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

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

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

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

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

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

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/$\mathrm{Cy_2}$ 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 (λ > 420 nm) of $\mathrm{Mn_2(CO)_{10}}$ (1.3 mM) in the presence of CyBr (1.6 M) and **2** (21 mM) resulted in the formation of $\mathrm{Mn(CO)_5Br}$ (1.5 mM) and $\mathrm{Ir(PMe_3)_2[C(O)Cy]ClBr}$ (8 mM); **1** reacted similarly. Presumably these reactions proceed via abstraction of Br$^{\bullet}$ by $^{\bullet}\mathrm{Mn(CO)_5}$,[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.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. A.S.G. thanks the Dreyfus Foundation for a Distinguished New Faculty Grant. We thank Zheng Wang for the synthesis of $\mathrm{Ru(CO)_3(dmpe)}$ and Johnson-Matthey for generous loans of rhodium and iridium.

Supplementary Material Available: Table of data of 28 carbonylation experiments, calculation of the upper limit of the ratio of CyCHO/$\mathrm{Cy_2}$ formation based on the assumption of rate-limiting attack by Cy$^{\bullet}$ on free CO, experimental data for the formation of $\mathrm{Cy_2}$ and other side products in reactions with 0.0-4.0 mM **2**, and synthesis and characterization of $\mathrm{Ir(PMe_3)_2[C(O)\text{-}Cy]ClBr}$ (5 pages). Ordering information is given on any current masthead page.

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[12] **2** is generated in situ from $\mathrm{Ir(PMe_3)_2(CO)Cl}$ under a CO atmosphere. The equilibrium constant for CO addition is 14.6 $\mathrm{atm^{-1}}$ at 25 °C; thus 9.6% of the iridium is present as dicarbonyl **2** under 2 atm of CO. The rate dependence on CO pressure for iridium-catalyzed eq 1 is similar to that found for **1** (which does not add CO even under 1000 psi). This argues against the likelihood of $\mathrm{Ir(PMe_3)_2(CO)Cl}$ being the active species since its concentration, unlike [**1**], is CO-pressure dependent.

[13] (a) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038. (b) Reference 8, p 383.

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

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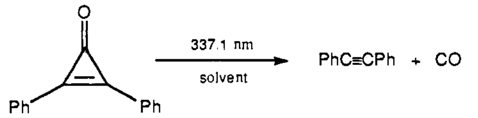
Photoacoustic calorimetry (PAC) has recently become an established tool for the determination of enthalpies of photoinitiated processes.[1] For the majority of work to date, it has been assumed that the photoacoustic signals detected in organic solvents arise exclusively from the thermal relaxation of 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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ΔH_{rxn}[eq1] by PAC.[4,5] Differences remain between the gas- and liquid-phase measurements; while developing our approach, we were able to resolve many of the apparent conflicts.

The observed photoacoustic signal (S_{obsd}) (eq 2) is the sum of two terms, an enthalpic contribution ($S_{thermal}$), from the adiabatic expansion of the solvent upon heat deposition, and a reaction volume contribution (S_{volume}), from differences between solvated reactant and product (eq 3). $S_{thermal}$[1,4,5] depends on the incident

$$S_{obsd} = K'E_p(1 - 10^{-A})f_h^{obsd}X_s \tag{2}$$

$$= S_{thermal} + S_{volume} \tag{3}$$

$$= K'E_p(1 - 10^{-A})f_hX_s + K'E_p(1 - 10^{-A})\frac{\Delta V_{chem}}{h\nu} \tag{4}$$

laser energy E_p, the sample absorbance A, the fraction of absorbed photon energy redeposited as heat f_h, the thermal expansivity[6] of the solvent X_s, and an empirical instrument constant K'. S_{volume} can be similarly expanded using K', E_p, A, the observed volume change ΔV_{chem}, and the photon energy $h\nu$. Note that $E_p(1 - 10^{-A})/(h\nu)$ is simply the number of photoexcited molecules. Equations 2 and 4 can be combined to give eq 5. If f_h and ΔV_{chem}

