

Reduction of Thiocyanate Complexes of Fe(III) in the Presence of Activated Carbon

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ABSTRAK

Kehadiran karbon teraktif didapati menurunkan Fe(III) yang berkompleks dengan SCN^- kepada Fe(II). Kadar susutan ketumpatan kompleks telah ditentukan dengan menggunakan spektrofotometer. Tindakbalas didapati menurut tertib pertama terhadap ion Fe(III). Entalpi dan entropi keaktifan adalah masing-masing $100 \pm 10 \text{ kJ/mol}$ dan $14.1 \pm 0.8 \text{ J/mol-K}$. Seseengah daripada Fe didapati terjerap pada permukaan mangkin di mana tindakbalas penurunan itu dijangka berlaku. Tindakbalas pengoksidaan seiring yang utama dicadangkan sebagai pengoksidaan ion tiosianat yang terjerap pada titik-titik positif pada mangkin.

ABSTRACT

Fe(III) complexed with SCN^- was found to be reduced to Fe(II) in the presence of activated carbon. The rate of disappearance of the complex was determined spectrophotometrically and was found to be first order with respect to Fe(III). The enthalpy and entropy of activation are $100 \pm 10 \text{ kJ/mole}$ and $14.1 \pm 0.8 \text{ J/mole-K}$ respectively. Some Fe was found to be adsorbed on the catalyst where the actual reduction was suggested to take place. The accompanying oxidation reaction has been suggested to be mainly that of the thiocyanate ions adsorbed at the positive centres on the catalyst.

Keywords: activated carbon, thiocyanate complexes of Fe(III), quinone/hydroquinone, thiocyanate ion, reduction of Fe(III)

INTRODUCTION

Activated carbon has been known to act as a catalyst in many chemical reactions (e.g. Bente and Walton 1942). It is widely used in teaching laboratories during some inorganic preparations (e.g. Lambert and Muir 1973; Rendle *et al.* 1976). Short reviews on the subject have also been written (Hassler 1974; Kalra *et al.* 1989). Activated carbon is similar to other heterogeneous catalysts in that its catalytic behaviour is a manifestation of its ability to adsorb reacting species. Thus it was suggested that the oxidation of CN^- to CNO^- in the presence of activated carbon, for example, occurred through the reaction of the adsorbed CN^- with dissolved oxygen or the adsorbed oxygen on the same carbon surface

(Bernadin 1973). More recent work in this area mainly concerned the removal of toxic substances such as Hg and CN^- from industrial and mining wastes (Parentich and Kinsella 1984; Saito 1984; Tsuchida and Muir 1986a, 1986b).

Much has been published concerning the complexation of Fe(III) with SCN^- (Korondan and Nagypal 1983 and references therein). Despite the common belief that the complex is hexa-coordinated, it has been shown that at concentrations less than 0.1M, virtually all the ions are present as FeSCN^{++} and $\text{Fe}(\text{SCN})_2^+$ (Betts and Dainton 1953). Even at higher concentrations, only a small fraction of tetra- and penta-thiocyanateiron(III) were formed (Korondan and Nagypal 1983). It has also been shown that the complex undergoes thermal and perhaps photochemical decomposition even at room temperature (Betts and Dainton 1953; Sultan and Bishop 1982). The results reported herein show that the rate of decomposition of the complex is enhanced in the presence of activated carbon.

MATERIALS AND METHODS

A solution of Fe(III) was prepared by dissolving 2.34 g iron sheet (Goodfellow, 99.99% pure) in a beaker containing 100 ml HNO_3 6M (Merck, selectipur). When the rate of reaction decreased, the solution was heated to near boiling for five hours to ensure complete dissolution of the metal. It was allowed to cool to room temperature before being quantitatively transferred into a one-litre volumetric flask. The volume was made up with HNO_3 (1M). The concentration of the stock solution (0.042M) was determined by AAS with solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Ajax, AR) being used for standardization.

A 0.6M solution of KCNS was prepared by dissolving about 6.0 g KCNS (Merck, pure) in 100 ml distilled water.

Preparation of Carbon

Large pieces of activated carbon were prepared by a method described earlier (British Patent 1984). A fairly flat piece was ground with sandpaper into a disc having a diameter of about 15 mm and thickness of 1.8 mm. The disc, which weighed 0.3605 g, was boiled in 1M HCl for one week and then was continuously washed with distilled water in a Soxhlet apparatus for another week. It was left soaking in distilled water until it was used. As the same piece was used for all kinetic measurements, the same washing procedure was followed after each experiment.

