this way would be expected to prevent both whole-molecule tumbling and metal–tripod rotation. The mechanical spectrum of the sample is shown in Figure 1. The observed peak appears to be the most conclusive evidence for the assignment of the phenomenon responsible for the absorption in the mechanical spectrum of organometallic complexes containing arene or Cp ligands to rotation of the ring about the ring–metal axis.

Registry No. 7, 12082-08-5; $C_6H_6Cr(CO)_2PPh_3$, 12278-67-0; $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5PPh_3$, 14917-12-5; PPh_3, 603-35-0; $C_6H_5C_2H_5Cr(CO)_3$, 12203-31-5; polystyrene, 9003-53-6.

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Thermal Decomposition of the Pentacyanoaquoferrate(II) Ion in Aqueous Solution

José A. Olabe* and Hugo O. Zerga

A wide number of substitution[1-8] and electron-transfer[9-11] reactions involving the pentacyanoaquoferrate(II) ion, Fe-$(CN)_5H_2O^{3-}$, have been investigated. This species is known to be the primary product of the thermal and photochemical decomposition of hexacyanoferrate(II), a reaction that ultimately can lead to a variety of products, depending mostly on pH and air content of the medium.[12,13]

$Fe(CN)_5H_2O^{3-}$ is known to be susceptible to autoxidation and dimerization processes; however, these can be put under control if air is rigorously excluded and work is carried out in sufficiently dilute solutions, respectively.[14] An additional complication relates to the thermal decomposition of the complex, which is known to be significant in aged solutions. The nature of this last reaction is not well understood; previous studies throw some light on this question, but the working material is known to be a complex mixture of monomeric and polymeric species.[15] The availability of a cleaner method of generating the monomeric aquo ion[16] calls for a reinvestigation

of the stoichiometry, as well as of the kinetic and mechanistic aspects of the decomposition reaction, which is important in its own right, as well as helpful in controlling the properties of solutions containing $Fe(CN)_5H_2O^{3-}$.

Experimental Section

Solutions of $Fe(CN)_5H_2O^{3-}$ (5×10^{-5}–10^{-3} M) were prepared from solid $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$, which was synthesized by conventional procedures.[17] Doubly distilled and deoxygenated water was used, and analytical grade reagents were employed in the control of pH and ionic strength (NaCl). A slight excess of ascorbic acid was also added to prevent oxidation of $Fe(CN)_5H_2O^{3-}$.

Measurements were initiated about 10 min after the dissolution of the solid; this time allowed the complete aquation of the Fe-$(CN)_5NH_3^{3-}$ ion to proceed, the transfer of the solution (syringe techniques were used), and adequate thermostating of the spectrophotometric cell. Most of the work was carried out by measuring the decay of the 440-nm absorption of the pentacyanoaquoferrate(II) ion with a Shimadzu UV-210A double-beam spectrophotometer. A pseudo-first-order rate constant, k_{obsd} (s^{-1}) was obtained from the linear plot of $\ln (A_t - A_\infty)$ vs. time, where A_t is the measured absorbance at time t. At least two measurements were made in every case, and measured k_{obsd} were accurate to within approximately 5%. Temperature and ionic strength dependence of k_{obsd} were determined within the ranges of 20–50 °C (±0.1 °C) and 0.1–1 M, respectively, with a concentration of the reactant ion c of 5×10^{-5} M. pH was varied in the range 4–7.

At intermediate concentrations of the aquo complex (ca. 2×10^{-4} M), dispersion effects were operative, due to the slow formation of a colloidal precipitate; although the final A_t values were most probably affected by some error, the linear plots were well-behaved up to 3 half-lives and led to slightly lower numerical k_{obsd} values compared to those obtained with diluted solutions. At higher concentrations (ca. 10^{-3} M), no decay of the 440-nm band was observed; instead, a continuous shift of the maximum to lower wavelengths as well as an increase in absorbance was seen in the successive spectra, while the solution became cloudy. After several hours, a white precipitate was formed, which turned blue if air was allowed to enter the reaction medium.

