associated with the conjugate acid of the amide base used in their formation.[12] Numerous deuterium-incorporation experiments strongly support the conjecture that such postenolization complexes remain intact in solution. Likewise, we now suggest that the conflicting reports of the ability of LiHMDS to enolize bulky ester and amide substrates are due to the formation of relatively stable preenolization complexes as characterized herein.

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Supplementary Material Available: Atomic numbering schemes and tables of crystallographic data, atomic positional parameters and thermal parameters, bond lengths and angles, and selected torsion angles for the LiHMDS/*tert*-butyl isobutyrate complex **1a** and the LiHMDS/*tert*-butyl pivalate complex **1b** and IR spectra of **1a**, **1b**, and the LiHMDS/methyl pivalate ester complex (28 pages). Ordering information is given on any current masthead page.

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Photochemical Cyclohexane Carbonylation Cocatalyzed by d^8 Transition Metal Carbonyls and Aromatic Ketones and Aldehydes

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The catalytic functionalization of alkanes is of great current interest;[1] a potentially important example is carbonylation. $Rh(PR_3)_2(CO)Cl$ (**1**, R = Me) has been found to photochemically catalyze hydrocarbon carbonylation.[2,3] Recently it was reported that the rate of cyclohexane carbonylation upon irradiation of a 1:1 benzene/cyclohexane solution is 10 times greater than that of a solution of **1** in pure cyclohexane.[4] This observation was attributed to the inhibition "of secondary photoreactions of cyclohexanecarboxaldehyde including decarbonylation due to the filter effect of benzene".[4]

We find that the *initial* rate of cyclohexane carbonylation ($\lambda > 340$ nm) in a benzene/cyclohexane solution of **1** (7.0 mM) is less than that of a pure cyclohexane solution of **1** ($\phi_{rel} = 2.9 \times 10^{-5}$).[5] However, added benzaldehyde (0.10 M) increases the reaction rate 200-fold ($\phi = 5.8 \times 10^{-3}$, $\phi_{adj} = 0.20$).[5] Presumably benzaldehyde produced in the benzene/cyclohexane mixtures is responsible for the increased rate of cyclohexane carbonylation.

$$\mathrm{CyH} + \mathrm{CO} \xrightarrow[\text{aromatic ketone or aldehyde}]{\text{metal carbonyl } h\nu\ (\lambda > 340\text{ nm})} \mathrm{CyCHO}$$

$$(\mathrm{Cy} = \text{c-}C_6H_{11}) \qquad (1)$$

Benzophenone, acetophenone, or *p*-(trifluoromethyl)acetophenone have a similar effect on reaction 1. 2-Nonanone and 1-nonanal do not absorb the incident irradiation ($\lambda > 340$ nm) and do not affect the rate. Triphenylene and anthracene absorb 366-nm light and are good triplet sensitizers[7] like the aromatic carbonyls, but do not accelerate reaction 1. Unlike the aromatic carbonyls, however, their lowest excited states are π–π^*, not n–π^*, and therefore they do not abstract hydrogen from alkanes, which is a well-known reaction of photoexcited ketones and aldehydes.[8]

The role of the organic carbonyl as the photoactive species in this system is demonstrated by experiments in which the concentration of **1** was varied. An *inverse* dependence of the reaction rate ($\phi_{rel} = 4.5 \times 10^{-2}$–$5.4 \times 10^{-3}$) on [**1**] is observed over the range 0.70–7.0 mM **1** as the fraction of light absorbed by $(p\text{-}CF_3C_6H_4)C(O)CH_3$ (in competition with **1**) varies in this range from 0.31 to 0.043 ($\phi_{adj} = 0.12 \pm 0.02$). A similar dependence is observed by varying $[Ir(PMe_3)_2(CO)_2Cl]$ (**2**; vide infra). When [**2**] is held constant, the rate shows a positive dependence on the concentration of acetophenone over the range 0.0060–0.10 M ($\phi_{rel} = 1.2 \times 10^{-2}$–$8.4 \times 10^{-2}$) as the fraction of light absorbed by the ketone increases from 0.020 to 0.25. The quantum yield is invariant (±5%) over a 10-fold intensity range (2 mM **2**, 0.10 M acetophenone), arguing against the possibility of a two-photon mechanism.

