

Organometallic alkane and noble-gas complexes in conventional and supercritical fluids*

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Abstract: Fast time-resolved infrared (TRIR) spectroscopy has been used to study a wide range of organometallic alkane and noble-gas complexes at ambient temperature. We have shown that the reactivity of the *n*-heptane complexes decreases both across and down Groups V, VI, and VII, and that the corresponding xenon complexes have similar reactivities.

INTRODUCTION

Organometallic alkane complexes are of fundamental interest particularly because they are key intermediates in the C–H activation process. There have been several recent reviews of the area [1]. Organometallic alkane and noble-gas complexes have a long history. 16-electron coordinatively unsaturated metal carbonyl intermediates are highly reactive even toward seemingly inert molecules. More than 20 years ago, Perutz and Turner [2] showed that photolysis of Cr(CO)₆ in low-temperature (12 K) matrices generated Cr(CO)₅(L) (L = Ar, Kr, Xe and CH₄). Although matrix isolation is a powerful technique for the characterization of unstable species at low temperature, it does not provide any kinetic information quantifying the reactivity of these species at room temperature. Early flash photolysis experiments showed [3] that in solution, Cr(CO)₅(cyclohexane) is formed at room temperature within 50 ns following UV flash photolysis of Cr(CO)₆ in cyclohexane, and, subsequently, ultrafast transient spectroscopy demonstrated that the solvation process for Cr(CO)₅ occurs *within the first picosecond* following UV irradiation [4].

Fast time-resolved infrared spectroscopy (TRIR), a combination of UV flash photolysis and fast infrared detection, is a particularly useful technique for characterizing these solvated intermediates. TRIR measurements can be performed on the milli-, micro-, nano-, pico-, and even femtosecond timescales in the gas phase, solution (liquid or supercritical fluid), polymers and zeolites [5]. For slower measurements (>10 ns) there are two widely used approaches for obtaining TRIR spectra. The first uses the “point-by-point” principle where the change in IR intensity is measured at a fixed frequency following a UV–vis laser flash. TRIR spectra are built up by repeating the measurement at different frequencies and plotting the change in absorbance versus frequency. Globars [6] or diode lasers [7] may be used as the IR sources for these measurements. The second technique is based on a *step-scan* FTIR interferometer [8]. The time-resolved *step-scan* FTIR (*s*²-TRIR) technique involves the moveable mirror of the interferometer being displaced in a step-wise manner. At each mirror position, the time-dependent change in IR intensity is measured following excitation, producing time-dependent interferograms. Fourier transformation of an interferogram at a particular time delay following excitation yields the spectral intensity changes at that particular time slice, which are converted to the corresponding absorption spectra. We have used both IR laser TRIR and step-scan FTIR to probe the reactivity of organometallic alkane and noble-gas complexes in solution at room temperature.

*Lecture presented at the XVIIIth IUPAC Symposium on Photochemistry, Dresden, Germany, 22–27 July 2000. Other presentations are published in this issue, pp. 395–548.

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RESULTS AND DISCUSSION

Organometallic alkane complexes

Organometallic alkane complexes can be generated by photolysis of metal carbonyls in alkane solution and are key intermediates in many photochemical pathways, e.g., the photosubstitution of $\text{CpTa}(\text{CO})_4$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) by H_2 in *n*-heptane to yield the dihydride $\text{CpTa}(\text{CO})_3\text{H}_2$ (see Fig. 1).