The buildup of Fe^{2+} was followed either by adding 1,10-phenanthroline (phen) initially to the reaction medium or by treating periodically extracted aliquots of the reacting mixture with the same reagent. In both cases, the graph of A_t (absorbance at 510 nm, maximum of $Fe(phen)_3^{2+}$) vs. t showed an S-shaped behavior, although the induction period was in fact very short (about 3–4 min). Neglecting the first points, the plot of $\ln (A_\infty - A_t)$ vs. t was linear, with an essentially equal numerical value of k_{obsd} compared to that obtained from the decay at 440 nm. The treatment of kinetic data based on the growth of $Fe(CN)_6^{4-}$ concentration did not lead to well-behaved linear plots, probably because of overlapping spectra or dispersion effects.

A search for significant concentrations of reaction intermediates was made by adding ethylenediamine (about 1 half-life after initiating the reaction) under oxidizing conditions in an alkaline medium; this test has been successfully used in the identification of $Fe(CN)_4en^{2-}$, which turns red when oxidized to the diimine complex $Fe(CN)_4diim^{2-}$ (diim = NH=CH—CH=NH), and could be indicative of the presence of $Fe(CN)_4(H_2O)_2^{2-}$ in our solutions.[18] Alternatively, neutral $Fe(CN)_2(H_2O)_4$ was investigated by treating the reacting solution with phen in the presence of chloroform at different times. In both cases negative results were obtained.

Results and Discussion

The stoichiometry of the thermal decomposition reaction conformed to eq 1, as shown by concentration changes of the

$$Fe(CN)_5H_2O^{3-} \rightarrow {}^5/_6Fe(CN)_6^{4-} + {}^1/_6Fe^{2+} + H_2O \qquad (1)$$

reactant anion as well as those for both products of the reaction. A set of successive spectra shows that the decay of the peak centered at 440 nm is accompanied by the appearance
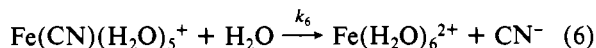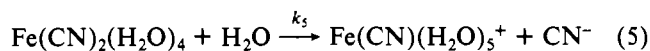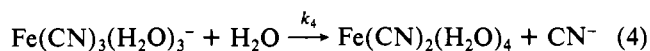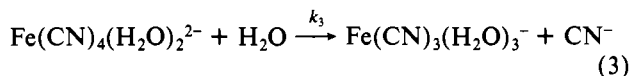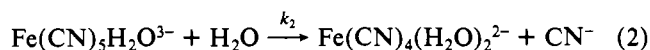
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of a new peak at ca. 325 nm, characteristic of $Fe(CN)_6^{4-}$. At higher concentrations a secondary precipitation reaction occurs probably due to formation of $Na_2FeFe(CN)_6$,[12] a compound that must be easily oxidized in the presence of air to generate a Prussian Blue type compound; this is the origin of the kinetic complications mentioned above.

The presentation of our kinetic data is simplified by first referring to our suggested reaction mechanism, as shown in Scheme I.

Scheme I

$$Fe(CN)_5H_2O^{3-} + H_2O \xrightarrow{k_2} Fe(CN)_4(H_2O)_2^{2-} + CN^- \quad (2)$$

$$Fe(CN)_4(H_2O)_2^{2-} + H_2O \xrightarrow{k_3} Fe(CN)_3(H_2O)_3^- + CN^- \quad (3)$$

$$Fe(CN)_3(H_2O)_3^- + H_2O \xrightarrow{k_4} Fe(CN)_2(H_2O)_4 + CN^- \quad (4)$$

$$Fe(CN)_2(H_2O)_4 + H_2O \xrightarrow{k_5} Fe(CN)(H_2O)_5^+ + CN^- \quad (5)$$

$$Fe(CN)(H_2O)_5^+ + H_2O \xrightarrow{k_6} Fe(H_2O)_6^{2+} + CN^- \quad (6)$$

Although reactions 2–6 are in fact reversible, they are presently considered as irreversible steps, as cyanide is quantitatively scavenged by $Fe(CN)_5H_2O^{3-}$ according to reaction 7. Reaction 7 is also written as an irreversible step owing to

