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Photoacoustic Calorimetric and Time-Resolved Infrared Studies on Unstable Dinitrogen and Dihydrogen Complexes in Hydrocarbon Solution; Estimation of V–L Bond Dissociation Enthalpies in [(η^5-C_5H_5)V(CO)$_3$L] Compounds (L = N_2 and η^2-H_2)

Frank P. A. Johnson,[a] **Vladimir K. Popov,***[b] **Michael W. George,***[a] **Viktor N. Bagratashvili,**[b] **Martyn Poliakoff***[a] **and James J. Turner**[a]

[a] *Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK. Fax: 0602 705874*

[b] *Laser Chemistry Department, Scientific Research Centre for Technological Lasers, USSR Academy of Sciences, 142092 Troitzk, Moscow Region, USSR. Fax: 095 334 0201*

Photoacoustic calorimetry (PAC) is used to measure energy changes associated with the photochemical reaction of [cpV(CO)$_4$] (cp = η^5-C_5H_5) with H_2 and N_2 in n-heptane solution; fast time-resolved IR spectroscopy (TRIR) is used to establish the timescale of these reactions and to verify the quantum yields so that enthalpy changes can be calculated from the PAC signals and hence bond dissociation energies can be estimated.

The knowledge of bond dissociation energies is a prerequisite for a full understanding of chemical reactions.[1] Such data are particularly important in the study of reactions of H_2 with transition metal centres where a delicate balance of interactions determines whether dihydrides or non-classical dihydrogen compounds are formed.[2,3a] Unfortunately, thermochemical measurements on organometallic compounds remain a relatively difficult area and, despite the intensive study of dihydrogen complexes over recent years, surprisingly little information is available about the energetics of the M–(η^2-H_2) interaction, apart from elegant calorimetric, kinetic and spectroscopic experiments by Hoff and coworkers.[3] These studies have provided comprehensive data for the reactions of [Cr(CO)$_3$(PR$_3$)$_2$] and its group 6 congeners with H_2 and N_2 but deriving precise values for bond dissociation energies is complicated by the presence of an intramolecular agostic interaction in the M(CO)$_3$(PR)$_3$ complexes. There have been a number of theoretical estimates of the M–(η^2-H_2) bond energy[4] but few other experimental measurements have been made.† At Nottingham, we have exploited the photochemical reaction of transition metal carbonyl complexes with H_2 as a general route to a wide range of non-classical dihydrogen complexes in hydrocarbon,[5a] noble gas[5b] or supercritical fluid[5c] solution, [eqn. (1)]. These complexes have been characterized either by FTIR or by fast Time-Resolved IR spectroscopy (TRIR), a combination of UV flash photolysis and nanosecond IR spectroscopy.[6]

$$[L_nM(CO)_x] + H_2 \xrightarrow{UV} [L_nM(CO)_{x-1}(\eta^2\text{-}H_2)] + CO \quad (1)$$

Photoacoustic calorimetry (PAC) is by now a well established technique for investigating photochemical processes and has been elegantly applied to a number of organometallic systems.[7–9] In this Communication, we combine the PAC expertise from the laboratory at Troitzk[10] with the photochemical techniques at Nottingham to study the energetics of the reaction of H_2 with [cpV(CO)$_4$] (cp = η^5-C_5H_5) in solution, a reaction which we recently showed[11] to lead to the formation of the [cpV(CO)$_3$(η^2-H_2)], the first non-classical dihydrogen complex of a group 5 metal.

The principles of PAC in solutions have been discussed elsewhere.[7] Briefly, irradiation of a UV absorbing compound with a pulsed UV laser gives rise to an acoustic signal, detectable by a sensitive microphone which, given suitable calibration, can be used to measure directly the amount of energy transferred from the compound to the solution. Under identical irradiation conditions (*i.e.* identical laser pulse energy, absorbance of solution *etc.*), less energy will be transferred to the solution by a compound undergoing an endothermic photochemical process than by a compound which is photochemically inert (*e.g.* ferrocene). The enthalpy of the photochemical reaction is then given by the expression,‡ $\Delta H = (E_{ref} - E_p)/\Phi$, where E_{ref} and E_p are the energies transferred to the solution

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† The activation energy for the reaction of [(toluene)Cr(CO)$_2$(η^2-H_2)] with CO in supercritical xenon, 70($\pm$ 5) kJ mol^{-1}, was tentatively equated with Cr–(η^2-H_2) bond dissociation energy.[5c]

‡ This assumes that the absorbance of the solutions is relatively low (*i.e. ca.* 0.1) and that the UV energy absorbed is sufficiently low that the number of absorbed photons is very much less than the number of molecules in the irradiated volume.

respectively by the reference and photoactive compounds and Φ is the quantum yield for the reaction.

