in THF, slow hydrogen gas evolution takes place continuously over the reaction period. Upon hydrolysis of the intermediate reduction products, 9,10-dihydroanthracene, (ArH_2 when hydrolyzed with H_2O) and 9,10-dihydroanthracene-*9-d* (ArHD and ArD_2 when hydrolyzed with D_2O) are obtained. On the other hand, when the above reaction is carried out by using $LiAlD_4$ under the identical reaction conditions, hydrolysis with H_2O again produced both ArHD and ArH_2. These results indicate the presence of a solvent-separated ion pair ($Ar^{-}\cdot,M^+$ as well as ArH^-M^+ or ArD^-M^+) prior to hydrolysis. In the reaction with $LiAlH_4$ more ArD_2 is formed than ArHD (when hydrolyzed with D_2O), and in the reaction with $LiAlD_4$ more ArH_2 is formed than ArHD (when hydrolyzed with H_2O), indicating that more of the reaction is proceeding via pathway b than pathway a. The mechanism of hydrolysis had been studied earlier by previous workers; however, we are actively studying the later part of the reaction.

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(12) G. Levin, C. Sutphen, and M. Szwarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972).

(13) A. Rainis, S. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 659 (1973).

(14) A. Rainis and M. Szwarc, *J. Am. Chem. Soc.*, **96**, 3008 (1974).

(15) We are grateful for support of this work by the National Science Foundation (Grant No. MPS 7504127).

(16) H. M. Assenheim, "Introduction to Electron Spin Resonance", Hilger and Watts Std, London, 1966, pp 115–118.

(17) E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958).

Photogeneration of Very Active Homogeneous Catalysts Using Laser Light Excitation of Iron Carbonyl Precursors

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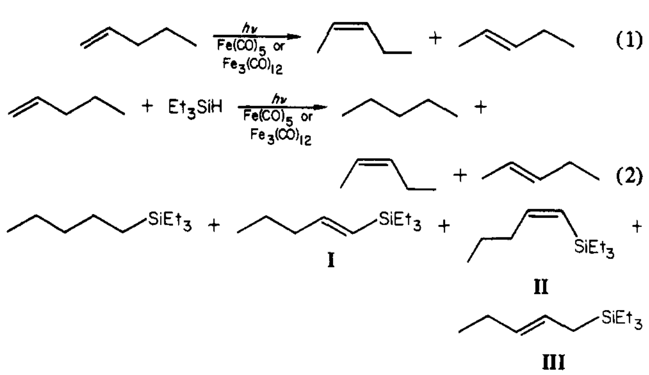
Photoinitiation of homogeneous catalysis by irradiation of thermally inert iron carbonyl catalyst precursors has been demonstrated to be a procedure for effecting olefin isomerization, hydrogenation, and hydrosilation reactions at low temperature[1-3] compared to thermal catalysis.[4] However, there has been very little quantitative information concerning the activity of photogenerated catalysts. In this communication we wish to report preliminary experiments that show that $Fe(CO)_5$ and $Fe_3(CO)_{12}$ are photochemical precursors to thermally active catalysts that rival the fastest homogeneous catalysts known.[5] The catalytic chemistry studied has been that represented by eq 1 and 2 and the question addressed has been what is the turnover rate for the photogenerated catalysts? Answering such a question is important in establishing whether photoinitiation of catalysis can provide products at a useful rate. But the answer is not straightforwardly obtained, since the actual catalyst in this system is not well characterized. We have taken an approach that allows us to put some lower limits on the activity of the catalyst.



The observed quantum yield for consumption of 1-pentene according to (1) or (2) significantly exceeds unity[1-3] and indicates that an active catalyst is generated photochemically. But the quantum yield at a single light intensity only gives the efficiency for utilizing incident quanta. The quantum yields from $Fe(CO)_5$ or $Fe_3(CO)_{12}$ photocatalyzed reactions are not found to be infinite; catalysis does not persist in the dark after photoinitiation in these systems. Sealed reaction vessels lead to the possibility of the catalyst back reacting with photoejected CO while purging with an inert gas to remove the CO leads to clusters that are catalytically inactive. This chemistry complicates the determination of catalyst turnover rate. Thus, the approach we have taken has been to determine the observed rate of 1-pentene consumption by using very high light intensity excitation where the catalyst turnover rate, not photogeneration of the catalyst, could become the rate-limiting feature. The results are given below.

