of hydroxyl from axial to equatorial (**22** → **23**) by SmI_2 reduction of a cyclohexanone.[21]

Supplementary Material Available: Experimental data for compounds listed in the paper (8 pages). Ordering information is given on any current masthead page.

---

[21] (21) This research was assisted financially by grants from the National Institutes of Health and the National Science Foundation. We are most grateful to Dr. Günther Wess for many helpful discussions and early studies on the crucial cationic cyclization step in the series leading to successful synthesis of cafestol.[8]

Asymmetric Hydrooligomerization of Propylene

P. Pino,* P. Cioni, and J. Wei

Institut für Polymere, Swiss Federal
Institute of Technology, 8092 Zürich, Switzerland

Received April 8, 1987

Recently optically active homogeneous catalysts have been used to polymerize propylene to isotactic polymers;[1] the synthesized high polymer did not have a detectable optical activity in solution and in the melt as expected.[2] However, with the same catalysts optically active isotactic oligomers of propylene with detectable optical rotation should be produced.[2] Knowing the sign of optical rotation of the isotactic oligomers it is possible to relate enantioface of the α-olefin, prevailingly reacting, with the known structure[3] of the chiral catalyst precursor, thus obtaining further important indications on the regio- and stereospecific polyinsertion mechanism.

The polymerization of propylene at 0 °C in toluene solution (400 cm^3; C_3H_6 = 2.4 mol/L) for 72 h in the presence of hydrogen (eq 1) (p_{H_2} between 1 and 4 bar during the polymerization) using

$$\mathrm{CH_2{=}CHR} \xrightarrow[\mathrm{H_2}]{\text{catalyst}} \mathrm{H\text{-}[CH_2\text{-}CH(R)]_{\mathit{n}}\text{-}H} \qquad (1)$$

$$\mathrm{R = H,\ alkyl}$$

a catalyst obtained from a mixture of (−)-(*R*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethylzirconium,[3] **1** [42 mg, $[\alpha]_{436}^{25°}$ = −540° (*c* = 3.4 mg/mL in benzene)], and methylaloxane[4] (388 mg; $\bar{M}_n$ = 1200) yields a mixture of hydrogenated isotactic polypropylenes and liquid hydrogenated oligomers (288.5 g). The solid high polymers (230.2 g) were purified and fractionated as usual[5] (Table I, fractions F–J). From the toluene solution, after elimination of the catalyst residues, the low-boiling oligomers were separated by distillation[6] (1.4 g, fraction A, Table I). The higher boiling oligomers (56.9 g) were fractionated by dissolution with a series of solvents at room temperature (fractions B–E, Table I). The IR and ^{13}C NMR spectra of the fractions indicate the presence of *n*-butyl, *n*-propyl, and isobutyl groups with a large prevalence of *n*-propyl groups; no bands corresponding to olefinic carbon atoms could be detected, and therefore the reaction can be considered as a "hydrooligomerization". The above results show that (i) hydrogenolysis of zirconium–carbon bonds is much faster than β-hydrogen elimination, (ii) polypropylene chains start and grow according to "1-2"-insertion (presence of *n*-propyl groups and isopropyl groups as chain ends; no detectable amount of -$CH(CH_3)$-CH_2-CH_2-$CH(CH_3)$ sequences[7] in fraction J), and (iii) occasional "2-1"-insertions lead, after reaction with hydrogen, to chain termination (presence of *n*-butyl groups as chain ends). Furthermore ^{13}C (Table I footnote *o*) and ^{1}H NMR spectra indicate that the oligomers have an isotactic structure.[8,9]

