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Influence of Pressure and Temperature on the Non-Radiative Relaxation in Solution of Excited States of Di(tertiaryphosphine) Complexes of Nickel(II)

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Although the study of the influence of pressure on the reactivity of the photo-excited states of transition metal complexes can yield mechanistically significant information, it has been pointed out [1–3] that ambiguities may arise in the interpretation of experimental data due to the difficulty of separating the effects of pressure on the competing photophysical and photochemical pathways. Investigation of the pressure dependence of photophysical processes alone is therefore of considerable importance.

We have recently shown [4], that pulsed laser excitation in the ligand-field bands of planar, diamagnetic Ni(II) complexes of the type $NiLX_2$ (X = halogen; L = bidentate phosphine ligand) results in the formation of triplet, tetrahedrally distorted excited states which, in non-coordinating solvents undergo exponential, non-radiative decay to the singlet, planar ground states. These complexes therefore afford an opportunity of studying the influence of pressure on unimolecular, excited state decays which involve spin and concomitant structural change.

We now present some results of excited state decay measurements as a function of pressure in the range 1–1200 bar for the complexes** $Ni(dpe)Cl_2$, $Ni(dpe)Cl_2$, $Ni(dpe)Br_2$ and $Ni(VPP)Br_2$ in the solvents dichloromethane and bromomethane. As a complement to the high pressure studies, the influence of temperature on the relaxation was also investigated in both solvents over the range 25 °C to –40 °C.

Experimental

The complexes $Ni(dpe)Cl_2$, $Ni(dpe)Br_2$ and $Ni(VPP)Br_2$ were synthesized according to published procedures [5, 6]. Solutions (~5 × 10^{-4} mol dm^{-3}) were prepared in CH_2Cl_2 and C_2H_5Br which had been dried (molecular sieve 4A) and fractionally distilled.

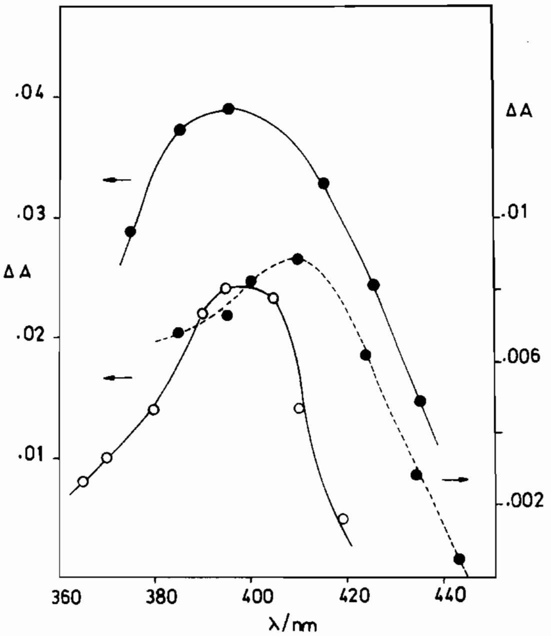

Fig. 1. Transient absorption spectra produced by laser pulse excitation of $NiLX_2$ at 530 nm. ○: $Ni(dpeCl_2$ in CH_2Cl_2; ●----●: $Ni(dpe)Br_2$ in CH_2Cl_2; ●——●: $Ni(dpe)Br_2$ in C_2H_5-Br.

Excited state decays over the pressure range 1–1200 bar were measured in a stainless steel high pressure reaction vessel fitted with four sapphire windows. The technique will be described in more detail elsewhere [8]. A 1 cm square fluorimeter cell was used for the studies at 1 bar in the temperature range 25 °C to –40 °C and the solutions were purged with argon prior to an experimental run.

Samples were excited at 530 nm using pulses of 5–25 ns duration from a pulse-sliced, Q-switched Nd^{3+}/glass laser and the excited state decays monitored spectrophotometrically using a pulsed Xe arc as the analysing source, [4, 7]. The transient signals were captured on a Tektronix 7912 AD digitizer controlled by a Commodore 3032 microcomputer. The computer programme used to analyse the decay traces was based upon the Guggenheim method for 1st order kinetics.

Results and Discussion

Nanosecond irradiation at 530 nm of the planar $NiLX_2$ complexes in either CH_2Cl_2 or C_2H_5Br

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**Ligand abbreviations: dpe = 1,2-bis(diphenylphosphine)-ethane; VPP = *cis*-1,2-bis(diphenylphosphine)ethylene.

