composition of $[(NH_2CH_2CO_2^-)_2Cu^{III}-CH_3(aq)]_R$ is 0.1 s^{-1}. Therefore, the steady-state concentration of this complex is $[[NH_2CH_2CO_2^-)_2Cu^{III}-CH_3]_R]_{ss} \approx 3 \times 10^{-7}/0.1 \approx 3 \times 10^{-6}$ M. Under these conditions, in solutions containing 1.0×10^{-3} M $Cu^{II}(NH_2CH_2CO_2^-)_2$, the yield of ethane is 2.0 and that of methane is 1.6 (Table II). This means that of the methyl radicals $(2.0 + 1.6)/(2 \times 2.0 + 1.6) = 3.6/5.6$ react via reaction 7 whereas 2.0/5.6 react via reaction 11. Therefore, $1.0 \times 10^{-3} \times k_7/3 \times 10^{-6} \times k_{11} = 3.6/2.0$; i.e., $k_7/k_{11} = 5.4 \times 10^{-3}$. Assuming that $k_7 = 2.5 \times 10^7$ M^{-1} s^{-1}, the value obtained at the low-dose-rate experiments, one obtains therefore $k_{11} = 2.5 \times 10^7/5.4 \times 10^{-3} \approx 5 \times 10^9$ M^{-1} s^{-1}. However, clearly this value of k_7 contains a contribution of reaction 11, and therefore, the calculated k_{11} is an upper limit. The conclusion that k_{11} approaches the diffusion-controlled limit is not surprising, as similar rates were recently reported for analogous reactions.[13-16]

The spectra of $[(NH_2CH_2CO_2^-)_2Cu^{III}-CH_3]$ and $[(NH_2CH_2CO_2^-)_2Cu^{III}-CH_3(aq)]_R$ should be compared with those of (peptidate)Cu^{III}-R, where R = alkyl. The results clearly indicate a significant blue shift when the amino acid is replaced by its peptides. This result is in accord with the assignment of these bands to ligand to metal charge-transfer bands, taking into account that the redox potential of the peptide complexes is considerably lower than that of the glycine complex.[17] The reason for the dependence of the apparent absorption coefficient on the dose per pulse (Table I) is the competition between reactions 7 and 11.

It should be noted that we do not observe the formation of $Cu^{III}(NH_2CH_2CO_2^-)_2^+$ as predicted by reaction 9, as the specific rate of decomposition of the latter complex is considerably faster than k_9.[11]

A comparison of the reaction of $^{\bullet}CH_3$ radicals with $Cu^{2+}(aq)$ and with $Cu^{II}(NH_2CH_2CO_2^-)_2$ sheds some light on the effect of ligands on the mechanism of reaction of copper(II) ions with aliphatic free radicals. In both reactions a transient with a copper(III)-carbon σ bond is formed. However, the rate of reaction with $Cu^{II}(NH_2CH_2CO_2^-)_2$ is faster by about 2 orders of magnitude than that with $Cu^{2+}(aq)$.[18] This effect probably stems from the lowering of the oxidation potential by the amino acid ligand. Furthermore $Cu^{III}-CH_3(aq)$ decomposes into $Cu^+(aq) + HOCH_3$ whereas $(NH_2CH_2CO_2^-)_2Cu^{III}-CH_3(aq)$ decomposes into $Cu^{III}[(NH_2CH_2CO_2^-)_2^+(aq) + CH_4$, a fact that clearly stems from the effect of the ligands on the redox potential of the central copper ion.

The difference in the mechanism of reaction observed for methyl radicals, this study, and benzyl radicals, reaction described in ref 2, with $Cu^{II}(NH_2CH_2CO_2^-)_2$ is probably due to the fact that methyl radicals are considerably stronger oxidizing agents and that they are less stabilized by resonance.

Finally, we wish to point out that these results indicate that aliphatic free radicals can oxidize copper(II) complexes with available biological ligands under physiological conditions. As it is reasonable to assume that the tervalent copper complexes thus formed have biologically deleterious effects, these observations suggest that this might be another mechanism contributing to the radiosensitization by copper ions, which is usually attributed to a reduction of the copper complexes by the free radicals followed by a Fenton like reaction. Thus, aliphatic free radicals might cause deleterious effects, which are usually attributed to the reaction of hydroxyl free radicals.

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Registry No. $Cu(NH_2CH_2CO_2)_2$, 13479-54-4; CH_3, 2229-07-4; CH_4, 74-82-8; C_2H_6, 74-84-0; $(NH_2CH_2CO_2)_2CuCH_3$, 129916-84-3.

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Pentacyanoamminechromate(III). Synthesis, Characterization, and Photochemistry

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The $Cr(CN)_5(NH_3)^{2-}$ ion was synthesized by irradiation of $Cr(CN)_6^{3-}$ in methanol and reaction with NH_3, isolated as the potassium salt, and characterized by analysis, chromatography, aquation, absorption spectroscopy (λ_{max} at 397 and 320 nm, as predicted theoretically), and phosphorescence (λ_{max} at 777 nm, $\tau = 32$ μs at 20 °C in Me_2SO). Ligand field excitation causes release of both NH_3 and CN^-. The respective quantum yields are 0.08 and 0.06 in H_2O, 0.05 and 0.007 in Me_2SO, and 0.11 and 0.003 in dimethylformamide. The prevalence of NH_3 loss is in agreement with the angular overlap model but not with previous photolysis theories. The medium markedly affects the absorption spectrum, the emission behavior, the photoreaction efficiencies, and especially the Φ_{NH_3}/Φ_{CN^-} ratio; the changes are interpreted in terms of solvent orientation and hydrogen bonding. The phosphorescence is observed in aprotic solvents but not in H_2O and is quenched by $Co(sep)^{3+}$. In Me_2SO, at least 90% of each photoreaction mode remains unquenched upon complete doublet-state quenching. Both photoprocesses are concluded to proceed from the lowest quartet excited state prior to intersystem crossing. Results for $Cr(CN)_6^{3-}$ photolyzed in Me_2SO in the absence and in the presence of $Co(sep)^{3+}$ are also reported, and the two systems are compared.

