CATALYTIC EFFECT OF COPPER(II) IONS ON REACTIONS WITH POTASSIUM HEXACYANOFERRATE(III)

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Copper(II) ions in trace concentrations considerably increase rate of reaction of hexacyanoferrate(III) ion with cyanide, hydrazine, mercaptoacetic acid, thiosulphate, and sulphite. Oxidation of thiosulphate is a complex reaction and copper(II) ions affect the rate of reaction as well as kinetics of the reaction. Alternative mechanisms of catalyzed reactions are presented.

Potassium hexacyanoferrate(III) is a common monoequivalent oxidizing agent, whose reactions with various substrates have been many times studied. Oxidizing action of hexacyanoferrate(III) ion is presumably *via* one-electron transfer, or if a multivalent substrate is involved, *via* several subsequent one-electron transfers. A more detailed kinetic study, however, reveals effects unsatisfactorily explainable by this mechanism. Effects of the concentration of the reacting components[1], hexacyanoferrate(II) ion[2], reaction products[3], and inert electrolytes[4], which can be explained with difficulty only, have been presented in the literature.

Recently, we have studied specific effects of inert electrolytes on the reaction of hexacyanoferrate(III) ion with sulphite[5]. We have found the reaction to be catalyzed by traces of copper(II) ions whose catalytic activity is influenced by nucleophilic particles present in the reaction system. Kinetics of the reaction therefore depends on the quantity of copper(II) ions contained as trace impurities in the reagents used and on the nature of anions. In this paper we have examined, whether concentrations of copper(II) ions affect course of other oxidation–reduction reactions of hexacyanoferrate(III) ion and to what extent the trace catalysis is responsible for hardly explainable effects observed when studying these reactions. Reactions of hexacyanoferrate(III) ion with thiosulphate[4], mercaptoacetic acid[6], hydrazine[7,8], hydroxylamine[9], sulphite[5], cyanide[1], glucose[10], arsenite, and formaldehyde[11] have been studied.

EXPERIMENTAL

Reagents and Apparatus

All the reagents used were A.R. grade purity. Potassium hexacyanoferrate(III) and oxidized substrates except formaldehyde were repurified by double crystallization from the water solution.

Rate of reduction of hexacyanoferrate(III) by various substrates was examined colorimetrically at a wave-length of 418 nm. The reaction was followed continuously in an apparatus making possible recording transmittance of the reaction mixture[5].

Composition of the reaction mixtures and their pH was chosen so that the reaction should not proceed within a time interval shorter than 1 minute and longer than several tens of minutes. The initial concentration of potassium hexacyanoferrate(III) was $1 . 10^{-3}$ mol/l, that of the substrate $2·5 . 10^{-4}—1 . 10^{-1}$ mol/l. The reactions occurred in the Britton–Robinson buffer medium at constant ionic strength obtained by additions of sodium nitrate under a nitrogen atmosphere. Nitrogen was freed from oxygen traces by chromium dichloride.

Thin-layer chromatography (Silufol sheets 150×150 mm, Kavalier Votice) was applied to identifying products of the reaction of hexacyanoferrate(III) with thiosulphate. As solvent, the n-propanol–methanol–ammonium hydroxide–water solution (10 : 10 : 1 : 2) was employed. Ammoniacal solution of silver nitrate was used for the detection.

Concentration of hexacyanoferrate(III) and substrates was determined by conventional titrimetric methods.

RESULTS AND DISCUSSION

Effect of Copper(II) *Ions on Initial Reaction Rates*

Effect of additions of copper(II) ions and those of ethylenediamine tetraacetic acid (EDTA) on the course of reactions of hexacyanoferrate(III) with thiosulphate, mercaptoacetic acid, hydrazine, hydroxylamine, sulphite, cyanide, glucose, arsenite, and formaldehyde has been investigated. All these reactions follow at the beginning kinetic equation of the second order of magnitude, later on, they deviate from this course to various extent[1-10]. Catalytic effect of copper(II) ions and inhibiting effect of EDTA were therefore considered using values of rate constant $k(\text{mol}^{-1} . 1 . \text{s}^{-1})$ at time $t = 0$. In Table I values of the rate constants for reaction taking place without additions of catalyzing ions, with Cu^{2+} $(1 . 10^{-5}$ mol/l) as well as EDTA $(2 . 10^{-4}$ mol/l) additions are summarized. There are considerable differences between values of the rate constants of individual reactions, and the dependences of the rate constants on pH are likewise different. It was not therefore possible to examine reactions at equal pH, but adjustment of pH of the reaction mixtures was needed so that the reactions might proceed at a rate adequate to the experimental arrangement.

