The total free surface determines the crystal packing energy for moderately polar substances. A linear relationship is found between this energy and the free surface (or the total number of valence electrons). The relationship between packing forces and atomic free surfaces is a very important one. It appears that while the more exposed atoms have larger energetic relevances (that is, provide a larger amount of cohesive energy in crystals), the crystalline edifice is built so as to let any atom reach an average, constant atomic relevance. These arguments are, in fact, a (although partial) quantification of the close-packing principle: in the ideal close-packed crystal all atoms are exposed equally and have the same energetic relevance, corresponding to the maximum of intermolecular contacts in their coordination sphere. Future work along these lines may lead to a better understanding of crystal formation and growth.

A precise evaluation of molecular surface can be of great aid in studies of mutual molecular recognition, such as host–guest interactions in clathrates, or the reactant–substrate interplay in catalytic reactions (especially the biological ones). A natural extension of the method allows the computation of the free surface of biological polymers and its connection to effective or contact surfaces of biological interest.

Finally, it may be mentioned that the method can be adapted to give molecular area cross sections for studies of the deposition of monolayers on single-crystal metallic surfaces.[13]

(12) To give just two examples: (a) Adams, S. P.; Whitlock, H. W. *J. Am. Chem. Soc.* **1982,** *104,* 1602 (for the steric barrier to passage of arenes through the cavity of [8.8]paracyclophanes). (b) Seeman, J. I.; Viers, J. W.; Schug, J. C.; Stovall, M. D. *J. Am. Chem. Soc.* **1984,** *106,* 143 (for the dependence of reactivity to methylation in substituted pyridines from a geometrical accessibility factor at a crowded nitrogen atom).

(13) Gavezzotti, A.; Simonetta, M.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.,* in press.

All the computer software needed to perform the surface calculations is incorporated in the OPEC program[3,4] and is available for distribution upon request.

Note Added in Proof. Further work and discussion have brought to the author's attention the following points: (a) the exposure ratio, E_R, should be renamed to shielding ratio, since it is a minimum for linear and a maximum for globular molecules; (b) comparison with Bondi's work[5] (Table III) is at some points obscured by a different apportioning scheme for >C= and by differences in the oxygen and fluorine van der Waals radii; (c) S_M and S_{ai}'s provide a useful guide to strain and accessibility at molecular sites, and their relationship to steric hindrance should be viewed in this light; (d) the S_{ai}'s can be used to calculate how much of the molecular surface is hydrophobic (coming from C, H) and how much is hydrophilic (coming from N, O), giving hints to intermolecular and solvation properties of the molecule; (e) heavily fluorinated compounds are found to deviate from the correlation of eq 7, since fluorine has many valence electrons under a small surface.

The author is grateful to E. Maverick and K. Trueblood for useful discussions.

Photochemical Disproportionation of (MeCp)₂Mo₂(CO)₆ (MeCp = η⁵-CH₃C₅H₄) by Halides

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Abstract: The photochemical disproportionation of (MeCp)₂Mo₂(CO)₆ by halides in acetone, acetonitrile, or dimethyl sulfoxide proceeds according to the equation

$$(MeCp)_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu} (MeCp)Mo(CO)_3X + (MeCp)Mo(CO)_3^-$$

The quantum yields for the disproportionation are dependent on the absorbed intensity of the exciting light but are independent of the concentration of X⁻. At low exciting light intensities, the quantum yields are greater than one. The following chain pathway is proposed to account for these observations: (1) (MeCp)₂Mo₂(CO)₆ ($h\nu,\phi$) → 2(MeCp)Mo(CO)₃; (2) (MeCp)Mo(CO)₃ + solvent → (MeCp)Mo(CO)₃(solvent); (3) (MeCp)Mo(CO)₃(solvent) + (MeCp)₂Mo₂(CO)₆ → (MeCp)Mo(CO)₃(solvent)⁺ + (MeCp)₂Mo₂(CO)₆⁻; (4) (MeCp)₂Mo₂(CO)₆⁻ → (MeCp)Mo(CO)₃⁻ + (MeCp)Mo(CO)₃; (5) (MeCp)Mo(CO)₃(solvent)⁺ + X⁻ → (MeCp)Mo(CO)₃X + solvent. The following results are consistent with this pathway: (1) (MeCp)₂Mo₂(CO)₆ will disproportionate in neat acetone, CH₃CN, or Me₂SO without added X⁻; (2) (MeCp)₂Mo₂(CO)₆ will not disproportionate in benzene containing added X⁻. Kinetic analysis of the mechanism reveals that the quantum yield for (MeCp)₂Mo₂(CO)₆ disappearance (Φ) will be linearly proportional to $I^{-1/2}$. This prediction was experimentally verified. In THF solvent, the quantum yield is dependent on the halide concentration. A mechanism involving direct reaction of the halide with the (MeCp)Mo(CO)₃ primary photoproduct is proposed. Analysis of the ligand concentration dependence data leads to a value of $\phi_{405} = 0.41$ in THF.

