of propylene preferentially reacts when the catalyst is prepared from **1**.[21]

A simplified stereochemical model[22] of a possible transition state for the olefin insertion step is represented in Figure 1. In the model it is assumed that the catalyst precursor **1** maintains its configuration, (*R*), in the catalytic complex and that the active species is a tight ion pair[23] of the type $[Zr]^+[X(Al(CH_3)–O–)_n]^-$, with only the cation being represented in the figure. The experimental results indicate that the quadrant in which less steric hindrance exists, (Q1), is not occupied by the methyl group of the monomer (which is preferentially located in Q2[24]) but by the last monomeric unit of the growing chain in agreement with the proposal of Corradini and co-workers.[25] On this basis stereoregulation, for propylene polymerization, at least with the catalytic system prepared from **1**, arises from the chirality of the catalytic center which compels the last monomeric unit of the growing chain to occupy the less crowded quadrant (Q1).

Acknowledgment. We thank Montedison S.p.A. (Milano, Italy) for partial support of this work and Professor H. H. Brintzinger and collaborators (Universität Konstanz) for help with the synthesis and enantiomer separation of the zirconium procatalyst.

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(21) With use of catalysts prepared from (+)-(*S*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, all the oligomer fractions have negative optical rotation.

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(23) Eisch, J. J.; Pitrowski, A. M.; Brownstein, S. K.; Gabe, E. G.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

(24) The methyl group cannot be preferentially located in quadrants Q-1 and Q-2 because of the presence of the $–CH_2–CH_2–$ bridge of the ligand. The back face of the complex is less accessible to the monomer due to the presence of the two tetrahydroindenyl groups the CR–Zr–CR angle being 125.0° (CR = centroid of the Cp ring[3]).

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Chemical Kinetics in Dilute Solution: Photoacoustic Detection of Small Absorbance Changes in Chemical Reactions

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Received June 8, 1987

The most frequently used experimental technique for the determination of chemical rate constants is based on spectrophotometric recording of absorbance changes. While this method is widely applicable, there are two restrictions that limit the range of experimental conditions where data can be obtained: first, a suitable change in optical density (on the order of 10^{-2} absorbance units) must take place, and, second, the rate of reaction must not exceed the response time of the spectrophotometer. In this note we show that photoacoustic[1–4] monitoring of absorbance changes in a reaction provides a significant improvement over conventional spectrophotometric detection and that the photoacoustic technique can be used when the absorbance changes are on the order of only 10^{-4} units. The utility of this method is demonstrated with an inorganic, an organic, and a biochemical enzyme reaction.

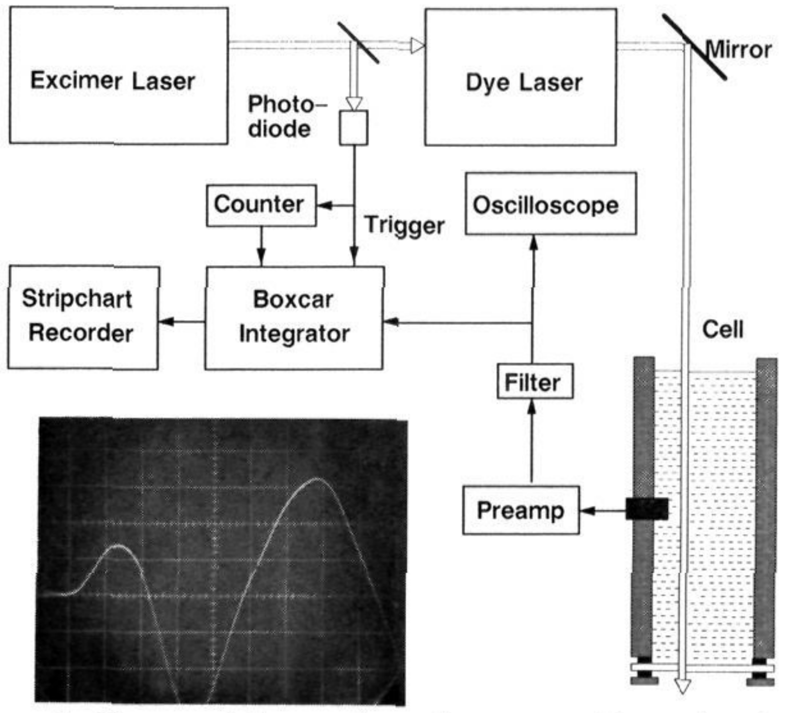

Figure 1. Diagram of the experimental apparatus. The excimer laser (Lamda Physik Model 102MSC) operated at 308 nm (XeCl) with a pulse length of about 15 ns. The dye laser output was attenuated to give 0.3 mJ per pulse and collimated with an adjustable iris. The acoustic cell was left open at the top to provide easy access. The oscilloscope trace shows the signal from a single pulse (*x* axis is 2 μs/div).