Kinetic Studies

2.50 ml of the Fe(III) stock solution was pipetted into a 100-ml volumetric flask followed by 1 ml of KCNS 0.6M. The flask was then filled to the mark with HNO_3 1M. The solution ($1.05 \times 10^{-3}\text{M}$ in Fe^{3+} , $6.00 \times 10^{-3}\text{M}$ in SCN^-) was then transferred into a Pyrex glass reaction vessel of about 200 ml

capacity. Nitrogen gas was bubbled through the solution for the duration of the experiment. The reaction vessel was placed in a water bath which was covered to eliminate light and maintained at various temperatures as given in Table 1. Before the start of a kinetic run, about 3 ml of the solution was withdrawn for spectrophotometric measurement at $\lambda = 454$ nm (Shimadzu UV-160).

TABLE 1
Rate constants for the bleaching of ferricthiocyanate in the presence of activated carbon

t(deg C)	10^5 (sec)	$1/T \times 10^3$ (K ⁻¹)	ln(k/T)
23.5	$1.93 \pm .04$	3.37	-16.55
25.5	$2.57 \pm .24$	3.35	-16.27
29.5	$2.94 \pm .05$	3.30	-16.15
34.5	$5.95 \pm .14$	3.25	-15.46
37.5	$13.66 \pm .31$	3.21	-14.64
43.5	$25.51 \pm .21$	3.16	-14.03

The carbon disc was dried with soft tissue paper and was dropped into the reaction vessel. The progress of the reaction was followed spectrophotometrically by measuring the absorbance as a function of time for periods of at least five hours. Initial and final absorbance readings were taken for control solutions at each temperature to determine the extent of autodecomposition of the complex in the absence of activated carbon over the period of reaction. The autoreduction of the complex was also followed as a function of time at 30°C for the solution in the absence of carbon.

Product Analyses

The reaction mixture was left standing overnight at room temperature (23.5°C) on completion of the experiment. After the carbon disc was removed, the total Fe in the solution was determined by AAS. Four 5 ml portions were subjected to the following analyses:

- (i) Addition of a few drops of ferricyanide solution,
- (ii) Addition of a few drops of ferrocyanide solution,
- (iii) Addition of a few drops of Fe(III) stock solution followed by a few drops of H₂O₂ (RDH, 35%)
- (iv) Addition of a few drops of KCNS solution, followed by a few drops of H₂O₂.

RESULTS

The results obtained from the control experiments (Table 2) showed that the thiocyanate complex of Fe(III) was stable throughout the duration of the experiments over the concentration and temperature ranges used in this investigation. Hence, the marked decrease with time of the absorbance due to the Fe(III) complex in the presence of carbon has been attributed to the catalytic reduction to Fe(II). The kinetic data show that the decrease in absorption is first order. Sample first-order plots are given in *Fig. 1*. An Eyring plot is given in *Fig. 2*. The activation enthalpy and entropy have been calculated to be 100 ± 10 kJ/mole and 14.1 ± 0.8 J/mol-K respectively.

TABLE 2
Initial and final* readings for the absorbance at 454 nm
for ferricthiocyanate and final times

t(deg C)	(with Activated C)		(without Activated C)		Final time (min)
	Initial	Final	Initial	Final	
23.4	2.480	0.371	2.480	2.479	1680
25.5	2.466	1.414	2.466	2.457	420
29.5	2.475	0.165	2.475	2.470	1530
34.5	2.490	0.776	2.477	2.470	330
43.5	2.470	0.019	2.470	2.460	310

* Final reading was the reading taken at the final time for a given kinetic run and was not the absorbance at infinite time. Final times for samples with and without activated carbon were the same at the same temperature.

The qualitative tests gave the following results:

- (i) The product solution became dark green with slight precipitation upon the addition of a few drops of ferricyanide reagent, indicating the presence of Fe(II).
- (ii) The addition of ferrocyanide turned the solution to light blue which indicated the presence of Fe(III).
- (iii) The addition of Fe(III) caused the solution to become slightly darker red in colour indicating the presence of SCN⁻ but in a quantity much less than the original amount. When the addition of Fe(III) solution was followed by the addition of a few drops of H₂O₂ there was no apparent change in the colour intensity despite the increase of Fe(III) through reoxidation of Fe(II).
- (iv) The addition of SCN⁻ caused the solution to become faintly red. However, when SCN⁻ was followed by H₂O₂, the solution instantly

