J. Am. Chem. Soc. **1981**, *103*, 6089-6092 6089

A Flash Photolysis Study of the Metal–Metal Bond Homolysis in Dimanganese Decacarbonyl and Dirhenium Decacarbonyl[1]

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Abstract: Hexane solutions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been subjected to flash photolysis. Under 1 atm of CO pressure, the absorbance due to the dinuclear species returns to the original value in accordance with a simple bimolecular rate law. This behavior suggests that the only process of importance in the solutions is bimolecular recombination of $M(CO)_5\cdot$ radicals. The bimolecular rate constants obtained at 22 °C are $k_r = 9.5 \times 10^8\ M^{-1}\ s^{-1}$ for $Mn_2(CO)_{10}$ and $3.7 \times 10^9\ M^{-1}\ s^{-1}$ for $Re_2(CO)_{10}$. When the solutions are thoroughly degassed prior to flash photolysis, a more complex behavior is noted. Intermediates that are more strongly absorbing in the 350–500-nm region than the $M_2(CO)_{10}$ species are formed and then disappear over a period of 200–400 ms. The maximum in absorbance due to the intermediates occurs in the 50–100-ms time interval. The intermediates are ascribed to $M_2(CO)_8$ and $M_2(CO)_9$, formed via loss of CO from the $M(CO)_5\cdot$ radicals in a thermal process following their formation. The $M(CO)_4$ thus formed reacts with $M(CO)_5\cdot$ or $M(CO)_4$ to form the postulated intermediates. Computer modeling of the proposed reaction scheme yields moderate agreement with observations.

Photochemical homolysis of the metal–metal bond has become a well-established route to formation of metal-centered carbonyl radicals. Gray and co-workers were the first to assign an absorption feature in the near-UV spectrum of $Mn_2(CO)_{10}$ to an allowed transition from the metal–metal σ-bond orbital to the corresponding σ^* orbital.[2] Irradiation into this absorption feature results in efficient rupture of the metal–metal bond to form $Mn(CO)_5\cdot$. Wrighton and co-workers have used this and closely related photochemical routes to form 17-electron metal–carbonyl radicals.[3] A transition which also occurs in the near-UV spectrum of many dinuclear carbonyls, assigned as $d\pi$–σ^*, also leads to efficient metal–metal bond homolysis.[4] The σ–σ^* excitation in a dinuclear metal–carbonyl compound containing a single metal–metal bond has the effect of reducing the metal–metal bond order to zero. A molecular beam study of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in the gas phase showed that the absorption bands ascribed to the σ–σ^* transition are indeed polarized parallel to the M–M bond axis and that the excited states live only a few picoseconds before dissociation occurs.[5] The fragments formed in the case of $Re_2(CO)_{10}$ were shown to be $Re(CO)_5\cdot$; that is, there is no loss of CO from the metal in the dissociation process.

Meyer and co-workers carried out flash photolysis studies of $Mn(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in cyclohexane and THF.[6,7] In the case of $Mn_2(CO)_{10}$, bleaching of the 343-nm absorption occurs following the flash. Absorption reappears at a rate consistent with bimolecular recombination of $Mn(CO)_5\cdot$ radicals. The bimolecular rate constant observed in cyclohexane, defined by the rate law $-d[Mn(CO)_5]/dt = 2k_r[Mn(CO)_5]^2$, was reported as $3.9 \times 10^9\ M^{-1}\ s^{-1}$ at 20 °C. This is of a magnitude expected for a diffusion-controlled process. However, an additional distinct transient spectral change in cyclohexane was observed. The second, slower process was reported to be first-order and independent of added CO. The rapid, second-order recovery of $Mn_2(CO)_{10}$ was also observed in THF, with a bimolecular rate constant at 20 °C of $1.9 \times 10^9\ M^{-1}\ s^{-1}$. In addition, a long-lived intermediate, which could also be generated by steady-state photolysis in THF, was also noted.

