The effect of temperature on photoprocesses in acetone solutions of $Cr(NH_3)_2(NCS)_4{}^-$

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Abstract

The photolysis yields and emission lifetimes for solutions of $Cr(NH_3)_2(NCS)_4{}^-$ in fluid acetone have been recorded as a function of temperature in the range -93 to 10 °C. The ^2E levels are quenched by O_2 and the relative contributions of the fast and slow photoreactions have been determined by comparing the photolysis yields in deaerated and O_2 saturated solutions. The quantum yield of the prompt process is 0.02 and is temperature independent. The thermal enhancement of the slow photolysis correlates with depopulation of ^2E and the results are consistent with back-intersystem crossing as the pathway for this process.

Introduction

The several processes that follow $^4T_2 \leftarrow {}^4A_2$ excitation are shown in Fig. 1. The risetime for the population of ^2E is very short, 1–10 ps [1, 2], and prompt intersystem crossing (pisc) might compete with vibrational relaxation [3]. In addition, a slower intersystem crossing can arise from a vibrationally relaxed and thermalized $^4T_2$ distribution (isc). Any reaction that occurs in $^4T_2$ or in
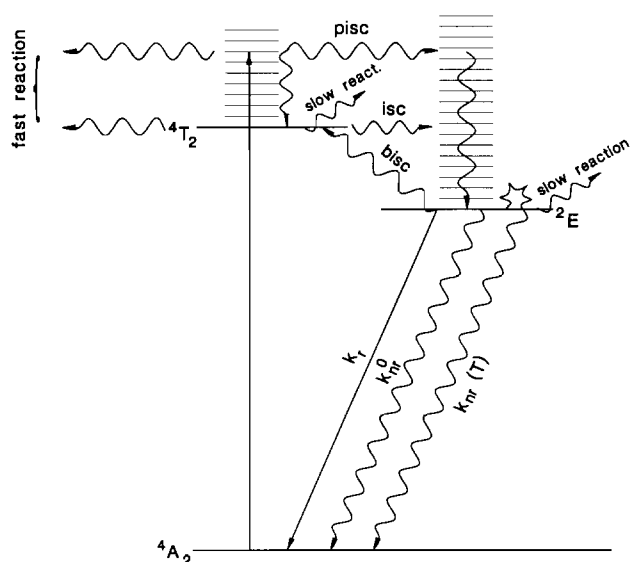

Fig. 1. Energy levels and excited state relaxation pathways in Cr(III) complexes.

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higher vibrational levels of ^2E prior to achievement of a Boltzmann distribution in the latter state will be fast and unaffected by quenching of ^2E. The slow reaction involves complexes that have passed through thermalized ^2E and the photosolvation yield will be reduced as ^2E is quenched [4, 5]. If the fast reaction originates in a non-thermalized distribution, it can be invariant to temperature change. In the pioneering study of Adamson [6], the overall photolysis yield for $Cr(NH_3)_2(NCS)_4{}^-$ was found to be temperature dependent even in the range where the alcohol–water solvent was glassy, but the fast and slow contributions to the overall photoreaction were not distinguished. The total quantum yield for this complex at -65 °C was 0.01 and 50% of the reaction was quenchable but the temperature dependence was not examined [7]. We have now determined the photosolvation yields for the quenchable and unquenchable processes in acetone solution from the melting point to near ambient temperature.

Experimental

$(NH_4)[Cr(NH_3)_2(NCS)_4]$ was obtained from Alfa and Janssen Chimica and purified by recrystallization. Acetone solutions of approximately 5×10^{-2} M concentration were prepared in dim red light and irradiated at 514 nm with a slightly defocussed 2–10 mW beam from an Ar^+ laser. The solutions were stirred by a stream of N_2 or O_2 gas and temperature control was achieved by placing the sample in an optical dewar

and directing cold nitrogen gas onto the cuvette. Quantum yields were referenced to aqueous solutions at room temperature ($\Phi_{rx} = 0.30$ [8]) and were independent of excitation intensity or the use of a $3 \times$ beam expander, indicating that the stirring was adequate to prevent local depletion during photolysis. The NCS^- release was monitored by addition of Fe^{3+} and determination of the resultant absorbance at 450 nm [8]. Correction was made for the very small thermal reaction. The optical densities at 514 nm were determined spectrophotometrically in a 1 cm cell at room temperature. The absorbance (0.5–0.7) increase due to the volume contraction at low temperatures (c. 20%) was counterbalanced by a concomitant decrease in the extinction coefficient, but the net result of these effects was not determined.

Lifetimes were computed by digitizing and signal averaging the decay following excitation with an N_2 laser. The emission was monitored at 755 nm where interference from the photoproduct was minimized.

