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Further kinetics studies of intermediates formed by flash photolysis of Mo(CO)₆

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Dedicated to Professor Robert J. Angelici.

Abstract

Kinetics studies of the behavior of $Mo(CO)_5(CH)$ in the presence of radical initiators were conducted in cyclohexane (CH) solution by laser flash photolysis with time-resolved infrared detection. Activation parameters were determined for reactions of $Mo(CO)_5(CH)$ with toluene and with photochemical radical generator dibenzylketone (DBK) in the presence of excess CO. © 2008 Elsevier B.V. All rights reserved.

Keywords: Molybdenum; Carbonyl; TRIR; Kinetics; Mechanism

1. Introduction

Although the chemistry and photochemistry of group VI metal carbonyls have been extensively studied [1–3], these and related complexes continue to attract the attention as catalyst precursors. An example is the carbonylation of ethylene catalyzed by molybdenum hexacarbonyl with ethyl iodine [4,5], proposed to proceed by molybdenum carbonyl radical intermediates. The present study was undertaken in order to evaluate whether such intermediates might be generated by flash photolysis of a mixture of Mo(CO)₆ and a potential radical precursor in solution.

As background, previous studies have shown that flash photolysis of $Mo(CO)_6$ solutions leads to immediate dissociation of one CO (<1 ps) followed by formation of the solvated complex $Mo(CO)_5(sol)$ as identified by time-resolved infrared (TRIR) and optical (TRO) spectroscopy (Eq. (1)) [6]. The latter species undergo further reaction with CO and other ligands at rates that are dominated by the strength of the metal–sol interactions [7–10]. The photo-

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chemical behavior of cyclohexane (CH) solutions of $Mo(CO)_6$ under a CO atmosphere was recently reexamined in this laboratory using a high pressure/variable temperature (HP/VT) flow cell that allows for examining the reactions over much wider ranges of CO pressures (P_{CO}) and temperatures (T) than previously studied. In this manner, an accurate activation enthalpy (ΔH_{CO}^{\dagger}) was determined for the reaction of $Mo(CO)_5(CH)$ with CO. This proved to be significantly less than the Mo–CH bond enthalpy determined previously, so an interchange dissociative (I_d) ligand substitution mechanism was proposed [10].

A question posed when initiating the present study was whether these pathways would significantly altered by the simultaneous generation of radicals. For example, dibenzylketone (DBK) has been shown to generate radicals upon photolysis by a step-wise process to give two equivalents of the benzyl radical (Bz' = PhCH₂') plus CO with an overall quantum yield of ~0.7 [11]. There is significant overlap of the electronic spectra of DBK and Mo(CO)₆, so photolysis of cyclohexane solutions containing both should lead to simultaneous benzyl radical formation from the former and CO photodissociation from the latter ($\sigma_{CO} \sim 0.75$) [12,13] to give Mo(CO)₅(CH). The goal of

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the present study was to evaluate whether such radicals affected the products or reaction dynamics of the subsequent reactions of the intermediate $Mo(CO)_5(CH)$.

2. Experimental

2.1. Materials

Cyclohexane and toluene (Aldrich) were dried and distilled under N₂ according to published procedures [14]. Mo(CO)₆, and dibenzylketone (DBK) were purchased from commercial sources and dried under vacuum prior to storing in the glovebox without further purification. All the solutions were prepared on the glovebox under Ar. The Mo(CO)₆, was weighed and dissolved in cyclohexane (CH), then precise volumes of toluene (TOL) and or other reactants were measured with micro-syringes, such that the concentrations were known with accuracy. Solution concentrations of CO were calculated from published solubility data and the measured pressures [15]. All gases used for flash photolysis experiments were passed through an Oxyclear oxygen scrubber, all the samples were prepared in an inert atmosphere glovebox under argon, and the CO was 99.999% pure.

2.2. Flash photolysis studies

Photolysis studies were carried out in a custom-built HP/VT IR flow cell described previously [16]. This cell allows excellent control of the reactant gas pressures and the temperature while insuring that the sample will not be subject to repetitive excitation to generate secondary photoproducts. Solutions were excited by pulsed lasers, and the temporal IR absorbances were studied using the time resolved infrared (TRIR) point-by-point detection system described before [10,16]. The excitation pump sources were either a Lambda Physik XeCl excimer laser at (308 nm operating at 2 Hz) or a Nd:YAG pulse laser using the third harmonic (355 nm) operating at 2 or 10 Hz. The excitation pulses had an energy of \sim 15–20 mJ/pulse with a width of 10–20 ns.