When applied to organometallic reactions, PAC has a major limitation, namely that data can only easily be obtained on processes which occur within *ca.* 1 μs of the laser pulse. Extracting information about slower processes requires relatively sophisticated deconvolution procedures.[7b,d] As a consequence many PAC studies on metal carbonyl compounds[7–9] have involved the primary fission of the M–CO bond and subsequent solvation of the naked metal centre by hydrocarbon solvents [eqn. (2)], a process which typically occurs on a subnanosecond timescale.[12] Reaction with ligands [eqn. (3)] is typically much slower (*e.g.* $t_{1/2}$ *ca.* 10 μs) and it therefore requires more complex time-resolved PAC techniques. Such

$$[\mathrm{L}_n\mathrm{M(CO)}_x] \xrightarrow{\mathrm{UV}} [\mathrm{L}_n\mathrm{M(CO)}_{x-1}] + \mathrm{CO} \xrightarrow{\text{solvent}} [\mathrm{L}_n\mathrm{M(CO)}_{x-1}(\text{solvent})] \qquad (2)$$

$$[\mathrm{L}_n\mathrm{M(CO)}_{x-1}(\text{solvent})] + \mathrm{L} \longrightarrow [\mathrm{L}_n\mathrm{M(CO)}_{x-1}\mathrm{L}] + \text{solvent} \qquad (3)$$

limitations do not apply to cpV(CO)$_4$ because its photochemical reactions[13] are more than an order of magnitude faster than comparable reactions of group 6 or 7 metals.[14] The TRIR kinetic traces in Fig. 1 show that the overall reaction with N$_2$ [eqn. (4)] is essentially complete within < 1 μs, a timescale compatible with direct PAC measurements.§ Reaction with H$_2$, CO and other ligands occurs at similar rates.[13]

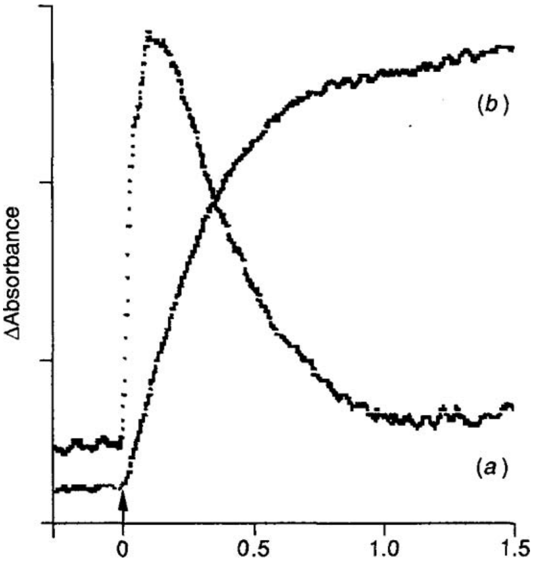

Fig. 1 Time-resolved IR kinetic traces¶ recorded during the 308 nm flash photolysis of [cpV(CO)$_4$] in n-heptane solution under 1.5 atm pressure N$_2$; (*a*) the transient formation of [cpV(CO)$_3$(heptane)], monitored at 1895 cm^{-1} and (*b*) the formation of [cpV(CO)$_3$(N$_2$)], monitored at 1916 cm^{-1}. Note that [cpV(CO)$_3$(heptane)] was identified by comparison with the IR spectrum of [cpV(CO)$_3$] in low temperature matrices.[16] *Note that the two traces have been normalized to the same arbitrary absorbance scale.*