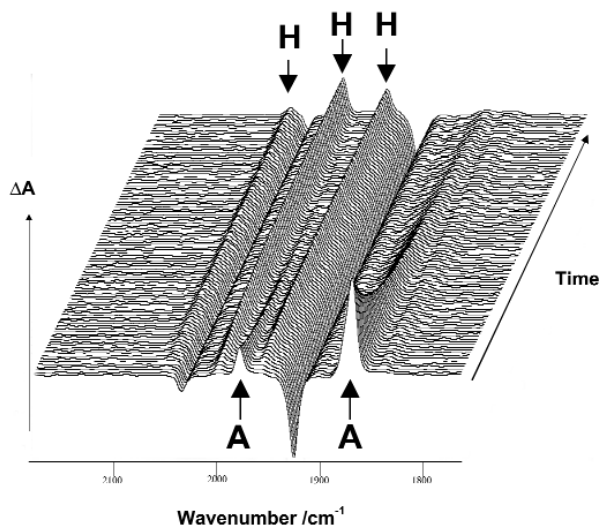


Fig. 1 Step-scan FTIR waterfall plot obtained following UV irradiation of $\text{CpTa}(\text{CO})_4$ in *n*-heptane saturated with H_2 . The two initially produced bands (**A**) are due to the instantaneous formation of the alkane complex, $\text{CpTa}(\text{CO})_3(\textit{n}\text{-heptane})$. These bands decay to form the dihydride, $\text{CpTa}(\text{CO})_3\text{H}_2$ (**H**). The spectra are taken at 1- μs intervals after the initial irradiation.

In order to understand the factors governing the stability of organometallic alkane complexes we have performed a systematic study on the early transition-metal carbonyl alkane complexes. We have used the second-order rate constant for the reaction of the alkane complex with CO to compare the reactivity of these complexes. We have shown [9,10] that the reactivity of organometallic alkane complexes decreases both across and down Groups V, VI, and VII, with the $\text{CpRe}(\text{CO})_2(\textit{n}\text{-heptane})$ complex reacting 50 000 times slower than $\text{CpV}(\text{CO})_3(\textit{n}\text{-heptane})$, Table 1. Group VIII and IX metals form less stabilized alkane complexes, with $\text{CpCo}(\text{CO})$ having no detectable interaction with cyclohexane and $\text{Cp}^*\text{M}(\text{CO})$ ($\text{M} = \text{Rh, Ir}$) reacting with alkanes to form C-H activated products [1d]. The stability of $\text{CpRe}(\text{CO})_2(\textit{alkane})$ is significant, and Ball and Geftakis [11] have been able to characterize $\text{CpRe}(\text{CO})_2(\text{cyclopentane})$ at low temperature (~ 180 K) using ^1H NMR spectroscopy. The factors governing the reactivity of unstable alkane complexes have been investigated. Johnson *et al.* found that the reactivity of $(\eta^5\text{-C}_5\text{R}_5)\text{Mn}(\text{CO})_2(\textit{n}\text{-heptane})$ ($\text{R} = \text{H, Me, and Et}$) toward small molecules such as CO, N_2 , and H_2 in *n*-heptane solution steadily increased in the order $\text{H} < \text{Me} < \text{Et}$ while the reactivity toward PPh_3 did not change [12]. These results indicated that steric rather than electronic factors governed the reactivity of these alkane complexes. Long and coworkers [13] found that the reactivity of $(\eta^6\text{-C}_6\text{R}_6)\text{Cr}(\text{CO})_2(\text{cyclohexane})$ ($\text{R} = \text{H, Me, and Et}$) toward CO in cyclohexane also increased in the order $\text{H} < \text{Me} < \text{Et}$. Changing the solvent from cyclohexane to longer and longer linear alkanes, resulted in an increased rate of reaction between $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2(\textit{alkane})$ and CO. We have subsequently

Table 1 Second-order rate constants, k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$), for the reaction of early transition-metal *n*-heptane complexes with CO in *n*-heptane solution at 298 K.

V	VI	VII
CpV(CO) ₃ (<i>n</i> -heptane) ^a 1.3×10^8	Cr(CO) ₅ (<i>n</i> -heptane) ^c 9.3×10^6	CpMn(CO) ₂ (<i>n</i> -heptane) ^d 8.1×10^5
CpNb(CO) ₃ (<i>n</i> -heptane) ^b 4.5×10^6	Mo(CO) ₅ (<i>n</i> -heptane) ^c 7.8×10^6	—
CpTa(CO) ₃ (<i>n</i> -heptane) ^b 2.0×10^6	W(CO) ₅ (<i>n</i> -heptane) ^c 1.8×10^6	CpRe(CO) ₂ (<i>n</i> -heptane) ^d 2.5×10^3

a) ref [9], b) ref [15], c) ref [16], d) ref [14]

shown [14] that CpM(CO)₂(cyclopentane) (M = Mn, Re) complexes are longer-lived than the corresponding heptane complexes, and the activation parameters for the reaction with CO suggest that the major factor controlling the relative reactivity of these alkane complexes is the difference in activation entropy.

