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Photochemical Substitution Reactions of Manganese Nitrosyl Tetracarbonyl

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The photochemical substitution reaction of $Mn(NO)(CO)_4$ show a quantum yield which is dependent upon the nature of the nucleophile and also upon the concentration of the better nucleophiles. When $Mn(NO)(CO)_4$ is irradiated at 427 nm, the quantum yield, Φ, for its photochemical reaction with $As(_6H_5)_3$ is 0.15. For $P(C_6H_5)_3$ the quantum yield depends on the concentration of the nucleophile. This is interpreted in terms of a mechanism involving two pathways. For poor nucleophiles, a S_N1 pathway is postulated and the deviation of the quantum yield from 1.0 is discussed in terms of the absorption band being irradiated. For better nucleophiles both S_N1 and S_N2 photochemical pathways are indicated.

Introduction

Photochemical techniques have been used in the preparation of organo-metallic compounds for many years. As several recent reviews indicate,[1-8] little quantitative work has been reported on the photochemical substitution reactions of metal carbonyls. The exception to this is studies on Group VI carbonyls. The quantum yields for the photochemical substitution reactions of these carbonyls are reported as $\Phi = 1.0$. The mechanism of these reactions are interpreted as the photochemical loss of CO to give a coordinately unsaturated intermediate which is then attacked by a nucleophile to give the product.

Photochemical reactions of $Fe(CO)_5$ have been extensively used in the preparation of iron carbonyl derivatives; however, little data are available on the mechanism of the reactions and no quantum yield data. Studies on $Fe(CO)_5$ indicate that, like the Group VI carbonyls, the photochemical process is proposed to be the loss of CO to give $Fe(CO)_4$ as the reacting intermediate.[9,10]

The compounds $Fe(CO)_5$ and $Mn(NO)(CO)_4$ are isoelectronic and isostructural. Thermal substitution reactions of $Fe(CO)_5$ are predominately S_N1 in nature,[11] whereas similar reactions with $Mn(NO)(CO)_4$ are S_N2 in nature.[12] Since some information is available on the mechanism of the photochemical reactions of $Fe(CO)_5$, it was of interest to investigate the photochemical reaction mechanism of $Mn(NO(CO)_4$.

Experimental Section

Preparation of Compounds. The compound $Mn(NO)(CO)_4$ was prepared according to the method of Stone and co-workers[13] as detailed by King[14] and it was stored at −78°C under vacuum in the dark. The reagents $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $P(n{-}C_4H_9)_3$ were obtained commercially. The $P(C_6H_5)_3$ was recrystallized from C_2H_5OH and dried under vacuum. The $As(C_6H_5)_3$ was dissolved in hot CH_3OH and filtered, while hot, through activated charcoal. The solution was then allowed to crystallize and the solid filtered and dried under vacuum. The $P(n{-}C_4H_9)_3$ was distilled and stored under N_2. The solvents used were of reagent grade and were dried, distilled, and stored under an atmosphere of N_2.

The compounds used in this study were all known compounds[12] and were prepared using standard vacuum line and Schlenk tube techniques[15] Stock solutions of $Mn(NO)(CO)_4$ in CH_2Cl_2 and $n{-}C_6H_{12}$ were prepared by degassing a volume of solvent in a flask equipped with a rubber septum cap and stopcock. The $Mn(NO)(CO)_4$ was stilled into the flask and N_2 added. Samples of the solution could be withdrawn through the septum cap using syringes. The solutions of $Mn(NO)(CO)_4$ were prepared fresh immediatel before use.

Calculation of Extinction Coefficients. The spectrum of $Mn(NO)(CO)_4$ is shown in Figure 1. The band maximum is at 428 nm. The spectra of $Mn(NO)(CO)_3L$ ($L = P(C_6H_5)_3$ and $As(C_6H_5)_3$) are qualitatively the same with the band maxima at 409 nm and 404 nm, respectively.

