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Rates and Mechanism of Substitution Reactions of Dimanganesedecacarbonyl and Some of its Derivatives

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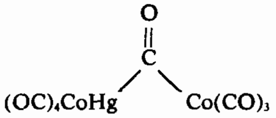
The rates of substitution reactions of $Mn_2(CO)_{10}$ and some of its derivatives are reported. The rate of reaction of $Mn_2(CO)_{10}$ with various reagents is first-order in carbonyl and zero-order in reagent concentrations. For poor nucleophiles the rate of reaction is largely decreased with the addition of CO and the activation parameters for reaction are $\Delta H^* = 37$ kcal/mole and $\Delta S^* = +20$ e.u. These observations suggest that substitution reactions of $Mn_2(CO)_{10}$ in p-xylene solution take place by a CO dissociation mechanism. Similar results were obtained for the reaction of monosubstituted derivatives $Mn_2(CO)_9L$, but the kinetic behavior of $Mn_2(CO)_8[P(C_6H_5)_3]_2$ is different.

Introduction

Extensive studies have been made on substitution reactions of metal carbonyls and excellent reviews of the subject were written recently by Brown[1] and by Angelici.[2] Also considerable effort is currently being spent on the synthesis of new metal-metal bonded carbonyls and investigations of their properties and structures.[3] In spite of this the kinetics and mechanisms of very few such systems have been examined.

Some of the metal-metal bonded systems that have been examined include the reactions of acetylenes[4] with $Co_2(CO)_8$ and its exchange with ^{14}CO[5] and reaction with $P(C_6H_5)_3$.[6] The kinetics of ^{14}CO exchange with acetylene derivatives of the type $Co_2(CO)_6C_2RR'$ have been reported.[7] These compounds contain a cobalt-cobalt bond but may also have groups bridging the metals.[8]

Substitution reactions of three metal-metal bonded systems that do not contain bridging groups have also been examined. The exchange of ^{14}CO with $Hg[Co(CO)_4]_2$ was found to be first-order and it was suggested[9] that this perphas involved a mercury-cobalt bond cleavage by means of a ligand migration process to generate the active intermediate



$$(OC)_4CoHg\overset{\overset{O}{\|}}{C}Co(CO)_3$$

Haines, Hopgood, and Poë[10a] have recently reported results of investigations on the rates of substitution reactions of $Mn_2(CO)_{10}$ with $P(_6H_5)_3$ in decalin solution. The reaction is first-order but only partially inhibited by added CO. On the basis of this, as well as the rate of the reaction of I_2 with $Mn_2(CO)_{10}$ and its decomposition in the absence and presence of oxygen, it was suggested that the substitution reaction proceeds by two paths. The minor path (about 27%) proceeding by a dissociation mechanism (loss of CO) and the major path involving the homolytic cleavage of $Mn_2(CO)_{10}$ to form the reactive $Mn(CO)_5$ radicals in a solvent cage. It was also suggested that the radicals need not be the active intermediate but rather it might be a carbonyl bridged species of type (I), $(OC)_5MnCOMn(CO)_4$.

This intermediate is now favored,[11] and it appears that it can form by means of a ligand migration reaction similar to that proposed for the $Hg[Co(CO)_4]_2$ system.[9] Similar results have also been obtained for the reaction of $Re_2(CO)_{10}$ with $P(C_6H_5)_3$.[10b]

This paper reports the rates of substitution reactions of $Mn_2(CO)_{10}$, and some of its derivatives with different reagents in *p*-xylene solution. Preliminary observations[12a,b] on some of these reactions indicated that they proceed by a dissociative process rather than by the homolytic cleavage of the Mn-Mn bond to form reactive radical intermediates. The results of our kinetic studies are largely in accord with this interpretation,[12c]

Experimental Section

Compounds and Solvents. The solvents used were purified by distillation, deoxygenated and carefully dried. $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $As(C_6H_5)_3$ (Eastman Or-

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ganic Chem.), $Sb(C_6H_5)_3$ (Matheson Co.), $P(n\text{-}C_4H_9)_3$ (Eastman Organic Chem. and Aldrich Chem. Co.) were commercial products, $P(C_2H_5)_3$ was prepared from PBr_3 and C_2H_5MgBr. Solids were recrystallized from methanol; $P(OC_6H_5)_3$ was distilled over sodium in a stream of N_2 at reduced pressure, $P(n\text{-}C_4H_9)_3$ and $P(C_2H_5)_3$ were dried over BaO and were purified by distillation in a stream of nitrogen. The $Mn_2(CO)_{10}$ was freshly sublimed before use.

