A kinetic study of photosubstitution of carbon monoxide and triphenylphosphine in complexes $Mn(\eta^5\text{-}CH_3C_5H_4)\text{-}(CO)_{3-n}(PPh_3)_n$ ($n = 0$, 1 and 2)
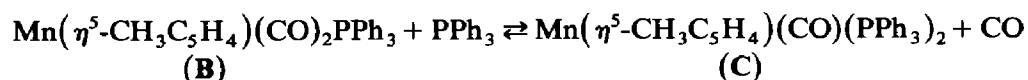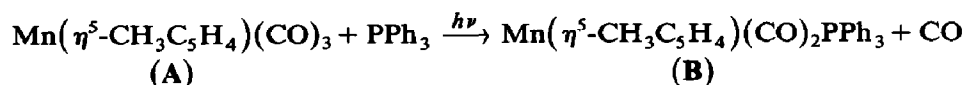
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Abstract

The kinetics of photosubstitution of carbon monoxide and triphenylphosphine in complexes $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_{3-n}(P(C_6H_5)_3)_n$ ($n = 0$, 1, 2) have been studied at an irradiation wavelength of 366 nm. The kinetics of the reaction occurring upon the irradiation of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$ (A), in the presence of PPh_3 in n-hexane are consistent with the following reaction sequence:

$$Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3 + PPh_3 \xrightarrow{h\nu} Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3 + CO$$
$$(\mathbf{A}) \qquad\qquad\qquad\qquad\qquad (\mathbf{B})$$

$$Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3 + PPh_3 \rightleftarrows Mn(\eta^5\text{-}CH_3C_5H_4)(CO)(PPh_3)_2 + CO$$
$$(\mathbf{B}) \qquad\qquad\qquad\qquad (\mathbf{C})$$

The quantum yields for the carbon monoxide substitution by PPh_3 are 0.77 ± 0.05 and 0.59 ± 0.05 for derivatives **A** and **B**, respectively. In the case of **C** no replacement of the ligand carbon monoxide was observed. With **B**, the triphenylphosphine ligand was not replaced by CO, but with **C** the replacement took place with a quantum yield of 0.88 ± 0.05. The ratio between rate constants for the recombination reactions, i.e. of the intermediate $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2$ with CO, (K_1) or with PPh_3, (K_2), is K_1/K_2 0.5 The analogous ratio for the intermediate $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)PPh_3$ with CO (K_3) or with PPh_3 (K_4) is K_3/K_4 3.5.

Introduction

Carbon monoxide photosubstitution in metal carbonyl complexes has attracted much interest [1], because of the synthetic applications of such reactions, and the advantages of their high quantum yields. In view of our interest in the carbon

monoxide photosubstitution reactions [2] some results reported for $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ in the presence of triphenylphosphine [3] prompted us to carry out a detailed study of the photochemical interconversion kinetics, of the derivatives $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_{3-n}(PPh_3)_n$ ($n = 0, 1, 2$) in order to determine the relevant kinetic parameters.

It is noteworthy that whereas with $Mn(\eta^5\text{-}C_5H_5)(CO)_2(NC_5H_5)$ the pyridine is the photolabile ligand in substitution [3], with the related phosphine complex $Mn(\eta^5\text{-}C_5H_5)(CO)_2PPh_3$, it is the carbonyl ligand that is photosubstituted under analogous conditions [3,4]. Our study of the derivative $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3$ confirmed the photolability of the carbonyl ligand.

The quantum yield of 1.0 for the substitution of carbon monoxide in $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ by CH_3COCH_3 or $PhC{\equiv}CPh$ [5,6] suggests that dissociation is the controlling step. On the other hand, in the replacement of carbon monoxide by pyridine in $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ the quantum yield is 0.65 [3]; this can be attributed to an influence of the entering group or to a less efficient photochemical dissociation. In this paper we use a kinetic approach that throws light on that influence, and allows not only measurement of the quantum yield for the primary dissociation process following the light absorption, but also determination of the ratio of the rate constants for the intermediate competition of the entering and leaving groups.

