

## The Effect of Pressure on the Photochemistry of Tris(bipyridyl)chromium(III) Ion

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The quantum yield for the photoaquation of  $\text{Cr}(\text{bpy})_3^{3+}$  in basic medium decreases with increasing pressure, with an apparent volume of activation of  $3.8 \pm 1.0 \text{ ml mol}^{-1}$ . From this value and that associated with the phosphorescence lifetime, the volumes of activation for non-radiative decay to the ground state and for formation of photoproduct are derived as  $-1.6$  and  $+2.9 \text{ ml mol}^{-1}$ , respectively. The latter value is consistent with either an associative process with water entering from pockets between the ligands or a dissociative process involving one or both bonds to a bipyridyl ligand.

### Introduction

The photochemistry of chromium polypyridyl complexes has been extensively studied and has been recently reviewed [1]. The parent compound,  $\text{Cr}(\text{bpy})_3^{3+}$ , is one of the best documented examples for which the major fraction of the photochemistry is postulated to occur directly from the doublet state manifold [2]. The reaction, consisting of aquation of one bipyridyl ligand, has a constant but small quantum yield for strongly acid solutions, and a larger quantum yield, 0.15, for pH values above 9.5. Because the quantum yield in the intermediate region varies with pH in exactly the same manner as does the rate constant for the thermal reaction [3], it has been proposed that the photochemical reaction and the thermal reaction occur via the identical intermediate.

This intermediate was suggested to be a seven-coordinate complex formed by associative attack of water on the ground state (thermal reaction) or on the doublet excited manifold (photochemical reaction) of  $\text{Cr}(\text{bpy})_3^{3+}$  [2]. A dissociative reaction involving ring opening to a one-ended bipyridyl was considered unlikely because no acid catalysis of either

thermal or photochemical reaction was found even in 1 M HCl. In a previous study, we reported [4] that the lifetime of the emitting state of  $\text{Cr}(\text{bpy})_3^{3+}$  decreases at high pressure. For the total rate constant representing decay of the phosphorescence,  $k_{\text{decay}}$ , the apparent volume of activation is  $-0.9 \pm 0.1 \text{ ml mol}^{-1}$ . We pointed out that this experimental activation volume,  $\Delta V_{\text{decay}}^\ddagger$ , would be a weighted sum of all of the activation volumes for the decay processes of the doublet state manifold, proposed to be only: (i) non-radiative deactivation (nr); (ii) phosphorescence (rad); (iii) formation of the aquo intermediate (rx). This latter intermediate must react to product except in acid solution, where it mainly returns to the ground state.

The weighting factors in this sum are just the efficiencies,  $\eta_i$ , of each process [4]. Also, since  $\phi_{2E}$  has been found to be very close to one, the  $\eta_i$  are equal to the observed quantum yields. Since  $\eta_{\text{rad}} = 10^{-3}$ ,  $\Delta V_{\text{rad}}^\ddagger$  makes no appreciable contribution to  $\Delta V_{\text{decay}}^\ddagger$ . Also since  $\eta_{\text{rx}} = 0.15$ ,  $\Delta V_{\text{rx}}^\ddagger$  makes only a minor contribution to  $\Delta V_{\text{decay}}^\ddagger$ . Consequently, the observed activation volume of  $-0.9 \text{ ml mol}^{-1}$  implies  $\Delta V_{\text{rx}}^\ddagger \approx -6 \text{ ml mol}^{-1}$  if it is assumed that  $\Delta V_{\text{nr}}^\ddagger$  is  $\approx 0$ .

Measurement of the pressure dependence of the photochemical reaction itself, however, would provide a more reliable estimate of  $\Delta V_{\text{rx}}^\ddagger$  and  $\Delta V_{\text{nr}}^\ddagger$  and thus some mechanistic information about the process leading to the intermediate. We report here the results of such an investigation.

### Experimental

Photolyses were carried out with 365 nm light at 22 °C on deaerated solutions. The quantum yield was redetermined in conventional apparatus with ferrioxalate actinometry. The photochemical aquation

was then studied in the cell previously described [4] at ambient pressure and at a number of different high pressures. The quantum yield at high pressure was measured relative to that at ambient pressure in alternate experiments identical in all respects except for the pressure.

Solutions were outgassed immediately prior to photolysis. To allow for compression of the solution at high pressure while maintaining separation from the hydraulic fluid, both piston and membrane systems were tried. A rubber tube membrane was found to be most satisfactory, and allowed for effective outgassing prior to pressurization. No losses of bipyridine, one of the products, to the membrane were found in check experiments.