Preparations. All operations were carried out in the dark and under an atmosphere of nitrogen using anhydrous, oxygen-free solvents. The compounds $Mn_2(CO)_8[P(C_6H_5)_3]_2$, $Mn_2(CO)_8[P(n\text{-}C_4H_9)_3]_2$, and $Mn_2(CO)_8[P(OC_6H_5)_3]_2$ were prepared in small volumes of *p*-xylene at 120°C from $Mn_2(CO)_{10}$ and $P(C_6H_5)_3$ (1:4.5, 12 hrs), $P(n\text{-}C_3H_9)_3$ (1:2.5 7 hrs) or $P(OC_6H_5)_3$ (1:5, 12 hrs). They were recrystallized from xylene, methanol or hexane, respectively. The preparation of $Mn_2(CO)_9P(C_6H_5)_3$ was described previously.[12] $Mn_2(CO)_9P(n\text{-}C_4H_9)_3$ was isolated from a reaction of 650 mg of $Mn_2(CO)_{10}$ and 330 mg of $P(n\text{-}C_4H_9)_3$ in 10 ml of *p*-xylene after heating at 125°C for 6 hr. The solvent was evaporated, the residue was dissolved in hexane and chromatographed over Al_2O_3 (anhydrous). Evaporation of the eluate yielded a yellow oil. 400 mg, 43%. *Anal.* Calcd. for $Mn_2(CO)_9P(n\text{-}C_4H_9)_3$: C, 44.70; H, 4.82. Found: C, 43.90; H, 4.66.

$Mn_2(CO)_9P(OC_6H_5)_3$ was prepared in the same way from 450 mg $Mn_2(CO)_{10}$ and 350 mg $P(OC_6H_5)_3$. After heating at 125°C for 18 hr, the solvent was evaporated in a vacuum. The residue was chromatographed in hexane over Al_2O_3 (3% water). Yellow $Mn_2(CO)_9P(OC_6H_5)_3$ crystallized from the concentrated eluate at –78°C. At room temperature, it exists as a wax. Yield 320 mg, 42%. *Anal.* Calcd. for $Mn_2(CO)_9P(OC_6H_5)_3$: C, 48.24; H, 2.25. Found: C, 47.65; H, 2.23%.

Kinetic Studies. Purified, anhydrous *p*-xylene was used as the solvent in all of the experiments. The reaction mixtures were kept at constant (±0.1°) temperature, in the dark, and under an atmosphere of nitrogen during the kinetic runs. All of the kinetics were carried out under pseudo-first-order conditions, using at least a ten-fold excess of reagent. The rates of reaction were followed spectrophotometrically as described below. Measurements were usually made over a period of three half-lives. If not mentioned specifically, all reactions went to completion and the data gave good linear plots of $\log(A\text{-}A_\infty)$ *vs.* time, where A is the absorbance at time t and A_∞ is the absorbance at infinite time. Rate constants were reproducible to within 10% or better. Errors in activation parameters are estimed to be ±1 kcal/mole for ΔH^* and ±2 e.u. for ΔS^*.

The rates of reaction were followed by monitoring changes in the ir spectra of the reaction mixtures using a Perkin-Elmer Spectrophotometer, Model 337 and Model 237. This was done by observing changes in the C–O stretching regions of the spectra to record the disappearance of starting material and/or appearance of product. Samples were removed from the reaction flasks by means of a syringe inserted through a rubber serum cap. In order to avoid a partial vacuum and introduction of oxygen as a result of removal of aliquots, the reaction flasks were kept under a slight positive pressure of nitrogen.

To study the influence of carbon monoxide on the rates of reaction, certain volumes of CO gas were introduced to the reaction flasks (50 ml volumetric flasks, filled with 25 ml reaction solution) by means of a gastight syringe yielding a partial pressure of CO of *ca.* 60-300 mm Hg at room temperature. Assuming the validity of Henry's Law and a solubility of CO in *p*-xylene at 100°C of $\alpha = 0.15 \frac{\text{N cm}^3\ (\text{CO})}{\text{cm}^3\ (\text{solvent})\text{atm}}$[13], this corresponds to concentrations of CO in solution of *ca.* $0.5\text{–}3 \times 10^{-3}$ *M*.

Results

The observed pseudo-first-order rate constants, k_{obs}, for reaction (1)

$$Mn_2(CO)_{10} + L \longrightarrow Mn_2(CO)_9L + CO \qquad (1)$$

where L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ at different temperatures are listed in Table I. Experiment (6e), measured in the presence of CO, approached an equilibrium leaving 50% $Mn_2(CO)_{10}$ unreacted; k_{obs} in this instance was estimated from the initial slope of the rate plot of $\log(A\text{-}A_\infty)$ *vs.* time using the value for 100% reaction for A_∞. The sance assumption was made to estimate the rate constants of the reactions with $As(C_6H_5)_3$. These reactions, although eventually leading to consumption of the total starting material, became slower as the reaction proceeded; the first order rate plots were linear only over ca. 20-30% of the reaction.