Recent papers have demonstrated the utility of studying the quantum yields of organometallic reactions as a function of exciting light intensity.[1–3] As part of our study of the photochemical disproportionation reactions of metal–metal bonded carbonyl

(1) Fox, A.; Poe, A. *J. Am. Chem. Soc.* **1980,** *102,* 2497–2499.
(2) Tyler, D. R. *J. Photochem.* **1982,** *20,* 101–106.
(3) Stiegman, A. E.; Tyler, D. R. *J. Photochem.* **1984,** *24,* 311–314.

dimers,[4] we investigated the intensity dependence of the disproportionation of (MeCp)₂Mo₂(CO)₆ by halides (eq 1).[5] We report

$$(MeCp)_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu}$$
$$(MeCp)Mo(CO)_3X + (MeCp)Mo(CO)_3^- \quad (1)$$
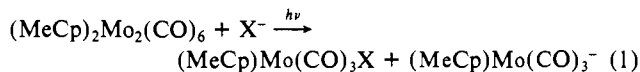
$$X = Cl, Br, I; \text{ solvent} = \text{acetone, Me}_2SO, CH_3CN$$

Table I. Disappearance Quantum Yields for the Disproportionation of $(MeCp)_2Mo_2(CO)_6$ $(1.2 \times 10^{-3}M)$ in Acetone Containing 0.1 M $N(n\text{-Bu})_4Cl$

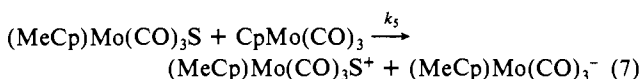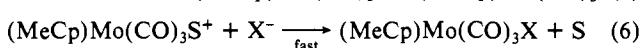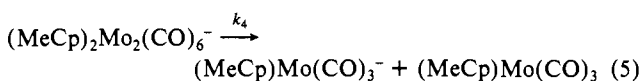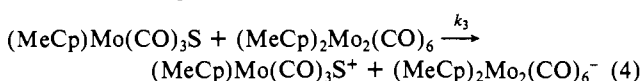| I, (einsteins/ min) $\times 10^9$	$I^{-1/2}$, (einsteins/ min)$^{1/2}$ $\times 10^{-2}$	Φ
	405 nm	
1540	8.06	0.64 ($\pm$ 0.09)
1060	9.72	0.72 ($\pm$ 0.06)
134	27.3	0.98 ($\pm$ 0.11)
106	30.7	0.94 ($\pm$ 0.09)
42.3	48.6	1.32 ($\pm$ 0.12)
10.6	97.2	1.93 ($\pm$ 0.14)
3.35	173	2.43 ($\pm$ 1.03)
	505 nm	
215	21.6	0.47 ($\pm$ 0.04)
21.5	68.2	0.66 ($\pm$ 0.30)
2.15	216	1.26 ($\pm$ 0.80)

Table II. Disappearance Quantum Yields (Φ) for the Disproportionation (λ = 405 nm) of $(MeCp)_2Mo_2(CO)_6$ $(1.2 \times 10^{-3}$ M) by Cl^- in Acetone[a]

$[Cl^-]$[b]	Φ
1.0×10^{-1}	0.64 ($\pm$ 0.09)
1.0×10^{-2}	0.61 ($\pm$ 0.06)
1.0×10^{-3}	0.71 ($\pm$ 0.06)
1.0×10^{-4}	0.64 ($\pm$ 0.05)
0.0 (neat acetone)	0.63 ($\pm$ 0.05)

[a] $I = 1.54 \times 10^{-6}$ einstein/min. [b] Added as $N(n\text{-Bu})_4Cl$.

Figure 1. A plot of the disappearance quantum yields (Φ) for the disproportionation of $(MeCp)_2Mo_2(CO)_6$ at 405 nm in acetone containing 0.1 M $N(n\text{-Bu})_4Cl$ vs. $I^{-1/2}$ ((einsteins/min)$^{-1/2}$). [$(MeCp)_2Mo_2(CO)_6$] = 1.2×10^{-3} M.

here the results of intensity-dependent quantum-yield measurements which show that reaction 1 follows a chain pathway and which also demonstrate that 19-electron complexes are important intermediates in the disproportionation reaction.