Evidence has accumulated from kinetic and mechanistic studies that 17-electron metal–carbonyl species are highly labile with respect to replacement of CO by other nucleophiles such as phosphine.[3,8-10] Whether this substitution occurs via a dissociative loss of CO or by an associative interaction of $Mn(CO)_5\cdot$ with L is still not entirely clear.[8,11] However, there are substantial grounds for believing that the process is dissociative in character in many of the systems studied. These kinetic and mechanistic evidences were not in hand at the time Meyer and co-workers published their flash photolysis results. There has been an element of inconsistency in the flash photolysis results reported for cyclohexane solutions and the expectations based on the evidence from kinetic and mechanistic studies. It therefore seemed advisable to reinvestigate the flash photolysis behavior of this system, which represents an important prototype, and to compare the results with those for $Re_2(CO)_{10}$, which has not previously been studied using flash photolysis.

Experimental Section

The flash apparatus has been described elsewhere.[12] In brief, the flash is generated in a pair of EG and G type FX-142C xenon flash tubes. The flash has a duration of about 35 μs at half-amplitude width. Filtering of the lamp output was accomplished with Pyrex plates of 2-mm thickness to reduce the incidence of short wavelength photons. The temperature of the flashed solutions was in all cases about 22 °C.

The detector employed was a Hamamatsu type R269 photomultiplier tube, with output to a variable gain amplifier with variable DC offset. The output of the amplifier passes to a storage oscilloscope for viewing and through an 8-bit A/D converter to a Data General Nova 820 minicomputer for storage on disk. Data acquisition in each flash is limited to 150 points, with variable acquisition rate, from 10 to 10^4 μs per point. The only software available for use during these experiments was for normalization of voltages and printout of voltage vs. time.

Solutions were prepared by weighing out suitable quantities of metal carbonyl into volumetric flasks in the laboratory, followed by gentle flushing with prepurified N_2. The flasks were then taken into a glovebox with N_2 atmosphere and carefully purified hexane added. Solutions were diluted as appropriate to produce concentrations in the range from 1 to 2×10^{-5} M for use in the flash experiments.

Solutions that were to be free of CO were transferred to a suitable cell fitted with a threaded Teflon vacuum stopcock. The cell was taken from the box and transferred to a vacuum line, where it was degassed via five

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(1) This research was supported by the National Science Foundation through research Grants NSF CHE76-17570, CHE-7950001, and DMR-77-23999.

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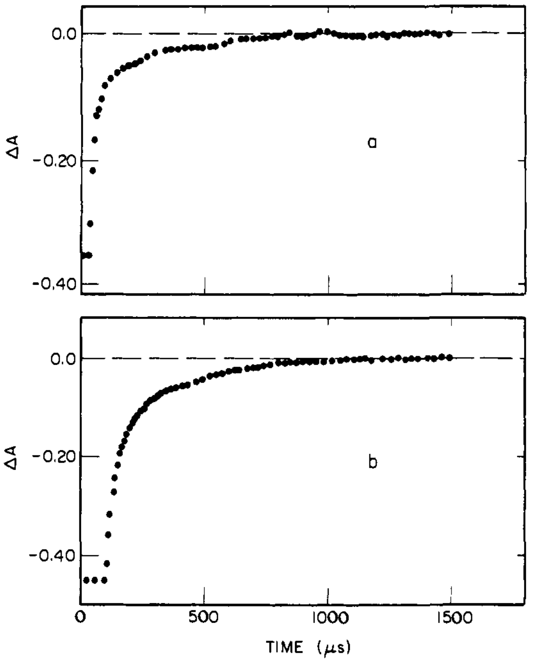

Figure 1. Change in absorbance vs. time on flash photolysis of a 1 × 10^{-5} M hexane solutions of (a) $Re_2(CO)_{10}$ and (b) $Mn_2(CO)_{10}$, under 1 atm of CO.

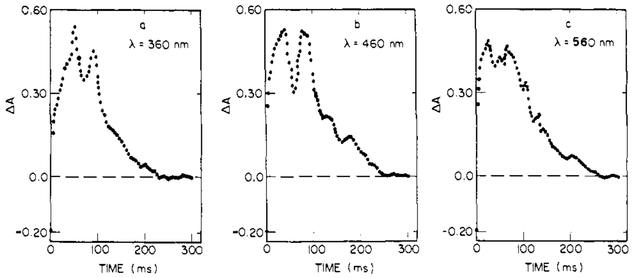

Figure 2. Change in absorbance vs. time on flash photolysis of a 1 × 10^{-5} M solution of $Mn_2(CO)_{10}$ which has been thoroughly vacuum degassed before flashing.

