Inorganica Chimica Acta, 22 (1977) 35–38

Kinetics of Oxidation of Pentacyano(sulphito)ferrate(II) by Peroxydisulphate

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Received July 20, 1976

The kinetics of oxidation of pentacyano(sulphito)ferrate(II) by peroxydisulphate follow the rate law

$$-d\,[Fe(CN)_5SO_3^{5-}]/dt = k_0[Fe(CN)_5SO_3^{5-}] + 2k_1[Fe(CN)_5SO_3^{5-}]\,[S_2O_8^{2-}]$$

where $k_0 = 5.0 \times 10^{-4}$ *sec*$^{-1}$ *at pH = 10 and 25 °C.* k_1 *showed marked dependence on the type and concentration of cation present. Two products have been identified,* $Fe(CN)_5SO_3^{4-}$ *and* $Fe(CN)_5OH^{3-}$*; the first resulted from an outer-sphere oxidation mechanism, and the second was produced from a side reaction in which the complex* $Fe(CN)_5SO_3^{5-}$ *loses* SO_3^{2-} *before oxidation.*

Introduction

The rate of oxidation of hexacyanoferrate(II) by peroxydisulphate has been observed to be markedly dependent upon the type and concentration of cations present [1–3]. The effect of the cations is seen to be due to the formation of ion-pairs which are more reactive than the parent ions [1, 2].

The kinetics of oxidation of pentacyano(sulphito)ferrate(II) by peroxydisulphate are described in this study. The rate of this reaction is expected to show a similar dependence on the type and concentration of cations present as exhibited by the hexacyanoferrate(II)-peroxydisulphate reaction.

Experimental

Analytical grade chemicals were always used, whenever available, without further recrystallisation. General grade Sodium peroxydisulphate (BDH) was recrystallised at 50 °C. Solutions of sodium and potassium peroxydisulphates were standardised [4]. Fresh solutions were always used. The complex $Na_5Fe(CN)_5SO_3 \cdot 4H_2O$ was prepared according to Hofmann's method [5]. The complex was purified by the modified method of Asperger *et al.* [6] and verified by analysis and absorption spectra.

Buffer solutions of known concentrations were made from carbonate and hydrogencarbonate both as sodium and potassium salts. Sodium and potassium nitrates were used to vary the concentration of sodium and potassium cations respectively. Doubly distilled water was used.

A weighed quantity of the complex was added to a thermally equilibrated buffered solution of the peroxydisulphate. This was thoroughly mixed and quickly transferred to an absorption cell. The change in absorbance with time was recorded at 340 nm using a Unicam SP 700 spectrophotometer equipped with thermostatted cell-holder. At 340 nm the absorbance (A) of the product $[Fe(CN)_5SO_3]^{4-}$ is appreciably higher than that of the reactant $[Fe(CN)_5SO_3]^{5-}$. The reaction was carried out under pseudo first-order conditions with the peroxydisulphate concentration being in excess over that of the complex. pH of the reaction solution was measured on a Radiometer pH meter model PHM 63.

Results

With the peroxydisulphate concentration in excess over that of the complex ion at pH 10.0, $[Na^+] = 0.175$ *M* and temperature 25 °C, the oxidation of pentacyano(sulphito)ferrate(II) exhibited first-order kinetics. Plots of $\log(A_\infty - A_t)$ as a function of time gave straight lines to beyond 90% of the reaction. Table I gives the values of the pseudo first-order rate constant (k_{obs} sec^{-1}) over the range in which the concentration of the complex was varied.

TABLE I. Order with respect to $[Fe(CN)_5SO_3^{5-}]$.[a]

$[Fe(CN)_5SO_3^{5-}] \times 10^4$ *M*	$10^3\ k_{obs}$, sec^{-1}
10.0	1.49
7.5	1.47
5.0	1.45
4.0	1.46
2.5	1.44

[a] $[S_2O_8^{2-}] = 1.0 \times 10^{-2}$ *M*, $[Na^+] = 0.175$ *M*, pH = 10.0, T = 25 °C.

