

also been carried out using SF<sub>6</sub> as an infrared sensitizer.<sup>8</sup> However, SF<sub>6</sub> is less effective than SiF<sub>4</sub>. Under the same conditions as in run 5, if SF<sub>6</sub> is used as a sensitizer, methylacetylene begins to appear only after 50 pulses.

Our studies on the use of SiF<sub>4</sub> as an infrared sensitizer for inducing chemical reactions in the gas phase by high power infrared lasers are continuing.

**Acknowledgment.** We thank Professor E. Grunwald and Dr. K. Olszyna for helpful discussions.

### References and Notes

- (1) Support from NSF and Research Corporation is gratefully acknowledged.
- (2) S. S. Levush, S. S. Abadzhev, and V. U. Shevchuk, *Neftekhimiya*, **9**, 215 (1969).
- (3) Y. Sakakibara, *Bull. Chem. Soc. Jpn.*, **37**, 1262 (1964).
- (4) (a) A. Lifshitz, M. Frenkloch, and A. Burcat., *J. Phys. Chem.*, **79**, 1148 (1975); (b) J. N. Bradley and K. O. West, *J. Chem. Soc., Faraday Trans. 1*, **71**, 967 (1975); (c) R. Walsh, *ibid.*, **72**, 9 (1976).
- (5) K. J. Olszyna, E. Grunwald, P. M. Keehn, and S. P. Anderson, *Tetrahedron Lett.*, 1609 (1977).
- (6) (a) S. Mukamel and J. Jortner, *Chem. Phys. Lett.*, **40**, 150 (1976); (b) D. M. Larsen and N. Bloembergen, *Opt. Commun.*, **17**, 254 (1976).
- (7) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, N.Y., 1976, p 370.
- (8) J. Tardien de Maleissye, F. Lempereur, C. Marsal, and R. I. Ben-Aïm, *Chem. Phys. Lett.*, **42**, 46 (1976).

Chris Cheng, Philip Keehn\*

Department of Chemistry, Brandeis University  
Waltham, Massachusetts 02154

Received April 18, 1977

### Observation of a Rapid Ionic Photoassociation Reaction in the Q-Switched Laser Photolysis of a Planar Complex of Nickel(II) in Solution

Sir:

Among transition metal complexes examples of photoassociation are very rare. The first case was reported<sup>1</sup> in 1972, and more recently, exciplex formation in an Ir(III) complex has been described.<sup>2</sup> We wish here to report a novel example of an ionic photoassociation reaction. The phenomenon was observed during the Q-switched laser photolysis at 530 nm of the complex 1,1,7,7-tetraethyldiethylenetriaminenickel(II), [Ni(Et<sub>4</sub>dien)Cl]Cl. In acetonitrile solutions of this complex, two planar diamagnetic species, Ni(Et<sub>4</sub>dien)Cl<sup>+</sup> and a solvent-separated ion pair NiEt<sub>4</sub>dienCl<sup>+</sup>||Cl<sup>-</sup>, are present in equilibrium with paramagnetic five-coordinate Ni(Et<sub>4</sub>dien)Cl<sub>2</sub>, according to the scheme<sup>3</sup> (L = Et<sub>4</sub>dien):

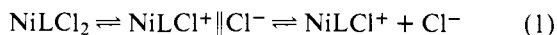
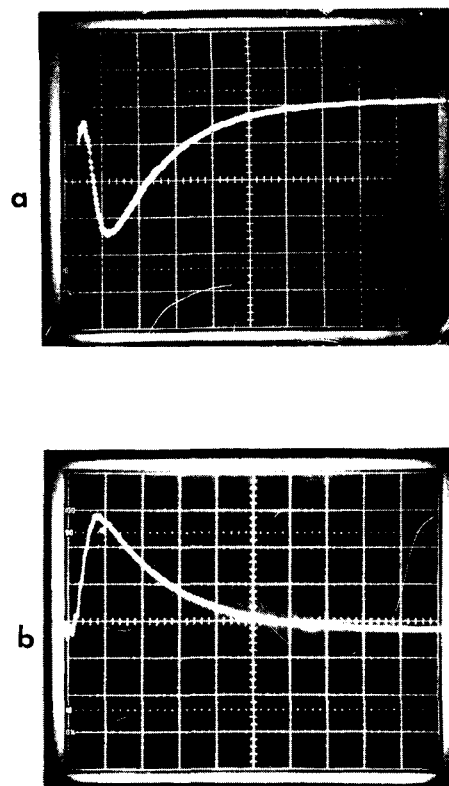


Figure 1 shows the transient conductivity changes, monitored by the voltage divider method,<sup>4</sup> which occurred when acetonitrile solutions of the complex were irradiated with Q-switched neodymium laser pulses (60-ns duration) at 530 nm (trace a) and 1060 nm (trace b). In trace b, the rapid increase and subsequent decay in conductivity as a result of 1060-nm irradiation mark the photochemical formation (within the laser pulse) of planar NiLCl<sup>+</sup>||Cl<sup>-</sup> from five-coordinate NiLCl<sub>2</sub>, the principal absorbing species at 1060 nm, followed by relaxation of the perturbed equilibria (eq 1). This is in line with the interpretation put forward in a previous paper,<sup>3</sup> of the transient optical density changes observed in the same system following 1060-nm irradiation.