$$Fe(CN)_5H_2O^{3-} + CN^- \xrightarrow{k_7} Fe(CN)_6^{4-} + H_2O \quad (7)$$
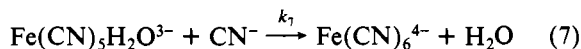
the well-known inertness of $Fe(CN)_6^{4-}$ toward substitution.[19] As shown below, the conversion of the mixed-ligand complex $Fe(CN)_5H_2O^{3-}$ to $Fe(CN)_6^{4-}$ and $Fe(H_2O)_6^{2+}$ ions (eq 1) is accompanied by a net decrease in free energy.

According to this scheme, the decay of $Fe(CN)_5H_2O^{3-}$ is interpreted by considering a set of competitive, consecutive second-order reactions,[20] i.e. (2) and (7); the rate law should be

$$-d[Fe(CN)_5H_2O^{3-}]/dt =$$
$$k_2[Fe(CN)_5H_2O^{3-}][H_2O] + 5k_7[Fe(CN)_5H_2O^{3-}][CN^-]$$

A limiting case is easily solved when $k_2 \ll k_7$, in which case the second step is a rapid follow-up to the first;[20] then the observed rate will be simply that of a pseudo-first-order process. The assumption is strongly supported by available kinetic data for reaction 7[2] ($k_7[CN^-]$ should be at least 1 order of magnitude higher than $k_2[H_2O]$ in our working conditions) and, certainly, by our rigorous first-order results, $k_{obsd} = 1.25 \times 10^{-4}$ s^{-1} (25 °C, $I = 1$ M). k_{obsd} may therefore be equalized to $k_d = k_2[H_2O]$, the dissociation rate constant for the loss of cyanide from $Fe(CN)_5H_2O^{3-}$. A remarkable difference of 3 orders of magnitude is found by comparing with the slower loss of cyanide from hexacyanoferrate(II) ($k = 4.0 \times 10^{-7}$ s^{-1}).[19]

Activation parameter data are also in accordance with the previous interpretation of k_{obsd}. Our value for $\Delta H^{\ddagger} = 109 \pm 3$ kJ mol^{-1} is of the same order as values obtained[21,22] for the dissociative loss of L from different $Fe(CN)_5L^{n-}$ (including L = CN^-);[19] besides, the positive number found for $\Delta S^{\ddagger} = 46 \pm 9$ J K^{-1} mol^{-1} is also in agreement with a dissociatively controlled process,[23] as also found in $Fe(CN)_5L^{n-}$.

No ionic strength effects were found for k_{obsd} in the range studied, as expected for a reaction between a charged species with a neutral one;[20] a very slight increase at lower I (see Table

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Table I. Rate Constants, k_d, for Cyanide Dissociation from $Fe(CN)_5H_2O^{3-}$ at Different Temperatures, pHs and Ionic Strengths[a]

T, °C	$10^4 k_{obsd}$, s^{-1} [b]	T, °C	$10^4 k_{obsd}$, s^{-1} [d]
20.0	0.56	40.0	10.7
25.0	1.25[c]	45.0	20.2
30.0	2.89	50.0	42.6
35.0	4.95		

pH	$10^4 k_{obsd}$, s^{-1} [d]	pH	$10^4 k_{obsd}$, s^{-1} [d]
4.0	1.40	7.0	1.30
6.0	1.30		

I	$10^4 k_{obsd}$, s^{-1} [e]	I	$10^4 k_{obsd}$, s^{-1} [e]
0.1	1.40	0.3	1.30

[a] Measured as the first-order rate of decay of the 440-nm absorption. [b] pH = 5.0; I = 1 M (NaCl). [c] Alternative runs were performed by measuring the growth of Fe(phen)$_3^{2+}$ concentration, $k_{obsd} = 1.20 \times 10^{-4}$ s^{-1}. [d] T = 25.0 °C; I = 1 M (NaCl). [e] T = 25.0 °C; pH = 5.0.

