Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 197 (2008) 335–341

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

A photoacoustic calorimetric characterization of the reaction enthalpy and volume for the preparation of a reactive intermediate from $CpMn(CO)_3$

Kevin W. Davies, David Maivald, Joseph J. Grabowski*

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, United States

Received 2 June 2005; received in revised form 22 January 2008; accepted 25 January 2008
Available online 6 February 2008

Abstract

Photoacoustic calorimetry (PAC) allows measurement of the energetics of reactive intermediates. Here, we report the examination of the metal carbonyl η^5-$CpMn(CO)_3$ (Cp, cyclopentadiene) via time-independent PAC, in a homologous series of solvents. The measured heat releases allow one to determine simultaneously the enthalpy and volume change resulting from the photodissociation of $CpMn(CO)_3$. While the photoacoustic signal results from both of these processes, it has often been assumed that the volume change contribution to the observed photoacoustic signal is negligible for small molecules undergoing photodissociation. The current study tests the assumption of a negligible reaction volume by using a more complete treatment. The reaction of an equimolar number of photons and $CpMn(CO)_3$ molecules, the subsequent photodissociation of the Mn–CO bond, and the ligation of a solvent molecule in an alkane solvent yields $\Delta H_{obs} = 32.7 \pm 0.7$ kcal/mol and $\Delta V_{chem} = 11.0 \pm 1.3$ mL/mol, both of which are independent of the quantum yield of photodissociation. A detailed analysis of the quantum yield is included (using both previously reported measurements, and new data from this work), from which we determine $\Phi_{diss} = 0.635$. This quantum yield allows us to determine $\Delta H_{rxn} = 51.6$ kcal/mol and $\Delta V_{rxn} = 17.3$ mL/mol. These results demonstrate that if the contribution of the reaction volume change to the photoacoustic signal is ignored, the reaction enthalpy derived would underestimate the true value by 7%. We also estimate the BDE$\{Cp(CO)_2Mn–CO\}$ to be 59.4 kcal/mol.

Keywords: Photoacoustic calorimetry; Photodissociation; Bond enthalpy; Thermodynamics; Metal carbonyl

1. Introduction

Over the last few decades, organometallic systems have been the focus of a number of detailed studies due to their increasingly appreciated role in biological and synthetic systems [1–6]. Transition metal reagents have been quite successful to date in C–C and C–H bond activation of otherwise unreactive bonds [4–6], but much remains unknown about how to tailor reagents to approach those desirable capabilities found in biological systems. To that end, better knowledge of the energetics of these molecules may help to understand the interactions that drive these organometallic reactions.

Photoacoustic calorimetry (PAC, also known as laser-induced optoacoustic calorimetry, LIOAC) has been used to determine the reaction enthalpies of photoinduced processes [7–13], to determine the heats of formation of reactive intermediates [14–16], to determine quantum yields [17], and to determine the kinetics and lifetimes of transient intermediates [18–21] (citations are representative, not exhaustive). In PAC, a molecule undergoes photoexcitation followed by thermal relaxation; a pressure wave results, which may be measured and analyzed to recover kinetic and enthalpic information simultaneously. In many PAC studies carried out in organic solvents, the entire photoacoustic signal has been assigned to the thermal relaxation of the photoexcited species, i.e. assuming that $\Delta V_{rxn} = 0$. In this study, we examine the contribution of ΔV_{rxn} to the photoacoustic signal to probe the acceptability of the assumption of a negligible reaction volume. To date, few examples of the ΔV_{rxn}'s contribution to photoacoustic signals have been documented for systems in organic solvents. For aqueous systems, where the solvent expansivity is often a factor of 10 or more smaller than for organic solvents, consideration of non-thermal contributions to the photoacoustic signal typically are treated explicitly [16,22–25]. To separate the contribution of the volumetric and enthalpic changes to the photoacoustic signal, solvent expansivity can be varied by: (i) changing the temperature (if the solvent has significant expansivity dependence on temperature as is the case for water) [16]; (ii) varying the pressure

---

* Corresponding author. Tel.: +1 412 624 8632; fax: +1 412 624 8611.
E-mail address: joeg@pitt.edu (J.J. Grabowski).

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.01.012

[26]; (iii) or using a homologous series of solvents over which ΔH_{rxn} will be unaffected [27]. This last method, which utilizes linear alkanes as its solvent series (in which relative solvation effects are constant, but for which the solvent expansivity varies [28]) is considerably easier to experimentally conduct than the high-pressure approach [26].

Here, we report the use of a series of linear alkanes as solvents in the determination of the reaction enthalpy for the photodissociation of a carbon monoxide from a metal compound, while explicitly accounting for the reaction volume contributions to the photoacoustic signal. ΔH_{rxn} is considered both with/without accounting for ΔV_{rxn} in order to ascertain the magnitude of neglecting the volumetric term. We chose $\mathrm{CpMn(CO)_3}$ (Cp, cyclopentadiene) because of its usefulness in synthetic routes [29] as well as the fact that it has been examined in several previous kinetic and thermodynamic studies. The photodissociation of CO from $\mathrm{CpMn(CO)_3}$ has been studied by PAC in heptane [30–35]; in those studies, the entire photoacoustic signal was attributed to the thermal expansion of the solvent due, in turn, to the heat released following the absorption of a photon and photofragmentation (Eq. (1)).

$$\mathrm{CpMn(CO)_3} + h\nu \xrightarrow[\text{solvent}]{} \mathrm{CpMn(CO)_2(solvent)} + \mathrm{CO} + \text{heat} \tag{1}$$

$$\mathrm{CpMn(CO)_2(solvent)} + \text{nucleophile} \xrightarrow[\text{solvent}]{} \mathrm{CpMn(CO)_2(nucleophile)} + \text{solvent} \tag{2}$$

