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The oxidation of potassium hexacyanoferrate(II)trihydrate by potassium dibromodicyanoaurate(III) in acidic solution: a kinetic study

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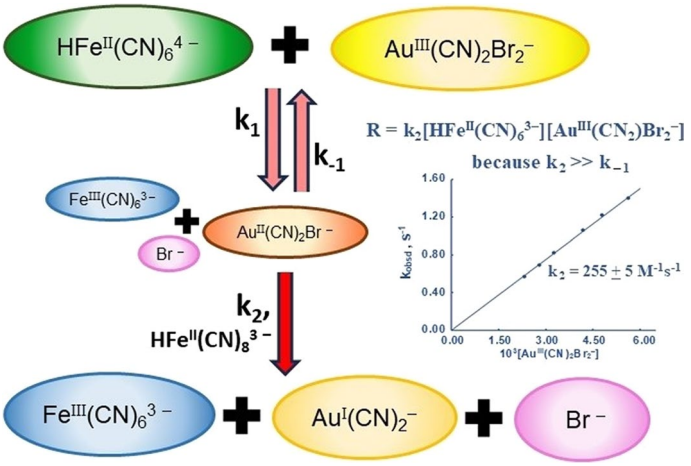
Abstract

The reduction of the dibromodicyanoaurate(III) ion by hexacyanoferrate(II)trihydrate was studied in an acidic medium. The reaction was first order in both $Au(CN)_2Br_2^-$ and $Fe(CN)_6^{4-}$ and a second order rate constant of $k_2 = 255 \pm 5\ M^{-1}\ s^{-1}$ at $[H^+] = 2.041 \times 10^{-4}$ M, an ionic strength of 0.51 M (NaBr) and 20.0 ± 0.1 °C was found for the reaction. The reaction rate decreases with increasing $[H^+]$ in the region $0.0004 \leq [H^+] \leq 0.065$ M. An equilibrium constant of $K_a = (3.00 \pm 0.01) \times 10^{-3}$ M ($pK_a = 2.52$) at 20.0 ± 0.1 °C was found for the deprotonation of $H_2Fe(CN)_6^{2-}$. Activation parameters of $\Delta H^{\#} = 47.8 \pm 0.9$ kJ mol^{-1} and $\Delta S^{\#} = -37 \pm 3$ J K^{-1} mol^{-1} have been obtained by a least squares fit of temperature data directly to the Eyring equation.

Graphical abstract



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Keywords Redox kinetics · Acidic medium · Mechanism · Rate law · Activation parameters

Introduction

Kinetic studies of the reduction of gold(III) ions by one-electron reducing agents such as thiosulfate [1], iodide [2, 3], alkyl sulfides [4], thiocyanate [5], hydroxyl amine [6], L-histidine [7], hydrazoic acid [8], sulfite and hydrogen sulfite [9] and oxalic acid [10] have been reported and provide evidence for a common intermolecular reaction mechanism [4]. The rate determining step was suggested to be the attack of the nucleophile on the coordinated ligand followed by a bridged electron transfer to the metal centre [4].

In contrast to the information available regarding the substitution kinetics of d^8 species, of which Au(III) is a member, the two-electron reduction of gold(III) complexes is much lesser known. Redox studies show first order kinetics in both the Au(III) and the reducing agent concentration, except for oxalic acid reduction where a fractional order in oxalic acid was observed [10]. In all of the mentioned studies the hydrogen ion concentration in the reaction mixture has a decreasing effect on the reaction rate with increasing $[H^+]$.

The reduction of $AuCl_4^-$ with metal ions and metal ion complexes as reducing agents have also been reported [11–13]. The rate of the $AuCl_4^-/Fe^{2+}$ reaction show an increasing trend in the rate with increasing $[Cl^-]$ in the reaction mixture [11]. In the oxidation of $Pt(CN)_4^{2-}$ by $AuCl_4^-$ [12] three reactive Au(III) species have been identified due to the $[Cl^-]$ in the reaction mixture. For $[Cl^-] < 2 \times 10^{-4}$ M and pH 0, the neutral Au(III) and $AuCl_3(H_2O)$ are the predominant Au(III) species. A relative high $[Cl^-]$ suppress hydrolysis of $AuCl_4^-$ and therefore with $[Cl^-] \geq 0.20$ M and pH 0, the exclusive oxidant species is $AuCl_4^-$ [12].

