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.

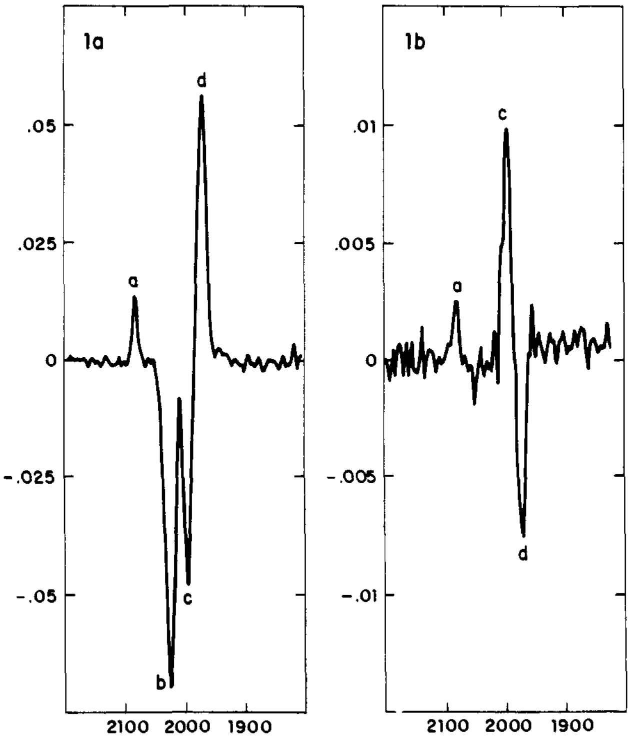

Figure 1. Infrared spectral changes in the carbonyl region of the $Fe(CO)_5$ photocatalyzed isomerization of 1-pentene (a) during irradiation and (b) after the light is turned off. Peaks are at (a) 2077, (b) 2020, (c) 1995, and (d) 1969 cm^{-1}.

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.

[†] Contribution No. 2839.

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

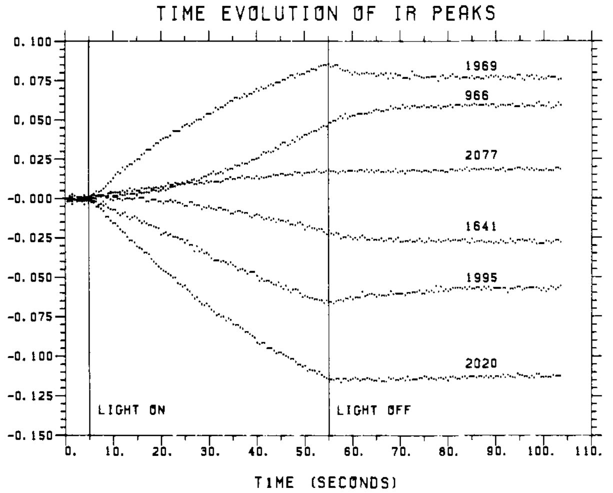

Figure 2. Time evolution of principal infrared bands before, during, and after irradiation of a mixture of $Fe(CO)_5$ and 1-pentene.

Both disappearance of 1-pentene and appearance of 2-pentene show an induction period suggesting that the active catalyst is not formed directly from pentacarbonyliron by a one-quantum process. The lifetime of the active catalytic species is determined by adding (with the proper signs) the absorption changes in both the olefin and carbonyl bands from the time the light is turned off to the end of the experiment. Ten seconds of the resulting composite trace is fit to an expression of the form $OD = C + A \exp(-Bt)$ where $1/B$ is taken as the catalyst life (assuming a first-order decay process). The measured lifetimes varied from 7 to 28 s and seem to depend most strongly on the concentration of 1-pentene present when the light is turned off. Thus the higher quantum yield observed in neat 1-pentene compared to dilute solutions[2] is more the result of longer catalyst life in this medium rather than a change in the intrinsic turnover rate.

