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Properties of triethylphosphite complexes of pentacyanoferrate(II) and (III). Cyanide photolabilization in a pentacyanoferrate(II) complex with a monodentate ligand

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Abstract

$Na_3[Fe(CN)_5P(OCH_2CH_3)_3]$ was synthesized and characterized by electronic ($\lambda_{max}=320$ nm ($^1A_1 \rightarrow {}^1E$), $\epsilon=314$ M^{-1} cm^{-1}) and IR spectroscopies, cyclic voltammetry ($E°'=0.40$ V versus SCE) and elemental analysis. The Fe(III) species was synthesized by PbO_2 oxidation of the corresponding $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ complex ion. The $[Fe(CN)_5P(OEt)_3]^{2-}$ and $[Fe(CN)_5P(OEt)_3]^{3-}$ species do not undergo aquation reactions for a period of at least three weeks. Irradiation of the complex ion $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ in aqueous solutions with light of 313 nm leads to phosphite and cyanide aquations, with quantum yields $\phi_{CN} \cong 0.08$ and $\phi_{P(OEt)_3} \cong 0.13$ mol/einstein, respectively.

Introduction

A large amount of information is available on chemical reactions of pentacyanoferrate ions with different ligands [1, 2]. In our laboratories the chemistry of phosphites as ligands for Ru(II) and (III) ammines has been extensively investigated [3–5]. In an attempt to gain further insight into the basic chemistry of phosphorus as a ligand we have extended our studies to the pentacyanoferrate(II)/(III) systems. A smaller 3d orbital radial extension compared to that of the 4d orbitals, the presence of CN^-, a good π-acid ligand, in the Fe(II) coordination sphere, instead of the π innocent NH_3 ligand present in the Ru(II) compound, should have a different effect on the metal–phosphorus bond in the Fe(II) and Ru(II) systems.

The photochemical behavior of the $Fe^{II}(CN)_5L$ complexes, where L is an unsaturated ligand, was explained [6] in terms of the tuning model. The photoreactive $Fe^{II}(CN)_5L$ complexes are reported [2] to undergo photoaquation as the sole photoreaction. The clinical uses of sodium nitroprusside are well known [7] and since pentacyanoferrates are being considered in photochemical dynamic therapy (PDT) the investigation of their photochemical behavior became mandatory.

The aim of this work was to prepare the corresponding triethylphosphite cyanoferrate complexes and study their chemical and photochemical reactivities. The data upon the chemical behavior of these $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-/2-}$ complexes when compared with those of ruthenium(II)/(III) ammines will provide information about the systematics of the interaction between the metal centers and ligands and variations in their chemical reactivity.

Experimental

Materials

Sodium amminepentacyanoferrate(II) and methylpyrazinium *p*-toluenesulfonate were prepared following methods described in the literature [3, 8]. All solvents and chemicals used were analytical reagent grade (Aldrich). The experiments and syntheses were carried out under argon or nitrogen atmospheres.

Physical measurements

IR spectra were recorded on a Bomen FTIR model MB-102 spectrophotometer in the 400 to 4000 cm^{-1} range using solid samples dissolved in KBr pellets. The distinction between $\nu(C{\equiv}N)$ axial and $\nu(C{\equiv}N)$ equa-

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torial has been performed assuming that ν(C≡N) axial occurs at higher energy than ν(C≡N) equatorial, according to Tosi [9] assignments for $Na_2[Fe(CN)_5NO]$.

NMR spectra were recorded using a Brukcr AC-200 instrument with D_2O (99.8%) as solvent and 2,2-dimethyl-2-silapentane-5-sodium sulfonate (DSS) as internal standard. UV–Vis spectra were carried out using a Hewlett Packard diode array spectrophotometer model 8452A. Cyclic voltammetry and electrolysis were performed with a potentiostat/galvanostat model 173 from Princeton Applied Research. Glassy carbon saturated calomel electrode (SCE) and a platinum wire were used as working, reference and auxiliary electrode, respectively. All electrochemical experiments were performed in aqueous solution, ($\mu = 0.10$ $NaCF_3COO$, 25 °C).

Mössbauer spectra were obtained with a standard instrument with constant acceleration, with the ^{57}Co source in a rhodium matrix, and operating at room temperature. Sodium nitroprusside was taken as reference.