Results and Discussion

The quantum yields[6] of reaction 1 (X = Cl; solvent = acetone; λ = 405 and 505 nm) at various irradiation intensities are shown in Table I. Two points are of initial importance. Note that the quantum yields are intensity dependent and the quantum yields at lower intensities are greater than one. This latter point establishes that the mechanism has a chain component. The dependence of the disproportionation quantum yield on the concentration of Cl^- is shown in Table II. Clearly, the quantum yield is independent of ligand concentration. Similar results showing the independence of the quantum yield on Cl^- concentration were obtained in acetonitrile solution. A mechanism that accounts for the intensity dependence, the ligand concentration independence, and the quantum yields being greater than one is shown below in Scheme I. This pathway is analogous to the chain pathways
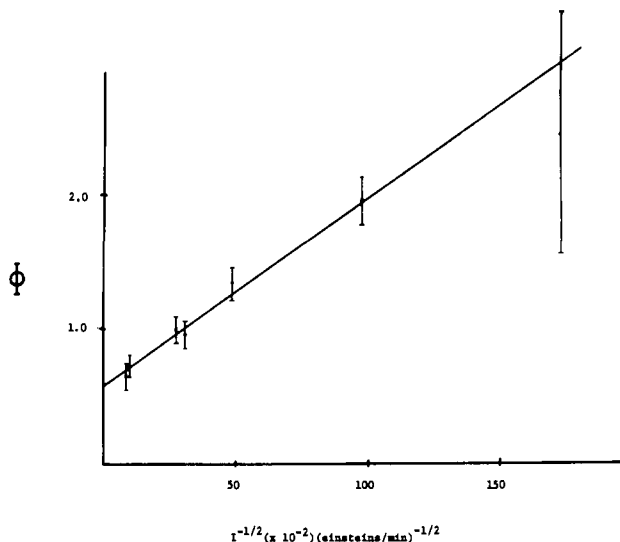
Scheme I

$$(MeCp)_2Mo_2(CO)_6 \underset{k_{-1}}{\overset{h\nu, \phi}{\rightleftarrows}} 2(MeCp)Mo(CO)_3 \quad (2)$$

$(MeCp)Mo(CO)_3$ +

$$S \underset{k_{-2}}{\overset{k_2, slow}{\rightleftarrows}} (MeCp)Mo(CO)_3S \quad (S = solvent) \quad (3)$$

$(MeCp)Mo(CO)_3S + (MeCp)_2Mo_2(CO)_6 \overset{k_3}{\longrightarrow}$

$$(MeCp)Mo(CO)_3S^+ + (MeCp)_2Mo_2(CO)_6^- \quad (4)$$

$$(MeCp)_2Mo_2(CO)_6^- \overset{k_4}{\longrightarrow}$$
$$(MeCp)Mo(CO)_3^- + (MeCp)Mo(CO)_3 \quad (5)$$

$$(MeCp)Mo(CO)_3S^+ + X^- \underset{fast}{\longrightarrow} (MeCp)Mo(CO)_3X + S \quad (6)$$

$$(MeCp)Mo(CO)_3S + CpMo(CO)_3 \overset{k_5}{\longrightarrow}$$
$$(MeCp)Mo(CO)_3S^+ + (MeCp)Mo(CO)_3^- \quad (7)$$
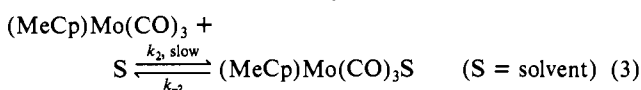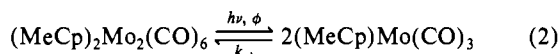
proposed for the disproportionation reactions of $Cp_2Mo_2(CO)_6$

(4) (a) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037. (b) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 527–529.
(5) Burkett, A. R.; Meyer, T. J.; Whitten, D. G. *J. Organomet. Chem.* **1974**, *67*, 67–73.
(6) At long irradiation times, the following secondary reaction occurs.[5]

$$CpMo(CO)_3X + X^- \overset{h\nu}{\longrightarrow} CpMo(CO)_2X_2^- + CO$$
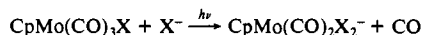
With the short irradiation periods of our quantum yield measurements, however, this reaction does not occur to a significant extent. In addition, control experiments showed that the extent of the following back reaction was negligible:[7]

$$CpMo(CO)_3X + CpMo(CO)_3^- \rightarrow Cp_2Mo_2(CO)_6 + X^-$$

$$X = Cl, Br, I$$

by phosphines and of $Mn_2(CO)_{10}$ by nitrogen-donor ligands.[4] Termination steps include the reverse of reaction 2 and the reaction in eq 7 (followed by reaction 6).

Kinetic analysis of the mechanism above is algebraically complex but tractable if we make the assumption that $k_{-2} \gg k_3[(MeCp)_2Mo_2(CO)_6]$ and $k_{-2} \gg k_5[(MeCp)Mo(CO)_3]$. (This assumption, justified in the Appendix, essentially means that the $(MeCp)Mo(CO)_3S$ species is in equilibrium with $(MeCp)Mo(CO)_3$ and S.) With this assumption and using the steady-state approximation for the concentration of all the intermediates, the following expression for the quantum yield of disappearance can be derived

$$\Phi = \phi\left(1 - \frac{k_{-1}}{k_{-1} + K[B]}\right) + \left(\frac{K'[B]}{(k_{-1} + K[B])^{1/2}}\right)(\phi/I)^{1/2} \quad (8)$$

where $K' = k_2k_3[M_2]/(k_{-2})$, $K = k_5k_2/k_{-2}$, B = solvent, and I = the absorbed intensity. If [$(MeCp)_2Mo_2(CO)_6$] is essentially constant during the photolysis, then Φ will be linearly proportional to $I^{-1/2}$.

