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High-pressure photoacoustic calorimetry of chromium hexacarbonyl: volumes of heptane displacement from chromium pentacarbonyl heptane

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Abstract

We have developed high-pressure photoacoustic calorimetry to determine the volume of reaction for organometallic compounds. This allows the calculation of reaction enthalpies from the photoacoustic data. The photoacoustic signal for chromium hexacarbonyl with acetonitrile in heptane was examined from near ambient pressure to 100 MPa. Two components of the signal were resolved at 10–20 mM acetonitrile. The fast component is attributed to CO displacement by heptane (<10 ns), while the slow component (~1 μs) is attributed to the subsequent displacement of heptane by acetonitrile. The amplitude of both components were pressure dependent demonstrating that the volumes of each reaction made a significant contribution to the photoacoustic signal (-21 and 17 ml mol^{-1}, respectively). The enthalpies of CO displacement by heptane are 28 kcal mol^{-1} and heptane displacement by acetonitrile is -22 kcal mol^{-1}. Neglect of the volumes of reaction in the PAC experiments can lead to an error of 6 kcal mol^{-1}. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Coordinatively unsaturated metal complexes are proposed intermediates in many reactions, and the structure and properties of these intermediates are important in understanding their reactivity [1]. Studies of $M(CO)_6$ ($M = Cr, Mo, W$), in particular, have been important in advancing the understanding of transition metal intermediates. Early matrix isolation studies of $M(CO)_6$ (see Eqs. (1) and (2)) were the first to show that coordinatively unsaturated complexes like $M(CO)_5$ can coordinate alkanes at what previously had been assumed to be a vacant coordination site [2].

$$M(CO)_6 + \text{alkane} \xrightarrow{h\nu} M(CO)_5(\text{alkane}) + CO \quad (1)$$

$$M(CO)_5(\text{alkane}) + L \xrightarrow{h\nu} M(CO)_5L + \text{alkane} \quad (2)$$

Subsequent kinetic studies have shown that the activation barrier is significant for displacement of a coordinated alkane solvent with various Lewis bases. For example, the activation enthalpy for dissociative heptane displacement by 1-hexene was found to be 8.3 kcal mol^{-1} for $W(CO)_5$(heptane) [3]. It has been proposed that this represents a lower limit for the W–heptane bond energy. Photoacoustic calorimetry (PAC) offers an alternative method to determine the M–alkane bond energy. With PAC, the heat of reaction is measured via an ultrasonic transducer that detects a sound wave caused by laser initiated reactions. The M–alkane bond energy can be determine from the heat of CO displacement by an alkane (reaction 1) since the heat of this displacement is equal to the difference in bond energies formed and broken. PAC results have given M–alkane bond energies greater than that estimated from activation enthalpies, in some cases, 10 kcal mol^{-1} greater; therefore, we have reexamined the experimental methods and theory for discrepancies [4].

The determination of the heat of a reaction by PAC is not always straightforward. While the photoacoustic signal depends on thermal expansion caused by the liberation of heat, it can also depend on the volume of reaction, i.e. the difference in partial molar volumes of reactants and products or intermediates. Previously, the volume of reaction for metal carbonyls was either ignored or it was suggested that it was not significant, since the volume increase for CO dissociation would be offset by solvent coordination [4–6]. Furthermore, the thermal expansion of organic solvents is large, and by comparison the reaction volume contribution was expected to be negligible. While these arguments seemed reasonable, the fact remained that the volumes of these

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reactions had never been determined. Since the metal–alkane bond is weak, the volume decrease during bond formation could be small and may not offset the volume increase of CO dissociation. In general, the change in the solvent organization around the reaction species is not well understood.