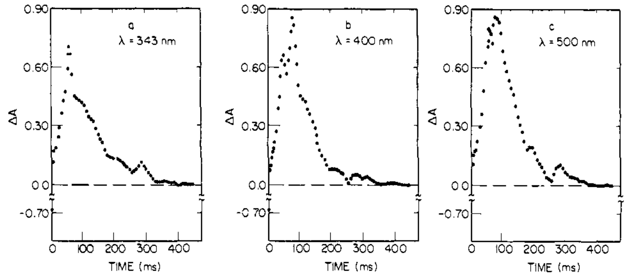

Figure 3. Change in absorbance vs. time on flash photolysis of a 1 × 10^{-5} M solution of $Re_2(CO)_{10}$ which has been thoroughly vacuum degassed before flashing.

freeze–pump–thaw cycles by using a vacuum system with attainable vacuum of 10^{-5}mmHg. The cell was then closed off for use. In the cases where a CO atmosphere was to be present, CO gas was purified by passage through activated manganese(II) oxide[13] and type 4A molecular sieve columns and then bubbled through the solution for about 20 min before the cell was closed off under a CO atmosphere.

Results

Under CO atmosphere, when a 1 × 10^{-5} M solution of $Mn_2(CO)_{10}$ in hexane which has been saturated with CO under 1 atm of pressure is flashed, nearly all of the bleaching which occurs in the 343 nm absorption returns within a few milliseconds. However, a small amount (less than 2%) of irreversible behavior is noted. After a few flashes, a completely stable base line is achieved. At this point less than 2% decomposition of the $Mn_2(CO)_{10}$ has occurred. In later flashes the behavior of the system is entirely reversible. Figure 1a shows a graph of ΔA vs. t, where ΔA represents the change in absorbance at 343 nm at time t from that characteristic of the solution just before and long after the flash.

We interpret the lack of complete reversibility in the first few flashes to the presence of traces of O_2 or other impurities present in low concentrations which react with the radicals produced in the flash. However, once these impurities have been scavenged, the behavior of the system is entirely photochromic.

In most respects our results parallel those observed by Hughey, Anderson, and Meyer.[6] However, we have observed no evidence for the long-lived intermediate reported by these workers as a minor photoproduct, which they continued to observe even after disappearance of the irreversible bleaching characteristic of the first few flashes. Attempts to build up an observable concentration of this species by repeated flashing were unsuccessful.

Entirely analogous results were obtained with $Re_2(CO)_{10}$, for a monitoring wavelength of 311 nm. In this case, however, the change in absorbance upon flashing is much smaller, probably because the maximum absorbance in the σ–σ* transition for $Re_2(CO)_{10}$ occurs at much shorter wavelength, 311 nm, and the integrated absorbance across the spectral range of photons that reach the cell is not large. In any case, considerably higher gains were required to attain sufficiently large changes in voltage. Figure 1b shows the results of a typical flash experiment on a 1 × 10^{-5} M $Re_2(CO)_{10}$ solution. Again, it is evident that the system is entirely photochromic.

When $Mn_2(CO)_{10}$ is photolysed in hexane solutions which have been thoroughly degassed by several cycles of freeze–pump–thaw, dramatically different behavior from that noted above results. Following the flash there is an initial rapid recovery of absorption. However, on a longer time scale the absorbance continues to increase beyond that characteristic of the initial solution as illustrated in Figure 2. The maximum increase in absorbance is generally much larger than the initial decrease in absorbance following the flash. These results, including the small transient occurring at about 60 ms, proved to be entirely reproducible. Some decomposition of the metal carbonyl was observed in these solutions following the first few flashes. Typically the extent of decomposition was between 1 and 2%. After the first few flashes the system became entirely photochromic. The time required for return of the absorbance to its initial value was typically about 300–500 ms, much longer than in the solutions containing CO.

Similar results were seen when hexane solutions of $Re_2(CO)_{10}$ initially free of CO were flashed, as shown in Figure 3.

