The Primary Photoproducts of $Mn_2(CO)_{10}$: Direct I.R. Observation and Decay Kinetics of $Mn(CO)_5$ and $Mn_2(CO)_9$ in Hydrocarbon Solution at Room Temperature

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Time-resolved i.r. spectroscopy is used to show that $Mn(CO)_5$ and CO-bridged $Mn_2(CO)_9$ are the primary photoproducts of $Mn_2(CO)_{10}$ in hydrocarbon solution; $2Mn(CO)_5 \rightarrow Mn_2(CO)_{10}$ and $Mn_2(CO)_9 + CO \rightarrow Mn_2(CO)_{10}$ are established as the recombination processes.

Photolysis of $Mn_2(CO)_{10}$ is now believed to result in both homolytic cleavage of the Mn–Mn bond [reaction (1)] and loss of CO [reaction (2)]. The latter process has received little attention so far, although reaction (1) was found not to be the sole primary process in the photoreaction of $Mn_2(CO)_{10}$ with CCl_4,[1] and an intermediate other than $Mn(CO)_5$ was suggested in an early flash photolysis study.[2] Only recently has $Mn_2(CO)_9$ been postulated as the second photoproduct of $Mn_2(CO)_{10}$ in both flash photolysis experiments[3,4] and matrix isolation studies.[5,6] Here, we present the first i.r. spectra of the transients $Mn(CO)_5$ and $Mn_2(CO)_9$ in solution, and we show that $Mn_2(CO)_{10}$ is reformed by two pathways [reactions (3) and (4)].

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

$$Mn_2(CO)_{10} \xrightarrow{h\nu} Mn_2(CO)_9 + CO \qquad (2)$$

$$2Mn(CO)_5 \xrightarrow{k_3} Mn_2(CO)_{10} \qquad (3)$$

$$Mn_2(CO)_9 + CO \xrightarrow{k_4} Mn_2(CO)_{10} \qquad (4)$$

The technique for obtaining time-resolved i.r. spectra has been described previously.[7,8] Rigorous sample preparation procedures[8] were followed throughout. Flash photolysis of 8×10^{-4} M $Mn_2(CO)_{10}$ in argon-saturated cyclohexane (C_6H_{12}) or n-heptane (C_7H_{16}) generated two initial transients. They were distinguishable by their decay kinetics and are assigned to $Mn(CO)_5$ [$t_{1/2}$ *ca.* 50 µs in C_7H_{16}, *ca.* 80 µs in C_6H_{12}; Figure 1(a)] and to $Mn_2(CO)_9$ [$t_{1/2}$ *ca.* 1 ms in C_7H_{16}, *ca.* 7 ms in C_6H_{12}; Figure 1(b)]. Under these conditions approximately 5—8% of $Mn_2(CO)_{10}$ was converted into photoproducts in one flash.

Only one i.r. band was observed for $Mn(CO)_5$ which, by comparison with the spectrum of $Mn(CO)_5$ in low temperature CO matrices[9] (Table 1), is assigned to a superposition of the e and low-frequency a_1 vibrations of the square pyramidal $Mn(CO)_5$ fragment. Its decay in n-heptane, monitored at 1988 cm^{-1}, followed second-order kinetics, with k_3 in C_7H_{16} (Table 1) being in accord with previously determined rate constants for reaction (3).[2,4,10,11] The nearly diffusion-controlled recombination reaction (3) proved to be the only process responsible for the decay of $Mn(CO)_5$ in both argon and CO saturated solution. No evidence was found for facile dissociative loss of CO as claimed by Brown and co-workers.[10]

$Mn_2(CO)_9$ exhibited five terminal CO stretching vibrations and, as already observed in low-temperature matrices,[5,6] a bridging CO band at 1760 cm^{-1} (Table 1). Considering

Table 1. Rate constants and i.r. and visible absorptions of $Mn(CO)_5$ and $Mn_2(CO)_9$.