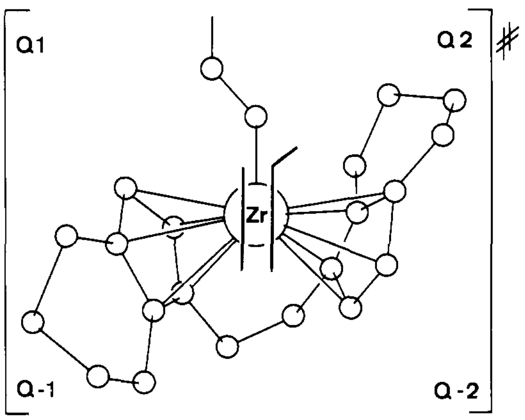


Figure 1. Simplified stereochemical model of a transition state for propylene insertion in the Zr–C< bond of the catalytic system prepared from **1**. The Zr atom and the first carbon atom of the growing chain lie in the plane of the drawing, and the incoming propylene molecule, with the *Re* enantioface directed toward the catalyst, is projected on the same plane.

The molar rotation of all the fractions, $[\Phi]_D^t$, (Table I) is positive and not very different, as expected for polymer chains which do not have largely preferred (e.g., helical) conformations in solution.[10,2] The gas chromatograms of fractions A and B (Carbowax 15%, 4 m) at 200 °C revealed a series of peaks that appeared as pairs. Fraction A was reexamined with GC–MS at lower temperature (80–150 °C), and three pairs of peaks were observed. The products corresponding to the two peaks[11] of each pair have the same molecular weight, that is for the three pairs 128, 170, and 212, respectively. The two compounds having MW 128 were identified as 2,4-dimethylheptane, **2**, and 4-methyloctane, **3**, respectively, by comparison of the ^{13}C NMR spectrum of their mixtures and of their mass spectrum with that of the corresponding authentic samples.

The isomer of molecular weight 170 with the shorter retention time[6] was identified by ^{13}C NMR as a single diastereoisomer of the 2,4,6-trimethylnonane, **4**. The ^{1}H NMR spectrum of this compound when compared to the spectrum of meso and racemic 2,4,6,8-tetramethylnonane[12] reveals that the asymmetric carbon atoms in position 4 and 6 have opposite absolute configuration[13] and is therefore the u[13] diastereoisomer. The isomer with higher retention time was identified as (u)-4-6-dimethyldecane, **5**, on the basis of ^{1}H and ^{13}C NMR spectra of its mixture with **4** (75% of **5** by GC analysis) by subtracting the spectrum of **4** from the spectrum of the mixture of **4** and **5**. The identification was

---

[1] (1) Kaminsky, W. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodanska: Tokyo, 1986; p 293.

[2] (2) Pino, P. *Adv. Polym. Sci.* **1966**, *4*, 395.

[3] (3) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63. Schäfer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *328*, 87.

[4] (4) Kaminsky, W.; Häuser, H. Germ. Offen. DE 3240383, 1982.

[5] (5) Natta, G.; Pino, P.; Mazzanti, G. *Gazz. Chim. Ital.* **1957**, *87*, 528.

[6] (6) A spinning band distillation system (Perkin Elmer 251 auto annular still) was used for separating the low-boiling components from toluene. The 2,4,6-trimethylnonane investigated contains some toluene (30%).

[7] (7) No detectable band at 752 cm^{-1} in the IR spectrum: Tosi, C.; Zerbi, G. *Chim. Ind.* (*Milan*) **1973**, *55*, 334.

[8] (8) In high molecular weight polypropylenes the methylene protons of the isotactic diastereomers give resonances centered at 1.36 and 0.9 ppm[9] (*o*-dichlorobenzene at 150 °C). The methylene protons of syndiotactic polypropylene give resonances centered at 1.07 ppm (*o*-dichlorobenzene at 150 °C). The methynes and the methyl protons give resonances above 1.45 and below 1.05 ppm, respectively. We have assumed the ratio between the intensity of the resonances at less than 1.05 ppm (methyl protons + one methylene proton of the -CH_2-$CH(CH_3)$-units) and the intensity of the resonances above 1.45 ppm as a good indication for the isotacticity of the oligomers synthesized. The experimental values (Table I), are in very good agreement with the values calculated according to the structure **6** and **7** (**6**/**7** = 2 from GC). The measurements were made in *o*-dichlorobenzene at 130 °C.