3. Results and discussion

In our recent photochemical study of Mo(CO)₆ in cyclohexane [10], the TRIR difference spectrum seen upon flash photolysis (355 nm) exhibited three features in the v_{CO} region. These were the prompt transient bleach at 1987 cm⁻¹ corresponding to depletion of Mo(CO)₆ and the prompt transient absorptions at 1965 (strong) and 1931 (medium) cm⁻¹ corresponding to formation of the pentacarbonyl intermediate Mo(CO)₅(CH). The back reaction of Mo(CO)₅(CH) with CO to regenerate Mo(CO)₆ (Eq. (1)) followed second order kinetics with a rate constant $k_{CO} = 4.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, and temperature dependence studies gave $\Delta H_{CO}^{\ddagger} = 33 \pm 3 \text{ kJmol}^{-1}$. Given that ΔH_{CO}^{\ddagger} was less than the Mo–CH bond energy $(45 \pm 4 \text{ kJ mol}^{-1})$ determined by Burkey et al. [17] using photoacoustical techniques, an interchange dissociative (I_d) mechanism was proposed [10].

$$Mo(CO)_5(CH) + CO \Longrightarrow Mo(CO)_6 + CH$$
 (1)

A cyclohexane solution of $Mo(CO)_6$ and DBK would be characterized by the overlapping absorption spectra of these two species, so as a result, irradiation at either 308 nm (XeCl excimer laser) or 355 nm (3rd harmonic of Nd:YAG laser) results in excitation of both. After flash photolysis, the solution also include the solvento derivative $Mo(CO)_5(CH)$ plus $Mo(CO)_5(DBK)$ and various radical intermediates. For this reason, the flash photolysis of $Mo(CO)_6$ was first studied in the presence of an aromatic ligand (toluene) for which radical intermediates were not anticipated.

3.1. Reactions with toluene

Flash photolysis of the Mo/toluene/CO/cyclohexane system led to a bleach on the signal at 1987 cm^{-1} owing to the depletion of $Mo(CO)_6$ and the appearance of transient absorbances (TA) at 1964 and 1930 cm⁻¹ corresponding to the "prompt" formation of Mo(CO)₅(CH). New transient absorbances (TA) at 1954 and 1920 cm^{-1} (weaker), not seen for experiments in cyclohexane alone, were also apparent and these were attributed to formation of the complex $Mo(CO)_5(Tol)$ (Tol = toluene) (Eq. (2)) by analogy to similar Mo(CO)₅L spectra. The TA at 1954 cm^{-1} reached a maximum in 10–20 µs with a magnitude dependant on the toluene concentration [Tol]. In the absence of CO, no appreciable further changes in the 1954 cm⁻¹ absorption were observed on the experimental timescale, which had an upper limit of about 1 s, but under CO, the signal at decayed in the ms time-scale. The latter process was assigned to be the reaction of Mo(CO)₅(Tol) with CO to regenerate $Mo(CO)_6$ (Eq. (3)).

$$Mo(CO)_5(CH) + Tol \Rightarrow Mo(CO)_5(Tol) + CH$$
 (2)

$$Mo(CO)_5(Tol) + CO \rightarrow Mo(CO)_6 + Tol$$
 (3)

Both the appearance and the slower disappearance of the TA at 1954 cm⁻¹ for a solution having a fixed CO pressure of 6.1 atm (0.055 M) proved to be first order giving the apparent rates constants $k_{obs}(2)$ and $k_{obs}(3)$ that were dependent on [Tol]. The first step was accelerated by increasing [Tol] and a plot of $k_{obs}(2)$ values versus [Tol] was linear with a slope $k_{tol} = 6.2 \ (\pm 0.7) \times 10^6 \ M^{-1} \ s^{-1}$ (298 K). Thus the reaction of Mo(CO)₅(CH) with toluene (Eq. (2)) is modestly faster than the analogous reaction with CO (see above). The disappearance of $Mo(CO)_5(Tol)$ in the second step was, in contrast, slowed by the higher toluene concentrations as illustrated by the linear plot of the reciprocal rate constant $1/k_{obs}(3)$ versus [Tol] (Fig. 1). This behavior is consistent with the formation of an intermediate I in the reaction of the toluene complex with CO as illustrated by Scheme 1.



