II is a strong base (vide infra) it reacts readily with I, so that maximum amounts of II arise at low conversions of reaction 1.

Ion II reacts in a completely different manner from its isomer, acetaldehyde enolate (III). It is a strong base, and m/z 43 is converted completely into m/z 44 by reaction with D_2O (eq 2).

$$CH_3\bar{C}{=}O + D_2O \rightarrow \left[\begin{matrix} O \\ \| \\ CH_3{-}C{-}D \cdot OD^- \end{matrix}\right] \quad (2)$$

$$\downarrow$$

$$\begin{matrix} O^- \\ | \\ CH_2{=}C{-}D \\ \text{III} \\ m/z\ 44 \end{matrix} + HOD$$

No DO^- is produced in this reaction, which suggests that the first step is endothermic or thermoneutral and that II is less basic than hydroxide ion ($\Delta H°_{acid}(H_2O)$ = 391 kcal/mol).[12] This conclusion is strengthened by the observation of a small amount of allyl anion when II is allowed to react with a large excess of propylene ($\Delta H°_{acid}$ = 391 kcal/mol).[12] If we postulate $\Delta H°_{acid}$ = 390 ± 2 kcal/mol for the acyl hydrogen in acetaldehyde, the electron affinity of the acetyl radical $CH_3\dot{C}{=}O$ can be calculated to be 0.42 (±0.10) eV (10 kcal/mol), and indeed a small amount of O_2^- is formed when an excess of O_2 (EA = 0.44 eV)[13] reacts with II.[14] These conclusions are strongly supported by preliminary photodetachment data of Nimlos et al.,[15] which give EA($CH_3\dot{C}{=}O$) = 0.438 (±0.020) eV.

The acetyl anion is highly reactive and atom transfer is observed with N_2O,[16] COS,[17] and CS_2.[18] The main products of its reaction with oxygen[19] also involve atom transfer.[20]

$$CH_3\bar{C}{=}O + N_2O \rightarrow CH_3CO_2^- + N_2 \quad (3)$$

$$CH_3\bar{C}{=}O + COS \rightarrow CH_3COS^- + CO \quad (4)$$

$$CH_3\bar{C}{=}O + CS_2 \rightarrow CH_3COS^- + CS \quad (5)$$

$$CH_3\bar{C}{=}O + O_2 \xrightarrow{0.5} CH_3CO_2^- + O \quad (6)$$

$$\xrightarrow{0.5} CH_2CO_2^- + HO \quad (7)$$

It also undergoes addition reactions, for example with CO_2.[16]

$$CH_3\bar{C}{=}O + CO_2 \rightarrow CH_3COCO_2^- \quad (8)$$

It seems likely that this method will prove general for the formation of acyl anions in the gas phase, and further investigations are currently in progress.

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Registry No. CH_3CO^-, 64723-93-9; $(CH_3)_3SiCOCH_3$, 13411-48-8; F^-, 16984-48-8; CH_3CO, 3170-69-2.

(11) The (M - 1) ion from I is a minor product (<10%). Traces of ions corresponding to $(M + F - CH_4)^-$ and $(M + F - C_2H_4O)^-$ are also detected.

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(14) For this calculation we have used a value of 86 kcal/mol for the bond dissociation energy of the carbon-hydrogen bond (McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493-532) and 313.6 kcal/mol for the ionization potential of the hydrogen atom (Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables"; NSRDS-NBS-37, 2nd ed., National Bureau of Standards, Washington, DC, 1971). From this value for the electron affinity of the acetyl radical the heat of formation of acetyl anion can be calculated to be $\Delta H_f°_{298}$ = -17 kcal/mol. These results are in perfect agreement with those calculated by Schleyer[8] when zero-point energy corrections are included in the latter.

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(20) A referee has noted that atom transfer *from* N_2O or COS *to* the acetyl anion cannot be distinguished by mass from methide ion transfer *from* the acetyl anion *to* these reagents. However, we do not believe that methide ion transfer occurs based on the fact that this process is not observed with CS_2 nor with hexafluoroacetone. The decomposition of the acetyl anion to methide and CO is endothermic by 24 kcal/mol. We hope to find alkide ion-transfer reactions with substituted acetyl anions for which the analogous decomposition is less endothermic.