[9] (9) Ferguson, R. C.; Trans. *N.Y. Acad. Sci.* **1967**, *29*, 495.

[10] (10) Birshtein, T. M., Gotlieb, Yu.Ya.; Ptitsyn, O. B. *J. Polym. Sci.* **1961**, *52*, 77.

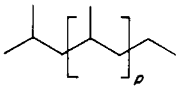
[11] (11) The gas chromatogram shows that in the pair with the lowest retention time a small impurity (~2%) is present having a retention time intermediate between the two major components.

[12] (12) Pino, P.; Pucci, S.; Benedetti, E.; Bucci, P. *J. Am. Chem. Soc.* **1965**, *87*, 3263. Suter, U. W. Thesis no. 5133, ETH-Zürich, 1973, p 21.

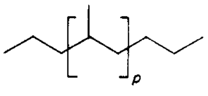
[13] (13) For the diastereoisomers containing more than one asymmetric carbon atom the descriptors (l) and (u) have been used as proposed by the following: Prelog, V.; Helmchen, G. *Angew. Chem.* **1982**, *94*, 621.

0002-7863/87/1509-6189$01.50/0

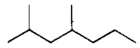
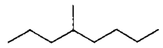
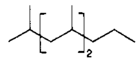
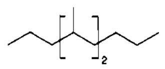
Table I. Properties of the Hydrooligomers Identified and of the Hydrooligomer and Polymer Fractions Isolated from the Products Obtained by using (−)-(*R*)-(EBTHI)Zr$(CH_3)_2$, **1**, and $[-Al(CH_3)-O-]_n$ as Catalyst Precursors



6



7

compd or fraction[a,b,v] (%)	$\bar{M}_n$[c]	mp[d] (°C)	isotacticity index[e] (%)[f]	structure	chiroptical properties: experimental $[\Phi]_D^{60}$[i]	experimental α_D^{60}[i]	calculated[q]: abs config	calculated[q]: $[\Phi]_D^{20}$
A **2**					+11.2[o,r,u]		4*S*[o]	+10
3 (0.5)					+2.9, ∓1[p,s,u]		4*S*[p]	+2
4	155	n.d.	n.d.		+18.4[u]		4*R*6*S*	+15
5					+2.2[t,u]		4*S*6*R*	+3
B (1)	310	n.d.	n.d.	**6** $\bar{p}$ = 5.3 **7**	+15.09	+3.71	4*R* (*p* = 6) 4*S* (*p* = 6)	+20 +4
C (6)	380	−50	4.6 (∼100)	**6** $\bar{p}$ = 7 **7**	+14.63	+2.99	4*R* 4*S*	
D (8.1)	490	20	4.4 (∼100)	**6** $\bar{p}$ = 9.6 **7**	+14.52	+2.34	4*R* 4*S*	
E (4.6)	670	62.1	n.d.	**6** $\bar{p}$ = 13.9 **7**	+13.64	+0.28	4*R* (*p* = 14) 4*S* (*p* = 14)	+25.7 +5.1
F (8.5)	420	35.9	4.5 (∼100)	**6** $\bar{p}$ = 7.95 **7**	+13.44	+2.51	4*R* 4*S*	
G (5.6)	840	76.1	4.2 (99)	**6** $\bar{p}$ = 17.95 **7**	+13.51[j]	+0.07[j,k]	4*R* 4*S*	
H (4.6)	965[g]	96.9	3.9 (93)	**6** $\bar{p}$ = 20.9 **7**	+11.75[j,l]	+0.013[j,l]	4*R* 4*S*	
I (51)	2040[g]	138.0	3.6 (90)	**6** $\bar{p}$ = 46.5 **7**	+11.7[j,m]	+0.008[j,m]	4*R* (*p* = 47) 4*S* (*p* = 47)	+28.7 +5.7
J (10.1)	[h]	150.9	4.0[n]	n.d.	n.d.	n.d.		