The quantum yield data in Table I for acetone are plotted vs. $I^{-1/2}$ in Figure 1. It is evident that Φ is linearly proportional to $I^{-1/2}$. There is a simple physical explanation why Φ will decrease with increasing I. Essentially, as I increases so does the steady-state concentration of $(MeCp)Mo(CO)_3$. As the concentration of $(MeCp)Mo(CO)_3$ increases, reaction 7 and the other termination steps (e.g., coupling reactions) become more favorable relative to reaction 4, i.e., the second-order (in intermediates) chain-terminating steps become more efficient relative to the first-order chain-propagating steps. The quantum yield will decrease, of course, as the relative efficiencies of the chain-terminating reactions increase.[2]

According to the proposed mechanism, it is the solvent and not X^- that bonds to $(MeCp)Mo(CO)_3$ (eq 3). This result explains why the quantum yield will be independent of $[X^-]$, an expected result if the electron transfer from the 19-electron intermediate

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Table III. Disappearance Quantum Yields for the Disproportionation (λ = 405 nm) of $(MeCp)_2Mo_2(CO)_6$ (1.2×10^{-3} M) in Acetone Containing 0.1 M X^-.[a]

X^- [b]	Φ
Cl^-	0.64 ($\pm$ 0.09)
Br^-	0.73 ($\pm$ 0.05)
I^-	0.63 ($\pm$ 0.03)

[a] $I = 1.54 \times 10^{-6}$ einstein/min. [b] Added as $N(n\text{-}Bu)_4X$.

Table IV. Disappearance Quantum Yields for the Disproportionation (λ = 405 nm) of $(MeCp)_2Mo_2(CO)_6$ (1.2×10^{-3} M) in Acetonitrile and Me_2SO as a Function of the Absorbed Intensity

I, einstein/min	Φ[a]
CH₃CN	
1.06×10^{-6}	0.020
1.06×10^{-7}	0.13
Me₂SO	
1.06×10^{-6}	0.086
1.06×10^{-7}	0.15
1.06×10^{-8}	0.31
3.3×10^{-9}	0.81

[a] Errors in these values are 10–30%.

is the rate-limiting step in the thermal sequence of reactions. This aspect of the proposed pathway can be checked by three experiments. First, no disproportionation should occur in noncoordinating solvents containing X^-. This prediction has been verified: irradiation (λ = 405 nm) of $(MeCp)_2Mo_2(CO)_6$ in benzene solution containing 0.1 M Cl^- (KCl was solubilized by adding 18-crown-6) gave no disproportionation products as monitored by infrared spectroscopy. Second, the quantum yield for disproportionation should be independent of the halide. The data in Table III show that the quantum yields are identical within experimental error for $X^- = Cl^-$, Br^-, and I^- (at constant concentration of X^- in acetone). Third, the disproportionation should occur in coordinating solvents even in the absence of X^-. Indeed, irradiation (λ = 405 nm) of $(MeCp)_2Mo_2(CO)_6$ (10^{-4} M) in neat Me_2SO or CH_3CN forms $(MeCp)Mo(CO)_3^-$ ($\nu(C\equiv O)$ = 1892, 1773 cm^{-1} (CH_3CN); $\nu(C\equiv O)$ = 1891, 1770 cm^{-1} (Me_2SO)) and $(MeCp)Mo(CO)_3(solvent)^+$ ($\nu(C\equiv O)$ = 2049, 1968 cm^{-1} (S = Me_2SO); $\nu(C\equiv O)$ = 2069, 1989 cm^{-1} (S = CH_3CN)).[8] (Table IV shows that the quantum yields for disproportionation in CH_3CN and Me_2SO are also intensity dependent, as required by the mechanism.)

Similar irradiations in acetone at room temperature do not yield net disproportionation because the back reaction in eq 9 is apparently very fast.[7] (Similar back reactions between (MeCp)-

$$(MeCp)Mo(CO)_3(acetone)^+ + (MeCp)Mo(CO)_3^- \xrightarrow{\text{dark, RT}}$$
$$(MeCp)_2Mo_2(CO)_6 + \text{acetone} \quad (9)$$
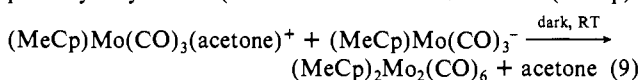
$Mo(CO)_3X^+$ (X = Cl^-, Br^-, SCN^-, Me_2SO, CH_3CN) and $(MeCp)Mo(CO)_3^-$ also occur but at much slower rates than eq 9.[5]) However, the back reaction in eq 9 does not take place at low temperature. Thus, irradiation (λ = 405 nm) of $(MeCp)_2Mo_2(CO)_6$ in neat acetone at -78 °C forms (MeCp)-$Mo(CO)_3^-$ and $(MeCp)Mo(CO)_3(acetone)^+$ ($\nu(C\equiv O)$ = 1898 and 1779 cm^{-1} and 2067 and 1955 cm^{-1} for the anion and cation, respectively).[7] Addition of $N(n\text{-}Bu)_4Br$ to this solution gives the stable products $(MeCp)Mo(CO)_3Br$ and $(MeCp)Mo(CO)_3^-$.