Discussion

By relating the measured voltage changes to changes in absorbance, it is possible to test whether the recovery of absorbance following the flash obeys second-order kinetics. For this purpose it is necessary to assume that the transients produced in the flash do not contribute significantly to the absorbance at the monitor wavelength, 343 nm in the case of $Mn_2(CO)_{10}$ and 311 nm in the case of $Re_2(CO)_{10}$. Let A_∞ be the absorbance of the solution before the flash and a long time after the flash, A_t be the absorbance at time t following the flash, and A_0 be the absorbance immediately following the flash. For an entirely photochromic system and taking account of the fact that two $M(CO)_5\cdot$ are formed for each $M_2(CO)_{10}$ absorbing molecule, the appropriate rate expression is

$$\frac{1}{\Delta A_t} - \frac{1}{\Delta A_0} = k_r t \tag{1}$$

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where k_r is the bimolecular rate constant for recombination of the radicals, $\Delta A_t = A_\infty - A_t$, and $\Delta A_0 = A_\infty - A_0$. Figure 4 shows typical graphs of $1/\Delta A_t$ vs. t for both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, for the solutions saturated with CO at 1 atm. Note that the intercepts at $t = 0$ provide an estimate of the extent of initial bleaching of the solutions. As expected, the bleaching is considerably more extensive for $Mn_2(CO)_{10}$ than for $Re_2(CO)_{10}$. Note also that very satisfactory linear plots are obtained. These results confirm that the major kinetic process associated with the change in absorbance following the flash is the bimolecular recombination of $M(CO)_5\cdot$ radicals to form the dinuclear species. The second-order rate constants obtained from these studies are $k_r = 9.5 \times 10^8\ M^{-1}\ s^{-1}$ for $Mn_2(CO)_{10}$ and $k_r = 3.7 \times 10^9\ M^{-1}\ s^{-1}$ for $Re_2(CO)_{10}$. *No other process than simple bimolecular recombination is observable in these solutions.*

The situation is much more complex for those solutions that are initially CO free. The fact that the absorbance increases beyond that characteristic of the solution before the flash requires that one or more species that absorb more strongly at the monitor wavelength than the starting carbonyl compound are formed in the time following the flash. Figures 2 and 3 show that the absorption occurs rather strongly across a broad wavelength range. The fact that there is no evidence of these species in solutions containing excess CO suggests that the absorption is due to coordinatively unsaturated metal carbonyl species. Second, the fact that the absorbances grow in rather slowly and reach a maximum concentration only after about 60 ms or longer demonstrates that they are not the product of a prompt CO loss, e.g., as a component of the primary photochemical step.

We propose the following mechanistic scheme (eq 2-7) to account for the observations.

$$2M(CO)_5\cdot \xrightarrow{k_r} M_2(CO)_{10} \qquad (2)$$

$$M(CO)_5 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M(CO)_4 + CO \qquad (3)$$

$$M(CO)_4 + M(CO)_5 \xrightarrow{k_3} M_2(CO)_9 \qquad (4)$$

$$M(CO)_4 + M(CO)_4 \xrightarrow{k_4} M_2(CO)_8 \qquad (5)$$

$$M_2(CO)_8 + CO \xrightarrow{k_5} M_2(CO)_9 \qquad (6)$$

$$M_2(CO)_9 + CO \xrightarrow{k_6} M_2(CO)_{10} \qquad (7)$$

In this mechanism the loss of CO from the $M(CO)_5\cdot$ radical competes with recombination of the radicals to reform $M_2(CO)_{10}$. When excess CO is present, the reverse reaction in eq 3 is rapid with respect to any other processes that might involve $M(CO)_4$, so that the sole process observed is the radical recombination process, with bimolecular rate constant k_r. However, when there is very little or no CO present, the bimolecular reaction of $M(CO)_4$ with another $M(CO)_4$ or with $M(CO)_5\cdot$ competes with reaction with CO, and coordinatively unsaturated species $M_2(CO)_9$ and $M_2(CO)_8$ are formed. We propose that these dinuclear species give rise to the excess absorbance that develops following the flash.