Fig. 1 diagrams the processes occurring upon photoexcitation which occur during the time resolution window of our instrument. Upon photoexcitation with a near-UV photon, $\mathrm{CpMn(CO)_3}$ is promoted to an excited state, followed by CO dissociation from the metal center [38]. A solvent molecule is then agostically bound in the empty ligand site [39]. Both the photodissociation and the solvent ligation processes occur much faster (70 fs and 120 ps) [16,38,39] than the resolution limit of our detector (10 ns). In the absence of a nucleophile, the reaction proceeds as summarized in Eq. (1), and the 'too-fast' PAC treatment applies (i.e. the processes are indistinguishable from a concerted reaction) [19]. If a nucleophile (e.g., pyridine) were to be present, the nucleophile would replace the ligated solvent molecule on a 10^{-7}–10^{-6} s time scale (depending on nucleophile concentration) (Eq. (2)) [40]. The simultaneous heat depositions would result in a unique waveform containing contributions from each of the two heat release pathways (Eqs. (1) and (2)), causing a phase-shift in the observed photoacoustic signal with respect to the reference wave. The signal may be deconvoluted into its composite waveforms to recover information about processes in the resolvable time scale (10^{-8}–10^{-5} s) via the 'time-resolved' treatment [19,41,42].

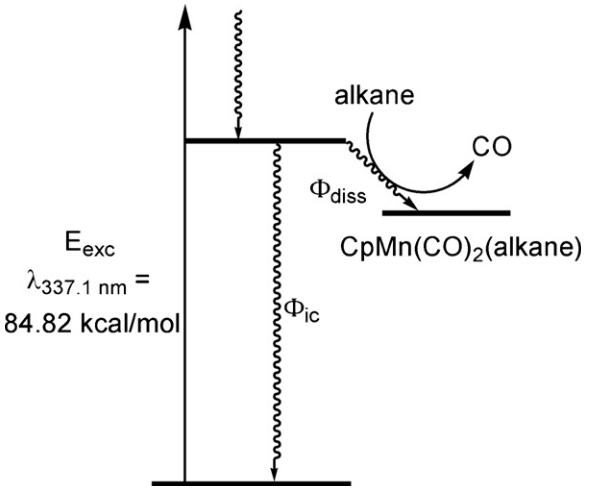

Fig. 1. Jablonski diagram for the photoprocesses relevant to the PAC experiment. As the lifetime of $\mathrm{CpMn(CO)_2}$ (alkane) is on the order of seconds [36] in the absence of nucleophiles, its decay pathways are too slow to impact the PAC measurement [37].

Previous work on $\mathrm{CpMn(CO)_3}$, both photoacoustic and otherwise [30–35], has focused on measuring the enthalpy or the kinetics (or both) of the processes shown in Eqs. (1) and (2), and did not consider ΔV_{rxn}. In this study, we test the assumption that volume treatment is unnecessary for $\mathrm{CpMn(CO)_3}$, and report the difference in results between the volume-dependant and volume-independent treatments for $\mathrm{CpMn(CO)_3}$ photodissociation and thereby. In doing so, we are able to establish the best value for the enthalpy of the liquid-phase reaction shown in Eq. (1). Furthermore, by comparing that result to an estimate of the agostic interaction, we are able to derive the BDE$\{\mathrm{Cp(CO)_2Mn{-}CO}\}$.

2. Experimental

2.1. General

All compounds used in this work were of the highest purity available, and all solvents were reagent grade; all were obtained from commercial sources. $\mathrm{CpMn(CO)_3}$ was purified by vacuum sublimation. Ferrocene (FER) was recrystallized twice from hexane. Tetraphenylethylene (TPE) was recrystallized from ethanol/hexane. 2,4-Dihydroxybenzophenone (DHBp) was used as received. Pentane and octane were used both as received and after purification by washing with basic $\mathrm{KMnO_4}$ and drying with $\mathrm{CaCl_2}$. As no difference in photoacoustic measurements were observed in pentane or octane purified in this manner/used as received, all subsequent measurements were performed without further preparation. In our quantum yield measurements, potassium ferrioxalate, pyridine, and 1,10-phenanthroline were used as received.

2.2. Photoacoustic calorimetry

The photoacoustic calorimeter used has been previously described in detail and so only the key aspects are summarized here [16]. Sample absorbances (as measured by a Hitachi U-2000 spectrophotometer) ranged from 0.130 to 0.260, and all solutions were matched within 0.005 absorbance units in a single experiment. A nitrogen laser (Laser Photonics Model LN-1000, 337.1 nm, fwhm ~1 ns, 1.3 mJ/pulse, ~2 Hz repetition rate) was used for photoexcitation, while a computer-controlled shutter ensured the sample was only irradiated during data acquisition.

The excitation pulse passed sequentially through a 1 mm circular aperture and then through a 10 mm quartz cuvette containing ferrocene/acetonitrile of varying optical density. These two components worked together to reduce the excitation pulse to ≤15 μJ; these low pulse excitation energies are used to minimize the occurrence of multiphoton events. The laser pulse then passed through a beam splitter where ∼30% of the pulse was reflected into a reference cell containing a photoacoustic standard (either ferrocene or tetraphenylethylene). The photoacoustic signal generated by this reference cell served as a relative measure of pulse energy. The remaining portion of the beam passed through a photoacoustic cell containing the sample. A third cell containing a photoacoustic standard (the 'transmitted' cell) was placed such that it measured the portion of the beam remaining after excitation of the sample; this cell allowed in situ monitoring of the sample absorbance. Each photoacoustic cell (sample, reference, and transmitted) consisted of a 10 mm quartz cuvette spring-loaded against a custom-built piezoelectric microphone, described elsewhere [43]. The photoacoustic standards used, FER [44], DHBp [45], and TPE [46], are known to absorb at 337.1 nm excitation without occurrence of photoinitiated reactions and to release all absorbed energy as heat faster ($\tau < 10$ ns) than the resolution of our transducer (i.e., $f_h = 1.00$). The signal recorded for the standard was used to determine the instrumental response factor (κ', described in Section 3). If in the sample waves a phase-shift were to be observed versus the reference waves, it would indicate the need to use 'time-resolved' PAC. The time window, during which the photoacoustic signal (Fig. 2) was acquired, was chosen such that pre- and post-laser-firing were recorded in order to capture baseline and the first positive and negative excursions.