Experimental

$Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$ (Aldrich) was purified by column chromatography on alumina. Compounds $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_{3-n}(PPh_3)_n$ ($n = 1, 2$) were synthesized by published methods [7]. Other chemicals were of analytical grade. Preparative photolysis and quantum yield determinations were carried out under the conditions described previously [2].

Quantum yields were corrected for the light absorption by reagents and products. The total incident light was measured by ferrioxalate actinometry [8] (I_0-7.3 × 10^{-7} Einstein min^{-1} at 366 nm).

The reactions were carried out in n-hexane, with the solutions degassed by three cycles (freeze-pump-thaw) to 1.3×10^{-2} Pa. Saturation with carbon monoxide was achieved by admiting carbon monoxide to the sample at 1.3×10^{-2} Pa. The concentrations of reagent and products were determined by using a simultaneous spectrophotometric analysis at two different pairs of wavelengths; the two sets of results were the same within experimental error.

Some slight decomposition, noted after long irradiation periods may have introduced small errors in calculations of the equilibrium concentrations.

A value of 1.3×10^{-2} mol l^{-1} was used for the concentration of carbon monoxide in saturated solutions of n-hexane on the basis of data for n-heptane [9].

No thermal reactions of compounds $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_{3-n}(PPh_3)_n$ with carbon monoxide or triphenylphosphine were observed under the conditions used.

Results

Irradiation of solutions of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$ and PPh_3 on a preparative scale, in a Pyrex jacket fitted with a medium pressure 90 W mercury lamp yielded the derivatives $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_{3-n}(PPh_3)_n$ ($n = 1, 2$), which were identified
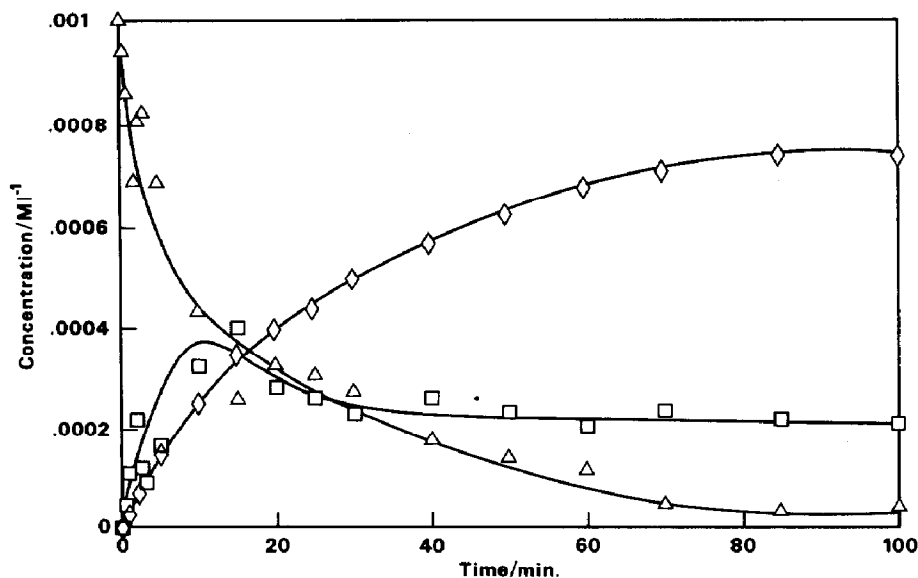
Fig. 1. Time dependence of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_{3-n}(PPh_3)_n$ concentration, $n = 0, 1, 2$ in the presence of phosphine (1/3). $\triangle = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$; $\square = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3$, $\lozenge = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)(PPh_3)_2$.

by elemental analysis and by comparison of their IR spectra with those of authentic samples synthesized by published methods [5]. The time dependence of the concentration of derivatives $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_{3-n}(PPh_3)_n$ ($n = 0, 1, 2$) obtained by irradiation of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$ in the presence of PPh_3 (Fig. 1), is in agreement with $\mathbf{A} \rightarrow \mathbf{B} \rightleftarrows \mathbf{C}$ kinetics.