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TABLE I. Lifetimes and Activation Parameters for Excited State Decay in $NiLX_2$.

X	L	τ_0 [a] (ns)	$\Delta H^{\ddagger}$ (kJ mol^{-1}) [b]	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}) [b]	$\Delta V^{\ddagger}$ (cm^3 mol^{-1}) [c]
Solvent CH_2Cl_2					
Cl	dpe	64 ± 3	11.4 ± 0.6	−68 ± 3	−9.6 ± 0.5
Br	dpe	23 ± 3	7.4 ± 0.6	−74 ± 3	−9.1 ± 0.4
Br	VPP	23 ± 2	7.5 ± 0.5	−74 ± 3	−8.3 ± 0.4
Solvent C_2H_5Br					
Cl	dpe	195 ± 10	13.7 ± 0.9	−70 ± 3	−12 ± 2
Br	dpe	54 ± 4	10.1 ± 0.5	−71 ± 2	−11 ± 2
Br	VPP	49 ± 4	9.0 ± 0.5	−74 ± 4	−10 ± 2

[a] Excited state lifetimes at 1 bar and 20 °C. [b] Errors are standard deviations. [c] Errors for CH_2Cl_2 data are standard deviations; errors for C_2H_5Br are estimated (see text).

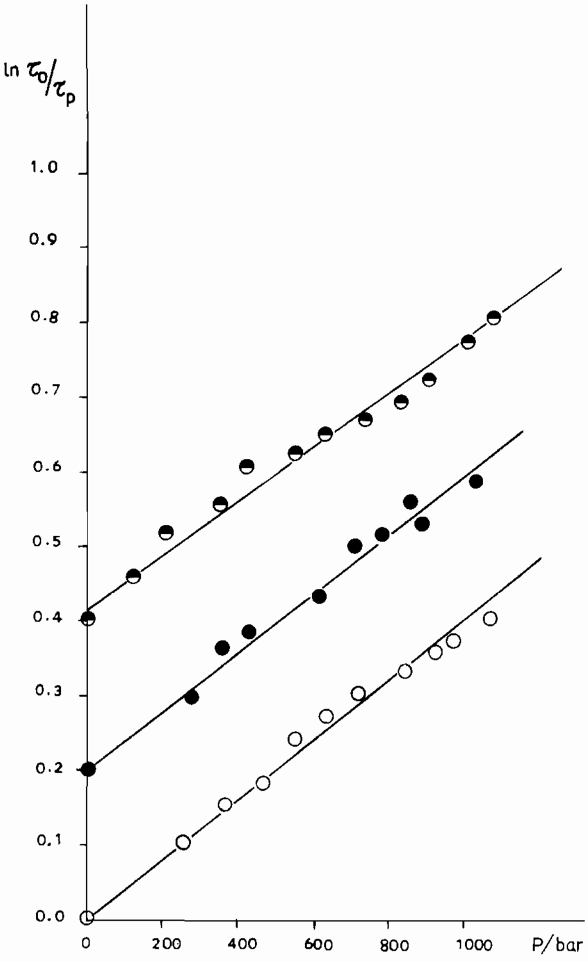

Fig. 2. Pressure dependence of the excited state relaxation of $NiLX_2$ in CH_2Cl_2. ○: $Ni(dpe)Cl_2$; ●: $Ni(dpe)Br_2$; ◒: $Ni(VPP)Br_2$. τ_0 denotes the relaxation time at 1 bar. For clarity of presentation, the ordinates of the plots for $Ni(dpe)Br_2$ and $Ni(VPP)Br_2$ have been shifted upwards from the true origin.