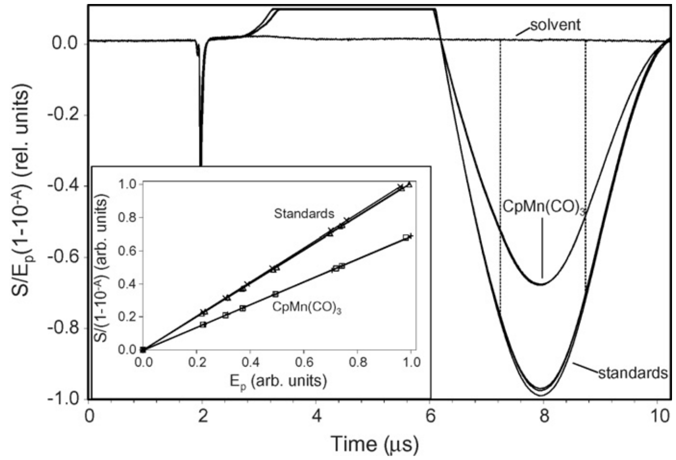

Fig. 2. Averaged waves (30 shots) from a typical PAC experiment at a single laser energy. Shown are three waves from standards (2 ferrocene, 1 DHBp) and two from $CpMn(CO)_3$, along with that for pure solvent. The noise spike at ∼2 μs corresponds to the firing of the laser. Data before this point serves to define the baseline for wave integration. Integration limits are shown by dashed lines. To maximize sensitivity of the 8-bit digitizer, the baseline of the acoustic wave is deliberately offset to ensure the first negative excursion of the wave is recorded with the best possible S/N ratio. The first positive excursion of the wave is therefore 'clipped' and not fully captured. Inset: PAC signals for $CpMn(CO)_3$ and two standards plotted according to Eq. (3).

2.3. *Quantum yield determination*

In photoacoustic calorimetry, a quantum yield (Φ = (# of events)/(# of molecules absorbing a photon)) is needed to extract the fundamental thermodynamic properties of the system under investigation (vide infra, Eqs. (7) and (8)). The quality of ΔH_{rxn} and ΔV_{rxn} determined is limited in part by the how well Φ_{diss} is known. For this study, where we will examine the photoacoustic signal for one reaction across a homologous series of solvents, it is important to ascertain if the quantum yield of photodissociation for $CpMn(CO)_3$ varies over the solvents used. To determine if there is a solvent dependence for this quantum yield, Φ_{diss} was determined in both hexane and hexadecane, the extrema of the solvent range (pentane was not used out of concern over its fast rate of evaporation and the resulting possibility of an unaccounted for increase in concentration).

In order to perform the actinometry experiments, the photoacoustic calorimeter was used in a slightly modified form. Laser intensities were maintained at the same level used in photoacoustic experiments (≤15 μJ/pulse). The output from the nitrogen laser was passed through the optical trigger and shutter to the beam splitter; the shutter reduced the laser beam diameter to ∼6.5 mm. The light passing through the beam splitter illuminated a 10 mm quartz cuvette (the sample cell), containing either the chemical actinometer or the $CpMn(CO)_3$ sample; this cell was housed within a temperature-controlled brass block (22.0 ± 0.1 °C) coupled to a NESLAB RTE-110 refrigerated bath. The reflected portion of the laser was directed through a 1 mm aperture (to maintain signal intensity on par with that of a photoacoustic experiment), then into a photoacoustic cell containing ferrocene in acetonitrile. This cell served as a relative measurement of the incident laser energy, just as in the traditional PAC experiment.

Ferrioxalate was used as the actinometer [47–49], allowing calibration of the photoacoustic signal to the incident number of photons. All solutions were freshly prepared, and all measurements were performed in a single experiment. A 0.006 M potassium ferrioxalate solution in 0.1N H_2SO_4 was prepared under red photosafe light, and both it and aqueous 0.1% 1,10-phenanthroline were stored in the dark until needed. 2 mL of the ferrioxalate solution was irradiated with 50–400 laser shots ($<10^{-8}$ Einsteins incident), after which a 1 mL aliquot was removed from the cuvette. The irradiated ferrioxalate aliquot was added to 0.5 mL of the phenanthroline solution and 1 mL of acetate buffer solution (600 mL 1N CH_3COONa, 360 mL 1N H_2SO_4 diluted to 1 L), then diluted to 5 mL with deionized water. These samples were stored for 1 h at room temperature in the dark to allow the phenanthroline to complex with the photoreduced Fe^{2+}, after which their absorbance at 510 nm was determined. By using known quantum yields for the photoconversion of the actinometer [47], the number of photons incident on the cell was correlated to the relative intensity as measured by the photoacoustic cell. 0.005 g $CpMn(CO)_3$ were added to 20 mL of solvent (0.0012 M) and 100 μL pyridine (0.061 M). 2 mL of this solution were irradiated for either 200 or 400 laser shots using hexane or hexadecane as the solvent. Formation of $CpMn(CO)_2$pyridine was monitored at 412 nm ($\varepsilon_{412} = 5100\,M^{-1}\,cm^{-1}$) [37] to determine the amount of $CpMn(CO)_3$ photolyzed. This portion of the experiment was performed under room lighting (Giordano et al. [37] have shown that in the presence of excess pyridine, $CpMn(CO)_2$pyridine is quantitatively regenerated making it effectively photostable) and immediately measured via the spectrophotometer.

