Photochemistry of Pentacyanonitrosylferrate(2−), Nitroprusside

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Solutions containing pentacyanonitrosylferrate(2−), nitroprusside [$(NC)_5FeNO^{2-}$], were photolyzed using unfiltered light of wavelength greater than 300 nm and monochromatic light at 366 and 436 nm. Changes in $[H^+]$, $[O_2]$, and $[(NC)_5Fe^{III}H_2O^{2-}]$ were observed as a function of photolysis time. Quantum yields with respect to pentacyanoaquoferrate(III) formation, $\Phi_{(NC)_5FeH_2O^{2-}}$, were determined under varying experimental conditions and found to be dependent only on photolysis wavelength. At 436 nm, $\Phi_{(NC)_5FeH_2O^{2-}}$ was 0.18 mol einstein^{-1} and, at 366 nm, was 0.35 mol einstein^{-1}. Isotopic labeling experiments with H_2O (^{18}O) were performed in attempting to elucidate the primary photochemical process. Evidence from this study indicates that excitation of the iron $d_{xz,yz} \rightarrow \pi^*(NO)$ absorbance band of nitroprusside, *ca.* 400 nm, results in expulsion of nitric oxide as a direct result of photon absorption: $(NC)_5FeNO^{2-} + h\nu \rightarrow (NC)_5(Fe^{III})^{2-} + NO$. Rapid aquation of the pentacyanoferrate(III) intermediate yields $(NC)_5Fe^{III}H_2O^{2-}$. The changes observed in $[H^+]$ and $[O_2]$ in these investigations and those of other workers can be rationalized by secondary reactions of nitric oxide.

There have been several recent examinations of the photochemistry of pentacyanonitrosylferrate(2−), $(NC)_5FeNO^{2-}$, nitroprusside. Mitra and his coworkers[1,2] have observed several parameters of the system using unfiltered light ($\lambda > 300$ nm) and suggested the primary photochemical process as
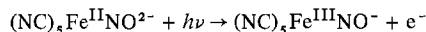
$$(NC)_5Fe^{II}NO^{2-} + h\nu \rightarrow (NC)_5(Fe^{II})^{3-} + NO^+$$
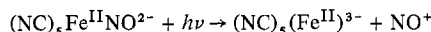
They found a pH decrease upon photolysis[1,2] and attributed this to hydrolysis of the nitrosyl cation

$$NO^+ + H_2O = H^+ + HNO_2$$
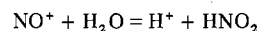
Buxton, Dainton, and Kalecinski[3] studied some qualitative aspects of the aqueous nitroprusside system using light of wavelength greater than 300 nm and suggested both nitric oxide production

$$(NC)_5Fe^{II}NO^{2-} + h\nu \rightarrow (NC)_5(Fe^{III})^{2-} + NO\cdot \quad (1)$$
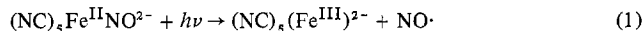
and photoelectron production

$$(NC)_5Fe^{II}NO^{2-} + h\nu \rightarrow (NC)_5Fe^{III}NO^- + e^-$$

Jezowska-Trzebiatowska, *et al.*,[4] studied the photolysis utilizing a monochromatic light source. Their observations at 329 nm indicated production of Fe^{3+} as a product of nitroprusside decomposition and they cited the nitroprusside absorption band ($d_{xz,yz} \rightarrow d_{x^2-y^2}$)[5] located at this wavelength as photochemically active.

Much of the theory of Mitra, *et al.*, rests on the spectral identification of the product of photolysis as pentacyanoaquoferrate(II). However, recently Emschwiller[6] and Espenson and Wolenuk[7] have shown the species with λ_{max} at 395 nm to be pentacyanoaquoferrate(III), $(NC)_5Fe^{III}H_2O^{2-}$. This lends credence to the primary process, which has also been proposed by Buxton, *et al.*,[3] as nitric oxide production, described by eq 1.

This work reports a study of the photochemistry of nitroprusside and a mechanism is proposed to account for the observations made on the system in this work and the work of others.

Experimental Section

Instruments. Absorbance measurements were conducted on a Cary Model 14 recording spectrophotometer (Applied Physics Corp.) with temperature control of $\pm0.2°$. A Du Pont Model 310 curve resolver was used in resolving the nitroprusside spectral envelope. Reported[5] estimated molar absorptivities and wavelengths of maxima estimated from shoulders agree well with those obtained from envelope resolution. Oxygen concentrations were observed using a Beckman Fieldlab oxygen analyzer, Model 1008. The oxygen concentration readings

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were standardized against literature values[8] at constant ionic strength. A Beckman Expandomatic pH meter, which was calibrated against commercial standard buffers, was used in all pH measurements. The pH was assumed to represent hydrogen ion concentration. This approximation introduced no significant errors in the studies performed herein.