Results

The photolysis yields as a function of temperature in deaerated and O_2 saturated solutions are compared to the reciprocal of the ^2E lifetime in Fig. 2. The total photolysis yield (Φ_{rx}) is the sum of the fast unquenchable
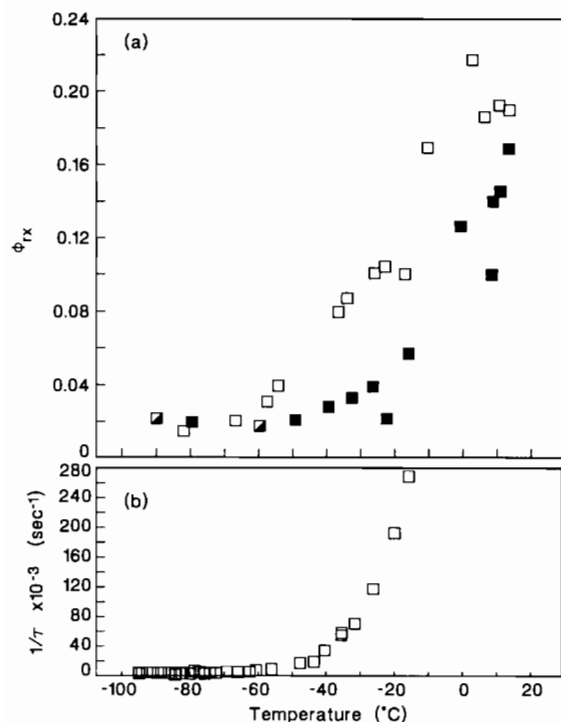

Fig. 2. (a) Photosolvation yields: $\square$, N_2 bubbled; $\blacksquare$, O_2 bubbled; $\blacksquare$, same value for N_2 and O_2 bubbled; (b) ^2E decay rates in acetone solutions of $Cr(NH_3)_2(NCS)_4^-$.

and the slow quenchable reaction yields. The ^2E lifetime at $-90\,°C$ is reduced from 300 μs in an N_2 bubbled solution to 10 μs in a solution equilibrated with ambient air. This confirms that O_2 is an efficient quencher of the ^2E level and that the difference between Φ_{rx} in N_2 and O_2 bubbled solutions can be used to estimate the contribution of the slow reaction to the overall quantum yield.

The solubility of O_2 in acetone at ambient temperatures is 0.011 M at one atm and this quantity is not very temperature dependent [9]. The quenching constant for O_2 can be estimated from the Stern–Volmer equation, $\tau°/\tau = 1 + \tau°k_Q[O_2]$. This yields $k_Q = 5 \times 10^7\ M^{-1}\ s^{-1}$ at $-90\,°C$ and $6 \times 10^7\ M^{-1}\ s^{-1}$ at $-54\,°C$ where the lifetime is 95 μs in N_2 bubbled and 7 μs in air-saturated solutions. That k_Q is considerably less than the usual diffusion controlled value at low viscosities, $10^{10}\ M^{-1}\ s^{-1}$, has also been established for O_2 quenching of $Cr(1,10\text{-phenanthroline})_3^{3+}$ and $Cr(CN)_6^{3-}$ [10]. The effectiveness of quenching is diminished as the lifetime decreases and there is only a slight decrease in the fluorescence intensity when O_2 is bubbled through a deaerated solution at ambient temperatures where $\tau° = 157$ ns [11].

The major points that emerge from examination of Fig. 2 are:

(i) below $-70\,°C$, the photosolvation yields in N_2 and O_2 bubbled solutions are the same, 0.02;

(ii) above $-70\,°C$, O_2 quenching reduces the photoreduction but Φ_{rx} is essentially constant between -90 and $-50\,°C$ in O_2 bubbled solutions;

(iii) in N_2 bubbled solutions the thermal enhancement of Φ_{rx} correlates with the marked increase in the ^2E relaxation rate ($1/\tau$).

Discussion

The viscosity of fluid acetone varies from 0.295 to 2.148 cp in the temperature interval 30 to $-92.5\,°C$ [12]. Consequently, for all temperatures between ambient and the freezing point, the solvent motions are fast on the ns timescale and thermal activation is not due to changes in viscosity.

The near constancy of Φ_{rx} in O_2 bubbled solutions between -50 and $90\,°C$, coupled with the very efficient quenching of the fluorescence in this range, is clear evidence that the yield of the fast unquenchable reaction is small and not thermally activated. We assume that the increase in Φ_{rx} above $-50\,°C$ in O_2 saturated solutions is due to incomplete ^2E quenching when the lifetime is short and that the unquenchable yield is constant throughout the entire temperature range. This behavior is expected if the fast reaction precedes thermalization in $^4T_2$ [3]. Since only a small fraction of Φ_{rx}

is due to prompt reaction at ambient temperatures where the preponderance of the reaction arises from complexes that have passed through a thermalized population in ^2E, the near independence of Φ_{rx} to excitation wavelength [8] can be understood.