The interpretation of a reaction mechanism by which two-electron oxidizing agents such as $AuCl_4^-$ reacts is simplified when it reacts with stable one-electron reducing agents. The reduction of $AuCl_4^-$ by the cyano complexes $Fe(CN)_6^{4-}$, $W(CN)_8^{4-}$ and $Mo(CN)_8^{4-}$ as reducing agents have been reported [13]. These reactions show a decrease in reaction rate with an increase in $[H^+]$ in the reaction mixture. The reactions of $Fe(CN)_6^{4-}$ and $W(CN)_8^{4-}$ are independent of $[Cl^-]$ in the reaction mixture for $[Cl^-] \geq 0.20$ M but the reaction between $Mo(CN)_8^{4-}$ and $AuCl_4^-$ shows a decreasing effect in the reaction rate with an increase in $[Cl^-]$ in the reaction mixture.

The reduction of dicyanodibromoaurate(III) and dicyanodichloroaurate(III) by sulfite and hydrogen sulfite has also been reported [9]. For both the reactions the rate of the reactions decreases with an increase in $[H^+]$ of the reaction mixture. The reduction of *trans*-$Au(CN)_2Br_2^-$ is independent of $[Br^-]$ and that of *trans*-$Au(CN)_2Cl_2^-$ is independent of $[Cl^-]$ in the reaction mixture.

In contrast to the wealth of kinetic information available on the reduction of $AuCl_4^-$, almost no kinetic information is available on the reduction of $Au(CN)_2Br_2^-$. We present with this paper results of a kinetic study of the

two-electron reduction of $Au(CN)_2Br_2^-$ by the one-electron reductant $Fe(CN)_6^{4-}$. This choice of reductant followed from the advantageous of mechanistic clarifications offered by enforcing one-electron transfer steps in the reaction mechanism.

Experimental

Trans-$KAu(CN)_2Br_2 \cdot 3H_2O$ was synthesized by the oxidation of $KAu(CN)_2$ as previously described [14] and were standardized with an iodometric process [15] and EDTA [16]. Fresh solutions of $K_4Fe(CN)_6 \cdot 3H_2O$ (Merk pro analise) were prepared frequently as this complex is unstable towards oxidation [17]. Solutions of $Fe^{II}(CN)_6^{4-}$ were standardized as previously described [18, 19] directly before use. Double distilled water was used throughout.

The reaction was monitored by measuring the formation of $[Fe^{III}(CN)_6^{3-}]$ ($\lambda_{420}\{Fe^{III}(CN)_6^{3-}\} = 1000\ M^{-1}\ cm^{-1}$) at 420 nm and 20 °C on a Durrum D110 stopped-flow spectrophotometer connected to a Tektronix 5103 N oscilloscope. The $Fe^{II}(CN)_6^{4-}$ and the $Au^{III}(CN)_2Br_2^-$, as well as the reaction product of the latter compound, do not contribute to the absorbance at this wavelength. The reaction was performed with the $[Au^{III}(CN)_2Br_2^-]$ in excess of between 4 and 11 fold over the $[Fe^{II}(CN)_6^{4-}]$. These conditions were deemed sufficient for pseudo first order conditions as Lente explanied in his book [20], that an excess of fourfold is sufficient for a flooding (pseudo first order) process in chemical kinetics. This minimum concentration requirement for pseudo first order conditions has previously been tested and confirmed as valid [13, 21–23].

The temperature of the reaction mixtures were controlled to within 0.1 °C with a Fryka-Kaltetechnic KB 300 waterbath with a Thermomix 1440 thermostat, connected to the Durrum D110 stopped-flow spectrophotometer.