$$f_h^{obsd}h\nu X_s = f_hh\nu X_s + \Delta V_{chem} \tag{5}$$

remain constant for a range of X_s, then the enthalpic contribution ($f_hh\nu X_s$) can be distinguished from the reaction volume (ΔV_{chem}) by measuring f_h^{obsd} as a function of X_s. The true reaction enthalpy ΔH_{rxn} for that series of solvents is calculated from f_h, the quantum yield for photodissociation Φ_{diss}, and eq 6; the true reaction volume ΔV_{rxn} is calculated from eq 7. Because X_s of water has a large

$$f_h = \frac{h\nu - \Delta H_{rxn}\Phi_{diss}}{h\nu} \tag{6}$$

$$\Delta V_{chem} = \Delta V_{rxn}\Phi_{diss} \tag{7}$$

temperature dependence, there are several examples in the literature where the enthalpy and the reaction volume have been resolved by examining the photoacoustic signal as a function of temperature in aqueous solution.[4,7] In contrast, the values of X_s in organic solvents are not strongly temperature dependent and all compounds of interest are not soluble in water. One can, however, vary X_s by using a series of homologous solvents, provided that changing solvents has no effect on the intrinsic reaction enthalpy or volume.[8,9]

Our photoacoustic calorimeter has been described previously.[10] The photodissociation of DPCP in alkanes is complete within 100 ns, obviating the need for time-resolved analysis.[11] The signal was integrated and normalized by $(1 - 10^{-A})$ (Figure 1, inset A). From a plot of $S_{obsd}/(1 - 10^{-A})$ vs E_p (Figure 1, inset B), the ratio of the slope of the sample to those of ferrocene and tetraphenylethylene, the standards, yields f_h^{obsd} in a given solvent. The quantum yield Φ_{diss} in alkanes was determined to be 1.0 by measuring the extinction coefficient and photolysis rate of DPCP relative to those values in benzene.[11] By combining the values of f_h^{obsd} and X_s for the series of alkanes with eq 5, f_h and ΔV_{chem} can be recovered from the slope and intercept, respectively (Figure 1). On the basis of 15 independent measurements, over eight alkanes, we find $\Delta H_{rxn} = -6.7 \pm 1.2$ kcal mol^{-1} and $\Delta V_{rxn} = 23 \pm 4$ cm^3 mol^{-1} for the photodissociation of DPCP.

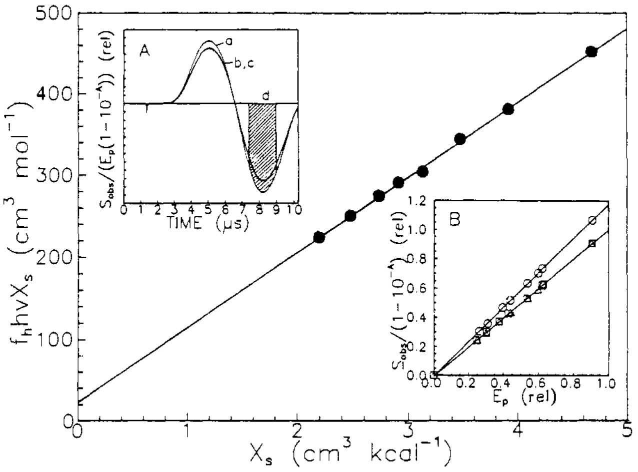

Figure 1. Plot of $f_h^{obsd}h\nu X_s$ vs X_s for the photodissociation of DPCP in alkanes (i.e., eq 5). Inset A: Normalized photoacoustic signal $S_{obsd}/[E_p(1 - 10^{-A})]$ in pentane (a, DPCP; b, ferrocene; c, tetraphenylethylene; d, pentane). Inset B: Representative plot of $S_{obsd}/(1 - 10^{-A})$ vs E_p in nonane (○, DPCP; □, ferrocene; △, tetraphenylethylene).