The reaction products $Mn_2(CO)_9L$ and $Mn_2(CO)_8L_2$ for L = $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ were unstable and were not accumulated during the reaction. However, their preparation at high temperatures as well as their instability above 100°C were reported previously.[14,15,16,17] Thus the assumption of the initial formation of $Mn_2(CO)_9L$ followed by its decomposition seems reasonable. The presence of $Mn_2(CO)_9As(C_6H_5)_3$ was clearly detected in the reaction solutions by means of ir spectra. Experiments (3c, d), (4d, e), (8d), (9d, e) of Table I were carried out in an atmosphere containing carbon monoxide at the partial pressures of CO designated.

The activation parameters for reaction (1) with L = $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ are:

L	ΔH^*, kcal/mole	ΔS^*e.u.
$P(C_6H_5)_3$	37±1	+19±2
$P(OC_6H_5)_3$	38±1	+21±2

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Table I. Rate Constants for Reaction (1) in *p*-Xylene at Different Temperatures

Exp.	T, °C	$[Mn_2(CO)_{10}]$, *M*	L	[L], *M*	k_{obs}, sec^{-1}
1a	120	3.6×10^{-4}	$P(C_6H_5)_3$	3.98×10^{-3}	2.4×10^{-4}
1b	120	5.4×10^{-4}	$P(C_6H_5)_3$	8.84×10^{-2}	2.5×10^{-4}
1c	120	5.8×10^{-4}	$P(C_6H_5)_3$	1.03×10^{-1}	2.5×10^{-4}
1d	120	6.3×10^{-4}	$P(C_6H_5)_3$	1.89×10^{-1}	2.6×10^{-1}
1e	120	4.2×10^{-4}	$P(C_6H_5)_3$	7.74×10^{-3}	2.2×10^{-4} [a]
1f	120	4.4×10^{-4}	$P(C_6H_5)_3$	$7.5\ \times10^{-2}$	2.4×10^{-4} [a]
2a	120	5.2×10^{-4}	$P(OC_6H_5)_3$	$9.6\ \times10^{-3}$	2.3×10^{-4}
2b	120	6.1×10^{-4}	$P(OC_6H_5)_3$	4.57×10^{-2}	2.4×10^{-4}
2c	120	5.2×10^{-4}	$P(OC_6H_5)_3$	1.55×10^{-1}	2.4×10^{-4}
3a	120	2.8×10^{-4}	$As(C_6H_5)_3$	9.75×10^{-2}	2.4×10^{-4}
3b	120	5.0×10^{-4}	$As(C_6H_5)_3$	1.03×10^{-1}	2.4×10^{-4}
3c	120	5.4×10^{-4}	$As(C_6H_5)_3$	9.35×10^{-2}	$<10^{-6}$ [a]
3d	120	5.0×10^{-4}	$As(C_6H_5)_3$	1.01×10^{-1}	$\sim1\times10^{-4}$ [b]
4a	120	3.5×10^{-4}	$Sb(C_6H_5)_3$	4.77×10^{-3}	1.4×10^{-4}
4b	120	4.5×10^{-4}	$Sb(C_6H_5)_3$	4.57×10^{-2}	2.2×10^{-4}
4c	120	4.8×10^{-4}	$Sb(C_6H_5)_3$	7.58×10^{-2}	2.2×10^{-4}
4d	120	3.6×10^{-4}	$Sb(C_6H_5)_3$	1.09×10^{-2}	no reaction [a]
4e	120	4.2×10^{-4}	$Sb(C_6H_5)_3$	6.21×10^{-2}	2.6×10^{-5} [a]
5a	110	5.6×10^{-4}	$P(C_6H_5)_3$	7.43×10^{-3}	6.8×10^{-5}
5b	110	6.0×10^{-4}	$P(C_6H_5)_3$	4.53×10^{-2}	6.5×10^{-5}
5c	110	5.3×10^{-4}	$P(C_6H_5)_3$	1.59×10^{-1}	6.8×10^{-5}
6a	100	5.6×10^{-5}	$P(C_6H_5)_3$	8.85×10^{-4}	1.8×10^{-5}
6b	100	2.8×10^{-4}	$P(C_6H_5)_3$	4.51×10^{-3}	1.6×10^{-5}
6c	100	4.7×10^{-4}	$P(C_6H_5)_3$	7.18×10^{-2}	1.7×10^{-5}
6d	100	5.6×10^{-4}	$P(C_6H_5)_3$	2.43×10^{-1}	1.8×10^{-5}
6e	100	4.2×10^{-4}	$P(C_6H_5)_3$	5.25×10^{-3}	1.1×10^{-5} [a]
6f	100	5.3×10^{-4}	$P(C_6H_5)_3$	7.55×10^{-2}	1.6×10^{-5} [a]
7a	100	6.7×10^{-4}	$P(OC_6H_5)_3$	6.84×10^{-3}	1.5×10^{-5}
7b	100	6.3×10^{-4}	$P(OC_6H_5)_3$	8.08×10^{-2}	1.6×10^{-5}
8a	100	2.2×10^{-4}	$As(C_6H_5)_3$	7.0×10^{-3}	1.2×10^{-5}
8b	100	1.9×10^{-4}	$As(C_6H_5)_3$	9.2×10^{-2}	1.9×10^{-5}
8c	100	3.9×10^{-4}	$As(C_6H_5)_3$	9.2×10^{-2}	1.7×10^{-5}
8d	100	3.6×10^{-4}	$As(C_6H_5)_3$	9.3×10^{-2}	$\sim5\times10^{-6}$ [c]
9a	100	2.9×10^{-4}	$Sb(C_6H_5)_3$	6.75×10^{-3}	$\sim1.2\times10^{-5}$
9b	100	2.3×10^{-4}	$Sb(C_6H_5)_3$	8.20×10^{-2}	1.7×10^{-5}
9c	100	4.5×10^{-5}	$Sb(C_6H_5)_3$	8.25×10^{-2}	1.7×10^{-5}
9d	100	4.8×10^{-4}	$Sb(C_6H_5)_3$	$8.0\ \times10^{-2}$	3.2×10^{-6} [c]
9e	100	4.8×10^{-4}	$Sb(C_6H_5)_3$	8.0×10^{-2}	6.4×10^{-6} [d]