Energetics of a Homogeneous Gas-Phase Photocatalytic System: The Hydrogenation of Ethylene by $Fe(CO)_4(C_2H_4)$

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An interesting class of photochemical reactions consists of those processes in which photofragmentation generates an active thermal catalyst. Particularly important examples exist for which the catalyst and its precursor are organometallic complexes. In such cases, when the photochemical initiation step is reversible, photocatalytic activity can be maintained almost indefinitely, and the overall conversion process is highly efficient in its use of photons. The kinetics of the reversion step are critical; its rate regulates the turnover number and irreversible loss of photoprepared catalysts.[1,2]

Recent work in our laboratory has concentrated on the elementary kinetics of photoinitiated homogeneous catalytic processes of organometallic complexes in the *gas phase*.[1,2] There the distinction between various competing *molecular* interactions is particularly sharp, and the importance of reversion becomes a natural focus.

Our system of principal interest has been the iron carbonyl photocatalyzed hydrogenation of ethylene, Scheme I.

We have recently measured[2] the rate constant for catalyst, $Fe(CO)_3(C_2H_4)$, recombination with CO to be nearly 3 orders of magnitude smaller than that determined elsewhere for $Fe(CO)_4$.[3] The present paper traces the source of this kinetically important difference to a substantial activation energy for the reaction of CO with the ethylene-substituted complex.

Figure 1 shows quantum yields for C_2H_4 hydrogenation measured[1,2] as function of laser repetition rate at three temperatures. The yield per photon declines at high repetition rates because successive laser pulses perturb catalytic cycles still working from previous pulses. The point at which this perturbation becomes significant allows us to estimate the lifetime of the catalyst, $\tau = (k_R[CO])^{-1}$. Taken together with a knowledge of the low repetition rate, maximum quantum yield, Φ_{max}, this lifetime information gives the turnover rate (TOR) of the catalyst:

$$TOR = \Phi_{max}/\tau \quad (1)$$

The results are summarized in Table I. We obtain an Arrhenius temperature dependence for TOR yielding an activation energy for the substrate-saturated cycle of 9.4 ± 1.3 kcal/mol.

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(2) Miller, M. E.; Grant, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 4635-4636.

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Table I. Kinetic Data on the $Fe(CO)_3(C_2H_4)$ Catalyzed Hydrogenation of Ethylene Giving the Lifetime of the Cycle (τ), Its Turnover Rate (TOR), and the Rate Constant for the Recombination of Catalyst with CO (k_R)

temp, °C	τ, s	Φ_{max}	TOR, s^{-1} [a]	k_R/TOR, M^{-1}	k_R, $M^{-1}\ s^{-1}$
23	0.066 ± 0.008	19 ± 1	820 ± 100	62 ± 3	$5.1 \pm 0.7 \times 10^4$
32	0.064 ± 0.005	28 ± 1	1300 ± 110	49 ± 1	$6.2 \pm 0.5 \times 10^4$
43	0.045 ± 0.003	35 ± 2	2200 ± 180	41 ± 1	$9.1 \pm 0.8 \times 10^4$

arrhenius params	TOR	k_R
E_a, kcal/mol	9.4 ± 1.3	5.5 ± 1.3
A	$6 \times 10^9\ s^{-1}$	$5 \times 10^8\ M^{-1}\ s^{-1}$

[a] See ref 9.

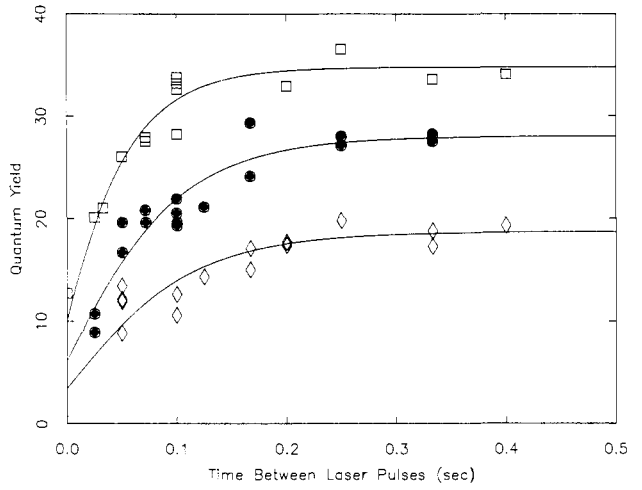


Figure 1. Quantum yield vs. time between laser pulses (reciprocal of repetition rate) at 23 (diamonds), 32 (solid circles), and 43 °C (open boxes). Initial substrate pressures: $Fe(CO)_5$, 0.3 torr; CO, 3 torr; ethylene, 400 torr; hydrogen, 1400 torr. The curves are theoretical fits.[2]

An accurate measure of k_R can be made by adopting the linearized form of eq 1:[2]

$$\Phi_{max}^{-1} = \frac{k_R}{TOR}[CO] \qquad (2)$$

Data plotted according to eq 2 show good linearity yielding slopes given as k_R/TOR in Table I. k_R extracted from these data is also temperature dependent yielding an activation energy E_R = 5.5 ± 1.3 kcal/mol (see Figure 2).