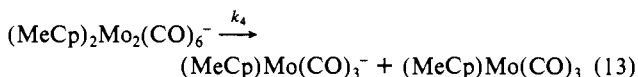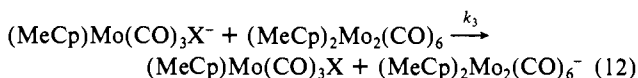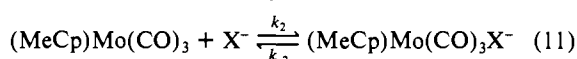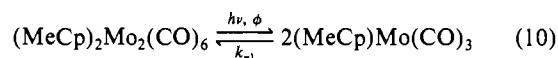Meyer has also reported on the photochemical disproportionation of $Cp_2Mo_2(CO)_6$ by halides.[5] One of the solvents in his study was THF. Unlike our results in acetonitrile and acetone, he found the disproportionation quantum yields to be dependent on the halide ion concentration in THF. In light of Meyer's results, we decided to repeat our experiments using THF as the solvent. As Table V shows, we, too, found a concentration dependence in THF.

(7) Hughey, J. L.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 947–949.
(8) (a) King, R. B.; Bisnette, M. B.; Fronzaglis, A. *J. Organomet. Chem.* **1966**, *5*, 341–356. (b) Beck, W.; Scholter, K. Z. *Naturforsch., B: Inorg. Chem., Org. Chem.* **1978**, *33B*, 1214–1222.

Table V. Disappearance Quantum Yields for the Disproportionation (λ = 405 nm) of $(MeCp)_2Mo_2(CO)_6$ (1.6×10^{-3} M) in THF as a Function of Br^- Concentration ($I = 2.03 \times 10^{-6}$ einstein/min)

$[Br^-]$	Φ	Φ (calcd, least squares)
0.25	0.48 ($\pm$ 0.02)	0.48
0.10	0.44 ($\pm$ 0.03)	0.42
0.07	0.40 ($\pm$ 0.03)	0.39
0.05	0.36 ($\pm$ 0.02)	0.36
0.01	0.18 ($\pm$ 0.02)	0.19
0.007	0.14 ($\pm$ 0.02)	0.15
0.005	0.13 ($\pm$ 0.02)	0.12
0.001	0.12 ($\pm$ 0.04)	0.032
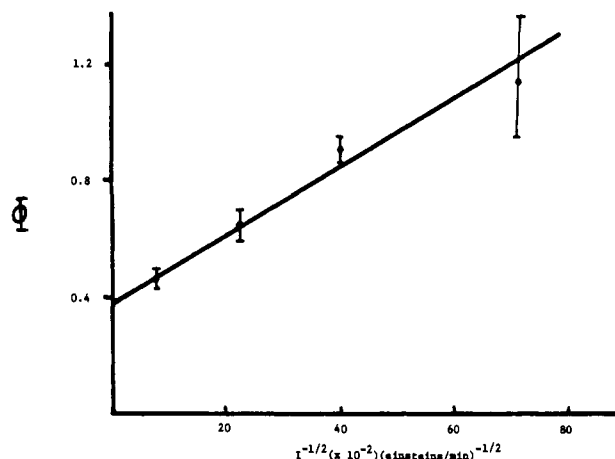
Figure 2. A plot of the disappearance quantum yields (Φ) for the disproportionation of $(MeCp)_2Mo_2(CO)_6$ at 405 nm in THF containing 0.1 M PPh_4Br vs. $I^{-1/2}$ ((einsteins/min)$^{-1/2}$). $[(MeCp)_2Mo_2(CO)_6] = 1.6 \times 10^{-3}$ M.

Given that disproportionation occurs with halides in THF, the dependence on halide concentration in THF is expected because pure THF will not disproportionate $(MeCp)_2Mo_2(CO)_6$. For example, irradiation (λ = 405 nm) of a THF solution of $(MeCp)_2Mo_2(CO)_6$ for several hours produces no changes. Even irradiations at -78 °C produced no ionic products, unlike in acetone. THF is apparently such a poor coordinator and electron donor that the 19-electron species $(MeCp)Mo(CO)_3(THF)$ (if formed) will not transfer an electron to the dimer. A 19-electron reducing species can only form in the THF solution by coordination of the halide (eq 11). This being the case, the quantum yield will depend on the halide ion concentration. The proposed mechanism for the disproportionation in THF is shown in Scheme II.