Introduction

Pentacyanochromates(III) constitute a potentially rich yet little explored class of anionic complexes that may be regarded as a counterpart of the widely investigated pentaamminechromium(III) cations. Although several $Cr(CN)_5X^{z-}$ species have been mentioned in the literature, their study has probably been limited by difficulties in the isolation of suitable amounts of these compounds. Thus, acid hydrolysis of $Cr(CN)_6^{3-}$ results in solutions of $Cr(CN)_5(H_2O)^{2-}$ mixed with products of subsequent aquation,[1] and Cr(II)-catalyzed CN^- loss in alkaline medium leads to equilibria between $Cr(CN)_6^{3-}$ and $Cr(CN)_5(OH)^{3-}$.[2,3] Similarly, reaction of $Cr(NCS)_6^{3-}$ with KCN yields mixtures of all the $Cr(CN)_{6-n}(NCS)_n^{3-}$ ions, from which the $n = 1$ component can be

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separated by either ionophoresis[4] or chromatography.[5]

$Cr(CN)_5X^{2-}$ are the photolysis products of $Cr(CN)_6^{3-}$ in various solvents. The complexes with X = H_2O,[6] Me_2SO,[7] and MeCN[8] were more or less characterized through the spectral changes of irradiated solutions, and that with X = DMF (dimethylformamide) was also isolated chromatographically.[9] Except for the reported preparation of $K_3[Cr(CN)_5(OH)]\cdot H_2O$,[10] in no other case were solid salts obtained.

It is noteworthy that the spectral transitions of a number of pentacyanochromates(III) unknown to date were anticipated two decades ago on the basis of ligand field (LF) theory.[11] Regarding the photochemistry, some data have recently appeared on the CN^- photoaquation of the species with X = H_2O and OH^-.[12]

As we have long been interested in the ground-state[13-15] and excited-state[16-22] properties of chromium(III) cyano ammines, it was natural to direct our attention to the X = NH_3 system. This paper deals with the synthesis and characterization of $K_2[Cr(CN)_5(NH_3)]$, as well as with its photophysical and photochemical behavior; the preparative procedure itself involves a photochemical step. Notable features of the new complex are its phosphorescence in solution at room temperature, the occurrence of two photosubstitution reactions, and the large energy spacing between the photochemically relevant, lowest quartet and doublet LF excited states.

Experimental Section

Materials. $K_3[Cr(CN)_6]$,[23] $(Ph_4P)_3[Cr(CN)_6]$,[24] $[Co(NH_3)_5F](ClO_4)_2$,[25] and $[Co(sep)](PF_6)_3$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane)[26] were prepared according to literature procedures. Anion-exchange experiments were performed with a Sephadex QAE A-25 resin; gel filtration chromatography employed a Sephadex G 15 resin. Dimethyl sulfoxide (Me_2SO) and dimethylformamide (DMF) were dried with 4-Å molecular sieves (Merck). All other chemicals and solvents were of reagent grade.

Potassium Pentacyanoamminechromate (III). A filtered solution of 2.0 g of $(Ph_4P)_3[Cr(CN)_6]$ (1.6×10^{-3} mol) in 12 mL of methanol was irradiated in a quartz spectrophotometer cell of 4.0-cm path length, under continuous stirring at room temperature. The irradiation band, of 380-nm maximum and 40-nm half-width, was selected by a monochromator from a 200-W, high-pressure Hg lamp. The photoreaction was followed spectrophotometrically by periodical sampling and was protracted until the 382-nm maximum of $Cr(CN)_6^{3-}$ virtually disappeared, being progressively replaced by a band centered at 432 nm. Conversion of about three-fourths of the reactant to $Cr(CN)_5(MeOH)^{2-}$ occurred in ca. 500 h. An 80-mL volume of a saturated solution (ca. 4 M) of NH_3 in methanol was then added, and the mixture was kept at 50 °C for 4–5 h in a stoppered flask. After NH_3 degassing at room temperature, rotary evaporation of the solvent left a yellow-orange solid consisting of $(Ph_4P)_2[Cr(CN)_5(NH_3)]$ and unreacted $(Ph_4P)_3[Cr(CN)_6]$.

Isolation of the product by gel filtration chromatography required conversion of the above water-insoluble salts into water-soluble compounds, which was accomplished by reprecipitation from ethanol with a saturated ethanolic solution of CH_3COOK, centrifugation, and repeated washing with ethanol. An aqueous solution of the potassium salts was eluted with water through a 40 × 2 cm column of G 15 resin. A faster moving, orange-red band contained minor amounts of species other than the reactant and the product. The main, orange-yellow fraction separated into two bands, consisting of $Cr(CN)_6^{3-}$ and $Cr(CN)_5(NH_3)^{2-}$, in order of recovery. As some band overlap remained, the mixed-complex portion was eluted once more through the same column, after being concentrated by rotary evaporation at 30 °C under reduced pressure. The eluates containing the pentacyano complex were combined and rotary-evaporated to dryness as above. The yellow solid was washed with ethanol and vacuum-dried. All operations were carried out in dim light. The yield of $K_2[Cr(CN)_5(NH_3)]$ was 0.25 g, or 55% of the theoretical. Analysis gave a Cr:CN:NH_3 proportion of 1.00:(4.93 ± 0.12):(0.99 ± 0.03). A 20–25% amount of inert material, mostly CH_3COOK, was present. Its mole ratio to the complex close to 1 suggests possible coprecipitation. Despite this occurrence, chromatography and spectra (absorption, emission, excitation) warranted the absence of extraneous complexes, so that the product was employed without further recrystallization, to avoid a yield reduction of as much as 50%.

Analyses and Instrumentation. Cr was determined spectrophotometrically at 374 nm (ϵ 4745 M^{-1} cm^{-1}) after oxidation to CrO_4^{2-} by alkaline H_2O_2. Because of the inertness of cyano complexes in basic media (vide infra), a preliminary acid treatment was necessary to promote removal of CN^- as in analogous instances.[13,14] The samples were heated with 10 M $HClO_4$ at 80 °C for 10 min. (*Caution*! Me_2SO and DMF solutions must be diluted with water to ca. 5:1 before adding $HClO_4$, in order to avoid possible explosion.) After cooling, they were alkalinized with NaOH pellets and boiled for another 10 min to complete decomposition, which was followed by H_2O_2 addition and further heating.

