concentration of singlet molecular oxygen. In a photooxidation experiment, we would expect the oxirane:dioxetane ratio to increase with increasing light intensity.

Another useful experiment suggested by our calculations is the photooxidation of a bulky olefin such as 2,2′-biadamantylidene in the presence of ethylene. We predict ethylene to trap the initially formed peroxirane of 2,2′-biadamantylidene via reaction 3, since the approach of ethylene is sterically feasible and since ethylene is a better reducing agent than singlet molecular oxygen.

Finally, we note that, in the transition state for reaction 2, the oxygen molecule is electronically polarized (see Figure 1). In cases for which reactions 1 and 2 are competitive,[3-5] the oxirane:dioxetane ratio in the product is expected to increase with increasing ability of the solvent to stabilize such a polarized oxygen molecule.

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Flash Photolysis Evidence for Metal–Metal Bond Cleavage and Loss of CO in the Photochemistry of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$[1]

Sir:

The photochemistry of metal-metal bonds appears to be extensive, although quantitative studies have begun to appear only recently.[2] The results of many reactions can be reconciled in terms of initial metal–metal bond cleavage (eq 1).[2b]

$$M\text{–}M \xrightarrow{h\nu} 2M \tag{1}$$

However, several different types of photoproducts have been observed, and it is reasonable to suspect that alternate photopathways may exist. For example, the dimer, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$,[3] undergoes net light-induced substitution, disproportionation, and oxidation[4-7] with relatively high efficiencies.[8,9]

In the electronic spectrum of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ there are two well-defined absorption bands at 387 (ϵ 21,000) and 510 nm (ϵ 1870).[10] The band at 387 nm is probably the $\sigma \rightarrow \sigma^*$ transition of the metal-metal bond by analogy with the assignments made by Levenson, Gray, and Ceasar for the intense, near-uv bands of $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$.[11] The relatively low-intensity band at 510 nm is probably a $d \rightarrow d$ transition, since the spectra of related compounds without metal-metal bonds (e.g., $(\eta^5\text{-}C_5H_5)Mo(CO)_3Br$, $(\eta^5\text{-}C_5H_5)Mo(CO)_2Br_2^-$)[8] are qualitatively similar in the visible (ϵ ~500). Our work has shown that *either* uv (366 nm) *or* visible (546 nm) photolysis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in THF (tetrahydrofuran) can give efficient substitution, disproportionation, and oxidation reactions.[8,9]

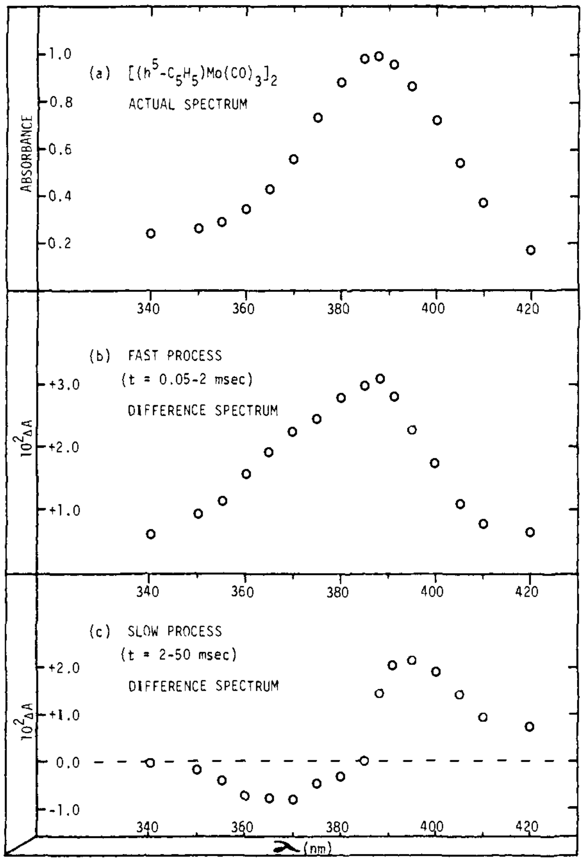

Figure 1. Comparison of the difference spectrum obtained by visible (λ ≥460 nm) flash photolysis of 2×10^{-5} $M[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ *in* cyclohexane: (a) actual spectrum (2.5-cm pathlength) of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ taken before flash photolysis, (b) difference spectrum for the fast process (t = 0.05-2 msec) after being corrected for the slow process, and (c) difference spectrum for the slow process (t = 2-50 msec).

By applying conventional flash photolysis techniques to solutions of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in cyclohexane, THF, and acetonitrile, we find direct evidence for the appearance of *two* distinct intermediates, immediately following photolysis. The intermediates subsequently react by independent thermal processes, which regenerate $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ quantitatively.[12] The intermediates are both present at the earliest experimental observation times ($t \geq 50$ μsec), and both appear following either uv or visible photolysis.[13]

One of the following thermal processes is ~50–100 times faster than the other, which has allowed us to resolve the difference spectra between regenerated $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and both intermediates (Figure 1). For the fast process (t ~0.05-2 msec), the difference spectrum (Figure 1b) closely matches the intense uv absorption band of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (Figure 1a) suggesting that in the intermediate, the metal-metal bond has been lost. For the slower process (t ~2-50 msec), the difference spectrum (Figure 1c) shows that the intermediate absorbs strongly in the $\sigma \rightarrow \sigma^*$ (Mo-Mo) spectral region, since there is an isosbestic point close to the uv λ_{max} for $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$.[14]