Scheme II

$$(MeCp)_2Mo_2(CO)_6 \underset{k_{-1}}{\overset{h\nu, \phi}{\rightleftharpoons}} 2(MeCp)Mo(CO)_3 \quad (10)$$

$$(MeCp)Mo(CO)_3 + X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (MeCp)Mo(CO)_3X^- \quad (11)$$

$$(MeCp)Mo(CO)_3X^- + (MeCp)_2Mo_2(CO)_6 \xrightarrow{k_3}$$
$$(MeCp)Mo(CO)_3X + (MeCp)_2Mo_2(CO)_6^- \quad (12)$$

$$(MeCp)_2Mo_2(CO)_6^- \xrightarrow{k_4}$$
$$(MeCp)Mo(CO)_3^- + (MeCp)Mo(CO)_3 \quad (13)$$

$$(MeCp)Mo(CO)_3X^- + (MeCp)Mo(CO)_3 \xrightarrow{k_5}$$
$$(MeCp)Mo(CO)_3X + (MeCp)Mo(CO)_3^- \quad (14)$$
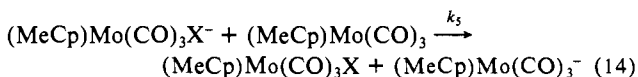
With use of the same method outlined in Appendix I for the solvent-assisted pathway, the following relationship between the quantum yield of disappearance, $[X^-]$, and I can be derived for the pathway in Scheme II

$$\Phi = \phi\left(1 - \frac{k_{-1}}{k_{-1} + K[X^-]}\right) + \left(\frac{K'[X^-]}{(k_{-1} + K[X^-])^{1/2}}\right)(\phi/I)^{1/2} \quad (15)$$
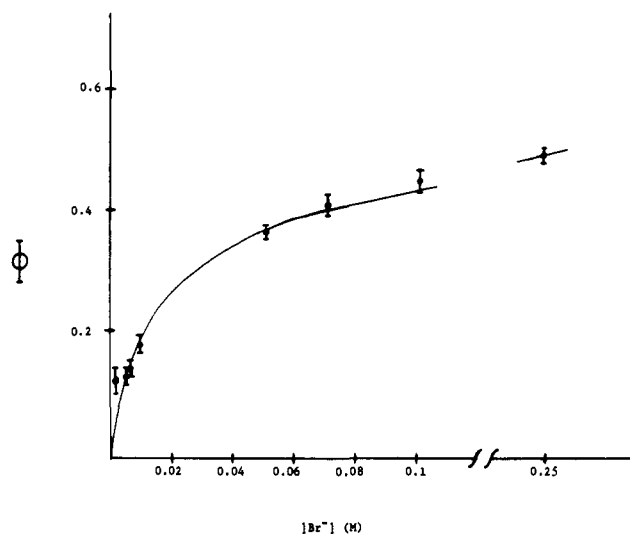
Figure 3. A plot of the disappearance quantum yields (Φ) for the disproportionation of $(MeCp)_2Mo_2(CO)_6$ at 405 nm in THF vs. [Br$^-$]. I = 2.03 $\times$ 10^{-6} einstein/min. The line is a least-squares fit of the data points to eq 15. See text for details.

As in eq 8, a linear dependence of Φ on $I^{-1/2}$ is predicted. Figure 2 shows a plot of Φ vs. $I^{-1/2}$ for the disproportionation of $(MeCp)_2Mo_2(CO)_6$ with Br$^-$; note the linear relationship. The dependence of Φ on [Br$^-$] (Table V) is shown by the points in Figure 3 (I = 2.03 $\times$ 10^{-6} einstein/min). A nonlinear least-squares fit of these points to eq 17 is shown by the curve in Figure 3. The best fit was obtained for the following values (k_{-1} = 2 $\times$ 10^9 M^{-1} s^{-1}, see below): ϕ = 0.41; K = 1.58 $\times$ 10^{11}; K' = 21.3 where K = $k_5k_2/(k_{-2})$ and K' = $k_2k_3[(MeCp)_2Mo_2(CO)_6]/(k_{-2})$. A similar analysis of the data in Figure 2 leads to similar values: ϕ = 0.41; K = 1.44 $\times$ 10^{11}; and K' = 31.0. Note that ϕ = 0.41 is similar to the values of ϕ reported by other workers.[1,9]

The fundamental question here is why is there a ligand dependence in THF solution but not in acetone or CH$_3$CN? We suggest that there actually is a ligand dependence in acetone and CH$_3$CN because there are two pathways: a coordinated solvent pathway (Scheme I) and a coordinated halide pathway (Scheme II). In good coordinating solvents (such as Me$_2$SO, CH$_3$CN, or acetone) the former pathway is quite efficient and therefore predominates; the contribution from the less-efficient halide pathway is effectively unobservable, and, hence, there is no ligand dependence. In noncoordinating solvents such as THF, the latter pathway is the only one available so there is a ligand dependence.

