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Inorganica Chimica Acta 357 (2004) 143–148
Inorganica Chimica Acta
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# Activation parameters in flash photolysis studies of $Mo(CO)_6$

Ceyhan Kayran [1], Margaret Richards, Peter C. Ford *

*Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA*

Received 30 May 2003; accepted 7 June 2003

## Abstract

Reported is a combined time-resolved optical (TRO) and infrared (TRIR) spectroscopic investigation of the flash photolysis of $Mo(CO)_6$ in cyclohexane solution. TRIR studies using 308 nm excitation led to transient bleaching of the strong $\nu_{CO}$ band at 1987 $cm^{-1}$ of $Mo(CO)_6$ and appearance of new bands at 1931 and 1964 $cm^{-1}$ attributed to $Mo(CO)_5(Sol)$. Using a high pressure/variable temperature flow cell, the kinetics of back reaction with CO ($k_{CO}$) to regenerate the hexacarbonyl was studied over the $P_{CO}$ range 1–20 atm and at five temperatures. These data gave $k_{CO} = 4.6 \pm 0.2 \times 10^6$ $M^{-1}$ $s^{-1}$ (298 K) and the activation parameters $\Delta H^{\ddagger}_{CO} = 32.6 \pm 3$ kJ/mol and $\Delta S^{\ddagger}_{CO} = -7.3 \pm 11$ J $mol^{-1}$ $K^{-1}$ from which an interchange mechanism was proposed. The analogous species seen in the TRO experiment displayed a transient absorbance at 420 nm and analogous kinetics properties although at lower $P_{CO}$ self-trapping with $Mo(CO)_6$ (to give $Mo_2(CO)_{11}$) is a competitive process. The $Mo(CO)_5(Sol)$ transient could also be trapped by $^nPrBr$ ($k_{RBr} = 5.3 \pm 0.7 \times 10^7$ $M^{-1}$ $s^{-1}$).

*Keywords:* Molybdenum carbonyl; TRIR; Kinetics

## 1. Introduction

This laboratory has had a long-term interest in applying time-resolved infrared (TRIR) and optical (TRO) spectroscopy to characterize reactive intermediates of various homogeneous catalysts [1]. For examples these studies have probed the reaction dynamics of intermediates in H–H and C–H activation by rhodium phosphine complexes [2] and the formation of carbon–carbon bonds via CO migratory insertion into metal–alkyl bonds of manganese, cobalt and iron carbonyl models for hydroformylation catalysts [3]. Another homogeneous carbonylation catalyst is one based upon $Mo(CO)_6$ as the metal bearing precursor active for the selective "single step" hydroxycarbonylation of ethene under relatively mild conditions [4]. Notably, the Group VI carbonyls have also drawn attention as homogeneous catalysts in processes such as the oxidative carbonylation of urea and the polymerization of alkynes [5].

The pentacarbonyl species $Mo(CO)_5(Sol)$ (Sol = solvent) is proposed to be an intermediate in the formation of the chain carrying complexes responsible for the ethene hydroxycarbonylation pathways [4]. Under catalytic conditions reactive intermediates are present only in small steady state concentrations even at elevated temperatures. However, the pentacarbonyl is readily generated and its reactivity investigated in using laser flash photolysis techniques. Indeed the flash photolysis of $Mo(CO)_6$ and its chromium and tungsten analogs have been favorite topics for testing new photophysical techniques (for example [6,7]). These studies have demonstrated that photoexcitation is followed by very fast (<1 ps) reactive decay to give a vibrationally excited pentacoordinate intermediate followed by cooling and trapping by solvent to give the solvated pentacarbonyl complex $Mo(CO)_5(Sol)$ (Eq. (1)). A slower, second-order reaction with added ligands L (among them CO) leads to formation of the product $Mo(CO)_5L$ (Eq. (2)). The relative stabilities of various $Mo(CO)_5(Sol)$ have been determined and the kinetics of Eq. (2) have been investigated for several ligands [8]. However, the reaction with

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* Corresponding author. Tel.: +1-805-893-2443; fax: +1-805-893-4120.
*E-mail address:* ford@chem.ucsb.edu (P.C. Ford).

[1] Present address: Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey.

0020-1693/$ - see front matter
doi:10.1016/S0020-1693(03)00384-0

L = CO is complicated by the competition with $Mo(CO)_6$ itself to generate an intermediate dinuclear species, presumably $Mo_2(CO)_{11}$ (for example [6b,9]).