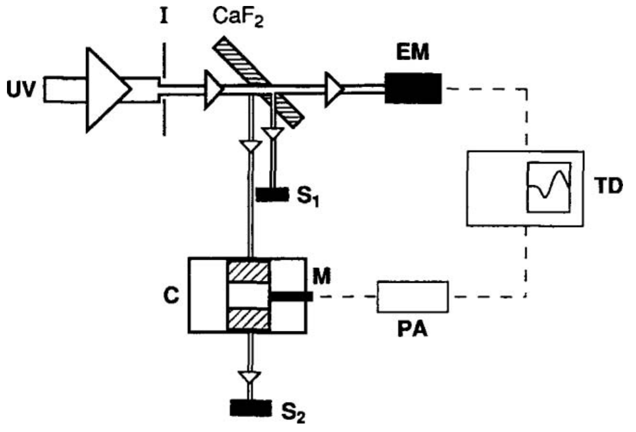

Fig. 2 Plan view of the PAC apparatus. The components are labelled as follows: **UV**, 308 nm beam from XeCl excimer laser, 15–20 ns pulse; **I**, 2 mm iris for collimating the UV beam; **CaF$_2$**, uncoated CaF$_2$ beam splitter: thickness 6 mm; **EM**, piezoelectric energy meter with a lead zirconate/titanate ceramic element; **S$_1$**, beam stop to intercept UV reflection from rear surface of the beam splitter; **C**, nickel plated brass flow cell, 10 mm pathlength, CaF$_2$ windows; **M**, lead zirconate/titanate ceramic microphone; **PA**, 60 dB preamplifier, 10 MHz bandpass, Laser Monitoring Systems MPA3; **TD**, Gould 4072 100 MHz transient Digitizer, 1 μs timebase; **S$_2$**, beam stop. With this optical arrangement the laser energy reaching the PAC cell was < 200 μJ. The cell and microphone were built in Troitzk and all experiments were carried out in Nottingham.

$$[\mathrm{cpV(CO)}_4] \xrightarrow[+\,\text{heptane}]{308\ \text{nm},\ -\mathrm{CO}} [\mathrm{cpV(CO)}_3(\text{heptane})] \xrightarrow[+\,\mathrm{N}_2]{-\,\text{heptane}} [\mathrm{cpV(CO)}_3(\mathrm{N}_2)] \qquad (4)$$

Both [cpV(CO)$_3$(N$_2$)] and [cpV(CO)$_3$(η^2-H$_2$)] are too unstable for conventional quantum yield measurements. However, the quantum yield has been measured,[15] at 436 and 366 nm, for the substitution reaction of [cpV(CO)$_4$] with PPh$_3$. The value, 0.80(± 0.02), shows little wavelength dependence and, in the presence of excess PPh$_3$, is not concentration dependent. TRIR provides a simple means of comparing the quantum yield for substitution of H$_2$, N$_2$ and PPh$_3$ by comparing the depletion of cpV(CO)$_4$ (monitored at 1934 cm^{-1}) in the presence of each ligand under identical irradiation conditions.‖ Assuming that the mean value of our measurements for PPh$_3$ corresponds to a quantum yield of 0.8, we obtain quantum yields of 0.83 (± 0.07) for H$_2$ and 0.78(± 0.06) for N$_2$. Thus, the three quantum yields are the same within experimental error.

Fig. 2 shows the configuration of our PAC apparatus. It differs somewhat from previous designs;[7–9] the ceramic microphone is in direct contact with the solution and the windows of our IR flow cell are IR transparent so that TRIR and PAC measurements can be made in the same cell. Table 1 details the PAC measurements for the various reactions of [cpV(CO)$_4$] and the enthalpy changes are summarized in Scheme 1. Test measurements on other carbonyl compounds were in satisfactory agreement with literature values, see footnote *c* of Table 1.