Disappearance quantum yields of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$ (A) in the presence of
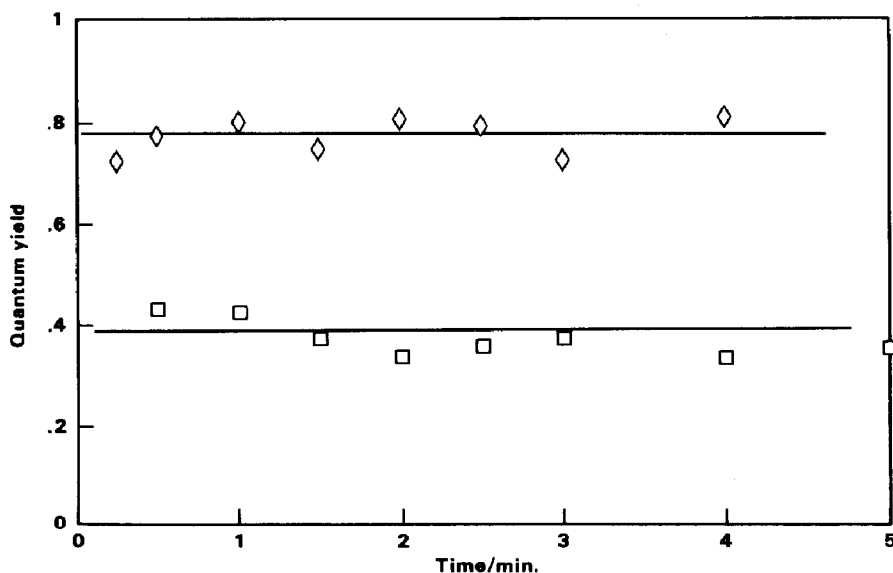
Fig. 2. Disappearance quantum yields of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$. $\lozenge$ refers to reactions in absence of added carbon monoxide; and $\square$ to solutions saturated with carbon monoxide.

Table 1

Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_{3-n}$(PPh$_3$) ($n = 0, 1, 2$) disappearance quantum yields in n-hexane at 366 nm

Compound	Initial concentrations		Quantum yield
	[PPh$_3$] [a]	[CO]	
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_3$	(1/3)	–	0.77
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_3$	(1/20)	saturated	0.64
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_2$PPh$_3$	(1/3)	–	0.59
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_2$PPh$_3$	–	saturated	no reaction
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)(PPh$_3$)$_2$	(1/1)	–	no reaction
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)(PPh$_3$)$_2$	(1/20)	saturated	0.88

[a] In parentheses (compound/phosphine) ratio concentration. A ratio of 1/3 suffies to meet the condition [PPh$_3$] $\gg$ [CO], in no CO is added to the solution, since only a fraction of CO remains in solution.

excess of PPh$_3$ obtained at 366 nm, either in a CO saturated solution or in the absence of added carbon monoxide remain constant with time. The smaller value found in the first case can be attributed to a recombination step involving carbon monoxide (Fig. 2 and Table 1).