Preparation of the iron cyanometallate complexes

$Na_3[Fe(CN)_5P(OCH_2CH_3)]$

$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ (100 mg) was dissolved in 10 ml of distilled water, under argon atmosphere. $P(OCH_2CH_3)_3$ (2 ml) was dissolved in 5 ml of distilled and deaerated ethanol, and then added to the iron complex solution. After 1 h of reaction, 50 ml of ethanol were added to the resulting solution and a white solid precipitate was produced. The precipitate was collected under nitrogen atmosphere, washed with copious quantities of ethanol, dried and stored in a vacuum desiccator over silica gel, in the absence of light. Yield 80%. *Anal.* Calc. for $Na_3[Fe(CN)_5P(OCH_2CH_3)_3]\cdot 1H_2O$: C, 30.09; N, 15.95; H, 3.87. Found: C, 29.80; N, 15.85; H, 3.78%.

$Na_2[Fe(CN)_5P(OCH_2CH_3)_3]$

This compound was obtained by oxidation of the $Na_3[Fe(CN)_5P(OCH_2CH_3)_3]\cdot 1H_2O$ complex with PbO_2 in aqueous solution. 100 mg of iron(II) complex were dissolved in 5 ml of H_2O. With the addition of PbO_2 (45.2 mg), the colorless $Na_3[Fe(CN)_5P(OCH_2CH_3)_3]$ solution turned red. After 30 min, a red precipitate was formed upon the addition of ethanol. The precipitate was collected and washed with copious quantities of ethanol, dried and stored in a vacuum desiccator in the absence of light. Yield 80%. *Anal.* Calc. for $Na_2[Fe(CN)_5P(OCH_2CH_3)_3]\cdot 5H_2O$: C, 27.06; N, 14.35; H, 5.12. Found: C, 26.90; N, 13.98; H, 5.25%.

Photolysis experiments

The photolysis of the triethylphosphitepentacyanoferrate(II) complex was performed using an Osram 150 xenon lamp in an Oriel model 8500 Universal arc lamp source with an Oriel interference filter for monochromatization (≅10 mm band pass) and IR filter, and a thermostated cell holder. Photolysis reactions were carried out in aqueous solutions of $NaClO_4$, $\mu = 0.20$ at pH 3.0 and 4.0. Ferrioxalate actinometry was used for light intensity measurements. Solutions for photolysis and dark reactions were prepared in a Zwickel flask and transferred to the 1.0 cm pathlength quartz cell ($V = 4.0$ ml) using an all-glass apparatus. During photolysis, the solution was kept stirred by a small magnetic bar in the cell. All photolysis were carried out at 25.0 ± 0.1 °C. Corrections were made to take into account thermal reactions during photolysis by using a dark sample prepared similarly do that used for the photolyzed sample. The corrections were negligible.

Photoaquation of CN^-

The pH changes were used to evaluate the release of cyanide from the Fe(II) coordination sphere. After photolysis the pH values of the dark and irradiated solutions were determined. The quantum yields ϕ_{CN^-} were calculated from differences in the hydrogen ion concentration of these solutions The solutions used for the determination of cyanide photoaquation had an initial pH≅4.00.

Photoaquation of phosphite

The photoaquation reaction was followed by measuring the formation of $[Fe(CN)_5Mepz]^{2-}$ Photolysis of the phosphite complex results in $[Fe(CN)_5(H_2O)]^{3-}$ which reacts promptly with [1] *N*-methylpyrazinium $(Mepz)^+$ forming the thermodynamically [2, 10] stable ($K_{eq} = 2.0 \times 10^6$ M^{-1}) and the thermally and photochemically inert complex $[Fe(CN)_5Mepz]^{2-}$ [2, 10, 11], which absorbs at 660 nm with a relatively high molar absorptivity coefficient ($\epsilon = 1\ 23 \times 10^4$ M^{-1} cm^{-1}) [2] which is very convenient for the determination of $[Fe(CN)_5(H_2O)]^{3-}$ formed at a low extent of reaction. Initial pHs of the solutions for phosphite quantum yield measurements were adjusted to ≅3.0. Corrections were made to take into account thermal reactions during photolysis.

