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Registry No. I, 64867-63-6; Na[$Fe(CO)_4C(O)CH_3$], 91128-40-4.

Supplementary Material Available: List of atomic coordinates, thermal parameters, and selected bond angles and distances for $HFe_3(CO)_9BH_4$ (3 pages). Ordering information is given on any current masthead page.

Relaxation Kinetics in the Homogeneous Gas-Phase Photocatalytic Hydrogenation of Ethylene by $Fe(CO)_4(C_2H_4)$

Michael E. Miller and Edward R. Grant*

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

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Photogenerated coordinatively unsaturated organometallic species are well noted for their catalytic activity in solution.[1-6] As a result, interest in the elementary chemistry of such species has been intense,[7-14] with a number of recent studies isolating relevant elementary reaction pathways and rate processes for reactions in the gas phase.[15-22] Significant among these is work in our own laboratory,[22] which has demonstrated for the first time that free photogenerated organometallic fragments can function as potent homogeneous catalysts for gas-phase organic transformations.

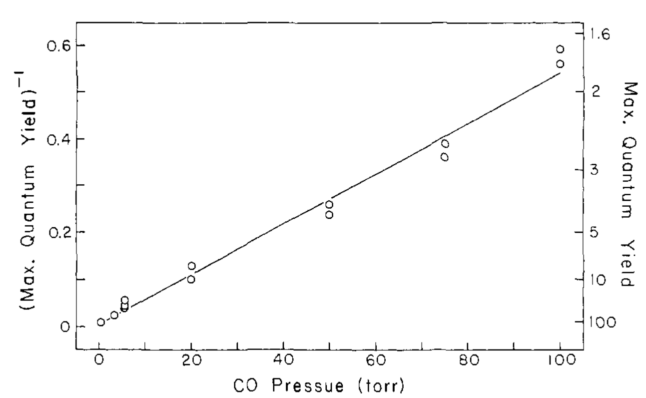

Figure 1. Reciprocal of the quantum yield vs. the total CO pressure at 43 °C and a laser repetition rate of 4 Hz. Initial substrate pressures: $Fe(CO)_5$, 0.3 torr; ethylene, 400 torr; hydrogen, 1400 torr. The plot is linear as predicted by eq 3, but there is a small positive y intercept due to catalyst/precatalyst interactions which also shut off catalytic activity.

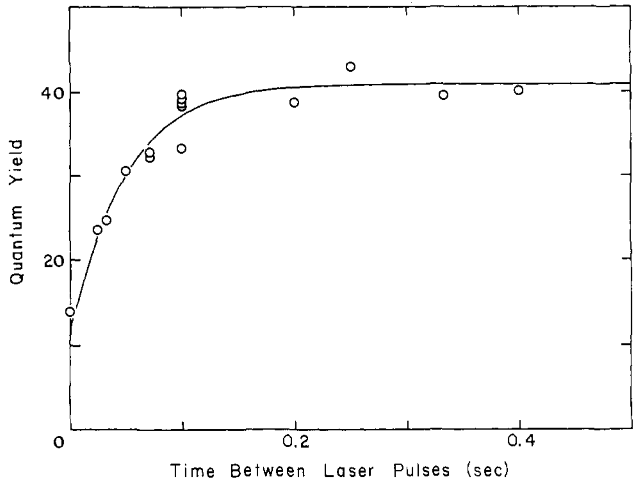

Figure 2. Quantum yield vs. time between laser pulses (reciprocal of repetition rate) at 43 °C. Initial pressures: $Fe(CO)$, 0.3 torr; CO, 3 torr; ethylene, 400 torr; hydrogen, 1400 torr. The solid curve is our theoretical fit (see text). The continuous wave ($\Delta t = 0$) experiment was carried out with a filtered Xe arc lamp (λ 300-410 nm).

