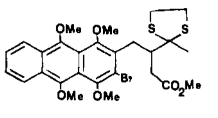

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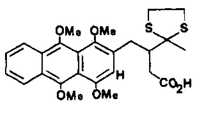

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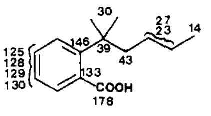
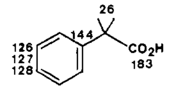
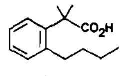
(11) Structure 7 is preferred rather than the isomeric iii on the basis of ^{1}H and ^{13}C NMR and mass spectral fragmentation. The ^{13}C NMR assignment is as shown below:







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Sequential Two Photon Photoredox Chemistry of Transition Metal Compounds. Nonlinear Intensity Effects in Photochemistry of the Reineckate Ion[1]

Sir:

Two photon photochemical effects appear to play a major role in the photochemistry of chlorophyll.[2] Two photon processes have been investigated in the luminescence of some dye molecules,[3] in the spectroscopy of a variety of substrates,[4,5] and in gas phase photochemical studies.[6] There have been few systematic investigations of two photon photochemical processes with condensed phase substrates.[7-9]

The reineckate ion, $Cr(NH_3)_2(NCS)_4^-$, has become an important chemical actinometer for visible radiation.[10] The use of the reineckate ion as a chemical actinometer depends upon the photoaquation of NCS^- (eq 1). However, near-ultraviolet excitations of $Cr(NH_3)_2(NCS)_4^-$ do lead to the formation of $(NCS)_2^-$ and Cr^{2+} in small yields ($\phi \sim 10^{-3}$) (eq 2).[11,12] Thus using $Co(NH_3)_5F^{2+}$(7×10^{-3} M) to scavenge for Cr^{2+} (eq 3)[13-15] we find that $\phi_{Co^{2+}} = 3.4 \times 10^{-3}$ for 337-nm irradiations (xenon lamp with cut-off filter and monochromator) and 7.7×10^{-3} for 254-nm excitations (low pressure mercury lamp). In these same experiments, we found the quantum yields for NCS^- aquation to be 0.25 and 0.30,[15,16] respectively.

$$Cr(NH_3)_2(NCS)_4^- + h\nu \xrightarrow[H_2O]{} Cr(NH_3)_2(NCS)_3(OH_2) + NCS^- \quad (1)$$

$$Cr(NH_3)_2(NCS)_4^- + h\nu \xrightarrow[H^+]{} Cr^{2+} + 2NH_4^+ + (NCS)_2^- + 2NCS^- \quad (2)$$

$$Cr^{2+} + Co(NH_3)_5F^{2+} \xrightarrow[H^+]{k_3} CrF^{2+} + 5NH_4^+ + Co^{2+} \quad (3)$$

While investigating the suitability of the reineckate ion as an actinometric reference for visible-near-UV laser and dye laser systems, we have found that both these product yields increase for 337-nm pulsed nitrogen laser excitations (1 MW, 10-ns pulse width). For example, at the highest power levels[17] we found $\phi_{NCS^-} \simeq 0.5$ and $\phi_{Co^{2+}} \simeq 0.015$.[18] Under these conditions both ϕ_{NCS} and $\phi_{Co^{2+}}$ are intensity dependent, the former decreasing with I_a and the latter increasing with I_a (Figure 1). For moderate intensities $\phi_{Co^{2+}}$ is proportional to I_a, but at the highest power levels $\phi_{Co^{2+}}$ approaches an intensity independent limit (Figure 1). This is suggestive of a "saturation" effect of the sort expected when the ^{2}E concentration is significantly depleted by the absorption of a second photon and the accompanying photoredox processes. Such a "saturation" effect could only be important when the rate of excited-state light absorption becomes equal to or greater than the normal rate of excited state decay.