Free CN^- and NH_3 were respectively measured by means of Amel 201-CN and Orion 95-12 selective electrodes, connected with a Radiometer PHM-84 potentiometer. In both cases the pH was adjusted to ca. 11 with NaOH. Dimethyl sulfoxide samples were diluted to 5:1 with water prior to analysis, in order to avoid damage and/or malfunction of the electrodes. Calibration was performed during each run by use of a series of fresh KCN + NaOH or NH_4Cl + NaOH standards. The presence of complexes did not cause analytical interference for at least 30 min after alkalinization, as thermal CN^- release of either the reactant or the products was negligible at pH < 11. The reproducibility was ±4% for CN^- and ±6% for NH_3. The NH_3 content of complexes (either as solids or in solution) was determined by a semimicro Kjeldahl method.

Optical densities were measured by a Beckman DU spectrophotometer. UV–vis absorption curves were recorded by either a Cary 17 instrument or a Hewlett-Packard 8452A diode-array spectrophotometer. The spectra of $Cr(CN)_5(NH_3)^{2-}$ were quantified by determination of chromium in the solution samples. Emission spectra were obtained by means of a Perkin-Elmer 650-10S spectrofluorometer, equipped with an R928 photomultiplier. No correction for instrument response was attempted, as the phototube output is fairly constant in the range of interest, allowing wavelength identification of the sharp emission peaks. Phosphorescence lifetimes were determined by the use of a J & K System 2000, frequency-doubled ruby laser, delivering 20-ns pulses of 200-mJ energy at 374 nm. The emission decays, monitored by a Hamamatsu R928 tube, were recorded on a Tektronix 468 storage oscilloscope, digitized, and computer-processed. All solutions to be used for either absorption or emission measurements were filtered through 0.45-μm Millipore filters.

Procedures. The photolysis apparatus was that employed earlier,[16-22] equipped with a thermopile calibrated by ferrioxalate[27] and Reinecklate[28] actinometry. The pH of aqueous solutions was either 3.3 ($HClO_4$) or 7.2 (0.01 M NaH_2PO_4/0.01 M Na_2HPO_4). Filtered aliquots of 2.5-mL volume were irradiated in 10-mm, square cuvettes at 20.0 ± 0.5 °C under stirring. Complex concentrations were ca. 5×10^{-3} M. As samples were partially transparent, the absorbed energy was determined as previously described.[29] In quenching experiments, both $Co(NH_3)_5F^{2+}$ and $Co(sep)^{3+}$ were 1×10^{-5}–5×10^{-4} M. Since the LF spectral maxima of the cyano complexes around 400 nm match the minima of the quenchers (ϵ 10–15), the latter absorbed less than 2% of the exciting light, so that correction for mixed absorption was smaller than experimental uncertainty. In order to reduce error sources in comparing quantum yields in the presence and in the absence of quenchers, photolyses were carried out simultaneously by alternating short, partial irradiations of the two types of samples under identical conditions. Total photodecomposition was

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Table I. Ligand Field Spectral Data for Chromium(III) Cyano Ammine Complexes

complex	solvent	absorption: λ, nm[a] $^4A_{2g} \rightarrow {}^4T_{2g}$[b]	$^4A_{2g} \rightarrow {}^4T_{1g}$[b]	emission: λ, nm $^2E_g \rightarrow {}^4A_{2g}$[b]	$E(Q_1^0-D_1^0)$,[c] cm^{-1}	ref[d]
$Cr(NH_3)_6^{3+}$	H_2O	464	350	654	4000	33, 36
$Cr(NH_3)_5(CN)^{2+}$	H_2O	451	347	680	5500	13, 20
trans-$Cr(NH_3)_4(CN)_2^+$	H_2O	440	344	698	5900	14, 20
cis-$Cr(NH_3)_4(CN)_2^+$	H_2O	436	342	700	6400	14, 20
$Cr(CN)_5(NH_3)^{2-}$	H_2O	397 (90)	320 (54)			*e*
	Me_2SO	406 (77)	324 (58)	777	9300	*e*
	DMF	406 (72)	316 (66)	777	9300	*e*
$Cr(CN)_6^{3-}$	H_2O	377 (86)	307 (60)			1
	Me_2SO	386 (78)	313 (56)	800	11300	*e*
	DMF	391 (78)	317 (53)	803	11200	37

[a] For the anionic complexes extinction coefficients are given in parentheses, with an uncertainty of ±1 $M^{-1}\ cm^{-1}$. The values for the pentacyano complex are based on the chromium content of solution samples. [b] O_h approximation. [c] Energy differences between the lowest thermally equilibrated quartet and doublet excited states, evaluated according to ref 63. [d] First reference: absorption. Second reference: emission. [e] This work.

generally 15–20%. While in Me_2SO, DMF, and pH 7.2 aqueous solution, thermal CN^- loss was unappreciable within analytical accuracy, some aquation did occur at pH 3.3. In all cases, however, such reactivity was allowed for by analyzing in parallel photolyzed and dark samples.

Results

Preparation. The main nuisance in the obtainment of fair amounts of $Cr(CN)_5X^{z-}$ species by conventional methods is the reaction cascade resulting in mixtures that often contain low percentages, if any, of the desired product.[1-5,10] The present alternative route combines the selectivity of photosubstitution[30,31] (eq 1) with an efficient thermal process (eq 2).

$$Cr(CN)_6^{3-} + MeOH \xrightarrow{h\nu} Cr(CN)_5(MeOH)^{2-} + CN^- \quad (1)$$

$$Cr(CN)_5(MeOH)^{2-} + NH_3 \xrightarrow{kT} Cr(CN)_5(NH_3)^{2-} + MeOH \quad (2)$$

Reactions such as (1) are well-known to follow LF excitation in various solvents.[6-9] Since the LF maxima of the reactant (382 nm) and the product (432 nm) are sufficiently separated, narrow-band irradiation induces clean replacement of one ligand up to 75% photosolvation, as indicated by the permanence of isosbestic points at 396 and 353 nm (Figure 1). The red spectral shift is consistent with substitution of CN^- by a spectrochemically weaker, oxygen-coordinated species. An unavoidable drawback is the long irradiation period. If polychromatic light is employed to reduce the reaction time, the isosbestic behavior is soon lost, as secondary photolysis leads to uncontrolled displacement of more CN^- groups.