				Absorptions		
Compound	Medium	Temperature (K)	Rate constants ($dm^3\,mol^{-1}\,s^{-1}$) k_3	I.r. (cm^{-1})	Visible (nm)	Ref.
$Mn(CO)_5$	C_7H_{16}	R.t.[d]	$1 \times 10^{9\,a}$	1988		
	C_6H_{12}	R.t.	$7 \times 10^{8\,b}$	1990	820[c]	
			8.8×10^{8}			4
	EtOH	R.t.			830	11
	CO	20		1993,[e] 1988,[e] 1978	798	9
			k_4			
$Mn_2(CO)_9$	C_7H_{16}	R.t.	$2.7 \times 10^{6\,f,g}$	2058, 2022, 2008 1996, 1968, 1760		
	C_6H_{12}	R.t.	$1.2 \times 10^{6\,f,g}$	2058, 2020, 2006, 1994, 1966, 1760	480[c]	
			$5 \times 10^{5\,h}$			
			$7.5 \times 10^{5\,i}$			
			$1.2 \times 10^{5\,h}$			4
	3-Methylpentane	77		2055, 2017, 1986, 1760		5
	Argon	12		2058, 2037, 1993, 1977, 1764		6

[a] Calculated from $k_3/\varepsilon(1988\ cm^{-1}) = 1 \times 10^5\ s^{-1}\,cm$ of the i.r. transient spectrum and, assuming the molar absorption coefficient of $Mn(CO)_5$ to be similar to that of $Mn(CO)_5$(halogen) compounds (ref. 18), an estimated $\varepsilon(1988\ cm^{-1})$ *ca.* $10^4\ dm^3\ mol^{-1}\ cm^{-1}$. [b] Calculated from the visible transient spectrum using $\varepsilon(830\ nm) = 800\ dm^3\ mol^{-1}\ cm^{-1}$ for $Mn(CO)_5$ in EtOH (ref. 11). [c] Band also reported by Yesaka *et al.*[4] in C_6H_{12}. [d] R.t. = room temperature. [e] Matrix-split e mode. [f] Measured from the i.r. transient spectrum with added CO (1.3 bar CO, 1.5×10^{-2} M in C_7H_{16} and 1.2×10^{-2} M in C_6H_{12}; see ref. 13). [g] *Cf.* $k = 3 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ for the reaction of $Cr(CO)^5$ in C_6H_{12} with CO (ref. 14). [h] Measured from the visible transient spectrum in argon-saturated solution; calculated using an estimated $\varepsilon(500\ nm) = 1000\ dm^3\ mol^{-1}\ cm^{-1}$ (ref. 4). [i] Measured from the visible transient spectrum with added CO.

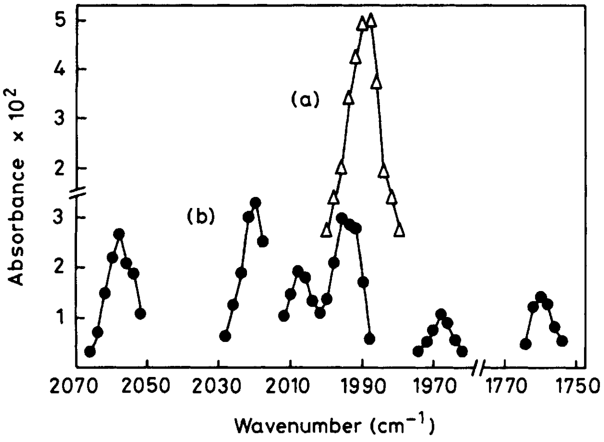

Figure 1. Transient i.r. spectra of the photoproducts of $Mn_2(CO)_{10}$ in n-heptane solution immediately after the flash. (a) $Mn(CO)_5$ (upper absorbance scale). (b) $Mn_2(CO)_9$ (lower absorbance scale); note the prominent bridging CO band at 1760 cm^{-1}.

