Photolysis of Aquopentacyanoferrate(III) in Aqueous Solution in the Presence of *o*-Phenanthroline with Reference to the Photolysis of Nitroprusside

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Although it is a well-known fact that the initial act of the photochemical decomposition of the nitroprusside ion in aqueous solution at pH 6 gives NO and $[Fe(CN)_5H_2O]^{2-}$ [1], the subsequent decomposition of the aquopentacyanoferrate(III) ion has not been studied in detail and it is supposed that intermediates are produced by successive hydrolytic steps, giving $[Fe(H_2O)_6]^{2+}$ as the final product [2]. Attempts to trap these intermediates with *o*-phenanthroline gave results which were only qualitative and inconclusive [2]. We undertook a study of the photolysis of the $[Fe(CN)_5H_2O]^{2-}$ ion in aqueous solution in the presence of *o*-phenanthroline to get more information on this reaction.

Irradiation was done at room temperature with light from a medium pressure mercury lamp filtered through Pyrex glass. All chemicals used were reagent grade. Aqueous solutions of $[Fe(CN)_5H_2O]^{2-}$ were prepared by previously described procedures [3]. Solutions for the photolytic work were freshly prepared by further dilution to *ca.* 10^{-4} *M* and addition of enough NaCl to give 1.0 *M* total ionic strength. These solutions were not deoxygenated because the presence of dissolved oxygen produces no change in the photochemical reaction. $[Fe(CN)_2(o\text{-phen})_2]$ was extracted from the reaction mixture with chloroform and the other components were separated with a column of Sephadex G-25. The fractions obtained were analyzed spectrophotometrically (UV–visible) and results showed the presence of $[Fe(CN)_4(o\text{-phen}]^{2-}$, $[Fe(o\text{-phen})_3]^{2+}$ and $[Fe(CN)_6]^{3-}$. Electronic spectra reproduced in Figs. 1–5 are representatives of reproducible spectra of reacting solutions obtained under the above conditions.

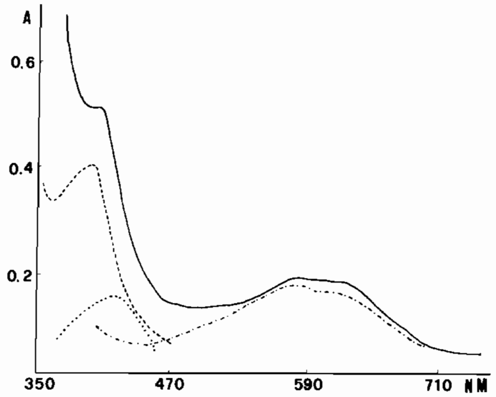

Fig. 1. Spectral changes observed in a solution of $[Fe(CN)_5H_2O]^{2-}$ 5 × 10^{-4} *M* and 2 × 10^{-2} *M* in *o*-phenanthroline irradiated during 5 minutes (——). The spectra of $[Fe(CN)_5H_2O]^{2-}$ (- - - -), $[Fe(CN)_6]^{3-}$ (·······) and $[Fe(o\text{-phen})_3]^{3+}$ (– · –) are also included in an arbitrary scale for the sake of comparison.

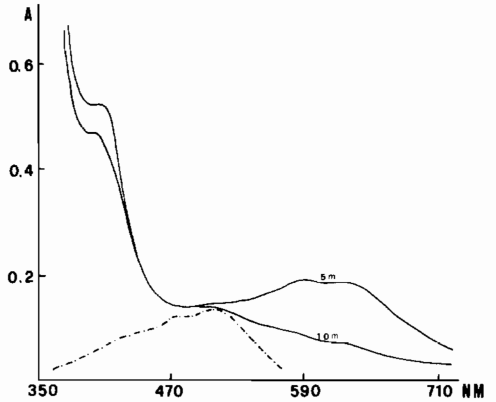

Fig. 2. Transformation of $[Fe(o\text{-phen})_3]^{3+}$ into $[Fe(o\text{-phen})_3]^{2+}$ when the irradiation time is increased from 5 to 10 minutes. Characteristic bands of $[Fe(o\text{-phen})_3]^{2+}$ are also reproduced (– . –).

After brief irradiation, only $[Fe(o\text{-phen})_3]^{3+}$ and $[Fe(CN)_6]^{3-}$ were detected in the solution, together with unreacted $[Fe(CN)_5H_5O]^{2-}$. Figure 1 reproduces the spectral changes observed in a solution of $[Fe(CN)_5H_2O]^{2-}$ 5 × 10^{-4} *M* and 2 × 10^{-2} *M* in *o*-phenanthroline when irradiated for five minutes. The $[Fe(o\text{-phen})_3]^{3+}$ ion is stable only in acid solution; in neutral solutions it gradually turns into $[Fe(o\text{-phen})_3]^{2+}$ [4]. As UV light accelerates this transformation, this ion is detectable only at a very short irradiation time. Figure 2 shows the transformation of $[Fe(o\text{-phen})_3]^{3+}$ into $[Fe(o\text{-phen})_3]^{2+}$ when the irradiation time is increased to ten minutes. When the solution is irradiated for 15 minutes, the presence of $[Fe(o\text{-phen})_3]^{3+}$ can no longer be detected, and a concentration ratio of 4.75: 1 between

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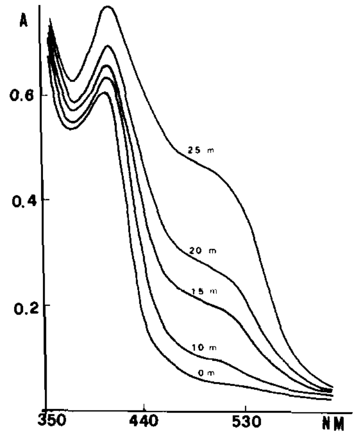

Fig. 3. Successive spectral changes observed in a solution of $[Fe(CN)_5H_2O]^{2-}$ 7 × 10^{-4} *M* and 2 × 10^{-2} *M* in *o*-phenanthroline irradiated during 10, 15, 20 and 25 minutes.