No development of absorbance in the UV–Vis region of the spectra was observed upon mixing solutions containing $[Fe(CN)_5P(OEt)_3]^{3-}$ and $Mepz^+$, respectively.

Photolysis runs did not exceed 2% of the reaction for phosphite photoaquation and 10% of the reaction for CN^- photoaquation. Quantum yields $\phi_{P(OEt)}$ and ϕ_{CN^-} were calculated by plotting quantum yield versus percent reaction and extrapolating back to 0% Reported quantum yields are the average for at least three independent determinations.

Results and discussion

The $[Fe(CN)_5H_2O]^{3-}$ species exhibits a well defined ligand field (LF) absorption on the visible region of the spectra (λ_{max}, 444 nm; ϵ, 450 M^{-1} cm^{-1}) due to the ($^1A_1 \rightarrow E_{(1)}$) transition [2, 10]. When the H_2O ligand is replaced by triethylphosphite in the coordination sphere of the pentacyanoferrate(II) complex, a hypsochromic shift is observed (λ_{max}, 320 nm; ϵ, 314 M^{-1} cm^{-1}) in the position of the LF transition. The blue shift observed for the LF transition on the triethylphosphite–iron(II) complex, in accordance with the same transition in the aquo–iron(II) analog, reflects a higher LF splitting and further stabilization of the t_{2g} orbitals upon $P(OCH_2CH_3)_3$ coordination. This is consistent with the position of triethylphosphite and water ligands in the spectrochemical series [2, 10, 11]: $NO^+ > CO > CN^- \geqslant P(OEt)_3 > DMSO > SO_3^{2-} > P(Ph)_3 \cong NH_3 > H_2O$.

According to the literature [11] for the $[Fe(CN)_5P(OEt)_3]^{3-}$ species two other bands, $^1A_1 \rightarrow {}^1A_2$ (400 nm) and $^1A_1 \rightarrow E_{(2)}$ (488 nm) transitions, were expected to appear. These transitions were not unequivocally detected by us, even using deconvolution techniques. Only one weak absorption band at 405 ± 10 nm ($\epsilon < 40$ M^{-1} cm^{-1}) was found. A third band due to its weak absorptivity could probably be hidden by the other two.

The UV–Vis spectrum of the $[Fe(CN)_5P(OCH_2CH_3)_3]^{2-}$ species exhibits two absorptions: $\lambda_{max} = 410$ nm, $\epsilon = 835$ M^{-1} cm^{-1} and $\lambda_{max} = 528$ nm, $\epsilon = 262$ M^{-1} cm^{-1}, which despite the low extinction coefficients of the latter, have been tentatively attributed to an LF and an LMCT transition, respectively, by comparison with similar systems [2].

The $E^{\circ\prime}$ values of 0.27 and 0.40 V for the Fe(II)/(III) couples in the $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ complexes suggest that $P(OCH_2CH_3)_3$ is more efficient than CN^- on the stabilization of Fe(II) with respect to Fe(III) in these systems. However, the energy of the LF transition is almost the same for both species, $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$, suggesting that the 10 *Dq* values in both complexes should be quite similar. Therefore, the more positive $E^{\circ\prime}$ value observed for the monophosphite complex probably reflects the lower thermodynamic stability of the Fe(III)–$P(OCH_2CH_3)_3$ bond when compared with the Fe(III)–CN^- bond.

It is well accepted [2, 9–11] that with Fe(II) → CN^- backdonation the electron population of the C≡N antibonding orbital is increased and as a consequence the ν(C≡N) stretching vibration shifts to lower energies relative to that of a non-coordinated cyanide. When NH_3, a good σ-donor ligand, is changed for the moderate σ-donor and good π-acceptor $P(OCH_2CH_3)_3$ ligand on the $[Fe(CN)_5L]^{3-}$ complex, the ν(C≡N) axial increases in energy from 2088 to 2105 cm^{-1} and the ν(C≡N) equatorial is shifted in energy from 2043 to 2055 and 2074 cm^{-1}. These data which show good agreement with the literature data [12], reflect the perturbation in the Fe–CN bond upon coordination of $P(OCH_2CH_3)_3$ in the Fe(II) center, which is more intense in the axial cyanide than in the equatorial one, as expected [2]. The ν(C≡N) in the $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NH_3]^{3-}$ species are 2042 and 2043 cm^{-1}, respectively, and therefore an increase of about 25 cm^{-1} in ν(C≡N) is observed with respect to the triethylphosphite complex. These observations indicate that π^* cyanide orbitals are being depleted and suggest that the π-bonding of the $Fe(CN)_5^{3-}$ moiety with $P(OEt)_3$ is stronger than with CN^-. The ν(C≡N) axial data, for $[Fe(CN)_5L]^{3-}$ species, suggest that triethylphosphite is a very good π-acid, being only surpassed by NO^+ and CO [2, 11].

