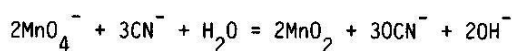


The Stoichiometry of the Reaction between Permanganate and Cyanide Ions in Aqueous Solution

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Summary: The stoichiometry between permanganate and cyanide ions in aqueous solution has been investigated. The reaction leading to the formation of a dark brown precipitate is represented by the equation



Interaction of excess of ice-cooled 3M aqueous potassium cyanide and 0.1 M aqueous potassium permanganate, initially produces an unstable manganese (IV) cyano species which is finally reduced to manganese (III) giving heptapotassium- μ -oxo-bis [pentacyanomanganate(III)] cyanide. The oxo bridged $[\text{Mn}_2\text{O}(\text{CN})_{10}]^{6-}$ ion appears to exist in solution.

Introduction

The cyano complexes of manganese (III) and manganese (II) are well known and formation of $\text{K}_2[\text{Mn}(\text{CN})_6]$ by the oxidation of $\text{K}_3[\text{Mn}(\text{CN})_6]$ with nitrosyl chloride has been described. Attempts to isolate the manganese (IV) complex by interaction of saturated potassium permanganate and 80% potassium cyanide, as reported by Yakimach[2], have failed. Goldenberg[3] was the first to repeat the preparation, and believed the product was a diamagnetic cyano complex of manganese (III), which he formulated as $\text{K}_3\text{Mn}_2(\text{CN})_9 \cdot 4\text{KOH}$. This improbable formula need not be taken at its face value because hydroxyl ion decomposes the cyanide complex of manganese (III) and also because Goldenberg's analyses, even for well-known compounds such as barium manganate, are highly approximate. Further the presence of KOH has been denied on the basis of infrared spectroscopic studies[4]. Because of the instability of the manganese (IV) cyano complex, believed to be initially present in solution before it is reduced to manganese (III) or

before manganese dioxide is precipitated in bulk, earlier attempts[5] to isolate and characterise the solid product were unsuccessful. Our early analytical results of the solid products, however, now seem to be in agreement of the formula $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$. We find that if the initial product, $\text{K}_7[\text{Mn}_2\text{O}(\text{CN})_{10}]\text{CN}$, is left in aqueous solution in presence of concentrated cyanide to prevent hydrolysis, for a longer period (removing from time to time the precipitated oxide of manganese), the final product is $\text{K}_3[\text{Mn}(\text{CN})_6]$. This work was carried out to reinvestigate in detail the reaction between permanganate and cyanide ions in aqueous solution and to establish the stoichiometry of the reaction. Evidence of short lived manganese (IV) cyano species in solution is provided.

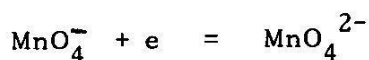
Experimental

All the chemicals used were of Analytical Reagent grade. Solutions of potassium permanganate and potassium

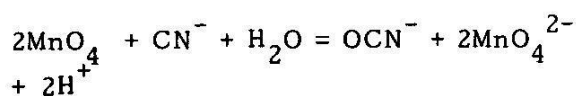
cyanide were standardised according to methods in reference [7a,b]. Oxidation states of manganese were determined by the oxalate method.

Results and Discussion

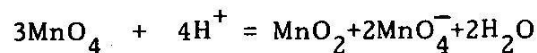
In acid solution, there is no reaction between permanganate and hydrogen cyanide even at 85°C, and it is often possible to oxidise the metal in a complex cyanide without affecting the ligand. In strongly alkaline medium, where the basic oxidising reaction is represented by the equation.



Drummond and Waters [8] showed that; if excess of barium ion is present to remove MnO_4^{2-} as barium manganate, the reaction



takes place quantitatively. When, however, potassium permanganate is added to potassium cyanide solution (pH approximately 10.5) in absence of added alkali, the green colour which appears on the first addition of the oxidising agent disappears when more is added, and a red brown solution is formed which after a short time deposits a dark brown precipitate of manganese dioxide resulting from the disproportionation



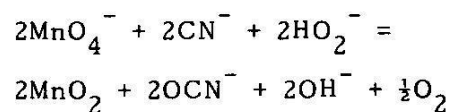
A. Interaction of permanganate and cyanide ions in the ratio $1\text{MnO}_4^- : 1\text{CN}^-$

Various volumes of the solution of permanganate and cyanide were mixed in order to locate the point at which the presence of excess of permanganate after the reaction was shown by the pink colour. It was observed that one mole of permanganate reacts with one

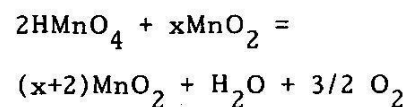
mole of cyanide to give a dark brown precipitate and a clear solution. The dried precipitate contained no nitrogen and its IR spectrum did not show any $\text{C}\equiv\text{N}$ stretching frequency. It was further observed that the precipitate did not contain any cyanide even if the $\text{MnO}_4^- : \text{CN}^-$ ratio was 1:10 and addition of KOCN (one of the reaction products) did not affect the 1:1 ratio. The oxidation state of manganese in the precipitate was 3.90. Therefore, the dark brown precipitate could be nothing but hydrated manganese dioxide.