[a] $p_{CO}\sim300$ mm Hg; [b] $p_{CO}\sim60$ mm Hg; [c] $p_{CO}\sim200$ mm Hg; [d] $p_{CO}\sim100$ mm Hg.

Table II. Rate Constants of Reaction (1) in p-Xylene at Different Temperatures

Exp.	T, °C	$[Mn_2(CO)_{10}]$, *M*	L	[L], *M*	$k_{init.}$, sec^{-1}
1a	120	5.2×10^{-4}	$P(n\text{-}C_4H_9)_3$	1.29×10^{-2}	2.6×10^{-4}
1b	120	5.5×10^{-4}	$P(n\text{-}C_4H_9)_3$	1.67×10^{-1}	2.7×10^{-4}
2a	120	5.1×10^{-4}	$P(C_2H_5)_3$	2.13×10^{-2}	2.4×10^{-4}
2b	120	4.9×10^{-4}	$P(C_2H_5)_3$	3.04×10^{-1}	2.3×10^{-4}
2c	120	4.8×10^{-4}	$P(C_2H_5)_3$	1.54×10^{-1}	3.2×10^{-4}
2d	120	2.2×10^{-4}	$P(C_2H_5)_3$	1.51×10^{-1}	3.1×10^{-4}
3a	100	4.8×10^{-4}	$P(n\text{-}C_4H_9)_3$	$1.3\ \times10^{-2}$	2.0×10^{-5}
3b	100	4.8×10^{-4}	$P(n\text{-}C_4H_9)_3$	1.52×10^{-1}	1.9×10^{-5}
3c	100	1.9×10^{-4}	$P(n\text{-}C_4H_9)_3$	1.61×10^{-1}	2.2×10^{-5}
4a	100	5.6×10^{-4}	$P(C_2H_5)_3$	1.92×10^{-2}	2.5×10^{-5}
4b	100	5.2×10^{-4}	$P(C_2H_5)_3$	1.39×10^{-1}	2.3×10^{-5}
4c	100	2.5×10^{-4}	$P(C_2H_5)_3$	1.38×10^{-1}	2.6×10^{-5}
4d	100	5.9×10^{-4}	$P(C_2H_5)_3$	2.87×10^{-1}	2.0×10^{-5}

Of the many rate constants obtained for the reactions of $Mn_2(CO)_{10}$ with $P(n\text{-}C_4H_9)_3$ and $P(C_2H_5)_3$ only a few selected values are listed in Table H. With ratios of $P(n\text{-}C_4H_9)_3/Mn_2(CO)_{10}>30$ and for all experiments with $P(C_2H_5)_3$, the first order rate plots for the disappearance of $Mn_2(CO)_{10}$ were non-linear, showing increasing rates as the reaction proceeded. Rate constants reported were calculated from the initial slopes of the rate plots, corresponding to 10-30% consumption of substrate. In these instances errors of the rate constants are greater than 10%, however, because of their reproducibility within this limit in a great number of experiments they are believed to bear significance. Carbon monoxide had little influence on the rate of the reaction with $P(C_2H_5)_3$. However, reactions with $P(n\text{-}C_4H_9)_3$, which displayed constantly increasing rates in the absence of CO, were strongly influenced even by very low concentrations of CO. After a slow induction period of about 15-20% (with $k_{init.}$ similar to k_{obs} of Table I) they showed good first-order dependance on the concentration of $[Mn_2(CO)_{10}]$ over several half-lives, and with increasing CO pressure the rate constant calculated from the slope of these plots approached the low limiting values of Table I. The ir spectra of reactions showing non-first-order dependance in [$Mn_2(CO)_{10}$] also indicated that the initial products $Mn_2(CO)_9L$ and $Mn_2(CO)_8L_2$ reacted with excess ligand to give unidentified secondary products. These secondary reactions were suppressed to various degrees in CO containing solutions and by carbon monoxide evolved during the reactions.