Irradiation of solutions of Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_2$PPh$_3$ (**B**) in the absence of added phosphine but in carbon monoxide saturated solutions produces no spectral changes, demonstrating the inertness towards photosubstitution of the phosphine ligand in the complex. This behaviour contrasts with that of the analogous complex Mn(η^5-C$_5$H$_5$)(CO)$_2$(NC$_5$H$_5$), the pyridine ligand of which is photochemically replaced by other nucleophiles [3]. Irradiation of the same compound in presence of added phosphine but in the absence of added carbon monoxide (Fig. 3) leads to an equilibrium of mixture of **B** and Mn(η^5-CH$_3$C$_5$H$_4$)(CO)(PPh$_3$)$_2$ (**C**) showing not only the photolability of the carbon monoxide ligand in **B**, but also the photolability of the phosphine ligand in **C**.
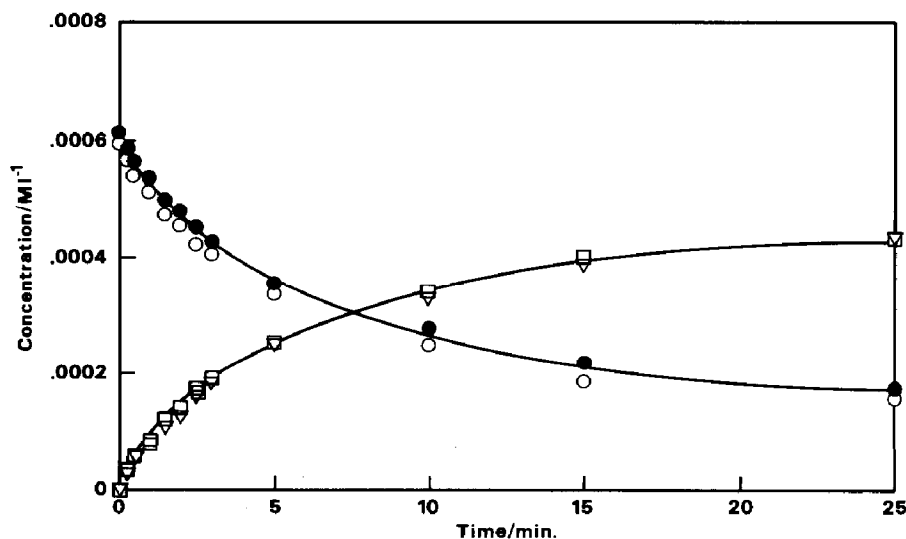

Fig. 3. Time dependence of Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_2$(PPh$_3$) concentration in the presence of phosphine (1.3) ○,● = Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_2$PPh$_3$. □,▽ = Mn(η^5-CH$_3$C$_5$H$_4$)(CO)(PPh$_3$)$_2$. ●,▽ monitored at 310, 340 nm; ○,□ monitored at 320, 340 nm.
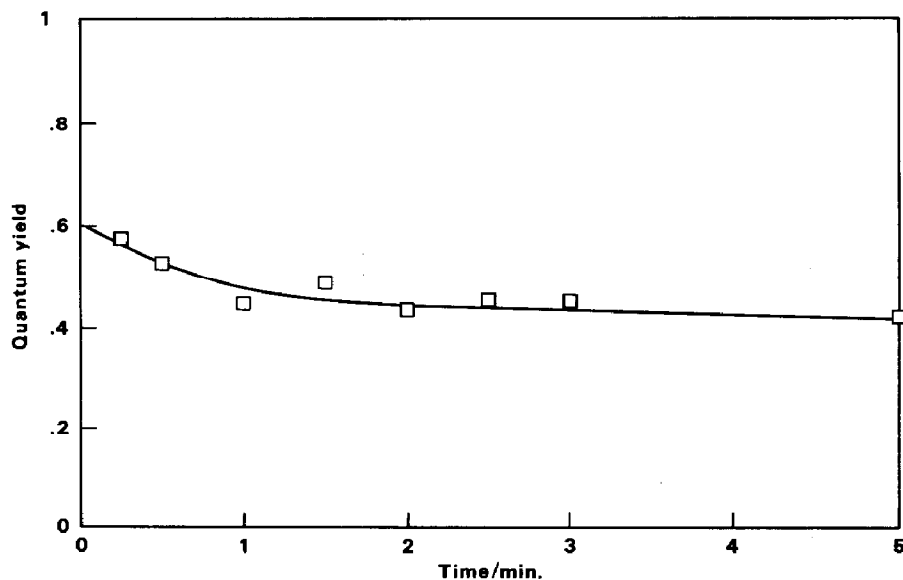
Fig. 4. Disappearance quantum yield of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3$ in absence of added carbon monoxide.