Formation of $M(CO)_4$ might be expected to occur concertedly with formation of $M(CO)_5\cdot$, as a result of excess energy remaining in the photofragments following bond homolysis. This possibility cannot be ruled out for photolysis of $Mn_2(CO)_{10}$; however, Freedman and Bersohn were able to establish that CO loss does not accompany Re–Re bond homolysis following irradiation of $Re_2(CO)_{10}$. These authors, however, point out that the available energy over that required for metal–metal bond rupture is higher in $Mn_2(CO)_{10}$ and the Mn–CO bond energies are probably lower. Thus, CO loss as an integral part of the photolysis process cannot be ruled out a priori for $Mn_2(CO)_{10}$. However, we have already noted that the $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ solutions are remarkably alike in their photochemical behavior. In neither case is the species giving rise to the excess absorbance present immediately following the flash. Rather, in both cases the absorbance builds up over a period of about 50 ms. Thus, the loss of CO as part of the initial photochemical process can be excluded as a source of the absorbing species, in both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ solutions, whether that CO loss occurs from the radical species in the course of metal–metal bond homolysis or as a direct photochemical CO dissociation. We are left with the sole possibility that the CO loss process is thermal in character and involving one or more of the species formed in the primary photochemical event. We propose that this CO loss occurs from the 17-electron, mononuclear metal–carbonyl fragment.

Once formed, $M(CO)_4$ is likely to undergo reaction with 17-electron or 15-electron species, eq 4 and 5, with bimolecular rate constants approaching the diffusion-controlled limit. These processes thus account for formation of the intermediate species which give rise to the excess absorbance at times in the vicinity of 50–100 ms. On a longer time scale both $M_2(CO)_8$ and $M_2(CO)_9$ react with CO, eventually reforming $M_2(CO)_{10}$.

For a test of the general feasibility of the scheme proposed in eq 2–7, the rate expressions for the elementary processes were numerically integrated for various assumed values of rate constants and initial concentrations of various relevant reacting species. The numerical integration was carried out by using a modified version of the program HAVCHM, which employs the Gear algorithm for efficient integration of "stiff" differential equations.[14] Using such a numerical approach, it is possible to test the feasibility of a given complex mechanistic scheme, by exploring the range of rate constants and concentrations that provide a suitable fit with experimental results.

The constraints imposed on suitable solutions are that the $M_2(CO)_{10}$ recovers its initial value in a period of less than 450 ms following the time at which initial conditions were established. The initial conditions were set to correspond to those observed for $Re_2(CO)_{10}$. That is, the initial concentration of $Re(CO)_5\cdot$ at $t = 0$ was taken to be twice the extrapolated initial concentration change for $Re_2(CO)_{10}$ on the basis of data such as those shown in Figure 4b. A value of 5.0×10^{-7} was chosen. The initial concentration of CO was chosen to be either zero or 5.0×10^{-7} M. The latter value was chosen on the basis that some small degree of decomposition of $Re_2(CO)_{10}$ occurs during the first few flashes. If half of the CO on the molecules involved in the decomposition are liberated, the CO concentration would thus be on the order of 5×10^{-7} M. (Since no IR absorptions due to CO-containing decomposition products were observed, the assumption that half the CO is released seems a conservative estimate for illustrative purposes.) Finally, the solutions were required to lead to the formation of a maximum concentration of $M_2(CO)_9$ and/or $M_2(CO)_8$ at about 50 ms, the time at which the excess absorbance is observed to reach its maximum value.

The values chosen for the rate constants given in the reaction scheme, eq 2–7 are as follows: $k_r = 3.7 \times 10^9\ M^{-1}\ s^{-1}$; $k_2 = 10^2\ s^{-1}$; $k_{-2} = 5 \times 10^6\ M^{-1}\ s^{-1}$; $k_3 = 3 \times 10^9\ M^{-1}\ s^{-1}$; $k_4 = 3 \times 10^9\ M^{-1}\ s^{-1}$; $k_5 = 10^7\ M^{-1}\ s^{-1}$; $k_6 = 10^8\ M^{-1}\ s^{-1}$. The value of k_r is available from the experimental results in the presence of excess CO. We chose k_3 and k_4 to also be at about the diffusion-controlled limit, inasmuch as there is no reason to expect any barrier for formation of the metal–metal bond in either of these processes. Rate constants k_5 and k_6 are chosen to be large, as is typical of 16-electron metal centers in their reactions with CO.[15,16] It could be argued that each of these putative species might be stabilized to at least some extent and thus not react so readily with CO. For example, the $Mn_2(CO)_9$ might be stabilized by formation of a semi-bridging CO interaction across the metal–metal bond, as observed in $Mn_2(CO)_5(Ph_2PCH_2PPh_2)$[17] or $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$.[18] $M_2(CO)_8$ should possess a triple metal–metal bond of bond order 3; there might be some free energy barrier to the