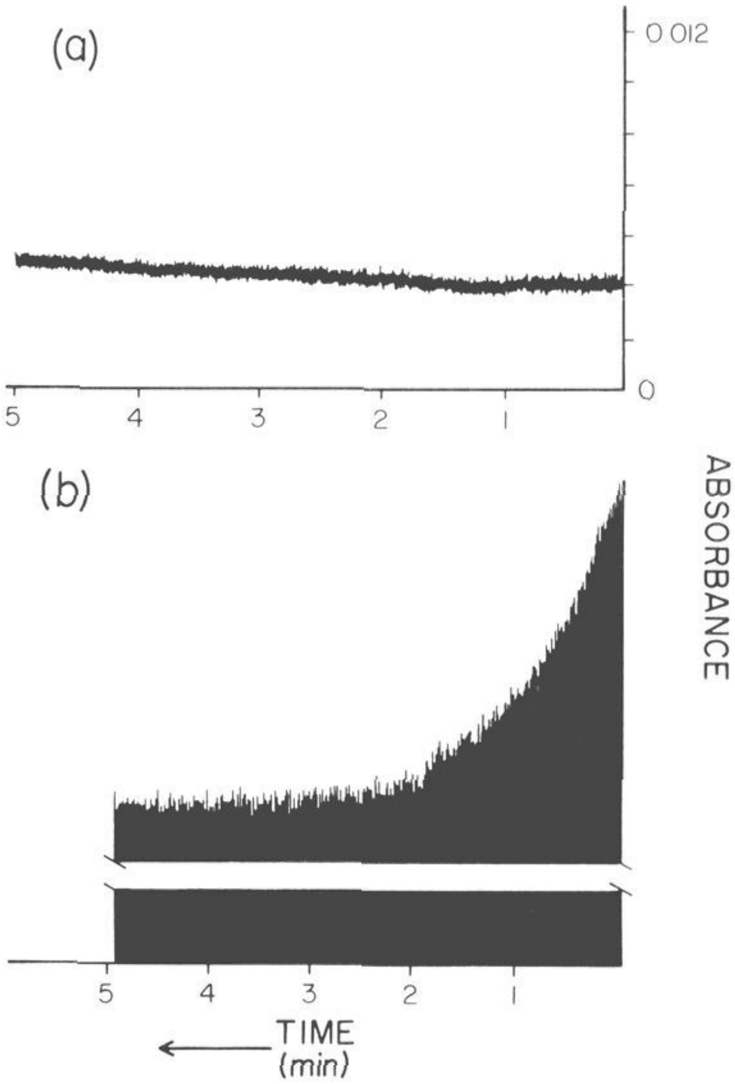

Figure 2. Photoacoustic monitoring (b) of reaction 1 at 385 nm in acetonitrile with a metal complex concentration of 2.5×10^{-7} M and a diphos concentration of 5.0×10^{-6} M. The laser was operated at 8 Hz with the integrator reset after 64 pulses giving a time constant of 8 s. The signal amplitude at the end of the reaction has contributions from the acoustic signal generated in the solvent as well as a deliberately introduced constant offset produced by the boxcar averager. Trace (a) is the signal obtained at the same reactant concentrations in a 1-cm quartz cell with use of a Gilford Model 250 spectrophotometer.

As the first example, reaction 1 was studied in purified acetonitrile[5] with use of an excimer laser pumped dye laser operating

