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Solid-State Photoreactions of *trans*-$[Cr(en)_2X_2]Y \cdot xH_2O$ Compounds

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A number of salts of *trans*-$[Cr(en)_2X_2]^+$ (where X = Br^-, Cl^-, F^-, and NCS^-) have been surveyed for solid-state photoreactions. The large majority were photoinert, but it was found that *trans*-$[Cr(en)_2Br_2]Br \cdot H_2O$ underwent a very efficient photoaquation reaction to yield *cis*-$[Cr(en)_2H_2OBr]^{2+}$, determined by ion-exchange chromatography. In contrast, the anhydrous bromide salt was photoinert. A similar solid-state photoaquation was observed for the corresponding chlorine-containing monohydrated compound. Measurements of the quantum yield of the bromide photoaquation on powdered samples yielded values in the range 0.45 ± 0.2 varying with extent of conversion and method of calculation, showing that the efficiency of photoaquation in the solid state is very similar to that for the reaction in solution.

Introduction

Although a large number of solution studies of photochemical processes in chromium(III) complexes exist,[1-3] little quantitative information has been reported on any solid-state photochemical processes. This is so despite many qualitative observations of degradations of chromium complexes when exposed to light. There have been some studies of solid-state photoreactions of complexes of other metals, and for the large majority the observed processes have transpired to be photoredox processes.[4] Some $Cr(en)_3X_3$ (X = Br^-, Cl^-, NCS^-) compounds undergo ethylenediamine loss[5] with acido ligand insertion to give $[Cr(en)_2X_2]X$ species with cis configuration for Cl^- and Br^- but trans for NCS^-. The corresponding iodide was reported[6] to photolyze to a monodentate ethylenediamine/iodide-substituted metastable intermediate. More recently, hydroxide and chloride photoanation reactions have been observed[7] in solutions of $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5(H_2O)]^{3+}$, and $[Cr(NH_3)_2(NCS)_4]^-$ in frozen aqueous and ethanolic glasses.

The present study was motivated by casual observations that the bromide salt of *trans*-$[Cr(en)_2Br_2]^+$ was particularly light sensitive and rapidly underwent a dramatic color change from green to red on exposure to room light. This suggested the possibility of a solid-state photoisomerization reaction, and initially the process was studied as a possible entry route to synthesis of *cis*-$[Cr(en)_2XY]$ compounds by photolysis of $[Cr(en)_2X_2]Y$. We report here our results showing that in fact the process is one of photoaquation involving crystal water, a type of solid-state photochemical process previously unreported.

Experimental Section

Preparation of Materials. *trans*-$[Cr(en)_2Br_2]Br \cdot H_2O$ was prepared from *trans*-$[Cr(en)_2F_2]^+$ chloride or perchlorate by the method of Fee, Harrowfield, and Jackson.[8] Although the yield from the chloride was lower, the product was cleaner than from the perchlorate. Use of a polypropylene beaker also avoided much contamination of the product. The monohydrate salt was readily dehydrated by washing with 100% ethanol, or by drying at 70 °C, and could be rehydrated by washing with 95% ethanol. The water of crystallization was determined by thermogravimetric analysis in a slow stream of dry nitrogen. The results corresponded closely to the theoretical for both the anhydrous bromide and the monohydrate. Anal. Calcd for $[Cr(en)_2Br_2]Br \cdot H_2O$: Cr, 12.08; C, 11.17; H, 4.22; N, 13.04; Br, 55.77. Found: Cr, 12.11; C, 11.50; H, 4.17; N, 13.10; Br, 53.62.

trans-$[Cr(en)_2Cl_2]Cl$ and its monohydrate were prepared in an analogous manner, and *trans*-$[Cr(en)_2(NCS)_2]ClO_4$ was obtained as described in the literature.[9]

Salts with various other counterions were prepared from a concentrated, slightly acidic (pH 3) aqueous solution of the dibromo bromide by precipitation with an excess of the appropriate sodium, potassium, or ammonium salt. In this way were obtained the iodide, chloride, perchlorate, thiocyanate, cyanate, nitrate, and dicyanoargentate. The method failed for the cyanide, acetate, chlorate, oxalate, and sulfate. Thermogravimetric analysis of the compounds obtained showed them all to be anhydrous. With the exception of the thiocyanate, which was commonly contaminated with excess KSCN, the purity of the compounds was greater than 95% as determined by chromium analysis.