The optical cell used in the high pressure vessel was a 1.5 cm high, 1 × 1 cm square cell fused to a 1 cm OD tube in the upper part to minimize the non-irradiated volume but to allow for the significant volume change of the solution at the highest pressures. The pressure was calibrated up to 3,500 atm by comparison of measurements of the compressibility of water with tabulated data [5].

Solutions of  $1.0 \times 10^{-3} M$   $\text{Cr}(\text{bpy})_3(\text{ClO}_4)_3$  in a Britten-Robinson buffer at pH 10, with the ionic strength adjusted to unity with NaCl, as used previously [2], were photolyzed at several pressures up to 2350 atm. Released bipyridine was extracted from the solution with n-heptane and analyzed spectrophotometrically as described in the literature [3]. Particular attention was paid to having the alternate runs at high and at ambient pressure under otherwise the same conditions. Light intensities were measured by chemical actinometry combined with monitoring photocells. No correction was required for increase in absorbance with pressure because the solutions were nearly totally absorbing. In all runs, conversions to the hydrolyzed product were kept to less than 10%.

## Results

Measurements at atmospheric pressure of the limiting quantum yield for photoaquation in conventional equipment gave values of  $0.15 \pm 0.01$  at 22 °C, consistent with the range of values in the literature [1]. In addition, the lifetime found for decay of phosphorescence in deaerated solutions, 73  $\mu\text{s}$ , agrees with the accepted value [6].

Figure 1 shows a plot of the logarithm of the ratio of the quantum yield at pressure  $P$ ,  $\phi_P$ , to that at 1 atm,  $\phi_1$ , against the pressure. The least squares line through zero at  $P = 1$  shown there gives  $\Delta V^\ddagger_{\text{photochem}} = 3.8 \pm 1.1 \text{ ml mol}^{-1}$ . Although the data show a downward curvature, their precision does not warrant any attempt to evaluate either  $\beta^\ddagger$  ( $-\partial \Delta V^\ddagger / \partial \Delta P$ ) or  $\{\partial \ln(\phi_P / \phi_1) / \partial P\}_{P=1}$  from that curvature. In addi-

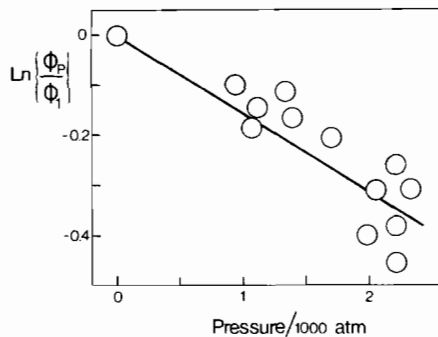


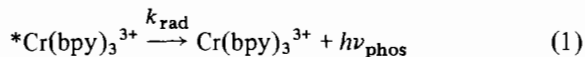
Fig. 1. Logarithm of the ratio of quantum yield for photoaquation at pressure  $P$  to that at 1 atm plotted against the applied pressure.

tion, the small apparent curvature is in a sense opposite to that generally observed in thermal studies, and hence probably does not represent a real curvature in the data. In any case, the limiting  $P = 1$  slope is well within the generous error limits quoted for  $\Delta V^\ddagger_{\text{photochem}}$ .

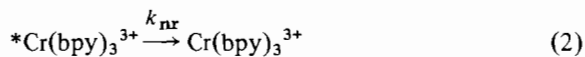
## Discussion

Previous descriptions [1, 2] of the photochemistry and luminescence behaviour of  $\text{Cr}(\text{bpy})_3^{3+}$  suggest that excited molecules in the doublet excited state manifold (\*) undergo the three reactions:

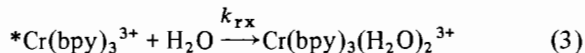
Phosphorescence:



Non-radiative deactivation:



Formation of an intermediate:



At pH 9.5 and above, the intermediate in eqn. 3 is converted completely and irreversibly into  $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$  through ring opening and subsequent loss of a bipyridyl ligand. The quantum yield for formation of this product, 0.15 at 22 °C and 1 atm in deaerated solution, is assumed to represent also the quantum yield for formation of the intermediate in both acid and basic media. However, in acid solution, the intermediate reverts to the original reactant by two parallel paths, one acid independent and the other acid dependent, with only a minor fraction,  $\phi = 0.007$ , leading to aquated product [7].