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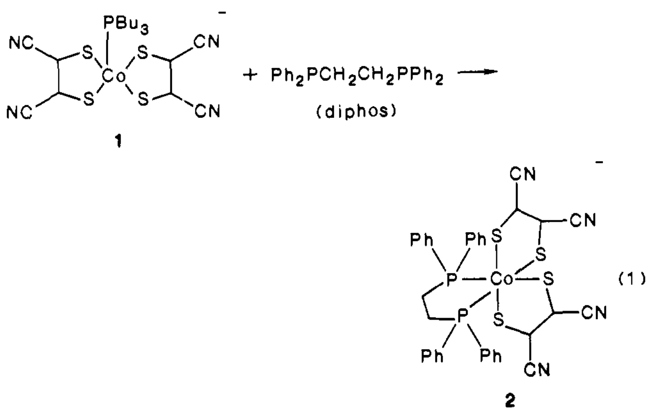
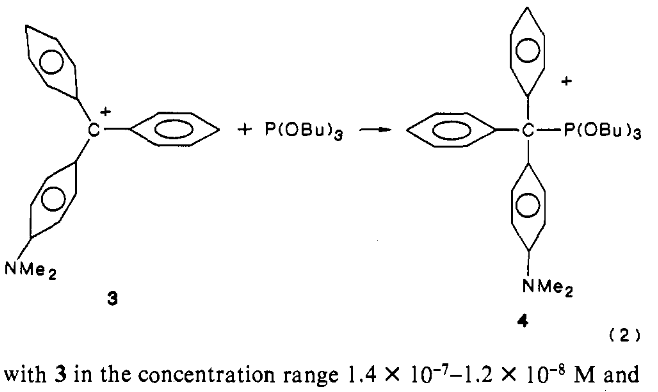
at 385 nm. At this wavelength **1** has an extinction coefficient



of 3740 cm^{-1} M^{-1}, whereas **2** has a negligible extinction coefficent by comparison. As shown in Figure 1, the output from the dye laser was positioned a few millimeters in front of a piezoelectric transducer in a stainless steel cell as described in ref 1. The signal from the transducer was fed to a charge sensitive preamplifier[6] followed by a high pass filter and was processed with a boxcar averager gated to detect only the incident acoustic signal. The boxcar averager was operated as a linear integrator so that charge was added to the integrator with each firing of the laser. After a fixed number of pulses, the averager was reset to zero giving what resembles a histogram on a strip chart recorder. Figure 2 shows a typical recorder output for reaction 1; a spectrophotometer output is shown for comparison. Inspection of the signal-to-noise ratios in a number of experiments showed the photoacoustic technique to be approximately 100 times more sensitive than spectrophotometric detection under normal operating conditions.[7] Photoacoustic measurements of absorbance versus time were easily obtained for reaction 1 with the concentration of **1** in the range 5.0×10^{-6}–2.5×10^{-8} M. In contrast, spectrophotometric detection required a concentration of **1** greater than 2×10^{-6} M in order to give an acceptable signal-to-noise ratio. The rate law for reaction 1 was determined by holding the concentration of **1** fixed and varying the diphos concentration, which was kept in pseudo-first-order excess. Standard treatment of the photoacoustic data established the rate law[8] as k[diphos][**1**], with the rate constant k equal to 300 ± 30 M^{-1} s^{-1}. Spectrophotometric data (obtained at [**1**] = 5×10^{-6} M) gave the same value for k within experimental error limits.

An analogous study was made of reaction 2 in acetonitrile at 460 nm, where **3** has an extinction coefficient of 2.6×10^4 cm^{-1} M^{-1} and **4** has negligible absorption. The reaction was studied



with **3** in the concentration range 1.4×10^{-7}–1.2×10^{-8} M and with P(OBu)$_3$ in pseudo-first-order excess. The rate constant for the forward step was found to be 2.6 M^{-1} s^{-1}, which agrees with spectrophotometric results obtained here as well as in a previous report.[9] The sensitivity of the photoacoustic method, however, permitted rate data to be obtained at concentrations approximately 100 times lower than was possible with the spectrophotometer.

As a further example, the well-known[10] enzyme-catalyzed reduction of nicotinamide adenine dinucleotide (NAD$^+$) by glucose-6-phosphate (G6P) was studied photoacoustically in aqueous solution. A 0.01 M, pH 8 Tris–buffer solution was prepared in

$$\mathrm{NAD^+ + G6P \xrightarrow[\text{dehydrogenase}]{\text{G6P}} NADH + 6\text{-phosphoglucono-}\delta\text{-lactate}} \quad (3)$$

distilled, deionized water and filtered through a 0.025 μm filter. After the reactants were mixed and placed in the cell, glucose-6-phosphate dehydrogenase was added to initiate the reaction. The appearance of NADH was monitored at 308 nm by using the attenuated output of the excimer laser. At this wavelength NADH is a moderately strong absorber (ϵ = 3200 cm^{-1} M^{-1}), whereas the other species in reaction 3 are essentially transparent. The reaction could be monitored at NAD$^+$ concentrations as low as 6×10^{-7} M (with [G6P] = 1.75×10^{-4} M), which constitutes a factor of 5 improvement in sensitivity over that obtained spectrophotometrically.