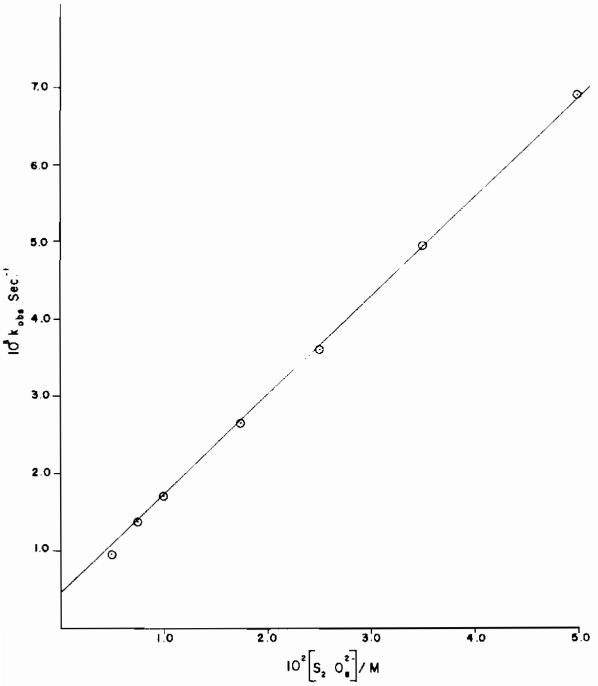

Figure 1. Dependence of k_{obs} on $[S_2O_8^{2-}]$ • $[Fe(CN)_5SO_3^{5-}] = 10^{-3}$ *M*, $[Na^+] = 0.255$ *M*, pH = 10.0, T = 25 °C.

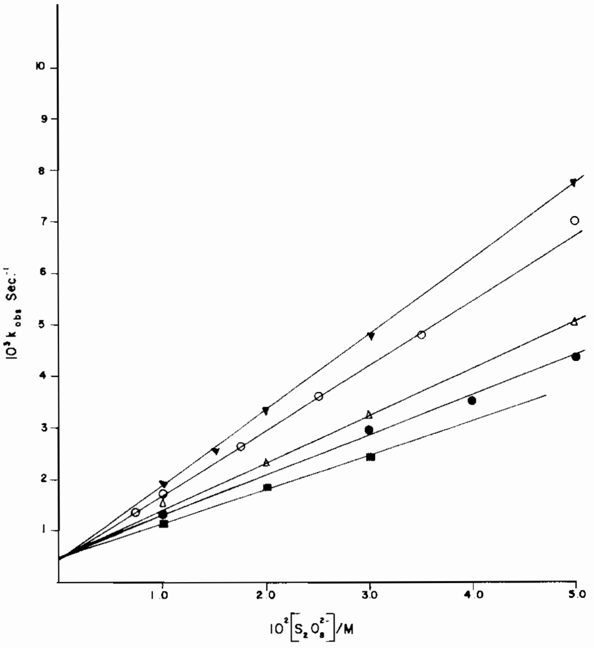

Figure 2. Dependence of k_{obs} on $[Na^+]$ • $[Fe(CN)_5SO_3^{5-}] = 10^{-3}$ *M*, pH = 10.0, T = 25 °C. $[Na^+]$: ■ = 0.095 *M*, ● = 0.137 *M*, △ = 0.180 *M*, ○ = 0.255 *M*, ▼ = 0.337 *M*.

The dependence of k_{obs} on the peroxydisulphate concentration was investigated over the range 0.50–5.0 × 10^{-2} *M* at pH 10.0, $[Na^+] = 0.255$ *M* and 25 °C.