A recent study by Ouderkirk et al.[21] has established the rate of a key reaction for gas-phase photocatalysis, the recombination of an unsaturated organometallic fragment with CO to reform a stable photocatalyst precursor. They found that $Fe(CO)_4$ recombines with CO at an extraordinarily fast rate ($k \sim 10^7$ M^{-1} s^{-1}), while $Fe(CO)_3$ and $Fe(CO)_2$ react two orders of magnitude faster.

Our system adds hydrogen and ethylene to $Fe(CO)_5$, and despite the above-cited fast rate for recombinative deactivation, we find very efficient photocatalytic production of ethane. This suggests that our gas-phase organometallic photocatalytic system possesses a characteristic that sets it apart from one composed of unsubstituted $Fe(CO)_x$ fragments. The aim of the present study is to uncover that difference by examining the CO recombination kinetics of a functioning photocatalytic system.

Catalysis is initiated in our homogeneous gas-phase system by temporally distinct pulses of unfocussed light from a Lambda Physik EMG-101 excimer laser (operated on N_2, 337-nm, 1-mJ pulse energy). This light is absorbed only by the iron carbonyl component of our samples. For many experiments excess CO is

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added, though in all cases our samples contain a concentration of free CO at least as large as the initial concentration of $Fe(CO)_5$. A thermopile detector measures attenuation of light by the reaction mixture, while product (ethane) yields are monitored at intervals by flame ionization gas chromatography.

The catalyst precursor, $Fe(CO)_4(C_2H_4)$, is prepared in situ by irradiation of $Fe(CO)_5$ in the presence of reactants.[23] This precatalyst is a stable species that does not revert to $Fe(CO)_5$ but photodecomposes to form the coordinatively unsaturated active catalyst, $Fe(CO)_3(C_2H_4)$, which promotes hydrogenation until it recombines with CO.

We find that CO added to the reaction mixture decreases the quantum yield (defined as the number of product molcules formed per photon absorbed). This decrease is systematic, yielding the inverse dependence of the quantum yield on CO pressure shown in Figure 1. The observed quantum efficiency also depends on the repetition rate of the laser, falling from a maximum value which is constant at low repetition rates to intersect the minimum quantum yield found under conditions of continuous wave illumination (see Figure 2).

The elementary behavior of the catalytic system responsible for these two observations can be understood by examining the simple kinetics of catalytic hydrogenation in competition with catalyst–CO recombination, viz.

$$Fe(CO)_3(C_2H_4) \xrightarrow[\text{TOR}]{H_2,C_2H_4} C_2H_6 + Fe(CO)_3(C_2H_4) \qquad (1)$$

$$Fe(CO)_3(C_2H_4) \xrightarrow[k_R[\text{CO}] = \tau^{-1}]{\text{CO}} Fe(CO)_4(C_2H_4) \qquad (2)$$

Here we associate a turnover rate (TOR) with the formation of product, and since the concentration of free CO is always large compared to that of active catalyst, we assign a pseudo-first-order rate constant, $k_R[\text{CO}]$, to the relaxation of the system back to precatalyst.

Figure 2 shows that at low repetition rates the catalytic quantum yield is maximized. Under such conditions if we can assume that every photon absorbed produces a catalyst, we can write down a simple relation between the turnover rate, the relaxation rate, and this maximum quantum yield. The turnover rate is the number of product molecules produced per catalyst divided by the average amount of time the catalyst works before its reversion, τ. Under our assumption of one catalyst formed per photon absorbed, the amount of product per catalyst is the same as the amount of product per photon, or the quantum yield, $\Phi_{\max}$. Thus

$$\text{TOR} = \Phi_{\max}/\tau = \Phi_{\max}k_R[\text{CO}] \qquad (3)$$

As shown in Figure 1, a plot of $\Phi_{\max}^{-1}$ vs. CO pressure is indeed linear, yielding by its slope the ratio $k_R/\text{TOR} = 100 \pm 1\ \text{M}^{-1}$.