Quantitative and qualitative collection and sampling of gaseous products was conducted on a general-purpose vacuum line equipped with a Toepler pump. Analyses of gaseous products were conducted on a Consolidated Electrodynamics Type 21-104 180° sector mass spectrometer.

Chemicals and Solutions. $Na_2[(NC)_5FeNO]\cdot2H_2O$, NaCl, and $NaH_2PO_4\cdot H_2O$ were reagent grade and were used without further purification. NaN_3 was practical grade. Solutions of sodium azide were prepared and allowed to stand for *ca.* 2 hr whereupon filtering with a fine-frit sintered-glass filtering funnel removed impurities and resulted in a clear solution of greater than 99% purity. Comparison of spectral properties of sodium nitroprusside with reported values[5] ascertained that no decomposition of the salt had occurred. Solutions were prepared with deionized, distilled water. Prepared solutions of nitroprusside were protected from light to prevent photodecomposition. The phosphate buffered solutions were adjusted to 1 *M* ionic strength with sodium chloride. The solutions were generally 0.25 *F* in phosphate; however no variations of experimental results as a function of phosphate concentration were observed.

Photochemical Studies. A 550-W medium-pressure mercury vapor lamp (Hanovia Type 673 A)[9] was placed in a water-cooled Pyrex jacket held in a fixed position. Constant geometry of the system including placement of filters and cells was maintained throughout all photolyses. Five centimeter path length optical cells with a volume of 15 ml and an optically flat surface of *ca.* 3 cm^2 were taped with black electrical tape on the sides to minimize extraneous reflections. No attempt was made at focusing the light. Corning glass color filters (Corning Glass Works, Corning, N.Y. 14830) were employed in combination for isolation of mercury spectrum lines.

366 nm. Filters CS 5-60 (5.65-mm thickness) and CS 7-60 (4.56 mm) in tandem resolved the 366-nm line with 12% transmittance. Relative transmittance of the adjacent lines was less than 1%.

436 nm. This line was isolated employing filters CS 5-60 (5.65 mm) and CS 3-73 (1.50 mm) and resulted in 48% transmission of the 436-nm line. The relative contributions of the adjacent lines were less than 1%. Intensity dependence studies were made by reducing the incident light intensity of this line by addition of another filter, CS 4-67 (1.84 mm), which reduced the transmittance to 15.6%.

An Eastman Kodak Wratten filter (Aero No. 1, in B glass) with a cutoff wavelength (% $T < 1\%$) of 460 nm was utilized in examining long-wavelength photolyses.

The intensity of irradiation emitted from the lamp was measured using ferrioxalate actinometry which is well described by Calvert and Pitts.[9] Each actinometric run was made after the lamp had reached a stable and efficient operating temperature, *ca.* 1-2 hr. Runs were made over a period of several days with no more than two measurements made for any given lamp start up. The quantum yield for ferrous ion production in the photolysis of the ferrioxalate solution used in the intensity calculations was the value of $\Phi_{Fe^{2+}} = 1.26$ at 366
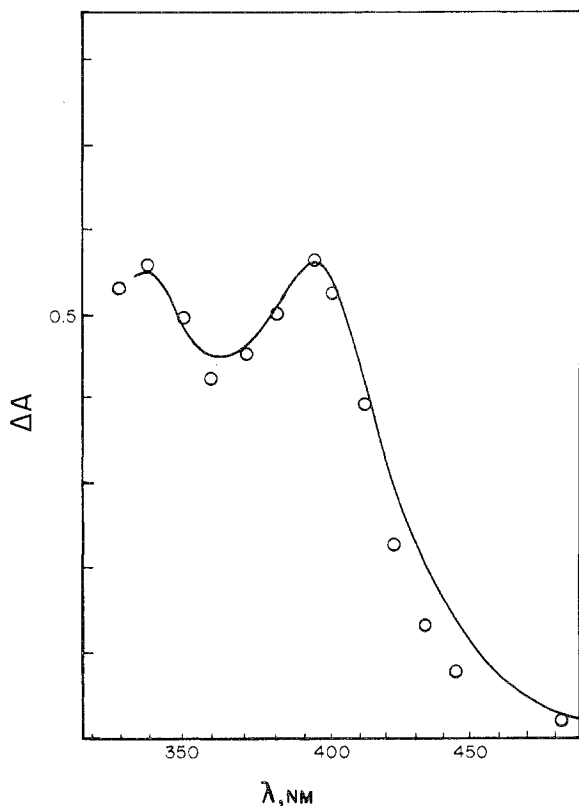
Figure 1. Difference spectrum of photolysis product of nitroprusside at 366 nm; 4.0×10^{-3} F $(NC)_5FeNO^{2-}$, pH 6.0 (phosphate), $\mu = 1.0$ (NaCl), $I_0{}^{366} = 1.26$ (± 0.06) $\times 10^{15}$ quanta sec^{-1}, 2-hr photolysis in 5-cm path length, 15-cm^3 cuvette. $\circ$ represents the spectrum of $(NC)_5FeH_2O^{2-}$ from ref 7 normalized at λ_{max} 395 nm.

nm given by Lee and Seliger.[10] This was chosen since their experimental conditions were more closely related to those performed here. The value obtained for the intensity incident in the cell, averaged over 10 trials, was 1.26 (± 0.06) $\times 10^{15}$ quanta sec^{-1} using the filtered 366-nm line. Further intensity measurements made from time to time showed no significant deviations. This value was then used in calculation of all quantum yields performed at 366 nm.