The work described here is a reexamination the reactivity of the pentacarbonyl intermediate(s) generated by flash photolysis and is part of broader investigation of these species' roles in relevant catalysts. We have utilized TRIR and TRO spectroscopy to determine the kinetics of the decay of the solvento species $Mo(CO)_5(Sol)$ (**A**) in cyclohexane solution in the presence of excess CO to give $Mo(CO)_6$ and the competitive reactions of **A** with added CO and with $^n$PrBr. A unique feature is the use of a high pressure/variable temperature (HP/VT) cell and flow system [9] that allows investigation of detailed kinetics and activation parameters for decay of **A** over a very wide range of CO pressures and reaction temperatures.

$$\mathrm{Mo(CO)_6} \xrightarrow{h\nu} \xrightarrow{-\mathrm{CO}} \{\mathrm{Mo(CO)_5}\}^* \xrightarrow{+\mathrm{Sol}} \mathrm{Mo(CO_5)(Sol)} \qquad (1)$$

$$\mathrm{Mo(CO)_5(Sol)} + \mathrm{L} \rightarrow \mathrm{Mo(CO)_5L} + \mathrm{Sol} \qquad (2)$$

## 2. Experimental

### 2.1. Materials

Cyclohexane used for flash photolysis was reagent grade (Aldrich) and was distilled by published procedures [10]. All gases used for laser flash photolysis experiments were passed through an Oxyclear oxygen scrubber and indicating oxygen trap prior to use. Gases used in synthesis were passed through a column of 4 Å molecular sieves, Drierite and a reduced chromium silica gel column to remove adventitious water and oxygen. Prepurified chromatographic grade (99.998%) argon was used in the glovebox. Reagent-grade CO was used for synthesis, and research grade (99.5%) CO (Liquid Carbonics or Spectra Gas) was used to prepare solutions for laser flash photolysis studies.

### 2.2. Instrumentation

Electronic absorption spectra were recorded for solutions in 1.0 cm path length quartz cells using a Hewlett–Packard 8452A diode array spectrophotometers. FTIR spectra were recorded with a Bio-Rad FTS-60 FTIR spectrophotometer.

### 2.3. Photolysis solutions

For TRIR experiments, $Mo(CO)_6$ solutions (0.23 mM) were prepared under an argon atmosphere in the glovebox and were loaded into foil-wrapped 50 ml gas-tight Hamilton syringes, equipped with shut-off valves and adapters for Leur-Lock connections. These were then transferred from the glovebox and loaded into the high-pressure flow system's sample reservoir of the HP/VT flow system. For TRO studies, solutions were prepared on a vacuum line using Schlenk techniques. The sample cell was a 1.0 cm path length square quartz fluorescence cell, which had been modified for attachment to vacuum lines. The solutions were frozen using liquid nitrogen and a freeze, pump and thaw (f–p–t) procedure was repeated three times to deaerate the solutions before equilibrating with the desired CO pressure. The concentrations of CO at various temperatures were calculated from published data [11].

### 2.4. Flash photolysis instrumentation

For TRO studies, the pump source was Nd:YAG pulsed laser operating in the third harmonic with the power attenuated to ~20 mJ/pulse and a pulse width of ~10 ns. For kinetics traces and point-by-point transient spectra, the probe beam was the output form ILC Technology Model R300-5 300W Xenon lamp passed through an IR filter and a high throughput Spex monochromator. The probe and pump beams were approximately collinear and were passed through a Spex Model 1680 Doublemate dual-grating monochromator after the sample to discriminate against the latter before detection at the RCA 8852 PMT. The PMT output was recorded by Tektronix TDS 540 digital oscilloscope and transferred to a computer for data analysis and storage. The TRIR apparatus using tunable single frequency detection (2150–1550 $\mathrm{cm}^{-1}$) has described in detail elsewhere [3]. In the present study the excitation source was a Lambda Physiks XeCl excimer laser (308 nm operating at 1 Hz).