The ^2E lifetime is given by the expression [13]

$$\tau^{-1} = \tau_o^{-1} + k_{nr}(T) + k_{rx} + (1 - \eta_{isc})k_{bisc} \qquad (1)$$

where k_{rx} is the rate constant for direct ^2E reaction, η_{isc} the intersystem crossing efficiency from a thermalized $^4T_2$ distribution and $\tau_o^{-1} = k_{nr}{}^o + k_r$ the decay rate at low temperatures. The lifetimes are 300 μs in fluid acetone just above the melting point and 400 μs at 77 K in solid acetone and alcohol glasses. We have chosen $\tau_o = 400$ μs in the Arrhenius plot for $\tau^{-1} - \tau_o^{-1} = A$ $exp(-E_a/RT)$ (Fig. 3), but the fitting is not sensitive to this choice in the high temperature region.

The onset of the enhanced ^2E decay and the increase in Φ_{rx} both occur at -60 °C, which suggests that the process responsible for the thermally activated ^2E relaxation is also the source of the slow reaction. However, this concordance does not tell us anything about the reaction pathway, a problem that has been the subject of extensive discussion [4, 13].

According to eqn. (1) three processes for thermal deactivation of ^2E have been identified: depopulation of ^2E to the ground state or to a reactive intermediate ($k_{nr}(T)$), direct reaction (k_{rx}) and back-intersystem crossing to $^4T_2$ (k_{bisc}) [4]. The slow photosolvation can then occur in ^2E, from a reactive intermediate or following repopulation of $^4T_2$. Rojas and Magde have suggested that back-transfer will be significant at room temperature if the ^2E–$^4T_2$ gap is <35 kJ mol^{-1} [14]. From the temperature dependence of the lifetime in aqueous

solutions of $Cr(NH_3)_2(NCS)_4{}^-$, they estimated the activation energy for back-transfer to be 26.9 kJ mol^{-1}, markedly smaller than the 42.4 kJ mol^{-1} value obtained by Walters and Adamson [15]. Both of these Arrhenius plots involved lifetime data in a limited temperature interval near ambient. The Arrhenius plot in acetone is quite linear above -65 °C with $A = 10^{14.8}$ and $E_a = 46$ kJ mol^{-1}. The activation energy exceeds the $^4T_2$–^2E gap obtained by inspection of the absorption and emission spectra [16]. Thus back-transfer is an energetically feasible process for ^2E decay at temperatures where the slow reaction is significant, but the kinetic results are consistent with all three of the pathways for the slow photosolvation. If the slow reaction occurs in $^4T_2$ after back-transfer the small activation energy at low temperatures is associated with $k_{nr}(T)$.

In summary, we have found that the prompt photosolvation yield is small and independent of temperature in a medium where solvent relaxation times are subnanosecond and not very sensitive to temperature. While the prompt reaction may be faster than solvent motions in acetone, there is ample time for solvent translation and rotation prior to the slow reaction and the activation energy for the slow process reflects a $^4T_2$–^2E gap that has been reduced by solvent relaxation. What remains to be determined is the effect of temperature on the fast and slow reaction rates in a glass-forming solvent where the solvent relaxation time can be altered over a wide range.

Acknowledgement

Fig. 3. Thermally activated ^2E relaxation rates ($\tau_o = 400$ μs).

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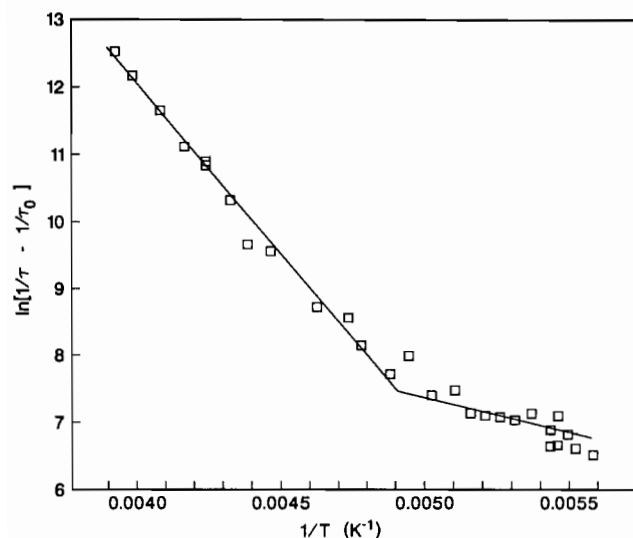10 M. Z. Hoffman, F. Bolleta, L. Moggi and G. L. Hug, *J. Phys. Chem. Ref. Data, 18* (1989) 219.

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