Thermogravimetric Analysis. On a Cahn electrobalance, 50-mg samples of the compounds were heated to 120 °C in a stream of dry nitrogen and their weight loss was continuously recorded. Most compounds showed only a fraction of a percent weight loss owing to adsorbed moisture.

Chromium Analysis. Chromium was determined spectrophotometrically as chromate ion, $\epsilon_{372nm} = 4.82 \times 10^{-3}$ L mol^{-1} cm^{-1}, after oxidation by H_2O_2 in sodium hydroxide solution.

Photochemical Studies. In the survey experiments, complexes of the solid compounds were exposed to fluorescent room light both in the atmosphere and also in desiccators to provide an anhydrous atmosphere. Extent of any photochemical reaction was determined visually from the accompanying color change (green → red for the dibromo compounds) and by ion-exchange chromatography.

For quantitative measurements, a 1000-W high-pressure capillary mercury arc source was employed together with a 436-nm interference filter and 5 cm^3 of water to remove heat. The extent of reaction was followed by the change in sample reflectance at 520 nm (a wavelength of maximum absorbance for the starting material) on a Cary type II integrating sphere reflectance accessory with a Cary 17 spectrophotometer. This instrument normally illuminates the sample with white light, but since this resulted here in rapid sample photolysis, the equipment was modified by adding a 520-nm interference filter in the light beam prior to the integrating sphere. In some of our early studies, reflectance was followed at 520 nm while photolyzing with the instrument white light source.

Ion-Exchange Chromatography. Samples were chromatographed on a 7.0 cm × 0.9 cm column of Hamilton HCX8 cation-exchange resin (20–25-μm diameter) using 0.5 M $(NH_4)_2SO_4$ in 10^{-3} M H_2SO_4 as the eluent. With a flow rate of 114 mL h^{-1}, elution times were 30, 44, and 75 min for *trans*-$[Cr(en)_2Br_2]^+$, *trans*-$[Cr(en)_2BrH_2O]^{2+}$, and *cis*-$[Cr(en)_2BrH_2O]^{2+}$, respectively. The number of theoretical plates was ~ 300.

Chromatograms were obtained on a Technicon autoanalyzer. The reaction chemistry was to mix the eluent with 2 vol of 1 M NaOH and 1 vol of 0.5% H_2O_2, heat at 90 °C for 20 min, cool, and measure the CrO_4^{2-} absorbance at 372 nm, with continuous readout on a recorder. Typical chromatograms are shown in Figure 1.

Results and Discussion

Photochemical Survey. Samples of *trans*-$[Cr(en)_2Br_2]X$, where X = NCS^-, ClO_4^-, NO_3^-, Br^-, I^-, NCO^-, and $Ag(CN)_2^-$, together with the bromide monohydrate, *trans*-$[Cr(en)_2Cl_2]Cl$ and its monohydrate, *trans*-$[Cr(en)_2F_2]Cl$, and *trans*-$[Cr(en)_2(NCS)_2]ClO_4$ were exposed to the laboratory fluorescent lighting for periods up to 1 month. Of these, the dibromo bromide monohydrate and the dichloro chloride monohydrate showed rapid

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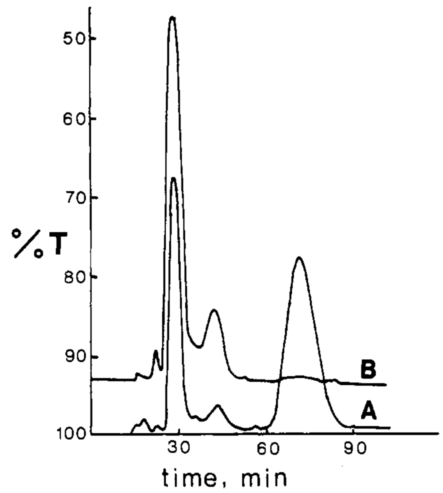

Figure 1. Ion-exchange chromatograms: (A) solid *trans*-$[Cr(en)_2Br_2]Br \cdot H_2O$ after prolonged exposure to light; (B) solid *trans*-$[Cr(en)_2Br_2]Br \cdot H_2O$ kept in the dark (curve displaced upward for clarity). The major peaks are *trans*-$[Cr(en)_2Br_2]^+$ at 30 min, *trans*-$[Cr(en)_2H_2OBr]^+$ at 44 min, and *cis*-$[Cr(en)_2H_2OBr]^{2+}$ at 70 min. The remaining small peaks represent less than 1% material; several are sulfate anation products from the thermal reaction with the eluant during solution preparation.

color changes while the remainder showed at most only small, slow color changes. When the exposures were repeated for several of these latter in a rigorously dry atmosphere, they were found to be photoinert.