Organometallic noble-gas complexes

We have recently shown [10,15,17,18] that organometallic noble-gas complexes can be observed in fluid solution at room temperature following irradiation of transition-metal carbonyls in supercritical fluids. Fast TRIR spectroscopy was used to characterize M(CO)₅L (M = Cr, Mo and W; L = Ar (W only), Kr and Xe), ($\eta^5\text{-C}_5\text{R}_5$)M(CO)₂L (M = Mn and Re; R = H, Me and Et (Mn only); L = Kr and Xe) and ($\eta^5\text{-C}_5\text{R}_5$)M(CO)₃Xe (M = Nb or Ta). The relative reactivity of these complexes is shown in Fig. 2. The comparison of the CO substitution kinetics for either the Xe or Kr complexes showed that ($\eta^5\text{-C}_5\text{R}'_5$)Mn(CO)₂(Xe) or ($\eta^5\text{-C}_5\text{R}'_5$)Mn(CO)₂(Kr) (R' = H and Me) have very similar reactivity toward CO, whereas ($\eta^5\text{-C}_5\text{Et}_5$)Mn(CO)₂L (L = Kr and Xe) are approximately twice as reactive [18]. This should be contrasted to the reactivity of the corresponding alkane complexes ($\eta^5\text{-C}_5\text{R}_5$)Mn(CO)₂(*n*-heptane) where the reactivity increased in the order, R = H < Me < Et [12]. The comparison of reactivity between organometallic noble-gas and alkane complexes is important. Surprisingly, we found that the rate constants for the Xe complexes, CpM(CO)_x(Xe) (M = Nb, Ta, x = 3; M = Mn, Re, x = 2) were very similar to those for the corresponding alkane complexes, CpM(CO)_x(*n*-heptane). CpRe(CO)₂(Xe) is only ×2 more reactive toward CO in scXe compared to CpRe(CO)₂(*n*-heptane) in *n*-heptane solution, and this means that the characterization of organometallic xenon complexes by NMR is a realistic goal.

CONCLUSIONS

There is a general decrease in the reactivity of both alkane and noble-gas complexes upon moving from Group V to Group VII. This has allowed the characterization of CpRe(CO)₂(cyclopentane) by NMR. We have shown that organometallic xenon complexes have a similar reactivity to alkane complexes, and, therefore, the characterization of a xenon complex by NMR is now a realistic goal. There is clearly still much to learn about organometallic alkane and noble-gas complexes, and it is likely that TRIR spectroscopy will prove increasingly useful for this purpose.

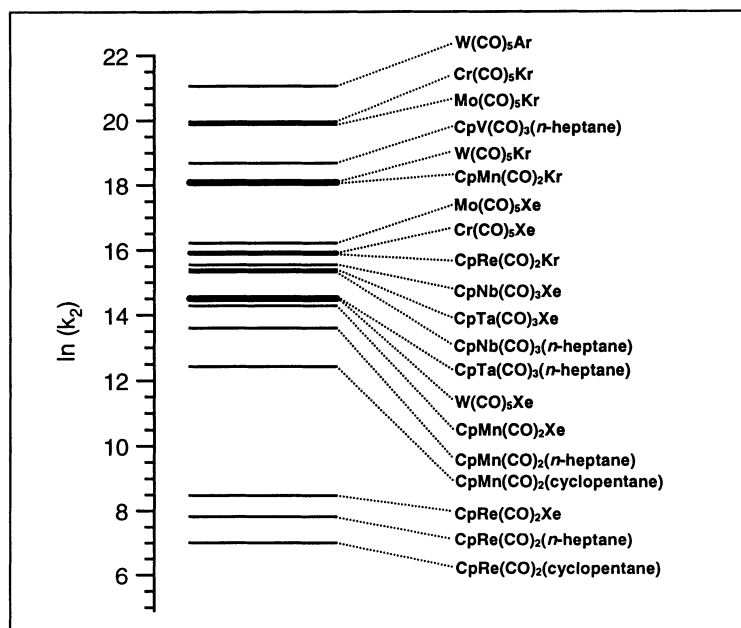


Fig. 2 Values of $\ln(k_2)$ for the reaction of alkane and noble-gas complexes with CO at 25 °C.

ACKNOWLEDGMENTS

We would like to thank all the technical staff in Nottingham for their invaluable help and support, in particular Mr. K. Stanley, M. Guyler, and D. Litchfield. We thank Profs. J. J. Turner and M. Poliakoff for their help and advice.

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