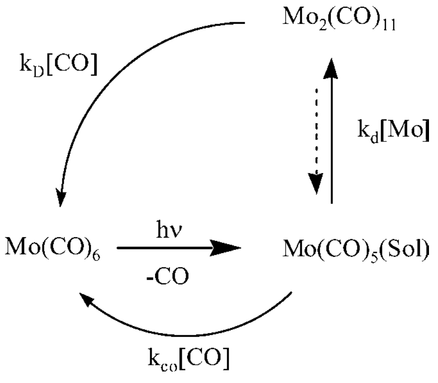
## 3. Results and discussion

### 3.1. TRO studies

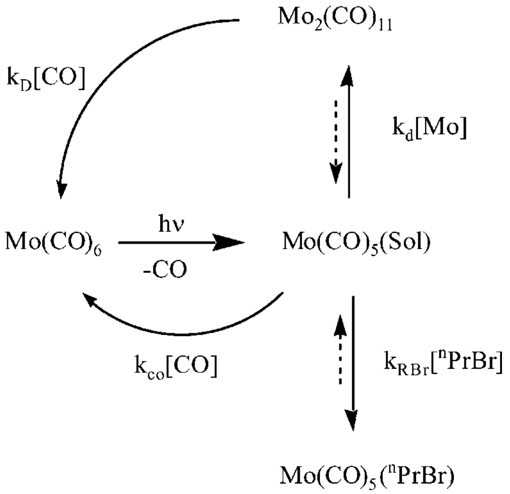
Flash photolysis studies with optical detection were carried out using 355 nm excitation. When a $Mo(CO)_6$ solution ($3.2 \times 10^{-4}$ M) in 298 K cyclohexane under 1.03 atm CO ($P_{\mathrm{CO}}$) was flashed, transient absorbance at 420 nm immediately formed that can be attributed to the solvento species, $Mo(CO)_5Sol$ (**A**, Sol = cyclohexane) (for example [6a]). The decay of this transient absorbance could be fit to a single exponential to give $k_{\mathrm{obs}} = (5.1 \pm 0.1) \times 10^4\ \mathrm{s}^{-1}$ although such fit required a residual absorbance about 23% that of the initial ΔAbs, implying that not all of the absorbance change was reversible. A better quality fit requiring only a small residual was obtained when a double exponential function was used to give $k_{\mathrm{obs}}(1) = 4.8 \times 10^4\ \mathrm{s}^{-1}$ and $k_{\mathrm{obs}}(2) = 1.2 \times 10^3\ \mathrm{s}^{-1}$. When analogous experiments were carried out at lower $P_{\mathrm{CO}}$, single exponential fits of the fast process left increasingly larger residuals implying that the species responsible for the residual absorbance is formed in competition with the reaction with CO to reform $Mo(CO)_6$. Double exponential functions with small residuals gave consistently good fits with both $k_{obs}(1)$ ($3.5 \times 10^4$, $2.4 \times 10^4$ and $1.4 \times 10^4$ $s^{-1}$) and $k_{obs}(2)$ ($0.96 \times 10^3$, $0.89 \times 10^3$ and $0.53 \times 10^3$ $s^{-1}$) responding to the change in $P_{CO}$ (0.75, 0.49 and 0.25 atm, respectively). Plots of $k_{obs}$ versus [CO] gave $k_{CO}(1) = 5.3 \pm 0.3 \times 10^6$ $M^{-1}$ $s^{-1}$ and $k_{CO}(2) = 8.8 \pm 1 \times 10^4$ $M^{-1}$ $s^{-1}$.

We interpret these results as being consistent with earlier reports (for example [6b,8e]) whereupon photolysis labilizes CO to form the pentacarbonyl solvento species **A**, which undergoes competitive trapping by CO or by the hexacarbonyl present in solution to give the dimeric species $Mo_2(CO)_{11}$ (**B**) (Scheme 1). The fast absorbance change is a combination of these two processes, but since **B** also absorbs at the monitoring wavelength, it is responsible for the residual absorption after the fast process. The slower change can be attributed to the reaction of the dimer with CO to regenerate $Mo(CO)_6$. Consistent with this argument, the residual absorbance after the fast process is quite large when the reaction is carried out under an argon rather than a CO atmosphere. On the other hand, when the photolysis was carried out at 1 atm CO but when a lower initial concentration of $[Mo(CO)_6]$ was utilized, the residual due to **B** was smaller.