Values for incident light intensity, I_0, at 436 nm were obtained for two different filter combinations and were $I_0{}^{436} = 4.08$ (± 0.21) $\times 10^{15}$ quanta sec^{-1} for the 3-73, 5-60 filter combination and $I_0{}^{436} = 1.37$ (± 0.08) $\times 10^{15}$ quanta sec^{-1} for the 3-73, 4-67, 5-60 filter combination.

In calculations involving the photolysis of sodium nitroprusside solutions at 1 M ionic strength, molar absorptivities of ϵ 20.1 M^{-1} cm^{-1} at 366 nm and ϵ 14.0 M^{-1} cm^{-1} at 436 nm were employed. The molar absorptivity of $(NC)_5Fe^{III}H_2O^{2-}$ is 743 M^{-1} cm^{-1} at 395 nm.[7] The product absorbance was determined by taking a difference spectrum with unphotolyzed solution as a reference. The correction for product absorbance of incident light which was applied to the calculated quantum efficiency with respect to $(NC)_5Fe^{III}H_2O^{2-}$ production assumed a linear relationship between transmittance and absorbance over small absorbance changes (less than 0.1) and small absorbance. The absorbance of the product at the photolyzing wavelength was divided by 2 to approximate the average absorbance over the photolysis time and this value was converted to represent average transmittance. The photolyses were conducted to less than 3% reaction in actinometric runs and ca. 10% for gas analysis experiments.

Results and Discussion

Photolyses at $\lambda > 300$ nm. Prussian Blue, HCN, and NO have been previously observed as the products of the photolysis of $(NC)_5FeNO^{2-}$ solutions.[11] Prolonged photolysis of unbuffered, air-saturated sodium nitroprusside solutions at room temperature with light of wavelength greater than 300 nm resulted in the formation of a dark blue precipitate, which was characterized as the sodium salt of Prussian Blue, Na-
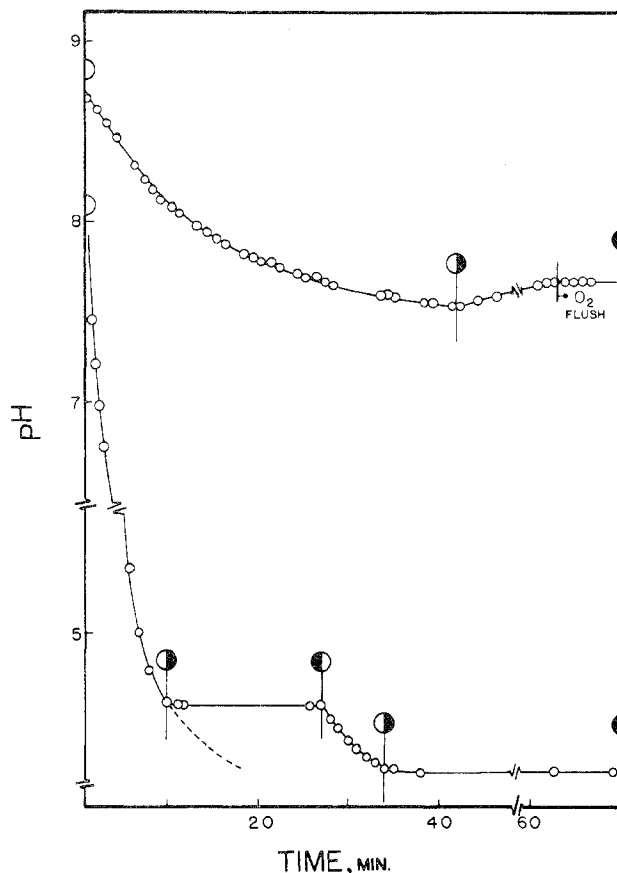

Figure 2. pH changes during photolysis of nitroprusside solution; 1.6×10^{-2} F $(NC)_5FeNO^{2-}$ initially, $\mu = 1.0$ (NaCl), constant I_0, λ 366 nm, 25°: upper curve, constant N_2 flush; lower curve, constant O_2 flush; $\circ$-$\circ$, photolysis; $\bullet$-$\bullet$, dark periods.

$[Fe^{III}Fe^{II}(CN)_6]$, by its infrared spectrum (ν_{CN} 2075 cm^{-1})[12] and qualitative analysis, reduction with dithionite resulting in Berlin White, $Na_2[Fe^{II}Fe^{II}(CN)_6]$.[11] Mass spectral analysis of gaseous products of the prolonged photolysis of 0.05 F $Na_2[(NC)_5Fe^{II}NO]\cdot 2H_2O$, which was outgassed under vacuum and irradiated with unfiltered light ($\lambda > 300$ nm), gives clear evidence for production of nitric oxide, cyanogen, and hydrogen cyanide.