3. Theory

$$S_{\mathrm{obs}} = \kappa' E_{\mathrm{p}}(1 - 10^{-A}) f_{\mathrm{h}}^{\mathrm{obs}} X_{\mathrm{s}} \tag{3}$$

$$S_{\mathrm{obs}} = S_{\mathrm{thermal}} + S_{\mathrm{volume}} \tag{4}$$

$$S_{\mathrm{obs}} = \kappa' E_{\mathrm{p}}(1 - 10^{-A}) f_{\mathrm{h}} X_{\mathrm{s}} + \kappa' E_{\mathrm{p}}(1 - 10^{-A}) \frac{\Delta V_{\mathrm{chem}}}{h\upsilon} \tag{5}$$

$$f_{\mathrm{h}}^{\mathrm{obs}} h\upsilon X_{\mathrm{s}} = f_{\mathrm{h}} h\upsilon X_{\mathrm{s}} + \Delta V_{\mathrm{chem}} \tag{6}$$

The photoacoustic signal is defined as shown in Eq. (3), where E_p is the incident photon energy, A is the absorbance of the sample, f_h^{obs} is the apparent fraction of absorbed energy released as heat, X_s is the thermal expansivity of the solvent, and κ' is an empirical instrument response factor. The observed signal (S_{obs}) results from the volume change accompanying thermal deposition ($S_{thermal}$) [7,10,14,50–58] to the solvent as well as any volume change due to chemical reaction (S_{volume}) (Eq. (4)). Eq. (3) can be restated as in Eq. (6) to expressly delineate the volumetric contributions. In Eq. (5), ΔV_{chem} is the volume change associated with the chemical reaction measured in the experiment. Eq. (5) can be simplified into Eq. (6). By measuring f_h^{obs} for different X_s (Fig. 3) over a homologous solvent series (we take linear alkanes to fill this requirement [28]) one can recover the actual fraction of energy converted to heat due to thermal deposition (f_h) and ΔV_{chem} of the system via Eq. (6). Eqs. (7) and (8) allow the recovery of the reaction enthalpy and reaction volume (ΔH_{rxn} and ΔV_{rxn}) from the measured photoacoustic results (f_h and ΔV_{chem}) by normalizing to the number of dissociative events (i.e., Φ_{diss}).

$$f_{\mathrm{h}} = \frac{h\upsilon - \Delta H_{\mathrm{rxn}} \Phi_{\mathrm{diss}}}{h\upsilon} \tag{7}$$

$$\Delta V_{\mathrm{chem}} = \Delta V_{\mathrm{rxn}} \Phi_{\mathrm{diss}} \tag{8}$$

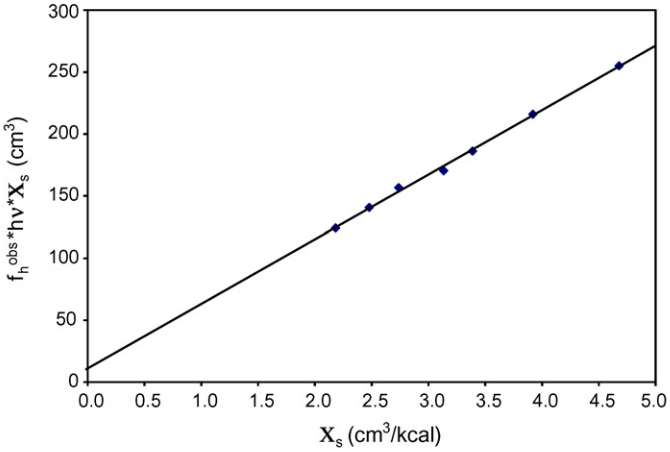

Fig. 3. Plot of $f_h^{obs} h\upsilon X_s$ vs. X_s (Eq. (6)) for the photoinitiated reaction of $CpMn(CO)_3$ in linear alkanes. The point size used is representative of the largest error in the entire series.

4. Results and discussion

4.1. Quantum yield

Quantum yield measurements were performed in hexane and hexadecane. The ferrioxalate actinometer ($\Phi_{337.1nm} = 1.23$, determined by interpolation of $\Phi_{334nm} = 1.23$ and $\Phi_{341nm} = 1.22$, no errors listed) [47] was used to calibrate the relative energy detector (E_p). No non-linear effects were observed in this experiment; this is unsurprising given that we are working at laser intensities similar to that of a PAC experiment. Knowledge of the amount of ferrioxalate photolysis product formed per unit of reflected signal allowed determination of the number of incident photons for any number of laser firings. ΔA_{412} was used to monitor the formation of $CpMn(CO)_2$(pyridine) (Eq. (9)) [37]. With the knowledge of the ratio of incident photons vs. signal (E_p) found from the ferrioxalate actinometer, Φ_{diss} for $CpMn(CO)_2$–CO was determined twice for each solvent. All Φ_{diss} determinations accounted for the absorbance of $CpMn(CO)_3$ used, and the errors derive from the uncertainty of the slope of the detector calibration ($n = 8$).

$$CpMn(CO)_3 + \text{pyridine} \xrightarrow[\text{solvent}]{} CpMn(CO)_2(\text{pyridine}) + CO \tag{9}$$

In hexane, we measured Φ_{diss} to be 0.570 ± 0.085 based on 200 laser pulses, and 0.572 ± 0.086 based on 400 laser pulses. In hexadecane, we measured Φ_{diss} to be 0.591 ± 0.088 based on 200 laser pulses, and 0.602 ± 0.090 based on 400 laser pulses. Evaluation of these results indicates that no significant difference in quantum yield exists for $CpMn(CO)_3$ between these two solvents (0.571 ± 0.060 in hexane, 0.596 ± 0.063 in hexadecane). These data demonstrate that the quantum yield for photodissociation is constant over the solvent range used; as such, we find $\Phi_{diss} = 0.584 \pm 0.044$. This is comparable to the value of 0.65 ± 0.10 for $CpMn(CO)_3$ in octane at 313 nm reported by Giordano et al. [37], as well as 0.67 ± 0.04 in heptane at 337.1 measured by Pang et al. [59]. In the analysis reported here, we use the average of these three known measurements ($\Phi_{diss} = 0.635 \pm 0.038$).