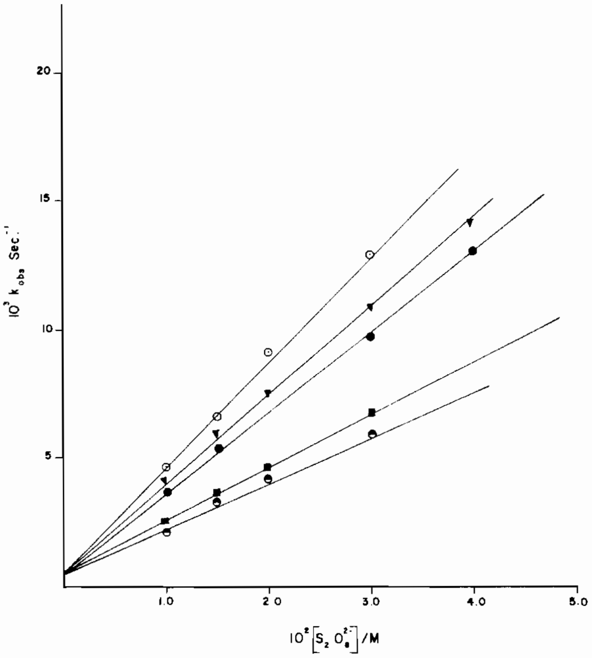

Figure 3. Dependence of k_{obs} on $[K^+]$ • $[Fe(CN)_5SO_3^{5-}] = 10^{-3}$ *M*, pH = 10.0, T = 25 °C. $[K^+]$: ○ = 0.075 *M*, ■ = 0.095 *M*, ● = 0.160 *M*, ▼ = 0.195 *M*, ⊙ = 0.255 *M*.

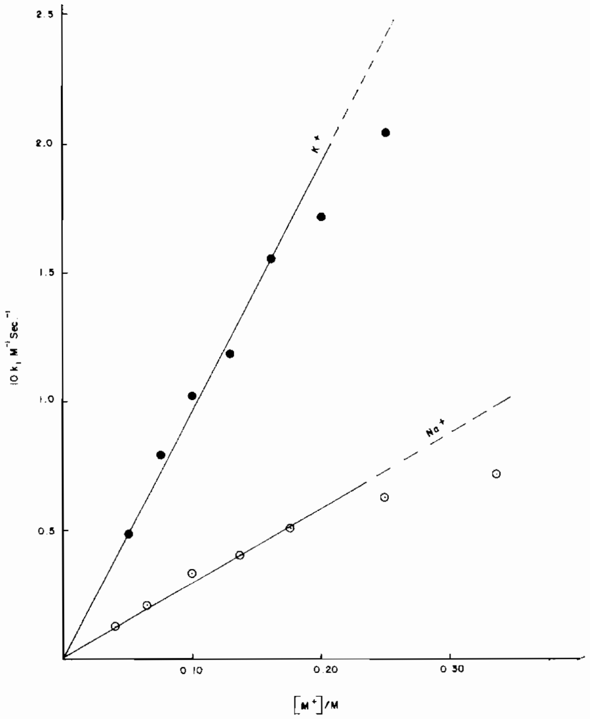

Figure 4. Variation of k_1 with alkali cation concentration. pH = 10.0, T = 25 °C.