Photolyses at 366 and 436 nm. Iron-Containing Product. Photolyses of nitroprusside solutions buffered at pH 6 (phosphate buffer, $\mu = 1.0$) at 366 or 436 nm yielded a species with the spectrum of Figure 1. This spectrum is nearly identical with that reported for $(NC)_5Fe^{III}H_2O^{2-}$.[7] In buffered solutions no decomposition products such as Prussian Blue or cyanogen were observed over photolysis periods up to 16 hr.

pH Change. Changes in hydrogen ion concentration as a result of photolysis have been reported by other workers.[1,2] Investigation of this phenomenon showed that photolysis of an unbuffered 1.6×10^{-2} M nitroprusside solution ($\mu = 1.0$, NaCl; λ 366 nm) under a constant oxygen flush resulted in a pH change of from initially near neutrality down to ca. pH 4 as illustrated in Figure 2. In a similar experiment under constant nitrogen flush only a small pH decline is observed (Figure 2). The final value, $[H^+]$ less than 10^{-7} M, is accountable for by interaction with a residual oxygen concentration. It was further observed that after termination of the nitrogen-flushed photolysis, addition of oxygen produced no pH change. After some initial buffering action the production of hydrogen ion in the earlier stages of photolysis is linear with respect to time at constant irradiation intensity in aerated solutions.

By titration with base Mitra, *et al.*, found 2 equiv of weak

acid produced upon photolysis per mole of $(NC)_5FeNO^{2-}$ photolyzed[2] and proposed 1 equiv to be due to a protonated form of product, $H[(NC)_5Fe^{II}H_2O]^{2-}$. The diprotonated species $H_2[(NC)_5Fe^{II}NO_2]^{2-}$, which they also suggested as a possible product, can be ruled out on the basis of the known reaction of $(NC)_5FeNO_2^{4-}$ with H^+ to give nitroprusside.[13] They found one of these acids to have a pK of *ca.* 8. Espenson and Wollenuk[7] have reported $(NC)_5Fe^{III}H_2O^{2-}$ to have a pK of 8.3.

A thermally reversible pH change and large hydrogen ion production in deoxygenated solutions, although less than in air-saturated solutions, were observed by other workers.[1] In solutions continuously flushed with the appropriate gas, we observed a small, partially reversible pH change in deoxygenated solutions ($[O_2] < 10^{-5}$ *M*) and no reversibility in the pH change in oxygenated solutions.

NO^+ vs. NO Production. Nitrosyl cation, NO^+, production has been suggested as responsible for this pH decline *via* hydrolysis

$$NO^+ + H_2O = HNO_2 + H^+$$
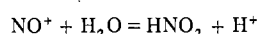
However, Mitra, *et al.*, observed a tenfold increase in hydrogen ion concentration in air-saturated solution *vs.* that observed in deoxygenated solutions.[1] Quantitative oxidation of nitrous acid
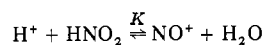
$$HNO_2 + {}^1/_2O_2 = H^+ + NO_3^-$$
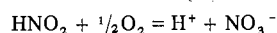
could only increase the hydrogen ion concentration by a factor of 2. Nitric oxide production accompanied by $(NC)_5Fe^{III}H_2O^{2-}$ production as a result of the photochemical process can account for these observations. In the absence of oxygen the ionization of the iron(III)–aquo species[7]

$$(NC)_5Fe^{III}H_2O^{2-} = (NC)_5Fe^{III}OH^{3-} + H^+ \quad (pK = 8.3)$$
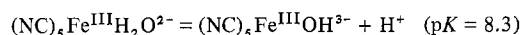
accounts for the small pH decline. In the presence of oxygen nitric oxide reacts to give dinitrogen tetroxide, followed by disproportionation, to yield nitric acid and nitrous acid, $K_a = 5 \times 10^{-4}$ (25°).[14] This is also in agreement with the previous observation that postphotolysis addition of oxygen to a nitrogen-flushed solution produced no pH change since the nitrogen would have swept out the nitric oxide. Nitric oxide does not react with water.[15] If nitrosyl cation and nitrous acid are involved in the equilibria

$$H^+ + HNO_2 \overset{K_2}{\rightleftharpoons} H_2NO_2^+ \quad (2)$$

$$H_2NO_2^+ \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} NO^+ + H_2O \quad (3)$$