The thiocyanate salt was a particularly interesting example in that it appeared at first to undergo a fairly efficient photoreaction, yielding ion-exchange chromatographic peaks for *cis*- and *trans*-$[Cr(en)_2BrH_2O]^{2+}$ and *cis*- and *trans*-$[Cr(en)_2NCSH_2O]^{2+}$. We think these results arise, however, by the following: (a) atmospheric water adsorption owing to the presence of some excess KSCN in the compound; (b) "solution" thermal and photochemical aquation to *trans*- and *cis*-$[Cr(en)_2BrH_2O]^{2+}$; (c) partial anation of this mixture to *trans*- and *cis*-$[Cr(en)_2NCSBr]^+$ in the presence of the KSCN solution; (d) later hydrolysis of these latter products under the chromatographic conditions to yield the observed *cis*- and *trans*-$[Cr(en)_2H_2ONCS]^{2+}$. This system was therefore not studied further, except to confirm the anation step by the observation of the growth of the Cr–NCS bond in the IR spectrum and to show that very carefully purified thiocyanate salt did not undergo any photoreaction. We conclude therefore that, except for the two monohydrate compounds noted above, all these compounds studied are photoinert and that solid-state photoisomerization or anation reactions are disfavored processes.

For the two genuine examples of solid-state photochemistry, ion-exchange chromatography showed that the product obtained was mainly *cis*-$[Cr(en)_2H_2OX]^{2+}$ with little or possibly no trans isomer. For the bromide salt specifically, greater than 90% of the product was in the cis configuration. The uncertainty implied in this lower limit arises owing to *trans*-$[Cr(en)_2H_2OBr]^{2+}$ produced by thermal reaction prior to the ion-exchange column. Figure 1B shows that trans product is produced thermally to an extent of about 8% (±2%), very likely during solution preparation and handling prior to the column exchange and probably not significantly in the solid state. This conclusion is supported by observation of peaks of similar area for both fresh and old unphotolyzed samples. In the photolysis of the sample of Figure 1A, the *trans*-aquobromo peak is about 6% of the unreacted dibromo peak, suggesting that essentially all of the observed trans aquobromo arises from thermal reaction. The solid-state photoaquation therefore apparently leads to the *cis*-aquobromo product alone. No significant peak (>2%), corresponding to *cis*-$[Cr(en)_2Br_2]^+$, was observed in the ion-exchange chromatograms, suggesting that trans → cis photoisomerism is not a significant photoprocess and denying our initial hypothesis as to the nature of the reaction. There is the qualification that *cis*-$[Cr(en)_2Br_2]^+$ rapidly loses bromide in aqueous solution to produce *cis*-aquobromo and might therefore remain unobserved. Nevertheless, no residual *cis*-dibromo was observed, and more convincing, no trans–cis isomerization was found for any of the other salts. Taken as a whole, therefore, the results strongly suggest that no photoisomerization occurs and that the sole observed photoprocess is a true photoaquation.

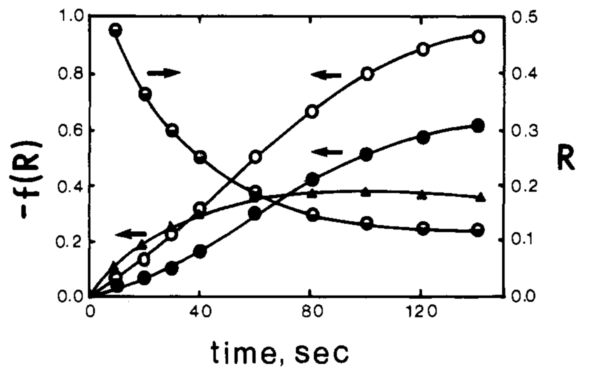

Figure 2. Reflectance changes and dependence of various reflectance functions on time for photolysis of solid *trans*-$[Cr(en)_2Br_2]Br \cdot H_2O$ using white light: ○, eq 1; ●, eq 2; △, eq 3 (left axis); ⊖, sample reflectance (right axis).