the intensity and position of this band [*cf.* $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$[12]], we propose that the CO bridge in $Mn_2(CO)_9$ is unsymmetrical and can be described as $\mu(\eta^1{:}\eta^2\text{-CO})$. Further support for this comes from low-temperature matrix polarization studies.[6] Clearly, no direct structural information of this kind is accessible by flash photolysis with u.v.–visible detection, but could only be provided by i.r. spectroscopy. In contrast to $Mn(CO)_5$, the decay of $Mn_2(CO)_9$ was affected by the addition of CO, reducing $t_{1/2}$ to *ca.* 50 μs in C_6H_{12} (at *ca.* 1.2×10^{-2} M CO) and *ca.* 20 μs in C_7H_{16} (at *ca.* 1.5×10^{-2} M CO).[13] The reactivity with CO (see Table 1 for k_4) is similar to that of $Cr(CO)_5$[14] which suggests that $Mn_2(CO)_9$ is not stabilised significantly by CO bridging. However, its decay was solvent dependent. In both argon and CO-saturated solutions, $Mn_2(CO)_9$ disappeared faster in C_7H_{16} than in C_6H_{12}. This behaviour is similar to that of $Cr(CO)_5$[15] which is known to co-ordinate solvent rapidly.[16]

In order to correlate the i.r. data of the two transients with their visible absorptions, flash photolyses were also carried out with u.v.–visible detection (excitation by either a Nd-YAG laser, 353 nm, or a xenon flash lamp, pulse durations 20 ns and 5 μs, respectively). Two initial transient bands observed at 820 and 480 nm are attributed to $Mn(CO)_5$ and $Mn_2(CO)_9$, respectively. The former assignment is made by comparison of absorption and decay kinetics with literature data (Table 1).[4,9,11] Significantly, $Mn_2(CO)_9$ also disappeared by second-order kinetics in argon-saturated C_6H_{12}, while upon saturation with CO the decay was accelerated and became pseudo first-order.† The second-order rate constants k_4 in C_6H_{12} reported for $Mn_2(CO)_9$ in this work, which range from 5×10^5 to 1.2×10^6 $dm^3\,mol^{-1}\,s^{-1}$ (Table 1), are somewhat higher than the previously quoted k_4 value, 1.2×10^5 $dm^3\,mol^{-1}\,s^{-1}$.[4]

The relative yields of $Mn(CO)_5$ and $Mn_2(CO)_9$ and the reformation rates of $Mn_2(CO)_{10}$ with both i.r. and u.v.–visible detection indicate, in accord with a previous finding,[4] that the initial concentrations of $Mn(CO)_5$ and $Mn_2(CO)_9$ are approximately the same, *i.e.*, dissociation of CO is certainly *not* a minor process.‡

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† A shortening of the lifetime of $Mn_2(CO)_9$ after many flashes in an argon-saturated solution can be attributed to CO liberation caused by some small decomposition of photoproducts, thus accelerating reaction (4).

‡ Occasional irregular kinetic behaviour of $Mn_2(CO)_9$ in the i.r. experiments, observed only in the first filling of the i.r. cell (argon-flushed C_6H_{12}), is due to addition of an as yet unidentified trace contaminant X of the instrumental system. $Mn_2(CO)_9$ decayed with a first-order rate constant of 2500 s^{-1} ($t_{1/2}$ *ca.* 280 μs) to $Mn_2(CO)_9X$ which has i.r. absorptions at 2026 (5), 1998 (8), 1980 (10), 1964 (5), and 1930 (3) cm^{-1} (approximate relative intensities in parentheses) and which disappeared with a first-order rate constant of 5 s^{-1} ($t_{1/2}$ *ca.* 140 ms). Comparison with known $Mn_2(CO)_9L$ derivatives[17] suggests that X is a strongly donating ligand occupying an equatorial position.