[a] Fractions A–E are soluble in toluene at 25 °C; fractions F–J are insoluble in toluene at 25 °C and were separated by filtration. [b] Weight of fraction/100 × weight of total products. [c] By vapor pressure osmometry in chloroform at 25 °C. [d] Measured by D.S.C. (Mettler, T. A. 3000 System D.S.C. 30). [e] By ^1H NMR; ratio between the intensity of the signals below 1.05 ppm and the intensity of the signals between 1.8 and 1.45 ppm; see ref 8. [f] (Experimental value/calculated value) × 100. [g] By vapor pressure osmometry in methylcyclohexane at 50 °C. [h] $[\eta]$ = 0.19 dl/g in tetraline at 134 °C; $\bar{M}_\eta$ = 17 000. [i] Neat. [j] In methylcyclohexane at 60 °C. [k] c = 45 mg/mL. [l] Value extrapolated from ORD according to Yang and Doty; α_{260} = +0.077 (c 11.5 mg/mL). [m] See footnote l; α_{320} = +0.041 (c 13.9 mg/mL). [n] 96% mmmm pentads from ^{13}C NMR (CH_3 band at 21.05 ppm, solvent *o*-dichlorobenzene-d_4 at 130 °C). [o] See ref 16. [p] See ref 17. [q] According to Brewster (see ref 18) for the isotactic diastereomers. [r] Value extrapolated from measurements in toluene according to ref 26. [s] Value calculated from measurements on a mixture of **2**, **3**, and **4** (composition of the mixture determined by gas chromatography). [t] Value calculated from measurements on a mixture of **4** and **5** (composition determined by gas chromatography. [u] At 25 °C. [v] A, mixture of C_9H_{20} and $C_{12}H_{26}$ oligomers;[6] B, methanol soluble (25 °C); C, methanol insoluble, acetone soluble (25 °C); D, acetone insoluble, ethyl acetate soluble (25 °C); E, ethyl acetate insoluble, diethyl ether soluble (25 °C); F, boiling methanol soluble;[5] G, boiling methanol insoluble, acetone soluble;[5] H, boiling acetone insoluble, boiling diethyl ether soluble;[5] I, boiling diethyl ether insoluble, boiling heptane soluble;[5] J, boiling heptane insoluble.[5]

confirmed by comparison with the ^{13}C and ^1H NMR spectra of a sample of the racemic (u)-4-6-dimethyldecane.[14]

The positive optical rotation found for **2** and **3** indicate[16,17] a substantial predominance (∼85/15) of the (*S*)-antipodes (Table I). For **4** Brewster calculations[18,19] give $[\Phi]_D^{20}$ of +15° for the (4*R*,6*S*) antipode (Table I), +30 for the (4*S*,6*S*) antipode, and −15° for the (4*S*,6*R*) antipode. The antipodes (4*R*,6*R*) and (4*S*,6*S*) are excluded on the basis of the ^1H NMR spectra;[15] therefore the prevailing antipode of **4** produced in the hydrooligomerization is the (4*R*,6*S*) one.

For **5** the antipodes (4*R*,6*R*) and (4*R*,6*S*) are excluded as Brewster calculations show that they have negative optical rotation. Between the (4*S*,6*S*)- and the (4*S*,6*R*)-diastereomers (optical rotation according to Brewster $[\Phi]_D^{20}$ +34.8° and $[\Phi]_D^{20}$ +3°, respectively) the first one can be discarded on the basis of the ^1H NMR spectrum[15] compared with that of an authentic sample of racemic **5**. The positive optical rotation of the isotactic fractions B–I (Table I) indicate that when **1** is used as a catalyst precursor the hydrooligomers having an *n*-propyl and an isopropyl group as terminal groups belong to the (4*R*) series and the oligomers having a *n*-propyl and an *n*-butyl as terminal groups belong to the (4*S*) series.

In both cases the asymmetric carbon atom following the *n*-propyl group, that is the first asymmetric carbon atom of the growing oligomer chain, has (*S*) configuration.