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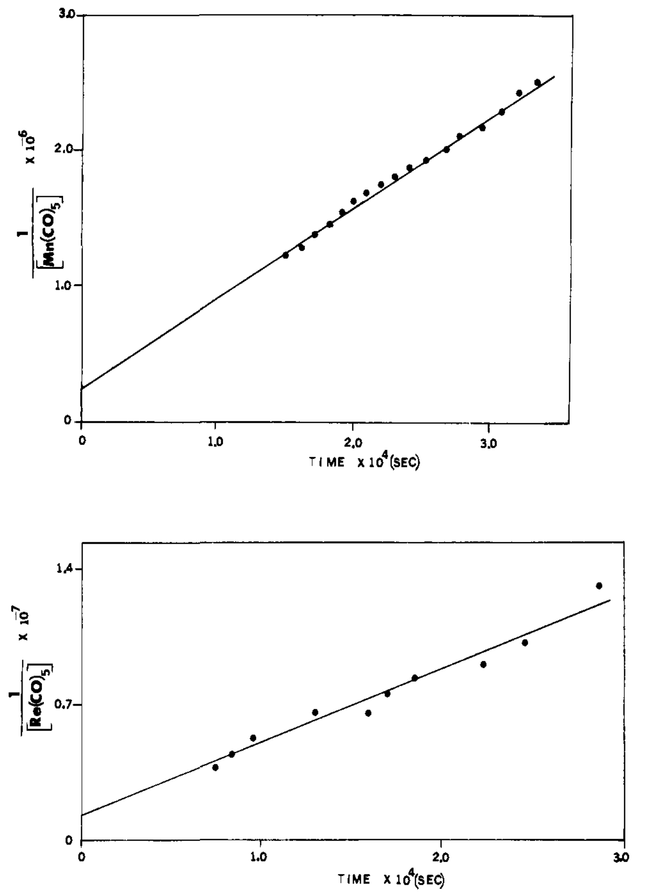

Figure 4. Inverse of the change in absorbance as a function of time upon flashing of 1 × 10^{-5} M solutions of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ in hexane, under 1 atm of CO.

interaction of such an intermediate with the incoming CO. However, in neither case is there any evidence for such stabilization, and it seems more appropriate in light of what we know to assume that the metal center behaves as a typical coordinatively unsaturated species in reacting rapidly with CO.

The most important single rate constant for the time development of the system is k_2, the rate constant for CO loss. We have found that a value for k_2 of about 100 s^{-1} is required to produce a maximum in the concentrations of $M_2(CO)_9$ and $M_2(CO)_8$ at about 50 ms. This value is in reasonable accord with what limited estimates have been made for the rate of CO loss from the 17-electron radicals. For example, Kidd and Brown estimate a *lower limit* of 10 s^{-1} for CO loss from $Mn(CO)_5$ to account for the photosubstitution results with $Mn_2(CO)_{10}$.[8]