The stoichiometry of the reaction has been determined volumetrically by titrating the formed $Fe^{III}(CN)_6^{3-}$ with ascorbic acid in the presence of $CdCl_2$ using variamine blue B hydrochloride (CI = 37,255) as indicator. The result was consistent with that of the $Fe^{II}(CN)_6^{4-}/Au^{III}Cl_4^-$ reaction as determined by Zakharov et. al [24] and the stoichiometric equation can be written as

$$2\ Fe^{II}(CN)_6^{4-} + Au^{III}(CN)_2Br_2^- \rightarrow 2\ Fe^{III}(CN)_6^{3-} + Au^{I}(CN)_2^- + 2\ Br^- \quad (1)$$

Results and discussion

The oxidation of $Fe^{II}(CN)_6^{4-}$ by dicyanodibromoaurate(III), $Au(CN)_2Br_2^-$, was performed under pseudo first order conditions [20] with $[Au(CN)_2Br_2^-]$ in a 4 to 11 fold excess over the limiting reagent $[Fe^{II}(CN)_6^{4-}]$. A non-linear least squares fit [25] of the data of the $Fe^{II}(CN)_6^{4-}/Au(CN)_2Br_2^-$ reaction traces (Fig. 1) to the exponential first order rate expression, Eqs. (2) or (3) [26],

$$\left\{\left[Fe^{III}(CN)_6^{3-}\right]_\infty - \left[Fe^{III}(CN)_6^{3-}\right]_t\right\} = \left\{\left[Fe^{III}(CN)_6^{3-}\right]_\infty - \left[Fe^{III}(CN)_6^{3-}\right]_o\right\} e^{(-kobsd.t)} \quad (2)$$

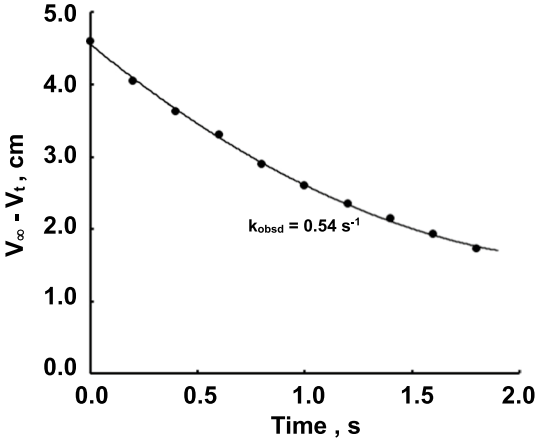

Fig. 1 A trace of the reaction between $Fe(CN)_6^{4-}$ and $Au(CN)_2(Br)_2^-$ (entry 6, Table S1). V_∞ = volts measured at time infinity on the oscilloscope, V_t = volts measured at time t. The difference $V_\infty - V_t$ was then measured in cm on the oscilloscope. $[Fe(CN)_6^{4-}] = 6.14 \times 10^{-4}$ M; $[Au(CN)_2(Br)_2^-] = 2.35 \times 10^{-3}$ M; $[H^+] = 2.04 \times 10^{-4}$ M; [NaBr] = 0.50 M; μ = 0.51 M; T = 20.0 ± 0.1 °C

or here

$$(V_\infty - V_t) = (V_\infty - V_o)\{e^{(-kobsd.t)} \quad (3)$$

indicate that the reaction is first-order in $Fe^{II}(CN)_6^{4-}$. Rate constants for the reactions are summarized in Table S1 (Supplementary Information). Since first order rate constant units are independent of concentration terms, concentration terms in Eq. (2) may be replaced by any quantity that is directly proportional to concentration. We substituted it with "volts", the quantity measured on the oscilloscope.

Variation of the $[Au(CN)_2Br_2^-]$ in the reaction mixture where $[Au(CN)_2Br_2^-]$ is 4 to 11 fold in excess of the limiting reagent, $Fe^{II}(CN)_6^{4-}$ (Table S1 entries 7 to 12 and Fig. 2) indicate the rate law shown in Eq. (4), with k_2 the 2nd order pH-dependent rate constant of 255 ± 5 $M^{-1}s^{-1}$ at an ionic strength (μ) of 0.51 M.