Table III. Rate Constants for Reaction (2) in p-Xylene at Different Tempreatures [$Mn_2(CO)_9P(C_6H_5)_3$] = 0.00045 *M*

Exp.	T, °C	$P(C_6H_5)_3$	[L], *M*	k_{obs}, sec^{-1}
1a	80	$P(C_6H_5)_3$	4.81×10^{-3}	6.2×10^{-5}
1b	80	$P(C_6H_5)_3$	1.23×10^{-2}	6.9×10^{-5}
1c	80	$P(C_6H_5)_3$	3.19×10^{-2}	6.6×10^{-5}
1d	80	$P(C_6H_5)_3$	5.71×10^{-2}	6.7×10^{-5}
2	80	$P(C_6H_5)_3$	5.42×10^{-2}	8.8×10^{-5}
3	80	$P(n\text{-}C_4H_9)_3$	4.98×10^{-2}	7.8×10^{-5}
4a	90	$P(OC_6H_5)_3$	2.9×10^{-2}	2.5×10^{-4}
4b	90	$P(C_6H_5)_3$	1.68×10^{-1}	2.4×10^{-4}
5a	100	$P(C_6H_5)_3$	3.08×10^{-2}	8.3×10^{-4}
5b	100		1.46×10^{-1}	8.1×10^{-4}

Table IV. Rate Constants for Reaction (2) in p-Xylene at Different Temperatures [$Mn_2(CO)_9L$] = 0.0004 *M*.

T, °C	L	[L], *M*	k_{obs}, sec^{-1}
80	$P(n\text{-}C_4H_9)_3$	8.83×10^{-3}	1.7×10^{-5}
80	$P(n\text{-}C_4H_9)_3$	5.08×10^{-2}	1.7×10^{-5}
80	$P(n\text{-}C_4H_9)_3$	1.71×10^{-1}	1.7×10^{-5}
80	$P(OC_6H_5)_3$	7.65×10^{-3}	1.6×10^{-6}
80	$P(OC_6H_5)_3$	4.54×10^{-2}	1.8×10^{-6}
80	$P(OC_6H_5)_3$	1.24×10^{-1}	1.7×10^{-6}
90	$P(n\text{-}C_4H_9)_3$	1.22×10^{-2}	5.8×10^{-5}
90	$P(n\text{-}C_4H_9)_3$	9.57×10^{-2}	6.2×10^{-5}
90	$P(OC_6H_5)_3$	1.08×10^{-2}	6.8×10^{-6}
90	$P(OC_6H_5)_3$	8.0×10^{-2}	6.4×10^{-6}
100	$P(n\text{-}C_4H_9)_3$	8.93×10^{-3}	2.3×10^{-4}
100	$P(n\text{-}C_4H_9)_3$	9.76×10^{-2}	2.5×10^{-4}
100	$P(OC_6H_5)_3$	9.26×10^{-3}	3.0×10^{-5}
100	$P(OC_6H_5)_3$	8.05×10^{-2}	3.3×10^{-5}

Rate constants for the reaction (2)

$$Mn_2(CO)_9L + L \longrightarrow Mn_2(CO)_8L_2 + CO \qquad (2)$$

are given in Table 3 and 4. The reaction of $Mn_2(CO)_9P(C_6H_5)_3$ went to completion only when $P(C_6H_5)_3$ was present in large excess (>100) or when CO evolved in the reaction was removed from the reaction flasks, Figure 1. Rate constants were calculated from the linear initial slopes of the first-order rate plots (20-70%). The activation parameters for reaction (2) are:

L	ΔH*, kcal/mole	ΔS*, e.u.
$P(C_6H_5)_3$	32±1	+13±2
$P(n\text{—}C_4H_9)_3$	34±1	+17±2
$P(OC_6H_5)_3$	38±1	+23±2

Data on ligand exchange reactions (3)

$$Mn_2(CO)_8[P(C_6H_5)_3]_2 + L \rightarrow Mn_2(CO)_8P(C_6H_5)_3L + P(C_6H_5)_3 \qquad (3)$$

where L = $P(OC_6H_5)_3$, $P(n\text{-}C_4H_9)_3$ are given in Table V. Because of overlapping ir bands of starting material and products, it was not always possible to follow the rate of reaction over the full range of three half-lives; the experimental error is therefore larger than usual (>10%).