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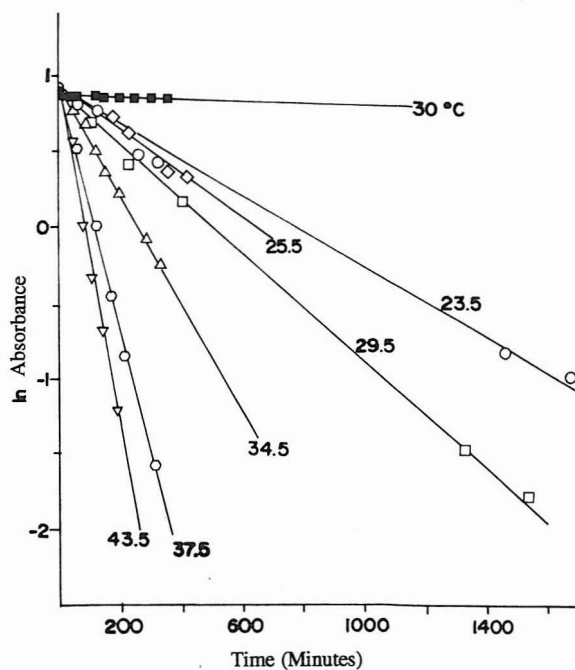


Fig. 1. First-order plots for the bleaching of Fe(III)-thiocyanate solutions in the presence of activated carbon (Filled squares: uncatalysed reaction)

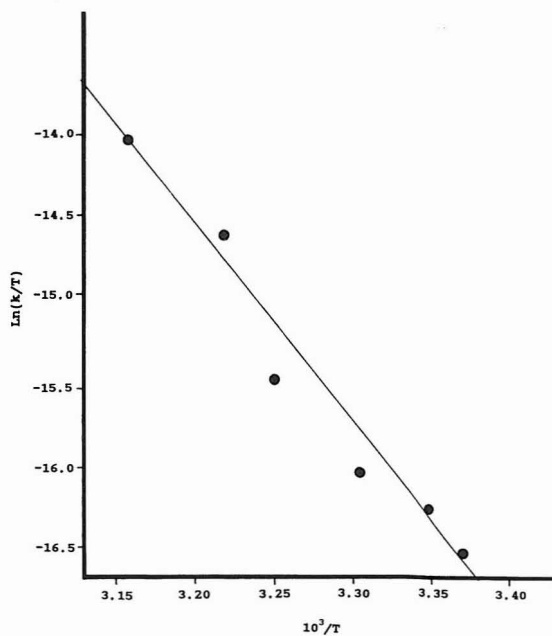


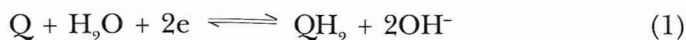
Fig. 2. Eyring plot for the bleaching of Fe(III)-thiocyanate solutions in the presence of activated carbon

became dark red. The evolution of heat and gas was observed. The reaction continued until the red colour faded completely.

The initial concentration of iron in solution at 23.5°C was $1.05 \times 10^{-3} \text{M}$ while after the reaction its concentration was $8.01 \times 10^{-4} \text{M}$ indicating that about 23.7% of the iron had been adsorbed onto activated carbon.

DISCUSSION

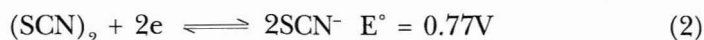
The qualitative analyses performed on the product samples clearly indicated that Fe(III) had indeed been reduced to Fe(II). A similar reaction has been observed for the cyanide complexes (Saito 1984). That the rate of reduction of the SCN^- complex in the presence of carbon was much faster than that in the absence of carbon indicates that some electroactive species on the surface of carbon was responsible for the transfer of electrons necessary for the reaction to occur. These electroactive species may be associated with quinone/hydroquinone, Q/QH_2 , structures which have been suggested to be present on the surface of activated carbon (Drushel and Hallum 1958; Jones and Kaye 1969; Epstein *et al.* 1971). The theoretical electrode potentials of these species have been estimated (Alt *et al.* 1972). The quinone/hydroquinone couple, for example,