Fig. 1. Plot of $(k_{obs}(2))^{-1}$ versus [Tol] for the slow decay of the 1954 cm⁻¹ band attributed to Mo(CO)₅(Tol) and generated by 308 nm flash photolysis of Mo(CO)₆ (0.72 mM) in 298 K cyclohexane solution under 6.1 atm CO.

$$Mo(CO)_{5}(Tol) \xrightarrow{k_{1}} I + Tol$$

$$I + CO \xrightarrow{k_{2}} Mo(CO)_{6}$$
Scheme 1.

Such an intermediate I might be $Mo(CO)_5$ or, more likely, $Mo(CO)_{5}(CH)$. For this scheme, the observed rate constant would be Eq. (4), and a plot of the reciprocal $(k_{obs}(3))^{-1}$ versus [Tol] is predicted to be linear with a slope $= k_{-1}/k_1k_2$ [CO] and an intercept $= k_1^{-1}$. The respective values of the slope and intercept k_1 . The respective values of the slope and intercept in Fig. 1 are $(2.3 \pm 0.1) \times 10^{-3}$ s M⁻¹ and $(93 \pm 9) \times 10^{-6}$ s. These would give $k_1 = \sim 1.1 \times 10^4$ s⁻¹ and a value for the ratio k_{-1}/k_2 of 1.33 \pm 0.2. This ratio is remarkably close to value of 1.35 for the ratio k_{tol}/k_{CO} , where k_{tol} is the second order rate constant for the formation of $Mo(CO)_5(Tol)$ (Eq. (2)) described above and k_{CO} is the second order rate constant for the reaction of Mo(CO)₅(CH) with CO to reform $Mo(CO)_6$ (Eq. (1)) as independently measured [10]. This agreement strongly suggests that I is Mo(CO)₅(CH). If this is the case, it may further be argued that the ratio k_{tol}/k_1 is the equilibrium K_{tol} for constant for the formation of Mo(CO)₅(Tol) from Mo(CO)₅(CH) plus toluene in cyclohexane solution (Eq. (2)), the value being $\sim 6 \times 10^2 \text{ M}^{-1}$.

$$k_{\rm obs}(3) = \frac{k_1 k_2 [\rm CO]}{k_{-1} [\rm Tol] + k_2 [\rm CO]}$$
(4)

The apparent activation parameters of the reactions indicated in Eqs. (2) and (3) were determined by measuring the $k_{obs}(2)$ and $k_{obs}(3)$ values at 25, 30, 35, 40 and 45 °C upon flash photolysis of a cyclohexane solution of Mo(CO)₆ for a specific set of conditions with [toluene] = 18 mM and $P_{CO} = 2.5$ atm. Several independent sets of experiments were carried out under these conditions using different excitation and monitoring wavelengths, with reasonable agreement for ΔH^{\ddagger} (apparent) = 34 ± 4 kJ mol⁻¹ and $\Delta S^{\ddagger}(\text{apparent}) = -32 \pm 16 \text{ J K}^{-1} \text{ mol}^{-1} \text{ for } k_{\text{obs}}(2)$ and $54 \pm 6 \text{ kJ mol}^{-1}$ and $41 \pm 24 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, for $k_{\text{obs}}(3)$. The ΔH^{\ddagger} for Eq. (2) is quite similar to that recorded for the reaction of Mo(CO)₅(CH) with CO and sufficiently less than the Mo(CO)₅-alkane bond enthalpy [17] of $45 \pm 4 \text{ kJ mol}^{-1}$. This suggests that the mechanism for Eq. (2) is also I_d. The substantially larger ΔH^{\ddagger} for Eq. (3) is likely due to the more stable molybdenum-to-toluene bond in Mo(CO)₅(Tol).

3.2. Flash photolysis in the presence of dibenzyl ketone

As noted above, the photolysis of DBK generates benzyl radicals. The mass spectra of the photoproduct solutions indicated the formation of diphenylethane consistent with this process. Furthermore, the FTIR spectrum of these solutions during the photolysis showed the progressive disappearance of the $v_{\rm CO}$ band at 1718 cm⁻¹ characteristic of DBK.