The use of methanol presents several advantages. (a) Due to its low coordinating ability, MeOH is readily replaced in reaction 2. (b) It dissolves large concentrations of NH_3. (c) Unlike other solvents, it is easily eliminated for product recovery. In fact, reactions 1 and 2 were also found to proceed in Me_2SO and DMF, with the additional benefit that, in the latter, secondary photolysis (consisting of DMF photoexchange, according to predictions; vide infra) does not subtract any monosubstituted product. However, these solvents hindered all other operations.

Photoreleased CN^- tends to recoordinate and, depending on the ratio between light intensity and complex concentration, photostationary states may be attained. Stage 2 is virtually complete, so that only two complexes of different charge and polarity are involved in the subsequent chromatographic separation. As expected, during this stage the above LF maximum moves back to the blue (397 nm). Exploratory work showed that other ligands, such as NCS^-, can be coordinated to the $Cr(CN)_5$ moiety by similar procedures.

Any attempt to react thermally $Cr(CN)_6^{3-}$ with NH_3, either as a liquid or in methanol solution, was unsuccessful. An additional observation is that minor quantities of $Cr(CN)_5(NH_3)^{2-}$ are formed along with other cyano ammines and can be isolated as the Li^+ salt, when $Cr(NH_3)_5(Me_2SO)^{3+}$ is treated with excess NaCN in Me_2SO. This route was not pursued, however, because of its complexity and scant yield.

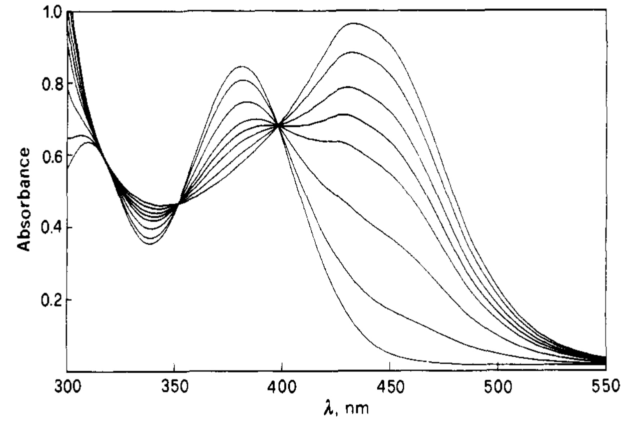

Figure 1. Spectral changes of a solution of $(Ph_4P)_3[Cr(CN)_6]$ in methanol, under irradiation with 380-nm light at room temperature: initial trace, maximum at 382 nm; final trace, maximum at 432 nm.

The novel compound was authenticated by elemental analysis, ion-exchange tests, aqueous reactivity, and absorption and emission spectroscopy. The 2– charge was confirmed by adsorption on the Sephadex anionic resin, followed by displacement with 1.5 M NaCl, of ionic strength insufficient to move $Cr(CN)_6^{3-}$.

$Cr(CN)_5(NH_3)^{2-}$ is remarkably inert in dipolar aprotic solvents and in neutral or alkaline aqueous solution, as indicated by its spectral constancy for several days at room temperature. On the contrary, acidification (2 M $HClO_4$) causes rapid and complete CN^- aquation (ca. 12 h at room temperature). The behavior is quite similar to that of $Cr(CN)_6^{3-}$[1] and other chromium(III) cyano ammines.[13-15] The LF absorption bands are progressively red-shifted, and the absence of isosbestic points denotes stepwise ligand loss. Also, the intense Cr → CN charge-transfer band (vide infra) disappears. The final spectrum, stable for at least 48 h at room temperature and at any pH between 0 and 2, presents maxima at 545 (ϵ 19) and 396 nm (ϵ 18), in good agreement with the literature data for $Cr(H_2O)_5(NH_3)^{3+}$.[32]

Spectra. The UV-vis absorption spectrum is shown in Figure 2. The two LF bands are assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ excitations in O_h approximation. The 20-nm bathochromic displacement relative to $Cr(CN)_6^{3-}$ is congruent with coordination of one lower field NH_3 ligand, as inferred from the LF data for the available terms of the $Cr(NH_3)_{6-n}(CN)_n^{3-n}$ series,[1,13,14,33] gathered in Table I. In the actual C_{4v} symmetry, both excited states are expected to split into the respective $^4E + {}^4B_2$ and $^4A_2 + {}^4E$ components, in order of increasing energy.[11] The sequence is the same as in the $Cr(NH_3)_5X^{z+}$ ions with X spectrochemically

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Table II. Photolysis Quantum Yields upon $^4A_{2g} \rightarrow {}^4T_{2g}$ Excitation[a] at 20 °C

complex	medium[b]	Φ_{NH_3}[c]	Φ_{CN^-}[c]	Φ_{NH_3}/Φ_{CN^-}
$Cr(CN)_5(NH_3)^{2-}$	H_2O, pH 3.3	0.079 ± 0.003 (2)	0.058 ± 0.006 (4)	1.3
	H_2O, pH 7.2	0.076 ± 0.004 (5)	0.059 ± 0.005 (2)	1.3
	Me_2SO	0.052 ± 0.007 (8)	0.007 ± 0.001 (9)	7
	Me_2SO, Q	0.049 ± 0.006 (4)	0.007 ± 0.001 (5)	7
	DMF	0.112 ± 0.010 (2)	0.003 ± 0.001 (2)	35
$Cr(CN)_6^{3-}$	H_2O		0.12[d]	
	Me_2SO		0.028 ± 0.004 (6)	
	Me_2SO, Q		0.026 ± 0.004 (3)	
	DMF		0.08[e]	
	MeCN		0.04[f]	

[a] O_h approximation. Irradiation band of 400-nm maximum and 14-nm half-width. [b] Q denotes photolyses in the presence of 5×10^{-4} M $Co(sep)^{3+}$. [c] Number of independent determinations in parentheses. The uncertainties are usually standard deviations, except for the data based on two runs, for which the range of results is given. [d] References 6 and 39. [e] Reference 9. [f] Reference 8.