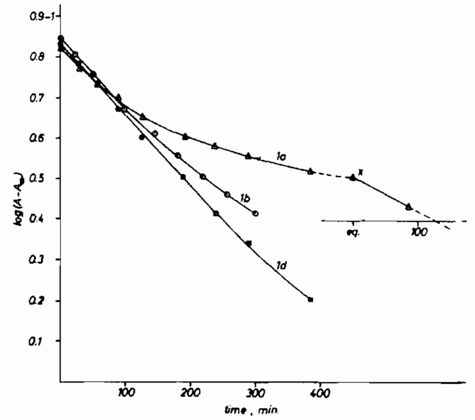

Figure 1. First order rate plots log(A—A∞) *vs.* time for reaction (2) at 80°C with L= $P(C_6H_5)_3$ (see text and Table III).

Table V. Rate Constants for Reaction (15) in p-Xylene at 51° [$Mn_2(CO)_8(P(C_6H_5)_3)_2$] = 0.0004 *M*

L	[L], *M*	k_{obs}, sec^{-1}
$P(OC_6H_5)_3$	8.49×10^{-3}	1.9×10^{-4}
$P(OC_6H_5)_3$	1.04×10^{-2}	2.0×10^{-4}
$P(OC_6H_5)_3$	1.42×10^{-2}	2.5×10^{-4}
$P(OC_6H_5)_3$	2.08×10^{-2}	3.9×10^{-4}
$P(OC_6H_5)_3$	2.44×10^{-2}	4.3×10^{-4}
$P(OC_6H_5)_3$	6.09×10^{-2}	8.4×10^{-4}
$P(OC_6H_5)_3$	8.28×10^{-2}	1.1×10^{-3}
$P(n\text{-}C_4H_9)_3$	3.6×10^{-3}	1.6×10^{-3}
$P(n\text{-}C_4H_9)_3$	9.9×10^{-3}	1.9×10^{-3}
$P(n\text{-}C_4H_9)_3$	3.94×10^{-2}	2.7×10^{-3}
$P(n\text{-}C_4H_9)_3$	6.57×10^{-2}	2.7×10^{-3}

Discussion

General Observations. Before discussing the results of our kinetic experiments, it appears useful to summarize the qualitative observations made in our laboratory and elsewhere on substitution reactions of $Mn_2(CO)_{10}$. Keep in mind that initially it was believed that reaction takes place by either of two active intermediates, the radical $.Mn(CO)_5$ or the CO deficient fragment $Mn_2(CO)_9$.

An important question, which is as yet unsettled, is whether compounds of the emperical formula $Mn(CO)_4L$ may exist as monomeric radicals or only as diamagnetic dimers. Hieber and Freyer[14] described the derivatives with Lewis bases such as $P(C_6H_5)_3$ or $P(C_2H_5)_3$ as radicals, $.Mn(CO)_4L$ whereas those with $P(C_6H_{11})_3$ and $P(OC_6H_5)_3$ were considered to be dimers, $[Mn(CO)_4L]_2$. The syntheses of these materials were carried out in the absence of light by means of thermal reactions. Using the same ligands, photochemical reactions were later found to yield only dimeric products.[15,16] The monosubstituted compound $Mn_2(CO)_9P(C_6H_5)_3$ was also prepared by a photosynthetic method.[18]

The results of our preparations[12a] show that compounds of the type $Mn_2(CO)_9L$ can also be prepared by thermal reactions. However, thermal reactions have not yielded the solid radical $.Mn(CO)_4P(C_6H_5)_3$. Even heating the solid $Mn_2(CO)_8[P(C_6H_5)_3]_2$ to *ca.* 200° in a high vacuum results in the sublimation of this compound along with $P(C_6H_5)_3$ and $Mn_2(CO)_9$-$P(C_6H_5)_3$, but there is no evidence of Mn-Mn bond cleavage. This method has been used to produce $.Co(CO)_4$ from $Co_2(CO)_8$,[19] but $Mn_2(CO)_{10}$ does not yield $.Mn(CO)_5$. Note that mass-spectrometric studies[20] give metal-metal bond energies of 11.5 and 18.9 kcal/mole for $Co_2(CO)_8$ and $Mn_2(CO)_{10}$, respectively.

Other attempts to obtain evidence for the existence of radicals of the type $.Mn(CO)_4L$ in solution also failed. Measurements of esr, ir, and molecular weights all indicated that only the diamagnetic dimer $Mn_2(CO)_8L_2$ is present. Molecular weights measured osmometrically in benzene at 37° for $Mn_2(CO)_8$-$[P(C_6H_5)_3]_2$ were low, as also observed previously[16] However the expected value for dimer was obtained in the presence of added $P(C_6H_5)_3$, which would not affect an equilibrium between the dimer and radicals but would suppress its dissociation to $Mn_2(CO)_8$-$P(C_6H_5)_3 + P(C_6H_5)_3$.