Irradiation of a solution of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)(PPh_3)_2$ (**C**), in the presence of added phosphine and the absence of carbon monoxide, causes no spectral changes, showing the inertness to photochemical substitution of the carbon monoxide ligand in this complex. On the other hand, the lability of the PPh_3 ligand in the same complex was confirmed by irradiation in the presence of added carbon monoxide and in absence of added phosphine, resulting in the derivative $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3$ (**B**). Disappearance quantum yields in the latter case are time dependent, showing an increase of the recombination reaction as the free phosphine concentration increased (Fig. 4).

The disappearance quantum yield of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)(PPh_3)_2$ in solutions saturated with carbon monoxide and containing a large excess of phosphine show a linear dependence on I_2/I_3, where I_2 and I_3 are the intensities of the light absorbed by $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3$ and $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)(PPh_3)_2$, respectively.

Discussion

Evidence for dissociative steps for photosubstitutions in the complexes $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ and $Mn(\eta^5\text{-}C_5H_5)(CO)_2(NC_5H_5)$ was previously presented by Wrighton [3], who suggested that disubstituted complexes $Mn(\eta^5\text{-}C_5H_5)(CO)X_2$ are formed by irradiation of $Mn(\eta^5\text{-}C_5H_5)(CO)_2X$ only when X is a fairly good π-acceptor ligand.

The results of our studies on complexes $Mn(\eta^5\text{-}CH_3C_5H_4)CO_{3-n}(PPh_3)_n$ ($n = 0, 1, 2$) suggest an overall kinetic of the type $A \rightarrow B \rightleftarrows C$, represented by the following scheme where $A = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$, $B = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3$, $C = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)(PPh_3)_2$, $X = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2$, and

$Y = Mn(\eta^5\text{-}CH_3C_5H_4)(CO)PPh_3$; and, α, β, γ are quantum yield of the dissociation excited states of **A**, **B** and **C** respectively.

$$\mathbf{A} \xrightarrow{\alpha I_1} X + CO \tag{1}$$

$$X + CO \xrightarrow{k_1} \mathbf{A} \tag{2}$$

$$X + PPh_3 \xrightarrow{k_2} \mathbf{B} \tag{3}$$

$$\mathbf{B} \xrightarrow{\beta I_2} \gamma + CO \tag{4}$$

$$\gamma + CO \xrightarrow{k_3} \mathbf{B} \tag{5}$$

$$\gamma + PPh_3 \xrightarrow{k_4} \mathbf{C} \tag{6}$$

$$\mathbf{C} \xrightarrow{\gamma I_3} \gamma + PPh_3 \tag{7}$$

$$\frac{d[\mathbf{A}]}{dt} = \alpha I_1 - k_1[CO][X] \tag{8}$$

$$\frac{d[\mathbf{B}]}{dt} = k_2[X][PPh_3] + k_3[Y][CO] - \beta I_2 \tag{9}$$

$$\frac{d[\mathbf{C}]}{dt} = k_4[Y][PPh_3] - \gamma I_3 \tag{10}$$

$$\frac{d[X]}{dt} = \alpha I_1 - k_1[X][CO] - k_2[X][PPh_3] \tag{11}$$

$$\frac{d[Y]}{dt} = \beta I_2 + \gamma I_3 - k_3[Y][CO] - k_4[Y][PPh_3] \tag{12}$$

Applying the stationary state hypothesis to X and Y we obtain

$$\phi_\mathbf{A} = \frac{\alpha k_2[PPh_3]}{k_1[CO] + k_2[PPh_3]} \tag{13}$$

$$\phi_\mathbf{B} = \frac{\beta k_4[PPh_3]}{k_3[CO] + k_4[PPh_3]} - \phi_\mathbf{A}\frac{I_1}{I_2} - \frac{k_3[CO]}{k_3[CO] + k_4[PPh_3]}\gamma\frac{I_3}{I_2} \tag{14}$$

$$\phi_\mathbf{C} = \frac{\gamma k_3[CO]}{k_3[CO] + k_4[PPh_3]} - \frac{k_4[PPh_3]}{k_3[CO] + k_4[PPh_3]}\beta\frac{I_2}{I_3} \tag{15}$$