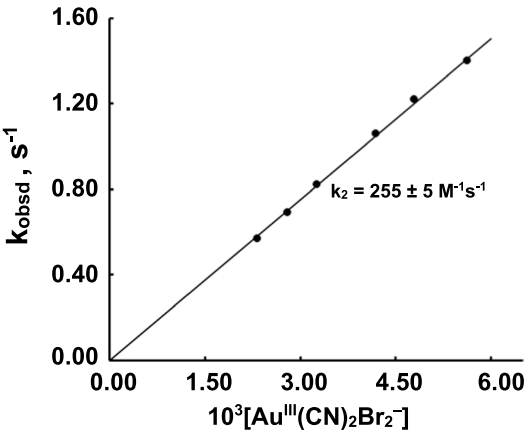

Fig. 2 Plot of k_{obsd} versus $[Au^{III}(CN)_2Br_2^-]$ for the variation of $[Au^{III}(CN)_2Br_2^-]$ in reaction mixtures. $[Fe^{II}(CN)_6^{4-}] = 5.11 \times 10^{-4}$ M, $[H^+] = 2.04 \times 10^{-4}$ M, $[Br^-] = 0.50$ M, μ(NaBr) = 0.51 M, T = 20.0 ± 0.1 °C

$$-\mathrm{d}\left[\mathrm{Fe^{II}(CN)_6^{4-}}\right]/\mathrm{dt} = \mathrm{k_2}\left[\mathrm{Fe^{II}(CN)_6^{4-}}\right]\left[\mathrm{Au^{III}(CN)_2Br_2^-}\right] \quad (4)$$

In studying the influence of reaction products and liberated Br^-, it was first noted that addition of $Fe^{III}(CN)_6^{3-}$ (entries 13–17, Table S1) and $Au^{I}(CN)_2^-$ (entries 18–23, Table S1) to the reaction mixture has no influence on the rate of $Fe^{II}(CN)_6^{4-}$ oxidation. The rate data of the reaction shows a slight decrease in the reaction rate with an increase in $[Br^-]$ in the reaction mixture (Table S1 entries 24 to 29) at $\mu = 0.51$ M (NaCl). This is indicative of an equilibrium step in the reaction mechanism, but the halide exchange reaction (5)

$$\mathrm{Au^{III}(CN)_2Br_2^-} + \mathrm{Cl^-} \rightarrow \mathrm{Au^{III}(CN)_2BrCl^-} + \mathrm{Br^-} \quad (5)$$

may also play a role. The most notable inhibiting effect by bromide is noted at high $[Br^-]$, but at low $[Br^-]$ and high $[Cl^-]$ (entries 24 and 25, Table S1), the mixed halogenated complex may form in noticeable quantities. The observed reaction rate acceleration at high $[Cl^-]$ is coherent with the known fact that Cl_2 is a better oxidizing agent than Br_2, which also means that Br^- is a stronger reductant than Cl^-. Therefore, replacement of a bromide ligand with a chloride ligand to form a mixed halide gold (III) complex may well increase the oxidizing power of this Au(III) complex and contribute to the faster reaction rates observed at low $[Br^-]$ but high $[Cl^-]$ in entries 24 and 25.

A theory for the influence of the ionic strength (I) of the reaction medium on the reaction rate was formulated by Brønsted and Bjerrum [27]. Application of this theory indicates that in water, if a plot of log k versus $\left(\frac{I^{1/2}}{1+I^{1/2}}\right)$ has a positive slope, the charges, Z_A and Z_B of reacting ions A and B are the same (i.e. both positive or both negative) and that the value of the slope should be approximately the product Z_AZ_B [13, 21, 23]. The data for varying the ionic strength of the reaction mixture for the $Fe^{II}(CN)_6^{4-}/Au^{III}(CN)_2Br_2^-$ redox reaction (Table S1 entries 30 to 37) show an increase in the reaction rate with an increase in ionic strength. The increasing effect (positive gradient) is also shown in Fig. 3 and is consistent with two negatively charge species reacting in the rate determining step of the reaction mechanism. Nothing can be read into the value of the slope (1.27), possibly because the Brønsted–Bjerrum theory is inaccurate at high ionic strength.