The catalyst lifetime may be determined by olefin dissociation from $(\text{olefin})Fe(CO)_3$ to give a fragment which rapidly decomposes to catalytically inactive species. At high concentrations of active catalyst such as might be produced by laser excitation, higher order kinetic processes might compete with the process found in this work.[5]

It is inappropriate to discuss quantum yields or catalyst cycles in these experiments, because the short path length in the IR cell allows most of the radiation to pass through unabsorbed and, at the low conversions studied, most of the pentacarbonyliron is only converted to the intermediate tetracarbonyl stage.

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Bridging the Gap between the Gas Phase and Solution: Transition in the Kinetics of Nucleophilic Displacement Reactions

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Now that techniques are available which allow the production of solvated ions in the gas phase, it has become possible to explore, in a quantitative manner, the transition in the kinetics and energetics of ion–molecule reactions from their solvent-free behavior to that observed in solution and so to deduce the absolute influence of solvent on such reactions.[1,2] Nucleophilic displacment reactions, for which we have shown that the specific rate can change by up to *20 orders of magnitude* in going from the gas phase to solution,[3] have received particular attention.[4,5] Here we report the first attempt to follow the transition in the kinetics of such reactions which ensues from the stepwise hydration of a nucleophile.[6] We have been able to follow this transition in the gas phase at room temperature for reaction 1 up to $n = 3$. The rate of this reaction in aqueous solution has been known for many years.[7]

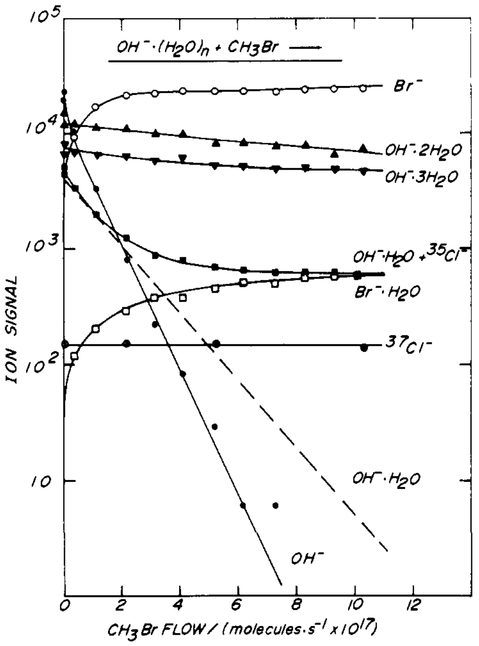

Figure 1. Variation of ion signals below m/e 100 recorded upon the addition of CH_3Br into a flowing H_2O/H_2 plasma in which unhydrated and hydrated hydroxide ions are initially present. The dashed curve represents the decay in $OH^-\cdot H_2O$ when account is taken of the contribution of $^{35}Cl^-$ to the measured m/e 35 signal. $P = 0.414$ torr, $T = 300$ K, $L = 60$ cm, $\bar{v} = 7.8 \times 10^3$ cm s^{-1}.

Table I. Room-Temperature Rate Constants Measured for Nucleophilic Displacement Reactions between Hydrated Hydroxide Ions and CH_3Br for Various Degrees of Hydration

hydroxide ion	rate constant
OH^-	$(1.0 \pm 0.2) \times 10^{-9}$ [a]
$OH^-\cdot H_2O$	$(6.3 \pm 2.5) \times 10^{-10}$
$OH^-\cdot(H_2O)_2$	$(2 \pm 1) \times 10^{-12}$
$OH^-\cdot(H_2O)_3$	$\leq 2 \times 10^{-13}$
$OH^-\cdot(H_2O)_n$	2.3×10^{-25} [b]

[a] In units of cm^3 molecule^{-1} s^{-1}. Each value represents the average of several measurements together with its estimated total accuracy. [b] In aqueous solution, from ref 7.

$$OH^-\cdot(H_2O)_n + CH_3Br \rightarrow Br^-\cdot(H_2O)_n + CH_3OH \qquad (1)$$

The measurements were carried out by using the flowing-afterglow technique.[8] Hydroxide ions (~10 ppb) were generated

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(1) We have followed the influence of stepwise hydration on the kinetics of proton transfer from the hydronium ion to a variety of bases in the gas phase: Bohme, D. K.; Mackay, G. L.; Tanner, S. D. J. Am. Chem. Soc. **1979**, *101*, 3724.

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