

In each case the exchange kinetics is second order as was observed with the analogous Co(II) and Ni(II) systems.^{10,11} For second-order kinetics $1/\tau_m = k_2[\text{ligand}]$ and $k_2 = (kT/h) \exp[(\Delta S^\ddagger/R) - (\Delta H^\ddagger/RT)]$. Table III gives the resulting kinetic parameters obtained from a plot of $\log(k_2/T)$ vs. $1/T$ along with the corresponding Ni(II) and Co(II) values for comparison.¹¹

TABLE III

Complex	$k_2(25^\circ)$ ($\pm 0.5 \times 10^{10}$)	ΔH^\ddagger , kcal/mole	ΔS^\ddagger , eu
L = TPP			
FeBr ₂	2.0×10^5	3.8 ± 0.5	-22 ± 3
NiBr ₂	6.9×10^3	4.7 ± 0.4	-25 ± 2
CoBr ₂	8.7×10^2	7.7 ± 0.5	-19 ± 3
L = TTP			
FeBr ₂	6.3×10^5	4.0 ± 0.8	-19 ± 5
NiBr ₂	6.1×10^3	5.2 ± 0.8	-24 ± 4
CoBr ₂	1.8×10^3	5.5 ± 0.9	-25 ± 4

The results are consistent with an associative mechanism involving a five-coordinate transition state. The trend in lability, Fe > Ni > Co, is apparent (particularly from the more accurate TPP data) and seems to be mainly an enthalpy of activation effect. Ligand field arguments predict that the tetrahedral d⁶ ground state will be stabilized to a lesser extent than that of the d⁷ and d⁸ analogs; this is consistent with the observed greater lability of the iron complexes. On the other hand, the same simple electrostatic model suggests that a pentacoordinate transition state of d⁶ will be less stable than of the d⁷ and d⁸ counterparts, which would predict an order of lability Co, Ni > Fe. Clearly these models are too crude to allow a realistic assessment of the relatively delicate energy balance which governs these ligand-exchange reactions. Nevertheless it seems apparent that d-electron effects are important in determining relative rates in reactions of this type.

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Mechanism of the Ferricyanide Oxidation of Thiols¹

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There have been relatively few investigations of the mechanism of the oxidation of organic substrates by ferricyanide. However, since these oxidations are almost universally base catalyzed, it seems attractive to suggest that the reactions generally involve electron

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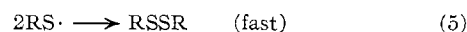
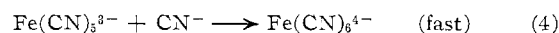
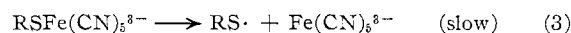
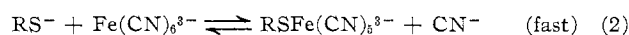
abstraction by ferricyanide from an anion derived from the substrate. Recently, however, Kolthoff and coworkers³ have suggested that the oxidation of thiols proceeds *via* a different path. We now wish to report a reinvestigation of this reaction.

In the previous work, *n*-octanethiol was found to be oxidized to the corresponding disulfide in aqueous acetone with the rate law being

$$v = k[\text{RSH}][\text{HO}^-][\text{Fe}(\text{CN})_6^{3-}]$$

Of particular significance was the rate depression observed on addition of potassium cyanide. Using equimolar amounts of thiol and ferricyanide ($7.25 \times 10^{-4} M$) a linear decrease in rate constant with increase in cyanide concentration was noted until at about $4 \times 10^{-4} M$ KCN the rate became almost independent of the cyanide concentration.

On the basis of these observations, the mechanism below was proposed



This scheme will explain the rate depression observed since cyanide ion will repress equilibrium 2. Presumably some other process must also be available to account for the small rate of oxidation in the presence of excess cyanide ion.

Although this scheme will account for the results, step 2 is surprising since cyanide ion itself will not exchange with ferricyanide⁴ under the conditions of the experiment. One may wonder why the mercaptide ion would be so much more effective than the cyanide ion. We have tested the mechanism by carrying out the reaction in the presence of cyanide-C¹⁴. Here, we would expect a facile induced exchange resulting from reactions 2 and 4. The potassium ferrocyanide isolated after essentially complete reaction showed less than 0.1% exchange. The absence of exchange indicates that the above mechanism cannot be correct.

It is clear that cyanide ion cannot interact with ferricyanide in such a way as to reduce its reactivity. However, it would not be unreasonable to expect the thiol to react with cyanide. The reaction of hydrogen sulfide with nitriles is known to be a facile reaction.⁵ This possibility was examined. The Raman spectrum of potassium cyanide in 60% aqueous acetone containing a pH 11.3 carbonate-bicarbonate buffer had a C≡N band at 2086 cm⁻¹.⁶ The addition of 1 equiv of 2-hydroxyethanethiol (*n*-octanethiol could not be used because of its low solubility) decreased the band

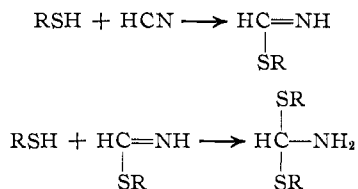
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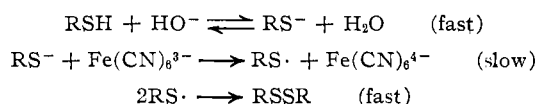
(6) We wish to thank the research group of Professor D. Hornig, Princeton University, Princeton, N. J., for their assistance in the use of the Cary 81 Raman spectrophotometer.

intensity to about half and after the addition of 2 equiv of the thiol, no 2086-cm⁻¹ band could be found. It is clear that the thiol added to the cyanide ion (or hydrogen cyanide) in a fashion such as



Attempts were made to isolate and characterize the product of the reaction which precipitates when the reaction is carried out in aqueous solution. However, it is quite unstable and we were not successful in characterizing it.