Then, from the equilibrium

$$H^+ + HNO_2 \overset{K}{\rightleftharpoons} NO^+ + H_2O$$

for which K is 2×10^{-7} (20°),[17] it is evident that

$$K_2(k_3/k_{-3}) = 2 \times 10^{-7} \text{ (20°)}$$

From the dissociation constant for nitrous acid and the rate of oxygen exchange between nitrite and water, $(2.6 \times 10^{8} \cdot [NO_2^-][H^+]^2)$(time in minutes),[18] Haim and Taube[19] calculated K_2k_3 as 2.1×10^3 M^{-1} sec^{-1} at 25°. Combining these data gives
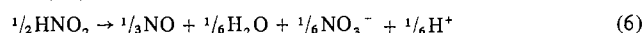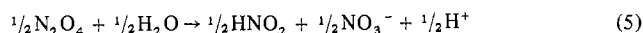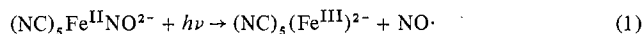
$$k_{-3} = 1.1 \times 10^{10} M^{-1} \text{ sec}^{-1}$$

for the rate constant for aquation of the nitrosyl cation, which is the magnitude expected for a diffusion-controlled bimolecular rate constant.[20] Thus, if the process

$$(NC)_5Fe^{II}NO^{2-} + h\nu \rightarrow (NC)_5(Fe^{II})^{3-} + NO^+$$
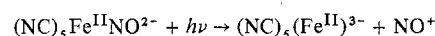
occurs in a primary process, prior to interaction with azide, oxygen exchange with the solvent would occur *via* eq 3 (also, the fact that the water concentration was 2500 times that of

the azide allows for considerable error in these calculations without affecting the resultant argument). The possibility of exchange was tested in two ways: first, photolysis of nitroprusside and azide solutions in isotopically labeled water (1.6% ^{18}O) gave only nitrous oxide of normal isotopic composition [*m/e* 46, 0.25 (±0.03)% *vs.* n.a. of 0.20%]; second, isotopically labeled nitroprusside [0.93 (±0.03)% ^{18}O] prepared,[16] and photolyzed in the presence of azide, gave quantitative labeling [0.90 (±0.05)%] of the nitrous oxide produced. This evidence supports the contention that free NO^+ is not formed during the photochemical process. However, the thermal reaction between nitroprusside and azide[16] decreases the sensitivity of these photochemical experiments.

Oxygen Consumption. The oxygen consumption during the course of the photolysis was found to be linear with respect to time at constant irradiation intensity and corresponded to 0.86 (±10%) mol of oxygen consumed/mol of $(NC)_5Fe^{III}H_2O^{2-}$ formed. If oxygen was only consumed through oxidation of nitric oxide, the O_2:$(NC)_5FeH_2O^{2-}$ ratio would be 0.5. However, other equilibria exist in these solutions. The disproportionation of nitrous acid would account for larger oxygen consumption *via*

$$(NC)_5Fe^{II}NO^{2-} + h\nu \rightarrow (NC)_5(Fe^{III})^{2-} + NO\cdot \quad (1)$$

$$NO + {}^1/_2O_2 \rightarrow {}^1/_2N_2O_4 \quad (4)$$

$${}^1/_2N_2O_4 + {}^1/_2H_2O \rightarrow {}^1/_2HNO_2 + {}^1/_2NO_3^- + {}^1/_2H^+ \quad (5)$$

$${}^1/_2HNO_2 \rightarrow {}^1/_3NO + {}^1/_6H_2O + {}^1/_6NO_3^- + {}^1/_6H^+ \quad (6)$$

Reaction 5 is always pseudo first order in aqueous solution with a half-life of less than 3 msec.[22] Reaction 6 is an equilibrium ($K_6 = 29$ atm^2 M^{-1})[17] which will lie largely to the left until nitric oxide is almost entirely consumed by reaction 4.[17] Reaction 4 is rate limiting in consumption of oxygen[17,23] and also indirectly limits the rate of hydrogen ion production. For oxygen in excess of nitric oxide concentration pseudo-second-order conditions prevail for this reaction (eq 4) and the estimated half-life for disappearance of nitric oxide is on the order of 10 sec. The cumulative effect of these reactions is the consumption of oxygen at a ratio of 0.75 mol of oxygen/mol of nitroprusside which undergoes photolytic decomposition.[24] The calculated value of 0.75 is at the limits of error of the observed O_2 production. Other photochemical and thermal pathways may also contribute.

The disproportionation of dinitrogen tetroxide is in agreement with the observation of nitrite formation in air-saturated photolyzed nitroprusside solutions by Buxton, *et al.*[3] A report of nitrite appearance in deoxygenated photolysis in another work[1] may possibly be due to use of air-saturated reagent solutions in the nitrite test.[25] Oxidation of residual free nitric oxide to form the product *via* eq 4 and 5 may then occur during the testing procedure.

