quenched by 0.05 M *p*-dimethoxybenzene, while the fluorescence of P was not quenched by *p*-dimethoxybenzene.

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Organic Chemistry by Infrared Lasers.[1] 1. Isomerization of Allene and Methylacetylene in the Presence of Silicon Tetrafluoride

Sir:

We wish to report here on the isomerization of allene and methylacetylene in the presence of SiF_4 as induced by a pulsed CO_2 megawatt infrared laser, demonstrating that under controlled conditions isomerizations can be carried out by this method and that competitive thermal decomposition of methylacetylene can be minimized.

Thermal isomerization of allene to methylacetylene in the temperature range of 900–1150 K has been studied by Levush et al.[2] who demonstrated that the reaction proceeds unimolecularly with an activation energy of ~55 kcal/mol. Though no rate constants were calculated, Sakakibara[3] demonstrated that structural isomerization was considerably faster than decompositions. Recently, Lifshitz et al.[4] studied this isomerization using a single-pulse shock tube technique in the temperature range of 1030–1220 K and found the isomerization to be "clean" and unimolecular with an activation energy of 61.2 ± 7.5 kcal/mol. They also found that the rate of the reverse action, methylacetylene to allene, was smaller than that of the forward reaction.

Recently[5] we demonstrated the usefulness of the inert sensitizer, SiF_4, for inducing chemical reaction of substrates which do not themselves absorb in the 9.2–11-μ region of the CO_2 laser. After absorption of laser energy at 1025 cm^{-1} the vibrational energy of the highly excited SiF_4 is sufficient, if converted adiabatically into random thermal energy, to produce temperatures in excess of 1000 K while the reaction vessel remains at ambient temperature. Although we do not know the detailed molecular dynamics[6] of energy transfer to the reactive substrate, reactions very similar to those in normal thermal decompositions take place. The effective reaction temperatures can be controlled by varying the concentration of SiF_4 or of reactant, or by varying the dose per flash of the laser beam.

In our studies, using the method described previously by Olszyna et al.,[5] various mixtures of allene and SiF_4 were irradiated at 1025 cm^{-1} using a pulsed megawatt CO_2 laser. The reactions were carried out in Monel cells (17-cm^3 volume) with KCl windows using two different dose levels. The results are given in Table I. It is obvious that at the lower dose (0.40 J/cm^2) the thermal decomposition of methylacetylene to methane and acetylene is minimized. At the higher dose, on the other hand, pyrolysis is favored even with fewer pulses. Thus, in run 7, after 25 pulses, all the allene has been isomerized and the presence of large quantities of CH_4 and C_2H_2 indicates the extensive secondary thermal decomposition of the methylacetylene. This is to be contrasted with run 1 where, after 50 pulses, the amount of methylacetylene is approximately the same, yet the presence of CH_4 and C_2H_2 is ~100 and 160 times less than that observed in run 7. This is probably due to the fact that the final temperature in run 1 is lower than that in run 7. Thermal decomposition of methylacetylene can also be minimized by decreasing the SiF_4 pressure. Runs 8–11 demonstrate that, even at the higher dose levels, isomerization can be controlled with a minimum of thermal decomposition. When these are compared with runs 1 and 2, it is obvious that the efficiency of the thermal isomerization is greater at the higher dose and low SiF_4 pressure.

Interestingly, in runs 1–4 and 8–11, the disappearance of allene per flash is greater in the earlier stages of the reaction. The results follow a pattern resembling the kinetics of reversible approach to a photostationary state[7] or an equilibrium state. That reversibility is indeed present, was demonstrated by the following experiments. (1) A mixture of SiF_4 (5 Torr) and methylacetylene (20 Torr) was irradiated at 0.73 J/cm^2. After 250 pulses the composition of the mixture was 10.0% allene, 80.0% methylacetylene, 0.3% methane, and 9.6% acetylene. This experiment, when compared with run 8, qualitatively implies that, by this method, the rate of isomerization of methylacetylene to allene is several times slower than the rate of isomerization of allene to methylacetylene. (2) Irradiation of a 17:16-Torr mixture of allene and methylacetylene in the presence of 16 Torr of SiF_4 at low dose (0.4 J/cm^2) showed no significant changes in the ratio of allene and methylacetylene even after 400 pulses.

It should finally be pointed out that this isomerization has

Table I

Run[a]	SiF_4 (Torr)	Allene (Torr)	Dose (J/cm^2) per flash	No. of pulses	% rxn[b]	% CH_4[c]	% $HC{\equiv}CH$[c]	% $CH_2{=}C{=}CH_2$[c]	% $H_3C{-}C{\equiv}CH$[c]
1	20	20	0.40	50	14.6	0.1	0.5	85.8	12.5
2	20	20	0.40	100	57.9	1.2	3.8	42.7	51.4
3	20	20	0.40	150	60.2	1.2	3.6	40.1	53.0
4[d]	20	20	0.40	400	72.9	8.4	23.4	20.7	45.5
5	20	20	0.73	1	13.9	0.8	4.6	92.1	2.5
6	20	20	0.73	5	54.5	4.2	25.6	54.0	16.3
7	20	20	0.73	25	99.5	8.7	79.6	<0.1	11.8
8	5	20	0.73	25	9.2	<0.1	0.4	87.3	12.3
9	5	20	0.73	50	42.6	0.5	1.7	55.7	41.2
10	5	20	0.73	75	46.3	0.9	2.7	45.6	49.8
11[d]	5	20	0.73	400	64.5	3.8	10.4	31.2	51.5

