AIP | The Journal of Chemical Physics

Laser photocatalytic isomerization and hydrogenation of olefins in the gas phase

Robert L. Whetten, KeJian Fu, and Edward R. Grant

Citation: The Journal of Chemical Physics **77**, 3769 (1982); doi: 10.1063/1.444244
View online: http://dx.doi.org/10.1063/1.444244
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/77/7?ver=pdfcov
Published by the AIP Publishing

Laser photocatalytic isomerization and hydrogenation of olefins in the gas phase

Robert L. Whetten,[a] Ke-Jian Fu,[b] and Edward R. Grant

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

(Received 9 June 1982; accepted 20 July 1982)

During recent studies of the primary photoprocesses of $Fe(CO)_5$ we have observed highly efficient vapor phase isomerization and hydrogenation of 1-pentene photocatalyzed by gaseous iron carbonyl.[1] Our findings remarkably show that both of these processes, necessarily involving complex catalytic cycles, occur homogeneously at pressures as low as 5 Torr. Under conditions employed in our experiments, minimum quantum yields (defined here as number of olefin molecules transformed divided by number of photons absorbed) approach 400 for isomerization and 20 for hydrogenation, indicating that the only function of our pulsed laser light source is to create a catalyst that is highly active at the ambient temperature of the medium.

The unusual catalytic and photochemical properties of organotransition metal complexes have been the objects of widespread investigation.[2-4] Work in this field has produced a number of systems that exhibit liquid phase photocatalytic behavior.[5] In such systems light is thought to initiate catalytic activity by photolytically removing ligands to generate a coordinatively unsaturated active catalyst under mild conditions. The liquid phase $Fe(CO)_5$ photocatalyzed isomerization and hydrogenation of olefins are among the most extensively studied systems.[6] For this case the repeating catalytic unit responsible for the binding and transforming of organic substrates is believed to be $Fe(CO)_3$. In the present report we show preliminary kinetic evidence which indicates that our gas phase catalytic behavior is entirely analogous to that found in liquids.

Our experiments use a Lambda Physik EMG-101 excimer laser, operated at one of several available wavelengths (351 nm, XeF, 308 nm, XeCl or 337 nm, N_2) all of which are strongly absorbed by $Fe(CO)_5$, but not absorbed by the hydrocarbon component of our systems. Laser irradiation is allowed to pass unfocussed through a 10 by 5 cm diam sample cell fitted with quartz windows. Following irradiations of from 5 to 45 min at fixed repetition rate from 3 to 20 Hz, samples are analyzed by gas chromatography.

Figures 1(a) and 1(b) show typical time dependence for laser-photocatalyzed isomerization and hydrogenation of 1-pentene under conditions of sustained, pulsed irradiation. Table I presents the full range of sample compositions examined.

With or without H_2, the isomerization reaction proceeds rapidly to the equilibrium mixture of the three pentenes, but in every case the observed rate increases during the early stages of the reaction.[8] In the presence of H_2, hydrogenation apparently competes with isomerization for the same catalytically active intermediates, as evidenced by the decreasing rate of isomerization with increasing H_2 pressure. The hydrogenation reaction also shows an induction period.

No reaction is observed in the absence of light, nor is any reaction observed when mixtures of substrates without $Fe(CO)_5$ are irradiated for extended periods. A gas cell visibly spoiled by prolonged irradiation of $Fe(CO)_5$ in the absence of potential ligands and then filled with 1-pentene and irradiated shows no catalytic activity. In experiments with substrate: catalyst ratios greater than 300 we observe no evidence for irreversible loss of catalyst; through identification of organo-

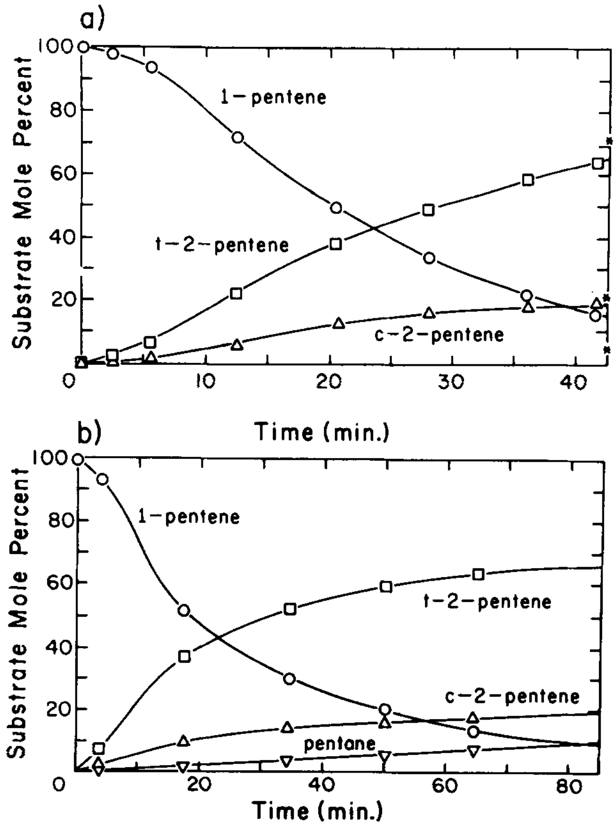

FIG. 1. Typical time dependence of gas-phase (a) photocatalytic isomerization and (b) photocatalytic hydrogenation under conditions of sustained, pulsed laser irradiation at 337 nm and 4 Hz. Initial sample compositions: (a) $Fe(CO)_5$ 1.0 mm Hg, 1-pentene 340 mm Hg; (b) $Fe(CO)_5$, 1.0 mm Hg; 1-pentene 400 mm Hg; H_2 800 mm Hg.