At the higher concentration of CO, the dominant contribution to this decay is the reaction with CO, and the second-order rate constant $k_{CO}(1)$ is a reasonable estimate of the $k_{CO}$ in Scheme 1. The $5.3 \times 10^6$ $M^{-1}$ $s^{-1}$ value determined agrees well with the values reported by other workers (for example [6a]). Furthermore, since the absorption spectra of the $Mo(CO)_5(Sol)$ and $Mo_2(CO)_{11}$ are likely to be similar, the residual absorbances after the fast process should indicate the amount of the dimer formed. From the magnitude of the residual, which increased as [CO] decreased, and the concentration of $Mo(CO)_6$ we estimate the value of $k_d$ to be $\sim 3 \times 10^7$ $M^{-1}$ $s^{-1}$, based on the assumption that the molar absorbances of **A** and **B** are nearly the same at 420 nm.



Scheme 1.



Scheme 2.

TRO studies were also carried out with another added solution ingredient, namely the halocarbon 1-bromopropane, $^n$PrBr. This was chosen in part because halocarbons are used as promoters in the molybdenum catalyzed hydroxycarbonylation mechanism mentioned above. When the flash photolysis of $Mo(CO)_6$ ($3.2 \times 10^{-4}$ M in cyclohexane solution) was carried out under CO (1 atm) in the presence $^n$PrBr ($3.2 \times 10^{-4}$ M), the decay of the prompt transient absorbance attributed to $Mo(CO)_5(Sol)$ was markedly accelerated. This decay could be fit to a single exponential ($k_{obs} = 7.4 \pm 0.2 \times 10^4$ $s^{-1}$) but with an increased residual relative to the observation in the absence of added RBr. This residual proved to be very long-lived; there was minimal decay on the longest time-scale (10 ms) of the TRO instrument. The $k_{obs}$ values increased with [$^n$PrBr] as expected if the halocarbon were competing directly with CO and with $Mo(CO)_6$ for the pentacarbonyl intermediate (Scheme 2). A plot of $k_{obs}$ versus [$^n$PrBr] proved to be linear with a slope ($k_{RBr}$) of $5.3 \pm 0.7 \times 10^7$ $M^{-1}$ $s^{-1}$ and a non-zero intercept $(5.2 \pm 0.6) \times 10^4$ $s^{-1}$ equal to the $k_{obs}$ determined in the absence of $^n$PrBr for $P_{CO} = 1$ atm (Fig. 1).

### 3.2. TRIR studies

A key advantage of the TRIR technique relative to the TRO method when working with compounds having strong IR chromophores is the greater opportunity to find detection frequencies where the absorption changes are specific to a single species, even though several may be present. For example, the $\nu_{CO}$ modes of $Mo(CO)_6$ occur at different frequencies than those of the pentacarbonyl intermediates. When a $Mo(CO)_6$ solution in cyclohexane was subjected to flash photolysis (308 nm excitation) in a

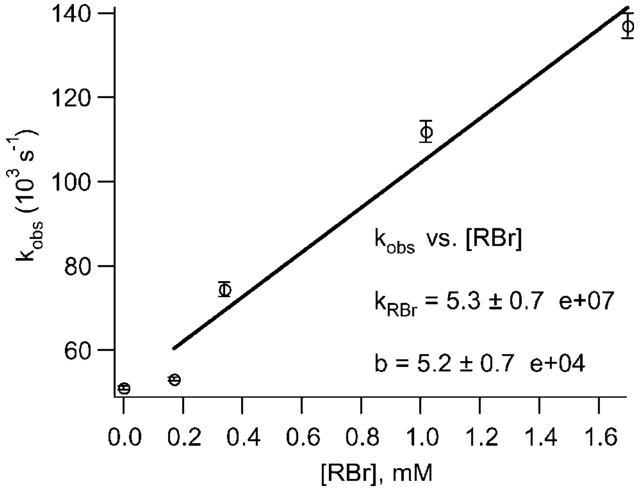


Fig. 1. Plot of $k_{obs}$ vs. [RBr] for the decay of transient, $Mo(CO)_5(Sol)$ in 298 K cyclohexane under $P_{CO} = 1.0$ atm.

