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Paper Electrophoresis and Polarography of the Reaction Product between the Chromium(III) Ion and Potassium Hexacyanoferrate(II)[1]

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In continuation of the previous work (Y. Matsumoto and M. Shirai, Bunseki kagaku, **12**, 608 (1963); Y. Matsumoto and M. Shirai, This Bulletin, **39**, 59 (1966).), results of a study of the colored products resulting from the reaction between the chromium(III) ion and potassium hexacyanoferrate(II) by paper electrophoresis and polarography will be presented in this paper. Paper-electrophoretical experiments illustrated that the negatively-charged complexes containing both Cr and Fe were gradually formed by reaction. In the presence of excess potassium hexacyanoferrate(II), the resulting complexes were constant in color and situation in the electrophoretical patterns, regardless of the molar ratio of reactants. On the other hand, in the case of a reactant molar ratio ($Fe(CN)_6^{4-}$ to Cr^{3+}) below 2.5, the patterns varied with the ratio. The product, sampled either in the form of a reaction mixture or as isolated state (Y. Matsumoto, M. Shirai, and H. Saito, This Bulletin, **41**, 2542 (1968).), was found to present no reduction wave of Cr^{3+} on polarography at the dropping mercury electrode.

The chromium(III) ion slowly reacts with potassium hexacyanoferrate(II) in an aqueous solution to form an orange-yellow to reddish-brown complex which is very soluble in water; this is in contrast with most heavy metal ions, which react rather quickly with the same reagent to form insoluble product.

This contrast, as well as the characteristic coloration, has attracted attention to the nature of the reaction product, especially to its structure in an aqueous solution, so that a number of approaches have been made[2-9] during the last ten years or so.

In the present work, the nature of the product in its aqueous solution, especially of the ion which composes the major moiety of this colored product, was studied using paper electrophoresis and polarography.

Experimental and Results

Electrophoresis was conducted on filter papers (2×40 cm, Toyoroshi Co., No. 51A), each saturated with a 0.1 M KCl solution, for 2 hr under an applied voltage of 200 V in a horizontal-type apparatus. The location of the chromium complex was detected by means of the diphenylcarbazide method.

One milliliter of a chrome alum solution (2 mg/m*l*

1) This work was partly presented at the 15th and 16th Symposia on Co-ordination Chemistry (1965 and 1966), and at the 19th and 20th Annual Meetings of the Chemical Society of Japan (1966 and 1967).

2) Y. Matsumoto and M. Shirai, *Bunseki kagaku*, **12**, 608 (1963).

3) Y. Matsumoto and M. Shirai, This Bulletin, **39**, 55 (1966).

4) Y. Matsumoto, M. Shirai, and H. Saito, This Bulletin, **41**, 2542 (1968).

5) Y. Matsumoto, M. Shirai, H. Saito, T. Kawashima, and Y. Sakabe, Proceedings of the 18th Symposium on Co-ordination Compounds (1968).

6) W. U. Malik, *J. Sci. Ind. Res.*, **18B**, 463 (1959).

7) W. U. Malik, *ibid.*, **20B**, 213 (1961).

8) W. U. Malik, *J. Indian Chem. Soc.*, **38**, 297 (1961).

9) W. U. Malik and J. Singh, This Bulletin, **39**, 2541 (1966).

for Cr^{3+}) was mixed with 3.2 m*l* of a potassium hexacyanoferrate(II) solution (50 mg/m*l* for $K_4Fe(CN)_6 \cdot 3H_2O$), the molar ratio of hexacyanoferrate(II) to Cr^{3+} being 10 : 1; the chromium concentration in the mixed solution was found to be about 10^{-2} M (reaction mixture 1). This yellow-colored reaction solution gave, on electrophoretical separation, two yellow spots (A and B), both located in the direction toward the positive electrode (Fig. 1). Extracts from both the spots, obtained with distilled water, were decomposed by (1+1) sulfuric acid, and then tested for the presence of Cr and Fe. The spot A proved to contain both Cr and Fe, while the spot B contained Fe alone. Upon the coloration test with diphenylcarbazide, the spot A turned purple, and the spot B, a grayish blue.

