frequencies. The red shifts of 41.3 and 33 cm^{-1} for ν_1 and ν_3, respectively, are somewhat larger in magnitude than those reported by Perry et al.[18] for the similar SnF_2/C_6H_6 reaction system, with shifts of 29 and 19 cm^{-1} for these same two fundamental vibrational modes.

Work is currently underway to broaden the present research to include isotopic substitution (both ^2H and ^{13}C) and concentration-dependency studies between ethylene and tin and tin(II) fluoride; in addition, the studies will be extended to include other main group 4 atoms and halides. Such investigations should yield much additional knowledge concerning bonding between group 4A species and organic reactants, especially information related to acceptor–donor bond strengths involving bare metal atoms and metal halides with organic π-electron system donor ligands in reaction (and subsequent trapping) environments. These exclude solvent effects and tend to minimize intermolecular contact factors that would be encountered in conventional solid-state and solution chemistry, factors such as crystal-packing effects and hydrogen bonding which are eliminated when the reactants and the ensuing products are kept in very low concentrations in the frozen matrices.

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Registry No. Sn, 7440-31-5; SnF_2, 7783-47-3; C_2H_4, 74-85-1.

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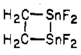
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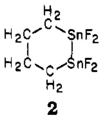
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from bulk cocondensation of SnF_2 with ethylene (analogous to SiF_2 condensation products[4a]) can also be postulated; however, the data obtained in the present study should be considered as only *very tentative* for any of these compounds. Consequently, all assignments in Table I refer to vibrational modes of the tin/tin(II) fluoride complexes of ethylene as resulting from a π-bonding interaction of the metal or metal fluoride species with the olefinic bond.
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Autocatalytic Chain Reaction in the Photochemical Decomposition of Tris(2,2′-bipyridyl)chromium(III) in Dimethylformamide[1]

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In an investigation of the excited-state properties of $Cr(bpy)_3^{3+}$ (bpy =2,2′-bipyridine) in DMF at room temperature, we have observed a chain reaction initiated by light leading to complete solvation of one bpy ligand. Previous work has demonstrated photoaquation of $Cr(bpy)_3^{3+}$ in alkaline solution.[2] Also in aqueous solution, some photoreduction of $Cr(bpy)_3^{3+}$ by such weak donors as $Ru(bpy)_3^{2+}$ and Fe^{2+} occurs followed by immediate back electron transfer, constituting therefore quenching of the phosphorescent state of $Cr(bpy)_3^{3+}$.[3]

We report evidence here that the chain carrier is a chromium(II) complex with bpy and that the chain reaction occurs via electron transfer.

Experimental Section

Tris(2,2′-bipyridyl)chromium(III) perchlorate, $[Cr(bpy)_3](ClO_4)_3$, was synthesized by a modification of published methods.[4–6] Addition of $Cr^{2+}(aq)$ to a nitrogen-saturated acidic aqueous suspension of excess bipyridine resulted in the immediate precipitation of purple-black microcrystals of $[Cr(bpy)_3](ClO_4)_2$ which were collected by filtration, washed with chloroform to remove excess ligand, and dried. This solid (which is stable in dry air[5]) was oxidized to $Cr(bpy)_3^{3+}$ by sprinkling it slowly (over the course of several hours) into 10 mL of 0.01 M $HClO_4$ which was continuously stirred and bubbled with oxygen or chlorine.[7] As the black solid dissolved and was oxidized, a yellow solution formed. The yellow $[Cr(bpy)_3](ClO_4)_3$ solid obtained on cooling was filtered and purified by recrystallization from dilute $HClO_4$.

This procedure gives a good yield and is superior to methods[4] in which the oxidizing agent is added slowly to a suspension of $[Cr(bpy)_3]^{2+}$. In acidic aqueous media, $Cr(bpy)_3^{3+}$ is inert, whereas $Cr(bpy)_3^{2+}$ is labile. Adding the reduced solid material slowly to an oxygen saturated acidic solution permits rapid oxidation to the Cr(III) form of the tris complex. Conversely, if the Cr(II) complex is allowed to equilibrate with an oxygen-free solution and then oxidized slowly, large amounts of pink crystals (presumably $[Cr(bpy)_2(H_2O)_2](ClO_4)_3$) are formed at the expense of the desired product.

Photolysis and emission measurements were carried out in DMF which was distilled daily at 25–30 °C under reduced nitrogen pressure. Sulfuric acid and copper sulfate were added to the still pot to prevent the formation of amine and formate impurities. Photolysis solutions were degassed for at least 1 h in a Zwickel flask with a stream of chromous-scrubbed, dried argon; a 3-mL aliquot was then transferred to a 1-cm spectrometer cell and sealed under 20 torr positive pressure of argon. The necessity for exhaustive degassing of the system cannot be overstressed. A He–Cd laser was used for irradiation at 325 or

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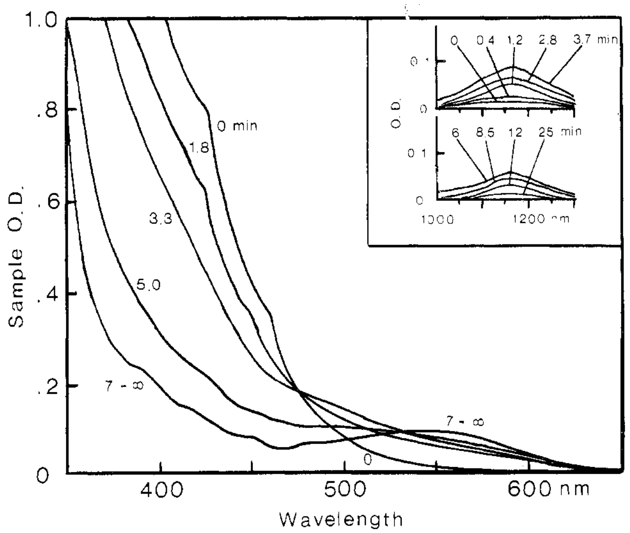