standing $CaF_2$ cell (0.5 mm pathlength), transient bleaching of the strong $\nu_{CO}$ band at 1987 $cm^{-1}$ characteristic of $Mo(CO)_6$ was observed, accompanied by the appearance of new $\nu_{CO}$ bands at 1931 and 1964 $cm^{-1}$ attributed to $Mo(CO)_5(Sol)$ (Sol = cyclohexane). Fig. 2 shows temporal absorbance data from such an experiment with $[Mo(CO)_6] = 2.3 \times 10^{-4}$ M and $P_{CO} = 1$ atm. The decay of the transient absorbance at 1931 $cm^{-1}$ fits well to a single exponential giving $k_{obs} = 5.0 \pm 0.1 \times 10^4$ $s^{-1}$ in excellent agreement with the rates seen for the TRO experiment under analogous conditions. The transient bleaching at 1987 $cm^{-1}$ shows a fast component with essentially the same rate constant ($k_{obs} = 4.7 \pm 0.1 \times 10^4$ $s^{-1}$) but a large residual bleaching that appeared to continue decaying but at a rate more than an order of magnitude slower (the TRIR system is not well suited for studying these slower decays).

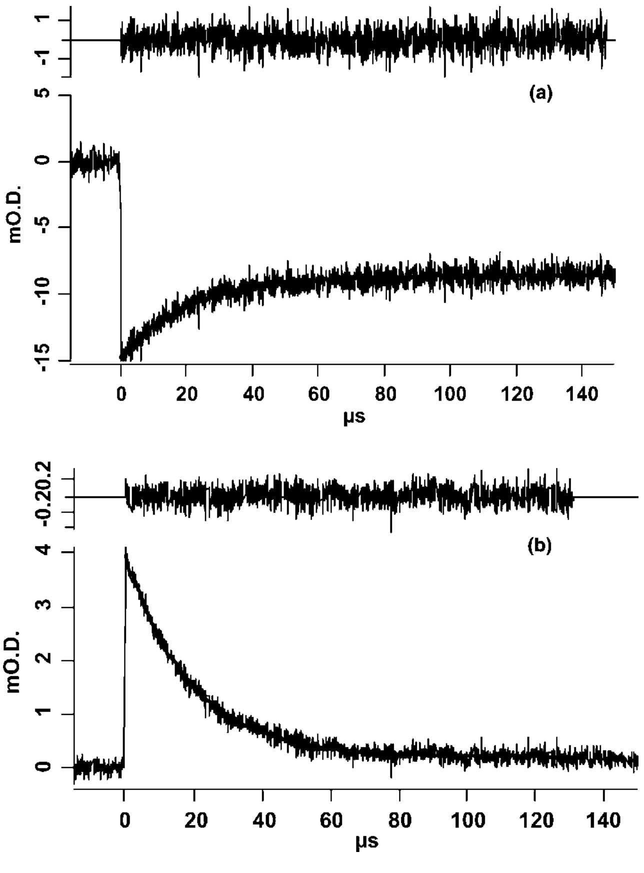


Fig. 2. Temporal absorbance changes at IR frequencies characteristic of (a) $Mo(CO)_6$ (1987 $cm^{-1}$) and of (b) $Mo(CO)_5(Sol)$ (1931 $cm^{-1}$) subsequent to 308 nm flash photolysis of $Mo(CO)_6$ in cyclohexane solution. $T = 298$ K, $P_{CO} = 1.0$ atm.

Another substantial advantage is the ability to control temperature and pressure (up to ~100 atm $P_{CO}$) in the HP/VT flow cell of the TRIR system. In contrast, the cells used in the TRO system are limited to pressures not significantly greater than 1 atm. With a system such as $Mo(CO)_6$, the ease of using much higher pressures allows one to evaluate CO dependent processes over a much wider range of $P_{CO}$ thereby avoiding some of the complications of the $Mo(CO)_6$ trapping of reactive intermediates. The HP/VT cell also provides excellent control of temperature and is well suited for determining kinetics activation parameters. The subsequent experiments in this series were carried out at much higher $P_{CO}$ (3–20 atm) under which conditions the residual bleaching was largely suppressed in accord with the predictions of Scheme 1.

