Photochemical Reactions of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (Mo–Mo) and Dark Reactions of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (Mo≡Mo) with $NaNO_2$ and $NaNO_3$: Reduction of NO_2^- and NO_3^- to Co-ordinated NO

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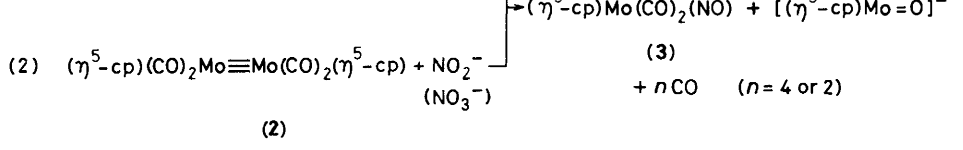
Photochemical reactions of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ with NO_2^- (irradiation at 507 or 391 nm) or dark reactions of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ with NO_2^- and NO_3^- give $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$.

In recent years there has been a growing interest in the photochemical behaviour of the Mo–Mo single bond in $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (**1a**)[1] and the reactivity of the Mo≡Mo triple bond in $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (**2a**).[2] However, comparative studies on the behaviour of both single and triple bonds towards particular substrates have been limited.

This communication reports a study of the reactivities of (**1a**) and (**2a**) toward NO_2^- and NO_3^- which have a strong affinity for low valent molybdenum.

Irradiation (at λ = 507, 391 nm or sunlight) of (**1a**) in a degassed tetrahydrofuran (THF) or THF–MeOH (1 : 1) solution containing excess $NaNO_2$ (3.3 equiv.) gave $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ (**3a**)[3] in a 90% yield [based on the stoicheiometry of equation (1)] and several oxide species including $\{[Mo(\eta^5\text{-}C_5H_5)(O)_2]_2O\}$ (**4a**)[4] [equation (1)]. When $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$ (**1b**) was used for the reaction instead of (**1a**), $[Mo(\eta^5\text{-}C_5Me_5)(CO)_2(NO)]$ (**3b**),[5] $\{[Mo(\eta^5\text{-}C_5Me_5)(O)_2]_2O\}$ (**4b**), and $[Mo(\eta^5\text{-}C_5Me_5)(O)_2]_2$ (**5b**) were



a; cp = C_5H_5
b; cp = C_5Me_5
Equation (1) photochemical reaction.
Equation (2) dark reaction.

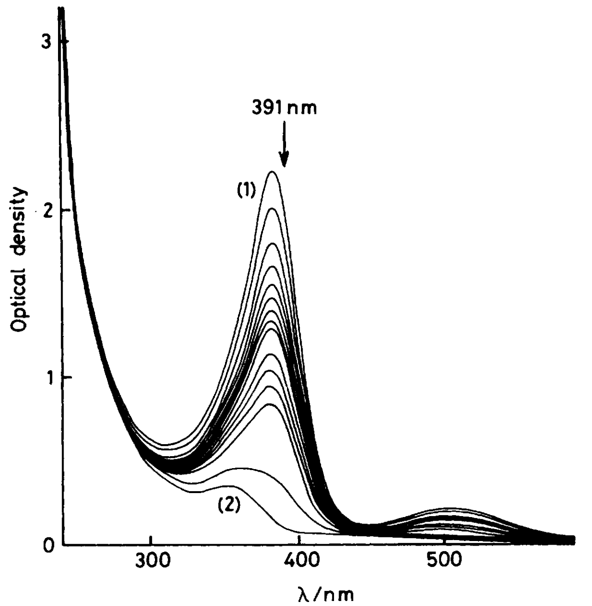
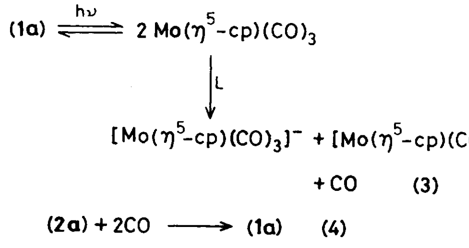


Figure 1. Absorption spectral changes of (**1a**) in MeOH–THF containing $NaNO_2$ with time on irradiation at 391 nm at 25 °C. Curves (1) and (2) represent the spectra after irradiation for 0 and 45 min, respectively. The initial concentrations of the starting complex and $NaNO_2$ were 0.13 and 7.3 mmol dm^{-3}, respectively.



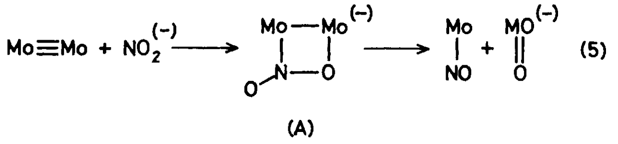
$$(1a) \xrightleftharpoons{h\nu} 2\,Mo(\eta^5\text{-cp})(CO)_3 \xrightarrow{L} [Mo(\eta^5\text{-cp})(CO)_3]^- + [Mo(\eta^5\text{-cp})(CO)_2L_2]^+ + CO \quad (3)$$

$$(2a) + 2CO \longrightarrow (1a) \quad (4)$$

L = THF or MeOH

isolated in 48, 42, and 37% yields, respectively.† The i.r. assay confirmed that the reactions did not generate CO_2 *in situ*, suggesting that one of the oxygen atoms in NO_2^- was transferred to the molybdenum atom but not to the co-ordinated CO to produce the oxide species.[6] Neither NO_2^- nor NO_3^- reacted thermally with (**1a**) in the dark.