As evident from the comparison of values k_0 (without addition) and k' (with Cu^{2+} addition), and k_0 and k_{EDTA} (with EDTA addition) for all the reactions, except the hexacyanoferrate(III) formaldehyde reaction, catalytic effect of copper(II) ions and inhibiting effect of EDTA were found. The reaction of hexacyanoferrate(III) with formaldehyde, which proceeds at a measurable rate at pH > 11 only, was studied in 1M sodium hydroxide. An addition of copper(II) ions or EDTA is of no effect on the value of the rate constant, but an addition of copper(II) ions in presence of EDTA increases somewhat value of the rate constant. In all other reactions, except for reaction of hexacyanoferrate(III) with arsenite, the rate constant value was in-

creased by $0.5-3$ orders of magnitude if $1 . 10^{-5}$ mol/l of Cu^{2+} was added, whereas addition of $2 . 10^{-4}$ mol/l of EDTA reduced value of the rate constant by $0-2$ orders of magnitude. For reaction of hexacyanoferrate(III) with arsenite, catalytic and inhibiting effects were found only at higher Cu^{2+} or EDTA concentrations (Table I).

It is interesting that the course of all the reactions mentioned is considerably affected, if the reaction mixture gets into contact with metallic copper. For example, by dipping a copper wire into the reaction mixture the rate of the hexacyanoferrate(III) reaction immediately rises two (oxidation of hydroxylamine, oxidation of glucose) to sixty times (oxidation of mercaptoacetic acid). Except for the oxidation of cyanide and arsenite the reaction takes place at enhanced rate even after the copper wire has been removed, this giving proof that the catalytic effect is due to an increased concentration of copper(II) ions in the solution. Also in this respect the hexacyanoferrate(III) reactions remind of typical "trace-catalyzed" reactions, as for instance of autooxidation of sulphite[11].

It has been found for the reactions of hexacyanoferrate(III) with thiosulphate, mercaptoacetic acid, hydrazine, hydroxylamine, sulphite, and cyanide that for $[Cu^{2+}] = 1 . 10^{-6}$ to $5 . 10^{-5}$ mol/l, relations

TABLE I
Effect of Cu^{2+} Ions and Na_2EDTA on Initial Rate of Reaction of Hexacyanoferrate(III) with Various Substrates

$[Fe(CN)_6^{3-}] = 1 . 10^{-3}$ mol/l; $[substrate^{n-}] = 2.5 . 10^{-4} - 4 . 10^{-2}$ mol/l; $25°C$; k_0 — without addition; $k' - [Cu^{2+}] = 1 . 10^{-5}$ mol/l; $k_{Cu} = (k' - k_0)/[Cu^{2+}]$; $k_{EDTA} - [EDTA] = 2 . 10^{-4}$ mol/l.