Activation parameters for the reaction of CO with $Mo(CO)_5(Sol)$ (Eq. (3)) were determined by measuring $k_{obs}$ values for at least 6 different $P_{CO}$ over the range 3–20 atm at each T. The $k_{CO}$ values were determined from the slopes of linear $k_{obs}$ versus [CO] plots at 25, 30, 35, 40 and 45 °C as shown in Fig. 3 and these values were used to generate the linear Eyring plot shown in Fig. 4. From the latter, the activation parameters $\Delta H^{\ddagger}_{CO} = 32.6 \pm 3$ kJ/mol and $\Delta S^{\ddagger}_{CO} = -7.3 \pm 11$ J $mol^{-1}$ $K^{-1}$ were extracted.

$$Mo(CO)_5(cyclohexane) + CO \xrightarrow{k_{CO}} Mo(CO)_6 + cyclohexane \qquad (3)$$

Considerable effort has been expended in attempts to evaluate quantitatively the strength of the bonding between unsaturated metal carbonyls and alkane solvents [12]. The most reliable studies would appear to be those based on photo-acoustical calorimetry (PAC), and PAC has been utilized to probe the $Mo(CO)_5$–solvento interaction. The accuracy of the PAC determination of the metal–solvent interaction is dependent on the accuracy of experimental parameters such as the quantum yield for CO photodissociation as well as corrections for volume changes upon reactions. This value is further dependent upon an accurate value for the $M(CO)_5$–CO bond dissociation energy. A recent study by Burkey and co-workers [12c] summarizes the possible uncertainties

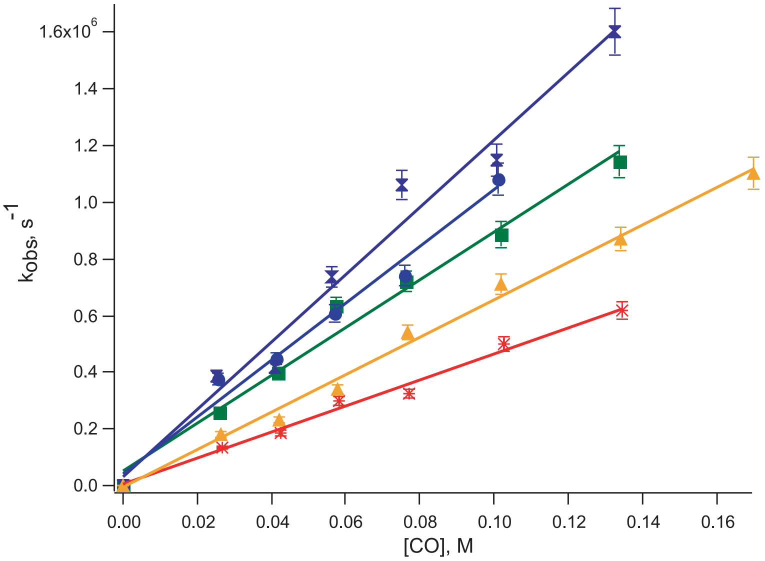


Fig. 3. Plots of $k_{obs}$ vs. [CO] for the decay of the transient $Mo(CO)_5(Sol)$ as monitored at 1931 $cm^{-1}$ in cyclohexane solution.

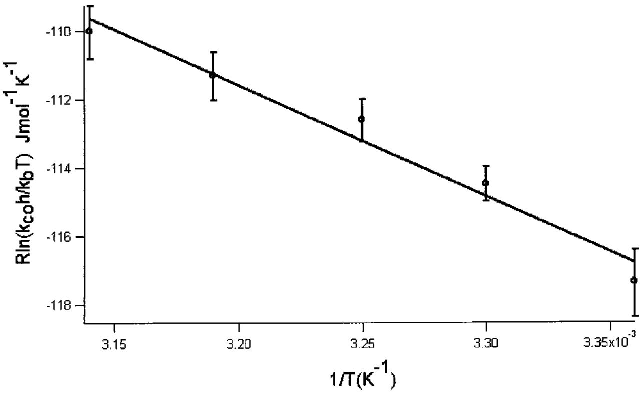


Fig. 4. Eyring plot of $k_{CO}$ data in Fig. 3 for the reaction of CO with $Mo(CO)_5(Sol)$ in cyclohexane solution.

in this determination and concludes that the $Mo(CO)_5$–alkane bond energy in alkane solution is 45 ± 4 kJ $mol^{-1}$. Notably this value is about 12 kJ $mol^{-11}$ larger than the $\Delta H^{\neq}_{CO}$ determined above for Eq. (3). In this context, one might safely argue that the rate limiting step of this substitution reaction is unlikely to be a limiting dissociative pathway since the activation energy of such a step would be expected to have a minimum value equal to or greater than the equilibrium bond energy. Similarly, one would expect a more positive entropy of activation than the $\Delta S^{\neq}_{CO}$ seen here. The near zero value of $\Delta S^{\neq}_{CO}$ would to be appear more consistent with a concerted or interchange substitution mechanism. In this context, we favor an interchange mechanism where there is considerable Mo–Sol bond breaking at the transition state given that $\Delta H^{\neq}_{CO}$ is about 75% that of the metal–alkane bond.