Various methods have been developed to resolve the contributions of thermal expansion and volume of reaction for PAC [5,7]. Each method depends on changing the thermal expansion of the solvent while maintaining the volume of reaction. This has been done previously by changing the temperature or using a series of linear alkanes. Changing the temperature works well in aqueous solutions where the thermal expansion is very dependent on temperature near 3°C. This is not a solution for the study of metal–alkane interactions since water would preferentially bind the metal. Changing the temperature of a hydrocarbon solution is not satisfactory, since the thermal expansion of hydrocarbons is insensitive to temperature. In another approach, a series of linear alkanes has been used successfully to change the thermal expansion, but this may not be an adequate method for studying metal–alkane bonding since the metal–alkane bond strength may also change [8].

Recently we have demonstrated that the thermal expansion for a single solvent can be varied for PAC by changing the pressure [9]. In the current study, we have examined the photoacoustic signal for photolysis of chromium hexacarbonyl in heptane at pressures up to 100 MPa. We report the enthalpy and volume for CO substitution by heptane, Eq. (1) ($M = Cr$), and for heptane substitution by acetonitrile, Eq. (2) ($L =$ acetonitrile). The results show that the volume of reaction can have a significant effect on the determination of the enthalpies of organometallic reactions in organic solvents.

2. Theory

The amplitude (S) of the PAC signal is dependent on pressure changes caused by thermal expansion (ΔP_{th}) or the volume of reaction (ΔP_V) as shown in Eq. (3) (K: instrument constant). The pressure change resulting from thermal expansion, expressed in Eq. (4), is a function of the total heat released (E_{th}), the coefficient of thermal expansion (β), heat capacity (C_P), density (ρ), photolyzed volume (V_0), and isothermal compressibility (κ). The pressure change due to the volume of reaction (ΔV) is expressed by Eq. (5), where $\Delta V = -\Delta V_0$. In contrast, the pressure change from a reference sample is dependent only on the energy of the absorbed light, as shown in Eq. (6), if the excited state returns by internal conversion to the ground state with a unit quantum yield. The ratio of sample and reference signal amplitudes represented by Φ in Eq. (7), is obtained by dividing Eq. (3) by Eq. (6) and making substitutions from Eqs. (4) and (5) for ΔP_{th} and ΔP_V. The heat from processes that are much faster than the transducer response (in this case $<10^{-7}$ s) are denoted with a subscript 1.

$$S = K\Delta P = K(\Delta P_{\mathrm{th}} + \Delta P_V) \tag{3}$$

$$\Delta P_{\mathrm{th}} = \frac{E_{\mathrm{th}}\chi}{V_0\kappa} \quad \left(\chi = \frac{\beta}{C_P\rho}\right) \tag{4}$$

$$\Delta P_V = \frac{\Delta V\Phi}{V_0\kappa} \tag{5}$$

$$\Delta P_{\mathrm{ref}} = \frac{h\nu\chi}{V_0\kappa} \tag{6}$$

$$\phi = \frac{S}{S_{\mathrm{ref}}} = \frac{\Delta P}{\Delta P_{\mathrm{ref}}} = \frac{E_{\mathrm{th}}}{h\nu} + \frac{\Delta V\Phi}{h\nu\chi} \tag{7}$$

As described in Eq. (8), the heat from these processes depend only on $h\nu$ and the enthalpy of fast reactions if there is no luminescence.[1] Taking into account that the enthalpy is pressure dependent as shown in Eq. (9), substitutions for E_{th} and ΔH and rearrangement of Eq. (7) yields Eq. (10). The solvent parameter χ changes with pressure, and ϕ_1 is determined experimentally, thus, a plot of $h\nu(1-\phi_1)/\Phi$ versus $(1/\chi - P)$ yields the enthalpy at ambient pressure (intercept) and the volume of reaction (slope).

$$E_{\mathrm{th}} = h\nu - \Phi\Delta H_1 \tag{8}$$

$$\Delta H_1 = \Delta E + \Delta VP = \Delta H_{P=0} + \Delta VP \tag{9}$$

$$\frac{h\nu\,(1-\phi_1)}{\Phi} = \Delta H_{1,P=0} - \Delta V_1\left(\frac{1}{\chi} - P\right) \tag{10}$$