The effect of triethylphosphite as a better π-acid ligand than cyanide is well illustrated by the IR spectra of $Na_2[Fe(CN)_5P(OCH_2CH_3)_3]$ complex. For this Fe(III) species, the ν(C≡N) is observed at 2129 cm^{-1}, which is consistent with the absence of backdonation from the Fe(III) center to the $P(OCH_2CH_3)_3$ and CN^- ligands. Comparison of the values of ν(CN) axial cyanide (2105 cm^{-1}) for the iron(II) complex with the above ν(CN) value for the iron(III) complex, illustrates the effect of electron density depletion in the iron(II) metal center as a consequence of the intense backbonding with the triethylphosphite ligand.

The Fe–CN bonding frequency increases in energy from 570 cm^{-1} in $[Fe(CN)_5NH_3]^{3-}$ to 579 cm^{-1} in $[Fe(CN)_5P(OEt)_3]^{3-}$. Again, this shift is due to the high Fe(II)–$P(OCH_2CH_3)_3$ backbonding which effectively increases the Fe(II) net charge and the energy of this vibration. Consistently, for the $[Fe(CN)_5P(OEt)_3]^{2-}$ species, this Fe–CN stretching frequency is further increased to 590 cm^{-1}.

The NMR (^1H) spectrum of the $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ complex ion exhibits a triplet signal at 1.06 ppm attributed to CH_3 groups and a quintuplet signal at 3.92 ppm, attributed to CH_2 groups. The phosphorus nuclear spins (^{31}P, $I = 1$) contribute as a doublet of quartets, with a weak coupling constant, supporting the appearance of a quintuplet.

The inductive effect of the oxygen atom over the electron density at the CH_2 and CH_3 groups is evident by comparing the NMR (^1H) spectra for the $P(OCH_2CH_3)_3$ and $P(CH_2CH_3)_3$ molecules [13]. The coordination of the ester to the M(II) center, considering only the σ component of the M(II) ← P(III) bond, contributes by decreasing the electron density over the CH_2 and CH_3 groups. The π component of M(II) → P(III), works in the opposite direction increasing the electron density over the P(III) center and over the P–O bond [4]. Therefore it is reasonable to expect a minimization of the σ-bond effect as a consequence of the backbonding M(II) → P(III). This causes an increase in the electron density over these protons with consequent shielding.

For the $[Ru(NH_3)_4(H_2O)P(OEt)_3]^{2+}$ ion, the observed proton chemical shifts are: $CH_3 = 1.02$ and $CH_2 = 3.78$ ppm. The straightforward comparison of the chemical shift values could suggest that the backbonding extension in the Ru(II) → P(III) and Fe(II) → P(III) complexes would be about the same. However, for the cyanometallates the anisotropic magnetic field of cyanides [14] and its effects over the CH_2 and CH_3 protons, must be considered. Also, for the $[Fe(CN)_5P(OEt)_3]^{3-}$ complex the competition between the CN^- and $P(OEt)_3$ ligands for the 3d electrons of the metal along the NC–Fe–P(OEt)$_3$ axis should be taken into account. These two effects are present in the $[Fe(CN)_5P(OEt)_3]^{3-}$ species, probably reducing the net Fe(II) → P(OEt)$_3$ backbonding effect over the CH_2 and CH_3 protons. Therefore as suggested by the NMR (^1H) spectra, the extension of the backbonding Fe(II) → P(OEt)$_3$ will be of the same order of magnitude of that existing in the Ru(II) → P(OEt)$_3$ bond in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$.