The quantum yield for the process in *trans*-$[Cr(en)_2Br_2]Br \cdot H_2O$ was measured by following the change in the powder reflectance spectrum at 520 nm, resulting from irradiation of a 1-mm thick layer, essentially opaque thickness, either with white light or with light at 436 nm, an isosbestic point for the reaction. As the reaction proceeded, the 520-nm reflectance of the sample decreased in a nonlinear fashion from an initial value of 0.482 to a final value of 0.067, measured against a $MgCO_3$ standard. Except for the differences in rate of photolysis, like reflectance changes were seen for the two modes of excitation. Quantitative experiments were carried out at two intensities of 436-nm irradiation.

Figure 1 shows a plot of reflectance vs. time for irradiation with white light. We have evaluated this and the data for monochromatic illumination by the methods proposed for thick powder samples by Simmons and co-workers.[10,11] They have suggested several different functional dependencies of reflectance on irradiation time and on other experimental parameters including the quantum yield. Because of the difficulty and uncertainty in evaluating quantum yields for reactions in powdered solids, three of these equations will be compared (eq 1–3), where n is the

$$(1 + R)^{-1} \ln [(f - f_P)/(f_A - f_P)] = -{}^2/{}_3 n^2 \phi \epsilon I_0 t \qquad (1)$$

$$(1 + R^2)^{-1} \ln \left[\frac{(\ln R)^2 - (\ln R_P)^2}{(\ln R_A)^2 - (\ln R_P)^2} \right] = -n^2 \phi \epsilon I_0 t \qquad (2)$$

$$\frac{1}{2} \ln \left[\frac{S}{S_A} \right] + \frac{f_P}{2(2f_P + f_P{}^2)^{1/2}} \ln \left[\frac{T}{T_A} \right] = -{}^2/{}_3 n^2 \phi \epsilon I_0 t \qquad (3)$$

refractive index, ϕ is the quantum yield, ϵ is the molar absorptivity, f represents the remission function $(1 - R)^2/2R$, $S = R^2/[1 - 2(1 + f_P)R + R^2]$, and $T = [R + 1 + f_P - (2f_P + f_P{}^2)]/[R + 1 + f_P + (2f_P + f_P{}^2)]$. No subscript appears for the sample reflectance, but subscripts A and P denote the values for starting material and final product, respectively. The cited references may be consulted for further details; eq 3 has been derived from the expressions given in Appendix A of ref 10, with correction of a sign error in equation A3.

Figure 2 shows plots of the left side of each of these equations for the reflectance/time data also shown in that figure. The following conclusions are evident. None of the equations gives a truly linear plot for the range of conversions of the surface material represented in the data, but all can be approximated as linear for very low conversions. We note that the sigmoidal shape

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Table I

I_0, einstein cm^{-2} s^{-1} × 10^9	conversion	ϕ_{cor}	
		eq 1	eq 2
3.5	high	0.50	0.65
3.5	high	0.41	0.56
1.43	high	0.29	0.45
3.5	low	0.38	0.45
3.5	low	0.38	0.44

of two of the plots is to be seen also in Simmons's published data.[10]

Equation 1 should have about $^2/_3$ the slope of eq 2, and for the higher conversions this prediction is obeyed well. For the lower conversions the factor is closer to 0.5. Equation 3 would be expected to yield values similar to those of 1 for low conversions, but instead it yields values closer to those of 2. In addition it shows a time dependence quite different from the other expressions. Since eq 1 and 2 seem to be in quite good agreement, we have based our quantum yield determinations on them. Table I shows quantum yields obtained by fitting the results to the best straight line for both low and high conversions at two monochromatic light intensities. The quantum yields have been corrected to take account of the fact that irradiation was at 436 nm where the sample has a constant, smaller reflectance than at 520 nm where the reflectance changes were analyzed. Since the light flux at the sample surface is proportional to $1 + R^2$, a correction factor $(1 + R_{436}{}^2)/(1 + R_{520}{}^2)$ was applied to the absorbed light intensity. This had the effect of reducing the quantum yields by 30%.