This mechanism predicts a quantum yield for reaction of:

$$\phi_{\text{photochem}} = \phi^2 \epsilon \eta_{\text{rx}} f(\text{pH}) \quad (4)$$

where  $\phi_{2E}$  is the quantum yield for formation of the doublet state manifold by intersystem crossing,  $\eta_{rx}$  is the efficiency of formation of the intermediate, given by:

$$\eta_{rx} = k_{rx}/(k_{rx} + k_{nr} + k_{rad}) \quad (5)$$

and  $f(\text{pH})$  is a function that is one for  $\text{pH} > 9.5$ , about 0.05 for  $\text{pH} < 2$  and has the intervening pH dependence given in previous work [2, 7].

The value of  $\phi_{2E}$  has been demonstrated to be at least 0.97 [2]. As we have shown [4], a step such as intersystem crossing that occurs with near 100% efficiency cannot contribute in other than a minor way to the activation parameters of the overall process. In the basic solution used in the present experiments,  $f(\text{pH})$  is also one, so that the reaction by which the intermediate is converted to product also does not make any contribution to the activation volume of the overall photochemical reaction. The volume of activation for the photochemical formation of  $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$  will therefore be given by:

$$\Delta V_{\text{photochem}}^{\ddagger} = -RT(\partial \ln \eta_{rx}/\partial P)_T \quad (6)$$

Substitution of eqn. 5 gives:

$$\Delta V_{\text{photochem}}^{\ddagger} = \Delta V_{rx}^{\ddagger} - (\eta_{rx}\Delta V_{rx}^{\ddagger} + \eta_{rad}\Delta V_{rad}^{\ddagger} + \eta_{nr}\Delta V_{nr}^{\ddagger}) \quad (7)$$

It may be noted that the weighting of the three volumes of activation is not the same. Recognizing that  $\eta_{rad}$  is of the order of  $10^{-3}$ , eqn. 7 reduces to:

$$\Delta V_{\text{photochem}}^{\ddagger} = \eta_{nr}(\Delta V_{rx}^{\ddagger} - \Delta V_{nr}^{\ddagger}) \quad (8)$$

The rate constant for the decay of the doublet state manifold is given by:

$$k_{\text{decay}} = k_{rx} + k_{rad} + k_{nr} = \tau_{\text{exp}}^{-1} \quad (9)$$

Associated with  $k_{\text{decay}}$  is the volume of activation:

$$\Delta V_{\text{decay}}^{\ddagger} = -RT(\partial \ln k_{\text{decay}}/\partial P)_T \quad (10)$$

Substitution of eqn. 9 yields:

$$\Delta V_{\text{decay}}^{\ddagger} = \eta_{rx}\Delta V_{rx}^{\ddagger} + \eta_{rad}\Delta V_{rad}^{\ddagger} + \eta_{nr}\Delta V_{nr}^{\ddagger} \quad (11)$$

Again, since  $\eta_{rad}$  is about  $10^{-3}$ , the middle term in eqn. 11 can be dropped, to give:

$$\Delta V_{\text{decay}}^{\ddagger} = \eta_{rx}\Delta V_{rx}^{\ddagger} + \eta_{nr}\Delta V_{nr}^{\ddagger} \quad (12)$$

Equations 8 and 12, when solved simultaneously, give the following for the volumes of activation of the two postulated elementary reactions, rx and nr:

$$\Delta V_{rx}^{\ddagger} = \Delta V_{\text{decay}}^{\ddagger} + \Delta V_{\text{photochem}}^{\ddagger} \quad (13)$$

and

$$\Delta V_{nr}^{\ddagger} = \Delta V_{\text{decay}}^{\ddagger} - \eta_{rx}\Delta V_{\text{photochem}}^{\ddagger}/(1 - \eta_{rx}) \quad (14)$$

Substitution of the experimental data for  $\eta_{rx}$  and for the two volumes of activation gives:

$$\Delta V_{rx}^{\ddagger} = 2.9 \pm 1.2 \text{ ml mol}^{-1} \quad (15)$$

and

$$\Delta V_{nr}^{\ddagger} = -1.6 \pm 0.2 \text{ ml mol}^{-1} \quad (16)$$

Before discussing the pathway to the transition state for this photoreaction, we need first to clarify some of the features of the intermediate species  $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ . The evidence that the intermediate has this constitution is reasonably good, but the assignment as seven-coordinate rather than six-coordinate is less sound and has been altered by more recent work [7]. The original argument against a six-coordinate intermediate was that since it would have a monodentate bipyridyl ligand which would be protonated in acid solutions, an increase in photochemical yield would be expected at low pH. The constancy of the quantum yield in the pH range below 6 was therefore taken to establish that the intermediate had no free base nitrogen available, and was therefore seven-coordinate.