Alkali metal ion catalysis was significant in previous redox studies of some cyano complex ions in both alkaline [28, 29] and acid medium [13]. The highly negative charged $Fe^{II}(CN)_6^{4-}$ suggest alkali metal cation association. Relative high association constants for alkali metal cation association with $Fe^{II}(CN)_6^{4-}$ have been reported [30]. This led to an investigation of alkali metal ion catalysis by varying the Cs^+ ion concentration in the reaction mixture. Variation of the $[Cs^+]$ in the reaction mixture (Table S2 entries 61 to 66) (Supplementary Information) show no effect on the reaction rate.

Oxidation studies of $Fe^{II}(CN)_6^{4-}$ in acidic reaction medium [31–34] have reported the involvement of the species $H_2Fe^{II}(CN)_6^{2-}$, $pKa = 2.22$ [35] and $HFe^{II}(CN)_6^{3-}$, $pKa = 2.72$ [35] at $\mu = 1.0$ M. Since the oxidation of $Fe^{II}(CN)_6^{4-}$ by

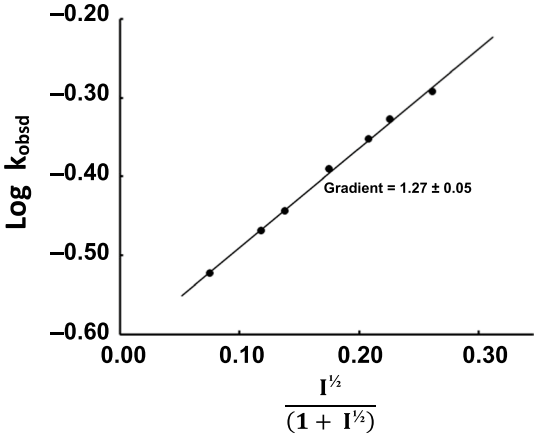

Fig. 3 Brønsted-Bjerrum plot of Log k_{obsd} *vs.* $\frac{I^{1/2}}{1+I^{1/2}}$ for varying the ionic strength (I, NaBr) of the reaction medium. $[Fe^{II}(CN)_6^{4-}] = 5.11 \times 10^{-4}$ M, $[Au^{III}(CN)_2Br_2^-] = 2.35 \times 10^{-3}$ M, $[H^+] = 2.054 \times 10^{-4}$ M, T = 20.0 ± 0.1 °C

$Au^{III}(CN)_2\ Br_2^-$ was studied in an acidic medium of $0.00012 \leq [H^+] \leq 0.2004$ M, protonated species of $Fe^{II}(CN)_6^{4-}$ should be involved and equilibrium 6 must form part of the reaction mechanism.

$$H_2Fe^{II}(CN)_6^{2-} \overset{K_a}{\rightleftharpoons} HFe^{II}(CN)_6^{3-} + H^+ \left(K_a = 0.0060\ \text{M};\ pK_a = 2.22\right) \tag{6}$$

The influence of $[H^+]$ on the reaction rate is indicated by the variation of $[H^+]$ in the reaction mixture (Table S2 entries 38–60). A sigmoid plot (S shaped plot) of k_{obsd} versus pH (Fig. 4, pH calculated from $-\log[H^+]$) indicate a pK_a in the experimental acidic range used. A K_a value of $(3.0 \pm 0.1) \times 10^{-3}$ M ($pK_a = 2.52$) at $\mu = 0.51$ M was obtained from a non-linear least squares fit [25] of the kinetic data in Table S2 to Eq. (7) [36–38].