The quantum yields of Table I range from 0.29 to 0.65. The lowest value found, but not shown in the table, 0.26, is obtained from the zero time tangent to the plot of eq 1. Although there is a fairly large, and difficult to assess, uncertainty in these values, they confirm the qualitative observation that this is a rather efficient solid-state photoaquation. It is particularly interesting that the value is of the same order as the solution photoaquation yield[12] of 0.27, an observation reminiscent of the situation reported for photoredox reactions in some oxalate complexes.[13]

It is unfortunate that the single-crystal X-ray structure of this monohydrate salt has not been reported. It might have proved interesting to see whether the water of crystallization is particularly favorably disposed toward entry into the coordination sphere. It is, to us, a particularly interesting observation that the photoaquation apparently obeys the same photostereochemical selection rules that apply in solution. Clearly in the solid there is ample room for rearrangement throughout the course of substitution of the excited state.

We found that the photoaquation yield dropped by a factor of 10 on cooling to liquid-nitrogen temperature but photolysis still occurred. In this respect, the behavior is similar to recent observations for frozen solutions,[7] where it was found that some glassy solution environments remain photochemically active down to low temperature. It may be that in a crystal the low-temperature process involves defects and dislocation sites.

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Registry No. *trans*-$[Cr(en)_2Br_2]Br\cdot H_2O$, 30852-95-0; *trans*-$[Cr(en)_2Br_2]NCS$, 94499-31-7; *trans*-$[Cr(en)_2Br_2]ClO_4$, 28074-55-7; *trans*-$[Cr(en)_2Br_2]NO_3$, 94499-32-8; *trans*-$[Cr(en)_2Br_2]Br$, 14240-27-8; *trans*-$[Cr(en)_2Br_2]I$, 94499-33-9; *trans*-$[Cr(en)_2Br_2]NCO$, 94499-34-0; *trans*-$[Cr(en)_2Br_2]Ag(CN)_2$, 94499-36-2; *trans*-$[Cr(en)_2Cl_2]Cl$, 14301-97-4; *trans*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$, 94499-37-3; *trans*-$[Cr(en)_2F_2]Cl$, 19581-00-1; *trans*-$[Cr(en)_2(NCS)_2]ClO_4$, 43176-07-4; *cis*-$[Cr(en)_2BrH_2O]^{2+}$, 60429-48-3; *cis*-$[Cr(en)_2NCSH_2O]^{2+}$, 25078-44-8; *trans*-$[Cr(en)_2BrH_2O]^{2+}$, 17979-12-3; *trans*-$[Cr(en)_2NCSH_2O]^{2+}$, 25125-60-4.

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Photodisproportionation of (μ-Oxo)bis((tetrakis(4-carboxyphenyl)porphinato)iron(III))

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The water-soluble complex (μ-oxo)bis((tetrakis(4-carboxyphenyl)porphinato)iron(III)) has been synthesized and characterized. Its photochemistry has been studied in the presence of reductive amines. Continuous photolysis in the presence of either EDTA or TEOA results in the two-electron oxidation of the amine with a strongly wavelength-dependent quantum yield. The observed quantum yield at 409 nm is 5.2×10^{-5}, about half the 1.0×10^{-4} value measured for the aprotic-soluble analogue $(FeTPP)_2O$. Flash photolysis confirms that the primary photoprocess is disproportionation and that the oxidation of amines by the ferryl complex is complete within 100 ns.

Introduction

Recently we reported that (μ-oxo)bis((tetraphenylporphinato)iron(III)) ($(FeTPP)_2O$) will photochemically disproportionate to yield the ferrous and ferryl complexes. The ferryl complex represents a strong one-electron oxidant that may be trapped by triphenylphosphine.[1]

$$(FeTPP)_2O \xrightarrow{h\nu} FeO(TPP) + FeTPP$$

$$FeO(TPP) + PPh_3 \rightarrow FeTPP + OPPh_3$$

This photoreaction represents an alternative approach to the conventional use of long-lived excited states to generate strong oxidants.[2-4] Perhaps the most discouraging aspect of that work was the small quantum yield obtained ($\phi_0 = 1.0 \times 10^{-4}$). This quantum yield no doubt reflects the effects of primary (cage) and secondary recombination, and hence the absolute quantum yield may well be substantially higher. The nature of the excited state responsible for this photoreaction also remains in question.

There has been much interest in the photochemical conversion of sunlight to useful energy, with much attention being paid to the splitting of water. We have begun the study of a water-soluble μ-oxo-bridged complex, (μ-oxo)bis((tetrakis(4-carboxyphenyl)porphinato)iron(III)) ($(FeTPPC)_2O$). It was anticipated that the quantum yield should increase since the products would be

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