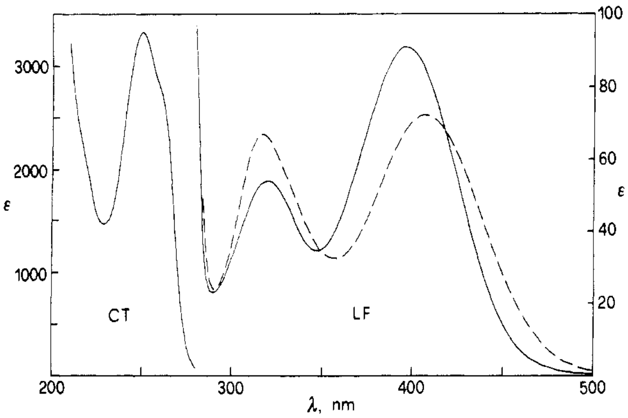


Figure 2. Charge-transfer (CT, left scale) and ligand field (LF, right scale) absorption spectra of $Cr(CN)_5(NH_3)^{2-}$ in water (solid line) and dimethylformamide (broken line).

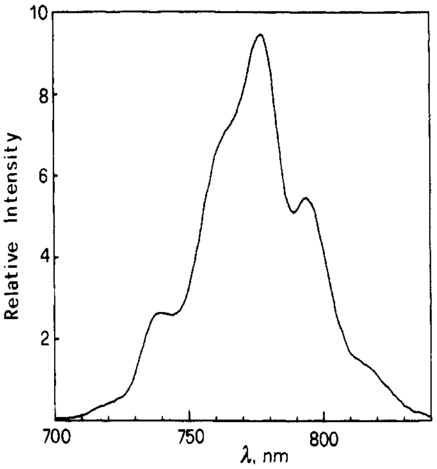


Figure 3. Emission spectrum of $Cr(CN)_5(NH_3)^{2-}$ in dimethylformamide solution at room temperature (uncorrected).

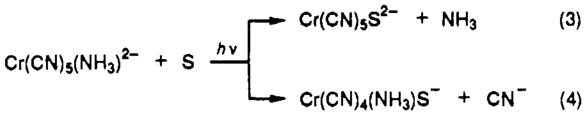
weaker than NH_3. Only for $Cr(NH_3)_5(CN)^{2+}$ are the splittings, of course, reversed.[13,16]

LF theoretical predictions are in good agreement with experiment: the four transitions from the $^4B_1$ ground state were calculated to occur at 397–377 and 319–312 nm.[11] The comparatively small separation between each pair of sublevels (ca. 1300 and 700 cm^{-1}, respectively) accounts for the lack of any splitting, even in the low-energy band. Remarkably, each maximum coincides with one of its predicted components: in particular the long-wavelength band matches the energy evaluated for the $^4B_1 \rightarrow {}^4E(^4T_{2g})$ transition. This is usually true with tetragonal chromium(III) complexes;[11] moreover, in most of the systems where the separation is observable, ^4E is indeed associated with a stronger absorption than $^4B_1$.[11,34]

The UV region displays a high-intensity band with maximum at 251 nm (ε 3300) and shoulders at 263 (ε 2450) and 220 nm (ε 1950). This is attributed to a metal-to-ligand, $t_{2g}(Cr) \rightarrow t_{1u}(\pi^*,CN)$ charge-transfer transition, on the grounds of its close resemblance in position, intensity, and shape with the analogous absorption of $Cr(CN)_6^{3-}$[35] and of its disappearance upon total CN^- aquation.

The pentacyano complex luminesces at room temperature in dipolar aprotic solvents but not in aqueous media. The moderately intense and structured emission band, reported in Figure 3, is assigned as phosphorescence from the $^2B_1/^2A_1$ lowest doublet state(s). The regularity of the emission maxima,[20,36,37] included in Table I, may be taken as additional proof for the ligand environment. As expected for an increasing number of coordinated cyanides, on one hand, the higher overall field strength raises the energy of the spin-allowed LF transitions, and on the other hand, the enhanced nephelauxetic effect lowers the energy of the spin-forbidden, intraconfigurational transitions.[33,38]

Photolyses and Quenching. The photobehavior was studied in water, Me_2SO, and DMF as solvents. While the thermal reactivity is one of exclusive CN^- loss, LF excitation induces simultaneous substitution of both types of ligands by the solvent S (eqs 3 and 4). Each of these reactions is in agreement with the observed



$$Cr(CN)_5(NH_3)^{2-} + S \xrightarrow{h\nu} Cr(CN)_5S^{2-} + NH_3 \quad (3)$$

$$Cr(CN)_5(NH_3)^{2-} + S \xrightarrow{h\nu} Cr(CN)_4(NH_3)S^- + CN^- \quad (4)$$

red shift of the LF bands. At pH 3.3 and 7.2 the photoproducts are expected to be in their aquo form, usually more stable than the hydroxo form. The pK_a for $Cr(CN)_5(H_2O)^{2-}$ is, in fact, 9.0,[2,10] and a similar value is reasonably assumed for $Cr(CN)_4(NH_3)(H_2O)^-$. Quantum yields were generally obtained at 20 °C. For pH 3.3 solutions, in which CN^- aquation is nonnegligible at room temperature, some measurements were repeated at 5 °C in order to restrain the thermal processes: the Φ_{CN^-} values do not differ significantly from those at 20 °C.

In DMF solution NH_3 cannot be determined, due to interference of the dimethylamine produced by hydrolysis of the solvent in the basic medium required by analysis. Since in this case the spectral variations are virtually unaffected by CN^- photorelease, which corresponds to only 2% of the photoreactivity, Φ_{NH_3} can be obtained from the absorption changes, on the basis of the known LF spectrum of $Cr(CN)_5(DMF)^{2-}$.[9] Postirradiation effects are ruled out by the stability for several hours of difference spectra between photolyzed and dark solutions. Table II summarizes the NH_3 and CN^- quantum yields upon irradiation of the low-energy LF band under various conditions.

The phosphorescence decay of $Cr(CN)_5(NH_3)^{2-}$ is monoexponential, with a lifetime of 32 μs in Me_2SO at 20 °C. Removal

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of dissolved oxygen by argon saturation does not modify appreciably both the intensity and the lifetime.

Addition of water to the dimethyl sulfoxide solution reduces the luminescence; the effect is rather modest, however, as a 40% v/v amount is necessary for 95% quenching. Also, the I^-, $Ni(aq)^{2+}$, and $Co(aq)^{2+}$ ions exert a moderate quenching action.

In the presence of $Cr(CN)_6^{3-}$, the drop of the 777-nm emission is accompanied by the rise of a new, partially overlapping band around 800 nm, typical of hexacyanochromate(III) (Table I), indicating energy transfer to the latter.

