ilar fashion having nearly the same σ and π ionization energies near 11.2 eV.

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Comparison of Photochemical and Temperature-Jump Perturbations. The Rate of Interconversion of Planar and Octahedral Configurations of a Nickel(II) Complex[1]

Sir:

Pulsed neodymium lasers are finding increasing application in the study of fast chemical reactions. One such application is the temperature-jump technique in which the laser is used to raise the temperature of a solution containing the system of interest by several degrees within a very short time; this is conveniently accomplished by using a laser wavelength that is absorbed strongly by the solvent, but not the solutes.[2-4] In a less common application, the laser is used to rapidly photochemically dissociate a reactant or convert it into a product of the reaction; in this case, the laser frequency is chosen so that solvent absorption is at a minimum but solute absorbance is high.[5,6] Following these perturbations, the rate of adjustment of the system to its new equilibrium position (relaxation rate) is followed. This rate provides information about the kinetics obtaining in the system. We wish to report the results of a rather novel kinetic study in which a neodymium laser was used to produce predominantly either temperature increases or concentration jumps in the same equilibrium system depending upon whether the wavelength of the laser radiation was 1.06 or 1.41 μ and the solvent H_2O or D_2O. In each case the subsequent relaxation of the system was followed spectrophotometrically.

The system chosen for study is the nickel(II) complex of the quadridentate ligand $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ (*N,N'*-bis(2-aminoethyl)-1,3-propanediamine).[7] The nickel complex exists as an equilibrium mixture of low-spin planar ($^1A_{1g}$) and high-spin octahedral ($^3A_{2g}$) forms in aqueous solution at room temperature.[7,8]

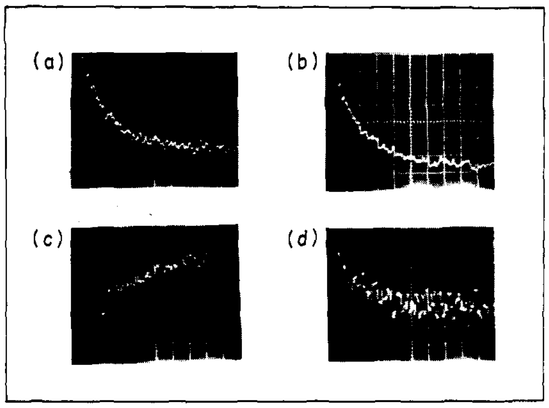

Figure 1. Absorbance at 440 nm as a function of time for solutions of $NiLCl_2$ ($L = NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$), with initial temperature 23°. The initial light intensity level was one major division above the bottom of the photograph, and the absorbance increases along the vertical axis. (a) 1.06 μ radiation, solvent H_2O, initial 440 nm absorbance is 0.32 ([Ni(II)] = 0.38 *M*, pathlength 0.08 cm), horizontal scale 0.2 μsec per major division, vertical scale 2% absorbance change per major division; (b) 1.06 μ radiation, solvent D_2O, initial 440 nm absorbance is 0.21 ([Ni(II)] = 0.13 *M*, pathlength 0.16 cm), horizontal scale 0.2 μsec per major division, vertical scale 3% absorbance change per major division; (c) 1.41 μ radiation, solvent H_2O, initial 440 nm absorbance is 0.32 ([Ni(II)] = 0.38 *M*, pathlength 0.08 cm), horizontal scale 0.1 μsec per major division, vertical scale 2% absorbance change per major division; (d) 1.41 μ radiation, solvent D_2O, initial 440 nm absorbance is 0.32 ([Ni(II)] = 0.38 *M*, pathlength 0.08 cm), horizontal scale 0.2 μsec per major division, vertical scale 0.6% absorbance change per major division.

$$NiL^{2+} + 2H_2O \rightleftharpoons NiL(H_2O)_2{}^{2+} \qquad (1$$

This reaction was previously found to be too rapid for study by conventional temperature jump techniques.[8] The system's relaxation times were, however, obtained in a study employing the neodymium laser radiation (1.06 μ) to rapidly perturb the above equilibrium by electronic excitation of the octahedral nickel complex ($\epsilon_{1.06\,\mu} \sim 2.0\ M^{-1}\ cm^{-1}$).[5] Following this perturbation, the return of the system to equilibrium was monitored by the absorbance decrease at 440 nm (an absorbance maximum for the planar complex). We have repeated these measurements on solutions 0.1–0.4 *M* in the chloride salt (both in H_2O and D_2O) using cells with path lengths of 0.08 and 0.16 cm. A typical relaxation is shown in Figure 1(a). It should be noted that there is a very rapid increase in the absorbance at 440 nm (rise time 30 nsec, the laser pulse width). This is followed by a slower absorbance decrease. The relaxation time for this decrease is 0.30 ± 0.02 μsec at 23° and independent of the concentration of the nickel complex, in accord with the previously reported results.[5] Also noteworthy is the observation that the "infinite time" absorbance is greater than the initial absorbance. This is due to a small displacement of the equilibrium resulting from the heating of the system. This effect is smaller, but not absent, in D_2O (Figure 1(b)). The temperature increase of the D_2O solution is primarily caused by the heat stemming from the nonradiative decay of the nickel excited state.

The interpretation of the observed relaxation de-

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pends on the fate of the excited octahedral complex. In the earlier study,[5] the excited complex was assumed to be very rapidly (*i.e.*, within the laser discharge time) converted to the *planar form in its ground state.*[9] The observed relaxation was then ascribed to the reestablishment of equilibrium *via* reactions of the ground-state octahedral and planar forms. In the absence of knowledge of the rate of conversion of the excited octahedral form to the ground-state planar complex or of the genuine relaxation rate for the ground-state complexes this interpretation is open to question. In an effort to resolve this difficulty we independently studied the relaxation of this system using the Raman laser temperature-jump technique.