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(1) E. L. Wehry, *Quart. Rev.* (*London*), *21*, 213 (1967).
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(14) R.B. King in « Organometallic Synthesis, vol. 1 », ed. by J.J. Eisch and R.B. King, Academic Press, New York, N.Y., 1965.
(15) D.F. Shriver, « The Manipulation of Air-Sensitive Compounds », MmGraw-Hill Book Co., New York, N.Y., 1969.

Table I. Extinction Coefficients for Compounds Used in this Study.

Compound	Solvent	ε_{427}nm, $M^{-1}cm^{-1}$	ε_{409}nm, $M^{-1}cm^{-1}$	ε_{1764}nm, $M^{-1}cm^{-1}$
$Mn(NO)(CO)_4$	$n-C_6H_{12}$	659±18	648±20	
	CH_2Cl_2	606±4	592±3	2257
$Mn(NO)(CO)_3P(C_6H_5)_3$	C_6H_{12}	662±9	694±12	
	CH_2Cl_2	605±9	665±9	
$Mn(NO)(CO)_3As(C_6H_5)_3$	CH_2Cl_2	618±6	696±6	

The extinction coefficients for $Mn(NO)(CO)_4$ at 427 nm and 409 nm were determined by transferring a weighed amount of $Mn(NO)(CO)_4$ under vacuum into a known volume of degassed solvent. Dilutions of this stock solution were made using a 1 ml syringe and a 10 ml volumetric flask equipped with a sidearm and stopcock so the dilutions could take place under N_2.

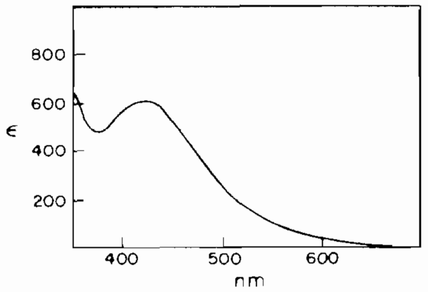

Figure 1. Ultraviolet-Visible Portion of the Spectrum for $Mn(NO)(CO)_4$ in CH_2Cl_2.

The extinction coefficients of $Mn(NO)(CO)_3As(C_6H_5)_3$ could not be isolated analytically pure, the extinction coefficients were determined *in situ* from a reaction mixture of $Mn(NO)(CO)_4$ and $As(C_6H_5)_3$. The original concentration of $Mn(NO)(CO)_4$ was determined from the absorbance of the solution in the infrared region at 1764 cm^{-1} and the visible region at 427 nm and 409 nm. As the reaction progressed, the concentration change of $Mn(NO)(CO)_4$ was followed using the nitrosyl absorption at 1764 cm^{-1} in the infrared. The contribution of $Mn(NO)(CO)_4$ to the absorbance at 427 nm and 409 nm could thus be calculated. The concentration and absorbance at these wavelengths of $Mn(NO)(CO)_3As(C_6H_5)_3$ were determined by difference.

Absorption spectra were taken in 1.000 cm quartz cuvettes (Helma Glass Co., No. 220QS) equipped with a right angle teflon vacuum stopcock (Kontes, No. K-826510). This type of stopcock was used in order that a stream of N_2 could be passed through the cuvette while the stopcock plug was removed and the solution syringed in.

The extinction coefficients are given in Table I.

Relative Quantum Yield Determinations. The relative quantum yields were determined using a MGR-500 Merry-Go-Round (Southern New England Ultraviolet Co.). The solutions were irradiated in 15 mm round Pyrex tubes using a Hanovia 100 watt high pressure mercury lamp. The cooling jacket of the lamp was wrapped in black tape and Corning 3-73 colored glass filters taped in the area of the reaction vessels. This sharp-cut filter has an absorbance greater than 1.0 at all wavelengths below 410 nm.