Photocatalysis experiments according to eq 1 and 2 were carried out by using an Ar ion laser as the excitation source to provide very high light intensity. Consumption of 1-pentene as a function of irradiation time proves to be a very fast process. Typically, we have monitored the chemistry by gas chromatography, but in these experiments we found that the reaction is so fast that we became concerned about the finite time interval involved in opening hermetically sealed ampules to quench any residual dark catalytic activity.

Irradiation of several samples for equal time followed by analysis of each at a different time after irradiation reveals no dark aftereffects; that is, it would appear that when the light is turned off catalysis ceases essentially instantly. The time resolution of this sort of experiment is <30 s, the time needed to quench any catalytic activity by exposing the solutions to O_2 by opening the hermetically sealed ampules. We have found that neat 1-pentene solutions can be quantitatively analyzed by near-infrared absorption spectroscopy. Figure 1 shows the results of catalysis on a portion of the near-infrared spectrum of 1-pentene. Independent measurement of the spectra of pure *cis*-2-pentene and pure *trans*-2-pentene in the same wavelength range shows that the spectral changes shown in Figure 1 are consistent with the chemistry represented by eq 1 where the ratio of *trans*-2-pentene to *cis*-2-pentene is roughly 3:1. The near-infrared spectrum of 1-pentene shows bands not present in the 2-pentenes and allows quantitative analysis of 1-pentene disappearance on a time scale much faster than gas chromatography. Comparison of a near-infrared spectrophotometric analysis and gas chromatographic analysis of 1-pentene disappearance shows that the near-infrared is a reliable quantitative technique. Monitoring the unique near-infrared absorbance of 1-pentene shows that catalysis persists for <5 s after irradiation of $Fe(CO)_5$/1-pentene mixtures is terminated. Flash photolysis followed by monitoring at 1330 nm shows that catalysis is over within a few seconds after the light is switched off (vide infra).

Table I summarizes typical data for photocatalysis experiments using high light intensity continuous laser excitation. The shortest convenient irradiation time was 5 s in such experiments, and roughly 25–50% conversion of neat starting material to product could be obtained by using either $Fe(CO)_5$ or $Fe_3(CO)_{12}$. In the reaction of $HSiEt_3$ with 1-pentene, the 2-pentenes account for only ~25% of the 1-pentene reacted; that is, 75% of the 1-pentene

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(1) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551; *J. Organomet. Chem.* **1977**, *128*, 345.

(2) (a) Asinger, F. Y.; Fell, B.; Schrage, K. *Chem. Ber.* **1965**, *98*, 372, 381. (b) Asinger, F.; Fell, B.; Collin, G. *Ibid.* **1963**, *96*, 716. (c) Carr, M. D.; Kane, V. V.; Whiting, M. C. *Proc. Chem. Soc., London* **1964**, 408.

(3) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *No. 168*, 189.

(4) (a) Howard, J. F.; Chalk, A. J. *Org. Synth. Met. Carbonyls* **1977**, *2*, 680–694. (b) Frankel, E. N.; Emken, E. A.; Peters, H. M.; Davison, V. L.; Butterfield, R. O. *J. Org. Chem.* **1964**, *29*, 3292, 3620.

(5) (a) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973. (b) Taqui Khan, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. I and II and references therein.

Table I. $Fe(CO)_5$ and $Fe_3(CO)_{12}$ Photocatalyzed Reactions of 1-Pentene[a]

catalyst precursor (concn, M)	irrdn. λ, nm (power, W)	irrdn. time, s	reaction	[1-pentene], M[c]	% 1-pentene[d] consumed	Φ[e]	turnover rate, 1-pentene/catalyst, min[f]
		Continuous Laser Irradiation[b]					
$Fe(CO)_5$ (8×10^{-3})	333, 351, 364 (2.5)	5	isomerization	9.14 (neat)	27	68	3700
		10			35	44	2400
$Fe_3(CO)_{12}$ (5×10^{-3})	514.5 (1.3)	10	isomerization	9.14 (neat)	7	11	700
		30			24	13	900
$Fe(CO)_5$ (1×10^{-2})	333, 351, 364 (2.5)	5	hydrosilation	3.66	42	42	1700
		10			50	24	1000
$Fe_3(CO)_{12}$ (5×10^{-3})	514.5 (7.5)	10	hydrosilation	3.66	42	5	1800
		20			59	3	1300
		Flash Photolysis Excitation[g]					
$Fe(CO)_5$ (1.4×10^{-2})			isomerization	9.14 (neat)	46		
$Fe(CO)_5$ (1.1×10^{-2})			hydrosilation	3.66	23		
$Fe_3(CO)_{12}$ (5.1×10^{-3})			hydrosilation	3.66	25		