We have obtained evidence for paramagnetic manganese carbonyl derivatives in some of these reaction mixtures. Prolonged heating of *p*-xylene solutions of $Mn_2(CO)_{10}$ containing excess $P(n\text{-}C_4H_9)_3$ with removal of CO evolved during reaction results in the consumption of the primary products $Mn_2(CO)_9P(n\text{-}C_4H_9)_3$ and $Mn_2(CO)_8[P(n\text{-}C_4H_9)_3]_2$. These solutions gave esr spectra showing hyperfine splitting due to ^{53}Mn. Similar results were obtained for the reaction of $Mn_2(CO)_{10}$ with $P(C_2H_5)_3$. The composition of these radicals is not known, but may be of the type $Mn(CO)_xL_{5-x}$ similar to the rhenium radicals $Re(CO)_3L_2$.[21] It should also be noted that the manganese radicals have a greater tendency to form when more carbonyl groups are replaced and when the ligands present are the more basic alkyl phosphines rather than aryl phosphines. This means the more basic the phosphines and the greater the extent of substitution, the more effective is the Mn-Mn bond weakening. A similar observation was made[22] on the reaction of $Co_2(CO)_6L_2$ with $SnCl_2$.

Prolonged heating of solutions of substituted manganese carbonyls in the absence of added ligands results in complicated disproportionation reactions of the type shown by (4) and (5).

$$Mn_2(CO)_9L \rightarrow Mn_2(CO)_{10} + Mn_2(CO)_8L_2 \qquad (4)$$

$$Mn_2(CO)_8L_2 \rightarrow Mn_2(CO)_9L + \text{paramagnetic residue} \qquad (5)$$

Similar light induced reactions have been reported[23] for the reaction of $Mn_2(CO)_8(NN)$, where (NN) = 1,10-phenanthroline or 2,2′-bipyridine, to yeld $Mn_2(CO)_{10}$ and $Mn_2(CO)_6(NN)_2$. It was assumed that these reactions proceed by means of radical intermediates. If so, the equilibria lie far on the side of the dimers, and it seems improbable that $Mn(CO)_4L$ radicals can be isolated in the pure form.

Reaction of $Mn_2(CO)_{10}$. The substitution reaction of $Mn_2(CO)_{10}$ with $P(C_6H_5)_3$ in decalin solution is said to proceed in part (73%) by Mn-Mn bond fission and in part (27%) by CO dissociation.[10] One reason for proposing a dual mechanism it that at 1 atm. of CO the reaction is retarded only by about 27% of the limiting rate. It was assumed that the Mn-Mn bond fission path would not be affected by the added CO, but that this negated the CO dissociation path.

The most significant observation made in this investigation is that the rate of reaction of $Mn_2(CO)_{10}$ with different reagents in *p*-xylene solution is very markedly affected by addition of CO. Data in Table I show that for the poorer nucleophiles $As(C_6H_5)_3$ and $Sb(_6H_5)_3$ even 0.5 atm. of CO is sufficient to almost prevent reaction. Thus the rate determining step for substitution cannot involve the formation of $.Mn(CO)_5$ radicals, because such a process would not be inhibited by the addition of CO . Likewise it does not appear that the rate of a ligand migration process would be inhibited by the addition of CO. This would require that the bridged species (I) be converted to a significant concentration of $(OC)_5Mn$-$COMn(CO)_5$ and there is no evidence of its presence. Furthermore the ligand migration reaction has been found[9,24] to have a low enthalpy and negative entropy of activation. Instead the reaction of $Mn_2(CO)_{10}$ has the activation parameters $\Delta H^* = 37$ kcal/mole and $\Delta S^* = +20$. These values are very similar to the values ($\Delta H^* = 38$ kcal/mole, $\Delta S^* = +18$ e.u.) reported[2] for substitution reactions of $Cr(CO)_6$ that take place by CO dissociation.

For this reason it appears that the substitution reactions of $Mn_2(CO)_{10}$ take place by a CO dissociation process and the kinetic data obtained are in accord with such a mechanism. This can be represented by means of eqs. (6) and (7).

$$Mn_2(CO)_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn_2(CO)_9 + CO \qquad (6)$$

$$Mn_2(CO)_9 + L \underset{k_{2-}}{\overset{k_2}{\rightleftharpoons}} Mn_2(CO)_9L \qquad (7)$$

Using a steady state approximation for the concentration of $Mn_2(CO)_9$, one obtains rate law (8) for the reaction of $Mn_2(CO)_{10}$.

$$-\frac{d[Mn_2(CO)_{10}]}{dt} = \frac{k_1k_2[Mn_2(CO)_{10}][L] + k_2k_{-2}[Mn_2(CO)_9L][L] - k_{-2}[Mn_2(CO)_9L]}{k_{-1}[CO] + k_2[L]} \qquad (8)$$