Cobalt(III) amine complexes, such as $Co(NH_3)_5F^{2+}$ and $Co(sep)^{3+}$, are efficient quenchers of the phosphorescence. Stern–Volmer plots for lifetime quenching are linear, with bimolecular rate parameters in Me_2SO at 20 °C of $k_q = 1.1 \times 10^9$ and 1.9×10^9 M^{-1} s^{-1}, respectively.

A number of photolyses in Me_2SO were performed in the presence of these ions, under conditions where ca. 97% of the emission is quenched. The results are included in Table II. The interaction with $Co(NH_3)_5F^{2+}$ is "noninnocent", in that the apparent NH_3 quantum yield increases: evidently, photosensitization of the quencher results in the liberation of extra amounts of ammonia. There is also spectral evidence that the cobalt(III) species may coordinate part of free cyanide, simulating a CN^- quenching effect.

$Co(sep)^{3+}$ rules out the above complications, as the cage-type ligand ensures complete thermal and photochemical inertness.[26] Addition of this complex leaves both the NH_3 and CN^- photosolvation yields unchanged, within an unavoidable experimental uncertainty of 10%. With a similar degree of reliability, the result is confirmed by difference spectrophotometry, which indicates the same extent of total photoreaction upon identical light exposure in the presence and in the absence of $Co(sep)^{3+}$.

Photochemistry of $Cr(CN)_6^{3-}$ in Me_2SO. The purpose of these experiments was to check the procedures and to supplement literature data for other solvents.[6,8,9,39] The quantum yield for CN^- photosolvation on 400-nm irradiation is reported in Table II.

The phosphorescence intensity, centered at 800 nm, is efficiently quenched by $Co(sep)^{3+}$ with a Stern–Volmer constant $k_{SV} = 2 \times 10^5$ M^{-1}. The emission lifetime was not determined; however, from its magnitude in other dipolar aprotic solvents[37] a k_q value of 10^8–10^9 M^{-1} s^{-1} may be estimated. Also in this system the photoreactivity is virtually unaffected, within error limits, by a quencher concentration able to extinguish ca. 97% of the emission.

Discussion

Ligand Photolabilization. Unlike the ground-state chemistry, characterized by a fair stability of the $Cr-NH_3$ bond even after complete CN^- loss, the LF excited-state chemistry is dominated by NH_3 solvation (Table II). The total photoreaction yields (ca. 0.14 in H_2O, 0.11 in DMF, and 0.06 in Me_2SO) are significantly lower than the values generally found for chromium(III) acido ammines but are in the range of those for $Cr(CN)_6^{3-}$.[30,31] Also, the decrease in photoreactivity on passing from water to nonaqueous solvents parallels our and literature data[6,8,9,39] on hexacyanochromate(III), entered for comparison in Table II.

To our knowledge, $Cr(CN)_5(NH_3)^{2-}$ is the first negatively charged, mixed-ligand chromium(III) species subject to two concurrent photosubstitution modes. There are relatively few other reports on anionic non-O_h complexes: *trans*-$Cr(NH_3)_2(NCS)_4^-$[28] and $Cr(en)(C_2O_4)_2^-$[40] are known to undergo photorelease of one type of ligand only, while for $Cr(EDTA)(H_2O)(CN)_2^{3-}$,[41] $Cr(CN)_5(H_2O)^{2-}$,[12] and $Cr(CN)_5(OH)^{3-}$,[12] CN^- photoaquation, but not H_2O photoexchange, was sought. It is therefore interesting to compare the present results with the theoretical expectations for competitive ligand photolabilization.

The lowest quartet excited state, to which all the models refer, is here ^4E as mentioned above, with a σ antibonding electron density prevalently localized on the $CN-NH_3$ axis (82% d_{z^2}).[42] The angular overlap approach of Vanquickenborne and Ceulemans,[42] presently recognized as a reliable standard, is considered first. Table III reports the bond energies, $I^*(Cr-L)$, for the various ligands in the ^4E state, calculated by means of the σ and π parameters of the two-dimensional spectrochemical series.[42] The results of Table II show that this procedure is successful in quantitatively predicting $\Phi_{NH_3} > \Phi_{CN^-}$, on the basis of the lowest strength for the $Cr-NH_3$ bond. Cyanide labilization is anticipated to occur in the axial position.

Table III. Bond Energies (cm^{-1}) for the ^4E Excited State of $Cr(CN)_5X^{z-}$ Complexes, Evaluated by Use of the Parameters and Procedures of Ref 42[a]

X	σ_X	π_X	$I^*(Cr-X)$	$I^*(Cr-CN)_{ax}$	$I^*(Cr-CN)_{eq}$
NH_3	7180	0	8480	10300	14520
Me_2SO	6400[b]	1720[b]	12480	9990	14670
DMF	5800	640	8400	9770	14780
H_2O	5940	500	8180	9820	14760
OH^-	8120	1390	14160	10720	14300

[a] $\sigma_{CN^-} = 8480$ cm^{-1}; $\pi_{CN^-} = -290$ cm^{-1}. While for chromium(III) acido ammines the LF parameter *B* is usually taken as 700 cm^{-1}, a value of 550 cm^{-1} is assumed here for cyano complexes (see ref 11); the difference, however, does not affect the relative bond energies. [b] Data from ref 43.

It should be noticed that this system proves particularly diagnostic toward the available theories. Inferences from earlier models in fact disagree with the experimental data. Adamson's semiempirical rules[44] would predict prevalent solvation of the strong field ligand (CN^-) on the weaker field axis ($CN-NH_3$). Similarly, qualitative σ/π MO treatments[45-47] envisage preferential CN^- release as a consequence of a general σ bond weakening along the *z* axis, coupled with the loss of π stabilization for CN^- (but not for NH_3), since the t_{2g} orbitals depleted by the transition are π bonding toward π-acceptor groups as cyanide. These discrepancies arise from the fact that the early approaches are based on excited-state bonding changes and do not take into account the initial, large ground-state strength of the $Cr-CN$ σ bond. The contribution of the latter continues to be experienced in the excited state and is believed to be responsible for the low, apparently anomalous quantum yields of $Cr(CN)_6^{3-}$.[30,31]

As this class of complexes has not been considered previously, it seems worthwhile to extend the theoretical comparison to other monosubstituted cyanochromates(III) for which some information has been obtained. Thus, the $I^*(Cr-L)$ values included in Table III are consistent with the observation that the photoproduct of $Cr(CN)_6^{3-}$ undergoes secondary photolysis in Me_2SO but not in DMF: $Cr(CN)_5(Me_2SO)^{2-}$ is, in fact, expected to lose axial CN^-, while $Cr(CN)_5(DMF)^{2-}$ would be more inclined to solvent photoexchange. Also, the reported Φ_{CN^-} values of 0.04 and 0.09 for the $Cr(CN)_5(H_2O)^{2-}$ and $Cr(CN)_5(OH)^{3-}$ ions[12] are in agreement with the respective preferences for H_2O and CN^- release.