A stock solution of $Mn(NO)(CO)_4$ was prepared as described above. Weighed amounts of $P(C_6H_5)_3$ and $As(C_6H_5)_3$ were placed in the Pyrex tubes. These tubes were equipped with an o-ring joint and right angle high vacuum Teflon stopcocks. The amount of nucleophile was chosen so as to make the volume change upon addition of $Mn(NO)(CO)_4$ stock solution insignificant. The stock solution (4 ml) was transferred in a syringe under positive N_2 pressure into the reaction vessels with the stopcock plug removed. Eight samples could be prepared and irradiated simultaneously using this technique. The extent of reaction of $Mn(NO)(CO)_4$ was determined by measuring the change in the absorbance of the nitrosyl band at 1764 cm^{-1}. The relative quantum yields were calculated as discussed below. The solutions were thermostatted at less than 20°C during the irradiation time so as to make the contribution of the thermal reaction unimportant.

Absolue Quantum Yields. The absolute quantum yields were determined using a Bausch and Lomb 33-86-07 monochromator equipped with Bausch and Lomb 33-86-31 variable slits. An Osram 33-86-36-01 super high pressure 200 watt mercury lamp was used as the irradiation source. An entrance slit of 3 mm and an exit slit of 1 mm were used. The solutions were prepared as described above except that 3 ml of the reaction mixture was then transferred under N_2 into the quartz cuvettes. During irradiation the solutions were stirred in the cuvettes using a micro stirring bar. The irradiation time was started and stopped using a manual shutter. The solutions were again thermostatted at less than 20°C.

The solutions were irradiated using the 434 nm line of mercury. The calculations of Φ were done at 427 nm, as the ε of $Mn(NO)(CO)_4$ at 427 nm and 434 nm were equal.

Kinetic Scheme for Determining Quantum Yields. A more general discussion of this scheme is given by Hautala[16] and by Balzani and Carassiti.[8] For a reaction scheme given by eq. 1, the quantum

$$B \xrightarrow{h\nu} B^* \longrightarrow C \qquad (1)$$

yield is defined by eq. 2. Appropriately substituting into eq. 2

$$\frac{-d(B)}{dt} = \Phi \bar{I}_0 \qquad (2)$$

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(16) R. Hautala, Ph. D. Dissertation, Northwestern University, 1970.

— where Φ = quantum yield and I_0 = quantity of light absorbed by the reactant in Einstein—l^{-1}—sec^{-1}. This term contains the correction for constant volume of reaction solution and cell geometry, since the same conditions were used for the actinometer solutions —.

and integrating, eq. 3 is obtained

$$[B_0]—[B]+\frac{1}{2.303\ \varepsilon L}\ln\frac{1—e^{-2.303\varepsilon L[B_0]}}{1—e^{-2.303\varepsilon L[B]}} = \frac{\Phi I 1000(t—t_0)}{L} \qquad (3)$$

— where L = pathlength of the cell. This equation is valid if equal volumes of both the reaction mixture and actinometer solution are irradiated under the same conditions —.

This can be rearranged to give eq. 4

$$A_0—A+\log\frac{1—T}{1—T_0}=\varepsilon\Phi I 1000(t—t_0) \qquad (4)$$

— where A and A_0 refers to the absorbance of the reactant and T and T_0 to transmittance of the reactant at times t=o and t, respectively. If the products also absorb at the same wavelength, as is usually the case, then the total absorbance and transmittance of the solution must be corrected. This correction was calculated in this work either by measuring the solution absorbance at two wavelengths or by using the concentrations calculated from the infrared absorbance data —.

Since I, the light intensity in Einsteins-cm^2-sec^{-1} can be evaluated using an actinometer, the quantum yield, Φ, can be determinde by measuring the absorbance as a function of time. The light intensity was evaluated using a solution of $K_3Fe(C_2O_4)_3$ as the actinometer.[17]

Because of the small absorbance changes involved in these reactions, the extent of the reaction, and therefore the contribution of $Mn(NO)(CO)_4$ to the total absorbance was determined using the nitrosyl absorption at 1764 cm^{-1} in the infrared. The absorbance terms were then calculated at 427 (434) nm and the value of Φ from eq. 4 determined. The use of this infrared data to solve eq. 4 was found to give better results than attempting to follow the change in absorbance at 427 nm and 409 nm as a function of time.