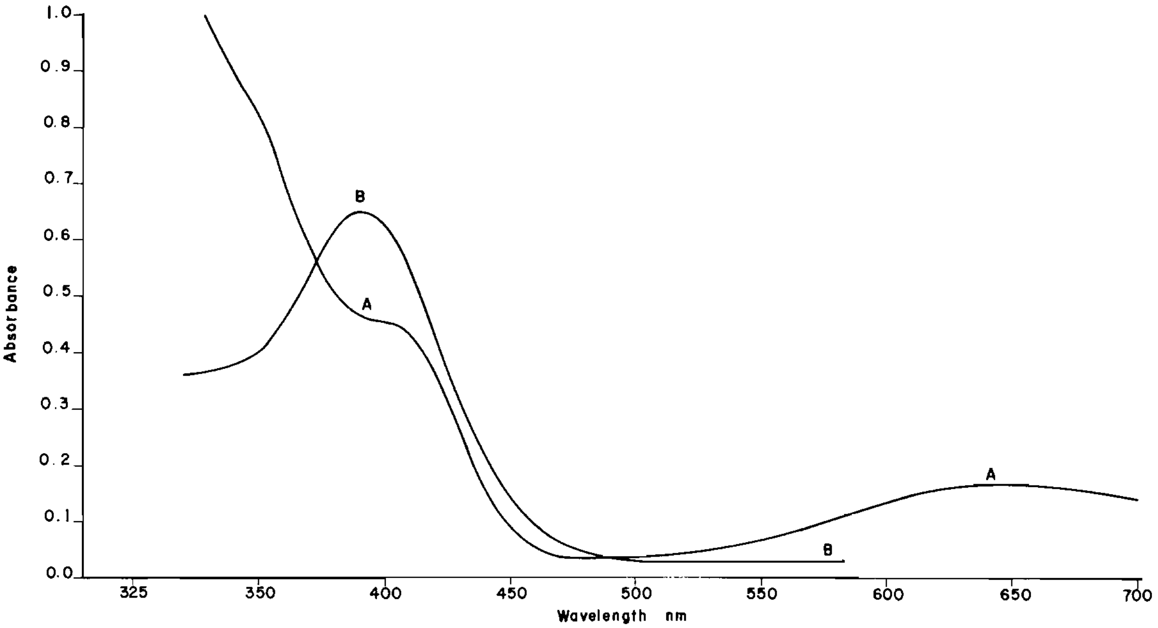

Figure 5. (A) UV–Visible absorption spectrum of $[Fe(CN)_5SO_3]^{4-}$ and (B) uv–visible absorption spectrum of the product of the side reaction believed to be $[Fe(CN)_5OH]^{3-}$

A plot of k_{obs} against $[S_2O_8^{2-}]$ agreed with Eq. 1 as can be seen from Figs. 1–3.

$$k_{obs} = k_0 + 2k_1\,[S_2O_8^{2-}] \qquad (1)$$

The factor 2 in Eq. 1 is used because $d[Fe(CN)_5SO_3^{4-}]/2dt = -d\,[S_2O_8^{2-}]/dt$. Values of k_0 and k_1 were obtained from the intercepts and the slopes of Fig. 1–3 respectively.

Figures 2 and 3 show the variation of k_{obs} with $S_2O_8^{2-}$ at different Na^+ and K^+ concentrations respectively at pH 10.0 and 25 °C. The value of k_0 (5.0×10^{-4} sec^{-1}) is clearly unaffected by the type or concentration of the cation present, whereas k_1 is affected by both. The variation of k_1 with Na^+ and K^+ concentrations is shown in Fig. 4. At low concentrations of Na^+ and K^+ cations k_1 showed a linear dependence on their concentrations. However, at [cation] 0.20 *M*, there is an obvious deviation as shown in Fig. 4. The dependence of k_1 on cation over the linear part is described by Eq. 2:

$$k_1 = k_{M^+}\,[M^+] \qquad (2)$$

where $k_{M^+} = 0.30$ and 0.97 M^{-2} sec^{-1} for $M^+ = Na^+$ and K^+ respectively at 25 °C.

The spectra of the two reaction products separated using an alumina column are shown in Fig. 5. The main product of the reaction, $[Fe(CN)_5SO_3]^{4-}$ (A), has a broad weak band at *ca.* 650 nm and a strongly absorbing band in the UV region. The product B which was eluted first (indicating a lower charge) has an absorption peak at *ca.* 392 nm.

Discussion

Oxidation of metal ion complexes by peroxydisulphate may proceed by either inner- or outer-sphere mechanisms [7]. Thus both the substitution inert complexes $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ appear to be oxidised by an outer-sphere mechanism [7], whereas an inner-sphere mechanism operates in the oxidation of $Cr(H_2O)_6^{2+}$ [8]. Parallel inner- and outer-sphere mechanisms have been proposed in the oxidation of Fe(II) complexes of N-2-(pyridylmethylene) analine by this oxidant [9]. The kinetics of this reaction showed a two-term rate law with one path independent of oxidant concentration.