1-Catalyzed benzene photocarbonylation is not accelerated by aromatic ketones. This selectivity is consistent with a proposed role of the photoexcited ketone as a hydrogen-abstraction agent since the aryl–hydrogen bond is too strong for the hydrogen to undergo abstraction. The presence of a good hydrogen donor, PhCHMeOH (1.0 M), reduces the rate of reaction 1 by 40% (2 mM **2**, 0.10 M acetophenone). Irradiation of a 1:1 C_6H_{12}/C_6D_{12} solution of **2** (4.0 mM) and Ph_2CO (0.033 M) yields the following ratio of isotopomers: $C_6H_{11}CHO$:$C_6H_{11}CDO$:$C_6D_{11}CHO$:$C_6D_{11}CDO$ = 70.9:12.2:14.8:2.1. The isotope effect, $k_H/k_D = 4.9$, is consistent with known isotope effects for H abstraction by photoexcited ketones[9] and contrasts with $k_H/k_D = 1.1$ for **1**-photocatalyzed benzene carbonylation.

Presuming the photoexcited ketone to cleave the alkane C–H bond, we considered that metal carbonyls other than **1** might also be effective cocatalysts. Indeed, the following metal carbonyls with d^8 electronic configurations are all effective (0.10 M PhC(O)Me): $RhL_2(CO)Cl$ (L = PPh_3, P^iPr_3), $Ru(CO)_3(dmpe)$, and **2**.[10] In the absence of ketone, none of these complexes significantly catalyze cyclohexane carbonylation.[11,12]

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[5] All photochemical experiments (cyclohexane solvent) were performed as described previously.[6] Relative quantum yields, ϕ_{rel}, were obtained based on rates relative to a carbonylation reaction for which the absolute ϕ was measured (0.22 mM h^{-1} CyCHO, 7 mM **1**, 0.10 M PhC(O)Me, $\lambda = 366$ nm, $I = 1.4 \times 10^{-7}$ einstein/s, 2.0 mL, $\phi = 1.0 \times 10^{-3}$). Use of a Corning CS-0-52 cutoff filter ($\lambda > 345$ nm) instead of a "monochromatic" (366 nm) filter combination (Corning CS-0-52 and Corning CS-7-60) yielded a rate of 0.62 mM/h. Thus $\phi_{rel} = \{(d[CyCHO]/dt)/(0.62\ mM\ h^{-1})\} \times 1.0 \times 10^{-3}$ (see supplementary material for experimental details). ϕ_{adj} is defined as moles of product per einstein absorbed by the ketone or aldehyde, i.e., $\phi_{adj} = \phi_{rel} \times \{([ketone]\epsilon_{ketone} + [M\text{–}CO]\epsilon_{M\text{–}CO})/[ketone]\epsilon_{ketone}\}$.

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[9] Reference 8, p 385.

[10] Cyclohexane photocarbonylation occurs to a slight extent in solutions of aromatic ketones in the absence of metal carbonyl under 800 Torr of CO ($\lambda = 366$ nm, 0.10 M $(p\text{-}CF_3C_6H_4)C(O)CH_3$, $\phi_{rel} = \phi_{adj} = 0.0028$). Yields are significantly higher under higher pressures: e.g., 400 psi of CO, $\phi_{rel} = \phi_{adj} = 0.077$). Boese, W. T.; Goldman, A. S., to be published.

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The observations above suggest a mechanism of the general form of eqs 2–5.

$$\mathrm{CyH + ArR'C{=}O \xrightarrow{h\nu} Cy^{\bullet} + ArR'C(OH)^{\bullet}} \quad (2)$$

$$\mathrm{Cy^{\bullet} + M(CO) \rightarrow {}^{\bullet}M[C(O)Cy]}$$

$$\mathrm{(M = RhL_2Cl,\ Ru(CO)_2(dmpe),\ Ir(PMe_3)_2(CO)Cl)} \quad (3)$$

$$\mathrm{{}^{\bullet}M[C(O)Cy] + ArR'C(OH)^{\bullet} \rightarrow HM[C(O)Cy] + ArR'C{=}O} \quad (4)$$

$$\mathrm{HM[C(O)Cy] + CO \rightarrow M(CO) + HC(O)Cy} \quad (5)$$

Equation 2 is well studied; known quantum yields[13] of ca. 0.5 are consistent with the quantum yields of eq 1 calculated on the basis of the fraction of incident light absorbed by the ketone, $\phi_{\mathrm{adj}} \leq 0.6$. Equation 4 is well precedented by β-hydrogen atom transfers from organic radicals to metal radicals which exhibit near diffusion controlled kinetics.[14]