Slower processes that occur on a time scale comparable to the transducer response time (10^{-7}–10^{-6} s) are denoted with a subscript 2. These processes cause a phase shift in the signal, and the amplitude of this contribution can be resolved from that of the faster processes [10]. Noting that the photon energy does not contribute to the heat observed on this slower time scale, the analogous expressions Eqs. (11) and (12) were derived. Deconvolution of the signal provides the relative amplitudes of the two components (ϕ_1 and ϕ_2) and the lifetime of the second component.

$$E_{\mathrm{th}} = -\Phi\Delta H_2 \tag{11}$$

$$\frac{-h\nu\phi_2}{\Phi} = \Delta H_{2,P=0} - \Delta V_2\left(\frac{1}{\chi} - P\right) \tag{12}$$

3. Experimental

Chromium hexacarbonyl (Aldrich) and ferrocene (Ethyl Corporation) were purified by vacuum sublimation. Heptane (Aldrich, HPLC) was distilled under argon after refluxing overnight over sodium. Acetonitrile was distilled from calcium hydride. Sample preparation for PAC experiments have been described previously [4]. In a typical experiment, a heptane solution of acetonitrile (20 mM) and

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[1] The rates of these processes cannot be determined or resolved from each other.

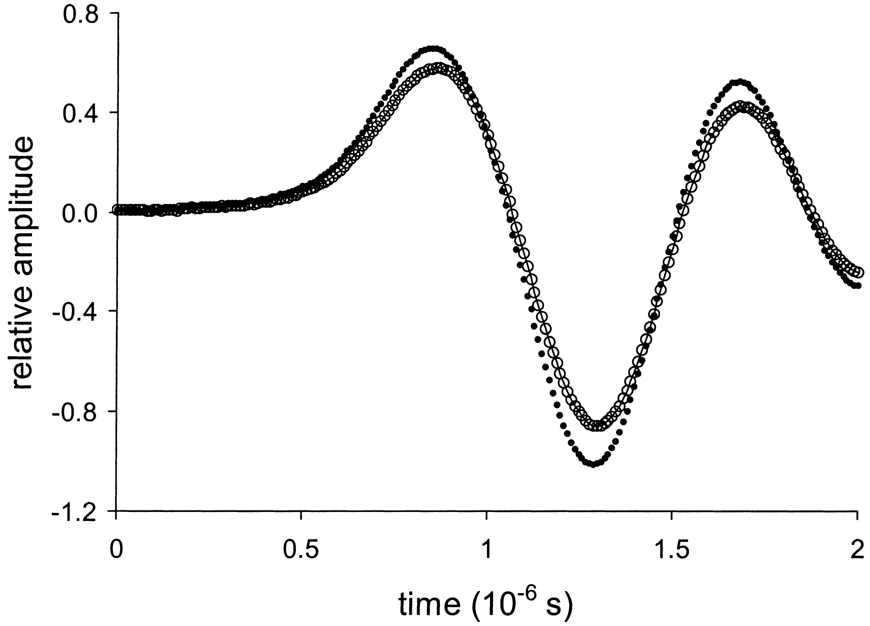

Fig. 1. Photoacoustic signals in heptane at 62 MPa for ferrocene (filled circles), chromium hexacarbonyl carbonyl and 10 mM acetonitrile (empty circles), simulation waveform (fitted line, $\phi_1 = 0.837$, $\phi_2 = 0.123$, $\tau = 4.9 \times 10^{-7}$ s).

chromium hexacarbonyl (0.2 mM) was prepared in a glove box and transferred to a stainless steel bellows. Ferrocene in heptane was used as the PAC reference solution. The concentration of the ferrocene (ca. 6 mM) was adjusted to match the absorbance of the chromium hexacarbonyl solution ($OD_{337} = 0.1$, 0.6 cm path length).