Emission Spectra. Reaction solutions of $Mn(NO)(CO)_4$ in CH_2Cl_2 were sealed in 13 mm pyrex tubes under vacuum. Light of 427 nm was used to excite the solutions under investigation for room temperature fluorescence.

Similar solutions were prepared in EPA mixed solvent (Matheson, Coleman, and Bell) in Pyrex phosphorescence tubes. These samples were sealed under vacuum and 427 nm light used as the exciting irradiation.

Spectra. Infrared spectra were recorded on a Perkin-Elmer 337 spectro-photometer equipped with an external recorder. Ultraviolet and visible spectra were recorded either on a Cary-14 or a Beckman DU-2 equipped with a Gilford attachment. Emission spectra were recorded on a Hitachi Perkin-Elmer MPF-4A spectrophotometer.

Results

Quantum yields for reaction 1 have been measured as a function of the concentration of the nucleophile. These measurements of the relative quantum

$$Mn(NO)(CO)_4+L\xrightarrow{h\nu}Mn(NO)(CO)_3L+CO \qquad (1)$$
$$[L=P(C_6H_5)_3 \text{ and } As(C_6H_5)_3]$$

yields were determined using a Corning 3-73 sharp-cut filter and in round tubes. In order to minimize the errors introduced by the use of round tubes, the reactions were allowed to go to only about 20% completion. Other experiments also showed that the extent of the reaction declined rapidly as the irradiating wavelength increased. This filter therefore gave reasonable aproximation of monochromatic light. The use of the merry-go-round to determine the relative quantum yields, $I\Phi$, insures that all of the reacting solutions were treated identically. The values of $I\Phi$ obtained in these experiments were reproducible. The ratio of $I\Phi_L/I\Phi_{L'}$ to $\Phi_L/\Phi_{L'}$ for $P(C_6H_5)_3$ and $As(C_6H_5)_3$ of 1.2/1 indicate the validity of the treatment. Table II shows the dependence of $I\Phi$ on the concentration of the nucleophiles. This table also shows values of $I\Phi$ for $P(n—C_4H_9)_3$; however, the reaction solutions for this ligand could not be thermostatted at such a temperature as to prevent the thermal reaction from occurring. These values are therefore too high. They are given to indicate the trend.

Table II. The Dependence of Φ on the Concentration of the Nucleophile.

L	$10_3[L]$ moles—l^{-1}	$I\Phi\times10^9$ moles—cm^{-2}—sec^{-1}
$P(C_6H_5)_3$	0.85	0.50
	2.00	0.55
	5.70	0.62
	19.90	0.69
$As(C_6H_5)_3$	1.14	0.42
	3.30	0.45
	6.20	0.44
	20.10	0.41
$P(n—C_4H_9)_3$	15.0	1.03 [a]
	17.7	1.14 [a]

[a] Includes some contribution from thermal reaction (see text)

Table III. Quantum Yields for the Reaction $Mn(NO)(CO)_4+L$ ($L=P(C_6H_5)_3$ and $As(C_6H_5)_3$) at 427 nm.

$10^3[L]$	Φ, moles—ein^{-1}
$P(C_6H_5)_3$	
19.9	0.19 [a]
$As(C_6H_5)_3$	
20.2	0.15 [a]

[a] Average of three determinations. The error is estimated to be ± 5%.

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[17] J.G. Calvert and J.N. Pitts, Jr., « Photochemistry », John Wiley and Sons, New York, N.Y., 1966, p. 783.

Table IV. Comparison between Calculated and Observed Absorbances in the 400 nm Spectral Region of An Irradiated Reaction Mixture of $Mn(NO)(CO)_4$ and $P(C_6H_5)_3$.