## Acknowledgements

This research was supported by a grant (DE-FG03-85ER13317) to PCF from Division of Chemical Sciences, Office of Basic Energy Research, US Department of Energy. C.K. thanks TUBITAK for financial support.

## References

[1] (a) P.C. Ford, J.S Bridgewater, S. Massick, J. Marhenke, Catal. Today 49 (1999) 419;
(b) P.C. Ford, S. Massick, Coord. Chem. Rev. 226 (2002) 39.
[2] J.S. Bridgewater, J.R. Schoonover, T.L. Netzel, S.M. Massick, P.C. Ford, Inorg. Chem. 40 (2001) 1466.
[3] (a) W.T. Boese, P.C. Ford, J. Am. Chem. Soc. 117 (1995) 8381;
(b) K.L. McFarlane, B. Lee, W.F. Fu, R. van Eldik, P.C. Ford, Organometallics 17 (1998) 1826;
(c) S. Massick, J. Rabor, S. Elbers, J. Marhenke, S. Bernhard, J. Schoonover, P.C. Ford, Inorg. Chem. 39 (2000) 3098;
(d) S.M. Massick, V. Mertens, J. Jon Marhenke, P.C. Ford, Inorg. Chem. 41 (2002) 3553;
(e) S.M. Massick, T. Büttner, P.C. Ford, Inorg. Chem. 42 (2003) 575.
[4] J.R. Zoeller, N.L. Buchanan, T.J. Dickson, K.K. Ramming, Catal. Today 49 (1999) 431.
[5] (a) J.R. McCusker, F. Qian, L.J. McElwee-White, Mol. Catal. A: Chem. 159 (2000) 11;
(b) H.C.M. Vosloo, J.A.K. Du Plessis, J. Mol. Catal. 79 (1993) 7.
[6] (a) H. Hermann, F.W. Grevels, A. Henne, K. Schaffner, J. Phys. Chem. 86 (1982) 5151;
(b) J.M. Kelly, C. Long, R. Bonneau, J. Phys. Chem. 87 (1983) 3344;
R. Bonneau, J.M. Kelly, J. Am. Chem. Soc. 102 (1980) 1220;
(c) J.A. Ganske, R.N. Rosenfeld, J. Phys. Chem. 93 (1989) 1959.
[7] (a) A.G. Joly, K.A. Nelson, Chem. Phys. 152 (1991) 69;
(b) T.P. Dougherty, E. Heilweil, J. Chem. Phys. Lett. 227 (1994) 1.

[8] (a) F.W. Grevels, J. Jacke, S. Ozkar, J. Am. Chem. Soc. 109 (1987) 7536;
(b) D.E. Marx, A. Lees, J. Inorg. Chem. 26 (1987) 620;
(c) S. Wieland, R. Van Eldik, J. Phys. Chem. 94 (1990) 5865;
(d) A. Shagal, R.H. Schultz, Organometallics 21 (2002) 5657;
(e) C. Breheny, J.M. Kelly, C. Long, S. O'Keeffe, M.T. Pryce, G. Russell, M.M. Walsh, Organometallics 17 (1998) 3690;
(f) D.J. Darensbourg, J.D. Draper, B.J. Frost, J.H. Reibenspies, Inorg. Chem. 38 (1999) 4705.

[9] S.M. Massick, P.C. Ford, Organometallics 18 (1999) 4362.

[10] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents: Physical Properties and Methods of Purification, John Wiley & Sons, New York, 1986.

[11] IUPAC Solubility Data Series: Vol. 43. Carbon Monoxide, Pergamon Press, Oxford, 1990.

[12] (a) G.K. Yang, V. Vaida, K.S. Peters, Polyhedron 7 (1988) 1619;
(b) J. Morse, G. Parker, T.J. Burkey, Organometallics 8 (1989) 2471;
(c) T. Jiao, G.-L. Leu, G.J. Farrell, T.J. Burkey, J. Am. Chem. Soc. 123 (2001) 4960.