This suggestion, however, brings up the problem concerning the inability of Cl$^-$ to disproportionate $(MeCp)_2Mo_2(CO_6$ in benzene solution; i.e., why is the halide-coordination mechanism in Scheme II not applicable in benzene just as it is in THF? A tempting explanation is that the lifetime of the $(MeCp)Mo(CO)_3$ primary photoproduct is shorter in benzene than in THF. However, Meyer's flash photolysis studies on the Cp$_2$Mo$_2$(CO)$_6$ complex[10] show no significant differences in the lifetimes of this species in cyclohexane vs. THF (k_{-1}(cyclohexane) = (5 $\pm$ 1) $\times$ 10^9, k_{-1}(THF) = (2 $\pm$ 1) $\times$ 10^9 M^{-1} s^{-1}). Another explanation may lie in the short lifetime of the $(MeCp)Mo(CO)_3X^-$ species in benzene. Conceivably, k_2 may be zero in benzene, indicating that $(MeCp)Mo(CO)_3X^-$ cannot form in a nonpolar solvent. Our research is continuing to probe this unanswered question.

Finally, note that eq 8 might explain the curious quantum yield results observed by Meyer.[5] He reported that the lower energy excited states were more reactive than the higher energy excited states (ϕ_{366} = 0.07 $\pm$ 0.02; ϕ_{546} = 0.36 $\pm$ 0.06; X$^-$ = Cl$^-$). This result probably arises because Φ is dependent on I. As Table I and Figure 1 show, ϕ_{405} is always larger than ϕ_{505} *for a given*

intensity. We suggest that Meyer's quantum yield results were obtained with a high irradiation intensity at 366 nm but a low intensity at 546 nm; it would then appear that the low-energy excited states were more reactive than the higher energy states.[11] There is nothing unusual about our observation that ϕ_{405} > Φ_{505} because two different absorption bands are being irradiated.[9] A similar observation was made by Wrighton; he demonstrated the wavelength dependence for the reaction of Cp$_2$Mo$_2$(CO)$_6$ with CCl$_4$ to give CpMo(CO)$_3$Cl (ϕ_{550} = 0.35; ϕ_{405} = 0.42).[9] Note that the intercept in Figure 1 is less than or equal to ϕ; thus, 0.56 < ϕ_{405}. ϕ is clearly solvent dependent because ϕ_{405} = 0.41 in THF whereas the data in Figure 1 are for acetone.

Experimental Section

$(MeCp)_2Mo_2(CO)_6$ was synthesized by literature methods[12] and recrystallized from cyclohexane. The tetrabutylammonium salts of chloride, bromide, and iodide were purchased from Aldrich and recrystallized in a drybox with use of literature methods.[13] Potassium chloride, Me$_2$SO (spectral grade), and benzene (spectral grade) were obtained from Fisher and used as received. Tetrabutylphosphonium bromide was also obtained from Aldrich. Acetone (Fisher) was distilled over potassium carbonate (anhydrous) under a nitrogen atomosphere. Acetonitrile (Aldrich) was refluxed with calcium hydride and distilled under nitrogen. 18-Crown-6 ether was purchased from Aldrich and used as received.

All photochemical reactions were performed under anaerobic conditions with use of a 200-W high-pressure mercury lamp (Oriel). Bands at 405 and 505 nm were isolated with use of interference filters obtained from Edmund Scientific.

Quantum yield measurements were made with the assistance of a Beckman DU spectrophotometer with use of matched quartz 1.00-cm cells fitted with rubber septum caps. All solutions were stirred during irradiation, and the disappearance of $(MeCp)_2Mo_2(CO)_6$ (10^{-3} M) was monitored at 508 nm. Lamp intensities were determined with use of ferrioxalate[14] (405 nm) and Reinecke's salt[15] (505 nm) actinometry. Lamp intensities were varied with neutral density filters obtained from Oriel. The error limits given in the tables are the standard deviations of multiple measurements.

Appendix

Derivation of Equations 8 and 12. For the mechanisms in Scheme I or II let M = $(MeCp)Mo(CO)_3$, B = solvent or halide, I = $I_{absorbed}$ = absorbed light intensity, and MB = the 19-electron species, then

rate of disappearance of M$_2$ = $-d[M_2]/dt$

$$= \phi I - k_{-1}[M]^2 + k_3[MB][M_2] \tag{1a}$$

Invoking the steady approximation we can write:

$$d[M]/dt = 0 = 2\phi I - 2k_{-1}[M]^2 - k_2[M][B] + k_{-2}[MB] + k_4[M_2^-] - k_5[M][MB] \tag{2a}$$

$$d[MB]/dt = 0 =$$
$$k_2[M][B] - k_{-2}[MB] - k_3[MB][M_2] - k_5[MB][M] \tag{3a}$$

$$d[M_2^-] = 0 = k_3[MB][M_2] - k_4[M_2^-] \tag{4a}$$

By adding eq 2a and 3a one obtains

$$0 =$$
$$2\phi I - 2k_{-1}[M]^2 - k_3[MB][M_2] + k_4[M_2^-] - 2k_5[MB][M] \tag{5a}$$

(9) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246–4251.