The kinetics of pentacyano(sulphito)ferrate(II)–peroxydisulphate reaction also require two parallel paths, one first order in each reactant (Eqs. 3 and 4):

$$[Fe(CN)_5SO_3]^{5-} + S_2O_8^{2-} \xrightarrow{k_3} [Fe(CN)_5SO_3]^{4-} + SO_4^{2-} + SO_4^{-} \qquad (3)$$

$$[Fe(CN)_5SO_3]^{5-} + SO_4^{-} \xrightarrow{fast} [Fe(CN)_5SO_3]^{4-} + SO_4^{2-} \qquad (4)$$

and the other first order in the Fe(II) complex and zero order in the oxidant. This second path is consistent with reaction 5 being rate-determining

$$Fe(CN)_5SO_3^{5-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Fe(CN)_5^{3-} + SO_3^{2-} \qquad (5)$$

where the intermediate $[Fe(CN)_5]^{3-}$ is rapidly oxidised to give $[Fe(CN)_5OH]^{3-}$ as indicated by the UV–visible spectrum of the yellow product (B) (Fig. 5) which is identical to that reported for this complex [10].

The rate law (6) is obtained from the above mechanism:

$$-d[Fe(CN)_5SO_3^{5-}]/dt = 2k_3[Fe(CN)_5SO_3^{5-}][S_2O_8^{2-}] + k_5[Fe(CN)_5SO_3^{5-}] \qquad (6)$$

where

$$k_{obs} = 2k_3[S_2O_8^{2-}] + k_5 \qquad (7)$$

which is identical to the experimental dependence of k_{obs} on $[S_2O_8^{2-}]$, Eq. 1, with $k_0 = k_5$ and $k_1 = 2k_3$.

The above reaction scheme indicates that both outer-sphere (Eq. 3) and dissociation mechanisms (Eq. 5) are operative. Pentacyano(sulphito)ferrate(II) is reported [6] to substitute the SO_3^{2-} by a limiting S_N1 mechanism forming the intermediate $[Fe(CN)_5]^{3-}$, which exhibited selective reactivity towards various ligands [11]; The magnitude of k_0 (5×10^{-4} sec^{-1}, pH 10.0 at 25 °C) is comparable to the rate constant reported for the loss of SO_3^{2-} from $[Fe(CN)_5SO_3]^{5-}$ (5.7×10^{-5} sec^{-1} pH 10.8 at 25 °C) if the first order dependence on $[H^+]$ was taken into consideration [12].

The dependence of k_1 on the nature and concentration of cations is not unexpected, as reactions between similarly charged ions have often displayed such effects [13]. The complex ion $[Fe(CN)_5SO_3]^{5-}$ is epxected to be extensively ion paired with alkali metal cations because of its high negative charge. Thus, it is not unreasonable to expect the formation of $[MFe(CN)_5SO_3]^{4-}$ and $[M_2Fe(CN)_5SO_3]^{3-}$ as reactive ions. Peroxydisulphate ion also forms ion pairs with alkali metal cations [3]. The deviation from linear dependence on cation concentration at [cation] >0.20*M* is not unexpected since increasing [cation] would lead to an increase in ionic strength and, therefore, a decrease in the ion-paris formation constants. The order of effectiveness of the alkali metal cations, $K^+ > Na^+$, as catalysts, has been observed before [1, 2]. The variation of k_1 with increasing [cation] may, in part, be due to a primary salt effect.

A comparison of the rate constants of the oxidation of pentacyano(sulphito)ferrate(II) and hexacyanoferrate(II) by peroxydisulphate under similar conditions, shows that the rate of oxidation of the former is greater. Thus at 25 °C, $[K^+] = 0.10$ *M* and pH = 10.0, the second order rate constants are 0.097 and 0.025 M^{-1} sec^{-1} respectively. The higher reactivity of $[Fe(CN)_5SO_3]^{5-}$, in spite of its higher negative charge, is likely to be due to the SO_3^{2-} ligand in which, probably, the oxidation state of the sulphur atom is changed from +4 to +5 and then rapidly to +4 by abstraction of an electron from Fe(II) in the complex. The sulphite ligand can act either as a donor or acceptor of electrons [14]. The very high absorption of the product $[Fe(CN)_5SO_3]^{4-}$ in the UV region is likely to be due to a charge transfer from the ligand SO_3^{2-} to the metal ion Fe(III).

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