Flash photolysis of a cyclohexane solution of $Mo(CO)_6$ plus DBK under CO with TRIR detection shows prompt signals corresponding to the formation of the transient complex Mo(CO)₅(CH) at 1964 and 1930 cm⁻¹ and the bleach at 1987 cm⁻¹ corresponding to depletion of the Mo(CO)₆. Subsequently, three new bands appear at 1944 (strong) and 1920 (medium) cm^{-1} that we attribute to the formation of Mo(CO)₅(DBK) by analogy with similar products such as $Mo(CO)_5(Tol)$, etc. The 1964 cm⁻¹ band of Mo(CO)₅(CH) decayed on the ms time scale, at a rate similar to the appearance of Mo(CO)₅(DBK) (Fig. 2). The temporal behavior of the 1944 cm^{-1} band in the TRIR experiment was analogous to that described above for the toluene complex; that is, it grew in exponentially in the first few µs, then decayed on the ms time-scale. A key difference was that it appeared faster,¹ and disappeared several orders of magnitude more slowly, than the comparable signals for the toluene complex under similar conditions. No other transient IR bands were seen that could be attributed to prospective intermediates such as the radicals $Mo(CO)_5(Bz)$ or $Mo(CO)_5(C(O)Bz)$.

Two excitation wavelengths ($\lambda_{irr} = 355$ nm or 308 nm) were utilized for the flash studies, but the kinetics results were essentially equivalent (within experimental uncertainties), so data from the 355 nm experiments will be reported here. In addition, varying the CO pressure over the reaction solution from $P_{CO} = 0$ (argon atmosphere) to 6.1 atm had no measurable effect on the rate for appearance of Mo(CO)₅(DBK) but showed a small, systematic increase in the rate for disappearance of Mo(CO)₅(CH). This would be expected given the much slower rate for reaction of the latter with CO. As Table 1 shows, the $\Delta H^{\ddagger}s$ determined for the disappearance of Mo(CO)₅(CH) are

¹ For example, with [L] = 28 mM and $P_{CO} = 6.1 \text{ atm}$, the formation of Mo(CO)₅L displayed k_{obs} values of $6.7 \times 10^5 \text{ s}^{-1}$ and $6.6 \times 10^6 \text{ s}^{-1}$ for L = Tol and DBK, respectively.



Fig. 2. TRIR absorbance changes after flash photolysis ($\lambda_{irr} = 308 \text{ nm}$) of a solution of Mo(CO)₆ and dibenzyl ketone in cyclohexane under 6.10 atm of CO (298 K): (a) at 1964 cm⁻¹ (disappearance of Mo(CO)₅(CH)), 5 µs time scale; (b) at 1944 cm⁻¹ (formation of Mo(CO)₅(DBK)), 5 µs time scale; and (c) at 1944 cm⁻¹ (disappearance of Mo(CO)₅(DBK)), 500 ms timescale.

Table 1

Apparent activation parameters determined for 355 nm flash photolysis of a cyclohexane solution of $Mo(CO)_6$ (0.0014 M) and DBK (0.014 M) under 6.1 atm CO

Monitoring frequency	ΔH^{\ddagger} (kJ mol ⁻¹)	$\frac{\Delta S^{\ddagger}}{(\mathrm{J}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1})}$
1964 cm ⁻¹ , disappearance of Mo(CO) ₅ (CH)	18 ± 3	-65 ± 12
1944 cm ⁻¹ , appearance of Mo(CO) ₅ (DBK)	20 ± 3	-79 ± 12
1944 cm^{-1} , decay of Mo(CO) ₅ (DBK)	71 ± 3	$+37\pm12$

considerably lower than for analogous reactions of $Mo(CO)_5(CH)$ with CO only or with CO and toluene, and the ΔS^{\ddagger} values are more negative. Furthermore, this

 ΔH^{\ddagger} is about half the enthalpy of Mo–CH bond dissociation enthalpy, so we again discount a limiting dissociative pathway as being the dominant mechanism for this substitution reaction.

$$Mo(CO)_{5}(CH) + DBK \rightleftharpoons Mo(CO)_{5}(DBK) + CH$$
 (5)

In this context we might consider two scenarios. The first would be that formation of Bz radicals, which occurs concurrently with the photodissociation of CO from Mo(CO)₆ owing to the overlapping absorptions at the excitation wavelength,² catalyzes the substitution of DBK for CH in the Mo coordination sphere thereby lowering ΔH^{\ddagger} . The second would be that the mechanism of ligand substitution with DBK as the entering ligand L is considerably more associative in character than when L = CO or Tol owing to its greater nucleophilicity. The higher donor strength of DBK is evidenced by the lower v_{CO} values seen for IR spectrum of Mo(CO)₅(DBK) relative to those seen for L = Tol or CH [18].