A further remark is that the strong solvent dependence of the quantum yields, and especially that of the ratio between photoreaction modes, points to the importance of chemical factors, besides the electronic ones, in determining the photochemical pattern: photolabilization is far from being a merely intramolecular process, as the models tend to assume.

Medium Effects. The pronounced influence of the solvent on both the photophysical and the photochemical properties can find a simple and common explanation in the possibility of hydrogen bonding in water but not in Me_2SO and DMF. Clearly, this is not the unique factor, but it must be significant enough to emerge among others.

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Table I and Figure 2 illustrate such an influence on the LF absorption maxima, especially on the long-wavelength one, which is the more sensitive to modification of the coordination sphere.[11,33,38] The higher transition energy in aqueous medium can be ascribed to a solvation shell tightened by CN–H_2O hydrogen bonding, enhancing the ligand perturbation on the central metal. In general, solvent effects on LF transitions are expected to be rather small,[38] and reports on this aspect are sparse.[34b,37,48,49] The literature data, as the present ones, reveal red shifts on going from aqueous to nonaqueous solutions; furthermore, anionic species, such as *trans*-$Cr(NH_3)_2(NCS)_4^-$[49] and $Cr(CN)_6^{3-}$,[37] appear to undergo larger variations (up to 950 cm^{-1}) than cationic ones, such as $Cr(NH_3)_5(CN)^{2+}$ and $Cr(NH_3)_4(CN)_2^+$.[20] The greater discrimination of anions between protic and nonprotic media can be understood in terms of orientation of the positive ends of the solvation molecules toward the complex, more appropriate for hydrogen-bond formation if protons are available.

Also, the appreciable changes in the extinction coefficients and in the ratio between the two maxima may be related to different extents of solvent participation in the vibronic interactions through which the Laporte-forbidden LF transitions gain intensity.

The same type of interaction can be invoked to justify the lack of any detectable emission in water. A good solute–solvent vibrational coupling would increase the rate of radiationless deactivation of the doublet state(s). Whatever the deactivation mechanism,[37,50] this result was not unexpected, in view of the analogous behavior of the $Cr(CN)_6^{3-}$ anion.[9,37]

The data of Table II indicate that solvent orientation and hydrogen bonding must also play a significant role in the photochemistry. The general reduction of the quantum yields in Me_2SO, compared to H_2O and DMF, can be explained by the need of solvent reorientation during the decay of the reacting state, in order to coordinate through the oxygen atom. The higher the viscosity [$\eta(\mathrm{DMF}) = 0.80$, $\eta(H_2O) = 0.89$, and $\eta(Me_2SO) = 1.98$ cP at 25 °C], the less favored solvent attack and ligand replacement. The above is in line with earlier observations on quantum yield/fluidity correlations for the *trans*-$Cr(NH_3)_2(NCS)_4^-$ anion.[51,52]

Of special interest here is the finding that, from H_2O to Me_2SO and DMF, Φ_{CN^-} decreases by 1 order of magnitude, in contrast with a much smaller change for Φ_{NH_3}. The dramatic variation (ca. 30-fold) of the mode *ratio* is accounted for by the capability of coordinated cyanide to hydrogen-bond with the facing H atoms of water molecules. This interaction is expected to assist solvent interchange with CN^- in H_2O, but not in Me_2SO or DMF, and possibly to facilitate quartet excited-state distortion. Within this line of reasoning, mixed-ligand anionic complexes are more suited than cationic ones to bring out solvent effects on the reactivity ratio. In the latter species the propensity to hydrogen-bond with the oppositely oriented solvation shell is larger for NH_3 than for CN^-. However, such bonding would now occur with the oxygen atoms, common to both protic and nonprotic molecules, and potential discriminations may be leveled off.

From another point of view, the different Φ_{NH_3}/Φ_{CN^-} ratios may be correlated with the different solvents' ability to stabilize the charge separation in the transition state, as was proposed for $Rh(NH_3)_5Cl^{2+}$.[53] The solvation of simple anions, such as Cl^- and CN^-, in fact decreases in the order $H_2O > Me_2SO >$ DMF,[54,55] while neutral NH_3 is expected to be much less sensitive to the solvent nature.

Finally, all the above chemical effects of solvent can be taken as a further clue in support of the associative nature of chromium(III) photosubstitution.[30,31]

Excited-State Reactivity. The present results are relevant to the longstanding question as to the possible involvement of the doublet state (D_1) in the photoreactivity.[30,31,56]

In a now classic study of $Cr(CN)_6^{3-}$, the phosphorescence in DMF was quenched by water, while Φ_{CN^-} was unaffected. Photosubstitution was thus demonstrated to occur entirely from the lowest quartet excited state (Q_1) prior to intersystem crossing.[9] The large Q_1–D_1 separation of hexacyanochromate(III) precludes back intersystem crossing (BISC), ruling out the ambiguity incurred with other chromium(III) systems, where the separation is smaller and emission quenching is accompanied by partial reaction quenching. In such instances, delayed Q_1 reaction following BISC is a potential path for photochemistry,[21,57,58] to be considered in addition to either direct D_1 reaction[59–61] or crossing from D_1 to a reactive ground-state intermediate.[56,62]

Table I reports an estimate of the gap between the lowest thermally equilibrated Q_1 and D_1 states (denoted by the superscript zero) of the known cyano ammines: the D_1^0 energies are taken from emission maxima, while the Q_1^0 ones are evaluated from absorption bands by use of the 5% empirical procedure.[63] As mentioned above, the larger the number of CN^- ligands, the wider the gap. It is seen that the $E(Q_1^0–D_1^0)$ value of $Cr(CN)_5(NH_3)^{2-}$ is somewhat smaller than that of $Cr(CN)_6^{3-}$, but still large (ca. 110 kJ mol^{-1}) enough to prevent BISC.