Time after Irradiation Stopped	Solution	$Mn(NO)(CO)_4$ $A_{1764\ cm^{-1}}$	$10^3[Mn(NO)(CO)_4]$ [a]	$10^3[Mn(NO)(CO)_3L]$ [b]	Calc. A_{427}	Obs. A_{427}
10 min.	A	0.309	1.37	0.74	1.279	1.324
20 min.	A	0.315	1.40	0.71	1.279	1.293
10 min.	B	0.319	1.42	0.69	1.279	1.358
20 min.	B	0.300	1.33	0.78	1.279	1.287

$[Mn(NO)(CO)_4]_0 = 2.11 \times 10^{-3}$ [a] Concentrations in moles per liter calculated from infrared absorption data. [b] Calculated by difference.

Table III shows the values of the quantum yields for the reactions with $P(C_6H_5)_3$ and $As(C_6H_5)_3$.

The two nucleophiles extensively studied in this work, $P(C_6H_5)_3$ and $As(C_6H_5)_3$ differed in their photochemical reaction behavior. In the case of $As(C_6H_5)_3$ the spectra were as expected for a smooth conversion of $Mn(NO)(CO)_4$ to $Mn(NO)(CO)_3L$ as the product. The quantum yields, both relative and absolute, were independent of the concentration of $As(C_6H_5)_3$.

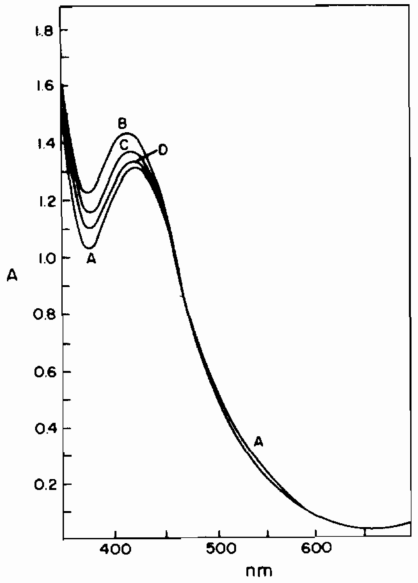

Figure 2. Spectra Changes of an Irradiated Reaction Mixture of $Mn(NO)(CO)_4$ and $P(C_6H_5)_3$ in CH_2Cl_2. A = original solution; B = after 1000 sec. hν; C = B + 10 min. in dark; D = B + 20 min. in dark.

In the case of $P(C_6H_5)_3$ however, the visible spectrum during irradiation exhibited a different behavior. When $Mn(NO)(CO)_4$ in the presence of $P(C_6H_5)_3$ was irradiated, both in CH_2Cl_2 and $n{-}C_6H_{14}$, the spectrum at 409 nm and 427 nm showed a large increase in absorption which could not be accounted for by the known components of the solution. When irradiation was stopped, the absorption spectrum decayed back toward that calculated for the mixture of product, $Mn(NO)(CO)_3\ P(C_6H_5)_3$ and unreacted $Mn(NO)(CO)_4$. Figure 2 shows the visible absorption demonstrating this decay process. The infrared spectra of such reaction mixtures showed that, during this decay process, the concentration of $Mn(NO)(CO)_4$ remained unchanged. This implies that the species responsible for this behavior goes on to product. Figure 3 shows such infrared spectra. and Table IV tabulates the absorbance data for the infrared and visible spectra.