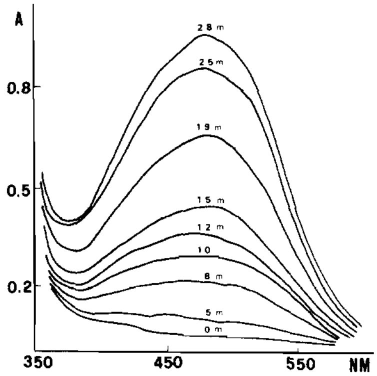

Fig. 5. Spectral changes observed in a solution of $[Fe(CN)_6]^{4-}$ 5 × 10^{-4} *M* and of *o*-phenanthroline 2 × 10^{-2} *M* irradiated 5, 8, 10, 12, 15, 19, 25 and 28 minutes.

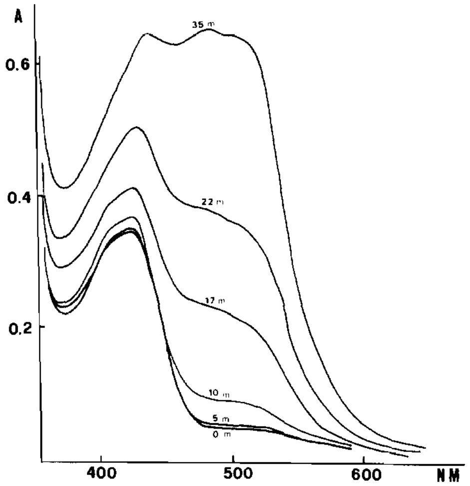

Fig. 4. Consecutive spectral changes noted in a solution 3 × 10^{-4} *M* in $[Fe(CN)_6]^{3-}$ and 2 × 10^{-2} *M* in *o*-phenanthroline when irradiated during 5, 10, 17, 22 and 35 minutes.

$[Fe(CN)_6]^{3-}$ and $[Fe(o\text{-phen})_3]^{2+}$ is found (Fig. 3). This indicates that the initial stoichiometry for the reaction is the following: $6[Fe(CN)_5H_2O]^{2-} + 3\ o\text{-phen} = 5[Fe(CN)_6]^{3-} + [Fe(o\text{-phen})_3]^{3+} + 6H_2O$. The production of $[Fe(o\text{-phen})_3]^{2+}$ as a result of the decomposition of $[Fe(CN)_5H_2O]^{2-}$ is confirmed by photolyzing a solution of nitroprusside in the presence of *o*-phenanthroline. In this case, after a short irradiation time a slightly soluble red solid of the composition $[Fe(o\text{-phen})_3][Fe(CN)_5NO]\cdot 2H_2O$ is formed. This salt is identical with the product obtained by mixing solutions of $Na_2[Fe(CN)_5NO]$ and $[Fe(o\text{-phen})_3]Cl_2$. Although its properties and structure will be reported separately [5] it should be noted here that they are similar to those found for $[Fe(bipy)_3][Fe(CN)_5NO]\cdot 4H_2O$ [6]. When the irradiation time of the $[Fe(CN)_5H_2O]^{2-}$ and *o*-phenanthroline solution is prolonged, the formation of $[Fe(CN)_4o\text{-phen}]^{2-}$ and $[Fe(CN)_2(o\text{-phen})_2]$ can be observed, as shown by Fig. 3 [7]. Apparently, the production of these mixed complexes is due to the photolysis of the hexacyanoferrate(III) ion. Figure 4 represents the consecutive spectral changes noted in a solution of ferricyanide and *o*-phenanthroline when irradiated.

It has been previously reported that photolysis of $[Fe(CN)_6]^{3-}$ gives first either $[Fe(CN)_5H_2O]^{3-}$ and $[Fe(CN)_6]^{4-}$ [8] or only the latter complex [9]. We have been unable to detect the presence of $[Fe(CN)_5H_2O]^{3-}$ in solutions irradiated shortly using nitrosobenzene [10] and N-methylpyrazinium [11] as analytical reagents. The presence of $[Fe(CN)_6]^{4-}$ is established by the spectral changes observed in the irradiated solution.

The irradiation of $[Fe(CN)_6]^{4-}$ in the presence of *o*-phenanthroline shows the successive substitution of cyanide ions giving $[Fe(CN)_5H_2O]^{3-}$ as the first reaction product. The presence of $[Fe(CN)_5H_2O]^{3-}$ can be detected in this case by its reaction with nitrosobenzene and by its characteristic absorption band at 440 nm. Figure 5 reproduces the spectral changes observed in an irradiated solution of $[Fe(CN)_6]^{4-}$ and *o*-phenanthroline. The presence of the mixed complexes with *o*-phenanthroline is also detected when irradiation time is prolonged enough.

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