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Charge-transfer Photochemistry under High Pressure: Reductive Elimination from *trans*-Diazidotetracyanoplatinate(IV)

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Abstract

The quantum yield for the reductive elimination of azide from *trans*-$Pt(CN)_4(N_3)_2{}^{2-}$ to yield $Pt(CN)_4{}^{2-}$ and molecular nitrogen in aqueous solution was studied as a function of pressure up to 200 MPa. The resulting volume of activation of 8.1 ± 0.4 $cm^3\ mol^{-1}$ is interpreted as evidence for the formation of a caged radical species via simultaneous scission of both $Pt-N_3$ bonds in the CT excited state. Similar measurements in ethanol result in a volume of activation of 14.3 ± 0.9 $cm^3\ mol^{-1}$. An additional deactivation route for the CT excited state is suggested to account for this result.

Introduction

The application of high pressure techniques in the elucidation of photochemical reaction mechanisms has received considerable attention in recent years. This has proved to be an effective tool for the evaluation of mechanistic information concerning the reactivity of excited state species participating in photosubstitution and photoisomerization reactions [1–7]. In contrast, only few data are available for the effect of pressure on photoredox reactions [8], which are in many cases complicated by competing substitution reactions.

We have now investigated the pressure dependence of the quantum yield for a simple photoredox reaction in which no competing substitution reactions occur. Vogler *et al.* [9, 10] studied the photoinduced reductive *trans*-elimination of azide from *trans*-$Pt(CN)_4(N_3)_2{}^{2-}$ at ambient pressure and found molecular nitrogen and $Pt(CN)_4{}^{2-}$ as the photolysis products in aqueous solution. Low temperature ESR measurements in ethanol indicated the generation of azide radicals in the primary photochemical step; no evidence for the formation of a Pt(III) intermediate could be found [10]. The azide radicals are unstable in water and decompose to yield molecular nitrogen. In ethanol they also abstract H atoms from the solvent to produce HN_3 and ethanol radicals. A significant advantage of the selected system is the absence of any net change in charge on the ionic species. Such effects usually complicate the interpretation of the volume of activation (obtained from the pressure dependence of the quantum yield) due to possible contributions from electrostriction effects [4, 7].

Experimental

trans-$K_2[Pt(CN)_4(N_3)_2]$ was prepared from *trans*-$K_2[Pt(CN)_4Br_2]$ [11] according to the following modified procedure [9]: *trans*-$K_2[Pt(CN)_4Br_2]$ dissolved in water was treated with a tenfold excess of KN_3 at 80 °C. A rapid colour change from light-yellow to orange indicates the formation of *trans*-$Pt(CN)_4(Br)N_3{}^{2-}$. Subsequent heating at 80 °C for 5 h, followed by cooling in ice, yielded orange crystals of the desired compound. Yield: 74% after recrystallization from water. The UV-Vis absorption spectra in both water and ethanol were practically identical to those reported previously [9], *viz.* ϵ_{max} (302 nm) = 18 700 compared to ϵ_{max} (302 nm) = 18 300 $M^{-1}\ cm^{-1}$. This transition was assigned to the (N_3-Pt)CT-type [9].

Complex solutions were irradiated at 313 nm under pressure up to 200 MPa using equipment described previously [4, 5]. Photochemical conversions were determined from the decrease in absorbance at 302 nm using a Perkin Elmer Model 551 spectrophotometer.

Results and Discussion

Irradiation of *trans*-$Pt(CN)_4(N_3)_2{}^{2-}$ at 313 nm and ambient pressure results in large spectral changes and clean isosbestic points in agreement with previously reported findings [9]. Irradiation under pressure resulted in similar spectral changes, indicating that the overall reaction is not influenced by the application of pressure up to 200 MPa.

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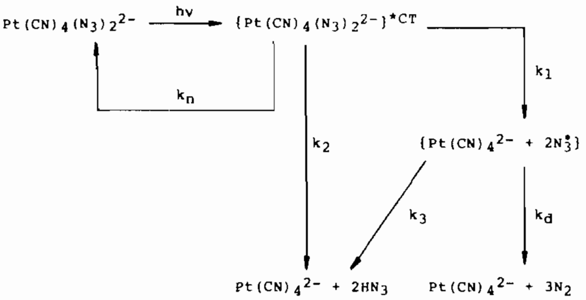
TABLE I. Quantum Yield as a Function of Pressure for the Disappearance of *trans*-$Pt(CN)_4(N_3)_2{}^{2-}$ upon CT-irradiation at 313 nm in Water and Ethanol [a]

Pressure (MPa)	ϕ_{H_2O}	ϕ_{EtOH}
1	0.35 ± 0.02	0.50 ± 0.02
25	0.34 ± 0.01	0.46 ± 0.02
50	0.32 ± 0.01	0.38 ± 0.02
75	0.31 ± 0.02	0.33 ± 0.02
100	0.28 ± 0.02	0.31 ± 0.02
125	0.28 ± 0.01	0.29 ± 0.02
150	0.26 ± 0.01	0.26 ± 0.02
175	0.25 ± 0.01	0.24 ± 0.02
200	0.21 ± 0.02	0.23 ± 0.02

[a] T = 25 °C, quantum yields in mol einstein^{-1}.