The same solutions that had been used in the 1.06 μ study were irradiated with 1.41 μ photons, obtained by using liquid nitrogen to Raman shift the 1.06 μ neodymium radiation.[3] The solutions were initially at 23°, and, in the case of H_2O solutions, temperature jumps of 2–3° were produced. The relaxation was again monitored at 440 nm. A typical trace for the H_2O solution is shown in Figure 1(c). Here the direction of the observed relaxation is opposite to that shown in Figure 1(a), but the relaxation time, 0.30 ± 0.02 μsec, is the same as that produced with the 1.06 μ radiation. The direction of the signal change, indicating an increase in the equilibrium concentration of the planar complex, is consistent with the exothermicity of eq 1 ($\Delta H° = -4.8 \pm 0.3$ kcal mol^{-1}).[5] Using 1.41 μ radiation for the H_2O solution favors temperature-jump over nickel photochemistry because of the relative absorbances of the complex and solvent at this wavelength (for H_2O, $A_{1.41} = 10$ cm^{-1}; for the nickel solution, $\epsilon_{1.41} \leq 1$ M^{-1} cm^{-1}). A relaxation of the kind found for 1.06 μ (but of smaller amplitude) is, however, seen when the D_2O solution is used at 1.41 μ (Figure 1(d)). Here again excitation of the octahedral nickel complex predominates because of the low absorptivity ($A = 0.07$ cm^{-1}) of D_2O at 1.41 μ.[2]

It is apparent from Figure 1(a), (b), and (c) that the signal changes obtained for photochemical and temperature-jump perturbations are of similar magnitude. For the photochemical perturbation at 1.06 μ the fractional increase in the concentration of planar molecule is given by[10]

$$\frac{\Delta[\mathrm{NiL}^{2+}]}{[\mathrm{NiL}^{2+}]} = \frac{2.3 \times 10^3 \epsilon I_0 K \phi}{N} \tag{2}$$

where ϵ (the molar absorptivity of the octahedral form at 1.06 μ) is 2.0 M^{-1} cm^{-1}, I_0 (the intensity of the incident laser beam) is 1.5×10^{19} photons cm^{-2} (3 J cm^{-2}), K (the equilibrium constant for reaction 1) is 6.25, N is Avogadro's number, and ϕ is the quantum efficiency for conversion of the excited octahedral complex to the planar form. Expression 2 reduces to 0.75ϕ. Since the observed 440 nm absorbance change corresponds to a 15% increase in the planar concentration, it follows that $\phi \sim 0.2$. In the case of temperature-jump perturbation for the H_2O solution at 1.41 μ, provided that the concentration of the planar form is much less than that of the octahedral, the fractional increase in the concentration of the planar complex is given by expression 3. Here ΔT is the temperature increase produced, 2.5° for 1 J cm^{-2} of 1.41 μ radiation, and $\Delta H°$ is the enthalpy change for reaction 1, 4.8 kcal mol^{-1}.

$$-\frac{\Delta[\mathrm{NiL}^{2+}]}{[\mathrm{NiL}^{2+}]} = \frac{\Delta T \Delta H°}{RT^2} \tag{3}$$

The concentration increase calculated for the planar form is 7%, in satisfactory agreement with the observed absorbance change of 9%. If the absorbance of the solvent at the wavelength of irradiation is less than 0.05, then the temperature jump produced is $\Delta T = 2.3 I_0 A/C$ where C is the heat capacity of the solution and A is the solvent absorbance per centimeter. Consequently the ratio of the displacements by the two perturbations (subject to the above conditions) is

$$-\frac{\Delta_{\text{photochem}}}{\Delta_{\text{temp jump}}} = \frac{7.0 \times 10^{-2} \epsilon K \phi T^2 C \lambda}{\Delta H° A} \tag{4}$$

where the energy units for C and $\Delta H°$ are calories and λ, the wavelength of the incident laser beam, is expressed in microns. The above equation neglects any temperature increase arising from absorption of the laser radiation by the solute. Equation 4 predicts the above ratio to be ~50 in H_2O at 1.06 μ, in good agreement with the observed value once allowance is made for the temperature increase resulting from the radiation absorption by the nickel complex.

It is worth reemphasizing that, in the present study, replacing H_2O by D_2O (with 1.41 μ radiation) converts a situation in which a *less* than equilibrium concentration of the planar complex is present immediately after the perturbation into one in which a *larger* than equilibrium concentration of the planar form is produced initially. A similar reversal in the direction of the perturbation is produced in H_2O by changing from 1.41 to 1.06 μ. Further, the agreement of relaxation times obtained by two independent methods is especially significant in that it adds credibility to the interpretation of the photochemically obtained results in terms of the reactions of ground-state species.

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Photoisomerizations of 2-Methylphenylcyclopropanes to 4-Phenylbutenes. Stereochemistry at the Benzylic Carbon

Sir:

The nature of the transition states in organic reactions is the object of continued investigation. Stereochemical criteria have been of great value in elucidating the nature of organic transition states, and the photochemical isomerization of 2-alkylphenylcyclopropanes to 4-phenylbutenes is amenable to such an experimental test.

Our working hypothesis was based on two reasonable mechanistic possibilities: (1) a σ^2s + σ^2s con-

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[9] The absorbance changes in Figure 1(a) and (b) may also be explained by postulating that the decay of the excited octahedral nickel complex yields a 440-nm absorbing, nonreactive species. This interpretation seems less plausible than that advanced above.

[10] Equation 2 obtains provided that the 1.06 μ absorbance of the solute is small (less than 0.05).