As polyinsertion occurs with cis stereochemistry,[20] the prevailing chirality of the hydrooligomers indicates that the *Re* enantioface

---

(14) We thank P. Prada for the preparation of samples of (u)- and (l)-5,6-dimethyldecane (see, also: Morozova, O. E.; Zemskova, Z. K.; Petrov, Al. A. *Neft. Khim.* **1973**, *13*, 478.).

(15) The ratios between intensities of the bands at 1.44–0.98 and 0.98–0.75 ppm is 1:2.0:5.4. These ratios are much nearer to that expected for the two antipodes (4*S*:6*R*) and (4*R*:6*S*) of the "isotactic" (u) diastereoisomer than to that expected for the (4*R*:6*R*) and (4*S*:6*S*) antipodes of the "syndiotactic" (l) diastereoisomer.[8,9,12]

(16) Levene, P. A.; Marker, R. E. *J. Biol. Chem.* **1931**, *92*, 455.

(17) Levene, P. A.; Marker, R. E. *J. Biol. Chem.* **1931**, *91*, 761.

(18) Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5475.

(19) Pino, P.; Ciardelli, F.; Zandomeneghi, M. *Ann. Rev. Phys. Chem.* **1970**, *21*, 567. The calculations of the optical activity according to ref 18 were made in collaboration with M. Galimberti and H. Wittwer.

(20) Natta, G.; Farina, M.; Peraldo, M. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1958**, *25*, (series 8) 424. Zambelli, A.; Giongo, M. G.; Natta, G. *Makromol. Chem.* **1968**, *112*, 183. Miyazawa, T.; Ideguchi, Y. *J. Polym. Sci. B.* **1963**, *1*, 389.

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.

---

(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.

(22) Pino, P.; Rotzinger, B.; von Achenbach, E. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodanska: Tokyo, 1986; p 461.

(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]).

(25) Corradini, P.; Barone, V.; Fusco, R.; Guerra, G. *Eur. Polym. J.* **1979**, *15*, 1133; **1980**, *16*, 835.

(26) Kauzmann W.; Clough F. B.; Tobias I. *Tetrahedron* **1961**, *13*, 57.

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

V. E. Anderson,* H. Z. Cheng, G. J. Diebold,* A. Mahmood, and D. A. Sweigart*

Brown University, Department of Chemistry
Providence, Rhode Island 02912

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.

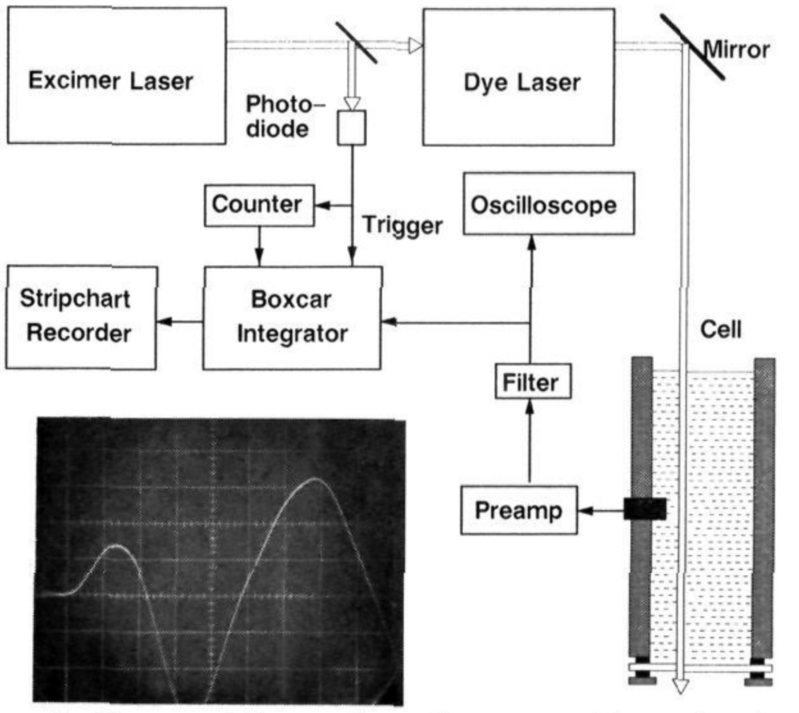


Figure 1. Diagram of the experimental apparatus. The excimer laser (Lamda Physik Model 102MSC) operated at 308 nm (XeCl) with a pulse length of about 15 ns. The dye laser output was attenuated to give 0.3 mJ per pulse and collimated with an adjustable iris. The acoustic cell was left open at the top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