The effect of varying DBK concentration on the $k_{obs}(5)$ values for the appearance of Mo(CO)₅(DBK) is summarized in Table 2. Notably, increasing [DBK] consistently leads to increasing $k_{obs}(5)$, although the net effect is not strictly linear. Nonetheless, at the lower concentrations of DBK, the apparent second order rate constant derived from the ratio $k_{obs}(5)/[DBK]$ is $\sim 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K. This would more than a factor of 50 more than that for L = CO and falls in a reactivity series DKB > $^{n}\text{PrBr} > \text{Tol} \sim \text{CO}$ consistent with the Lewis base strengths of such ligands. As a consequence, it would appear that the reaction of Mo(CO)₅(CH) with various ligands L is occurring by an interchange mechanism with increasing importance of Mo–L bond formation (associative character) with the more nucleophilic ligands.

With regard to the prospective radical-catalyzed pathway, the data in Table 2, argue strongly against this possibility, since a larger percentage of the energy from the initial flash is absorbed by DKB at higher [DBK]. As a consequence, substantial concentrations of Bz radicals are initially formed (in concentrations comparable to Mo(CO)₅-(CH)) and the generation of such radicals represents an increasingly larger fraction of the total photoreaction at these higher [DBK]. Yet the nonlinearity of data in Table 2 represents a decreasing net activity of DBK as its concentration increases, not the increased activity expected if the reaction were radical-catalyzed. An even more telling experiment was one where a 298 K cyclohexane solution of Mo(CO)₆ (0.42 mM) and DBK (18.2 mM) was subjected to flash photolysis at 308 nm under an argon atmosphere with the flash intensity varied by a factor of five from 5 mJ to 25 mJ. Although this should have raised the

² The different absorption of the chemicals at 308 and 355 nm shows that our work solution $(1.43 \times 10^{-3} \text{ M in } \text{Mo}(\text{CO})_6 \text{ and } 1.4 \times 10^{-2} \text{ M in } \text{DBK})$ at 308 nm ~33% of the light is absorbed by the Mo, while at 355 nm ~50% is absorbed.

Table 2

Rate constants $k_{obs}(5)$ measured for the formation of Mo(CO)₅(DBK) from Mo(CO)₅(CH) in cyclohexane solution (298 K) initiated by flash photolysis at 355 nm^a

[DBK](mM)	$k_{\rm obs}(5)$ (in $10^6 {\rm s}^{-1}$)	$k_{\rm obs}(5)/[{\rm DBK}]$ (in 10 ⁸ M ⁻¹ s ⁻¹)
11.4	3.0 (±0.2)	2.7
14.3	3.6 (±0.2)	2.6
17.5	3.9 (±0.2)	2.2
20.7	4.8 (±0.3)	2.3
28.5	6.6 (±0.2)	2.3
38.0	7.7 (±0.2)	2.0

^a [Mo(CO)₆] = 0.76 mM, $P_{CO} = 6.1$ atm CO. The rate constant $k_{obs}(5)$ was determined for the appearance of the strong v_{CO} band at 1942 cm⁻¹ assigned to Mo(CO)₅(DBK).

concentrations of Bz fivefold, there was no impact whatsoever of flash intensity on the first order rate constant $k_{obs}(5)$ for the formation of Mo(CO)₅(DBK) from Mo(CO)₅(CH).

In summary, flash photolysis studies of $Mo(CO)_6$ in the weakly coordinating solvent cyclohexane show that the first formed intermediate $Mo(CO)_5(CH)$ reacts with various ligands L give the $Mo(CO)_5L$ complexes via a rate law that is essentially second order. The second order rate constants k_L follow an order $L = DBK > ^nPrBr >$ toluene consistent with donor abilities of such ligands. Simultaneous generation of benzyl radicals PhCH₂ in significant solution concentrations had little or no influence on this ligand substitution reaction. Given the well known effects of radicals on catalyzing other ligand substitution reactions of metal carbonyls, a likely explanation of the absence of similar effect on $Mo(CO)_5(DBK)$ formation is that the high reactivity of the $Mo(CO)_5(CH)$ system makes it insensitive to such catalysis by a relatively stable radical such as Bz.

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