After removing the dark brown precipitate, the colourless filtrate forms white precipitate with silver nitrate. The X-ray powder photograph and reactions of the white precipitate were identical with those of AgOCN .

Thus the interaction of $1\text{MnO}_4^- : 1\text{CN}^-$ results in the reduction of permanganate to hydrated manganese dioxide and oxidation of cyanide to cyanate, presumably by the equation,



In this connection it is worth noting that ammonia (formed by hydrolysis of OCN^-) reduces MnO_4^- [9a], and that manganese dioxide is known to catalyse the decomposition of permanganate [9] according to the equation [9b]

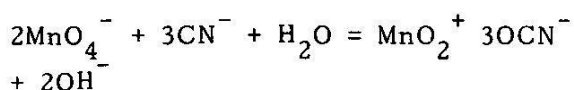


B. Interaction of permanganate with excess of cyanide ions

Potassium permanganate and cyanide solutions were mixed in the molar ratio 1:5 of reactants. The dark brown precipitate was filtered and washed with distilled water. The filtrate and the

washings were used to find out the unreacted cyanide by standard volumetric and gravimetric methods. Consistent results of one mole of permanganate reacting with 1.5 mole of cyanide were found. The oxidation state of manganese in the residue was again found to be 3.90.

These results suggest that in the presence of excess of cyanide ions, the permanganate is still reduced to hydrated manganese dioxide and that one mole of permanganate is not reacting with one mole of cyanide but instead with 1.5 mole of cyanide. The reaction in excess of cyanide then may be represented approximately by the equation,

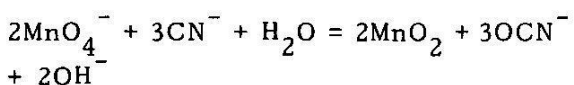


C. Interaction of permanganate and cyanide ions in the ratio $2\text{MnO}_4^- : 3\text{CN}^-$.

Potassium permanganate and cyanide solutions were mixed in the molar ratio 2:3 of reactants. Within five minutes of mixing a dark brown precipitate was formed and the filtrate was colourless indicating the absence of any unreacted permanganate. The colourless filtrate formed a white precipitate with silver nitrate solution. The white precipitate dissolved in 5M nitric acid giving a clear solution i.e. was silver cyanate. Thus when permanganate and cyanide ions are present in just 2:3 ratio, there is no excess of either permanganate or cyanide and one mole of MnO_4^- is reacting with 1.5 mole of CN^- .

D. Increase of the pH of the solution

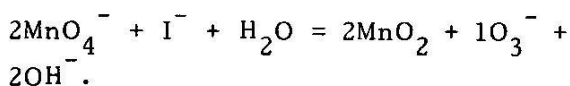
pH measurement were carried out to confirm the formation of hydroxyl ions in the solution by the interaction of permanganate and cyanide ions according to the equation,



Potassium permanganate solution (pH 6.90) and potassium cyanide solution (pH 10.50) were mixed in the ratio $2\text{MnO}_4^- : 3\text{CN}^-$. The dark brown precipitate was formed and the pH of the solution increased to 11.75. The pH of a solution of potassium cyanate corresponding to three moles of cyanide was found to be only 9.35.

A solution containing 115.40 mg of potassium cyanate in 13.20 ml of boiled and cooled distilled water was added to 6.33 ml of 0.15M KOH to give $3\text{OCN}^- : 2\text{OH}^-$ ratio. The pH of this solution was found to be 12.10.

A control experiment was performed to check the pH value on the interaction of potassium permanganate and potassium iodide where two hydroxyl ions are produced as shown by the following equation [10],



Aqueous potassium permanganate and potassium iodide were mixed in the ratio $2\text{MnO}_4^- : \text{I}^-$. A dark brown precipitate was formed and the pH of the solution was 11.70. A standard mixture containing $\text{IO}_3^- : 2\text{OH}^-$ was prepared. The pH of this solution was 12.05.

Potassium was found in the dark brown precipitate obtained either by interaction of potassium permanganate and potassium cyanide or potassium permanganate and potassium iodide.