4.2. Photoacoustic calorimetry

The results of 30 laser pulses were averaged for each photoacoustic wave (Fig. 2), and were normalized for both sample absorbance ($1–10^{-A}$) and incident energy (E_p) (Eq. (3)). Waveforms were visually inspected to ensure no change in cell alignment (i.e., a change in κ') had occurred and for indications of time-dependant behavior (none were found); such events are known to cause shifts in the observed waveform [60,61]. A portion of the first negative excursion of each waveform (typically 1.51 μs in length) was integrated to give S_{obs} (Fig. 2). In the

Table 1
Solvent parameters and $f_{\mathrm{h}}^{\mathrm{obs}}$ at 25 °C

	n^{a}	$f_{\mathrm{h}}^{\mathrm{obs}}$	S.D.	$\alpha^{\mathrm{b,c}}$ (1/°C)	MW (g/mol)	$C_{\mathrm{p}}{}^{\mathrm{b,d}}$ [cal/(mol °C)]	$\rho^{\mathrm{b,d}}$ (g/cm^3)	$X_{\mathrm{s}}{}^{\mathrm{e}}$ (cm^3/kcal)	$f_{\mathrm{h}}^{\mathrm{obs}}h\nu X_{\mathrm{s}}$	S.D.	% Error
Pentane	3	0.6431	0.0104	0.00161	72.15	39.96	0.6214	4.678	255.2	4.1	1.6
Hexane	3	0.6499	0.0214	0.001391	86.177	46.72	0.6548	3.918	216.0	7.1	3.3
Heptane	4	0.6482	0.0026	0.001234	100.2	53.72	0.6795	3.388	186.2	0.8	0.4
Octane	4	0.6410	0.0061	0.001164	114.23	60.74	0.6986	3.133	170.3	1.6	0.9
Decane	3	0.6624	0.0058	0.001051	142.28	75.18	0.7264	2.738	156.6	4.0	2.6
Dodecane	3	0.6696	0.0053	0.000974	170.34	89.86	0.7452	2.478	140.7	1.1	0.8
Hexadecane	3	0.6715	0.0079	0.000889	226.45	119.85	0.77	2.182	124.2	1.5	1.2

[a] Number of experiments.
[b] Organic Solvents: Physical Properties and Methods of Purification [75].
[c] Ref. [76].
[d] TRC Thermochemical Tables, vols. I and II, Thermodynamics Research Center, College Station, TX, 1986.
[e] $X_{\mathrm{s}} = \alpha\mathrm{MW}/C_{\mathrm{p}}\rho$.

determination of $f_{\mathrm{h}}^{\mathrm{obs}}$, the observed PAC waves from 7 different E_{p} intensities were analyzed according to Eq. (3) (Fig. 2 inset). The plots of $S_{\mathrm{obs}}/(1-T_{\mathrm{s}})$ vs. E_{p} demonstrated excellent linear form ($R^2 > 0.9980$). In each experiment (an experiment consists of a new set of solutions on a separate day) two to three sets of PAC waves were collected for the standards along with two sets for $\mathrm{CpMn(CO)_3}$, yielding slopes equal to $f_{\mathrm{h}}^{\mathrm{obs}}\,\kappa'$ for the standards and $\mathrm{CpMn(CO)_3}$. The slopes for the standards were then averaged to recover κ' (for standards, $f_{\mathrm{h}} = 1.00$, $\Delta V = 0$, $\tau < 10$ ns, no change in S_{obs} over >500 laser pulses), allowing the average $f_{\mathrm{h}}^{\mathrm{obs}}\,\kappa'$ of $\mathrm{CpMn(CO)_3}$ to be used to determine $f_{\mathrm{h}}^{\mathrm{obs}}$. Multiple experiments were performed in each solvent; the compiled results along with relevant solvent data are presented in Table 1.

The $f_{\mathrm{h}}^{\mathrm{obs}}$ were analyzed according to Eq. (6) (Fig. 3) to determine the f_{h} for Eq. (1) to be 0.614 ± 0.013, which can be represented as $\Delta H_{\mathrm{obs}} = 32.7 \pm 0.7$ kcal/mol ($\Delta H_{\mathrm{obs}} = \Delta H_{\mathrm{rxn}}\Phi_{\mathrm{diss}}$), and ΔV_{chem} was found to be 11.0 ± 1.3 mL/mol. The line obtained by fitting the data to Eq. (3) and used to derive the values just noted has excellent linear form ($R^2 = 0.9978$); note that the size of the points in Fig. 3 represents the largest error in the series. Using f_{h} and ΔV_{chem} along with $\Phi_{\mathrm{diss}} = 0.635$ and Eqs. (7) and (8), we determine $\Delta H_{\mathrm{rxn}}\{\text{Eq. (1)}\} = 51.6 \pm 3.5$ kcal/mol, and $\Delta V_{\mathrm{rxn}}\{\text{Eq. (1)}\} = 17.3 \pm 2.3$ mL/mol (errors include error propagated from both f_{h} and Φ_{diss}; the error in the quantum yield is often neglected in photoacoustic reports, and is the primary source of error in this measurement.)