If it is assumed that the CO concentration is initially zero, it is impossible to obtain a reasonable variation in the concentrations of $Mn_2(CO)_8$ and $Mn_2(CO)_9$ at times longer than 100 ms; the intermediates persist for much too long. The calculated variation in concentrations of $Mn_2(CO)_8$, $Mn_2(CO)_9$, and $Mn_2(CO)_{10}$ based on the above set of assumed rate constants are shown in Figure 5, for the case of [CO] = 5 × 10^{-7} M. The general outlines of the expected behavior are evident in Figure 5. However, there are serious shortcomings in the model. The rate at which the $Mn_2(CO)_8$ and $Mn_2(CO)_9$ appear is determined principally by the rate of CO loss from $Mn(CO)_5\cdot$. If k_2 is made too large, the intermediates reach their maximum concentrations at shorter times than observed. On the other hand, if k_2 is made much smaller than about 10^2 s^{-1}, the bimolecular recombination of $Mn(CO)_5\cdot$ radicals is a highly competitive process. In this case the maximum concentration of either $Mn_2(CO)_9$ or $Mn_2(CO)_8$ attained is very low. To account for the strong positive ΔA, it then is necessary in turn to postulate a value for ϵ at wavelengths in the range from 310 to 500 nm which is excessively large. The best approach to a reasonable model is obtained for k_2 about 100 s^{-1}. The model is deficient also in that it seems to make no provision for appearance of a double maximum, as seen in the $Mn_2(CO)_{10}$ flash results in the 0–100-ms time interval. Such a double maximum suggests that two strongly absorbing species are formed in the course of the overall reaction, at well-separated times. We have not succeeded in finding any set of reasonable rate constants k_2 through k_6 that leads to this behavior.

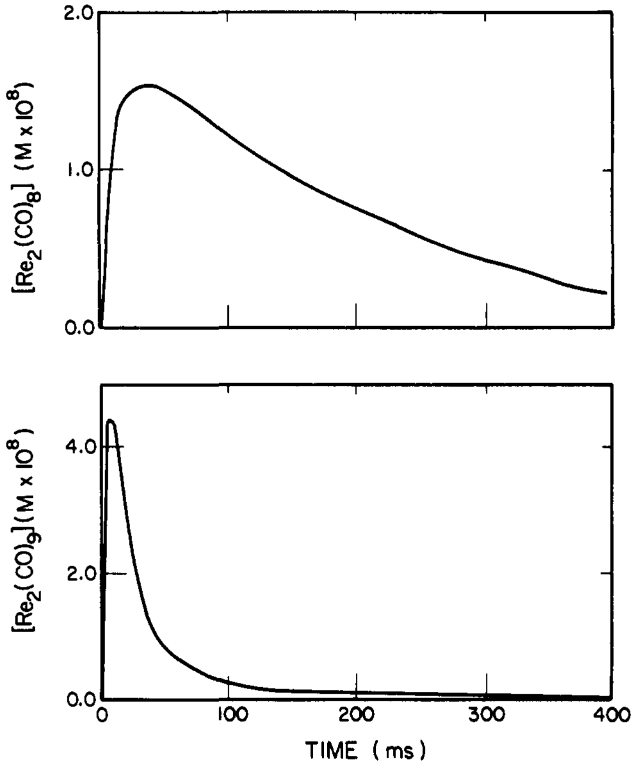

Figure 5. Variation in calculated concentrations of $Re_2(CO)_9$ and $Re_2(CO)_8$ with time following a flash, on the basis of the model of eq 2–7.

These limitations suggest that the proposed model needs additional refinement, but the experimental results in hand do not provide a basis for adding additional complexity. As it stands the model does account reasonably well for the observations. The model predicts that at a level of CO concentration on the order of 10^{-5} M the intermediates should still be formed (though the maximum concentrations attained will be much lower) and that they will be converted to $Mn_2(CO)_{10}$ more rapidly than in the case illustrated in Figure 3. When $Mn_2(CO)_{10}$ (1 × 10^{-5} M) is flashed in hexane under approximately 1mmHg pressure of CO atmosphere, a very small positive ΔA was noted, at a time of about 50 ms, as predicted.

The fact that the model successfully reproduces the effects of added CO and provides for generation of absorbing intermediates in a time interval in reasonable correspondence with that observed is positive support for the conclusion that loss of CO from either $Mn(CO)_5\cdot$ or $Re(CO)_5\cdot$ occurs in a relatively slow thermal process following formation of these radicals in a photochemical bond homolysis. In addition, the experimental results indicate that in the presence of ~0.01 M [CO] loss of CO from the radical is rapidly reversed, and the *sole* process observed that leads to return of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ is bimolecular recombination of the 17-electron radicals. In this connection, the present results rule against the intermediates proposed to account for some quantum yield observations in the photochemical reaction of $Mn_2(CO)_{10}$ with CCl_4.[19] Alternative pathways involving $Mn_2(CO)_8$ or $Mn_2(CO)_9$ may be involved, depending on the concentration of free CO in the system during the experiments.

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