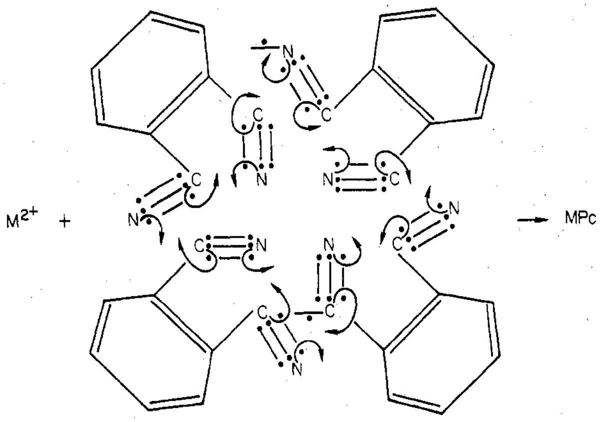

(3)

anion radical was the main byproduct separated and identified.

Finally, it is interesting to note that the attempts using UO_2^{2+} and Pb^{2+} ions in CH_3OH failed to produce MPc but produced instead H_2Pc.

The successful preparation of MPc using a two-compartment electrolytic cell described above might provide a valuable clue to the hitherto not well-elucidated mechanisms of the template reaction leading to the MPc. We are presently exploring the use of this method for a variety of reactions.

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Registry No. CuPc, 147-14-8; NiPc, 14055-02-8; CoPc, 3317-67-7; MgPc, 14325-24-7; PbPc, 15187-16-3; H_2Pc, 574-93-6; phthalonitrile, 91-15-6.

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Acidity of the Aquo Ligand in Aquopentacyanoferrate(II)

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The determination of the acidities of aquo ligands coordinated to low-spin transition-metal centers is a valuable contribution in view of their likely importance in both chemical and biochemical systems.

In a recent paper, Macartney and McAuley[1] reported a pH dependence in the visible spectrum of 10^{-4} M aqueous solutions of aquopentacyanoferrate(II) which led to an estimate of $K_{AH1} = (1.37 \pm 0.20) \times 10^{-8}$ M for equilibrium 1 at 25 °C.

$$(CN)_5Fe(H_2O)^{3-}(aq) \rightleftharpoons (CN)_5FeOH^{4-}(aq) + H^+(aq) \quad K_{AH1} \quad (1)$$

The distribution of iron(II) species derived from eq 1 was found to correspond closely to the pH profiles for the rates of substitution of thioureas and *N*-alkylthioureas, TU, at these proposed pentacyanoferrate(II) centers at the $(2–4) \times 10^{-5}$ M concentration level, leading to the conclusion[1] that reactions 2 and 3 proceed at significantly different rates. We cannot support the assignment of these data to reactions of monomeric aquopentacyanoferrate(II) centers.

$$(CN)_5Fe(H_2O)^{3-}(aq) + TU \xrightarrow{k_{H_2O}} (CN)_5FeTU^{3-} + H_2O \quad (2)$$

$$(CN)_5FeOH^{4-}(aq) + TU \xrightarrow{k_{OH^-}} (CN)_5FeTU^{3-} + OH^- \quad (3)$$

Our earlier work[2] describes the experimental problems encountered in making spectral measurements at the 10^{-4} M iron(II) concentration levels used by Macartney and McAuley,[1] even when *analyzed samples* of the precursor[3] $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$ are used.[4] In particular, we never observed the isosbestic spectral behavior anticipated from eq 1 from pH 6 to 1 M NaOH, and the time dependence of the spectra under these conditions was highly dependent on how the solutions were made up and treated.[2,6]

Reproducible rate data for substitution and redox reactions at monomeric aquopentacyanoferrate(II) centers can be obtained under carefully controlled conditions.[2] Published data actually indicate that 10^{-4} M aqueous solutions of pentacyanoferrate(II) species generated by rapid aquation[3] of $(CN)_5FeNH_3^{3-}$ contain both monomeric and dimeric species in time- and pH-dependent proportions.[2] Reactions of 10^{-4} M solutions containing such species with substituting ligands like X = pyrazine, nitrite, or *tert*-butyl hydroperoxide are easily distinguishable from their different rates.[2] The fastest process corresponds to reactions of monomeric species, as indicated by the observation of only one substitution process, at an identical rate, at $[Fe^{II}]_{TOTAL} \lesssim 10^{-5}$ M under identical pseudo-first-order conditions. Absorbance changes associated with formation of the common product $(CN)_5FeX^{n-}$ from reaction of X with monomeric and dimeric species present at higher concentration levels can be used to estimate the proportions of these species under a particular set of conditions.[2] At $[Fe^{II}]_{TOTAL} \lesssim 10^{-5}$ M, where monomers greatly predominate, absorption spectra exhibit a maximum at 440 nm which is unaffected by acidity variations in the pH 6–9 range.[7]

