Unusual Relaxation Kinetics in the Photo-induced Planar $\rightleftharpoons$ Tetrahedral Isomerization of Dibromo[1,3-bis(diphenylphosphino)propane]nickel(II) in Acetonitrile

By Louis Campbell and John J. McGarvey
(*Department of Chemistry, The Queen's University of Belfast, Belfast* BT9 5AG)

Summary Three relaxation processes observed during the *Q*-switched laser photolysis of the title complex in acetonitrile are assigned to the relaxation of coupled equilibria involving planar and tetrahedral isomers of the complex together with ion-pairs and free ions.

We recently described[1] a novel photochemical approach to the study of ground electronic state planar $\rightleftharpoons$ tetrahedral isomerization kinetics in ditertiary phosphine complexes of nickel(II), in which a *Q*-switched laser pulse was used to perturb the planar $\rightleftharpoons$ tetrahedral equilibrium. Readjustment of the equilibrium was characterized by a single, concentration-independent relaxation time. When the technique was applied to the complex dibromo[(1,3-bis-diphenylphosphino)propane]nickel(II), [Ni(dpp)Br_2], in CH_2Cl_2, this expected behaviour was found. However with the same complex in acetonitrile, we observed three distinct relaxation processes following the laser pulse. Spectral and conductivity measurements showed that, in addition to the anticipated isomerization equilibrium, partial ionic dissociation of the complex occurs in acetonitrile. We now present strong kinetic evidence that the three relaxations can be assigned to readjustment of equilibria involving the planar (SP-) and tetrahedral (tet-) isomers together with ion-pairs and free ions. For the kinetic studies, the use of both spectrophotometric and conductimetric detection methods proved advantageous.†

Distinct relaxation times τ_1 and τ_2 were measured at monitoring wavelengths of *ca.* 500 nm and *ca.* 410 nm, respectively, following laser irradiation at 1060 nm, where the tet isomer is the principal absorber. Traces (a) and (b) in the Figure illustrate the observed changes in absorbance. When the laser output was frequency-doubled to 530 nm, which is in the absorption region of the SP isomer, the absorbance traces were mirror images of (a) and (b), but yielded the same times τ_1 and τ_2. A third, slower relaxation time, τ_3 was monitored conductimetrically [trace (c)]. The Table summarises the data. All three times change with temperature, but whereas τ_3 also varies with concentration of complex, τ_1 and τ_2 are concentration independent.

TABLE

Relaxation times, τ at different irradiation (λ_i) and monitoring (λ_m) wavelengths as a function of temperature and [Ni(dpp)Br$_2$]

		λ_i 1060 nm		λ_i 530 nm		
	Temp./°C λ_m/nm	8	30	8	30	[Ni(dpp)Br$_2$] /mol dm^{-3}
τ_1/μs	500	0·55	0·24	0·5	0·2	10^{-3}
		0·5	0·23[a]	0·54	0·18	$2{\cdot}5 \times 10^{-4}$
τ_2/μs	410	0·22	0·14	0·2	0·15	10^{-3}
		0·2	0·13[a]	0·18	0·13	$2{\cdot}5 \times 10^{-4}$
τ_3/μs	conductimetric[b]	3·7				10^{-3}
		4·7				$7{\cdot}5 \times 10^{-4}$
		5·6				5×10^{-4}

[a] [Ni(dpp)Br$_2$] = 5×10^{-4} mol dm^{-3}; [b] temp. = 23 °C.

The dependence on irradiation wavelength of the direction of the absorbance changes shows that the net effect of the laser pulse is the reversible perturbation of the isomerization equilibrium, as in the earlier studies.[1] To account for three τ values in place of one we propose equation (1) (L = dpp), where [NiLBr]$^+$||Br$^-$ denotes a

$$\text{SP-}[\mathrm{NiLBr_2}] \underset{K_1}{\rightleftharpoons} \text{tet-}[\mathrm{NiLBr_2}] \underset{K_2}{\rightleftharpoons} [\mathrm{NiLBr}]^+||\mathrm{Br}^- \underset{\substack{k_{-3}\\ K_3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{NiLBr}]^+ + \mathrm{Br}^- \qquad (1)$$

solvent-separated ion pair and [NiLBr]$^+$ the complex cation with a solvent molecule presumably occupying the fourth co-ordination position. The configuration about the metal ion in these two entities is left unspecified.

The principal absorber at 500 nm is the SP isomer whereas the tet isomer absorbs more strongly at 410 nm.[1] We assign τ_1 and τ_2, respectively, to the relaxation of equilibria K_1 and K_2 following the ground-state depletion of tet-[NiLBr$_2$] by a 1060 nm pulse or its rapid production by a 530 nm pulse. The conductivity decrease [trace (c)] associated with the relaxation of K_3 which must follow that of K_2 is fully consistent with these assignments. Further, after a 530 nm pulse, the fast step at 410 nm was followed by an absorbance increase with a relaxation time equal to τ_3.