For the fast process, the difference spectrum suggests that the intermediate is relatively nonabsorbing in the near-uv region which allows us to estimate the second-order rate constants (at 20 ± 2°): $k_1 = (2 \pm 1) \times 10^9$ (THF), $(3 \pm 1) \times 10^9$ (acetonitrile), and $(5 \pm 1) \times 10^9\ M^{-1}\ \text{sec}^{-1}$ (cyclohexane). The values approach the estimated diffusion-controlled limits in the three solvents.[15] In THF, the rate of the fast process is unaffected by added inert electrolyte ($\text{N}(n\text{-C}_4\text{H}_9)^+\text{PF}_6^-$), ruling out reactions involving ions. The only reasonable interpretation is that light-induced cleavage of the Mo-Mo bond has occurred, followed by recombination of the monomeric fragments (eq 2).

$$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2 \xrightarrow{h\nu} 2(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3 \xrightarrow{k_1} [(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2 \qquad (2)$$

This interpretation is consistent with: (1) the loss of absorbance in the $\sigma \rightarrow \sigma^*$ (Mo-Mo) region, (2) the nearly diffusion-controlled rates in the range found for radical recombination reactions in solution,[16] and (3) the chemical evidence obtained in other work for radical byproducts.[17]

For the slow process, an estimate of the *maximum* second-order rate constant can be made (at 20 ± 2°), $k_2 = 3 \times 10^7$ (acetonitrile), 5×10^7 (THF), and $1 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ (cyclohexane), and a lower limit can be set at one-tenth of these values. For purposes of comparison, the value for the recapture of CO by Cr(CO)_5 in cyclohexane has been reported to be $(3 \pm 1) \times 10^6\ M^{-1}\ \text{sec}^{-1}$.[18] In THF, the slow process is also unaffected by added inert electrolyte, again ruling out an ionic reaction. The slow process appears to involve recombination with CO (eq 3),[19]

$$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{(CO)}_5 + \text{CO} \rightarrow [(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2 \qquad (3)$$

as shown by: (1) retention of the strong absorptivity in the uv, which implies the presence of a Mo-Mo bond in the intermediate, (2) the second-order kinetics with a rate constant in the range reported for the recapture of CO by Cr(CO)_5, and (3) the CO substitution behavior found for light-induced reactions between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ and neutral phosphine and phosphite ligands.[4,9]

The fact that *either* uv or visible photolysis gives *both* metal-metal bond cleavage and loss of CO implies that the two intermediates have a common origin, but it is not clear that the intermediate from which CO has been lost is a primary photoproduct. Metal-metal bond cleavage is expected following uv excitation into the $\sigma \rightarrow \sigma^*$ (Mo-Mo) band since the excited state should be antibonding with regard to the Mo-Mo bond, and, when thermally equilibrated, most likely consists of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3$ fragments in a solvent cage. Regardless of the detailed origin of the visible band, visible excitation could also lead to metal-metal bond cleavage. The energy of the thermally equilibrated $\sigma \rightarrow \sigma^*$ excited state can be estimated as <40 kcal/mol, since the metal-metal bond strength of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ in organic solvents appears to be significantly less than 40 kcal/mol.[9] Photolysis in the visible band ($\lambda \geq 460$ nm)[12] is sufficiently energetic to populate the thermally equilibrated $\sigma \rightarrow \sigma^*$ state. If there is an intersection between the $\sigma \rightarrow \sigma^*$ and d $\rightarrow$ d excited state surfaces, and if internal conversion and/or intersystem crossing efficiencies are high, efficient metal-metal bond cleavage is expected to occur, perhaps in competition with loss of CO.

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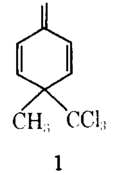
Light Intensity Effects on Ketone Photochemistry in Solution as a Consequence of Radical Quenching and Radical Chain Processes[1]

Sir:

We find that light intensity is a critical reaction variable in the photochemistry of cyclohexadienone (**1**) in 2-propanol (IPA) and other solvents and that intensity effects are related to unusual quenching behavior in this model system.[2] The fact that the role of light intensity (I^0) has been largely ignored by photochemists[3] may prove to have been a serious oversight, as demonstrated by the following observations.

The main products from irradiation of **1** in IPA are *p*-cresol (**2**), cyclopentenone ether (**3**), chloroform, and acetone. Compound **3** undergoes facile isomerization in the dark to **4** which is the material actually subjected to GLPC analysis. The ratio of **2** to **3** in preparative runs varied considerably using different light sources emitting over approximately the same wavelength range.[2j] Difficulty was also experienced in reproducing quantum yield measure-



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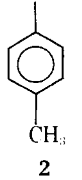

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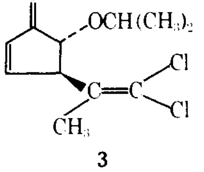

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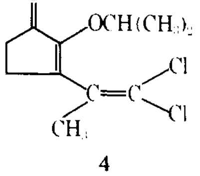

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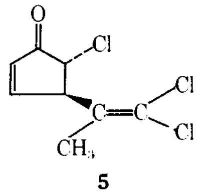

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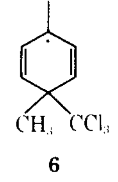

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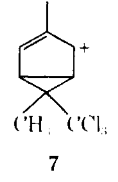

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