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Preliminary communication

PHOTOCHEMISTRY OF $Mn_2(CO)_{10}$

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Summary

Flash photolysis studies on $Mn_2(CO)_{10}$ in cyclohexane and THF show that the dominant photochemistry involves photolytic formation of 2 $Mn(CO)_5$ followed by recombination at rates near the diffusion-controlled limit. A second, relatively, long-lived intermediate is also observed and earlier observations of photodecomposition and photodisproportionation can be accounted for in terms of secondary photolysis of this intermediate. For the equilibrium:

$$Mn_2(CO)_{10} \rightleftharpoons 2\,Mn(CO)_5$$

$\Delta H \sim 36$ kcal/mol, $\Delta S \sim 32$ e.u., and $K(25°C) \sim 10^{-20}$ where the thermodynamic values have been estimated from kinetic measurements.

There is by now good photochemical evidence that photolysis of $Mn_2(CO)_{10}$ gives $Mn(CO)_5$ (eq. 1) and that $Mn(CO)_5$ is highly reactive [1—3]. Yet there are reports that photolysis in THF gives paramagnetic $Mn(CO)_5$ which is stable for extended periods [4—6].

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\,Mn(CO)_5 \qquad (1)$$

We have investigated the photochemistry of $Mn_2(CO)_{10}$ by flash photolysis *. In cyclohexane, bleaching of the intense $\sigma(Mn—Mn) \rightarrow \sigma^*(Mn—Mn)$ absorption band at 343 nm [8] occurs during the flash (310 nm $< \lambda <$ 380 nm) followed by two distinct transient spectral changes (Fig. 1) and, ultimately, complete regeneration of $Mn_2(CO)_{10}$. Regeneration occurs by both a rapid process which follows second-order, equal concentration kinetics (Fig. 2) and a slower first

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* Solvents used were purified as described previously [7]. Samples of $Mn_2(CO)_{10}$ ($\sim 1.4 \times 10^{-5}$ *M* in 2.5 cm cells) were subjected to at least six freeze-pump-thaw cycles and flame sealed at 3×10^{-6} Torr.

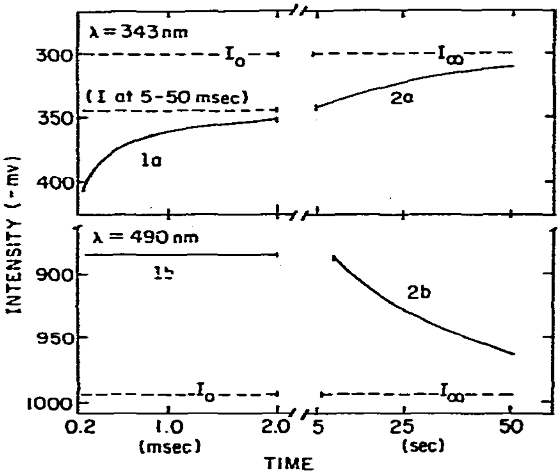

Fig. 1. Spectral changes at 490 and 343 nm following flash photolysis (310 nm $< \lambda <$ 380 nm) of $Mn_2(CO)_{10}$ (2×10^{-5} *M*) in cyclohexane: curves 1a and 2a following a single flash photolysis; curves 1b and 2b following a series of six rapid, successive flash photolyses.

order process. Both reactions are independent of added CO *.

The second-order process is almost surely the recombination reaction given in eq. 2, analogous to the recombination of $2(\eta^5\text{-}C_5H_5)Mo(CO)_3$ observed earlier by flash photolysis ** [9]. In the region 320—420 nm, the difference

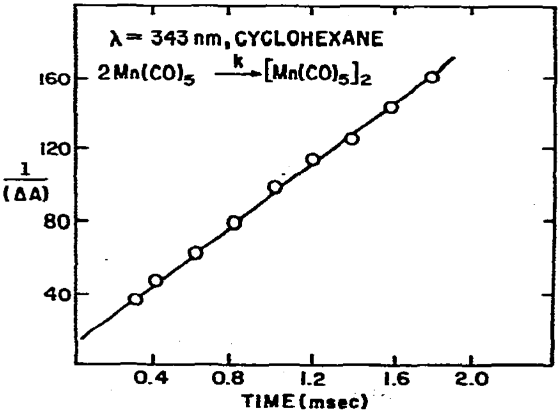

Fig. 2. Second-order, equal-concentration kinetic plot for reaction 3 using data like that shown in curve 1a of Fig. 1.