[a] Reactions were generally carried out at 25 °C; stirred, 1.0 mL of freeze–pump–thaw degassed solution was irradiated in hermetically sealed Pyrex ampules. Analysis for reaction was by gas chromatography or by near-infrared spectrophotometry (see text). Product ratios for isomerization were determined by using a 30 ft × $^1/_8$ in. 20% propylene carbonate on chromosorb P column operated at 20 °C and hydrosilation products were quantitated by using a 30-ft × $^1/_8$ in. β,β'-ODPN column operated at 50 °C. Control experiments show that no photoreaction occurs in the absence of $Fe(CO)_5$ or $Fe_3(CO)_{12}$; none is expected since 1-pentene and Et_3SiH are transparent to light transmitted by Pyrex. [b] The irradiation source was either a Spectra Physics Model 164 Ar-ion laser or a Coherent Radiation CR18 Ar ion laser tuned to the indicated wavelength and power. The beam diameter was ~2 mm. [c] For isomerization reactions the 1-pentene was used as solvent. For hydrosilation $HSiEt_3$ and 1-pentene were used in a 1/1 mol ratio (3.66 M/3.66 M) without any diluent but using *n*-hexane as an internal standard for gas chromatographic analyses. [d] Data shown are for total amount of 1-pentene consumed. For isomerization the only products are *trans*- and *cis*-2-pentenes but in the presence of $HSiEt_3$ the products also include *n*-pentane, (n-C_5H_{11})$SiEt_3$, and three isomers of (pentenyl)$SiEt_3$.[1] The percent of 1-pentene that reacts to form *n*-pentane and Si-containing material is ~75% under the conditions used; i.e., isomerization accounts for only ~25% of 1-pentene disappearance. [e] Number of 1-pentene molecules consumed per photon incident on the sample. [f] Turnover rate is given assuming all $Fe(CO)_5$ or $Fe_3(CO)_{12}$ forms a catalyst during the period indicated. Thus, these are lower limits on the turnover rate. [g] Flash photolysis was done by using a Xenon Corp. Model 710 apparatus and excitation was one 10-kV, 2000 J, <100-μs flash of a 1.0-mL degassed sample in a Pyrex ampule.

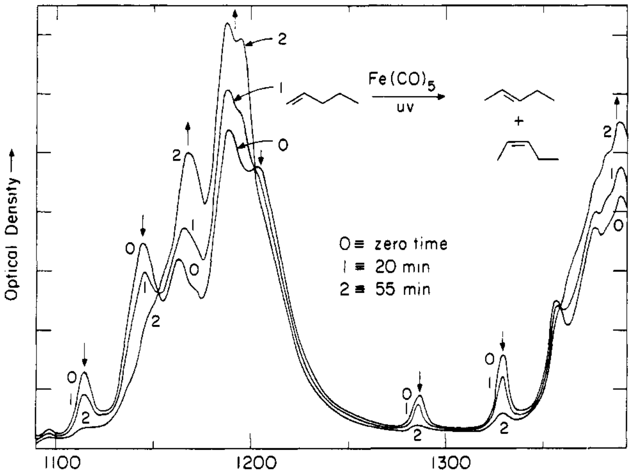

Figure 1. Near-infrared spectral changes accompanying ultraviolet irradiation [(335 ± 20) nm, ~2×10^{-6} einstein/min] of 2.0 mL of 1.86 × 10^{-2} M $Fe(CO)_5$ in neat 1-pentene. Features with an arrow pointing down are associated with the 1-pentene that is consumed; features with an arrow pointing up are associated with the *cis*- and *trans*-2-pentene products formed in a ~1:2.8 ratio.

yields *n*-pentane and Si-containing material. In all cases the observed quantum yield (Φ) (number of 1-pentene molecules consumed per incident photon) exceeded unity, and turnover rates generally exceeded 1000. The turnover rates given are based on the concentration of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ initially present and are thus lower limits. The data shown establish the catalyst from $Fe_3(CO)_{12}$ or $Fe(CO)_5$ to be among the most active homogeneous organometallic catalysts.

Determining turnover rates accurately depends on knowning the catalyst concentration and being able to simultaneously measure the reaction rate. Flash photolysis provides a way to generate a certain catalyst concentration, and catalytic chemistry could be monitored in the near-infrared. We find that catalytic chemistry is easily observable by using flash photolysis, and we had hoped that we could monitor the decline of the 1330-nm near-infrared overtone absorption following the excitation flash of <100-μs duration. Quantitative analysis (Table I) shows that a single flash can yield a large extent conversion. The difficulty is that flash photolysis of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ in 1-pentene yields a near-infrared absorbing transient with a lifetime of about 1 s, precluding a quantitative measure of the 1330-nm absorbance. The conclusion to be drawn now is that the catalytic chemistry is over within a few seconds after the excitation flash.[6] Continued effort is being directed to the use of flash photolysis to measure turnover rates.