resulted in the prompt appearance of transients absorbing in the wavelength range 360–440 nm. As the examples in Fig. 1 show, the absorbance difference spectra are very similar to the transient spectrum previously observed [4] for $Ni(dpe)Br_2$ in CH_2Cl_2. On the basis of arguments already presented for the latter system, [4, 9], we assign the spectra to tetrahedrally distorted, triplet excited states of $NiLX_2$, formed during the laser pulse. In each case, the transients decayed exponentially to the singlet ground state of the parent complex. The triplet → singlet lifetimes, τ were independent of complex concentration [(1–5) × 10^{-4} mol dm^{-3}] and of monitoring λ (380–430) nm but varied significantly with temperature, halogen ligand and solvent (Table I). More strikingly, the excited state decay in both solvents was also strongly enhanced by increasing pressure. This is shown for the decay in CH_2Cl_2 by the plots in Fig. 2 of ln τ_0/τ_P *vs.* P, where τ_0 denotes the lifetime at 1 bar. The volumes of activation, $\Delta V^{\ddagger}$ derived from the slopes of these and of the corresponding plots for the relaxation in C_2H_5Br are summarized in Table I. Despite a greater scatter in the measurements in the latter solvent, as reflected in the larger estimated errors in this case, the $\Delta V^{\ddagger}$ values are all consistently and markedly negative. A considerable contraction in volume in proceeding from the excited state to the transition state is clearly implied. In general, both intrinsic and solvational components may contribute to experimentally measured $\Delta V^{\ddagger}$ values. In the present instance, consideration of the parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ derived from the temperature dependence* of τ_0

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*Plots of ln $1/\tau_0$ T *vs.* $1/T$ were linear over the range 295–235 K. The use of transition state theory for the treatment of thermally activated radiationless decay of excited states is discussed in [15].

provides a significant pointer to the nature of the transition state and hence to the dominant contribution to the observed $\Delta V^{\ddagger}$. As Table I shows, the $\Delta S^{\ddagger}$ values are markedly negative, in parallel with $\Delta V^{\ddagger}$. Furthermore they are independent of the (complex + solvent) system, within experimental error. The variation of τ_0 with both halogen ligand and solvent is thus attributable to changes in $\Delta H^{\ddagger}$ alone. The interesting point is that for both solvents $\Delta H^{\ddagger}$, though basically small, is larger for the chloro than for the bromo complexes. This can be accounted for in terms of a planar, *triplet* transition state formed *via* a low energy torsional coordinate [10, 11] on triplet excited state surfaces. Such a state, with the electronic configuration (in C_{2v} symmetry) $(a_1)^2 (b_1)^2 (a_2)^2 (a_1)^1 (b_2)^1$, should lie at higher energies for the chloro complex because of the larger ligand field splitting in that case between the outer, singly occupied $a_1(xy)$ and $b_2(x^2 - y^2)$ orbitals. This interpretation implies that the b_2 orbital, which is σ-antibonding along Ni(II)–ligand axes [9], remains occupied during the activation step. Intrinsic contributions to the activation volume due to changes in Ni–ligand bond lengths should therefore be minimal and the principal contribution to the negative $\Delta V^{\ddagger}$ must be solvational. The contraction in volume can be envisaged as arising from tighter solvation of the planar transition state compared to the initial tetrahedral excited state. The data in Table I suggest that $\Delta V^{\ddagger}$ may be solvent dependent. More extensive measurements of the excited state decay in C_2H_5Br as a function of P are needed to substantiate this and also to look for evidence of the pressure dependence* of $\Delta V^{\ddagger}$ as a consequence of solvent reorganization in the activation step. In this context the small but readily discernible differences between the $\Delta H^{\ddagger}$ values for the decays in CH_2Cl_2 and C_2H_5Br may signal a contribution to the activation enthalpy from solvent reorganization.**

A more tightly and regularly solvated transition state also accounts for the strongly negative activation entropy characterizing the triplet → singlet decay, an interpretation which is reinforced by the $\Delta V^{\ddagger}$ data. Appreciably negative $\Delta S^{\ddagger}$ values are also a feature [12, 13] of the $^5T \rightarrow {}^1A$ and $^6A \rightarrow {}^2T$ spin conversions in iron(II) and iron(III) complexes respectively and have been attributed in both these cases [12, 14] to non-adiabaticity in the spin crossover. It appears from the present studies on Ni(II) that $\Delta V^{\ddagger}$ measurements should constitute a critical test [8] of such interpretations.

It has been argued [3] that the unimolecular, non-radiative decay of excited states should be associated with near-zero volumes of activation. The results of the present investigation indicate that this assumption requires qualification when configurational and solvational changes are prominent features of the excited state relaxation. In a broader sense, our findings draw further attention to the study of pressure effects [16] as a probe of the influence of solvent on excited state lifetimes and dynamics.

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*Although the plots in Fig. 2 display some hint of curvature, the experimental scatter is too large to warrant a non-linear analysis.

**Limited solubility of the complexes constrains investigations in a wider range of solvents.