The high-pressure PAC apparatus and operation have been described recently [9]. The high-pressure cell was maintained at 25.0 ± 0.1 C, and a 1 MHz transducer was used for all experiments (Panametrics V-103). Chromium hexacarbonyl solutions in the high-pressure cell were pulsed at 0.3 Hz (800 ps, 337.1 nm, 20 μJ per pulse). To ensure that only fresh chromium hexacarbonyl solution was irradiated, 0.12 ml was delivered to the cell between each laser pulse. Ferrocene solutions were measured within 5 min of the measurement of chromium hexacarbonyl solutions. In general, a measurement consisted of a signal averaged from 8 to 16 laser pulses. The averaged signal was corrected for variations in pulse energies, background signal obtained from pure heptane, and sample absorption. Corrected signals were analyzed with MQ or Sound Analysis 32 (Quantum Northwest, Spokane). At each pressure, measurements were obtained for five independently prepared solutions of chromium hexacarbonyl, and three to four measurements were recorded for each solution. The quantum yields and solvent properties at each pressure were obtained from the literature [11–13].

4. Results

The amplitude of the acoustic signal following photolysis of chromium hexacarbonyl with 10–20 mM acetonitrile (uncorrected for density changes) in heptane is less than, and phase shifted relative to that for ferrocene (Fig. 1). When the acetonitrile concentration is 200 mM, the amplitude of the signal for the chromium hexacarbonyl solution increases, and no phase shift is detected. On the other hand, when the acetonitrile concentration is 0.5 mM, the signal decreases and again no phase shift is detected. PAC measurements were recorded at 1.4, 20.7, 41.4, 62.0, 83, and 103 MPa. Deconvolution of the signal for chromium hexacarbonyl (10–20 mM acetonitrile) with a ferrocene signal at the same pressure revealed a fast (ϕ_1) and a slow (ϕ_2) component. As the pressure increased, ϕ_1 increased, ϕ_2 decreased, and the lifetime of ϕ_2 decreased (lifetimes were 2×10^{-7}–6×10^{-7} s depending on the pressure and acetonitrile concentration).[2] A plot of $h\nu(1-\phi_1)/\Phi$ versus $(1/\chi - P)$ is shown in Fig. 2, and plot of $-h\nu\phi_2/\Phi$ versus $(1/\chi - P)$ shown in Fig. 3.

5. Discussion

The assignment of ϕ_1 and ϕ_2 to reactions 1 or 2 (M = Cr; alkane = heptane; L = acetonitrile) varies with the concentration of added Lewis base. It has been established that photolysis of chromium hexacarbonyl leads to dissociation of CO followed by alkane solvent coordination on a sub-picosecond time scale [15,16]. Subsequently the solvent

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[2] After establishing that there was no signal on the timescale of the transducer for 0.5 and 200 mM, only one concentration (10 or 20 mM) was used at each pressure to determine ϕ_2. Although a single concentration is not appropriate for calculating a second-order rate constant, it can be estimated. For example, at 103 MPa the lifetime is 2.4×10^{-7} s at 22 mmol acetonitirile (density corrected) and yields 1.9×10^8 M^{-1} s^{-1} (assuming no zero-order reactions). For comparison, the rate constant is 2.6×10^8 M^{-1} s^{-1} at ambient pressure [14].

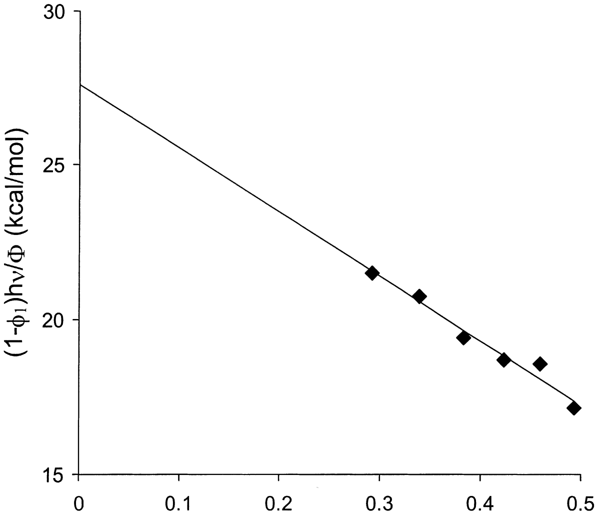


Fig. 2. Pressure dependence of ϕ_1 in Eq. (10) (the unshifted component of the photoacoustic signal) following 337 nm photolysis of chromium hexacarbonyl with acetonitrile (relative to ferrocene). Line is least-squares fit.