We next examine the effect of ignoring ΔV_{rxn} for the photodissociation of $\mathrm{CpMn(CO)_3}$, as well as the impact of the Φ_{diss} used. If, for the purposes of comparison, we reinterpret the value reported by Hester et al. in heptane [32] using the quantum yield found in this work, $\Delta H_{\mathrm{rxn}} = 47.9 \pm 2.2$ kcal/mol. If we then treat our $f_{\mathrm{h}}^{\mathrm{obs}}$ for heptane as f_{h} (i.e., neglect the contribution of ΔV_{rxn}), we would predict $\Delta H_{\mathrm{rxn}} = 47.0 \pm 2.8$ kcal/mol. Our results are in excellent agreement with the reinterpreted findings of Hester et al. Separation of the ΔV_{rxn} contribution results in a 7% underestimation of ΔH_{rxn} when the reaction volume is neglected. This comparison serves to illustrate that the data obtained in heptane in both Hester et al.'s study and this work are in superb agreement, and highlights that accounting for the volume of reaction is more important than previously appreciated (especially in order to ensure the most accurate determination of M–CO photodissociation reaction enthalpies).

If ΔV_{rxn} were equal to zero, our data also would imply a solvent dependency for ΔH_{rxn}. For linear alkanes smaller than pentane, a solvent-interaction energy dependence has been observed in $\mathrm{W(CO)_5}$ [62], though the trend appears to level off between pentane and hexane, consistent with our assumption that ΔH_{rxn} remains constant over our range of solvents.

We turn now to the determination and evaluation of the $\mathrm{BDE}\{\mathrm{Cp(CO)_2Mn{-}CO}\}$. The average bond dissociation energy of three Mn–CO bonds has been reported via bomb calorimetry [63], but this value cannot be compared to the value derived here. Hester et al. have reported 7.8 kcal/mol as a lower-bound for the Mn–heptane interaction in the solution phase, and state that the actual interaction strength is probably not substantially different [32]. Using this estimation of the agostic interaction, we are able to derive the rigorous lower limit of the $\mathrm{BDE}\{\mathrm{Cp(CO)_2Mn{-}CO}\}$ at 59.4 kcal/mol (Eq. (10)), and note that the actual value is not likely to be substantially different. To place this estimation into context, we point out three previous reports of $\mathrm{BDE}\{\mathrm{Cp(CO)_2Mn{-}CO}\}$. Li et al. reported $\mathrm{BDE}\{\mathrm{Cp(CO)_2Mn{-}CO}\}$ to be 43.4 kcal/mol as determined by TPEPICO (gas-phase) [64], while theoretical calculations by Fan and Hall place $\mathrm{BDE}\{\mathrm{Cp(CO)_2Mn{-}CO}\}$ at 52.7 kcal/mol [65]. The gas-phase $\mathrm{BDE}\{\mathrm{Cp(CO)_2Cr{-}CO}\}$ of the isoelectronic species $\mathrm{CpCr(CO)_3}^-$ was measured as 47.8 kcal/mol by Sunderlin and Squires [66] by energy-resolved collision-induced dissociation.

$$\begin{aligned}&\mathrm{BDE}\{\mathrm{Cp(CO)_2Mn{-}CO}\}-\mathrm{BDE}\{\mathrm{Cp(CO)_2Mn{-}solvent}\}\\&\quad = \Delta H_{\mathrm{rxn}} \qquad \{\text{Eq.(1)}\})\end{aligned} \tag{10}$$

The significant difference between threshold energy and PAC measurements prompted us to consider the validity of both our data, and the applicability of the TPEPICO-determined BDE's to metal carbonyls. As the PAC data is in complete agreement with previous studies (if ΔV_{rxn} were to be ignored) we focus here on the TPEPICO measurement. Few BDE measurements for $\mathrm{CpMn(CO)_3}$ have been reported, and so we examine a number of BDE reports for $\mathrm{Cr(CO)_6}$. Four gas-phase measurements of the first carbonyl dissociation for $Cr(CO)_6$ have been made by methods other than TPEPICO: 37.0, 36.8, 38.7, and 34.8 (avg. 36.8 ± 1.6 kcal/mol) [67–70]. Measurement by TPEPICO places the BDE$\{(CO)_5Cr–CO\}$ to be 27.1 kcal/mol [71], representing a 26% underestimation of the BDE of $Cr(CO)_6$. Similarly, TPEPICO measurement places the BDE$\{Cp(CO)_2Mn–CO\}$ for $CpMn(CO)_3$ 29% below that determined by PAC. Despite the similarities in the magnitude of underestimation, we believe them to be coincidental (i.e. not a scaling factor). We note that the use of the TPEPICO-determined BDE$\{Cp(CO)_2Mn–CO\}$, 43.4 kcal/mol [64], and our measured ΔH_{rxn}, 51.6 kcal/mol, in Eq. (10) a negative agostic interaction would result ($43.4 - 51.6 = -8.2$ kcal/mol) which is not possible. In summary, we find that for $CpMn(CO)_3$, the PAC determination of the BDE is more consistent.

Both Gitterman et al. [72] and Farrell and Burkey [73] have used PAC to determine ΔH_{rxn} and ΔV_{rxn} for metal carbonyls undergoing a similar process to that described in Eq. (1). For $Cr(CO)_6$ Farrell and Burkey found $\Delta H_{\mathrm{rxn}} = 27.6 \pm 0.8$ kcal/mol and $\Delta V_{\mathrm{rxn}} = 21 \pm 2$ mL/mol [73]. For $Mo(CO)_6$ in linear alkanes, Gitterman et al. found $\Delta H_{\mathrm{rxn}} = 27.2 \pm 1.9$ kcal/mol and $\Delta V_{\mathrm{rxn}} = 13 \pm 6$ mL/mol [72]. For $Cr(CO)_6$, Farrell and Burkey noted that ignoring the contribution of ΔV_{rxn} resulted in an error of 5–6 kcal/mol. For example, ignoring ΔV_{rxn}, their data would predict $\Delta H_{\mathrm{rxn}} = 21.5$ kcal/mol. Similarly, for $Mo(CO)_6$, Gitterman et al. showed that ignoring ΔV_{rxn} results in an error of 3.3 kcal/mol. These errors amount to 22% and 12% underestimates, respectively. To our knowledge, there are only three other simple metal carbonyls studied by PAC. ΔV_{rxn} may contain useful information, but at this time the data set is too small to be extendable.