where, $\phi_\mathbf{A}$, $\phi_\mathbf{B}$ and $\phi_\mathbf{C}$ are the quantum yields for the disappearance of **A**, **B** and **C**. Results for irradiation of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_3$ (**A**) in the absence of added CO and in presence of excess of PPh_3 indicates that $k_1|CO| \ll k_2|PPh_3|$ and that $\phi_\mathbf{A} = \alpha$, at least in the initial stages of the photosubstitution. If k_1, is much greater than k_2, then $\phi_\mathbf{A}$ decreases throughout the reaction, and α must be calculated by extrapolating the data to initial time.

Irradiation of the same compound, **A** in saturated CO solutions and in the presence of excess of PPh_3 gave a constant value of $\phi_\mathbf{A}$ (see eq. 13). The ratio k_1/k_2 can be calculated by using the value α obtained in the previous experiment (Fig. 2, Table 2 and 3).

Table 2

Kinetic parameters for CO and PPh$_3$ photodissociation in compounds Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_{3-n}$ (PPh$_3$)$_n$, ($n = 0, 1, 2$)

Compound	Leaving group	Parameter	Value
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_3$	CO	α	0.77
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_2$PPh$_3$	CO	β	0.59
Mn(η^5-CH$_3$C$_5$H$_4$)(CO)(PPh$_3$)$_2$	PPh$_3$	γ	0.88

In order to evaluate the remaining rate-constants it is convenient to use the data obtained by using Mn(η^5-CH$_3$C$_5$H$_4$)(CO)$_2$PPh$_3$ (**B**) as reagent. Under these conditions (since there is no **B** → **A** reaction) eq. 14 is transformed into eq. 16.

$$\phi_B = \frac{\beta k_4 [PPh_3]}{k_3 [CO] + k_4 [PPh_3]} - \frac{k_3 [CO]}{k_3 [CO] + k_4 [PPh_3]} \gamma \frac{I_3}{I_2} \tag{16}$$

From eq. 16 it is seen that quantum yield for disappearance of **B** explicitly depends on the light absorbed by species **B** and **C**, and this is a direct result of the reversibility of reaction **B** ⇌ **C**.

The parameter β can be obtained from eq. 16 by using the results for irradiation of Mn(η^4-CH$_3$C$_5$H$_4$)(CO)$_2$PPh$_3$ (**B**) in the absence of added CO but in the presence of an excess of PPh$_3$ (Tables 1 and 2). Similarly, use of data for irradiation of Mn(η^5-CH$_3$C$_5$H$_4$)(CO)(PPh$_3$)$_2$ (**C**) in the absence of added PPh$_3$ and in presence of excess of CO allows us to determine γ from eq. 15. When an excess of both CO and PPh$_3$ is used, a linear relation between ϕ_B and I_3/I_2 (eq. 16) or ϕ_C and I_2/I_3 (eq. 15) is expected, and this was observed for ϕC, as shown in Fig. 5.

Once β (or γ) are known from the first set of experiments, k_3/k_4 and γ (or β) can be evaluated by using the linear relations between ϕ_B and I_3/I_2 or ϕ_C and I_2/I_3 (Tables 2 and 3).

In order to gain further insight into the kinetic significance of the quantum yield, it is useful to divide the first three reactions in the kinetic scheme into the following steps:
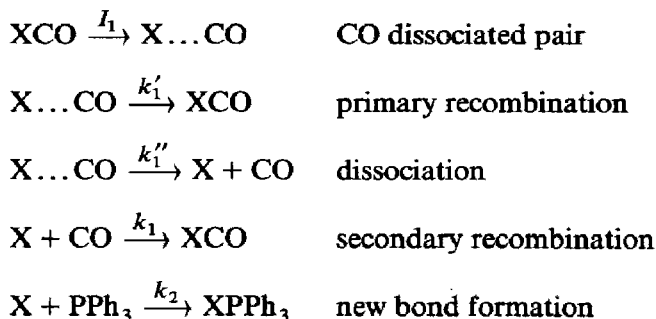
XCO $\xrightarrow{I_1}$ X...CO   CO dissociated pair