[a] Bright flashes of light are frequently observed during irradiation and a black sooty material (elemental carbon) is seen in the reaction vessel after irradiation. [b] Percent reaction is calculated by following the decrease in absorption of the allene 1970-cm^{-1} band in the infrared spectrum after a given number of pulses. [c] Identifications were made by IR and GC (flame ionization) analysis and percent composition of the mixtures after irradiation were calculated from integrated GC traces. [d] In these reactions ethylene is also observed by GC and IR analysis (0.5% in run 4 and 0.6% in run 11).

also been carried out using SF_6 as an infrared sensitizer.[8] However, SF_6 is less effective than SiF_4. Under the same conditions as in run 5, if SF_6 is used as a sensitizer, methylacetylene begins to appear only after 50 pulses.

Our studies on the use of SiF_4 as an infrared sensitizer for inducing chemical reactions in the gas phase by high power infrared lasers are continuing.

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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[1] in 1972, and more recently, exciplex formation in an Ir(III) complex has been described.[2] 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$_4$dien)Cl]Cl. In acetonitrile solutions of this complex, two planar diamagnetic species, Ni(Et$_4$dien)Cl$^+$ and a solvent-separated ion pair NiEt$_4$dienCl$^+$‖Cl$^-$, are present in equilibrium with paramagnetic five-coordinate Ni(Et$_4$dien)-Cl$_2$, according to the scheme[3] (L = Et$_4$dien):

$$\mathrm{NiLCl_2} \rightleftharpoons \mathrm{NiLCl^+\|Cl^-} \rightleftharpoons \mathrm{NiLCl^+ + Cl^-} \qquad (1)$$

Figure 1 shows the transient conductivity changes, monitored by the voltage divider method,[4] 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$^+$‖Cl$^-$ from five-coordinate NiLCl$_2$, 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,[3] 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.[5] It can be explained by the rapid 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$^-$ ion and *photoexcited* NiLCl$^+$ produced by irradiation at 530 nm where the principal absorber[6] is the ion pair, NiLCl$^+$‖Cl$^-$. This photoassociation displaces the ion pair $\rightleftharpoons$ five-coordinate equilibrium toward the latter species. The ensuing rapid relaxation ($\tau_1 < 0.2$ 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.[7] This ("slow") relaxation time, τ_2, 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_2 (μs) at 23 °C were measured at the concentrations indicated ([complex] × 10^{-4} mol dm^{-3}): 1.1 (2.5), 0.93 (5), 0.91 (7.5), 0.86 (10), 0.79 (25), yielding a curved plot for τ_2^{-1} against [NiLCl$^+$] + [Cl$^-$]. This is in accord with a standard kinetic analysis[8] of eq 1, taking τ_2 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.[7] 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.

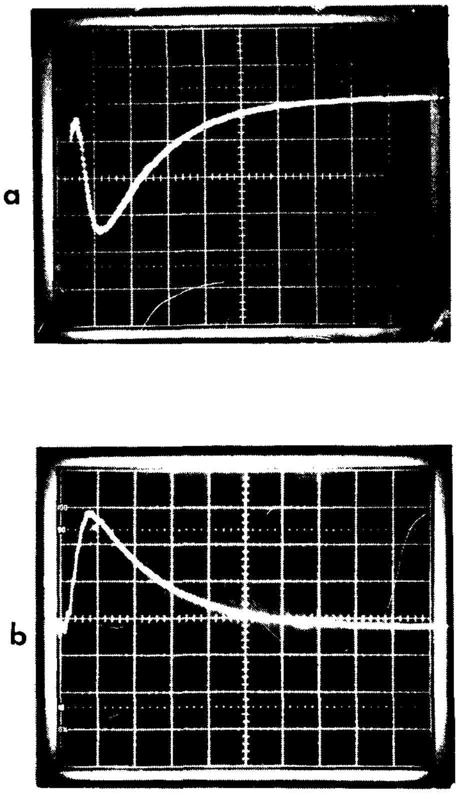

Figure 1. Transient conductivity changes in laser-irradiated Ni(Et$_4$dien)-Cl$_2$ in CH$_3$CN, monitored by the voltage divider method; applied voltage 200 V, solution resistance 14.5 kΩ, load resistance 400 Ω: (a) irradiation at 530 nm (vertical scale 2 mV/div, horizontal 0.5 μs/div); (b) irradiation at 1060 nm (vertical scale 5 mV/div, horizontal 0.5 μs/div).

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$^+$‖Cl$^-$ and NiLCl$^+$, are present