The measured quantum yields, determined in terms of the disappearance of *trans*-$Pt(CN)_4(N_3)_2{}^{2-}$ as a function of pressure and solvent, are summarized in Table I. The results at ambient pressure are in close agreement with those reported previously [9]. Our slightly lower quantum yield for the reaction in ethanol is within the error range usually observed for such photochemical measurements. The quantum yield ϕ shows a steady decrease with increasing pressure for both solvents. The corresponding volumes of activation were calculated from the slope of plots of $\ln[\phi/(1-\phi)]$ *vs.* pressure, which are linear within the experimental error limits. In this treatment it was assumed that the key photochemical reaction step occurs from the CT state directly populated during irradiation (see Scheme 1), and that the rate constant for radiationless deactivation is independent of pressure [4]. The resulting volumes of activation are 8.1 ± 0.4 and 14.3 ± 0.9 cm^3 mol^{-1} for the photolysis in water and ethanol, respectively.



Scheme 1.

The significantly positive $\Delta V^{\#}$ values clearly underline the dissociative nature of the photochemical process in both solvents. The difference in absolute values is significant and requires a more detailed interpretation. Despite the primitivity of the theoretical basis for charge-transfer photochemistry [12], several interesting mechanistic models have been proposed. Of these, Adamson's limiting radical pair model [13] has been adopted in many cases. However, it predicts a unitary yield for radical pair formation, which is not the case for the present system. In addition, the observed wavelength independence of the quantum yield [9] is also not in line with this model. We therefore prefer a charge-transfer excited state model as outlined in Scheme 1.

The reactive state in Scheme 1 is a thermally equilibrated ligand-to-metal CT excited state that undergoes radiationless deactivation to yield the educt species (k_n) and produces a caged radical species via simultaneous scission of both Pt–N_3 bonds (k_1). The latter species decompose to $Pt(CN)_4{}^{2-}$ and N_2 in water and ethanol (k_d) or interact with ethanol to produce HN_3 and ethanol radicals via the abstraction of hydrogen (k_3). For the photolysis in water $\phi = k_1/(k_n + k_1)$ and $\Delta V^{\#}(k_1) =$ 8.1 ± 0.4 cm^3 mol^{-1} under the assumption that $\Delta V^{\#}(k_n) \sim 0$ [4]. The azide radicals are very unstable in water and decompose rapidly to N_2 [14], $k_d =$ 6.8 × 10^9 M^{-1} s^{-1}. In ethanol an additional deactivation route for the CT excited state must be considered (k_2) to account for the production of HN_3 as byproduct [9, 10]. In this case $\phi = (k_1 + k_2)/(k_n + k_1 + k_2)$ and $\Delta V^{\#}(k_1 + k_2) = 14.3 \pm 0.9$ cm^3 mol^{-1}, such that the additional reaction accounts for the higher ϕ and $\Delta V^{\#}$ values. The increase in $\Delta V^{\#}$ especially favours the suggestion that the hydrogen abstraction originates from the CT excited state (k_2) and not from the caged radical species (k_3). The magnitude of $\Delta V^{\#}(k_1 + k_2)$ indicates that bond breakage is an important factor governing both processes, although the exact role of the ethanol molecule during the dissociative process remains unclear.

The suggested model outlined in Scheme 1 and described above, presents the most likely possibility. However, we cannot completely exclude the possibility that the reaction of the radical pair with ethanol to produce $HN_3(k_3)$ is the only additional step in ethanol as compared to water. In such a case ϕ and $\Delta V^{\#}$ should not be influenced by this subsequent reaction and alternative explanations for their higher values must be sought. A realistic possibility is that k_n and especially k_1 depend on the nature of the solvent, such that $\Delta V^{\#}$ may include a component due to solvent reorganization. Alternatively, the significantly different $\Delta V^{\#}$ values found for water and ethanol could, according to Neuman's suggestions [15], indicate that the reactions are 'two-bond scission' and 'one-bond scission' initiated processes, respectively. This would mean that, due to a specific solvent effect, the CT excited state can produce the radical pair according to a synchronous two-bond scission or a two-step, one-bond scission mechanism. Whatever the real reason may be, the results of this investigation clearly underline the dissociative nature of the radical pair formation process, and add another dimension to the understanding of charge transfer photochemistry.

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