$$k_{obsd} = \frac{k_{HA}\left[H^+\right] + k_A K_a}{[H^+] + K_a} \tag{7}$$

This kinetically determined K_a for the equilibrium in Eq. (6) correspond well with the potentiometric determined literature pK_a value of $pK_a = 2.22$ [35] at $\mu = 1.0$ M. Figure 4 showing kinetic data fitted to Eq. (7) also indicates that the $H_2Fe^{II}(CN)_6^{2-}$ species is not a strong enough reducing agent to reduce $Au^{III}(CN)_2Br_2^-$ as $k_{obsd} = k_{HA} = 0.0015 \pm 0.0004\ s^{-1}$ strived asymptotically to zero at low pH. Likewise, neat $HFe^{II}(CN)_6^{3-}$ reduces $Au^{III}(CN)_2Br_2^-$ with $k_{obsd} = k_A = 0.57 \pm 0.01\ s^{-1}$ under the conditions listed in Table S2.

Based on the arguments above we propose the mechanism for the oxidation of $Fe^{II}(CN)_6^{4-}$ by $Au^{III}(CN)_2Br_2^-$ in acidic medium, to be:

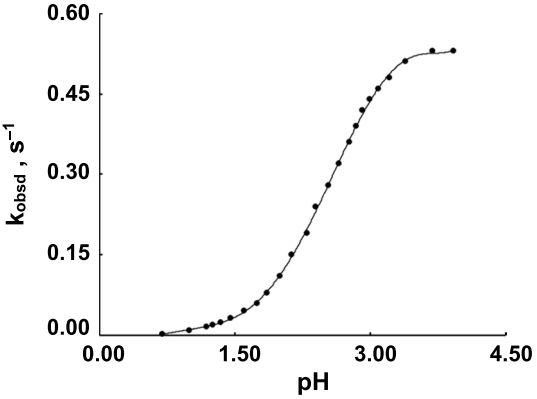

Fig. 4 Observed pseudo first order rate constant (k_{obsd}) *vs*. pH for the oxidation of $Fe^{II}(CN)_6^{4-}$ by $Au^{III}(CN)_2Br_2^-$. $[Fe(CN)_6^{4-}] = 7.42 \times 10^{-4}$ M; $[Au(CN)_2Br_2^-] = 3.67 \times 10^{-4}$ M; $\mu = 0.51$ M (NaBr); $T = 20.0 \pm 0.1$ °C (Data from Table S2)

$$H_2Fe^{II}(CN)_6^{2-} \underset{K_a}{\overset{Fast}{\rightleftharpoons}} HFe^{II}(CN)_6^{3-} + H^+ \tag{8}$$

$$HFe^{II}(CN)_6^{3-} + Au^{III}(CN)_2Br_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Au^{II}(CN)_2Br^- + HFe^{III}(CN)_6^{2-} + Br^- \tag{9}$$

$$HFe^{II}(CN)_6^{3-} + Au^{II}(CN)_2Br^- \xrightarrow{k_2} Au^{I}(CN)_2^- + HFe^{III}(CN)_6^{2-} + Br^- \tag{10}$$

The above mechanism is mutually consistent with the mechanism proposed for the reactions between $AuCl_4^-$ and $Fe(CN)_6^{4-}$, $W(CN)_8^{4-}$ and $Mo(CN)_8^{4-}$ [13]. Equation (9) is a reversible reaction with $k_1 >> k_{-1}$ and the forward k_1 reaction being the rate determining step. Application of a steady state approximation to the Au(II) intermediate, $Au^{II}(CN)_2Br^-$, yield the theoretical rate law 11 for the oxidation of $HFe^{II}(CN)_6^{3-}$ by $Au^{III}(CN)_2Br_2^-$.

$$\frac{d[HFe^{III}(CN)_6^{2-}]}{dt} = \frac{2k_1k_2\left[HFe^{II}(CN)_6^{3-}\right]^2\left[Au^{III}(CN)_2Br_2^-\right]}{k_{-1}[Br^-]\left[HFe^{III}(CN)_6^{2-}\right] + k_2\left[HFe^{II}(CN)_6^{3-}\right]} \tag{11}$$