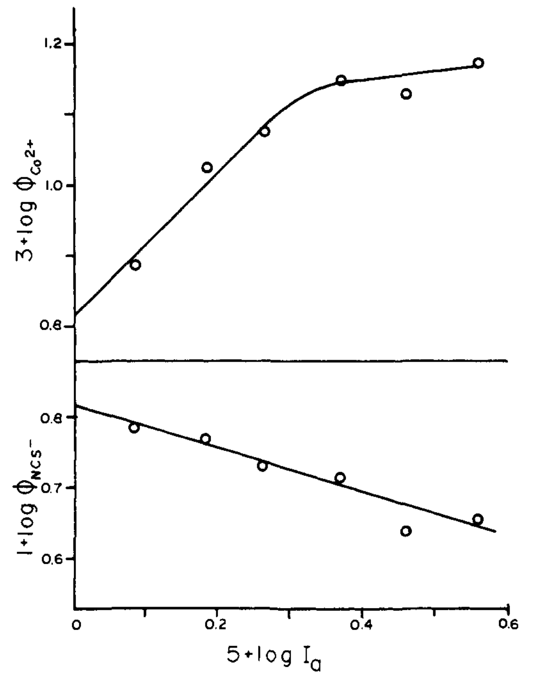

Figure 1. Variations of product quantum yields for redox (upper curve) and for NCS^- aquation (lower curve) with intensity during the 337-nm laser photolysis of *trans*-$Cr(NH_3)_2(NCS)_4^-$ in the presence of $Co(NH_3)_5F^{2+}$ in 0.01 M $HClO_4$.

If we take the NCS^- aquation process to be a characteristic reaction of quartet ligand field excited states,[19-21] then the laser induced processes may be described by eq 4-11 and

$$Cr(NH_3)_2(NCS)_4^- + h\nu \xrightarrow{I_a} {}^4CT^* \quad (4)$$

$$^4CT^* \longrightarrow Q^* \quad (5)$$

$$^4CT^* \xrightarrow[H^+]{\phi_0} Cr^{2+} + 2\,NH_4^+ + (NCS)_2^- + 2NCS^- \quad (6)$$

$$Q^* \longrightarrow Q_0 + \text{heat} \quad (7)$$

$$Q_0 \overset{K_8}{\rightleftharpoons} {}^2E \quad (8)$$

$$^2E + h\nu \xrightarrow{\phi' I_a'} Cr^{2+} + (NCS)_2^- + 2NCS^- + 2NH_4^+ \quad (9)$$

$$Q_0 \xrightarrow{k_{10}} Cr(NH_3)_2(NCS)_3OH_2 + NCS^- \quad (10)$$

$$Q_0 \xrightarrow{k_{11}} Cr(NH_3)_2(NCS)_4^- + \text{heat} \quad (11)$$

$$\phi_{Cr^{2+}} = \frac{\phi' \epsilon_D I_0 \delta \tau_D}{1 + \phi' \epsilon_D I_0 \delta \tau_D} + \phi_0 \quad (12)$$

$$\phi_{NCS^-} = \frac{k_{10} \tau_D}{1 + \phi' \epsilon_D I_0 \delta \tau_D} \quad (13)$$

Figure 2 where Q* designates ligand field states of quartet spin multiplicity, and Q_0 the thermalized state of the quartet

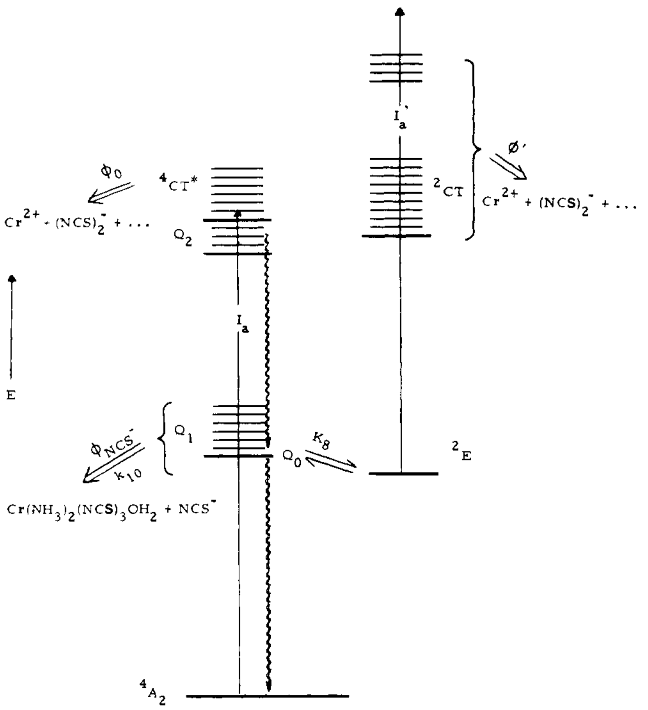

Figure 2. Schematic representation of photochemical and photophysical processes in *trans*-$Cr(NH_3)_2(NCS)_4^-$. The excited quartet ligand field states, Q_2, Q_1, etc., are represented by Q^* in the text while the thermalized states in the ligand field quartet manifold are indicated by Q_0. Photoaquation is regarded as a reaction characteristic of populations of ligand field excited states (Q_2, Q_1, Q_0, ^2E, etc.). Vibrational and internal conversion processes are indicated by wavy lines (k_v and k_{11}). The absorption of the ^2E state is indicated by ^2CT. Other terms are defined in the text.