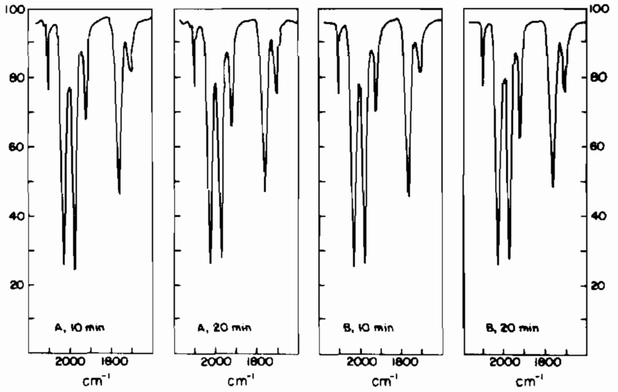

Figure 3. Infrared Spectra Carbonyl and Nitrosyl Region of Irradiated Mixture of $Mn(NO)(CO)_4$ and $P(C_6H_5)_3$. The solvent is CH_2Cl_2. (See Table IV for Calculations of Data).

The emission spectra of these reaction solutions were investigated in the possibility that the decay was caused by a long-lived intermediate, however no emission spectra were detected. The reaction solutions were also investigated for secondary photochemical reactions. No further photochemical reaction of the product, $Mn(NO)(CO)_3L$, was detected under the conditions used.

Discussion

The photochemical substitution reactions of metal carbonyl compounds have not been extensively studied. The photochemical substitution reactions of Group VI carbonyls have been studied and Strohmeier and Von Hobe[18] have shown the quantum yield to be $\Phi = 1.0$ and independent of the nature of the nucleophile. The mechanism is postulated as a dissociation of CO to give $M(CO)_5^*$ as the reaction intermediate. This intermediate has also been observed spectroscopically.[19] Gray and Beach[20] have proposed a molecular orbital scheme for $Cr(CO)_6$

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(18) W. Strohmeier and D. von Hobe, *Chem. Ber.*, *94*, 2031 (1961).

(19) I.W. Stolz, G.R. Dobson, and R.K. Sheline, *J. Am. Chem. Soc.*, *84*, 3589 (1962).

(20) N.A. Beach and H.B. Gray, *J. Am. Chem. Soc.*, *90*, 5713 (1968).

and the lowest energy transition is given to be $2t_{2g} \rightarrow 3e_g$ (d–d). Since this transition is σ^*(M–C) in character, irradiation in this region would weaken the M–C bond.

Work with $Fe(CO)_5$ indicates similar results. Matrix isolation work with $Fe(CO)_5$ indicates the presence of $Fe(CO)_4$ upon irradiation.[21] Lloyd and Schlag[22] have also discussed a molecular orbital scheme for $Fe(CO)_5$ in which the lowest energy transition is also σ^*(M–C) in character.

Thus previous work has shown that the photochemical process is a dissociation of CO followed by nucleophile attack. The photochemical substitution data for $Mn(NO)(CO)_4$ has several facts to be explained: 1) the rate of reaction with $P(C_6H_5)_3$; 2) reaction with $P(C_6H_5)_3$ produces a relatively stable intermediate, but such an intermediate is not observed for $As(C_6H_5)_3$; 3) the observed Φ of $P(C_6H_5)_3$ is dependent on the concentration of $P(C_6H_5)_3$, whereas it is concentration independent for $As(C_6H_5)_3$.

A mechanism with two pathways can account for this data. The kinetic derivation is given below.

Case I. Poor Nucleophiles

$$\mathrm{B} \xrightarrow{\Phi I} \mathrm{C}^* \xrightarrow{L} \text{Product}$$

$$\Phi_{obs} = \frac{\frac{-d[B]}{dt}}{I} \tag{5}$$

Case II. Better Nucleophiles

$$\begin{tikzcd}
 & & \text{Product} \\
\mathrm{B} \arrow[r, shift left, "\Phi_1'I"] \arrow[d, "\Phi_2'I"] & \mathrm{B}^* \arrow[l, shift left, "k_d"] \arrow[ur, "k_2[L]"] \arrow[dr, "k_{-2}[L]"'] & \\
\mathrm{C}^* \arrow[d, "L"] & & \mathrm{B} \\
\text{Product} & &
\end{tikzcd}$$

$$\frac{-d[B]}{dt} = \Phi_1'I - k_d[B^*] - k_{-2}[L][B^*] + \Phi_2'I \tag{6}$$

$$\frac{-d[B^*]}{dt} = -\Phi_1'I + k_d[B^*] + k_2[L][B^*] + k_{-2}[L][B^*] \tag{7}$$

$$\Phi_{obs} = \frac{\frac{-d[B]}{dt}}{I} \tag{8}$$

Using the steady state approximation for B*, and rearranging:

$$\frac{\Phi_1}{\Phi_{obs}-\Phi_2} = \frac{k_d}{k_2[L]} + \frac{k_2+k_{-2}}{k_2} \tag{9}$$