Substrate (L)	pH	pK_{HL}[12]	k_0 $l\,mol^{-1}s^{-1}$	k' $l\,mol^{-1}s^{-1}$	k_{Cu} $l^2mol^{-2}s^{-1}$	k_{EDTA} $k\,mol^{-1}s^{-1}$
$S_2O_3^{2-}$	6·0	1·72	1·7	8·8	$7.1 . 10^5$	$1.4 . 10^2$
$SHCH_2COO^-$	7·5	10·55	25·0	$\gg 5.0 . 10^2$	$\gg 4.8 . 10^7$	$3.4 . 10^{-1}$
N_2H_4	7·5	7·99	28·0	$4.0 . 10^3$	$4.0 . 10^8$	6·0
NH_2OH	7·5	5·98	1·6	35·0	$3.3 . 10^6$	$8.0 . 10^{-2}$
SO_3^{2-}	10·1	7·21	$1.9 . 10^{-1}$	1·7	$1.5 . 10^5$	$7.2 . 10^{-2}$
CN^-	12·0	9·22	$<1.3 . 10^{-3}$	2·8	$2.8 . 10^5$	$<1.3 . 10^{-3}$
$C_6H_{12}O_6$	12·0		$5.3 . 10^{-2}$	$1.4 . 10^{-1}$	$8.4 . 10^3$	$8.7 . 10^{-3}$
AsO_3^{3-}	0·2M-NaOH	9·22	$2.2 . 10^{-1}$	1.6^b	$6.9 . 10^3$	$7.6 . 10^{-2c}$
$HCOH$	1M-NaOH		$1.0 . 10^{-1}$	$2.6 . 10^{-1d}$		$1.0 . 10^{-1}$

^{a} [ref.[12]], ^{c} $[Cu^{2+}] = 1 . 10^{-4}$ mol/l; ^{b} $[EDTA] = 5 . 10^{-2}$ mol/l, ^{d} $[Cu^{2+}]$ $(1 . 10^{-4}$ mol/l) $+$ $[Na_2EDTA]$ $(1 . 10^{-3}$ mol/l).

$$v_0 \doteq k' \cdot \left[\text{Fe(CN)}_6^{3-} \right] \cdot \left[\text{substrate}^{n-} \right] , \tag{1}$$

$$k' = k_0 + k_{\text{Cu}} \cdot \left[\text{Cu}^{2+} \right] \tag{2}$$

hold. From the k_0 and k values, set out in Table I, the k_{Cu} values were calculated. Provided that relations (1) and (2) are valid, these values were calculated also for the reaction of hexacyanoferrate(III) with arsenite and with glucose.

It follows from Table I that there are great differences in the k_{Cu} values found for individual substrates. Owing to different pH values used for individual systems, the rate constants can be compared between one another with certain reservations only. If, however, $pK_{\text{HL}}^{\text{H}}$ values of protonized substrate forms are used instead $pK_{\text{ML}}^{\text{M}}$ values (which are not available for the most part of the systems studied) as a measure of interaction of Cu^{2+}-substrate^{n-} and if at equal or near pH values, the $pK_{\text{HL}}^{\text{H}}$ values are compared with the k_{Cu} values, it may be seen that even the k_{Cu} value decreases with the decreasing pK value.

The k_0 rate constant is obviously not a rate constant of a noncatalyzed reaction, but the rate constant of a reaction catalyzed by copper(II) ions traces present in the reaction systems as impurities. The addition of Na_2EDTA substantially decreases value of the rate constant in all cases except for the hexacyanoferrate(III) formaldehyde system (k_0 for the reaction of hexacyanoferrate(III) with formaldehyde was of such a low value that it was not possible to determine it using the given experimental arrangement). With respect to the value of the stability constant[12] of [CuEDTA] ($K_{\text{CuEDTA}} = 5 \cdot 10^{-18}$) and to the fact that addition of Na_2EDTA brings down concentration of copper(II) ions to a value less than 10^{-20} mol/l that is approximately by 13 orders of magnitude, one can note with surprise that maximum decrease of the rate constant value amounted to 3 orders of magnitude. This fact may have one or more reasons: the rate of the noncatalyzed reaction is not immeasurably low; the rate of the catalyzed reaction is not proportional to the concentration of copper(II) ions within the whole concentration range of copper(II) ions; the reaction is catalyzed by EDTA complexes with some other cations which are present in the system as trace impurities.

Effect of Copper(II) Ions on Kinetics of the Reaction of Hexacyanoferrate(III) with Thiosulphate

When examining course of the given reactions it was found that in some systems (reaction of hexacyanoferrate(III) with hydrazine, hydroxylamine, and thiosulphate) the concentration of copper(II) ions affects rate of the reaction and its kinetics. The most distinct effect of copper(II) ions was found for the hexacyanoferrate(III)-thiosulphate system; this reaction was therefore examined in a more detail.