Intense irradiation, and especially pulsed excitation, raises the possibility of unusually active species being formed. For example, the primary result of irradiating $Fe(CO)_5$ is believed to be that represented by eq 3.[7] When pulsed excitation is used, the leading

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO \tag{3}$$

edge of the pulse may effect the process represented by eq 3, while the trailing portion may effect further CO loss as in eq 4. The

$$Fe(CO)_4 \xrightarrow{h\nu} Fe(CO)_3 + CO \tag{4}$$

$Fe(CO)_4$ is known to be photosensitive with respect to CO loss in low-temperature matrices.[8] Photolysis of $Fe(CO)_5$ in the gas phase can even yield Fe atoms.[9,10] The consequences of such multiple coordinative unsaturation are not known, but we note no new products nor any change in the distribution of products in the photocatalyzed reactions of alkenes represented by eq 1 and 2. We have used a pulsed Nd–Yag laser (frequency tripled to yield 355-nm pulses) excitation of $Fe(CO)_5$ with <6-ns pulses, 20 mJ/pulse, and still find no unusual effects on catalytic product distributions. Likewise, 532-nm (<7 ns, 40 mJ/pulse) irradiation

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(6) For additional information concerning the nature of the catalyst and its lifetime after photogeneration, see: Chase, D. B.; Weigert, F. J. *J. Am. Chem. Soc.*, **1981**, *103*, following paper in this issue.

(7) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(8) (a) Poliakoff, M. *J. Chem. Soc.*, Dalton *Trans.* **1974**, 210. (b) Poliakoff, M., Turner, J. J. *J. Chem. Soc.*, Faraday *Trans.* **1974**, *70*, 93.

(9) Callear, A. B.; Oldman, R. J. *Nature* (*London*) **1966**, *210*, 730.

(10) Karny, Z.; Naaman, R.; Zare, R. N. *Chem. Phys. Lett.* **1978**, *59*, 33.

from a frequency-doubled Nd-Yag laser does not alter products from $Fe_3(CO)_{12}$ photocatalysis.

To summarize our main findings, we conclude that photolysis of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ yields an exceedingly active catalyst. The active catalyst is not likely to be an excited state species, since the excited lifetimes of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ are too short to effect catalysis.[7] The active species is likely to be an unsaturated ground-state species, photoproduced by loss of CO from $Fe(CO)_5$ or Fe–Fe bond cleavage in $Fe_3(CO)_{12}$.[1-3] Very high turnover rates for alkene isomerization and hydrosilation have been found. Moreover, very high turnover numbers (moles of product per mole of Fe initially present) are achieved. For example, when a single flash yields ~50% conversion of neat 1-pentene using $\sim 10^{-2}$ M $Fe(CO)_5$, the turnover number exceeds 400. Subsequent flashes yield an even greater extent conversion to ultimately completely equilibrate the linear pentenes.[1] High light intensity does not appear to alter the product distribution where a number of products are possible (alkene + $HSiEt_3$). The data show that very high light intensity can be used to produce product at a high observed rate and with high quantum efficiency ($\gg 1$).

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Fourier-Transform Infrared Measurement of the Catalyst Lifetime in the Pentacarbonyliron(0) Photocatalyzed Olefin Isomerization

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The iron carbonyl photocatalyzed olefin isomerization as studied by Asinger[1] and Wrighton[2,3] presents a paradoxical situation. Although quantum yields in the hundreds are measured,[2] "sustained alkene isomerization subsequent to irradiation is inefficient and somewhat irreproducible".[2] The gas chromatographic[2,3] and wet chemical[1] analytical methods used previously are neither fast enough nor sensitive enough to measure the small transient effects which must occur immediately after the light is turned off.

Infrared spectroscopy provides a sensitive method for monitoring the changes during photoisomerization, since individual bands associated with reactants, products, and catalytic species can be identified. Fourier transform techniques extend the possibilities of this experiment by allowing the simultaneous monitoring of many absorption bands during a single experiment with a temporal resolution of less than 1 s.

The infrared spectra were obtained with a Nicolet 7199 interferometer operating in the rapid scan mode. The spectral resolution was 4 cm^{-1} (Happ–Genzel apodization), and two scans were coadded to give a spectrum every 0.5 s. The sample configuration was modified to allow simultaneous data acquisition and irradiation with a 2000-W xenon lamp.[4] The output below 3000 and above 10 000 Å was filtered out.