I) could probably be assigned to medium effects, as was also found for some $Fe(CN)_5L^{n-}$.[24] Additionally, k_{obsd} was found to be independent of pH in the range 4–7, in contrast to previous results;[15b] in fact, our data are in accordance with the known acid–base properties of $Fe(CN)_5H_2O^{3-}$. pH 4 should be a reasonable lower limit to discard protonation effects on cyanide (pK_a for $HFe(CN)_5H_2O^{2-}$ = 2.6),[14,25] and on the other hand, pH 7 will ensure the irreversible aquation of $Fe(CN)_5NH_3^{3-}$. At this last pH, no disturbances are expected from the presence of hydroxo complexes.[26]

Our results indicate that the stationary concentrations of tetracyanoferrates and lower cyanide-containing species are very low during the course of the reaction; a set of successive spectra of periodically extracted aliquots treated with phen could always be interpreted (at least to a 5% uncertainty) as a simple mixture of $Fe(CN)_5H_2O^{3-}$ and $Fe(phen)_3^{2+}$ according to eq 1. Moreover, initially added phen had no effect in the rate of the overall process; these results are in accordance with previous work showing that tetracyanoferrates should not attain a significant concentration level at pH higher than 4.[27]

The alternative way of monitoring the progress of the reaction through the measurement of $Fe(phen)_3^{2+}$, thus obtaining an equal value for k_{obsd} (see Experimental Section), proves that reaction 2 is rapidly followed by reactions 3–6; in addition, it further supports the proposed mechanism, the fate of $Fe(CN)_5H_2O^{3-}$ being controlled by $k_d[Fe(CN)_5H_2O^{3-}]$ although with the provision that 6 mol of $Fe(CN)_5H_2O^{3-}$ are reacting for each mole of Fe^{2+} formed.

A thermodynamic calculation shows that $Fe(CN)_5H_2O^{3-}$ must be intrinsically unstable; the free energy change, $\Delta G_6°$, for the reaction Fe^{2+}(aq) + 6CN(aq) → $Fe(CN)_6^{4-}$(aq) is -201.7 kJ mol^{-1}, and from this a value of $10^{35.4}$ is obtained for β_6, the overall stability constant.[12] Equilibrium data for reaction 7 ($K = 10^8$ M^{-1})[12] allows the calculation of $\beta_5 = 10^{27.4}$ so that $\Delta G_5°$, the free energy of formation of $Fe(CN)_5H_2O^{3-}$, is equal to -157.3 kJ mol^{-1}. From these numbers, the free energy of reaction 1 can now be calculated: $\Delta G_r° = -10.5$ kJ mol^{-1} This is an expected low value, as an equal number of iron–cyanide bonds as well as iron–water bonds are present on both sides of eq 1, but it nevertheless reflects a significant tendency of the iron–cyanide–aquo system to generate a greatly stabilized species such as $Fe(CN)_6^{4-}$.

It is also remarkable that closely related behavior previously has been found for the thermal decomposition reactions of

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Na₃Fe(CN)₅L·nH₂O (where L = NH₃, ethylenediamine, pyridine, etc.) in the solid state.[28] In these cases, the endothermic peak associated with the removal of L was immediately followed by a slight exothermic peak, associated with a reorganization of primary products, i.e. Fe(CN)₅³⁻, to Fe(CN)₆Na₄ and Fe(CN)₆Fe₂; the stoichiometry was effectively the same as in the aqueous system.

It is clear that a significant slow reduction of reactant concentration should occur in aqueous solutions of Fe(CN)₅H₂O³⁻. On the other hand, it has been pointed out that the measurement of rates of substitution of water in Fe(CN)₅H₂O³⁻ by various ligands presents serious difficulties unless oxygen is excluded from the medium.[1] Even in this case, however, kinetic complications still show up as slow absorbance changes, which are claimed to arise from the dissociation of dimers generated from Fe(CN)₅H₂O³⁻.[29] We think that the presence of dimers at the dilution level usually employed (10⁻⁵ M) should be insignificant, as suggested by available data on the monomer–dimer equilibrium.[30] As shown in this work, Fe(CN)₆⁴⁻ is likely to be present in the system because of the decomposition reaction, and this species may react with the added Fe(CN)₅³⁻ scavenger through slow cyanide release.