The mechanism of Scheme I suggests ethylene insertion into an Fe–H bond as the rate-determining step for substrate-saturated turnover. The relatively small TOR A factor (see Table I) indicates a multicenter reaction pathway,[4] which is consistent with this supposition. The activation energy, E_{TOR}, is similar to the only other such value measured for an M–H ethylene insertion process, that of Rh–H in solution (12 kcal/mol).[5]

E_R is surprisingly high for the recombination of a good ligand with a coordinatively unsaturated organometallic. The activation energy for $Fe(CO)_4$ + CO recombination is not available. However, from the room-temperature data of Ouderkirk et al., we can estimate a value of 1.7 kcal/mol if we assume an A factor equal to ours. This is a moderate activation energy, not inconsistent with the higher observed reactivity of smaller fragments, such as $Fe(CO)_3$, nor with the fact that $Fe(CO)_4$ is a ground-state triplet, but far smaller than the 5.5 kcal/mol we measure for $Fe(CO)_3(C_2H_4)$. Thus, we look to a higher entrance channel barrier for $Fe(CO)_3(C_2H_4)$ + CO as an explanation for the CO recombination reactivity difference between $Fe(CO)_3(C_2H_4)$ and $Fe(CO)_4$.

Such a barrier suggests an interesting potential energy surface topography for recombination. No calculations of the transition state for this reaction are available; however, Albright et al.[6] have

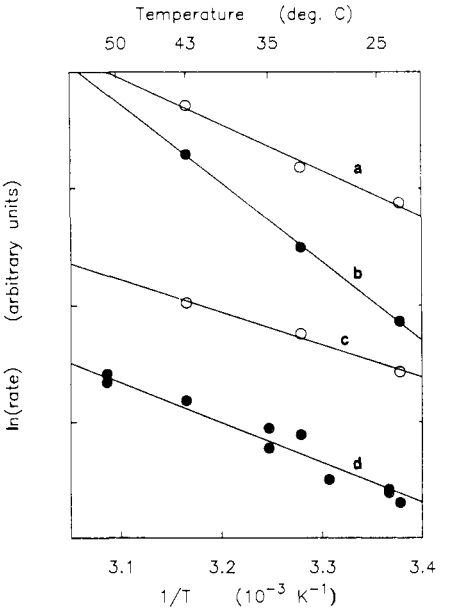
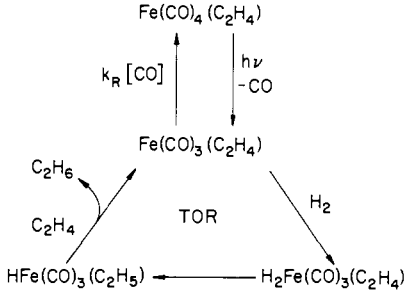


Figure 2. Arrhenius plots of the natural log of rate vs. the reciprocal of the absolute temperature. Rate = (a) k_R, (b) TOR, (c) TOR/k_R, and (d) Φ_{max}. The points on the bottom line correspond to a separate set of experiments in which the initial pressures are as follows: $Fe(CO)_5$, 0.3 torr; CO, 3 torr; ethylene, 400 torr; hydrogen, 1400 torr, with a laser repetition rate of 4 Hz. Note the agreement between (c) and the phenomenological temperature dependence (d) as predicted by eq 2.

Scheme I



determined a minimum-energy geometry for singlet ground state $Fe(CO)_3(C_2H_4)$, which predicts square-planar coordination, with the ethylene perpendicular to the molecular plane. The recombination product, $Fe(CO)_4(C_2H_4)$ is a trigonal bipyramid, with the ethylene in the equatorial plane.[7,8]

Acknowledgment. This work was supported by a grant from Koppers Co., Inc.

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(8) We thank Roald Hoffmann and Jerome Silvestre for discussions on the preferred geometries and relative energies of these species.
(9) Added in proof: New experiments[10] show that at 337 nm the quantum yield for photoproduction of catalyst $Fe(CO)_3(C_2H_4)$ from $Fe(CO)_4(C_2H_4)$ is not 1, as implied by eq 1, but rather 0.35, the competing channel being loss of C_2H_4 to form noncatalytic $Fe(CO)_4$. Turnover rates in Table I have been corrected accordingly. Estimates of k_R and both activation energies are unaffected.
(10) Miller, M. E.; Grant, E. R., unpublished results.