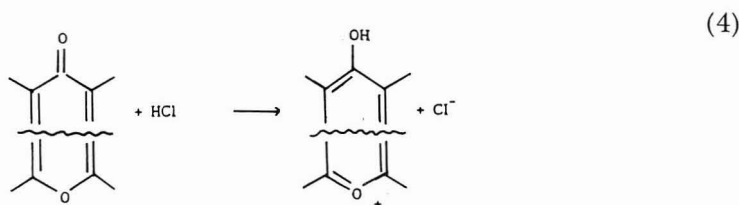
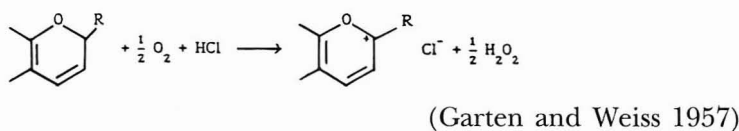
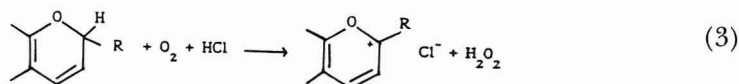
has been assigned a value of $E^\circ = 0.69\text{V}$ (CRC Handbook 1970-71) and was expected to be lower at lower pH. Since the potential for Fe(III)/Fe(II) couple is 0.77V, the overall emf would be at least 0.08V indicating that the reaction should be spontaneous.

Working with carbon black, Kinoshita and Belt (1973) observed that the concentration of Q/QH_2 on the surface of carbon was of the order of 10^{-10} - 10^{-11} mole/cm². The surface of activated carbon used in this investigation was about 190 m²/g (British Patent 1984). Therefore the total Q/QH_2 available for the reaction was of the order of 10^{-5} mole, a quantity certainly sufficient for its suggested catalytic function. The electron transfer was enhanced by the dynamic interconversion between Q and QH_2 . This affected the rate of the overall redox reaction (Fe(II) reduction/thiocyanate oxidation) in a positive manner.

The half-reaction likely to have been involved is that of the $(\text{SCN})_2/\text{SCN}^-$ couple:



The overall standard potential of this combination is zero. At the concentrations used in this experiment the potential would be positive and the reaction therefore spontaneous. SCN^- was found to be consumed in the reaction. Free SCN^- could be adsorbed on carbon moderately (Kunz and Gianelli 1976) perhaps through its interaction with the positive centres on the carbon surface. The following reactions might also have been responsible for the production of these positive centres



(Boehm and Voll 1970)

The quantity of $(\text{SCN})_2$ that would have been produced in the reaction would have been too small to observe. Also, any $(\text{SCN})_2$ produced would have undergone hydrolysis as shown in reaction 5 (Gauguin 1945, 1949; Cotton and Wilkinson 1972) to give soluble products such as CN^- and SO_4^{2-} with CN^- reacting further with carbon to yield products similar to those suggested for the cyanide system (Tsuchida and Muir 1986a, 1986b).



The fact remains that ferric thiocyanate has been reported to undergo thermal auto-reduction in aqueous solutions of perchloric acid (Betts and Dainton 1953). Competition of product (ferrous ion) with reactant (ferric ion) for the intermediate reactant $(\text{SCN})_2$ was said to retard the reduction. It appears that decomposition approached a limit of about 15% at 29.89°C in solution containing $(\text{Fe}^{\text{III}})_0 = 0.00230\text{M}$; $(\text{SCN}^-)_0 = 0.0784\text{M}$ in HClO_4 . Retardation was observed to begin after only 30 minutes at which time the solution had undergone about 5% decomposition. Control experiments in

nitric acid in this study showed a maximum of ~1.5% decomposition after a period of nine hours at 30°C in the absence of activated carbon. Solutions kept for ten days showed <20% decomposition. In the presence of activated carbon, the reduction of the Fe⁺⁺⁺ - SCN⁻ complex proceeded very rapidly. Fe⁺⁺⁺ - SCN⁻ solutions were eventually decolorized at all temperatures, i.e. A_∞ (454 nm) ~ 0.

As has been discussed by Sandell (1978), the spectrophotometric method for determining Fe³⁺ by complexation with SCN⁻ requires care with attention being given to SCN⁻ concentration which should be the same for all determinations and preferably in excess, to temperature which should be held constant, and to deviation from Beer's Law at low concentration of Fe³⁺ ion. Any error arising in accurate determination of Fe³⁺ using this method under the experimental conditions used in this work would be due only to deviation from Beer's Law. Any such error, however, is within the acceptable experimental error for these kinetic determinations and therefore would not invalidate the kinetic data reported herein.

CONCLUSION

It can be concluded that activated carbon catalyzed the reduction of Fe(III) in the form of thiocyanate complex to Fe(II). Quinone/hydroquinone redox couple that has been suggested to be present on the carbon surface might have been responsible for the catalytic behaviour but it seems that the ionic CNS⁻ species was the primary source of the electrons required for the reaction to go to completion. The reaction has been regarded to be of pseudo-first order even though it followed first-order kinetic equation in view of the fact that carbon also physically adsorbed the reacting species.

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