A calibration of the sensitivity of the photoacoustic apparatus using the known extinction coefficient of **1** gave a minimum detectable absorbance (determined by amplifier noise) of 6×10^{-6} cm^{-1} with a signal-to-noise ratio of two. Experiments with a number of common solvents (MeOH, MePh, MeCN, CCl$_4$, CH$_2$Cl$_2$, H$_2$O) showed that the limitation on reducing reactant concentrations in a kinetic study comes from the small but finite acoustic signal generated by the solvent which eventually masks the presence of the solute as concentrations are lowered. This is particularly evident in the experiments reported here in water where the comparatively large absorbance of water at 308 nm precludes reduction of the NAD$^+$ concentration from the figure reported above.

In summary, the photoacoustic effect provides a method of monitoring chemical dynamics in solution with a sensitivity significantly greater than is available with conventional spectrophotometers. This improved sensitivity can be used to advantage in several kinds of experiments where rate parameters are determined. First, depending on the reaction order, the use of low reactant concentrations permits the time scale for fast reactions to be lengthened, eliminating the need for rapid mixing of reactants. Alternatively, employment of photoacoustic detection with rapid mixing techniques can extend the range of experimentally accessible rate constants. Second, since the precision with which Michaelis constants are determined often depends critically on whether rate data can be obtained at low substrate concentrations, photoacoustic monitoring of reactions should permit more accurate measurements of such constants than is currently possible by using conventional spectrophotometric recording. The K_M for NAD$^+$ in reaction 3 is in the spectrophotometrically accessible range (> 1×10^{-5} M), but the Michaelis constants for many other reactions are too low to be routinely determined spectrophotometrically, e.g., isocitrate dehydrogenase,[11] 3-hydroxyacyl-CoA dehydrogenase,[12] and secondary metabolites in general. Third, it can be anticipated that some reactions that go to completion under ordinary conditions will not do so at the low concentrations permitted with the photoacoustic method. While such behavior may complicate the determination of forward rate constants, it offers the significant advantage of allowing the *direct* determination of reverse rate constants and equilibrium constants, all in the same series of experiments. Fourth, the ability to use smaller reactant concentrations should prove useful when there are re-

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(6) The charge sensitive preamplifier used here (Amptek Model A-225) gave a higher signal-to-noise ratio than the high impedance amplifier described in ref 1.

(7) This figure depends on the spectral band width of the spectrophotometer since the signal-to-noise (determined by shot noise) increases as the square root of the light intensity in this device. Comparison is made using a band width of 1 nm.

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strictions dictated by solubility, availability, or cost.

Acknowledgment. We are grateful for the support of this research by the U.S. Department of Health and Human Services and the National Science Foundation. D.A.S. is the recipient of an National Institutes of Health Research Career Development Award (1983–1988).

Energy Transfer in Solid Phases of Octasubstituted Phthalocyanine Derivatives[†][1]

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Received April 1, 1987

Octasubstituted phthalocyanine derivatives are well known to form columnar mesophases by segregation of the rigid aromatic cores and the flexible paraffinic side chains[2,3] (Figure 1). In the case of the dodecyl derivatives, the copper complex demonstrates a mesophase from 53 to more than 300 °C and the metal free compound from 80 to 260 °C.[2] It is possible to incorporate the copper complex $(C_{12}OCH_2)_8PcCu$ into the dihydrogeno compound $(C_{12}OCH_2)_8PcH_2$ as to form either mixed liquid crystals or solid solutions.[4] X-ray determinations at small angles have shown that the mesophases consist of ^2D hexagonal arrays of columns separated by about 31 Å.[2] In the solid phases present at room temperature, the columnar structure is preserved while a tilting angle of about 24° between the macrocycles and the axis of the columns induces an orthorhombic structure (a = 24.5 Å; b = 30.4 Å).[5] ESR studies have shown that the copper complex is randomly distributed within the columns composed of the metal free derivative.[4] In this paper the luminescence properties of the corresponding solid solutions are studied (Figure 2). The fluorescence of the dihydrogeno derivative is quenched in the presence of the copper complex in the solid[6,7] or in the solution.[13] Concentrations of Cu^{II} not inferior to 0.05% (m/m) could be attained due to the fact that copper cyanide is used in the chemical pathway leading to the final macrocycles.[3] For 16% of copper complex, the luminescence of $(C_{12}OCH_2)_8PcH_2$ is almost entirely quenched showing that energy migration processes are involved. For comparison, in unsubstituted phthalocyanine thin films, singlet excitation migrates over a distance of 300–500 Å.[8]