is displaced by various ligands at millimolar concentrations on a microsecond time scale [17,18]. At 200 mM acetonitrile, displacement of heptane by acetonitrile (reaction 2) is much faster than the response of the transducer, and the signal from this reaction cannot be resolved from that for CO dissociation (reaction 1). Consequently, both reactions 1 and 2 contribute to the amplitude of the signal without a phase shift relative to the reference sample, and only ϕ_1 is detected. Under these conditions, ϕ_1 is assigned to reactions 1 and 2. At 10–20 mM acetonitrile, where a phase shift is observed, the rate of reaction 2 is slower and comparable to the response of the transducer, thus two components are observed. Therefore, ϕ_1 is assigned to reaction 1 and ϕ_2 is assigned to reaction 2. At 0.5 mM acetonitrile, the rate of reaction 2 is too slow to be detected by the transducer, and only reaction 1 contributes to the signal, and ϕ_1 is assigned to reaction 1.

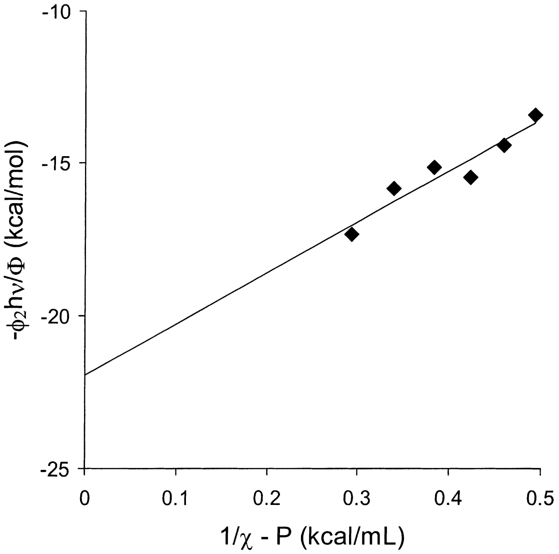
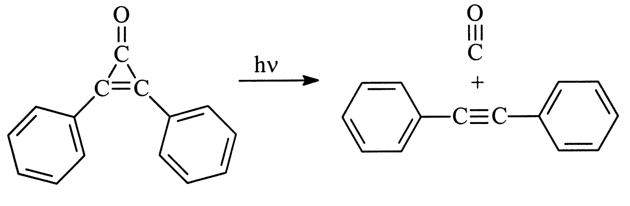


Fig. 3. Pressure dependence of ϕ_2 in Eq. (12) (the shifted component of the photoacoustic signal) following 337 nm photolysis of chromium hexacarbonyl with acetonitrile (relative to ferrocene). Line is least-squares fit.