The above treatment proposes that for $As(C_6H_5)_3$, Φ_{obs} should be independent of $[As(C_6H_5)_3]$. This is what is observed. For $P(C_6H_5)_3$, if Φ_2 is taken as the quantum yield for the $As(C_6H_5)_3$ reaction, then a plot of $1/\Phi_{obs}-\Phi_2'$ vs $1/[L]$ should yield a straight line. This is shown in Figure 4. Thus, a possible mechanism for the photochemical substitution reaction of $Mn(NO)(CO)_4$ is one consisting of two pathways. With poor nucleophiles, only a S_N1 type of pathway is important. With better nucleophiles, both S_N1 and S_N2 types of pathways are important. Rest[23] has shown that irradiation of $Mn(NO)(CO)_4$ at < 360 nm causes loss of CO to give a $Mn(NO)(CO)_3$ species.

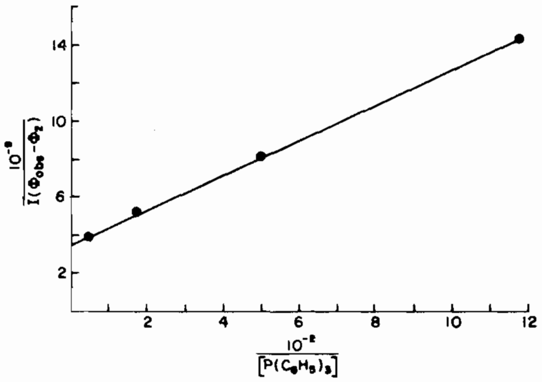

Figure 4. Plot of the Relative Values of $1/(\Phi_{obs}-\Phi_2)$ Versus $1/[P(C_6H_5)_3]$.

Since the spectrum of $Mn(NO)(CO)_4$ consists of two overlapping bands, see Figure 1, then absorption at 427 nm must be of two different electronic transitions. The tail of the higher energy band can be estimated to be responsible for about 20% of the absorption at 427 nm. Assuming this portion of the irradiation absorbed causes a dissociation process which is expected to occur with a quantum yield of 1.0, then a yield of approximately 0.2 is estimated which is in fair agreement with the experimental value of 0.15 for the reaction with the poor nucleophile $As(C_6H_5)_3$.

The mechanism for the photochemical reaction of $Mn(NO(CO)_4$ with $P(C_6H_5)_3$ therefore appears to involve two pathways, the S_N1 path discussed above and a S_N2 path. This latter pathway is probably the one which gives the stable intermediate observed in this reaction.

This intermediate may be caused by the interaction of a C_{4v}, tetragonal pyramid, stabilized excited state with $P(C_6H_5)_3$. Pearson[24,25] has recently discussed several symmetry rules for predicting the possible structures of molecules. For five-coordinate molecules the vibrations required to convert the D_{3h}, trigonal bipyramid, structure to the C_{4v} structures is of B_1 symmetry whereas the reverse process is of E' symmetry. Berry and co-workers[26] have calculated the orbital energy levels for two five-cordinate molecules PF_5 and AsF_5 which are known to be stereochemically non-rigid in the ground state.[27] These calculations

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[21] A.J. Rest, University of Cambridge, Cambridge, England, private communication.

[22] D.R. Lloyd and E.W. Schlag, *Inorg. Chem.*, *8*, 2544 (1969).