In conclusion, we find that the volume of reaction significantly contributes to the photoacoustic signal, and should be accounted for in this system. We also note that Farrell and Burkey and Jiao et al. [73,74] have observed a similar effect with $Cr(CO)_6$ and $Mo(CO)_6$, implying that a full accounting of enthalpic and volumetric contributions generally is called for in metal carbonyls to ensure accurate thermochemical determinations. For $CpMn(CO)_3$ in linear alkanes, we determine $\Delta H_{\mathrm{obs}} = 32.7 \pm 0.7$ kcal/mol and $\Delta V_{\mathrm{chem}} = 11.0 \pm 1.3$ mL/mol for the equimolar reaction of photons and $CpMn(CO)_3$ molecules as in Eq. (1), both of which are independent of the quantum yield of photodissociation. Knowledge of Φ_{diss} for $CpMn(CO)_3$ in linear alkanes (0.635) allows these values to be interpreted to yield the derived values $\Delta H_{\mathrm{rxn}} = 51.6$ kcal/mol and $\Delta V_{\mathrm{rxn}} = 17.3$ mL/mol. We further find the lower limit of the BDE$\{Cp(CO)_2Mn–CO\}$ to be 59.4 kcal/mol, and demonstrate the independence of Φ_{diss} over the range of linear alkanes examined.

Acknowledgements

KWD acknowledges the National Science Foundation's GK-12 Grant # 0338135 to JJG for financial (stipend) support that enabled him to complete this project.

References

[1] J.A. Cabeza, I. da Silva, I. del Rio, L. Martinez-Mendez, D. Miguel, V. Riera, Angew. Chem., Int. Ed. 43 (2004) 3464–3467.
[2] I.L. Franklin, A.M. Beale, G. Sankar, Catal. Today 81 (2003) 623–629.
[3] B.L. Tjelta, P.B. Armentrout, J. Am. Chem. Soc. 118 (1996) 9652–9660.
[4] M.D. Cavanaugh, B.T. Gregg, A.R. Cutler, Organometallics 15 (1996) 2764–2769.
[5] F.A. Cotton, Inorg. Chem. 41 (2002) 643–658.
[6] R.H. Crabtree, J. Organomet. Chem. 689 (2004) 4083–4091.
[7] T. Ni, R.A. Caldwell, L.A. Melton, J. Am. Chem. Soc. 111 (1989) 457–464.
[8] M.S. Herman, J.L. Goodman, J. Am. Chem. Soc. 111 (1989) 9105–9107.
[9] M. Bernstein, J.D. Simon, K.S. Peters, Chem. Phys. Lett. 100 (1983) 241–244.
[10] J.J. Grabowski, J.D. Simon, K.S. Peters, J. Am. Chem. Soc. 106 (1984) 4615–4616.
[11] J.C. Scaiano, C. Chen, P.F. McGarry, J. Photochem. Photobiol. A 62 (1991) 75–81.
[12] R.W. Larsen, Inorg. Chim. Acta 288 (1999) 74–81.
[13] K.B. Clark, D.D.M. Wayner, S.H. Demirdji, T.H. Koch, J. Am. Chem. Soc. 115 (1993) 2447–2453.
[14] L.J. Rothberg, J.D. Simon, M. Bernstein, K.S. Peters, J. Am. Chem. Soc. 105 (1983) 3464–3468.
[15] L.G. Arnaut, R.A. Caldwell, J.E. Elbert, L.A. Melton, Rev. Sci. Instrum. 63 (1992) 5381–5389.
[16] R.R. Hung, J.J. Grabowski, J. Am. Chem. Soc. 121 (1999) 1359–1364.
[17] S. Nonell, P.F. Aramendia, K. Heihoff, R.M. Negri, S.E. Braslavsky, J. Phys. Chem. 94 (1990) 5879–5883.
[18] R.P. Herbrich, R. Schmidt, J. Photochem. Photobiol. A 133 (2000) 149–158.
[19] J.E. Rudzki, J.L. Goodman, K.S. Peters, J. Am. Chem. Soc. 107 (1985) 7849–7854.
[20] R.R. Hung, J.J. Grabowski, J. Phys. Chem. 95 (1991) 6073–6075.
[21] R. Dunsbach, R. Schmidt, J. Photochem. Photobiol. A 83 (1994) 7–13.
[22] K.S. Peters, T. Watson, T. Logan, J. Am. Chem. Soc. 114 (1992) 4276–4278.
[23] J.A. Westrick, J.L. Goodman, K.S. Peters, Biochemistry 26 (1987) 8313–8318.
[24] W.P. Leung, K.C. Cho, S.K. Chau, C.L. Choy, Chem. Phys. Lett. 141 (1987) 220–224.
[25] K. Marr, K.S. Peters, Biochemistry 30 (1991) 1254–1258.
[26] J.A. Daffron, G.J. Farrell, T.J. Burkey, Rev. Sci. Instrum. 71 (2000) 3882–3885.
[27] R.R. Hung, J.J. Grabowski, J. Am. Chem. Soc. 114 (1992) 351–353.
[28] J. Morais, Jangseok Ma, Matthew B. Zimmt, J. Phys. Chem. 95 (1991) 3885–3888.
[29] K.G. Caulton, Coord. Chem. Rev. 38 (1981) 1–43.
[30] S. Hu, G.J. Farrell, C. Cook, R. Johnston, T.J. Burkey, Organometallics 13 (1994) 4127–4128.
[31] P.F. Yang, G.K. Yang, J. Am. Chem. Soc. 114 (1992) 6937–6938.
[32] D.M. Hester, J. Sun, A.W. Harper, G.K. Yang, J. Am. Chem. Soc. 114 (1992) 5234–5240.
[33] A.A. Sorensen, G.K. Yang, J. Am. Chem. Soc. 113 (1991) 7061–7063.
[34] J.K. Klassen, Matthais Selke, Amy A. Sorensen, Gilbert K. Yang, J. Am. Chem. Soc. 112 (1990) 1267–1268.
[35] T.J. Burkey, J. Am. Chem. Soc. 112 (1990) 8329–8333.
[36] G.I. Childs, D.C. Grills, X.Z. Sun, M.W. George, Pure Appl. Chem. 73 (2001) 443–447.
[37] P.J. Giordano, Mark S. Wrighton, Inorg. Chem. 16 (1977) 160–166.
[38] J. Full, C. Daniel, L. Gonzalez, Phys. Chem. Chem. Phys. 5 (2003) 87–96.
[39] P.T. Snee, C.K. Payne, K.T. Kotz, H. Yang, C.B. Harris, J. Am. Chem. Soc. 123 (2001) 2255–2264.
[40] T. Jiao, Z. Pang, T.J. Burkey, R.F. Johnston, T.A. Heimer, V.D. Kleiman, E.J. Heilweil, J. Am. Chem. Soc. 121 (1999) 4618–4624.
[41] J.A. Lavilla, J.L. Goodman, Chem. Phys. Lett. 141 (1987) 149–153.
[42] J.K. Klassen, G.K. Yang, Organometallics 9 (1990) 874–876.
[43] B. Fletcher, J.J. Grabowski, J. Chem. Educ. 77 (2000) 640–645.