Reaction 3 may proceed via initial attack of Cy$^{\bullet}$ on the metal center[15,16] or, alternatively, by direct attack on coordinated CO. Note that the attack of Cy$^{\bullet}$ on free CO may be considered an unlikely pathway (under 1 atm of CO[10]) on the basis of the slow rates known for radical addition to CO.[17] A steady-state analysis, in which the rate of Cy$^{\bullet}$ formation is assumed greater than or equal to the total rate of Cy-containing products,[18] predicts that the ratio of formation of CyCHO/Cy$_2$ would be less than 0.4:1 as compared with an experimental value of 95:1 (2.0 mM **2**, 0.10 M acetophenone).

The viability of eq 3 was confirmed by experiments in which cyclohexyl radicals were independently generated: irradiation ($\lambda > 420$ nm) of Mn$_2$(CO)$_{10}$ (1.3 mM) in the presence of CyBr (1.6 M) and **2** (21 mM) resulted in the formation of Mn(CO)$_5$Br (1.5 mM) and Ir(PMe$_3$)$_2$[C(O)Cy]ClBr (8 mM); **1** reacted similarly. Presumably these reactions proceed via abstraction of Br$^{\bullet}$ by $^{\bullet}$Mn(CO)$_5$,[20] followed by eq 3, and the resulting acylmetalloradical then abstracts Br$^{\bullet}$ from CyBr (propagating a chain reaction).

Aldehyde yields up to 110 mM have been realized from eq 1 (0.10 M acetophenone, 2.0 mM **2**). In a separate experiment, 9.5 catalytic turnovers based on acetophenone (6.0 mM) were obtained (2.0 mM **2**). Aldehyde decarbonylation (evidenced in experiments with added 0.1 M cyclooctanecarboxaldehyde) and ketone decomposition are yield-limiting factors.

In summary, we report that photochemical carbonylation of cyclohexane is catalyzed by various d^8 transition metal carbonyls and aromatic ketones. The mechanism involves cleavage of the cyclohexane C–H bond by the photoexcited ketone and attack of the resulting cyclohexyl radical on the metal carbonyl.

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Supplementary Material Available: Table of data of 28 carbonylation experiments, calculation of the upper limit of the ratio of CyCHO/Cy$_2$ formation based on the assumption of rate-limiting attack by Cy$^{\bullet}$ on free CO, experimental data for the formation of Cy$_2$ and other side products in reactions with 0.0–4.0 mM **2**, and synthesis and characterization of Ir(PMe$_3$)$_2$[C(O)-Cy]ClBr (5 pages). Ordering information is given on any current masthead page.

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Enthalpy Measurements in Organic Solvents by Photoacoustic Calorimetry: A Solution to the Reaction Volume Problem

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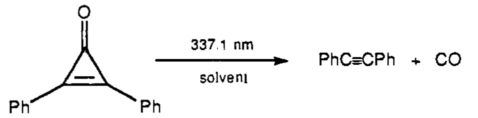
Photoacoustic calorimetry (PAC) has recently become an established tool for the determination of enthalpies of photoinitiated processes.[1] For the majority of work to date, it has been assumed that the photoacoustic signals detected in organic solvents arise exclusively from the thermal relaxation of the photoexcited chromophore. While this assumption leads to essentially no error for systems with no net photochemistry, differences between the partial molar volumes of the reactants and products should not be ignored for many studies in nonaqueous solution. In particular, photofragmentations and systems with large, photoinduced changes in polarity are subject to significant errors if the reaction volume is not explicitly considered. Here, we report a direct method, using a homologous series of alkane solvents, to resolve the thermal and the reaction volume contributions to the photoacoustic signal, and thus to improve the accuracy of the enthalpies determined by PAC.

We examined the photodissociation of diphenylcyclopropenone (DPCP), which yields diphenylacetylene (DPA) and carbon monoxide (eq 1). Because of the unique properties of cyclopropenones, there have been several thermochemical studies on DPCP,[2,3] including two widely different determinations of



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