X...CO $\xrightarrow{k_1'}$ XCO   primary recombination

X...CO $\xrightarrow{k_1''}$ X + CO   dissociation

X + CO $\xrightarrow{k_1}$ XCO   secondary recombination

X + PPh$_3$ $\xrightarrow{k_2}$ XPPh$_3$ new bond formation

Table 3
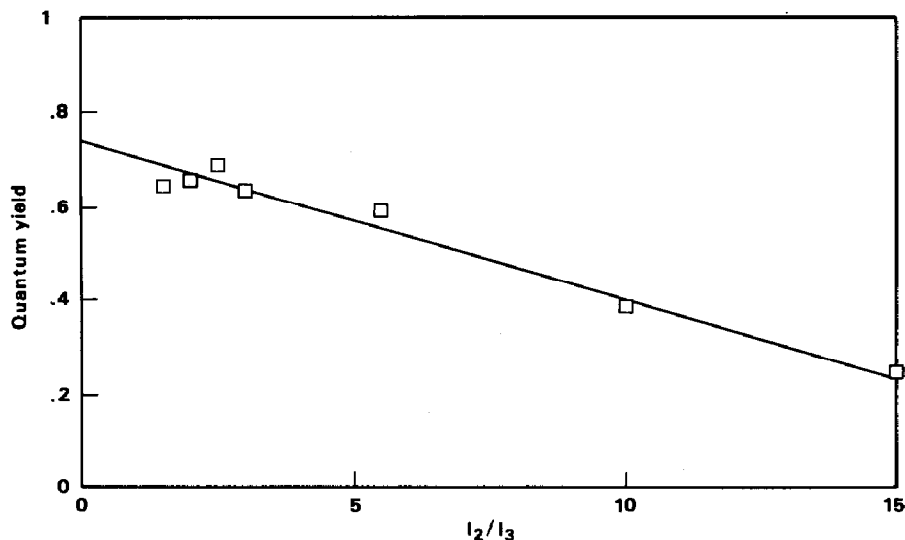
Recombination constants ratio

K_1/K_2	0.51
K_3/K_4	3.5

Fig. 5. Disappearance quantum yield of $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)(PPh_3)_2$ with added excess of carbon monoxide and phosphine as a function of the light absorbed by the reagent and the product $Mn(\eta^5\text{-}CH_3C_5H_4)(CO)_2PPh_3$.

In this way it can be seen that α is the ratio $k_{1''}/(k_{1''} + k_{1'})$, which represents the dissociation efficiency of A. A similar interpretation of β and γ, can be made.

The ratio k_1/k_2 is that between the rate constants for secondary recombination and new bond formation at X, and k_3/k_4 has a similar meaning for Y (eq. 5 and 6).

Conclusions

In most cases quantum yields reported in the literature are obtained under conditions in which the dissociation is the controlling step and the secondary recombination minimized. However, if k_1 is sufficiently greater than k_2, the influence of the secondary recombination can be important even during the early stages of reaction. The approach used in this work has enabled us to account for the influence of the secondary recombination, providing "a posteriori" test of the validity of the assumption $k_1[CO] \ll k_2[PPh_3]$.

The results obtained in this way agree with those previous reported by Wrighton [3] for the photochemistry of the analogous $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ with PPh_3, ($\phi = 0.65$), and in contrast with those reported for the photosubstitution of carbon monoxide by CH_3COCH_3 or $PhC{\equiv}CPh$ in $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ [8] for which $\phi = 1.0$, although this quantum yield was obtained under different conditions. The quantum yields α, β and γ are in principle independent of the entering group, but the involvement of the solvent through a cage effect makes comparison of quantum yields in irradiations in solvolytic and inert solvents especially doubtful, but this type of effect could not really account for the marked difference.

Acknowledgements

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