(10) Hughey, J. L., IV: Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 440–441.

(11) We used irradiation wavelengths of 405 and 505 nm because they correspond more closely to the peak maxima than do 355 and 546 nm.

(12) Birdwhistle, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergammon Press: Oxford, 1980.

(14) (a) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.*, **1976**, *80*, 2434.

(15) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394–403.

(16) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259–7264.

and from eq 4a we know

$$k_4[M_2^-] = k_3[MB][M_2] \qquad (6a)$$

Inserting this expression in 5a, one obtains

$$0 = 2\phi I - 2k_{-1}[M]^2 - 2k_5[MB][M] \qquad (7a)$$

Solving for [MB] in eq 3a, one gets

$$[MB] = \frac{k_2[M][B]}{(k_{-2} + k_3[M_2] + k_5[M])} \qquad (8a)$$

Making the assumptions that $k_{-2} \gg k_3[M_2]$ and $k_{-2} \gg k_5[M]$, eq 8a reduces to

$$[MB] = \frac{k_2[M][B]}{k_{-2}} \qquad (9a)$$

This expression for [MB] is now inserted in eq 7a.

$$0 = \phi I - k_{-1}[M]^2 - \frac{k_5 k_2[B][M]^2}{k_{-2}} \qquad (10a)$$

Letting $K = k_5 k_2 / k_{-2}$ and solving eq 10a for [M], one obtains

$$[M] = \left(\frac{\phi I}{k_{-1} + K[B]}\right)^{1/2} \qquad (11a)$$

By inserting eq 9a into the overall rate (eq 1a), one obtains

$$-d[M_2]/dt = \phi I - k_{-1}[M]^2 + \frac{k_3 k_2[B][M_2][M]}{k_{-2}} \qquad (12a)$$

The expression for [M] (eq 11a) is now inserted into eq 12a

$$-d[M_2]/dt = \phi I - \left(\frac{k_{-1}\phi I}{k_{-1} + K[B])}\right) + \left(\frac{k_2 k_3[M_2][B]}{k_{-2}}\right)\left(\frac{\phi I}{(k_{-1} + K[B])}\right)^{1/2} \qquad (13a)$$

Dividing through by I gives the final expression for Φ.

$$\Phi = \phi\left(1 - \frac{k_{-1}}{k_{-1} + K[B]}\right) + \left(\frac{K'[B]}{(k_{-1} + K[B])^{1/2}}\right)(\phi/I)^{1/2}$$

where

$$K' = k_2 k_3[M_2]/k_{-2}$$

Justification of the Assumptions. From eq 11a we know

$$[M] = \left(\frac{\phi I}{k_{-1} + K[B]}\right)^{1/2}$$

From Meyer's work,[10] $k_{-1} \simeq i \times 10^9$ and from the analysis of Figure 2 (when B = X⁻) $K = 1.58 \times 10^{11}$ $(M^{-1})^2$ s⁻¹. Thus, $K[B] = 1.58 \times 10^{11} \times 0.1 = 1.58 \times 10^{10}$ M⁻¹ s⁻¹ and

$$[M]_{max} = \left(\frac{0.41\dfrac{10^{-6}}{3\ mL}\dfrac{mol}{min}\dfrac{1\ min}{60\ s}\dfrac{1000\ mL}{1}}{1.8 \times 10^{10}\ M^{-1}\ s^{-1}}\right)^{1/2} \simeq 1 \times 10^{-8}\ M$$

To find $(k_5[M])_{max}$, assume reaction 14 is diffusion controlled; then $k_5 \simeq 10^9$ and so $(k_5[M])_{max} = 10^9 \times 10^{-8} = 10$ s⁻¹. Restated, our assumption is that $k_{-2} > 10$ s⁻¹. From pulse radiolysis studies it is known that values of k_{-2} for 19-electron organometallic halide complexes are very large. For example, Wojcicki[16] has put a lower limit of 10^7 s⁻¹ on the rate constant of the following reaction

$$Mn(CO)_5X^- \rightarrow Mn(CO)_5 + X^-$$
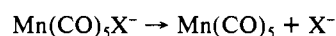
The rate constants for the analogous decompositions of CpMo-(CO)₃X⁻ are also, no doubt, very large so our assumption is justified for the case in which B = X⁻. We suspect that k_{-2} and $k_5[M]$ do not vary much from the values above when B = solvent. Our other assumption was that $k_{-2} \gg k_3[M_2]$. Recall

$$\frac{K}{K'} = \frac{k_5}{k_3[M_2]} = 7.4 \times 10^9$$

Thus,

$$\frac{k_5}{7.4 \times 10^9} = k_3[M_2] \quad or \quad \frac{(k_5)_{max}}{7.4 \times 10^9} > k_3[M_2]$$

We know

$$(k_5)_{max} \simeq 10^9 \quad and\ so\ \frac{1}{7.4} > k_3[M_2]\ and\ thus\ k_{-2} \gg k_3[M_2]$$