

PRODUCT DISTRIBUTION OF A PHOTOCHEMICAL REACTION AS A FUNCTION OF LIGHT INTENSITY

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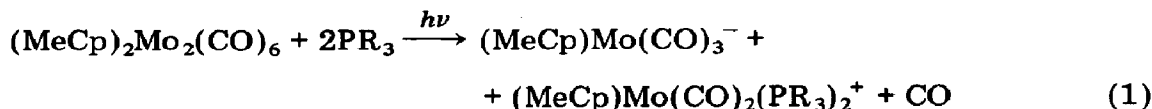
Summary

Disproportionation and substitution occur as parallel reactions when $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ ($\text{MeCp} \equiv \eta^5\text{-CH}_3\text{C}_5\text{H}_4$) is irradiated in the presence of $\text{P}(\text{OCH}_3)_3$. The products of the disproportionation reaction are $(\text{MeCp})\text{Mo}(\text{CO})_3^-$ and $(\text{MeCp})\text{Mo}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2^+$ while the product of the substitution reaction is $(\text{MeCp})_2\text{Mo}_2(\text{CO})_4(\text{P}(\text{OCH}_3)_3)_2$. The ratio of the quantum yield for disproportionation to that of substitution is dependent on the intensity of the exciting light. This result is in agreement with mechanisms proposed for the disproportionation and substitution reactions.

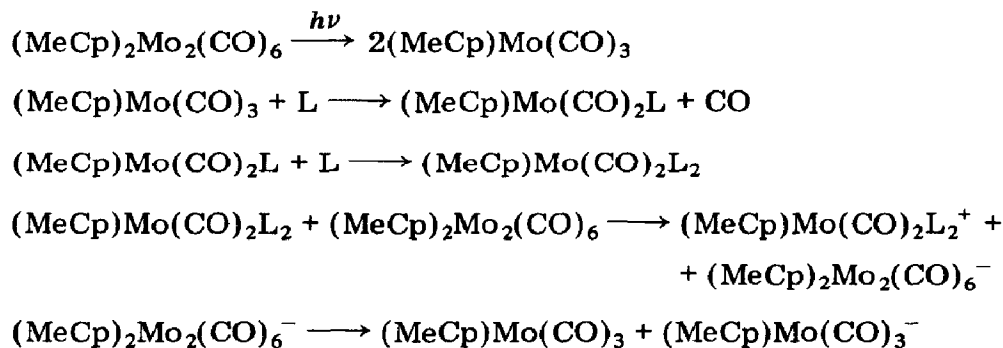
1. Introduction

It is well established that the product distribution of a photochemical reaction can be dependent on the solvent, the temperature, the concentration of the reactants and the wavelength of the exciting light. However, the effect of light intensity on the product distribution is generally ignored [1] (although the intensity can affect the quantum yield of a reaction [2]). A simple analysis (Appendix A) shows that, when an excited state (or a photo-generated intermediate) and a ground state molecule react in competition with another excited state (or another intermediate) to give different products, the product ratio will be intensity dependent. Surprisingly, examples of this phenomenon are rare [1], especially in the photochemistry of organometallic complexes. We report here an organometallic photochemical system in which the product distribution is intensity dependent.

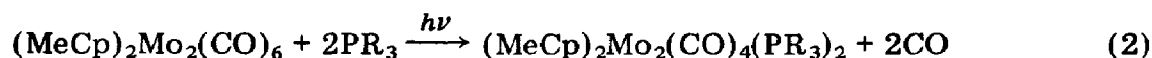
The photochemical disproportionation of $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ ($\text{MeCp} \equiv \eta^5\text{-CH}_3\text{C}_5\text{H}_4$) by phosphines and phosphites proceeds according to [3]



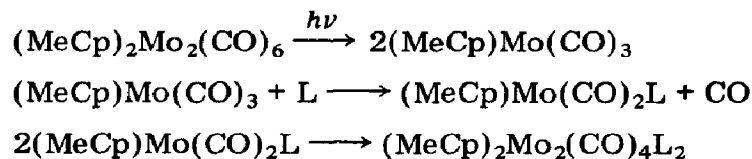
where PR_3 represents the phosphine or phosphite. (We use the MeCp ligand rather than the Cp ligand ($\text{Cp} \equiv \eta^5\text{-C}_5\text{H}_5$) because complexes of the former are more soluble in non-polar solvents.) We have shown that this reaction follows a radical chain pathway [3]:



where $\text{L} \equiv$ ligand. In addition to the ionic products formed in eqn. (1), substitution products of the type $(\text{MeCp})_2\text{Mo}_2(\text{CO})_4(\text{PR}_3)_2$ also form when $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ is irradiated in the presence of phosphines or phosphites:



Substitution reactions of metal-metal-bonded dimers are known to proceed via the following pathway [4]:



A comparison of the pathways in the above schemes shows that both pathways have the $(\text{MeCp})\text{Mo}(\text{CO})_2\text{L}$ intermediate in common. Disproportionation will occur if the $(\text{MeCp})\text{Mo}(\text{CO})_2\text{L}$ intermediate reacts with L before it can react with another $(\text{MeCp})\text{Mo}(\text{CO})_2\text{L}$ intermediate; if the $(\text{MeCp})\text{Mo}(\text{CO})_2\text{L}$ intermediate encounters another $(\text{MeCp})\text{Mo}(\text{CO})_2\text{L}$ before it reacts with L then the substitution product will form. The situation is thus one in which a photogenerated intermediate and a ground state molecule react in competition with another intermediate. The product distribution should be intensity dependent. Clearly, as the intensity of the exciting radiation is increased, the steady state concentration of $(\text{MeCp})\text{Mo}(\text{CO})_3$ (and thus $(\text{MeCp})\text{Mo}(\text{CO})_2\text{L}$) will increase and relatively more substitution product will form. This prediction has been experimentally verified. Table 1 shows the ratio of the quantum yield for substitution to that of disproportionation for the reaction of $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ with $\text{P}(\text{OCH}_3)_3$. The quantum yield for substitution increases relative to that for disproportionation as the intensity of the exciting light increases, in agreement with the analysis above.

TABLE 1

The ratio of the quantum yield of substitution to that of disproportionation as a function of exciting light intensity for the reaction of $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ with $\text{P}(\text{OCH}_3)_3$ ^a

Intensity (einstein min^{-1})	$\phi_{\text{sub}}/\phi_{\text{dispro}}$
1.2×10^{-6}	0.49
1.2×10^{-7}	0.21
1.2×10^{-8}	0.10

^a $[(\text{MeCp})_2\text{Mo}_2(\text{CO})_6] = 0.012 \text{ M}$; $[\text{P}(\text{OCH}_3)_3] = 0.25 \text{ M}$; $\lambda = 405 \text{ nm}$; in cyclohexane solution.

The effect of light intensity on product distributions is merely a curiosity when it is considered by itself. Of course, the real reason for investigating the effect of light intensity on product distributions is that, if a dependence is found, then the reaction mechanism must account for the dependence. Such a dependence can be a powerful check on a proposed mechanism. The intensity dependence of the product distribution for the reaction of $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ with $\text{P}(\text{OCH}_3)_3$ provides confirmation of the pathways in the above schemes.

2. Experimental details

$(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ was synthesized by methods reported in the literature [5] and recrystallized from cyclohexane. $\text{P}(\text{OCH}_3)_3$ was purchased from Aldrich, dried over sodium and distilled under nitrogen.

Photochemical experiments were performed under anaerobic conditions using an Oriel 200 W high pressure mercury arc lamp as the light source. 405 nm light was isolated using an interference filter obtained from Edmund Scientific. Lamp intensities were determined using ferrioxalate actinometry [6].

For the experiments described herein 0.6 g $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ in 10 ml of a 0.25 M solution of $\text{P}(\text{OCH}_3)_3$ in cyclohexane was irradiated at 405 nm. The product formation as a function of irradiation time was monitored using IR spectroscopy. IR spectra were obtained with a Perkin-Elmer 983 spectrophotometer. The disubstituted photoproduct $(\text{MeCp})_2\text{Mo}_2(\text{CO})_4(\text{P}(\text{OCH}_3)_3)_2$ has a carbonyl stretch at 1859 cm^{-1} ($\epsilon = 457 \text{ M}^{-1} \text{ cm}^{-1}$) and the anion $(\text{MeCp})\text{Mo}(\text{CO})_3^-$ produced in the disproportionation reaction has a carbonyl stretch at 1765 cm^{-1} ($\epsilon = 177 \text{ M}^{-1} \text{ cm}^{-1}$) [7, 8]. Lamp intensities were attenuated with Oriel Company neutral density filters.

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Appendix A

Let us consider a photochemical reaction in which an excited state can react with either another excited state or with a ground state molecule (Table A1). Then

$$\frac{\text{rate of formation of B}}{\text{rate of formation of D}} = \frac{k_1[A^*][A^*]}{k_2[A^*][C]} = \frac{k_1[A^*]}{k_2[C]}$$

TABLE A1

Reaction	Rate
$M \xrightarrow{h\nu} A^*$	I
$A^* + A^* \xrightarrow{k_1} B$	$k_1[A^*]^2$
$A^* + C \xrightarrow{k_2} D$	$k_2[A^*][C]$
$A^* \xrightarrow{k_3} M$	$k_3[A^*]$

Assuming the steady state condition for $[A^*]$, $d[A^*]/dt = 0$, then

$$[A^*] = \frac{-x + (x^2 + 8k_1I)^{1/2}}{2k_1}$$

where $x = k_2C + k_3$. Substituting this expression for $[A^*]$ into the rate ratio equation, we see that the amount of B which forms relative to the amount of D which forms is greater for larger values of the light intensity I . A similar but slightly more complicated expression is obtained for reactions involving intermediates rather than excited states.