Figure 1. Spectra resulting from photolysis of 1.2×10^{-3} M $Cr(bpy)_3^{3+}$ in argon-saturated DMF. After a 1-min photolysis at 442 nm, the sample was placed in the spectrometer and the sequential visible spectra showing the secondary dark reaction were run. Near-IR spectra (inset) show the growth (upper) and decay (lower) of the peak assigned to the $Cr(bpy)_3^{2+}$ intermediate. These spectra were run under continuous photolysis conditions in situ by using the unfiltered "white" light from the IR source of the Cary 14 as the photolysis irradiation source. This source is much less intense than the laser used for the visible spectra; hence longer irradiation times were needed for the near-IR measurements.

442 nm at incident intensities of 2×10^{-6} and 5×10^{-6} einstein min^{-1}, respectively.

Results and Discussion

Figure 1 shows that the photolysis is followed by a secondary dark reaction characterized by an induction period, followed by *quantitative* decomposition of the substrate within minutes. This can be followed in situ by monitoring either the ^2E emission at 728 nm or one of the substrate absorption bands as a function of time. The reaction is very sensitive to chemical quenching by oxygen or other oxidizing impurities.

The data, such as presented in Figure 1, are consistent with the following simplified mechanism:

$$Cr(bpy)_3^{3+} \xrightarrow{h\nu} Cr(bpy)_3^{3+*} \quad (1)$$

$$Cr(bpy)_3^{3+*} \rightarrow Cr(bpy)_3^{2+} \quad (2)$$

$$Cr(bpy)_3^{2+} \xrightarrow{DMF} Cr(bpy)_2(DMF)_2^{2+} + bpy \quad (3)$$

$$Cr(bpy)_3^{3+} + Cr(bpy)_2(DMF)_2^{2+} \rightarrow Cr(bpy)_3^{2+} + Cr(bpy)_2(DMF)_2^{3+} \quad (4)$$

Reactions 3 and 4 form a catalytic cycle which accounts for the rapid, quantitative decomposition of the substrate in a secondary dark reaction.

This mechanism is analogous to one proposed[4,6] for the thermal decomposition of aqueous mixtures of tris(bipyridyl)chromium(II) and -(III). Traces of Cr^{2+} produced electrochemically have been observed[2,8] to catalyze the decomposition of $Cr(bpy)_3^{3+}$. Redox catalysis is also implicated in the problems noted in the synthetic procedures for the tris complex.[6]

Further support for photoredox catalysis is provided by the following observations. When solid $[Cr(bpy)_3](ClO_4)_2$ was added to argon-saturated DMF, the violet solution produced faded with time. The initial near-IR absorption spectrum of this solution had a broad peak at 1170 nm. Such a peak was also observable in the photochemical intermediate (Figure 1). $[Cr(bpy)_3](ClO_4)_2$ is somewhat more stable in argon-saturated methanol. Its absorption spectrum in this solvent has a near-IR peak similar to that observed in DMF, and the entire spectrum agreed with that published by König and Herzog[9] for the dibromide salt in methanol.

When a trace of solid $[Cr(bpy)_3](ClO_4)_2$ was mixed with a solution of $Cr(bpy)_3^{3+}$ in argon-saturated DMF, the resulting reaction mimicked the secondary dark reaction observed in the photolysis. The disappearance of substrate absorbance and the appearance of the final product absorption spectrum with time were similar to the two cases. This supports the postulate that $Cr(bpy)_3^{2+}$ is involved as a catalytic intermediate in the photodecomposition of $Cr(bpy)_3^{3+}$ in DMF. Further support is provided by the fact that traces of oxygen, too small to quench the phosphorescence, do effectively quench the photodecomposition presumably by oxidizing the chain carrier. A large excess of bipyridine has also been found to inhibit the photochemistry. The quantum yield was not measured quantitatively as the *entire substrate decomposes* in the dark during the catalytic phase.

Much of the previous work on the electrochemistry[4,8] and photochemistry and photophysics[2,7,10-12] of $Cr(bpy)_3^{3+}$ has been done in aqueous solutions. Changing the solvent to DMF has profound effects on the properties of the complex. While the absorption and emission spectra have similar profiles in these two solvents, our photochemical quantum yield in DMF is orders of magnitude larger than those reported[2,7] for aqueous solutions. However, we have observed that the emission intensity is reduced by a factor of 15 in DMF compared with that in water. A previous report[10] that the excited-state lifetime is unchanged in nonaqueous solvents, including DMF, led us to reexamine carefully the solvent effect on the luminescence lifetime of $Cr(bpy)_3^{3+}$ in argon deaerated solutions, using a pulsed nitrogen laser for excitation. In water we obtained a value of 62.6 ± 0.9 μs, in excellent agreement with published data.[2,7] However, in DMF the lifetime is 3 ± 1 μs. The previous lifetime measurements[10] involved the decay of transient excited-state absorbance rather than luminescence decay and neat DMF was not used.[7]. We have found that $Cr(bpy)_3^{3+}$ emission in mixed water–DMF systems has an intensity *and* lifetime that vary monotonically with concentration between the values for water and DMF solutions.

Registry No. $[Cr(bpy)_3](ClO_4)_3$, 23539-86-8.

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