Quantum Yields. The production of $(NC)_5Fe^{III}H_2O^{2-}$ during photolyses at both 366 and 436 nm was quantitatively investigated. The observed quantum efficiency Φ of $(NC)_5Fe^{III}H_2O^{2-}$ production at 436 nm is 0.18 mol/einstein and at 366 nm is 0.35 mol/einstein (Table I). In buffered solution (pH 6, phosphate) the appearance of this iron-(III)–aquo species was linear with time at up to 5% reaction when irradiation intensity was corrected for product absorption. Data in Table I show that the quantum yield with respect to formation of $(NC)_5Fe^{III}H_2O^{2-}$ is independent of the presence of oxygen (the residual oxygen concentration in the deoxygenated solutions was less than 10^{-5} *M* and was therefore not present in sufficient quantity to account for the *ca.* 5×10^{-5} *M* quantities of $(NC)_5Fe^{III}H_2O^{2-}$ which were spectrally observed). Hydrogen ion production, as mentioned earlier, was dependent on oxygen.

The observed quantum yield for formation of $(NC)_5Fe^{III}H_2O^{2-}$ is also independent of ionic strength, buffer

Table I. Quantum Efficiency of $(NC)_5Fe^{III}H_2O^{2-}$ Production

	λ, nm	$[(NC)_5FeNO^{2-}]_0$, M	pH	μ^a	O_2, condition	$\Phi_{(NC)_5FeH_2O^{2-}}$ ^{d}
1^a	366	4.00×10^{-3}	6.0	1.0	Air satd	0.37
2^a	366	4.00×10^{-3}	6.0	1.0	Air satd	0.37 (± 0.01)^c
3^a	366	4.00×10^{-3}	6.0	0.5	Air satd	0.35
4^a	366	4.00×10^{-3}	4.0	1.0	Air satd	0.30^d
5^a	366	4.00×10^{-3}	2.3	1.0	Air satd	0.31^d
6^b	366	4.00×10^{-3}	6.0	1.0	O_2 satd	0.33
7^b	366	4.00×10^{-3}	6.0	1.0	Deoxygenated	0.34
8^b	366	4.00×10^{-3}	6.0	1.0	NO satd	0
9^b	366	1.6×10^{-2}	Unbuffered	1.0	Deoxygenated	0.34
10^e	436	4.00×10^{-3}	6.00	1.0	Air satd	0.18
11^e	436	4.00×10^{-3}	Unbuffered	0.5	Deoxygenated	0.18
12^e	436	4.00×10^{-3}	Unbuffered	0.01	Deoxygenated	0.21
13^e	436	8.00×10^{-3}	6.0	1.0	Air satd	0.20
14^f	436	4.00×10^{-3}	6.0	1.0	Air satd	$0.17_4{}^i$
15^g	436	4.00×10^{-3}	6.0	1.0	Air satd	$0.17_6{}^i$
16^h	436	4.00×10^{-3}	6.0	1.0	Air satd	0.18
17^h	436	4.00×10^{-3}	6.0	1.0	Air satd	0.18

^{a} Ionic strength adjusted with NaCl. ^{b} Intensity of $(1.26 \pm 0.06) \times 10^{15}$ quanta sec^{-1}. ^{c} Five points at different time intervals on same solution. ^{d} Φ's reported as observed at λ 395 nm. However there was a large lower wavelength absorption which caused considerable screening of incident light. ^{e} Initial intensity of $(4.08 \pm 0.21) \times 10^{15}$ quanta sec^{-1}. ^{f} Initial intensity of $(4.23 \pm 0.05) \times 10^{15}$ quanta sec^{-1}. ^{g} Initial intensity of $(1.42 \pm 0.02) \times 10^{15}$ quanta sec^{-1}. ^{h} Initial intensity of $(1.37 \pm 0.08) \times 10^{15}$ quanta sec^{-1}. ^{i} Runs made at carefully determined intensities to determine effect of changing intensity.

Table II. Electronic Spectrum of $(NC)_5FeNO^{2-}$

Obsd^a		Calcd^a	Resolved^b			Band assignments^{a,c}
$\bar{\nu}$, cm^{-1}	ϵ, M^{-1} cm^{-1}	$\bar{\nu}$, cm^{-1}	$\bar{\nu}$, cm^{-1}	λ, nm	ϵ, M^{-1} cm^{-1}	
20,080	*ca.* 8	20,540	19,600	510	7	$2b_2(^1A_1) \rightarrow 7e(^1E)$ $d_{xy} \rightarrow \pi^*(NO)$
25,380	25	25,090	25,100	400	23	$6e(^1A_1) \rightarrow 7e(^1A_1)$ $d_{xz,yz} \rightarrow \pi^*(NO)$
30,300 sh^d	$(40)^d$	30,770	31,200	320	47	$2b_2(^1A_1 \rightarrow 3b_1(^1A_2)$ $d_{xy} \rightarrow d_{x^2-y^2}$
37,800 sh^d	$(900)^d$	37,750				$6e(^1A_1) \rightarrow 5a_1(^1E)$ $d_{xz,yz} \rightarrow d_{z^2}$
42,000 sh^d	$(700)^d$	40,900				$6e(^1A_1) \rightarrow 3b_1(^1E)$ $d_{xz,yz} \rightarrow d_{x^2-y^2}$
50,000	24,000	49,900				$2b_2(^1A_1) \rightarrow 8e(^1E)$ $d_{xy} \rightarrow \pi^*(CN)$