Use of heats of formation ΔH_f(DPCP) = 75.9 kcal mol^{-1}, ΔH_f(DPA) = 96.2 kcal mol^{-1}, and ΔH_f(CO) = -26.4 kcal mol^{-1}, defines $\Delta H_{rxn} = -6.1$ kcal mol^{-1} in the gas phase.[2,12,13] Because solvent polarity is constant across the series of alkanes[14] and the solvation changes from reactant to product are small in nonpolar solvents,[15] the enthalpy determined in alkanes can be compared directly with the gas-phase value; our value for ΔH_{rxn} is in excellent agreement with that predicted by heats of formation. An early PAC study[4] reported ΔH_{rxn} in benzene to be -9.9 ± 2.9 kcal mol^{-1}, by attributing the entire photoacoustic signal to heat.[16] The enthalpy measured by PAC in aqueous solvent mixtures[5] was $+3.4 \pm 2.5$ kcal mol^{-1}; the value in aqueous mixtures is more endothermic than in alkanes since in a polar, protic environment DPCP is preferentially stabilized.

Cleavage of an average carbon–carbon bond results in a volume expansion[17] of ~10 cm^3 mol^{-1}. Our reaction volume for the photodissociation of DPCP of 23 ± 4 cm^3 mol^{-1} can be understood as the consequence of breaking two covalent bonds, accompanied by a minor rearrangement of the solvent upon relaxation of electrostriction. The volume change associated with the disappearance of the dipole moment of DPCP (5.1 D)[18] from the loss of electrostriction of the alkane around DPCP contributes 3–5 cm^3 mol^{-1} to the volume expansion.[19,20] The observed ΔV_{rxn} is

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(8) Because the solvent parameter X_s is not readily available for mixed solvent systems, Herman and Goodman (ref 5) make relative estimates of X_s, rather than using independently determined values. The reaction volume recovered from PAC experiments is very sensitive to X_s.

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(16) By assuming the reaction volume in benzene to be identical to that in alkanes, one calculates a ΔH_{rxn} of ~-3.1 kcal mol^{-1} in benzene. This estimate is consistent with the UV blue shift of DPCP and the red shift of DPA in benzene relative to alkanes, if one attributes the spectral shifts to differential ground-state stabilization.

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consistent with values observed for cycloadditions (25–40 cm^3 mol^{-1}).[21]

Because organic solvents possess large thermal expansivities, the reaction volume may only contribute a small fraction to the photoacoustic signal. One should be cautious, however, in interpreting enthalpies measured by PAC; if one does not explicitly account for the reaction volume, then the PAC measurement is only an estimate of the reaction enthalpy. By examining a reaction across the series of alkanes, PAC not only reliably determines the enthalpy of reaction but also yields the reaction volume and thereby provides insight into solvation phenomena.

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Supplementary Material Available: Table of solvent parameters α, MW, C_p, ρ, ϵ, and X_s and experimental values of f_h^{obsd} for DPCP measured against ferrocene and tetraphenylethylene at 337.1 nm (1 page). Ordering information is given on any current masthead page.

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(19) The effective radius of DPCP was estimated to be 3.6 Å by importing the X-ray structure into MacroModel 2.0. Tsukada, H.; Shimanouchi, H.; Sasada, Y. *Chem. Lett.* **1974**, 639–642. See ref. 17. Whalley, E. *J. Chem. Phys.* **1963**, *38*, 1400–1405. Brazier, D. W.; Freeman, G. R. *Can. J. Chem.* **1969**, *47*, 893–899.

(20) In aqueous mixtures, ΔV_{rxn} has been measured to be 63 ± 7 cm^3 mol^{-1} (ref 5). Theory predicts, however, that the volume associated with electrostriction around DPCP in water should be less than 1 cm^3 mol^{-1}, while the volume change due to fragmentation should remain the same as in alkanes (ref 17).