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* In an octane solution with P_{CO} = 450 torr, the first few flashes gave irreversible bleaching at 343 nm presumably because of reactions between $Mn(CO)_5$ and trace impurities introduced in the CO. After several flashes the system became photochromic and rate constants for the first and second order processes were obtained which were within experimental error of values obtained in the absence of CO.

** Evidence for a second intermediate whose properties are consistent with loss of CO and retention of the Mo—Mo bond ($(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5$) was also obtained by flash photolysis.

spectrum for the rapid process mirrors the absorption spectrum of $Mn_2(CO)_{10}$

$$2\,Mn(CO)_5 \xrightarrow{k_2} Mn_2(CO)_{10} \tag{2}$$

indicating that $Mn(CO)_5$ is relatively transparent in this region and allowing $k_2(20 \pm 2°) = 3.9 \times 10^9\ M^{-1}\ sec^{-1}$ to be calculated.

The long-lived intermediate I (reaction 3):

$$I \xrightarrow[(20\pm2°)]{k\,=\,0.027\ sec^{-1}} Mn_2(CO)_{10} \tag{3}$$

is apparently a relatively minor photoproduct which because of its lifetime ($t_{1/2}$ = 26 sec) can be built up by a series of successive flash photolyses. From the difference spectrum for reaction 3, I has λ_{max} at 500 ± 5 nm, an isosbestic point with $Mn_2(CO)_{10}$ at 370 nm and is relatively transparent below 370 nm compared to $Mn_2(CO)_{10}$. I can be generated by steady state photolysis in octane but is itself photosensitive and prolonged photolysis leads to permanent bleaching of the band at ~500 nm.

In cyclohexane the $Mn_2(CO)_{10}$ system is completely photochromic with both $Mn(CO)_5$ and I reverting to $Mn_2(CO)_{10}$. In THF, rapid, second-order recovery of $Mn_2(CO)_{10}$ was observed; $k_2\,(20 \pm 2°) = 1.9 \times 10^9\ M^{-1}\ sec^{-1}$. A long-lived intermediate also appeared with λ_{max} ~490 nm having an isosbestic point with $Mn_2(CO)_{10}$ at 375 nm. The intermediate could also be generated by steady state photolysis. After several flashes, the absorbance at 343 nm had decreased and a weaker absorption band had appeared at λ_{max} ~490 nm indicating the formation of an intermediate having an isosbestic point with $Mn_2(CO)_{10}$ at ~375 nm. Steady state photolyses of more concentrated solutions (~$10^{-3}\ M$) gave the intermediate which is itself photosensitive *. After the photolysis cell was opened, $Mn_2(CO)_{10}$ reappeared in part (~70%) within a few minutes as shown by an increase in absorbance at 343 nm. (Also see references 4 and 5) **.

Our conclusions are these: 1. The dominant primary product following photolysis of $Mn_2(CO)_{10}$ is $Mn(CO)_5$. For cases where quantum yields are high the observed photochemistry can be explained in terms of the high thermal reactivity of $Mn(CO)_5$ once generated by photolytic cleavage of the Mn—Mn bond [1—2]. In the absence of scavengers for $Mn(CO)_5$, the lifetime of $Mn(CO)_5$ is fixed by the nearly diffusion-limited recombination reaction (eq. 2) which is in the msec time range under our conditions. 2. A second intermediate also appears which is probably also a primary photoproduct. Given the excellent equal-concentration, second-order kinetics observed for reaction 2 (Fig. 2) it is unlikely that it arises from a thermal reaction of $Mn(CO)_5$. The intermediate, whose properties have been described in detail [4,5], may be an isomeric form of $Mn_2(CO)_{10}$ or perhaps a hydride which is relatively long-lived and noticeably so in THF. 3. The photodecomposition noted in alkane

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* In different experiments λ_{max} values varied in the range 470—495 nm. Prolonged photolysis resulted in permanent bleaching of the visible absorption band(s) and decomposition. The range in λ_{max} values may arise because of secondary photolysis of the initial intermediate with λ_{max} ~490 nm which leads ultimately to decomposition.