The ϕ_1 and ϕ_2 values obtained with 10–20 mM acetonitrile at various pressures were used in Eqs. (10) and (12) to determine the enthalpies and volumes of reaction for reactions 1 and 2, respectively. Plots of these equations in Figs. 2 and 3 show non-zero slopes, which demonstrate that the volumes of reaction make a significant contribution to the photoacoustic signals. From linear regressions of the data, we obtain $\Delta H_1 = 27.6 \pm 0.8\,\mathrm{kcal\,mol^{-1}}$, $\Delta V_1 = 20.8 \pm 1.9\,\mathrm{ml\,mol^{-1}}$, $\Delta H_2 = -22.0 \pm 1.1\,\mathrm{kcal\,mol^{-1}}$, and $\Delta V_2 = -16.7 \pm 2.8\,\mathrm{ml\,mol^{-1}}$. Furthermore, the enthalpy and volume of reaction for CO substitution by acetonitrile can be calculated from this data ($\Delta H_1 + \Delta H_2 = 5.6\,\mathrm{kcal\,mol^{-1}}$ and $\Delta V_1 + \Delta V_2 = 4.1\,\mathrm{ml\,mol^{-1}}$). Reaction 1 is expected to be endothermic since the bond formed (Cr–heptane) is weaker than the bond broken (Cr–CO). Likewise, reaction 2 is exothermic since the bond formed (Cr–acetonitrile) is stronger than the one broken (Cr–heptane). If we neglect the volumes of reaction by calculating ΔH_1 and ΔH_2 at a single pressure, then errors of 5–6 $\mathrm{kcal\,mol^{-1}}$ result. As an example, 21.5 and $-17.4\,\mathrm{kcal\,mol^{-1}}$ are obtained, respectively, at 1.4 MPa. The errors are even larger at higher pressures. On the other hand, the sum of these values ($4.1\,\mathrm{kcal\,mol^{-1}}$) is within experimental error ($1.5\,\mathrm{kcal\,mol^{-1}}$) of the ΔH_1 and ΔH_2 values obtained by correcting for the volume of reaction. Further studies are necessary to see if this is a general finding for the substitution of ligands of similar bond energies and symmetries.

Having accounted for the volumes of reaction, it is possible to calculate the metal–ligand bond energies. From the Cr–CO bond energy ($36.8 \pm 2\,\mathrm{kcal\,mol^{-1}}$) [19] and ΔH_1, the Cr–heptane bond energy is $9.8 \pm 2.2\,\mathrm{kcal\,mol^{-1}}$. Similarly, a Cr–acetonitrile bond energy of $31.2 \pm 2.4\,\mathrm{kcal\,mol^{-1}}$ can be calculated from the Cr–CO bond energy, ΔH_1, and ΔH_2.

The volume changes are large for both reactions 1 and 2. For reaction 1, the result is close to that observed for diphenylcyclopropenone ($24\,\mathrm{ml\,mol^{-1}}$, Scheme 1) [8,9,20,21]. It is obvious that there is a much greater change in the interatomic distance for atoms involved in bond breaking than for the atoms of unbroken bonds. Since $Cr(CO)_5$ and CO are no longer within the van der Waals radii of each



Scheme 1.

other, their volume must be greater than $Cr(CO)_6$ if $Cr(CO)_5$ and CO undergo little rearrangement (bond angles and lengths). This is supported by experimental and theoretical studies [22,23]. It is a general observation that there is about a 10 ml mol^{-1} activation volume for reactions with a single bond cleavage [24]. On this basis, we would interpret that a chromium-carbon double bond is being broken in chromium hexacarbonyl, yet this interpretation overlooks the complexity of the reaction. Unlike $Cr(CO)_5$, an organic radical apparently does not interact with a medium made up of closed shell molecules. The formation of a Cr–alkane bond is likely to have a negative volume contribution, but it is not clear how this bond forming process affects solvent organization around the $Cr(CO)_5$(alkane) complex. Studies of ligands that bond differently than CO or acetonitrile may provide clues to explain the role of Cr–alkane bonds in reaction volumes.

The factors affecting volume changes for reaction 1 should be similar to that for reaction 2. The volume decrease for heptane displacement by acetonitrile is somewhat less than for heptane displacement by CO. Since the symmetry of the two ligands is so similar, it is likely that the solvent reorganization for the two processes is also going to be similar. Although both CO and acetonitrile have σ and π bonds with the metal center, the bonding with CO is stronger (vide supra) and may be expected to be shorter, so a greater volume decrease is observed for the Cr–CO bond forming process.

In conclusion, the volume of reaction is large for heptane substitution of strongly binding ligands such as CO and acetonitrile on $Cr(CO)_5$ and significantly affects the photoacoustic signal in PAC measurements. Neglect of volume of reaction causes a large error in the calculation of the enthalpies for these reactions. On the other hand, the volume of reaction is small for CO substitution by acetonitrile, and its neglect causes a small error in the calculation of reaction or bond enthalpies.

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