manifold. The $Q_0 \rightarrow {}^2E$ intersystem crossing rate has been reported to be very rapid ($k_8 \geq 5 \times 10^{11}$ s^{-1})[22] and it is commonly held that a substantial portion of the ligand field photochemistry arises from $^2E \rightarrow Q_0$ back-intersystem crossing.[19-21] If this model be adopted, then our results are consistent with an equilibrium between the doublet and quartet states; our results do not require that the Q_0 and ^2E states be distinguishable. In the absence of the absorption of a second photon, the doublet lifetime is $\tau_D = 1/(k_{10} + k_{11})$ and an approximate stationary state treatment[23] of eq 4–11 results in analytic expressions (eq 12 13), which are consistent with the observed two photon effects (in obtaining eq 12 and 13 we have assumed that $\phi \ll \phi'$, and $I_a' \simeq \epsilon_D I_0 \delta [^2E]$ where ϵ_D is the molar absorptivity of ^2E at 337 nm and δ is a geometrical factor; ϕ_0 corresponds to the small intensity independent Cr^{2+} yield). For example a plot of $1/\phi_{Co^{2+}}$ vs. $1/I_0$ is reasonably linear.

$$\phi_{Cr^{2+}} = \frac{\phi' \epsilon_D I_0 \delta \tau_D}{1 + \phi' \epsilon_D I_0 \delta \tau_D} + \phi_0 \qquad (12)$$

$$\phi_{NCS^-} = \frac{k_{10} \tau_D}{1 + \phi' \epsilon_D I_0 \delta \tau_D} \qquad (13)$$

Equation 12 predicts a rather straightforward dependence of the yield of the two photon process, $\phi_{Cr^{2+}}$, on the excited-state lifetime, τ_D. We have found that τ_D may be varied over about an order of magnitude (from $\sim 2 \times 10^{-8}$ s to 2×10^{-7} s) increasing with increases in the percentage of acetone in aqueous solutions. Consistent with eq 12 plots of $1/\phi_{Co^{2+}}$ vs. $1/\tau_D I_0$ result in a single straight line for 0 M $\leq$ [acetone] $\leq$ 5 M and about a 10-fold range of τ_D.

There are several striking features of this study. (1) The values of $\phi_{Cr^{2+}}$ (proportional to $\phi_{Co^{2+}}$; solubility and absorbance problems do not permit us to scavenge all the Cr^{2+}; so $\phi_{Co^{2+}} < \phi_{Cr^{2+}}$[15]) at all pulsed laser intensities are larger than the yields for either 337- or 254-nm continuous irradiations. (2) The values of ϕ_{NCS^-} resulting from laser excitations are also greater than values obtained from continuous irradiations, but ϕ_{NCS^-} *decreases* with I_0 in contrast to the intensity dependence of $\phi_{Co^{2+}}$ and consistent with bleaching of the photoactive ligand field excited state. (3) The two photon effect appears to approach saturation of the redox yield at very high I_0. (4) The saturation effect is achieved at lower power levels as the excited state lifetime is increased.

Laser photolyses were performed with a Molektron UV1000 using a quartz focussing lens and Ealing neutral density filters. Lifetime measurements were performed with a frequency doubled, ruby flash photolysis system.[24] Chemical analyses for Co^{2+} [25] and NCS^- [9] were performed according to the literature methods.

References and Notes

(1) (a) Partial support of this research by the National Science Foundation and National Institutes of Health is gratefully acknowledged. (b) Reported in part at the 2nd Joint CIC-ACS Conference, Montreal, Canada, May 29–June 2, 1977, INOR 049.

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(24) We are grateful to Dr. Masaaki Ogasawara for his help in making these measurements and to Professor L. Kevan for making the laser photolysis system available to us.

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