^{a} Adapted from ref 5. ^{b} This work. ^{c} Predominant localized character. ^{d} Shoulder values estimated.

capacity, and a threefold variation in incident light intensity (Table I). The slight pH dependence on the spectrally observed quantity of $(NC)_5Fe^{III}H_2O^{2-}$ may be real, due to protonation of the nitroprusside cyanides, or may be an artifact of other equilibria involving the product. Pentacyanoferrate(II) complexes have been observed to undergo decomposition in acidic media,[26,27] with the rate being lower in more acidic solutions. The insensitivity of pentacyanoaquoferrate(III) formation to factors other than wavelength and the evidence for nitric oxide production suggest metal-to-ligand charge transfer followed by heterolytic cleavage of the metal–ligand σ bond, as the primary process following excitation of the λ_{max} 395 nm band (reaction 1). However, an associative mechanism

$$[(NC)_5Fe^{II}(NO^+)]^{2-} + h\nu \underset{-L}{\overset{L}{\rightleftharpoons}} [(NC)_5Fe(L)(NO)]^{2-} \rightarrow$$

$$(NC)_5FeL^{2-} + NO\cdot$$
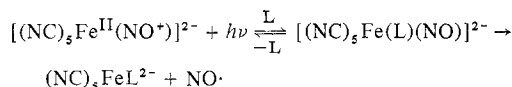
where $L \equiv H_2O$ or NO is not eliminated.

Manoharan and Gray[5] have performed extensive SCCC-MO calculations on sodium nitroprusside and have assigned the character of the absorption bands (Table II). A more recent MO study by Fenske and DeKock[28] gives the same orbital ordering. The nitrosyl moiety is coordinated along the z axis. Resolution of the nitroprusside spectral envelope at λ >300 nm in this work reveals the contributions of the individual bands. Molar absorptivities obtained from this resolution are presented in Table II. This resolved spectrum indicates the importance of using monochromatic light in irradiations so that the excitations taking place are known.

The lowest energy band, which occurs at *ca.* 500 nm, has been assigned to a $d_{xy} \rightarrow \pi^*(NO)$ transition.[5] This highest occupied molecular orbital is *ca.* 98% metal d_{xy} in character[29] and does not interact with the nitrosyl group in the ground state. Thus this transition to the $\pi^*(NO)$ orbital does not substantially affect the metal–nitrosyl bond strength. In fact,

photolysis at λ >480 nm evidenced no reaction.

The second band occurs at *ca.* 400 nm and is a $d_{xz,yz} \rightarrow \pi^*(NO)$ transition.[5] This transition has the instantaneous effect of shifting an electron from a predominantly metal-localized orbital (6e) (61% $d_{xz,yz}$; 25% $\pi^*(NO)$)[29] to an orbital (7e) centered primarily on the nitrosyl ligand (23% $d_{xz,yz}$; 73% $\pi^*(NO)$).[29] Since the 6e level is a bonding MO, a loss in metal-to-ligand bond strength occurs upon this transition to an excited state. The excited state may dispose of its excess energy in several ways, *e.g.*, photon emission, vibrational relaxation, electron emission, or translation *via* bond cleavage. Only the latter two give a detectable chemical change.

Photoexcitation of the 320-nm band results in d–d transitions. Ligand–metal bond cleavage in these reactions would be relatively nonspecific. It has been reported by Jezowska-Trzebiatowska, Kalecinska, and Kalecinski[4] that photolysis of aqueous nitroprusside at 329 nm results in decomposition, with ferric ion production. Also as observed here and elsewhere,[11,30] photolysis with unfiltered light of wavelength greater than 300 nm produces Prussian Blue.

Registry No. $(NC)_5FeNO^{2-}$, 15078-28-1.

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(24) Oxygen is consumed at a continuous proportion of ${}^1/_3$ mol/mol of nitrous acid formed. Then the total oxygen consumption, S_{O_2}, per mole of nitroprusside photolyzed is given by the expression $S_{O_2} = {}^1/_2 \sum_{n=0}^{\infty} ({}^1/_3)^n$. The sum of this series can be calculated from $S = a[(1 - r^n)/(1 - r)]$, where a is the first term of the series, ${}^1/_2$; r^n the last term, approaching zero; and r is the common ratio, ${}^1/_3$. Substitution gives S_{O_2} = 0.75.
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Spectroscopic Studies of Metal–Metal Bonding. VII. Absorption and Laser Raman Spectra and Vibrational Analyses of [(OC)5Re–M'(CO)5]- (M' = Cr, Mo, W)