[44] G.L. Geoffroy, M.S. Wrighton, Organometallic Photochemistry, Academic, New York, 1979.
[45] S.E. Braslavsky, G.E. Heibel, Chem. Rev. 92 (1992) 1381–1410.
[46] W.J. Leigh, D.R. Arnold, Can. J. Chem. 59 (1981) 3061–3075.
[47] C.G. Hatchard, C.A. Parker, Proc. Roy. Soc. A235 (1956) 518–536.
[48] A.D. Kirk, C. Namasivayam, Anal. Chem. 55 (1983) 2428–2429.
[49] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, Pure Appl. Chem. 76 (2004) 2105–2146.
[50] K.S. Peters, Pure Appl. Chem. 58 (1986) 1263–1266.
[51] T.J. Burkey, M. Majewski, D. Griller, J. Am. Chem. Soc. 108 (1986) 2218–2221.
[52] K.S. Peters, G.J. Snyder, Science 241 (1988) 1053–1057.
[53] J.M. Kanabus-Kaminska, B.C. Gilbert, D. Griller, J. Am. Chem. Soc. 111 (1989) 3311–3314.
[54] D. Griller, D.M. Wayner, Pure Appl. Chem. 61 (1989) 717–724.
[55] J.M. Morse Jr., G.H. Parker, T.J. Burkey, Organometallics 8 (1989) 2471–2474.
[56] T.J. Burkey, Polyhedron 8 (1989) 2681–2687.
[57] M.S. Herman, J.L. Goodman, J. Am. Chem. Soc. 110 (1988) 2681–2683.
[58] M.S. Herman, J.L. Goodman, J. Am. Chem. Soc. 111 (1989) 1849–1854.
[59] Z. Pang, T.J. Burkey, R.F. Johnston, Organometallics 16 (1997) 120–123.
[60] T.A. Moore, D. Benin, R. Tom, J. Am. Chem. Soc. 104 (1982) 7356–7357.
[61] C.K.N. Tam, A.C. Patel, Rev. Mod. Phys. 53 (1981) 517–553.
[62] C.E. Brown, Y. Ishikawa, P.A. Hackett, D.M. Rayner, J. Am. Chem. Soc. 112 (1990) 2530–2536.
[63] J.R. Chipperfield, J.C.R. Sneyd, D.E. Webster, J. Organomet. Chem. 178 (1979) 177–189.
[64] Y. Li, B. Sztaray, T. Baer, J. Am. Chem. Soc. 123 (2001) 9388–9396.
[65] H.-J. Fan, M.B. Hall, Organometallics 20 (2001) 5724–5730.
[66] L.S. Sunderlin, R.R. Squires, Int. J. Mass Spectrom. (1999) 149–161, 182/183.
[67] G. Pajaro, F. Calderazzo, R. Ercoli, Gazzetta Chimica Italiana 90 (1960) 1486–1494.
[68] K.E. Lewis, D.M. Golden, G.P. Smith, J. Am. Chem. Soc. 106 (1984) 3905–3912.
[69] T.R. Fletcher, R.N. Rosenfeld, J. Am. Chem. Soc. 110 (1988) 2097–2101.
[70] Y.J. Chen, C.L. Liao, C.Y. Ng, J. Chem. Phys. 107 (1997) 4527–4536.
[71] P.R. Das, T. Nishimura, G.G. Meisels, J. Phys. Chem. 89 (1985) 2808–2812.
[72] S. Gittermann, T. Jiao, T.J. Burkey, Photochem. Photobiol. Sci. 2 (2003) 817–820.
[73] G.J. Farrell, T.J. Burkey, J. Photochem. Photobiol. A 137 (2000) 135–139.
[74] T. Jiao, G.-L. Leu, G.J. Farrell, T.J. Burkey, J. Am. Chem. Soc. 123 (2001) 4960–4965.
[75] J.A. Riddick, W.B. Bunger, T.K. Sakano (Eds.), Techniques in Chemistry, vol. 2, 4th ed., Wiley and Sons, New York, 1986.
[76] W. Brostrow, Phys. Chem. Liquids 3 (1972) 91–113.