A novel aspect of $Cr(CN)_5(NH_3)^{2-}$ is the occurrence of two distinct photoprocesses: a possibility to be explored was that one reaction proceeded from Q_1 or Q_1^0, and the other from D_1^0. Within the attainable experimental precision, it can be concluded here that at least 90% of each photoreaction remains unquenched upon complete D_1^0 quenching. The direct or indirect participation of this state in chemical deactivation is therefore excluded for this complex also. With a similar degree of precision, the same result is established for $Cr(CN)_6^{3-}$, photolyzed in Me_2SO under identical quenching conditions so as to provide a fair comparison.

As to the quenching process, it may be pointed out that the relatively low D_1 energies of $Cr(CN)_5(NH_3)^{2-}$ and $Cr(CN)_6^{3-}$ bring about difficulties in finding efficient and "innocent" quenchers, like those able to quench the majority of the chromium(III) emitting species: the present investigation contributes with the suitability in this regard of $Co(sep)^{3+}$. The interaction with this ion is very likely one of energy transfer. This is energetically allowed, as the lowest triplets of cobalt(III) amines lie around 13 000 cm^{-1} (770 nm);[64] it is also consistent with the diffusional magnitude of the bimolecular rate constants[65] and the probable photosensitization of the electronically similar $Co(NH_3)_5F^{2+}$ ion. The exceptional inertness of $Co(sep)^{3+}$ warrants an "innocent" behavior.

The quenching efficiency is by 2 orders of magnitude higher than that of other species employed earlier with $Cr(CN)_6^{3-}$ in DMF solution,[66] and at least 10^5-fold that of H_2O. The latter

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circumstance makes the present tests more severe than the reported water quenching experiments in DMF.[9] The large H_2O concentration (ca. 20 M) needed to extinguish the emission is expected to modify substantially the environment (as inferred from the spectral changes; cf. Table I); moreover, preferential solvation, favored by hydrogen bonding, may enhance the H_2O content of the second coordination sphere. Since Φ_{CN^-} in H_2O is ca. 50% larger than Φ_{CN^-} in DMF (Table II), its invariance upon addition of water to DMF might result from compensation of some reaction quenching (i.e., the possible contribution of D_1 to the reactivity) with an increment of the CN^- yield.

As a last note, the evidence provided by $Cr(CN)_5(NH_3)^{2-}$ for the quartet as the only, or largely predominant, reaction precursor corroborates previous interpretations with other chromium(III) am(m)ine complexes where LF excitation gives rise to two[19,58b,67,68] or even three[21] different products. The following features are common to all these systems: (1) BISC is possible on energetic grounds; (2) the photoreactivity can be partially quenched; (3) the proportion of the various modes is the same for the quenchable and unquenchable photochemistry.

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Photoinduced Electron Transfer by Coordination Chemical Pathways across Pyrite/Electrolyte Interfaces

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Experiments are presented which show that, in the case of pyrite (FeS_2), interfacial transition-metal bridge complexes formed by attaching –O–, –CN–, or –CO– groups facilitate electronic charge transfer more efficiently by inner-sphere mechanisms (strong interaction) than may occur by tunneling (weak interaction). This is advantageous concerning electrode stability and catalytic activity. The described experiments also show that appropriate chemical surface modifications can channel photogenerated charge carriers through the interface of d-character materials at a high photocurrent density (~30 mA cm^{-2}) and with good stability. Individual –CN– groups attached to the FeS_2 interface pass photogenerated charge carriers at least 10^6 times before a side reaction occurs. New models have to be developed to describe the semiconductor/electrolyte interface in cases with strong chemical interaction. A first qualitative picture is presented.

Introduction

Semiconductors possessing valence bands with pronounced d character like MoS_2, RuS_2, and FeS_2 have proved to be reasonably efficient in converting light to electricity and fuels in electrochemical solar cells.[1,2] In addition, semiconducting materials containing transition-metal clusters have been shown to be catalytically active particularly for multielectron transfer reactions.[3,4] A proposed explanation for these favorable properties is the involvement of interfacial coordination chemistry. To substantiate the importance of chemical interaction at the semiconductor/electrolyte interface during electron transfer processes, a FeS_2 photoelectrode in contact with an Fe^{2+} containing electrolyte has been selected as a model system. As a semiconductor, FeS_2 is still a poorly explored material for which neither the stoichiometry nor the doping has yet been optimized. The synthetic samples used (grown by vapor transport) have a sulfur deficit[5] (most likely Fe_2S_3) causing a defect concentration of approximately 10^{20} cm^{-3}. These defects give rise to energy levels within the forbidden energy gap, which are probably responsible for the small photopotential (200 mV) but do not affect the very large quantum efficiency (80–90%) observed in the presence of appropriate electron donors (I^-, Br^-, $Fe(CN)_6^{4-}$). Previous experiments with FeS_2 have shown that the positively charged Fe^{2+} ion is an inefficient electron donor at the illuminated pyrite surface.[6] This has been interpreted as being caused by the ion's inability to interact with the interfacial iron states, where photogenerated holes are available for reaction.[2,6]

To facilitate coordination chemical transfer of holes from Fe states in the FeS_2 interface to Fe^{2+} ions in the electrolyte (which can only exchange electrons by tunneling), various bridge complexes can be made by introducing the appropriate ligand (=O, =CO, =CN) to the pyrite/electrolyte interface. The experimental aim of this work was to explore the advantage of such bridges for interfacial photoinduced electron transfer.

The theory of photoelectrochemical kinetics started with Gärtner's model,[7] and during the following 20 years scientists focused their attention mainly on the semiconductor part of the interface, describing physical properties such as charge separation, transport, and recombination within the solid-state phase.[8,9] In the presence of a sufficiently high concentration of the redox species and adequate mass transport conditions, interfacial electron transfer, assumed to occur via tunneling processes, typically appeared not to be rate limiting.[10,11] Lately, with the exploration of Fermi level pinning[12,13] and with kinetic suppression of corrosion via d-state photoelectrochemical reactions,[1] it became obvious that for some systems interfacial electron transfer is as important for the overall performance of the photoelectrode as semiconductor bulk properties. Classical theoretical models including interfacial reactions of a semiconductor with a redox couple in solution are based on quantum-mechanical tunneling, assuming weak interaction between the semiconductor and the redox couples in so-

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