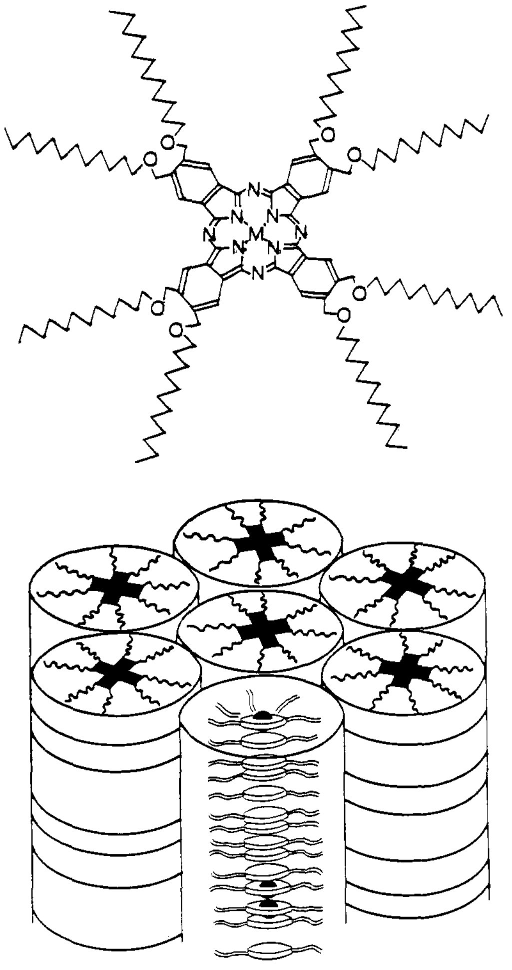

Figure 1. Schematic representation of the octadodecylphthalocyanine derivatives used: M = H_2, $(C_{12}OCH_2)_8PcH_2$; M = Cu^{II}, $(C_{12}OCH_2)_8PcCu$, and the structure of the corresponding columnar mesophases of mixed copper (solid circles) and metal free compounds.

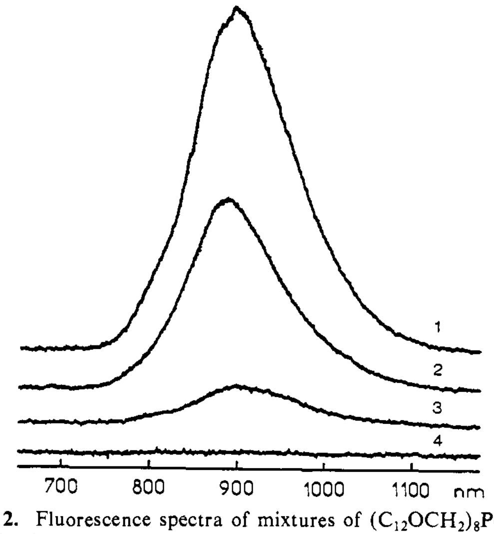

Figure 2. Fluorescence spectra of mixtures of $(C_{12}OCH_2)_8PcCu$ into $(C_{12}OCH_2)_8PcH_2$ at room temperature (excitation wavelength:514.5 nm): 1:0.05% (m/m); 2:0.45%; 3:4.5%; 4:16%.

The exciton diffusion length may be estimated knowing the probability $N(n)$ of having a sequence of n metal free molecules as a function of the copper concentration. It may be demonstrated that for a ^1D system if P_{ba} represents the probability of having the species A after the species B, then

$$N(n) = P_{ba} P_{aa}^{n-1} P_{ab} \qquad (1)$$

For a random distribution , the following is obtained[9] with y being the molar concentration of the species A in B.

$$N(n) = y^n(1 - y) \qquad (2)$$

The luminescence will be considered as quenched when the photon is absorbed in a region extending over $n_c/2$ A molecules

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[†] Work performed within the "Groupe de Recherches Interdisciplinaires sur les Matériaux Moléculaires" (G.R.I.M.M.).

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