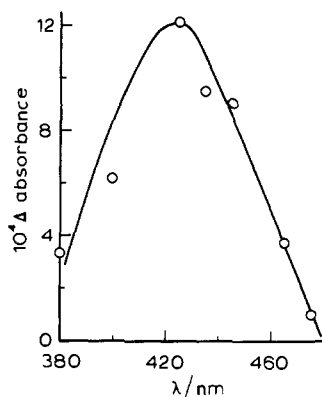
The novel feature we wish to highlight here is illustrated by trace a, from which it is evident that a rapid conductivity decrease follows the 530-nm laser pulse and a subsequent relaxation to equilibrium conditions takes place. This unexpected observation of an initial decrease in conductivity was verified in numerous experiments.<sup>5</sup> It can be explained by the rapid



**Figure 1.** Transient conductivity changes in laser-irradiated Ni(Et<sub>4</sub>dien)Cl<sub>2</sub> in CH<sub>3</sub>CN, monitored by the voltage divider method; applied voltage 200 V, solution resistance 14.5 kΩ, load resistance 400 Ω: (a) irradiation at 530 nm (vertical scale 2 mV/div, horizontal 0.5 μs/div); (b) irradiation at 1060 nm (vertical scale 5 mV/div, horizontal 0.5 μs/div).

relaxation of the equilibrium (see eq 1) between the solvent-separated ion pair and free ions following the occurrence within the laser pulse of an association reaction between Cl<sup>-</sup> ion and photoexcited NiLCl<sup>+</sup> produced by irradiation at 530 nm where the principal absorber<sup>6</sup> is the ion pair, NiLCl<sup>+</sup>||Cl<sup>-</sup>. This photoassociation displaces the ion pair ⇌ five-coordinate equilibrium toward the latter species. The ensuing rapid relaxation (τ<sub>1</sub> < 0.2 μs at room temperature) to a lower conductivity followed by a return to the initial level is consistent with the reaction scheme of eq 1 which should be characterized by two relaxation times. Clearly, only the slower of these two relaxations can actually be measured under the conditions of the experiments reported here.<sup>7</sup> This ("slow") relaxation time, τ<sub>2</sub>, should be the same as that measured when equilibria 1 are perturbed to the right by 1060-nm irradiation. In fact, the relaxation times derived from traces such as (a) and (b) agreed within experimental error and varied with the concentration of complex. In the 530-nm irradiation experiments the following values of τ<sub>2</sub> (μs) at 23 °C were measured at the concentrations indicated ([complex] × 10<sup>-4</sup> mol dm<sup>-3</sup>): 1.1 (2.5), 0.93 (5), 0.91 (7.5), 0.86 (10), 0.79 (25), yielding a curved plot for τ<sub>2</sub><sup>-1</sup> against [NiLCl<sup>+</sup>] + [Cl<sup>-</sup>]. This is in accord with a standard kinetic analysis<sup>8</sup> of eq 1, taking τ<sub>2</sub> to be associated with the (relatively) slow relaxation between five-coordinate complex and four-coordinate ion pair coupled to the faster relaxation between ion pair and ions.<sup>7</sup> As well as leading to a satisfactory kinetic analysis, the proposed photoassociation was supported by spectrophotometric measurements since transient absorbance increases within the laser pulse were seen in the wavelength range 420–500 nm when the complex was irradiated at 530 nm.

Further compelling evidence for an excited state association reaction as a consequence of irradiation at 530 nm was provided by studies of the complex in ethanol. In this solvent, only four-coordinate species, NiLCl<sup>+</sup>||Cl<sup>-</sup> and NiLCl<sup>+</sup>, are present



**Figure 2.** Absorbance difference spectrum for  $\text{Ni}(\text{Et}_4\text{dien})\text{Cl}_2$  in ethanol,  $10^{-3} \text{ mol dm}^{-3}$ . Laser irradiation at 530 nm.

and although the relatively high conductance of the solutions precluded transient conductivity studies, spectrophotometric measurements in the 380–500-nm range showed a rapid absorbance increase and subsequent decay with a first-order time constant of  $0.3 \mu\text{s}$  at  $20^\circ\text{C}$  when the solution was irradiated at 530 nm. The transient spectrum is shown in Figure 2 and is very similar in shape to the corresponding spectrum in acetonitrile, but with  $\lambda_{\text{max}}$  showing a slight blue shift. There can be little doubt that this is the spectrum of a five-coordinate species formed in an association reaction between  $\text{Cl}^-$  and the photoexcited  $\text{NiLCl}^+$  complex, especially since there is no evidence for the five-coordinate complex in ethanol in normal, equilibrium (“dark”) conditions.