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Biradicals and Spin-Correlated Radical Pairs Anchored to SiO_2 Surfaces: Probing Diffusion at the Solid/Solution Interface

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Flexible organic biradicals continue to attract the attention of chemists, because of the special relationship between their spin mechanics, chain dynamics, and chemical reactivity.[1] The interplay of these properties makes an analysis of the electron paramagnetic resonance (EPR) spectra of biradicals complex, yet provides distinct advantages for the study of diffusional dynamics, particularly in cases of restricted diffusion. Recently there have been many reports of spectroscopic measurements on organic intermediates in contact with or bound to silica surfaces, by optical and steady-state EPR methods.[2] We have initiated a program aimed at measuring, using time-resolved EPR spectroscopy, the dynamic properties of flexible biradicals and radical pairs at interfaces. We report here the results of our initial experiments on acyl/alkyl biradicals and radical pairs (RPs) covalently bound to polycrystalline SiO_2 surfaces. In a separate paper, EPR results on surface-anchored, noninteracting monoradicals will be reported.[3]

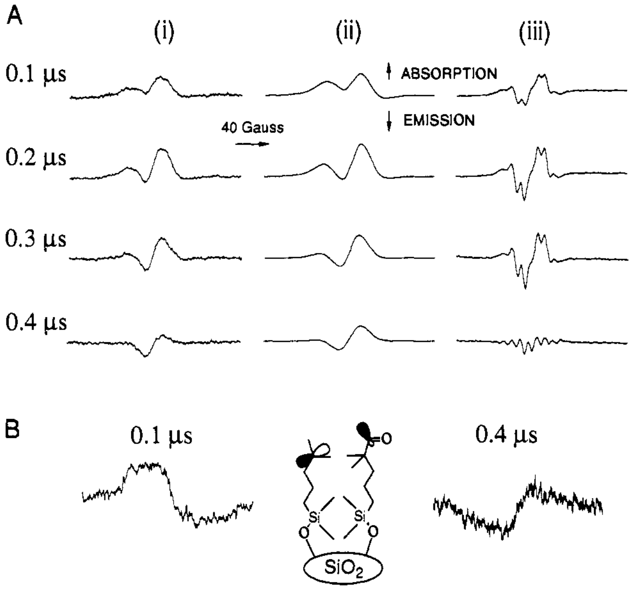
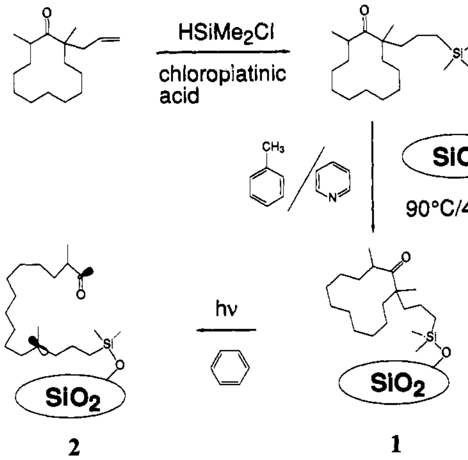


Figure 1. (A) (i) Time-resolved EPR spectra of surface-bound biradical **2** taken at the delay times shown at a temperature of 30 °C. All spectra are centered at 3385 G. Spectra taken at 0.1 μs are broadened due to instrument response. The intensities are normalized. (ii) Simulation using g(acyl) = 2.0008, g(alkyl) = 2.0025, a_H = 22.2 G (3 H), 17.8 G (4 H), LW = 22 ± 1 G, k_{en} = 7.2 ± 0.2 × 10^{10} s^{-1}, J = −180 ± 30 MHz, initial populations of T$^-$ = 0.35 and T^0 = 0.33. (iii) Spectra of the 1,12-acyl/alkyl biradical from the photolysis of a 0.084 M solution of 2,2,12,12-tetramethylcyclododecanone in benzene at 27 °C. (B) Spectra taken at the two delay times indicated for the spin-correlated radical pair shown. Experimental conditions and field axis scale are the same as in part A.

Scheme I



The surface attachment of precursor ketones was accomplished following literature procedures[4] which are summarized in Scheme I. Silicon oxide (PQ Corporation, BET surface area 366 m^2 g^{-1}) was treated by vacuum heating overnight before and after the

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