Although the experimental errors are substantial, a significant part is systematic. The cpV(CO)$_3$–(η^2-H$_2$) interaction is weaker by 29(± 9) kJ mol^{-1} than cpV(CO)$_3$–(N$_2$), a difference consistent with the observed thermal displacement of η^2-H$_2$ by N$_2$ in cryogenic solution.[11] Although coordination of η^2-H$_2$ does not involve a change in formal oxidation state of the V

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§ The TRIR experiments do not provide any evidence for significant transient slippage of the cp ring, an effect which has been observed on photolysis in low temperature matrices.[16]

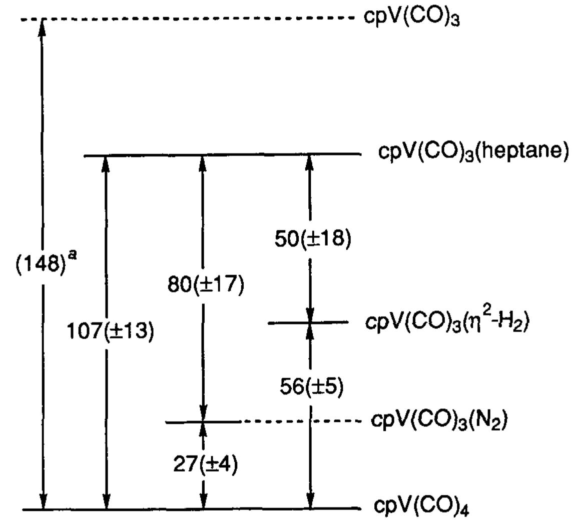
¶ For further details of the TRIR equipment in Nottingham (pulsed 308 nm XeCl excimer laser, cw CO IR laser, HgCdTe detector) see refs. 5*a* and 13. n-Heptane (Aldrich HPLC grade) was dried over CaH$_2$. [cpV(CO)$_4$] (Strem) was sublimed before use; ferrocene (Aldrich) and [cpMn(CO)$_3$] (Pierce and Warriner) were used without further purification. Carbonyl complexes were used at a concentration of *ca.* 1.0 × 10^{-5} mol dm^{-3} Ar, CO, N$_2$ and H$_2$ (BOC Research grade) were used at a pressure of 1.5 atm (*ca.* 0.15 MPa).

‖ Conditions for comparative measurement of quantum yields: [cpV(CO)$_4$], 1 × 10^{-4} mol dm^{-3} (0.55–0.6 absorbance units in 1 mm pathlength at 308 nm); gases, 1.5 atm pressure, *i.e.* H$_2$ (5 × 10^{-3} mol dm^{-3}) and N$_2$ (1 × 10^{-2} mol dm^{-3}); PPh$_3$ 10^{-2} mol dm^{-3}. In comparing the TRIR signals, allowance has to be made for the UV absorption of the free PPh$_3$ in solution. It was the complications introduced by this absorption which discouraged us from making PAC measurements on the reaction with PPh$_3$.

Table 1 Enthalpy changes measured by photoacoustic calorimetry[a]

Reaction	$\Delta H^{b,c}$/kJ mol^{-1}
$[\mathrm{cpV(CO)_4}] + \mathrm{heptane} \longrightarrow [\mathrm{cpV(CO)_3(heptane)}] + \mathrm{CO}$	107(± 13)
$[\mathrm{cpV(CO)_4}] + \mathrm{H_2} \longrightarrow [\mathrm{cpV(CO)_3(\eta^2\text{-}H_2)}] + \mathrm{CO}$	56(± 5)
$[\mathrm{cpV(CO)_4}] + \mathrm{N_2} \longrightarrow [\mathrm{cpV(CO)_3(N_2)}] + \mathrm{CO}$	27(± 4)
$[\mathrm{cpV(CO)_4}] + \mathrm{CO} \longrightarrow [\mathrm{cpV(CO)_4}] + \mathrm{CO}$	0(± 1)

[a] Assuming a quantum yield of 0.8 for all reactions. [b] All errors are maximum deviation of measured values. [c] All PAC measurements were made using reaction and reference solutions with very similar absorbance values (± 5%) at 308 nm as measured on Perkin-Elmer Lambda 5 spectrometer. Readings were normalized for laser pulse energy and minor differences in absorbance. Fresh reference measurements were made for reactant (*i.e.* under pressures of Ar, CO, H_2 and N_2). Each measurement was made 'single shot' and was repeated *ca.* 25 times to obtain a mean value and each experiment was itself repeated several times. Our measurements on other reactions gave values close to literature values, obtained with computer averaged PAC signals, in square brackets: $[\mathrm{Mo(CO)_6}] \longrightarrow [\mathrm{Mo(CO)_5(heptane)}] + \mathrm{CO}$, $\Delta H = 135(\pm 12)$ kJ mol^{-1}[133(± 5)][8b] $[\mathrm{cpMn(CO)_3}] \longrightarrow [\mathrm{cpMn(CO)_2(heptane)}] + \mathrm{CO}$, $\Delta H = 200(\pm 17)$ kJ mol^{-1} [196(± 6) kJ mol^{-1}].[9]