In accordance with the Sandved and Holte[3] data it has been found that the initial

rate of reaction in a system without additions of catalyzing ions is proportional to the concentration of hexacyanoferrate(III) and thiosulphate. The rate of reaction, however, is gradually accelerated by reference to the 2nd order of the reaction and magnitude of the deviation increases with the increasing initial concentration of thiosulphate. The initial slow course reminds of an induction period, and total dependence of the hexacyanoferrate(III) concentration upon time is of a character typical for autocatalytic reactions. Addition of tetrathionate greatly reduces induction period of the reaction; but neither at higher tetrathionate concentrations complies the reaction with the 2nd order reaction (Fig. 1). In contrast to this, potassium hexacyanoferrate(III) extends the induction period of the reaction similarly as the EDTA addition does (Fig. 1). Additions of the copper(II) ions affect the kinetics in accordance with the fact that with the increasing concentration of copper(II) ions, the deviation from the 2nd order decreases; and even at a $CuSO_4$ concentration of $1 . . 10^{-4}$ mol/l the reaction proceeds according to the 2nd order (Fig. 1).

The dependence of the initial rate of reaction on the concentration of copper(II) ions was followed within $1 . 10^{-6}$ to $1 . 10^{-4}$ mol/l. In a range of $1 . 10^{-6}$ to $5 . . 10^{-5}$ mol/l, the dependence of the initial rate of reaction upon concentration of copper(II) ions is linear. At higher concentration the "saturation effect" is applied and the initial rate of reaction rises with the increasing concentration of copper(II) ions more slowly than it would correspond to the linear dependence.

According to Sandved and Holte[3], and chromatographic measurements, tetrathionate is the only one product of the oxidation of thiosulphate by hexacyanoferrate(III) at the initial stage of the reaction. But in view of the polythionate[13] reactions described it is evident that in the reaction system containing thiosulphate and tetrathionate, reactions take place which result in the formation of polythionate and sulphite which likewise reduces hexacyanoferrate(III) in the subsequent reaction. The sequence of these reactions may be simply expressed by equations
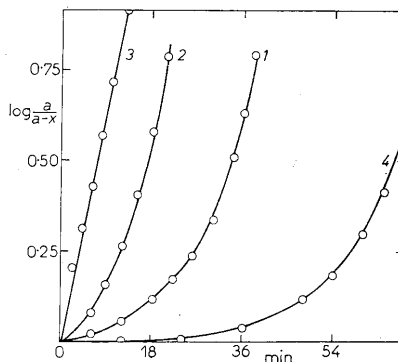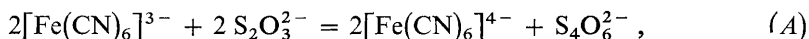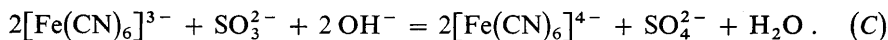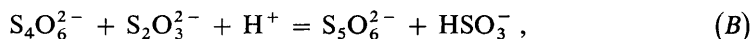
$$2[Fe(CN)_6]^{3-} + 2 S_2O_3^{2-} = 2[Fe(CN)_6]^{4-} + S_4O_6^{2-} , \qquad (A)$$

FIG. 1

Oxidation of Thiosulphate by Hexacyanoferrate(III)
$a = [Fe(CN)_6^{3-}]_{t=0} = 1 . 10^{-3}$ mol/l, $1 . 10^{-1}$ mol/l $Na_2S_2O_3$, $1 \cdot 0$ mol/l $NaNO_3$; pH 6, 25°C; 1 0, 2 $5 . 10^{-4}$ mol/l $Na_2S_4O_6$, 3 $1 . 10^{-4}$ mol/l $CuSO_4$, 4 $1 . 10^{-3}$ mol/l Na_2EDTA.

$$S_4O_6^{2-} + S_2O_3^{2-} + H^+ = S_5O_6^{2-} + HSO_3^- , \qquad (B)$$

$$2[Fe(CN)_6]^{3-} + SO_3^{2-} + 2\,OH^- = 2[Fe(CN)_6]^{4-} + SO_4^{2-} + H_2O . \quad (C)$$