In contrast to the above iron system, where the $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ ion complex is the only species formed, in pentaammineosmium(II), pentacyanoruthenium(II) and tetraammineruthenium(II) systems the product of reaction with triethylphosphite shows two molecules of this ligand in *trans* position [4, 15]

The chemical inertness of the phosphite ligand is another point that deserves comment. The free $P(OCH_2CH_3)_3$ molecule is quite reactive [16] towards hydrolysis and oxidation but becomes quite resistant [4, 17, 18] to the action of chemical reagents (H^+, Ce^{4+}, Br_2) when coordinated to Ru(II) and Ru(III) centers. A similar chemical behavior is observed for the ester in the $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ and $[Fe(CN)_5P(OCH_2CH_3)_3]^{2-}$ complex ions. As judged from UV–Vis spectroscopy and cyclic voltammetric experiments, these complex ions do not undergo cyanide or phosphite aquation reaction in aqueous solution, at room temperature (25 ± 2 °C) in a wide range of hydrogen ion concentration ($C_{H^+} = 10^{-1}$ to 10^{-7} M), for at least a three week period. The presence of the complex ions $[Fe(CN)_5L]^{3-}$ and $[Fe(CN)_4P(OEt)_3L]^{2-}$ (L = DMSO or pz) was not detected (UV–Vis spectroscopy) in solution containing $[Fe(CN)_5P(OEt)_3]^{3-}$ and DMSO (0.15 M) or pz (0.50 M) even after a three week standing period.

The thermal chemical inertness of the $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ species, despite the recognized strong *trans* effect and *trans* influence displayed by the $P(OCH_2CH_3)_3$ ligand in Ru(II) and Os(II) centers [4, 15], was in principle not expected since $P(OCH_2CH_3)_3$ is able to displace the *trans* cyanide ligand in *trans*-$[Ru(CN)_5P(OCH_2CH_3)_3]^{3-}$ and in *trans*-$[Ru(NH_3)_4(CN)P(OCH_2CH_3)_3]^+$ species [19].

An interesting observation was obtained from the Mössbauer spectra of $Na_3[Fe(CN)_5P(OCH_2CH_3)_3]$ and $Na_2[Fe(CN)_5P(OCH_2CH_3)_3]$ compounds. For the Fe(II) complex, the numerical values of the quadrupole splitting (ΔE_Q) and the isomer shift (δ) are 0.423 and 0 170 mm/s, respectively. The value of the quadrupole splitting is consistent [20] with a small distortion in the octahedral symmetry and suggests that the $P(OCH_2CH_3)_3$ and CN^- ligands in the pentacyanide-iron(II) complex would have a similar interaction with the Fe(II) center. The use of the equation: $Dt = 4.465 \times \delta - 0.857$, that correlates the parameter Dt and the isomer shift [20], allows the calculation of the value $Dt = -0.098$ kk which is consistent with axial compression along the z axis This small distortion is also consistent with the small value found for the quadrupole splitting and consistent with the similar isomer shift values exhibited by $[Fe(CN)_6]^{4-}$ (0.192 mm/s) and $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$.

In the plot of isomer shift versus quadrupole splitting, for $Fe(CN)_5L$ species, the $P(OCH_2CH_3)_3$ derivative falls on the 'σ-only' line [21] This suggests that $P(OCH_2CH_3)_3$ besides being a good π-acid and being the π acceptor capability dominant [12] in the Fe(II) complex, the phosphanes, behaves also as a good σ-base. This is coherent with the stability exhibited by $[Fe(CN)_5P(OCH_2CH_3)_3]^{2-}$, *trans*-$[Ru(NH_3)_4P(OCH_2CH_3)_3(H_2O)]^{3+}$ and *trans*-$[Ru(NH_3)_4(P(OCH_2CH_3)_3)_2]^{3+}$ species [3], where the backbonding M(III) → P(III) is absent

The isomer shift for the $[(CN)_5Fe^{II}L]^{n-}$ species increases as follows [20]: $NO^+ < CO < P(OCH_2CH_3)_3 < CN^- < SO_3^{2-} < PPh_3 < DMSO < NH_3 < H_2O$.