The increase of the pH of the solution containing potassium permanganate and potassium cyanide does indicate the formation of OH^- ions in the reaction product. The pH value observed is slightly lower than expected for $3\text{OCN}^- : 2\text{OH}^-$. This is not surprising because a similar lower pH value was observed for the permanganate and iodide reaction in which 2OH^- ions are

produced. The presence of potassium in manganese dioxide may be due to adsorption of some of the potassium hydroxide on manganese dioxide and this could also be the reason for the lower pH values of the solutions.

E. The existence of manganese (IV) cyano species in solution.

A dark brown solution was obtained when ice-cooled aqueous solutions of 0.1M potassium permanganate and 3M potassium cyanide were mixed in the $\text{MnO}_4^- : \text{CN}^-$ ratio of 1:30. The solution on standing decomposed forming hydrated manganese dioxide. The oxidation state of manganese in the dark brown solution was determined by oxalate method and found to be 3.85 ± 0.16 . This suggests that before decomposition a cyano complex of manganese (IV) is present in solution.

F. The attempted isolation and identification of the solid product.

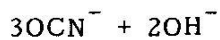
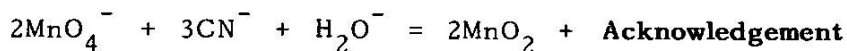
Ice-cooled aqueous solutions of 0.1M potassium permanganate and 3M potassium cyanide were mixed in the $\text{MnO}_4^- : \text{CN}^-$ ratio of 1:30. The dark brown solution so formed was treated with ice-cooled ethanol to precipitate the brown product. The brown product dissolved in water giving a clear dark brown solution which immediately decomposed forming manganese dioxide. The solid product was found to decompose on keeping in air or in vacuo, in light or in dark forming manganese dioxide. The oxidation state of manganese in the freshly precipitated dark brown product was found to be 3.70 ± 0.06 , lower than that found in solution. This supports the view that initially a cyano species of manganese (IV) is produced in solution by the reduction of permanganate which might be undergoing further reduction. The attempted precipitations of this cyano complex of manganese (IV) with

$(\text{CH}_3)_4\text{N}^+$, $\text{Co}(\text{NH}_3)_6^{3+}$ and Cs^+ cations were unsuccessful as these cations did not form any insoluble compounds.

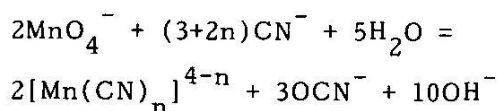
When the mixture of aqueous solutions of 0.1M potassium permanganate and 3M potassium cyanide in the ratio 1:30 was allowed to crystallize at room temperature, gold brown needles type of product was obtained which was contaminated by other reaction products. Therefore, it was not possible to get consistent analytical results of the dried product. However, by selecting the pure crystals, the analysis agreed well with the reported formula [6], $\text{K}_7[\text{CN}]_5\text{Mn-O-Mn}(\text{CN})_5\text{CN}$. This shows that the cyano species of manganese (IV) present in solution, is unstable and is rapidly reduced to manganese (III) giving oxo bridged $[\text{Mn}_2\text{O}(\text{CN})_{10}]^{6-}$ ion. When the product was left in aqueous solution in presence of cyanide for recrystallization, (removing from time to time the precipitated oxides of manganese) or on repeated precipitation with ice-cooled ethanol, the final product was found to be $\text{K}_3\text{Mn}(\text{CN})_6$.

An attempt was also made to isolate a solid manganese(IV) cyano complex by the interaction of aqueous 1M cyanide solution on potassium hexafluoromanganate (IV), a stable complex of manganese (IV), but the analytical data, X-ray powder photograph and IR spectrum of the red product showed that it was $\text{K}_3\text{Mn}(\text{CN})_6$. It seems that aqueous cyanide reduces manganese (IV) to manganese(III).

Results so far discussed supports the view that interaction of aqueous permanganate and cyanide in the ratio $2\text{MnO}_4^- : 3\text{CN}^-$ causes the reduction of manganese (VII) to manganese (IV) and oxidation of cyanide to cyanate according to the equation,



In excess of cyanide, the permanganate is still reduced and initially a cyano species of manganese (IV) is formed. Presumably and approximately the reaction in excess of cyanide could be represented by something like.



or similar equation involving formation of an oxycyano complex.

The exact nature of cyano species of manganese (IV), we believe to be present in solution, is not yet known. If we assume that $[\text{Mn}(\text{CN})_6]^{2-}$ ion is initially produced by the reduction of permanganate, it may be suggested that reduction to the oxo cyano complex of manganese (III) produced via the complex $[(\text{NC})_5 \overset{\text{IV}}{\text{Mn}} - \text{O} - \overset{\text{IV}}{\text{Mn}} (\text{CN})_5]^{4-}$.

The action of excess of aqueous cyanide on the reported complex $\text{K}_2[\text{Mn}(\text{CN})_6]$ might shed some light on this matter.

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