and Welo.[14] These data show that, in effect, half of the iron atoms are diamagnetic and the other half are paramagnetic, which Pauling[15] has interpreted to mean that half of the iron atoms are bonded by essentially covalent links (presumably to six surrounding carbon atoms) and half (presumably those surrounded by nitrogen atoms) are held by ionic bonds. We may now add that the iron–carbon bonds which are present in the hexacyanoferrate (II) and hexacyanoferrate(III) ions are not broken in the solid precipitate and remain intact when the precipitates are decomposed by the addition of dilute sodium hydroxide.

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Summary

1. An exchange of electrons between hexacyanoferrate(II) and hexacyanoferrate(III) ions in neutral solution, 1.0 *M* hydrochloric acid, and 0.05 *M* sodium hydroxide has been observed to occur within the time interval required for separation of the ions (one minute).

2. No exchange of iron atoms was observed between any of the following pairs of ions: iron (III) and hexacyanoferrate(III), iron(III) and hexacyanoferrate(II), iron(II) and hexacyanoferrate(II), and iron(II) and hexacyanoferrate (III).

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[9] Majer, *Z. physik. Chem.*, **A179**, 51 (1937).

[10] Libby, THIS JOURNAL, **62**, 1930 (1940).

[11] Nahinsky and Ruben, unpublished work.

[12] Seaborg, private communication.

[13] Keggin and Miles, *Nature*, **137**, 577 (1936).

[14] Davidson and Welo, *J. Phys. Chem.*, **32**, 1191 (1928).

[15] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 111.