It is interesting to note that Kolthoff found a maximum rate depression when the thiol:cyanide ratio was about 2:1 in agreement with the stoichiometry observed above. The slower oxidation at higher cyanide ion concentrations is probably due to oxidation of the thiol-cyanide complex. The simplest interpretation for the course of the thiol oxidation is then



Thus this reaction also appears to fall in the pattern suggested at the beginning of this paper.

Ligand displacement on ferricyanide has also been proposed as a step in the ferricyanide oxidation of sulfite ion.⁷ More recently, Swinehart has prepared the supposed intermediate and has found that it does not behave in the required fashion.⁸ We also have examined the reaction by adding excess labeled cyanide ion to the ferricyanide solution before the addition of sulfite ion. The ferrocyanide isolated at the end of the reaction had an activity corresponding to 0.01 ± 0.01% exchange. Thus, ligand displacement does not occur, and the reaction probably involves electron abstraction from sulfite.⁸

The ferricyanide oxidation of iodide ion has an unusual rate law,⁹ which might suggest ligand displacement. Again, the addition of labeled cyanide prior to the initiation of the reaction led to an insignificant amount of exchange, 0.014 ± 0.01%.

Since none of the typical good nucleophiles, CN⁻, RS⁻, S₂O₃²⁻, and I⁻, is able to effect reasonably rapid ligand displacement on ferricyanide, it appears unlikely that any ferricyanide oxidation will involve such a step. Ferricyanide appears to react uniquely *via* electron transfer.

Experimental Section

Reaction of 2-Mercaptoethanol with Cyanide Ion.—A 2 M aqueous potassium cyanide solution was found to have its C≡N Raman line at 2086 cm⁻¹. A 0.5 M solution of potassium cyanide in 60% acetone had a peak at the same position. The

addition of enough 2-mercaptoethanol to make a 0.5 M solution led to a decrease in the 2086-cm⁻¹ band to approximately half of its original intensity. When the amount of mercaptoethanol corresponded to a 1 M solution, the 2086-cm⁻¹ band disappeared.

When 2-mercaptoethanol was added to 1 M aqueous potassium cyanide, a pale yellow precipitate was formed which rapidly darkened on exposure to air.

Ferricyanide Oxidation of *n*-Octanethiol.—To a 250-ml flask was added 60 ml of acetone and a solution of potassium ferricyanide (0.24 g, 7.2 × 10⁻⁴ mole) in 40 ml of 2.5 × 10⁻³ M potassium carbonate–2.5 × 10⁻³ M potassium bicarbonate buffer. To this solution was added 7 ml (5.4 × 10⁻³ mole, 6.56 × 10⁶ dpm/ml) of potassium cyanide-C¹⁴ solution and 0.1 g (7.2 × 10⁻⁴ mole) of *n*-octanethiol. The mixture was cooled in an ice bath, and yellow crystals of potassium ferrocyanide precipitated over a period of 3 hr, giving 0.04 g (13%) after washing with 60% acetone. The ferrocyanide was dissolved in 1 ml of water and counted in a liquid scintillation counter using Cab-O-Sil and a toluene solution of PPO and POPOP.¹⁰ After correcting for the activity due to potassium an activity of 31 dpm was found. Thus, the maximum extent of exchange was 0.04%.

Oxidation of Sulfite Ion.—To a solution of 0.316 g (0.96 mmole) of potassium ferricyanide in 35 ml of water was added 5 ml of potassium cyanide-C¹⁴ solution (3.85 mmole, 5.16 × 10⁶ dpm/ml) and 0.114 g (0.72 mmole) of potassium sulfite. After 0.5 hr at room temperature, 60 ml of acetone was added and the mixture was cooled in an ice bath for 1 hr. The precipitate of potassium ferrocyanide was washed with 300 ml of cold 60% aqueous acetone in small portions and then with 50 ml of dry acetone. After drying under reduced pressure, titration with permanganate indicated it to be 99+ % potassium ferrocyanide. A solution of 0.05 g of the latter in 1 ml of water was counted in a liquid scintillation counter using Cab-O-Sil and a toluene solution of PPO and POPOP. After correcting for the activity due to potassium, the solution gave 5 dpm/0.1 mmole. Thus, the extent of exchange is no greater than 0.01%.

Oxidation of Iodide Ion.—To a solution of 0.593 g (1.8 mmoles) of potassium ferricyanide in 33 ml of water was added 7 ml (5.4 mmoles, 5.16 × 10⁶ dpm/ml) of potassium cyanide-C¹⁴ and 0.896 g (5.4 mmoles) of potassium iodide. After 1 hr, the potassium ferrocyanide was isolated as described above and counted giving 7 dpm/0.1 mmole. This corresponds to 0.014% exchange.

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The Aggregation of Alkylthiotricarbonylmanganese. Trimeric vs. Tetrameric Formulations

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Our interest in developing new synthetic routes to thiocyanatocarbonyl complexes of the transition elements has led to an investigation of reactions of the metal carbonyls with the organic thiocyanates. Re-

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