At high laser-pulse repetition rates, where the time between pulses is less than τ, a given pulse irradiates both precatalyst and still-active catalyst remaining from previous pulses, and we observe our assumption of one catalyst produced per photon absorbed to fail. The quantum yield, which is constant at slow repetition rates, diminishes with closer spaced pulses. Analysis of this time-between-pulses (rep rate) dependence allows us to calculate the average lifetime of the catalyst.

We consider four processes to occur with the advent of each laser pulse: (1) photoejection of CO from precatalyst with unit quantum efficiency to create active catalyst; (2) absorption of light by catalyst remaining from previous pulses, resulting in the irreversible loss of catalytic activity (again with unit efficiency); (3) catalyst recombination with CO; and (4) catalyst-promoted hydrogenation of ethylene. Processes 3 and 4 occur thermally whenever the appropriate reactants are present. From this model we obtain a recursion relation for the concentrations of catalyst and precatalyst after each successive laser pulse, which yields a geometric series in the limit of many pulses (>50). Taking into account the consumption of photons in both precatalyst and catalyst absorption channels, we calculate the quantum yield as a function of the time between laser pulses (Δt) for a given catalyst lifetime τ and catalyst absorption probability α:[24]

$$\Phi = \Phi_{\max} \frac{\alpha(1 - \alpha)e^{-\Delta t/\tau} + e^{\Delta t/\tau} - 1}{e^{\Delta t/\tau} - (1 - 2\alpha)} \qquad (4)$$

This model explains the behavior pictured in Figure 2. A two-parameter nonlinear least-squares fit of the data yields the theoretical curve shown for $\alpha = 0.42$ and $\tau = 0.045$ s. Thus from eq 3 we obtain for the present conditions TOR = $900 \pm 70\ \text{s}^{-1}$. This intrinsic rate is a thousand times faster than the fastest known liquid-phase hydrogenation system.[25] Equation 3 also yields $k_R = 9.0 \pm 0.7 \times 10^4\ \text{M}^{-1}\ \text{s}^{-1}$, which shows by comparison with the data of Ouderkirk et al.[21] that the substitution of ethylene for CO slows recombination of the unsaturated iron carbonyl fragment with CO by about 2.5 orders of magnitude.

The difference between $Fe(CO)_3(C_2H_4)$ and $Fe(CO)_4$ is interesting. We suspect that recombination in the case of the substituted carbonyl is slowed by an activation barrier, possibly associated with a required rearrangement of the ethylene ligand.[26] Temperature-dependence experiments to test this hypothess are presently underway.

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Registry No. $Fe(CO)_3(C_2H_4)$, 84520-95-6; $Fe(CO)_4(C_2H_4)$, 32799-25-0; $CH_2{=}CH_2$, 74-85-1.

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(23) The presence of this species together with its mechanistic significance is established by kinetic and spectroscopic evidence (see ref 1, 5, and 17).

(24) α is the product of the photon flux, catalyst extinction coefficient, and cell path length.

(25) See, for example: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 317–318.

(26) We thank C. P. Casey for discussions on this point.

Metallophosphorus Clusters: $Ru_5(CO)_{12}(\mu_4\text{-PPh})(\mu_3\text{-CCH}_2\text{-}i\text{-Pr})(\mu_2\text{-PPh}_2)$ and $HRu_5(CO)_{10}(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)$, Face-Capped-Octahedral and Pentagonal-Bipyramidal Clusters via Stepwise Reduction of an Acetylide

Karen Kwek, Nicholas J. Taylor, and Arthur J. Carty*

Guelph-Waterloo Centre, Waterloo Campus
Chemistry Department, University of Waterloo
Waterloo, Ontario N2L 3G1, Canada

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The incorporation of main-group atoms into the skeletal frameworks of transition-metal clusters offers new opportunities to compare the predictions of current bonding theories[1] and to improve on the degradative instability of high nuclearity, homonuclear compounds.[2] We report a new synthetic route to the interesting class of metallophosphorus clusters[3] involving sequential

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