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The absorption spectra (33–35,000 cm^{-1}) for the metal–metal bonded species ReCr(CO)$_{10}$-, ReMo(CO)$_{10}$-, and ReW(CO)$_{10}$- and the results of laser Raman measurements (0–2200 cm^{-1}), where obtainable, are reported. The vibrational spectral features have been assigned on the basis of C_{4v} symmetry, normal-coordinate analyses based on these assignments have been performed, and $k(\text{Re–M'})$ values have been found to be in the order $k(\text{Re–W}) > k(\text{Re–Mo}) > k(\text{Re–Cr})$. For isoelectronic species $k(\text{Re–Re}) > k(\text{Re–W})$ and $k(\text{Re–Mn}) > k(\text{W–Mn}) > k(\text{Re–Cr})$. Comparison of "$k(\text{M–M'})$" values of the ReM'(CO)$_{10}$- anions, of the previously investigated MnM'(CO)$_{10}$- species, and of the neutral decacarbonyls MM'(CO)$_{10}$ (M = M' = Mn, Re, Tc; M = Mn; M' = Re) is made.

Introduction

The compounds [(CO)5Re–M'(CO)5]- (M' = Cr, Mo, W) are members of the MM'(CO)$_{10}$ series of metal–metal bonded molecules in which changes in metal–metal bond strength, $k(\text{M–M'})$, can be studied as a function of both M and M'. The complete series of known species includes M2(CO)$_{10}$ (M = Mn, Tc, Re), MM'(CO)$_{10}$ (M = Mn; M' = Re), MM'(CO)$_{10}$- (M = Mn, Re; M' = Cr, Mo, W), and M2(CO)$_{10}$²- (M = Cr, Mo, W). Each of these is essentially isostructural with the others, and isoelectronic relationships exist between individual species to form three series: (1) Mn2(CO)$_{10}$, MnCr(CO)$_{10}$-, and Cr2(CO)$_{10}$²-; (2) Re2(CO)$_{10}$, ReW(CO)$_{10}$-, and W2(CO)$_{10}$²-; (3) ReMn(CO)$_{10}$, MnW(CO)$_{10}$-, and ReCr(CO)$_{10}$-. To investigate series 2 and 3, the values of $k(\text{M–M'})$ for ReCr(CO)$_{10}$- and ReW(CO)$_{10}$- are required, and to investigate the effect on $k(\text{M–M'})$ of changing M' from a first- to second- to third-row transition metal bound to the same M, the complete ReM'(CO)$_{10}$- series is of interest. With reported studies of MnM'(CO)$_{10}$- [2] and M2(CO)$_{10}$³⁻¹⁵ series and MnRe(CO)$_{10}$,[4] this study of ReM'(CO)$_{10}$- series permits investigation of nuclear charge distribution effects on $k(\text{M–M'})$ through isoelectronic series 2 and 3 above.

We report in this paper the infrared, laser Raman, and uv–visible spectra of the tetraethylammonium (Et4N+) salts of ReCr(CO)$_{10}$-, ReMo(CO)$_{10}$-, and ReW(CO)$_{10}$- and the tetraphenylarsonium (Ph4As+) salt of ReW(CO)$_{10}$-, their vibrational normal-coordinate analyses, and the bonding implications of the results in comparison with the related species discussed above.

Experimental Section

The compounds Et4NReCr(CO)$_{10}$, Et4NReMo(CO)$_{10}$, Et4NReW(CO)$_{10}$, and Ph4AsReW(CO)$_{10}$ were prepared by the procedure of Anders and Graham[16] using modifications described previously.[2] The reagents were purified by sublimation, recrystallization, and distillation, where appropriate, and the reactions were carried out under dry N2 or Ar. Samples of the compounds were prepared by recrystallization from 95% ethanol or by repeated recrystallization from tetrahydrofuran using *n*-pentane as the precipitating agent. The purity of each compound was established by elemental analyses (Re, M', C, H, N) and by the 5-μ infrared solution spectra. The analyses, performed by Baron Consulting Co. and Midwest Microlab, Inc., agreed with expected values to within 0.5% for the transition metals and 0.2% for C, H, and N. The 5-μ spectral measurements agreed with those of reported work.[16]

Solutions, mulls, powders, and pellets used for spectroscopic measurements were prepared and handled under a dry N2 atmosphere or *in vacuo* using dried and deaerated solvents and were sealed in N2-purged cells. Sealed capillary, fused-silica, and multipass Raman cells or sealed KBr, CsI, and high-density polyethylene far-infrared liquid cells were used where appropriate.

Infrared spectra were measured on a Beckman IR-11 or IR-12 spectrometer with a resolution and accuracy of *ca.* 1 cm^{-1} as determined by standard resolution tests and wave number calibration.[17] The mercury lamp (ir) source was filtered with carbon-filled polyethylene when used. The laser Raman spectra were measured on a Jarrell-Ash 25-300 Raman spectrometer, using He–Ne 632.8-nm laser radiation, with a resolution of *ca.* 3 cm^{-1} and an accuracy of 1 cm^{-1}. Uv–visible spectra were measured on a Cary 15 spectrometer.

Since these compounds are unstable in air and upon standing in solution, their 5-μ infrared spectra were recorded before, after, and from time to time during the measurement of the reported spectra,