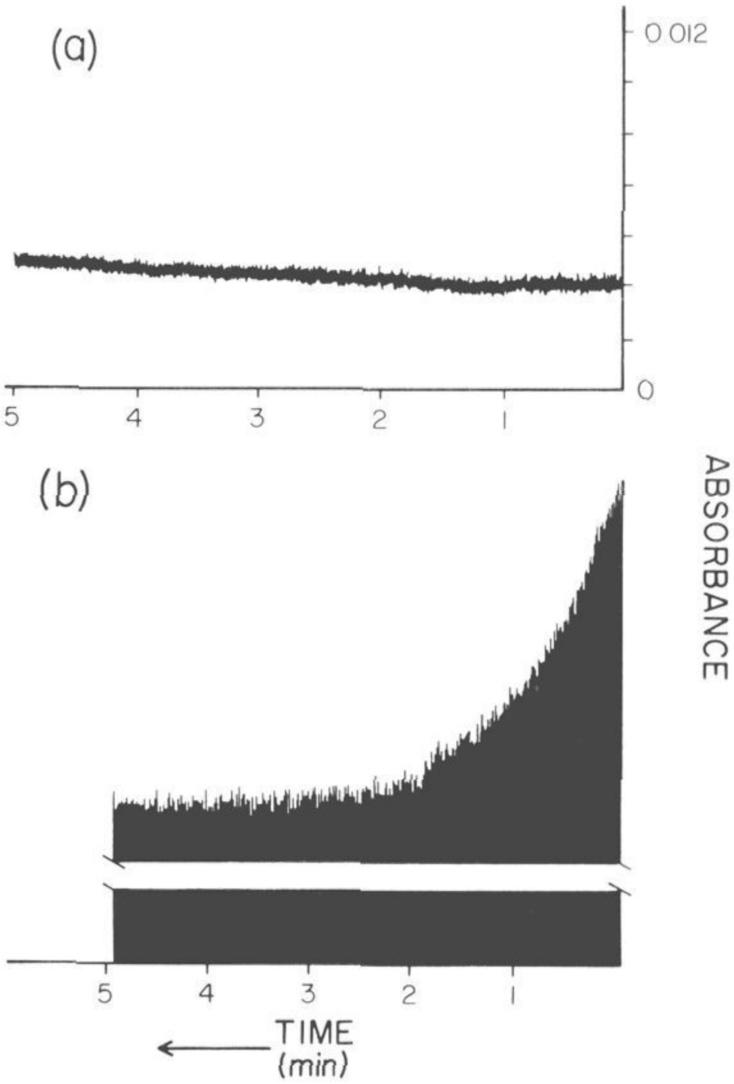


Figure 2. Photoacoustic monitoring (b) of reaction 1 at 385 nm in acetonitrile with a metal complex concentration of 2.5×10^{-7} M and a diphos concentration of 5.0×10^{-6} M. The laser was operated at 8 Hz with the integrator reset after 64 pulses giving a time constant of 8 s. The signal amplitude 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

---

(1) Patel, C. K. N.; Tam, A. C. *Rev. Mod. Phys.* **1981**, *53*, 517.

(2) Tam, A. C. *Rev. Mod. Phys.* **1986**, *58*, 381.

(3) Tam, A. C. In *Ultrasensitive Laser Spectroscopy*; Academic Press: New York, 1983.

(4) Sigrist, M. *J. Appl. Phys.* **1986**, *60*, R83.

(5) HPLC grade acetonitrile (Aldrich) was purified as described by Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents*, 4th ed.; J. Wiley: New York, 1986.

0002-7863/87/1509-6191$01.50/0 © 1987 American Chemical Society