Experimentally it was shown above that the oxidation of $HFe^{II}(CN)_6^{3-}$ by $Au^{III}(CN)_2Br_2^-$ is first-order in both reactants, and independent of the product concentration in the reaction mixtures. This is consistent with the proposed theoretical rate law 11 if $k_2 >> k_{-1}$ implying the $k_{-1}[Br^-][HFe^{III}(CN)_6^{2-}]$ term becomes negligible. This simplification implies Eq. (9) is for all practical purposes almost irreversible, that the retarding effect of Br^- is very limited which means Eq. (5) does play a role at high $[Cl^-]$, and leads to the experimental rate law shown in Eq. (12) where $2k_1$ is a 2nd order pH dependent rate constant.

$$\frac{d[HFe^{III}(CN)_6^{2-}]}{dt} = 2k_1\left[HFe^{II}(CN)_6^{3-}\right]\left[Au^{III}(CN)_2Br_2^-\right] \tag{12}$$

A hydrogen ion dependency was observed for the reaction (Table S2 and Fig. 4), which indicate that equilibrium 6 is significant for the reaction. From Eq. (8)

$$\left[Fe^{II}(CN)_6^{4-}\right]_T = \left[H_2Fe^{II}(CN)_6^{2-}\right] + \left[HFe^{II}(CN)_6^{3-}\right] \tag{13}$$

and

$$K_a = \frac{\left[H^+\right]\left[HFe^{II}(CN)_6^{3-}\right]}{\left[H_2Fe^{II}(CN)_6^{2-}\right]} \text{so that} \left[H_2Fe^{II}(CN)_6^{2-}\right] = \frac{\left[H^+\right]\left[HFe^{II}(CN)_6^{3-}\right]}{K_a} \tag{14}$$

Substitution of Eq. (14) into Eq. (13) and simplification gives

$$\left[Fe^{II}(CN)_6^{4-}\right]_T = \left[HFe^{II}(CN)_6^{3-}\right]\left[\frac{[H^+] + K_a}{K_a}\right]$$

$$\left[HFe^{II}(CN)_6^{3-}\right] = \frac{K_a[Fe^{II}(CN)_6^{4-}]_T}{[H^+] + K_a} \tag{15}$$

Substitution of Eq. (15) into Eq. (12) and simplification yield the rate law Eq. (16)

$$\frac{d[Fe^{II}(CN)_n^{4-}]_T}{dt} = \frac{2k_1\ K_a}{[H^+] + K_a}\left[Fe^{II}(CN)_6^{4-}\right]_T\left[Au^{III}(CN)_2Br_2^-\right] \tag{16}$$

and

$$k_{obsd} = \frac{2k_1\ K_a}{[H^+] + K_a} \tag{17}$$

Equation (16) is consistent with the experimentally observed decrease in reaction rate with an increase in the $[H^+]$ in the reaction mixture (Table S2) and Eq. (17) is mutually consistent with the experimentally determined Eq. (7) if $k_{HA} = 0\ s^{-1}$. A non-linear least squares fit [25] of the $[H^+]$ variation data for the oxidation of $HFe^{II}(CN)_6^{3-}$ by $Au^{III}(CN)_2Br_2^-$ (Table S2) to Eq. (17) yield the theoretical values $2k_1 = 2(0.290 \pm 0.004) = 0.580 \pm 0.008\ M^{-1}s^{-1}$ (k_a was determined to be 0.57 ± 0.01 in Eq. (7)) and $K_a = (2.7 \pm 0.1) \times 10^{-3}$ M ($pK_{a1} = 2.57$). The value of K_a obtained this way is similar to the experimentally determined value described above ($K_a = (3.0 \pm 0.1) \times 10^{-3}$ M, $pK_a = 2.52$ at $\mu = 0.51$ M) and also to the literature value [35], $pK_a = 2.22$ M at $\mu = 1.0$ M.