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Registry No. Fe(CN)₅NH₃³⁻, 18497-51-3.

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Fe–Fe π Bonding in Fe₂(CO)₆S₂?

Roger L. DeKock,*[1a,b] Evert Jan Baerends,[1a] and Ad Oskam*[1c]

Currently, dinuclear transition-metal complexes are the subject of numerous investigations. In particular, data from ultraviolet photoelectron spectroscopy (UPS) and molecular orbital (MO) calculations provide a foundation for understanding the electronic structure of these types of complexes.

Recent studies on Fe₂(CO)₆S₂ include the UPS measurements and self-consistent field–Xα–scattered wave (SCF–Xα–SW) of Andersen et al.[2] and the He I/He II UPS and minimal basis ab initio calculations of van Dam et al.[3] The general empirical assignment of the photoelectron (PE) bands made in both papers is essentially identical. However, the theoretical description of the metal–metal bonding interaction in the two studies is different. The ab initio calculation describes the Fe–Fe interaction in terms of a single "bent"

Table I. Calculated and Experimental Results for Fe₂(CO)₆S₂

IP,[a] eV		orbital level	% Fe 3d	% S	Fe–Fe Mulliken overlap population
exptl	calcd				
Band 1					
8.2 (sh)	8.14	15a₁	57	3	0.131
8.5 (sh)	8.49	14a₁	56	8	0.038
8.6	9.05	13a₁	69	9	0.022
	8.85	8a₂	80	0	−0.070
9.2 (sh)	8.54	12b₂	76	0	−0.073
	9.16	11b₂	75	2	−0.026
	8.57	9b₁	54	18	0.024
Band 2					
10.2	10.16	7a₂	15	62	−0.013
10.8 (sh)	10.87	8b₁	40	49	0.040
Band 3					
	12.46	12a₁	6	73	0.022
12.4	12.71	11a₁	16	68	0.039
	12.13	10b₂	9	61	−0.015

[a] sh = shoulder.

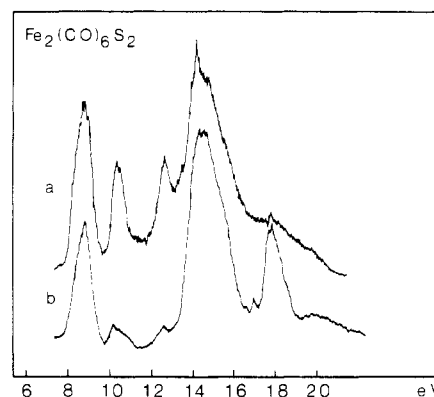**Figure 1.** UV PE spectra of Fe₂(CO)₆S₂: a, He I spectrum; b, He II spectrum.

a₁-bonding (highest occupied) MO, in agreement with earlier Fenske–Hall calculations on the same molecule.[4] In the Xα–SW scheme a "bent" Fe–Fe bond was also calculated as the HOMO, but at about 2 eV more stable in energy a b₁ orbital[5] is calculated to have a significant direct Fe–Fe π component induced by the interaction with the bridging sulfur ligand. In view of the disagreement between the two calculated methods and the relatively poor agreement between the calculated and experimental ionization potentials (IP's), we have carried out Hartree–Fock–Slater (HFS) calculations on Fe₂(CO)₆S₂ using a double-ζ basis set. Numerous previous studies employing the HFS method have shown it to give excellent results in comparison to UPS measurements.[6] Our intent is both to examine the nature of the Fe–Fe bonding and to compare computed and experimental IP's.

We present pertinent results in Table I. In computing the IP's we have employed the transition-state method for the same four transition states calculated by Andersen et al. For the other states we have employed an average of the calculated eigenvalues resulting from the four transition-state calculations. This procedure is justified since the eigenvalue shifts in each of the transition-state calculations is constant to within a few

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