** At least trace amounts of air (O_2) may be necessary for the reversion to $Mn_2(CO)_{10}$ to occur.

solvents [2] and the disproportionation products $Mn(THF)_6^{2+}$ + 2 $Mn(CO)_5^-$ in THF [6,10,11] must arise from secondary photolysis of the initial long-lived intermediate or of related intermediates which are photochemically derived from it. The long-lived intermediates may not themselves be paramagnetic and may play a role in explaining other features of the photochemistry of $Mn_2(CO)_{10}$.

However, perhaps the most important point arises from our rate data. Reaction 2 was studied as a function of temperature in cyclohexane in the range 10—55°C giving $\Delta H^{\ddagger} = -0.26 \pm 0.04$ kcal mol^{-1} and $\Delta S^{\ddagger} = -15.0 \pm 0.4$ cal mol^{-1} deg^{-1}. The rate data is consistent with a nearly diffusion-controlled process, although orientation effects and/or effects arising from spin statistics may be important [12]. Poë and his co-workers have studied the thermal decomposition of $Mn_2(CO)_{10}$ in decalin in the temperature range 80—135°C [13a]. The thermal decomposition reaction appears to occur via eq. 4 [13b]. By combining our data in cyclohexane with Poë's data in decalin (extrapolated to 25°), we are able to estimate for the metal—metal bond equilibrium in eq. 5 that $\Delta H \sim 36$ kcal mol^{-1}, $\Delta S \sim 32$ e.u., and $K(25°C) \sim 10^{-20}$. Clearly, the presence of the Mn—Mn bond has a profound effect on the energetics of the manganese carbonyl system

$$Mn_2(CO)_{10} \xrightarrow{k_1} 2\,Mn(CO)_5 \qquad (4)$$

$$Mn_2(CO)_{10} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,Mn(CO)_5 \qquad (5)$$

and at room temperature, the metal—metal bond is highly favored thermodynamically.

Acknowledgments

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References

1 M. Wrighton, Chem. Rev., 74 (1974) 471.

2 M. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 2065.

3 A. Hudson, M.F. Lappert, P.W. Lednor and B.K. Nicholson, J. Chem. Soc. Chem. Commun., (1974) 966.

4 S.A. Hallock, Ph.D. Thesis, Ohio State University, Columbus, Ohio, 1974.

5 S.A. Hallock and A. Wojcicki, J. Organometal. Chem., 54 (1973) C27.

6 C.L. Kwan and J.K. Kochi, J. Organometal. Chem., 101 (1975) C9.

7 J.L. Hughey IV, Ph.D. Thesis, The University of North Carolina, Chapel Hill, North Carolina, 1975.

8 R.A. Levenson, H.B. Gray and G.P. Ceasar, J. Amer. Chem. Soc., 92 (1970) 3653.

9 J.L. Hughey IV, C.R. Bock and T.J. Meyer, J. Amer. Chem. Soc., 97 (1975) 4440.

10 A.F. Hudson, M.F. Lappert and B.K. Nicholson, J. Organometal. Chem., 92 (1975) C11.

11 A. Hudson, M.F. Lappert, T.T. Macquitty, B.K. Nicholson, H. Zaimal, G.R. Luckhurst, C. Zannoni, S.W. Bratt and M.C.R. Symons, J. Organometal. Chem., 110 (1976) C5.

12 J.P. Lorand, Prog. Inorg. Chem., 17 (1972) 207; D.J. Carlsson and K.U. Ingold, J. Amer. Chem. Soc., 90 (1968) 7047.

13, (a) L.I.B. Haines, D. Hopgood and A.J. Poë, J. Chem. Soc. A, 421 (1968);
(b) A.J. Poë, D.M. Chowdhury, D. DeWit, J.P. Fawcett and M.V. Twigg, Proc. XIVth ICCC, Toronto, 1972, p. 120.