Scheme 1 Enthalpy changes in kJ mol^{-1}. [a] Activation energy taken from ref. 18.

centre, it is interesting to note that the enthalpy of reaction of $\mathrm{cpV(CO)_3}$–(heptane) with H_2 is similar [50(± 18) kJ mol^{-1}] to that estimated for oxidative addition of H_2 to a first row metal[17] but substantially smaller than that measured for a third row metal.[7e]

The values of the V–N_2 and V–(η^2-H_2) bond dissociation energies cannot be obtained without a value for the strength of the $\mathrm{cpV(CO)_3}$–(heptane) interaction. The V–CO bond dissociation energy of $\mathrm{cpV(CO)_4}$ in the gas phase is unknown but enthalpies of activation have been measured for thermal substitution reactions with $\mathrm{PR_3}$ of $\mathrm{cpV(CO)_4}$,[18] 148(± 2) kJ mol^{-1}, and (indenyl)$\mathrm{V(CO)_4}$,[19] 134 (± 1) kJ mol^{-1}. If these values are equated with the V–CO bond energy, subtraction of our PAC value [106 (± 13) kJ mol^{-1}] suggests that the energy of the $\mathrm{cpV(CO)_3}$–(heptane) interaction should lie in the range 30–40 kJ mol^{-1}, comparable to the values (20–40 kJ mol^{-1}) obtained for similar interactions of group 6 and 7 metals.[8c,9] Thus, combining a value of 40 kJ mol^{-1} for the V–(heptane) interaction with the enthalpy values in Scheme 1, we obtain the bond dissociation enthalpies shown in eqn. (5).

$$[\mathrm{cpV(CO)_3L}] \longrightarrow [\mathrm{cpV(CO)_3}] + \mathrm{L}$$

$$\Delta H(\eta^2\text{-}\mathrm{H_2}) = 90(\pm 20)\ \mathrm{kJmol^{-1}} \qquad (5)$$
$$\Delta H(\mathrm{N_2}) = 120(\pm 20)\ \mathrm{kJ\ mol^{-1}}$$

There has been considerable discussion[20] as to the origin of the exceptionally broad ν(H–H) bands observed in the IR spectra of non-classical dihydrogen complexes (in $[\mathrm{cpV(CO)_3(\eta^2\text{-}H_2)}]$, the ν(H–H) band[11] is *ca.* 90 cm^{-1} FWHM). One possible explanation is that the breadth is caused by vibrational predissociation of the dihydrogen ligand.[20] Our photoacoustic measurements suggest that this explanation is unlikely. The $v = 1$ level of the ν(H–H) vibration is 2642 cm^{-1} (31.6 kJ mol^{-1}) above the ground state, considerably less than our estimate of the bond dissociation energy of the V–(η^2-H_2) bond [90(± 20) kJ mol^{-1}]. It is interesting to note that our value is almost identical to the very recent molecular orbital prediction[4b] (93 kJ mol^{-1}) for the strength of the Cu–(η^2-H_2) bond in (η^2-H_2)CuCl.

In this Communication, we have demonstrated how TRIR and PAC measurements can be combined to study the bonding in highly labile complexes. TRIR unravels the mechanism and establishes the timescale of the reaction while PAC provides thermochemical information. Experiments of this type can clearly be extended to measuring the bond energies in a whole range of unstable organometallic systems. The present experiment has relied on the unusually fast reactions of $[\mathrm{cpV(CO)_3(heptane)}]$ to simplify the PAC measurements. However, TRIR allows the rates of such reactions to be monitored and, where necessary, the reactions of other less reactive species could be accelerated for PAC by using higher pressures of gases or higher concentrations of added ligands. A high pressure PAC cell is currently under construction in our laboratories.

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