In addition to the reaction of tetrathionate with thiosulphate, further polythionate reactions can take place in the reaction system under given conditions, leading to the increase of sulphur chains and even to the formation of colloidal sulphur[13,14]. At higher initial thiosulphate concentrations $(10^{-1}\ mol/l)$ also formation of colloidal sulphur within the reaction was well evident. Oxidation of thiosulphate by ferricyanide is therefore a complex reaction consisting of a series of side and successive reactions, some of which only being catalyzed by copper(II) ions. This allows to explain established deviations from the 2nd order as well as the fact that magnitude of these deviations decreases at higher concentrations of copper(II) ions which catalyze reactions (A) and (C).
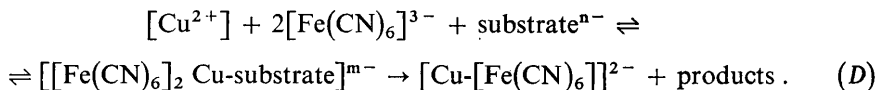
Mechanism of Catalyzed Reactions

The established catalytic effects of copper(II) ions on the oxidation reactions of hexacyanoferrate(III) may be accounted for three different mechanisms. Because of a lack of quantitative data on individual complexes involved in the reaction systems, it is difficult to decide for any of them:

1) The copper(II) ions, which can exist in a solution in three oxidation states, mediate electron transfer between one-electron oxidant and two-electron substrate on the basis of a chain mechanism which essentially is alternating oxidation and reduction of the ions. Oxidation of copper ions proceeds as two successive one-electron processes, whereas reduction involves a two-electron process. This mechanism serves to explain most oxidation-reduction reactions catalyzed by transition element ions[15].

2) All the substrates for which a distinct catalytic effect was proved, produce fairly stable complexes with metallic ions $(pK^{Cu^+}_{CuS_2O_3^-} = 10.35;\ pK^{Cu^{2+}}_{CuS_2O_3} > 6;\ pK^{Cu^+}_{CuSO_3^-} = 7.85;\ pK^{Cu^+}_{CuCN} > 8;\ pK^{Cu^{2+}}_{CuCN} > 6)$. It can be shown with use of tabulated data of the stability constants[12] that in some systems $[Cu^+] \ll [Cu\text{-substrate}^{(n-1)-}]$ or $[Cu^{2+}] \ll [Cu\text{-substrate}^{(n-2)-}]$ is valid. In these systems the one-electron transfer between $[Fe(CN)_6]^{3-}$ and $[Cu\text{-substrate}]^{(n-1)-}$ or $[Cu\text{-substrate}]^{(n-2)-}$ ions must be therefore also assumed. By means of this mechanism catalytic effect of copper(II) ions on oxidation of cystein[16] has been explained.

3) By reference to the interactions of ferricyanide-metallic ions[12] described, likewise associates of type $[Cu\text{-}[Fe(CN)_6]]^-$, $[[Fe(CN)_6 - Cu\text{-substrate}]^{m-}$ and $[[Fe.(CN)_6]_2 - Cu\text{-substrate}]^{p-}$ may be expected in the solution. Electron transfer between hexacyanoferrate(III) and substrate can therefore take place even inside these mixed complexes and the reaction mechanism may be defined, for instance,

by diagram (D). Mixed complexes have an extraordinary thermodynamic and kinetic properties and play an important role in some catalyzed reactions[17].

$$[Cu^{2+}] + 2[Fe(CN)_6]^{3-} + substrate^{n-} \rightleftharpoons$$

$$\rightleftharpoons [[Fe(CN)_6]_2 \, Cu\text{-substrate}]^{m-} \rightarrow [Cu\text{-}[Fe(CN)_6]]^{2-} + products \,. \qquad (D)$$

Analogously to other trace-catalyzed reactions a problem arises what are the values of the rate constants of the catalyzed reactions. As has been given here, this question cannot be for the time being satisfactorily replied. It cannot be excluded that in absence of catalyzing ions the reactions studied proceed [ref.[16]], similarly as other trace-catalyzed reactions, immeasurably slowly.

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