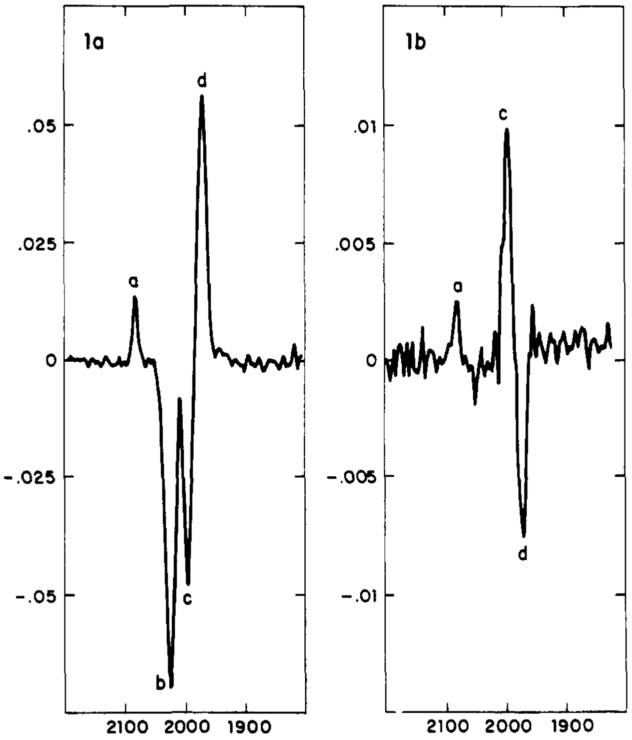

Figure 1. Infrared spectral changes in the carbonyl region of the $Fe(CO)_5$ photocatalyzed isomerization of 1-pentene (a) during irradiation and (b) after the light is turned off. Peaks are at (a) 2077, (b) 2020, (c) 1995, and (d) 1969 cm^{-1}.

A typical experiment involved placing the reactants in the IR cell, starting data acquisition with the sample in the dark, opening the shutter to the light, and, after a given period of time, closing the shutter. The spectrum taken at time $t = 0$ was then subtracted from each of the succeeding spectra to yield optical density changes as a function of irradiation time. The magnitude of these changes (ΔOD) was then plotted against time for the spectral features of interest.

Before irradiation the spectrum showed four carbonyl bands at 1800, 1969, 1995, and 2020 cm^{-1}, respectively. During irradiation the intensity of the two olefin bands at 1641 and 994 cm^{-1} decreased, and a new band characteristic of trans olefins appeared at 966 cm^{-1}. Cis olefin bands were obscured by the solvent benzene, but since gas chromatography had shown the trans/cis + trans) olefin ratio of 0.8 to be constant during the reaction, no information was lost. Although the carbonyl band at 1800 cm^{-1} did not significantly change during irradiation, the bands at 1995 and 2020 cm^{-1} decreased, while the band at 1969 cm^{-1} increased. A new weak band appeared at 2077 cm^{-1}. Between the time the light was turned off and the system reached steady state, only the three carbonyl bands at 1969, 1995, and 2077 cm^{-1} continued to change along with corresponding changes in the olefin bands. We assign the band at 1969 cm^{-1} to the active catalyst because it decreases when the light is turned off, but it must also have components from both the intermediate and pentacarbonyliron because it is present before irradiation and increases without an induction period when the light is turned on. Bands which decrease during irradiation must have a component of starting material, but the 1995-cm^{-1} band must also have a component of "$Fe(CO)_4$", because it increases again after the light is turned off. The changes in the carbonyl region of the spectrum during irradiation are shown in Figure 1a, while the changes after the light was turned off are shown in Figure 1b. The complete time evolution of some of these absorptions is shown in Figure 2 for a 20% solution of 1-pentene in benzene and an olefin/iron ratio of 300.

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† Contribution No. 2839.

(1) Asinger, F.; Fell, B.; Schrage, K. *Chem. Ber.* **1965**, *98*, 372.

(2) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551. Wrighton, M. S.; Graff, J. L.; Reichel, C. L.; Sanner, R. D. In "Transition Metal Mediated Organic Synthesis"; Slocum, D. W., Hughes, O. R., Eds.; New York Academy of Science: New York, 1980; Vol. 333, p 188.

(3) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.*, **1977**, *128*, 345.

(4) Chase, D. B., to be published.

0002-7863/81/1503-977$01.25/0