J. Chem. Phys. 77(7), 1 Oct. 1982 0021-9606/82/193769-02$02.10

TABLE I. Quantum yields for gas-phase photocatalytic isomerization and hydrogenation.[a]

Substrate pressure (mmHg)[b]		Quantum yields	
1-pentene	H_2	$\phi_{\text{isomerization}}$	$\phi_{\text{hydrogenation}}$
75	···	69	···
120	···	106	···
240	···	197	···
480	···	408	···
75	750	55	2.5
120	720	95	3.5
400	2200	225	18

[a] N_2 laser irradiation, $\lambda = 337$ nm, energy/pulse: 1 mJ, repetition rate: 4 Hz.

[b] $Fe(CO)_5$ partial pressure: 1.0 mmHg for all tabulated experiments.

metallic carbonyl compounds by infrared spectroscopy we are able to account for all the original $Fe(CO)_5$.[9]

In all our experiments we find initial quantum yields significantly greater than unity, as shown in Table I. For both hydrogenation and isomerization, the rate of reaction, and hence the quantum efficiency, is proportional to substrate pressure, indicating that the substrate concentrations used in these experiments are far below those needed to saturate the catalyst. In all cases that we have studied, isomerization is the more efficient process; however, in general, our gas phase photocatalytic hydrogenation quantum yields are much higher than those found in liquid phase photocatalysis, where quantum yields rarely exceed unity under any conditions.[5,6,10]

By varying the pulse repetition rate of the laser, we have been able to estimate the turnover rate of the gas-phase isomerization catalyst. We find, for a system with initial $Fe(CO)_5$ and 1-pentene pressures of 1.0 and 240 mm Hg, respectively, that the quantum efficiency of gas phase isomerization diminishes with increasing laser pulse rates above 4 Hz, indicating that at high repetition rates laser pulses are irradiating catalytic intermediates. Below 4 Hz the system apparently relaxes between pulses because the quantum efficiency is found to be independent of laser pulse rate. We thus estimate the lifetime of the catalyst under these conditions to be 0.2 s. Combining this number with the system's observed quantum yield (197) we calculate a turnover rate of about 1000 s^{-1}. Considering the present 1-pentene density, this turnover rate yields a bimolecular rate constant for the reaction of optically prepared unsaturated iron complexes of 2×10^{-16} cm^3 $molec^{-1}$ s^{-1}. To confirm this preliminary number, careful measurement of turnover rates over a range of substrate pressure are now in progress.

In other gas phase work we have used a PF_3 scavenging technique[7] to determine the initial yields of photofragments produced under the irradiation conditions of our catalysis experiments.[11] Results of these experiments clearly show that the effect of irradiation is to produce coordinatively unsaturated $Fe(CO)_4$ and $Fe(CO)_3$. We propose that the latter of these is a catalytic intermediate in our system, and present a mechanistic analysis in support of this view in a separate report on laser-induced photocatalysis in the liquid phase.[6(b)]

We gratefully acknowledge Koppers Company Inc. for generous support of this research.

---

a) National Science Foundation Graduate Fellow.

b) Permanent address: Institute of Physics, Chinese Academy of Sciences, Bijing, The People's Republic of China.

[1] Photocatalytic, used here according to the definition given in Refs. 5 and 6, refers only to systems which show substrate turnover numbers greater than unity with respect to both catalyst *and* photons.

[2] J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, Mill Valley, Calif., 1980).

[3] G. K. Geoffrey and M. S. Wrighton, *Organomettalic Chemistry* (Academic, New York, 1979).

[4] M. Bender, *Mechanisms of Homogeneous Catalysis: From Protons to Proteins* (Wiley–Interscience, New York, 1971).

[5] L. Moggi, A. Juris, D. Sandrini, and M. F. Manfrin, Rev. Chem. Intermed. 4, 171 (1981).

[6] (a) M. A. Schröder and M. S. Wrighton, J. Am. Chem. Soc. 98, 551 (1976); (b) R. L. Whetten, K.-J. Fu, and E. R. Grant, J. Am. Chem. Soc. **105**, 4270 (1982); (c) B. Fell, P. Krings, and F. Asinger, Chem. Ber. **99**, 3688 (1966); (d) R. D. Sanner, R. G. Austin, M. S. Wrighton, W. D. Honnick, and C. U. Pittman, Jr., Inorg. Chem. **18**, 928 (1979); (e) J. L. Graff, R. D. Sanner, and M. S. Wrighton, J. Am. Chem. Soc. **103**, 975 (1981); (f) D. B. Chase and F. J. Weigert, *ibid.* **103**, 977 (1981).

[7] G. Nathanson, B. Gitlin, A. M. Rosen, and J. T. Yardley, J. Chem. Phys. **74**, 361, 370 (1981).

[8] This is precisely the kinetic behavior observed in the corresponding liquid phase system and attributed to stepwise formation of the catalyst by the sequential absorption of two photons. See Refs. 6(a) and (b).

[9] It should be noted that at initial $Fe(CO)_5$ pressures greater than 3 Torr, or at initial substrate $Fe(CO)_5$ ratios less than 50, condensation of organometallic complex is observed during prolonged irradiation. This may be attributed either to low volatility of the stable $Fe(CO)_4$ (pentene) complexes or to clustering of reactive fragments in the absence of sufficient ligands. For substrate/catalyst ratios greater than 50 we find that quantum yields are independent of $Fe(CO)_5$ concentration.

[10] E. N. Frankel, E. A. Emkin, and V. L. Davison, J. Org. Chem. **30**, 2739 (1965).

[11] R. L. Whetten, K.-J. Fu, and E. R. Grant (to be published).