The explanation for the ready occurrence of the photoassociation reaction may lie in the distortion of the (vibrationally equilibrated) excited state produced by the laser pulse. Our previous studies<sup>4b,9</sup> of the laser flash photolysis of planar Ni(II) complexes, as well as earlier spectral and photochemical evidence,<sup>10</sup> strongly suggest that some of the ligand field excited states of  $d^8$  planar complexes may be tetrahedrally distorted. In the present system, repulsion between the filled  $d_{z^2}$  orbital in planar  $\text{NiLCl}^+$  and an approaching  $\text{Cl}^-$  ion might be lessened in the event of such a distortion of the complex away from a planar configuration. A parallel factor to be considered is the spin change accompanying the formation of paramagnetic five-coordinate product since in the altered electronic configuration the  $d_{z^2}$  orbital becomes singly instead of doubly occupied. The role of the solvent must also be taken into account,<sup>11</sup> and the details of the solvent and structural relaxation processes leading from the initially populated Franck–Condon state to the observed five-coordinate species remain a matter for future investigation.

The photoreversibility of the system widens the access to the kinetic parameters which characterize the ground electronic state interconversions and thus provides a check on the internal consistency of the assignments of the relaxation processes which follow photoexcitation. Systems of this type should also be useful models for testing some current proposals<sup>12</sup> concerning the similar nature of transition states for thermal reactions and the thermally equilibrated excited states which are thought to mediate the photochemical reactions of metal complexes.

**Acknowledgments.** We thank Drs. J. J. Rooney and S. M. Nelson for helpful discussions. The work was supported by a grant from the Science Research Council. L.C. thanks the Northern Ireland Department of Education for a postgraduate studentship.

## References and Notes

- (1) W. M. Bedford and G. Rouschias, *J. Chem. Soc., Chem. Commun.*, 1224 (1972).

- (2) R. Ballardini, G. Varani, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **96**, 7123 (1974).
- (3) H. Hirohara, K. J. Ivin, J. J. McGarvey, and J. Wilson, *J. Am. Chem. Soc.*, **96**, 4435 (1974).
- (4) (a) G. Beck and J. K. Thomas, *J. Chem. Phys.*, **57**, 3649 (1972); (b) L. Campbell and J. J. McGarvey, *J. Chem. Soc., Chem. Commun.*, 749 (1976).
- (5) Similar conductivity decreases were observed for the bromide complex and also in acetone as solvent. No conductivity changes could be detected when  $\text{Et}_4\text{NCl}/\text{CH}_3\text{CN}$  solutions of comparable resistance to the test solutions were irradiated at either 530 or 1060 nm.
- (6) As discussed in ref 3,  $\text{NiLCl}^+$  and  $\text{NiLCl}^+\|\text{Cl}^-$  have identical absorption spectra but the latter species is strongly favored at equilibrium.
- (7) Low-temperature experiments are in progress to study the faster relaxation. The two relaxations are evidently strongly coupled, and the observed  $\tau$  values will be approximations to the true relaxation times. Following the photoassociation, the relaxation spectrum is dominated by the ion pair  $\rightleftharpoons$  ion relaxation ( $\sim\tau_1$ ), while at a later time the major contribution comes from the five-coordinate complex  $\rightleftharpoons$  ion-pair relaxation ( $\sim\tau_2$ ).
- (8) See, e.g., C. F. Bernasconi, “Relaxation Kinetics”, Academic Press, London and New York, 1976, Chapter 3.
- (9) J. J. McGarvey and J. Wilson, *J. Am. Chem. Soc.*, **97**, 2531 (1975).
- (10) (a) For a recent discussion see P. C. Ford, R. E. Hintze, and J. D. Petersen in “Concepts of Inorganic Photochemistry”, A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, p. 237; (b) see also papers cited in ref 9.
- (11) Investigations on other four-coordinate Ni(II) complexes in polar media suggest a significant role for the solvent in the excited-state reactivity: C. J. Cairns, L. H. Campbell, and J. J. McGarvey, experiments in progress.
- (12) A. W. Adamson, ref 10a, p. 424.

Louis Campbell, John J. McGarvey\*

Department of Chemistry, The Queen's University of Belfast  
Belfast BT9 5AG, Northern Ireland

Received March 11, 1977

## Diels–Alder Reactions of $\alpha$ -Phenylsulfinylmethylene-carbonyl Compounds. The Synthesis of Disodium Prephenate Dimethyl Acetal

Sir:

Cyclohexadienones such as **1** might well service several synthetic objectives. If  $\text{R} = \text{H}$ , phenol **2** would be produced, presumably under the conditions of the formation of **1**. Alternatively, if  $\text{R} \neq \text{H}$ , decacylation (e.g., decarboxylation) of the vinylogous  $\beta$ -dicarbonyl system would lead to phenol **3**. Of course, acid-catalyzed dienone–phenol rearrangements<sup>1</sup> and photochemical transformations<sup>2</sup> could also be exploited.

In addition to such general possibilities, a suitable version of **1** might serve as a precursor to prephenic acid (**4**), a central