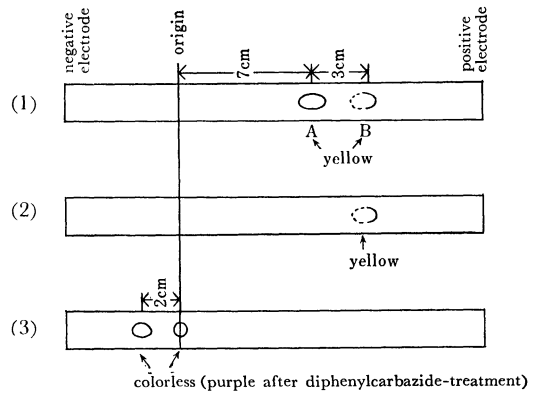

Fig. 1. Paper electrophoresis with (1) yellow-colored reaction mixture, (2) $K_4Fe(CN)_6$ soln, and (3) Cr^{3+} soln.

For reference, a potassium hexacyanoferrate(II) solution and a chrome alum solution of the same final concentrations as the corresponding concentrations in the sample solution were charged individually on other papers and then subjected to electrophoresis. On the reference paper charged with potassium hexacyanoferrate(II), one yellow spot was found in the position as far from the origin as the position B on the paper charged with the sampled solution, while Fe was not found at the position corresponding to A. On the reference paper for the Cr^{3+} solution, were observed two spots which proved to contain Cr by the diphenylcarbazide test; one of them was in the direction toward the negative electrode, and the other was at the point of origin. On the other hand, no chromium-containing spot other than A was observed on the electrophoretical pattern for the sample solution which had stood for an adequate reaction period.

The paper-electrophoretical study thus confirmed that the yellowish-orange-colored and negatively-charged complex ion, which contained both chromium and iron, existed predominantly in the reaction mixture resulting from the reaction between the chromium(III) ion and excess potassium hexacyanoferrate(II).

The process of the gradual formation of the chromium-containing complex from the chromium(III) ion, characterized in terms of the change to a negative species from a positive one, was successfully visualized by paper-electrophoretical patterns varying in the course of the progress of the reaction. A chrome alum solution of 2.5 m*l* (20 mg/m*l* for Cr^{3+}) was mixed with a potassium hexacyanoferrate(II) solution of 10 m*l* (200 mg/m*l* for $K_4Fe(CN)_6 \cdot 3H_2O$), the molar ratio of hexacyanoferrate(II) to Cr^{3+} being 5 to 1 (reaction mixture 2). The concentrations of the reactants in this reaction mixture were made larger than those in the foregoing one (reaction mixture 1) in order that the evidence for any transition state of chromium(III) ion from its free state to any other coordinated state could be observed distinctly; the reactant ratio of 5 : 1 was adopted after it had been confirmed that the reaction solution resulting from this reactant ratio gave qualitatively the same paper-electrophoretical pattern as was given by the solution with a reactant ratio of 10 : 1. The mixed solution of this reactant ratio were allowed to stand for varying periods of time (0, 2, 4 hr and 1 and 2 days) at room temperature after mixing; then they were subjected to paper electrophoresis. The coloration was done by means of the diphenylcarbazide method (Fig. 2).

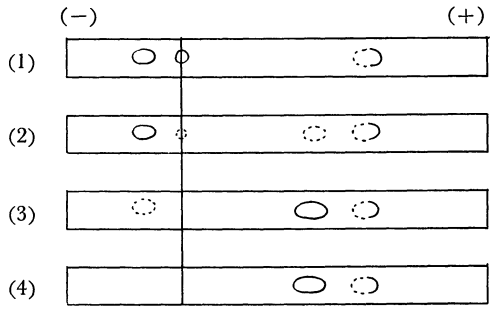

Fig. 2. Paper-electrophoretical patterns of the reaction mixture, altering in the course of the proceeding of the reaction: (1) immediately, (2) 2 hr, (3) 4 hr, and (4) 2 days after mixing reactants.

The results were as follows: (1) with the solution tested immediately after mixing, no colored chromium-containing spot was found, but two chromium-containing spots were detected by means of diphenylcarbazide coloration, one on the original point and another one at a distance from the point of origin in the direction of the negative electrode.

(2) With the solution which had stood for 2 hr after mixing, a yellow chromium-containing spot was found to appear in the direction of the positive electrode in addition to the visually colorless chromium-containing spots still present in the negative electrode direction and on the original point.

(3) With the solution allowed to stand for 4 hr after mixing, there appeared a chromium-containing yellow spot in the positive electrode direction, more intense in color, and a diphenylcarbazide-test-positive spot in the negative electrode direction, weaker in color, than in the foregoing case, *i.e.*, the case of the shorter reaction time. The former kind of spot became the more intense in color, and the latter kind became the weaker, the longer the time which elapsed after mixing. On the point of origin, no chromium-containing spot remained.

(4) Two days later after mixing, all the chromium was contained in the yellow complex which, on electro-

phoresis, is located in the positive electrode direction.