The kinetics of substitution at monomeric $(CN)_5Fe(H_2O)^{3-}$ centers have been investigated with a wide range of ligands X over the pH range 5.5–13. Except for X = pyrazine, which appears to be a special case,[2,8] a pH dependence of the rate is observed only for protic ligands, e.g., H_2O_2, where the dependence can be accounted for.[2] Our list[2] also includes kinetic data for substitution of thiourea,[1] which reacts with $(CN)_5Fe(H_2O)^{3-}$ in a second-order reaction whose constant

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(1) D. H. Macartney and A. McAuley, *Inorg. Chem.*, **18**, 2891 (1979).
(2) G. Davies and A. R. Garafalo, *Inorg. Chem.*, **15**, 1101 (1976), and references therein.
(3) J. M. Malin and H. E. Toma, *Inorg. Chem.*, **12**, 2080 (1973).
(4) Analyzed samples of $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$ (Fisher Certified) which had been recrystallized from concentrated ammonia solution and vacuum-dried were used throughout the studies reported in ref 2. We are concerned that no analytical data for this precursor are reported in ref 1 in view of difficulties we have experienced in reproducing published syntheses for a number of pentacyanoiron(II) species. If Brauer's procedure[5] is followed, it is likely that the product will contain significant proportions of monomeric and dimeric pentacyanoferrate(II) salts, in addition to $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$, since the ammonia ligand is known to be labile.[3]
(5) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed., Academic Press, New York, 1965, p 1511.
(6) Macartney and McAuley mention no time dependence of their spectra. As noted earlier,[2,7] the rate of change of the spectra of 10^{-4} M $(CN)_5Fe(H_2O)^{3-}$ solutions was highly dependent on pH even under closely controlled conditions.
(7) A. R. Garafalo, Ph.D. Thesis, Northeastern University, Boston, 1976.
(8) As reported earlier,[2] a 15% lower rate constant for formation of the pyrazine complex is observed on decreasing the reaction pH below 9.5. We were careful to discount the apparent $K_{AH1} \approx 2 \times 10^{-7}$ M (eq 1) suggested by the data (see ref 2 and text of this paper) and noted other peculiarities of this particular substituting ligand system which make it unsuitable as a means of determining K_{AH1}. The rate of the corresponding reaction with 2-methylpyrazine is essentially independent of acidity in the range pH 6–13 (A. Kwan and J. M. Malin, unpublished observations).

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is essentially *acid independent* over the pH range 7.8–12.1.[9]

To our knowledge, Macartney and McAuley's work[1] provides the only support for any significant dissociation of the aquo ligand in $(CN)_5Fe(H_2O)^{3-}$ over the pH range 6–13. Aside from the fact that their data stands apart from a large body of self-consistent work,[2,10] there are other considerations which indicate an incorrect assignment to reactions of monomeric species.

One would expect from well-known trends[11] in other aquo transition-metal systems that the iron(III) complex $(CN)_5Fe(H_2O)^{2-}$ would be substantially more acidic than the iron(II) complex $(CN)_5Fe(H_2O)^{3-}$, whereas Macartney and McAuley[1] conclude that the iron(II) complex is the more acidic.[12] Except for cases in which X is a good π acceptor, available evidence indicates that the $(CN)_5Fe^{II}$ center has a low affinity for σ-donor ligands like OH^- in the conjugate base $(CN)_5FeOH^{4-}$ (eq 1).[2] For this reason, we would expect that the latter would be more labile than its conjugate acid in eq 1, but Macartney and McAuley[1] report that the rate of substitution of X = thiourea on proposed monomeric aquopentacyanoferrate(II) centers *decreases* with increasing pH, which does not agree with experimental observations for other ligands and is not consistent with the above considerations.

We conclude that the spectral and kinetic data reported in ref 1 do not correspond to reactions of monomeric aquopentacyanoferrate(II) ions.

It may be that the spectral and kinetic measurements of ref 1 actually refer to iron(III)-containing species inadvertently produced in the synthesis of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ or in its subsequent isolation and treatment with methanol. We shall continue to follow the procedure of ref 2 for making up solutions of aquopentacyanoferrate(II) species from analyzed samples of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ under strictly anaerobic conditions.