However, other studies have demonstrated that for pH values less than 3, the overall rate of decay of transient bleaching, representing return of the intermediate to the ground state, is itself acid catalyzed [7], presumably a result of protonation of the coordinated water. In order for the quantum yield in strongly acid solution to be independent of  $[\text{H}^+]$ , as is observed, the pathway to product must also be acid catalyzed. In turn this implies the intervention of a free base nitrogen, *i.e.*, a one-ended bipyridyl ligand, either as part of the intermediate of eqn. 3 or of some subsequent species.

If the aquo intermediate is seven coordinate then it must involve an associative attack of water, as suggested previously [2]. However, in view of the above argument, it is possible for the intermediate to be six coordinate, and to be formed by either an associative or a dissociative process as extremes.

The interpretation of the volume of activation in terms of a mechanism is a difficult and controversial subject [8, 9, 10]. A pragmatic approach is to compare  $\Delta V_{\text{step}}^{\ddagger}$ 's for elementary steps of reactions whose mechanism is reasonably well understood. For water exchange reactions of octahedral complexes activation volumes range from +14 to -14  $\text{ml mol}^{-1}$  [8]. These represent the effective volume of an electrostricted water molecule modified by the volume change of the complex owing to changes in coordination number in the transition state. For the extreme positive volume of activation, the exchange reactions are dissociative with respect to formation of the transition state; for the extreme negative value, associative. Many reactions, however, are intermediate in character, and for these, the  $I_d$  and  $I_a$  nomenclature was proposed by Langford and Gray [11].

For reactions other than solvent exchange, when charges are altered or charge is redistributed significantly in the transition state, other major electrostrictive effects can contribute to  $\Delta V^{\ddagger}$ . We expect

electrostriction to make only a small contribution to  $\Delta V^\ddagger$  because the transition state leading to the intermediate in the photoaquation reaction of  $\text{Cr}(\text{bpy})_3^{3+}$  has the same charge as the reactant excited state molecule. The reaction involves the incorporation of solvent water into the primary coordination sphere of the complex. Hence the transition state will have a larger volume and the electrostrictive forces on the surrounding solvent will be slightly smaller than for the precursor.

We consider first the case that the transition state is formed by a dissociative process. Either ring opening to a one-ended bipyridyl or bond extension of both Cr–N bonds of a bipyridyl would represent the dissociative aspect. In this case the volume of a water molecule is not part of  $\Delta V^\ddagger$ , since water is assumed to enter in a non-rate-controlling step, subsequent to formation of the transition state. The expansion associated with bond rupture or bond extension of the bipyridyl ligand would provide a small positive  $\Delta V^\ddagger$ , consistent with the value found in this work.

The alternative mechanism, in which a water molecule enters the coordination sphere to form a seven-coordinate transition state, must be an associative path, although the water might not be fully coordinated in the transition state. If water enters from the second coordination sphere, there will be a large negative contribution to the volume of activation from the volume of that water lost. Expansion of the complex in the transition state might partially compensate, but it is extremely unlikely that the sign of  $\Delta V^\ddagger$  would be reversed. That is, the volume of activation should be negative and in the range of  $-5$  to  $-14 \text{ ml mol}^{-1}$ . This mode of formation of the transition state can therefore not be made consistent with the  $\Delta V_{\text{rx}}^\ddagger$  observed. By much the same argument, an associative reaction leading to a six coordinate intermediate can also be ruled out.

On the other hand, it has been demonstrated that water molecules can occupy 'pockets' between the ligands in polypyridyl complexes in the solid state [12]. Such water molecules, presumably also present in the complex in solution, are ideally positioned and oriented to substitute in the first coordination sphere of the complex. Involvement of this pocket water in the formation of the transition state provides an associative pathway that would have a positive  $\Delta V^\ddagger$  such as that found here. This is so because the water in the pocket is already part of the volume of the complex, and there would not be the large negative contribution from loss of water from the second coordination sphere. The increase in volume of the

complex in a seven-coordinate transition state, as well as the minor increase due to lessened electrostriction of the surrounding water, would provide the positive  $\Delta V^\ddagger$ .

We therefore conclude that the pressure effect on the photochemistry, although giving unique values for the volumes of activation for non-radiative deactivation and for reaction, does not let us distinguish between an associative and dissociative pathway for the reaction. We do conclude, however, that if the path is associative, the entering water molecule can not come from the second coordination sphere, but must be from water already located in pockets between the bipyridyl ligands. This conclusion is in agreement with the general effect of perchlorate on the photochemistry and excited state parameters [13].

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