In order to study the properties of the reaction products produced at varying reactant ratios, the solutions were also prepared by mixing 2.5 m*l* of a chromium(III) solution with the Cr^{3+} concentration of 20 mg/m*l* and 10-m*l* portions of potassium hexacyanoferrate(II) solutions with the salt concentrations of 200, 100, 80, 60, 40, and 20 mg/m*l* so that the resulting solutions contained potassium hexacyanoferrate(II) in ratios of 5, 2.5, 2, 1.5, 1, and 0.5 mol respectively to 1 gram ion of the Cr^{3+} ion. After having stood for two days, each colored reaction solution was centrifuged for 15 min at 3000 rpm; the supernatant was then subjected to paper electrophoresis.

The results are shown in Fig. 3. The products of the reaction at the reactant ratios (hexacyanoferrate(II) to Cr^{3+}) below 2.5 were visually similar to, but electrophoretically different from, those of the reactant ratios above 2.5. The lower the ratio of hexacyanoferrate(II) to Cr^{3+} the shorter the distance the corresponding chromium complex was shifted, and the more greenish became the color of the complex.

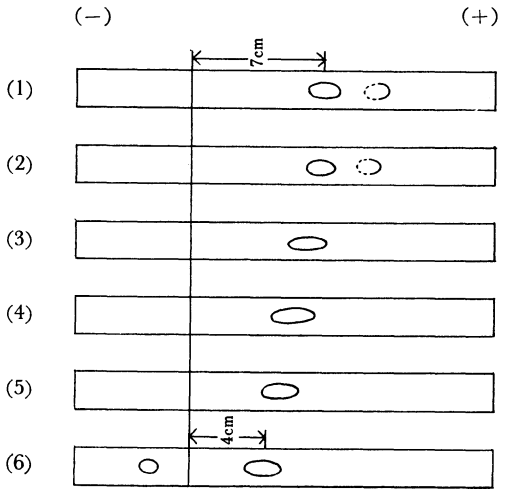

Fig. 3. Paper-electrophoretical patterns along with a variety of reactants ratios: (1) 5, (2) 2.5, (3) 2, (4) 1.5, (5) 1, and (6) 0.5 mol of $K_4Fe(CN)_6$ respectively to 1 gram ion of Cr^{3+}.

The remaining activity of Cr(III) in the reaction solution was further examined by polarography. The reaction mixture at the reactant ratio of 10 : 1 (chromium concentration 10^{-2} M), in which KCl had been added to 1 M, after which N_2 gas had been bubbled through the mixture, was examined by polarography *vs.* a saturated calomel electrode. The characteristic wave for Cr(III) was found to have disappeared, whereas, in the presence of the same concentration KCl, the solution of Cr^{3+} (chrome alum) gave the wave corresponding to $Cr^{3+} \rightarrow Cr^{2+}$, which was proportional in height to the concentration of Cr^{3+} salt in the range from 10^{-2} M (this concentration gave a wave having the reduction current of 18 μA and the $E_{1/2}$ of −0.9 V) to 10^{-3} M, indicating that the diffusion-controlled conditions hold for this concentration range of Cr^{3+}.

Malik reported[6] the disappearance of the reduction wave in these reaction mixtures at the same electrode, without giving interpretation about it.

In order to observe from what reactant ratio chromium(III) wave appears, solutions in molar ratios varying from 0.1 to 1 of potassium hexacyanoferrate(II) per Cr(III) ion were prepared, while the concentration of Cr^{3+} was kept at a constant value (10^{-2} M); the solutions were then allowed to react at 47°C for 2 hr. The reduction wave for Cr^{3+} diminished in height with an increase in the reactant ratio (hexacyanoferrate(II) to the Cr(III) ion) of the reaction solution and almost disappeared when the reactant ratio was raised to 0.5 : 1 (Fig. 4-a).

This depression of the reduction wave took place even immediately after mixing the reactants. The aqueous solutions of chrome alum and of potassium hexacyanoferrate(II) to which KCl had been added were both bubbled through with N_2 gas, and then they were mixed with each other to make a solution containing Cr^{3+}, $Fe(CN)_6^{4-}$, and KCl in concentrations of 10^{-2} M, 10^{-1} M and 1 M respectively; immediately afterwards, this mixed solution was subjected to polarography. The reduction wave could not be observed unless the molar ratio of hexacyanoferrate(II) to Cr(III) decreased to 0.8 : 1 (Fig. 4-b).