The fact that only τ_3 is concentration-dependent accords with equation (1) and is expected in consequence of the relative magnitudes of τ_1, τ_2, and τ_3 which also imply that the interconversions, SP $\rightleftharpoons$ tet $\rightleftharpoons$ ion-pair, are not rate-determining in the readjustment of the successive equilibria following perturbation. Since $\tau_3 >> \tau_1$, τ_2, equation (2) may be derived[2] by a standard kinetic analysis:

$$\tau_3^{-1} = k_{-3}([\mathrm{NiLBr}^+] + [\mathrm{Br}^-]) + k_3K_1K_2/[1 + K_1(1 + K_2)] \qquad (2)$$

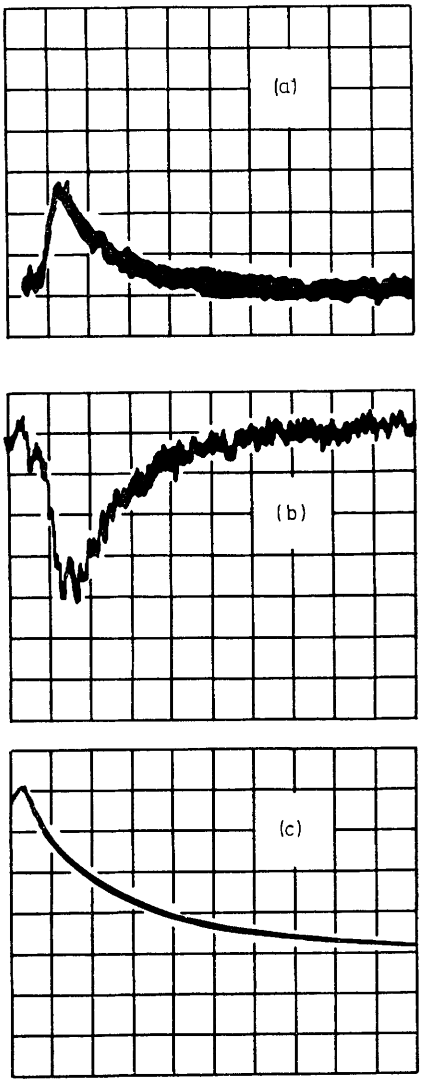

FIGURE. Transient absorbance and conductivity changes in [Ni(dpp)Br$_2$]–MeCN solution following laser irradiation at 1060 nm. Monitoring λ (absorbance increasing upwards): (a) 500 nm; (b) 410 nm; (c) conductimetric detection. Vertical scales: (a) 10 mV/div.; (b) 5 mV/div.; (c) 20 mV/div. Horizontal scales: (a) 0·2 μs/div.; (b) 0·1 μs/div.; (c) 2·0 μs/div. temp. *ca.* 25 °C in all cases.

A plot of τ_3^{-1} *vs.* [NiLBr$^+$] + [Br$^-$], the ion concentrations calculated from the dissociated constant, K_d which was measured conductimetrically (K_d *ca.* 2×10^{-6} mol dm^{-3}

at 25 °C), gave: slope, $k_{-3} = 3 \pm 2 \times 10^9$ dm^3 mol^{-1} s^{-1} at 23 °C and a ratio of intercept:slope $= K_1K_2K_3/[1 + K_1(1 + K_2)] = K_d = 10^{-6}$ mol dm^{-3}, in reasonable agreement with the measured K_d. The value of k_{-3} just approaches the lower end of the range expected for diffusion control and is close to the k recently measured[3] for ion recombination involving another complex of nickel(II) in acetonitrile.

The present results are a further illustration of the contribution which photochemical initiation can make to the study of ground electronic state chemical relaxation processes.[1,3] The system should also be amenable to complementary kinetic investigation by the dissociation field relaxation technique.[3,4]

We thank the S.R.C. for support, and the Department of Education (N. Ireland) for a postgraduate studentship (to L.C.).

(*Received*, 28*th June* 1976; *Com.* 717.)

---

† A minor modification of the voltage-divider method (G. Beck and J. K. Thomas, *J. Chem. Phys.*, 1972, **57**, 3649) was used. Applied voltages were in the range 90—120 V. The load resistance was 300—500 Ω and the solution resistance > 7000 Ω.

[1] J. J. McGarvey and J. Wilson, *J. Amer. Chem. Soc.*, 1975, **97**, 2531.
[2] G. Czerlinski, 'Chemical Relaxation,' Arnold, London, 1966, p. 53.
[3] H. Hirohara, K. J. Ivin, J. J. McGarvey, and J. Wilson, *J. Amer. Chem. Soc.*, 1974, **96**, 4435.
[4] H. Hirohara, K. J. Ivin, and J. J. McGarvey, *J. Amer. Chem. Soc.*, 1974, **96**, 3311.