[23] A.J. Rest, *Chem. Commun.*, 345 (1970).

[24] R.G. Pearson, *J. Am. Chem. Soc.*, *91*, 1252 (1969).

[25] R.G. Pearson, *J. Am. Chem. Soc.*, *91*, 4947 (1969).

[26] R.S. Berry, M. Tamres, C.J. Ballhausen, and H. Johanseh, *Acta Chem. Scand.*, *22*, 231 (1968).

[27] E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, *20*, 245(1966).

indicate that in the first excited state for these molecules, the C_{4v} structure is stabilized more relative to the D_{3h} structure than in the ground state. In the excited state the electron flow required to convert the $C_{4v} \rightarrow D_{3h}$ sructures is between $(3b_1)^2 \rightarrow (6a_1)^1$ orbitals, whereas the $D_{3h} \rightarrow C_{4v}$ conversion requires a flow between the $(4e)^3 \rightarrow (5e)^1$ orbitals. Qualitatively the $C_{4v} \rightarrow D_{3h}$ vibration should be more difficult in the first excited state than in the ground state while the $D_{3h} \rightarrow C_{4v}$ vibration is less affected. This trend of stabilization of the C_{4v} structure in the excited state is also shown by the calculations of the relative energies of the molecules.

Postulated configurations of *d*–orbitals for $Fe(CO)_5$ also indicate a possible preference for C_{4v} geometry in the excited state. However, the breaking of the Fe–C bond probably takes precedence.

The influence of the nitrosyl group makes it difficult to determine the relative ordering of the *d*–orbitals in $Mn(NO)(CO)_4$. Several things can possibly be said about the low energy transition in this compound. The thermal substitution reactions of nitrosyl complexes are postulated to have a mechanism in which a pair of electrons is isolated on the nitrosyl group, freeing a metal *d*–orbital for the entering nucleophile. If the low energy transition is of this nature and contains little σ^*(M–C) character, then the dissociation of CO would be of little importance for this excited state of $MnNO(CO)_4$ and might stabilize a C_{4v} tetragonal pyramid structure. The nucleophile $P(C_6H_5)_3$ can react with this stabilized C_{4v} structure to form a six-coordinate intermediate which, as the infrared data indicate, goes on to product. Since $As(C_6H_5)_3$ is a poorer nucleophile, it will not interact as strongly with this excited state and thus does not show this reaction pathway. The more basic $P(n\text{–}C_4H_9)_3$ will interact more strongly and with a higher quantum yield (Table III) than $P(C_6H_5)_3$. Figure 5 shows the postulated mechanism for this reaction.

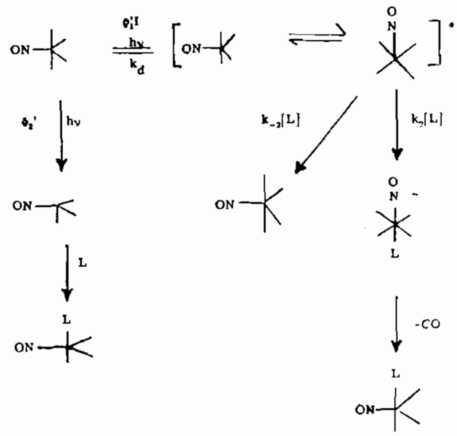

Figure 5. Proposed Mechanism for the Photochemical Substitution Reactions of $Mn(NO)(CO)_4$.

In contrast to other metal carbonyl systems studied a quantum yield of less than 1.0 was found for the photochemical substitution reaction of $MnNO(CO)_4$ irradiated at 427 nm. A reaction mechanism which can account for this difference has been postulated. It would now be of interest to examine other metal carbonyl compounds known to react thermally by S_N2 processes to determine if they undergo a similar photochemical behavior to that found for $MnNO(CO)_4$. However, studies regarding the nature of the energy levels in molecules such as these are needed before more definitive interpretations of their photochemical reactions can be given.

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