The Mössbauer parameters of the $[Fe(CN)_5P(OCH_2CH_3)_3]^{2-}$ complex ion exhibit an isomer shift value of 0.1 mm/s and a quadrupole splitting equal to 2.04 mm/s. The value of ΔE_Q is consistent with the oxidation state of the metal center where the $3d^5$ orbitals are asymmetrical relative to the C_{4v} symmetry. Also, the deshielding promoted by the electron unfilled 3d orbitals, increase the electron density at the ^{57}Fe nucleus, which decreases the isomer shift value. Unfortunately there is not enough available data on Mossbauer spectroscopy for Fe(III) complexes to allow comparisons.

The experimental data collected in this work suggest that in the title Fe(II) compounds the CN^- and $P(OCH_2CH_3)_3$ ligands are chemically very similar. This could be a consequence of a strong orbital matching along the CN–Fe–P(OCH$_2$CH$_3$)$_3$ axis, making the Fe–CN and Fe–P(OCH$_2$CH$_3$)$_3$ bonds chemically equivalent and, accordingly, explaining the inertness of the monophosphite complexes with regard to substitution reactions.

Irradiation of acidic deaerated aqueous solutions of $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$ with light of 313 or 365 nm leads to cyanide and triethylphosphite aquation, according to eqns. (1) and (2).

$$[Fe(CN)_5(POEt_3)]^{3-} \xrightarrow[\text{pH 3 0}]{h\nu} [Fe(CN)_5(H_2O)]^{3-} + POEt_3 \quad (1)$$

$$[Fe(CN)_5(POEt_3)]^{3-} \xrightarrow[\text{pH 4 0}]{h\nu} [Fe(CN)_4(H_2O)(POEt_3)]^{2-} + CN^- \quad (2)$$

Oxidation to the Fe(III) species was ruled out [2] by the absence of any absorption at 410 and 528 nm.

Table 1 shows the quantum yields of cyanide and $POEt_3$ photoaquation in $[Fe(CN)_5P(OEt)_3]^{3-}$. In eqns. (1) and (2), even considering the hydrolysis of the free phosphite to phosphonate, since this process is acid catalyzed [3–5], the free cyanide ion is the only species responsible for the pH change. Thus, cyanide photoaquation was detected by changes in the pH of the solution.

For the $[(HCN)Fe(CN)_4(H_2O)]^{2-}$ species, with a large variety of π-acids ligands L, the pK_a values are found in the 0.7–2.2 range [2, 10, 22], increasing the acidity as the π acceptor ability of L increases. The pK_a for the acid $[(HCN)Fe(CN)_4H_2O)]^{2-}$ is [2, 22] 2.63 but the pK_a value for $[(HCN)Fe(CN)_4P(OEt)_3]^{2-}$ is not known at the moment. However as judged from the voltammetric spectra of the $[Fe(CN)_5P(OEt)_3]^{3-}$ ion in 10^{-2}–10^{-5} M CF_3COOH ($\mu = 0.10$ $NaCF_3COO$) solutions and on the π acidity of the $P(OEt)_3$ ligand, the pK_a value for the acid $[(HCN)Fe(CN)_4P(OEt)_3]^{2-}$ should be smaller than 2.

The pK_a for the $[(HCN)Fe(CN)_4P(OEt)_3(H_2O)]^{2+}$ species is also not known but a value equal to 2.6, the same as for the $[(HCN)Fe(CN)_5(H_2O)]^{2-}$ species [2, 22], should be considered a reasonable estimate for it, taking into account the relative π acidity of $P(OEt)_3$ and CN^- ligands.

Since photodissociated $P(OEt)_3$ exists long enough [3, 16, 17] in aqueous solutions where $C_{H^+} \cong 4.0$ to regenerate $[Fe(CN)_5P(OEt)_3]^{2-}$ species, and cyanoiron(II) complexes in solutions were deprotonated under these experimental conditions, only the amount of released cyanide was quantified through pH measurements. Consequently the ϕ_{CN} quantum yields were calculated.