Acknowledgment. We wish to thank Drs. J. M. Malin and H. E. Toma for valuable discussion and Dr. A. McAuley for comments on this paper prior to publication.

Registry No. $(CN)_5Fe(H_2O)^{3-}$, 18497-51-3.

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[9] Macartney and McAuley[2] report a sharp rate decrease in this pH range.

[10] For recent data, see, for example, H. E. Toma, J. M. Martins, and E. Giesbrecht, *J. Chem. Soc., Dalton Trans.*, 1610 (1978), and references therein.

[11] L. G. Sillén and A. E. Martell, *Spec. Publ.—Chem. Soc.*, **No. 25** (1971).

[12] The acid dissociation constant of $(CN)_5Fe(H_2O)^{2-}$(aq) is $K_{AH_I} = 4.0 \times 10^{-9}$ M at 25 °C.[13]

[13] J. H. Espenson and S. Wolenuk, *Inorg. Chem.*, **11**, 1034 (1972).

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Photodissociation of the Iron Tricarbonyl Anion

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Unsaturated metal carbonyl compounds have been suggested as intermediates in the thermal and photochemical substitution reactions of transition-metal compounds,[1,2] but the corresponding neutral molecules have never been detected in solution or in the gas phase. While several papers have appeared predicting the geometry and d orbital energy levels of such molecules,[3,4] there are few experiments with which to compare these theories. These unsaturated molecules are unstable and cannot be isolated for study under conventional conditions, although they can be seen in low-temperature matrix experiments. Among those unsaturated species observed in this way,[5,6] $Fe(CO)_4$, $Fe(CO)_3$, and recently[7] $Fe(CO)_4^-$ have been formed by ultraviolet and vacuum ultraviolet irradiation of $Fe(CO)_5$. Visible irradiation of $Fe(CO)_4^-$ in a matrix leads to detachment of an electron[7] while in the gas phase dissociation occurs.[8]

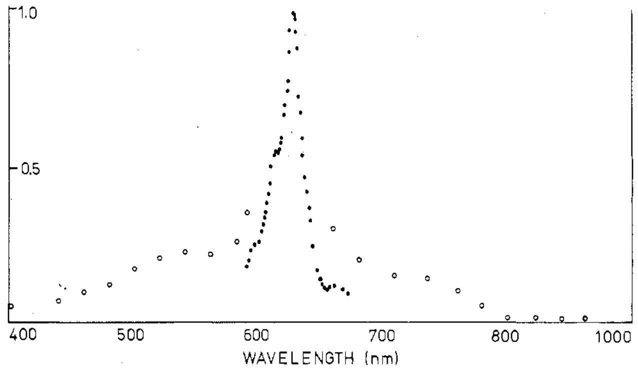

Figure 1. Relative photodissociation spectrum for photo increases of $Fe(CO)_2^-$ from $Fe(CO)_3^-$. The spectrum from 575 to 675 nm was taken at high resolution. The low-resolution spectrum has larger relative values due to the larger bandwidth of the monochromator.

The photodissociation of negative ions in an ion cyclotron resonance spectrometer has enabled us to study the electronic structure of an unsaturated iron carbonyl compound in some detail. This note is concerned with the electronic structure of $Fe(CO)_3^-$.

The interaction of light with gas-phase negative ions often results in the detachment of an electron, since the energy required to remove an electron from an anion is usually less than the energy required to break a bond. Dissociation can occur,[8] however, and when it does, it appears to involve reactions from excited states.[9] Thus, measuring photodissociation as a function of wavelength gives information about the absorption spectrum which cannot be recorded otherwise. The quantum yield for dissociation is generally assumed to be unity and wavelength independent so that the photodissociation action spectrum is taken to be equivalent to the absorption spectrum.[9] This therefore is a convenient way to study electronic excited states in ions.

Iron pentacarbonyl undergoes dissociative electron capture upon impact with low-energy electrons,[8,10–13] producing mainly $Fe(CO)_4^-$ and CO. Some $Fe(CO)_3^-$ is also produced, but no $Fe(CO)_2^-$ is present. (Product ions may also be lost via reaction with $Fe(CO)_5$ producing $Fe_2(CO)_6^-$.) Above energies of 3.0 eV $Fe(CO)_2^-$ is also present.

Ions were produced, trapped, and detected by using a Varian V-5900 ion cyclotron resonance (ICR) spectrometer. In-

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