Activation parameters for the reaction were calculated from the observed temperature variation data in Table S2 (entries 67–73) and Fig. 5 utilizing least squares mathematical fittings [25] applied directly to the Eyring equation [13, 21, 39, 40]. Values of $\Delta H^{\#} = 47.8 \pm 0.9$ kJ mol^{-1} and $\Delta S^{\#} = -37 \pm 3$ J K^{-1} mol^{-1} were obtained. Adherence to Eq. (18) proved the expected direct proportionality between the experimental errors of activation enthalpy, $\sigma\Delta H^{\#}$, and activation entropy, $\sigma\Delta S^{\#}$ [39]; details of applying data to this equation may be found elsewhere [23, 41].

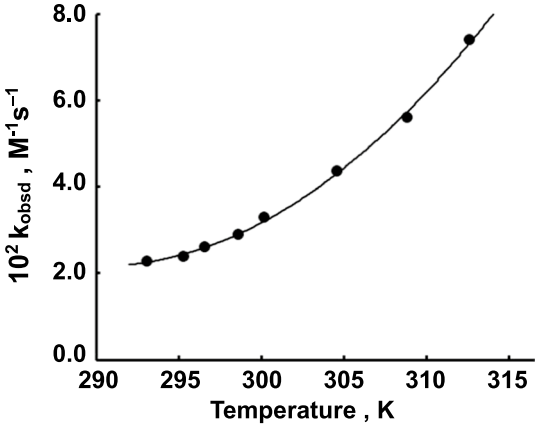

Fig. 5 A non-linear least squares fit of the second order rate constant (M^{-1} s^{-1}) and temperature (K) data to the exponential Eyring equation. $[Fe^{II}(CN)_6^{4-}] = 5.11 \times 10^{-4}$ M, $[Au^{III}(CN)_2Br_2^-] = 2.35 \times 10^{-3}$ M, $[Br^-] = 0.50$ M, $[H^+] = 2.054 \times 10^{-4}$ M, μ(NaBr) = 0.51 M

$$\sigma \Delta S^{\#} = \frac{1}{T_{av}} \sigma \Delta H^{\#} \tag{18}$$

In Eq. (18), T_{av} is the average temperature where experiments have been performed.

Conclusion

The reduction of the dibromodicyanoaurate(III) ion by hexacyanoferrate(II)trihydrate ions occur stoichiometrically in the ratio $Fe^{II}(CN)_6^{4-}$: $Au(CN)_2Br_2^- = 2{:}1$ and the reaction is first order in both reactants. The reactive form of $Fe^{II}(CN)_6^{4-}$ in the reaction in the acidic range 1.2×10^{-4} M to 0.2004 M is $HFe^{II}(CN)_6^{3-}$. Variation of the $[H^+]$ of the reaction mixtures yield a sigmoid relation and an acid dissociation constant of $K_a = (3.0 \pm 0.1) \times 10^{-3}$ M ($pK_a = 2.52$) at μ = 0.51 M and 20.0 ± 0.1 °C for the equilibrium.

$$H_2Fe^{II}(CN)_6^{2-} \overset{K_a}{\rightleftharpoons} HFe^{II}(CN)_6^{3-} + H^+ \tag{19}$$

This value is mutually consistent with the value obtained from the kinetic study of the oxidation of the hexacyanoferrate(II) ion by the $Au^{III}Cl_4^-$ ion [13] ($K_a = 9.1 \times 10^{-3}$ M; $pK_a = 2.04$) at μ = 1.2 M).

No specific ion effect was observed as the reaction rate was independent of $[Cs^+]$, but under low $[Br^-]$ and high $[Cl^-]$ conditions, it was found that the mixed halide species $Au^{III}(CN)_2BrCl^-$ does form and is slightly more reactive than $Au^{III}(CN)_2Br_2^-$.

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Author contributions JCS: Investigation, writing, editing, conceptualization, methodology, project admin, review. CRD: Investigation, writing, editing, methodology, project admin, supervision.

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Data availability No additional data available.

Declarations

Conflict of interest The authors are not aware of any conflict of interests.

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