TABLE 1. Photolysis quantum yields for the photoaquation of $P(OCH_2CH_3)_3$ and CN^- in $[Fe(CN)_5P(OCH_2CH_3)_3]^{3-}$

λ_{irr} [a]	ϕ_{CN^-} [b]	$\phi_{P(OCH_2CH_3)_3}$ [c]
313	0 084 ± 0 08	0 13 ± 0.01
365	0.015 ± 0 005	0 11 ± 0 01

[a] Irradiation wavelength in nm [b] In mole/einstein at initial pH ≅ 4 00, $C_{Fe(II)} = 10^{-3}$–10^{-4} M [c] In mole/einstein at initial pH ≅ 3.00, $C_{Fe(II)} = 10^{-2}$–10^{-3} M; $C_{Mepz^+} = 10^{-3}$–10^{-4} M.

Only experimental data corresponding to less than 10% of the photoreaction were considered in the cyanide photoaquation calculations.

The quantum yield for the $P(OEt)_3$ aquation was determined at pH 3.0 in the presence of excess *N*-methylpyrazinium ion [2]. At this pH no attempts to measure cyanide were made since in order to get any measurable and significant pH change the reaction should be allowed to proceed to a high extent. At this pH, any released $P(OCH_2CH_3)_3$ would undergo fast hydrolysis yielding diethylphosphite as product [3–5, 17]. The diethylphosphite, $P(OH)(OCH_2CH_3)_2$, exists in equilibrium [23] with diethylphosphonate, $P(O)(H)(OCH_2CH_3)_2$ in less than 5% of the diethylphosphonate concentration. From these two forms, $P(O)(H)(OCH_2CH_3)_2$ and $P(OH)(OCH_2CH_3)_2$, only the diethylphosphite is able to coordinate with the $Fe(CN)_5{}^{3-}$ moiety, but in the experimental conditions the $C_{P(OH)(OCH_2CH_3)_2}$ is smaller than 5×10^{-6} mol/l.

The second order specific rate data for the reaction

$$[Fe(CN)_5H_2O]^{3-} + P(OH)OCH_2CH_3)_2 \xrightarrow{K_1} [Fe(CN)_5P(OH)OCH_2CH_3)_2]^{3-} + H_2O$$

is not available at the moment. However, considering the $P(OH)(OCH_2CH_3)_2$ concentration in the photolyzed solutions, and the presence of the auxiliary ligand $Mepz^+$ which competes with $P(OH)(OCH_2CH_3)_2$ for the Fe(II) center, the formation of $[Fe(CN)_5P(OH)(OCH_2CH_3)_2]^{3-}$ species during the experiments has been disregarded.

The observed triethylphosphite photoaquation is similar to other L photoaquation [24–29] in $[Fe^{II}(CN)_5L]$ (L = pyridines, CO, $P(OCH_3)_3$, PPh_3, $AsPh_3$ or $SbPh_3$) species. Cyanide photoaquation was not reported in these latter complexes. Indeed, prolonged irradiation of $[Fe(CN)_5CO]^{3-}$ with light of 366 nm leads only [25] to trace amounts of cyanide with an estimated quantum yield of less than 10^{-2}. Cyanide aquation in pentacyanoferrate(II) complexes has already been observed photochemically only when chelating ligands are coordinated [24–29]. In this case cyanide release is followed by ring closure.

As it happens for the other above mentioned $[Fe^{II}(CN)_5L]$ complexes, the photosubstitution behavior of $[Fe(CN)_5(POEt_3)]^{3-}$ should come from low lying ligand-field excited states (LF*) through population of σ^* orbitals of e_g parentage [25–29].

As can be seen from Table 1, triethylphosphite photoaquation quantum yields are essentially the same for both irradiation wavelengths, and practically identical to the trimethylphosphite photoaquation quantum yield [27] at 366 nm, which is 0.14. However, cyanide photoaquation quantum yields show an irradiation wavelength dependence. These increases of the photodissociation of cyanides above the lowest LF band may be due to the proximity of the strong Fe(II)–CN MLCT bands in the UV region.

To our knowledge, the $[Fe(CN)_5P(OEt)_3]^{3-}$ system is the first case of unequivocal photochemical cyanide aquation in pentacyanoferrate(II) complexes with monodentate ligands. The cyanide quantum yield dependence on irradiation wavelength and the nature of cyanide labilized, *cis* or *trans*, or both, are currently being investigated in our laboratories. These studies are also being extended to the Fe(III) species.

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