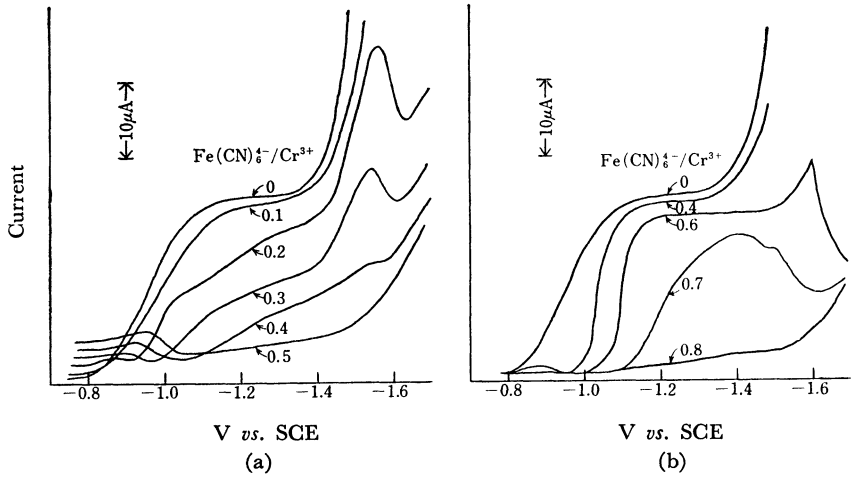

Fig. 4. The gradual disappearance of polarographical reduction wave for Cr^{3+} (10^{-2} M) with the increasing molar ratio of $K_4Fe(CN)_6$ to Cr^{3+} in two cases, (a) after the reaction time of 2 hr at 47°C, and (b) soon after mixing the reactants.

The solution containing the Cr^{3+} ion (10^{-2} M) and potassium hexacyanoferrate(II) (0.5 M), but not potassium chloride, lacked the reduction wave for Cr(III), too.

This disappearance of the reduction wave for Cr(III) was not, however, observed on the polarography of such other chromium(III) complexes, as potassium hexacyanochromate(III), even in the presence of excess potassium hexacyanoferrate(II). An aqueous solution of potassium hexacyanochromate(III) containing 0.5 M potassium hexacyanoferrate(II) as a supporting electrolyte was made using crystals of potassium hexacyanochromate(III) prepared[10] from chromium acetate and potassium cyanide. On polarography, the solution presented a very clear reduction wave corresponding to Cr(III) (Fig. 5).

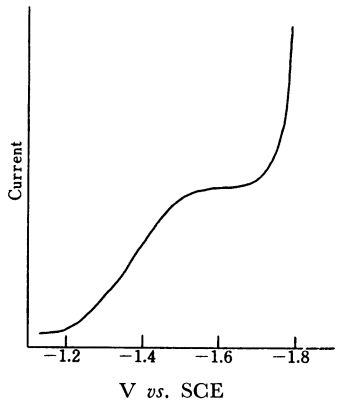

Fig. 5. Polarography of $K_3Cr(CN)_6$ in the presence of 0.5 M $K_4Fe(CN)_6$.

These waves were proportional in height to the Cr concentrations in the range from 10^{-2} to 10^{-3} M.

Recently, it was reported[4] that a reddish-yellow compound could be isolated in a pure form from the reaction mixture by Sephadex G-25 column chromatography. The Cr(III)-hexacyanoferrate(II) complex purified as has been described above was confirmed by paper electrophoresis to be free from the unreacted potassium hexacyanoferrate(II), and it showed no reduction wave on its polarogram.

It was surprising at first glance that even in the reaction mixture which stood only a short time after the mixing of the reactants and which was confirmed on paper electrophoresis still to contain many free Cr^{3+} ions, there was no reduction wave.

The paper-electrophoretical results indicate that this lack of a reduction wave can not be accounted for by presuming a particularly stabilized state of the chromium(III) ion coordinated with hexacyanoferrate(II), but it might well be attributed to the current-insulating effect of the deposition of an insoluble complex, the chromium(II)-hexacyanoferrate(II) complex, produced on the electrode surface by the polarographic reduction of Cr(III).

The insoluble film of the deposition, Cr(II)-hexacyanoferrate(II), would be formed either by the reduction of free Cr(III) ions in the presence of hexacyanoferrate(II) ions or by the reduction of the Cr(III)-hexacyanoferrate(II) complex already formed.

The author is grateful to Professor Yoshio Matsumoto for his help and advice throughout this work.

10) J. H. Bigelow and J. C. Bailar, Jr., "Inorganic Syntheses," Vol. 2, p. 203 (1946).