The disappearance of (**1a**) according to reaction (1) could be conveniently monitored by spectrophotometry (Figure 1).‡ The quantum yields of the reaction of (**1a**) with NO_2^- (60 equiv.) were 0.064 (irradiation at 507 nm) and 0.065 (at 391 nm) and did not show any marked wavelength dependence.§



$$Mo{\equiv}Mo + NO_2^{(-)} \longrightarrow \underset{(A)}{\underset{O\diagup N-O}{Mo-Mo^{(-)}}} \longrightarrow \underset{NO}{Mo} + \underset{O}{\overset{\|}{Mo^{(-)}}} \quad (5)$$

$\{[Mo(\eta^5\text{-cp})(O)_2]_2O\}$
(**4**)

$[Mo(\eta^5\text{-cp})(O)_2]_2$
(**5**)

a; cp = C_5H_5
b; cp = C_5Me_5

The irradiation of (**1a**) results in homolytic cleavage of the metal–metal bond with the concurrent formation of metal radical intermediates and in polar, co-ordinating solvents disproportionation sometimes occurs [equation (3)].[1] In reaction (1), however, a small dependence of the quantum yield on the NO_2^- concentration was observed.¶ It is therefore possible that the metal radical intermediate participates in the reaction to give the nitrosyl complex, although the true mechanism is still obscure.

However, the reactions of (**2a**) with a Mo≡Mo triple bond with excess of NO_2^- and NO_3^- in the dark (THF, 25 °C) gave (**3a**) [yields based on the stoicheiometry of equation (2): 23 and 14%, respectively], the molybdenum oxide species, and (**1a**) [equation (2)]. Complex (**1a**) could be formed by the subsequent reaction of the liberated CO with (**2a**), equation (4). In the reactions of $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ (**2b**) with the anions, (**3b**) and the molybdenum oxide species, (**4b**) and (**5b**), were also obtained (NO_2^-: 62, 27, and 36% yields, NO_3^-: 18, 34, and 10% yields, respectively). No carbon dioxide gas was generated in these reaction systems.

It is well known that molybdenum complexes reduce NO_3^- to NO_2 under anhydrous conditions.[7] In the present case, the reactions of (**2a**) and (**2b**) with NO_3^- also may give NO_2 in the initial step, which reacts directly with the Mo≡Mo bond to form the NO complexes without any disproportionation producing NO_3^- and NO_2^-.[8] Although the evolution of NO_2 was not examined, it was found that (**2a**) and (**2b**) react readily with NO_2 gas to give (**3a**) and (**3b**) under the same conditions.

A possible mechanism for the formation of the nitrosyl complexes from the dark reactions of (**2a**) or (**2b**) with NO_2^- and NO_2 is shown in equation (5). NO_2^- or NO_2 interacts with the Mo atoms before the oxygen atom is transferred on to one of them. Nitro groups are known to bridge two metal atoms through N and O atoms as in intermediate (A).[9]

The results presented here suggest that the Mo–Mo single bond is selective towards one electron reduction ($NO_2^- \rightarrow NO$) in the photochemical reaction while the Mo≡Mo triple bond can effect both the one electron reduction ($NO_2^- \rightarrow NO$) and three electron reduction ($NO_3^- \rightarrow NO$) in the dark reactions. The three electron reduction is thought to involve a two electron reduction of the NO_2 produced by the preceding one electron reduction of NO_3^-.

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† All new complexes gave satisfactory analyses and were characterized by molecular weight measurements and ^1H n.m.r. and i.r. spectroscopy.

‡ The starting material, (**1a**), has characteristic u.v.–visible absorption bands in the region 350—550 nm: $\lambda_{max.}$; 385 (ε 17 700, σ–σ* transition) and 505 nm (ε 1 650, dπ–σ* transition), while (**3a**) does not have an absorption maximum in the same region (ε 430 at 385 nm, ε 58.2 at 505 nm).

§ Quantum yield measurements were based on the disappearance of the band at 385 nm due to (**1a**). Irradiation intensities were measured by ferrioxalate actinometry at 391 or 507 nm. The light source was a 500-W xenon short-arc lamp with interference filters of 391 or 507 nm for wavelength selection.

¶ The quantum yields for the $NaNO_2$ concentrations of 7.3, 1.2, and 0.51 mmol dm^{-3} under a constant concentration of (**1a**) (0.13 mmol dm^{-3}) were 0.065, 0.051, and 0.043 respectively (error limits: ±0.007 in each) on irradiation at 391 nm.

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