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For a reaction going to completion it is reasonable to ignore $k_{-2}[Mn_2(CO)_9L]$. Then, independence of the observed rate constants, k_{obs}, on the concentration and nature of L is explainable when $k_2[L]$ is much reater than $k_{-1}[CO]$,, which simplifies the rate law to

$$-\frac{d[Mn_2(CO)_{10}]}{dt} = k_1[Mn_2(CO)_{10}] \qquad (9)$$

and $k_{obs}=k_1$. This behavior was observed for L= $P(C_6H_5)_3$ and $P(OC_6H_5)_3$. Linear first-order rate plots over several half-lives demonstrated that CO was never produced in sufficiently high concentrations to make the reverse reaction of (6) comparable to the forward reaction. This can be understood, since even at the lowest concentrations of $P(C_6H_5)_3$ used the final ratio of $P(C_6H_5)_3/CO_{total}$ was >7 and $[(C_6H_5)_3]/[CO]_{soluion}$ was >50. However, with increasing concentration of CO in solution $k_{-1}[CO]$ is no longer negligable compared to $k_2[L]$ and the reaction does not go to completion.

The rate constants for the initial part of the reaction, k_{obs}, making the assumption that initially $k_{-2}[Mn_2(CO)_9L]$ of eq. (8) is negligably small, is given by eq. (10).

$$k_{obs} = \frac{k_1k_2[L]}{k_{-1}[CO]+k_2[L]} \qquad (10)$$

Thus the k_{obs} is expected to decrease with increasing [CO]. Experiments confirm this pattern, *e.g.* at 100 °C and at a CO concentration of 3×10^{-3} mole/l the rate of reaction was not significantly retarded for $[P(_6H_5)_3]/[CO]>20$ and the reaction went to completion under these conditions (6f, Table I); however, for $[P(_6H_5)_3]/[CO]\approx1.5$ $k_{obs(init.)}$ was approximately 35% smaller than k_1 and the reaction approached an equilibrium with 50% consumption of $Mn_2(CO)_{10}$ (6e, Table I). It should be noted that without the addition of CO and at the lowest concentration of $P(C_6H_5)_3$ used, the same value of k_{obs} (6a, Table I) was obtained. This result was reproducible to within 5%, but it is at variance with the previous observation[10] that under similar conditions the value of k_{obs} is about three times less than its limiting value at the higher concentrations of $P(C_6H_5)_3$. We can offer no explanation for this experimental discrepancy.

Rates for the substitution of CO by the very weak nucleophiles $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ are also in agreement with this mechanism. At very low concentrations of these ligands, the reverse of equation (6) is observed even for the initial stages of the reaction, (which accounts for the smaller values of k_{obs} (4a, 8a, Table I). At higher concentrations of $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ and with no CO added, k_{obs} was identical with k_{obs} for $P(C_6H_5)_3$ and $P(OC_6H_5)_3$. But at CO concentrations which did not have any influence on the rate of reaction of $Mn_2(CO)_{10}$ with $P(C_6H_5)_3$, the substitution reactions with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ were slowed down significantly. This was to be expected making the reasonable assumption that k_2 will be smaller for these weaker nucleophiles than for $P(C_6H_5)_3$. (3c, d; e; 6f; 8d; 9d, e; Table I). Rate constants k_{obs} of exp. 9d, e, Table I, obtained at two different concentrations of CO (1:2) also reasonably agree with the gradation expected by inspection of eq. (10).

The reaction of $Mn_2(CO)_{10}$ with very strong nucleophiles like $P(n\text{-}C_4H_9)_3$ and $P(C_2H_5)_3$ are clearly autocatalytic as is indicated by a number of experiments of which only one is mentioned. A comparison of $-\Delta[Mn_2(CO)_{10}]/\Delta t$ at equal concentration of $Mn_2(CO)_{10}$ for two reactions, one where $-\Delta[Mn_2(CO)_{10}]/\Delta t$ represent the initial rate and another where $-\Delta[Mn_2(CO)_{10}]/\Delta t$ is measured after 50% reaction, demonstrates that in the latter case the rate has increased considerably due to the formation of a catalyst and the availability of a second catalytic reaction path. Analogous results were obtained for both ligands $P(n\text{-}C_4H_9)_3$ and $P(C_2H_5)_3$, but they were more distinctly marked for $P(C_2H_5)_3$. For $P(n\text{-}C_4H_9)_3$ the catalytic reaction became less important with increasing [CO] and the rate constants k_{obs} approached the limiting value of k_1 at high [CO]; the reaction with $P(C_2H_5)_3$ is less dependent on [CO]. Table II contains only rate constants for the initial rate of reaction at various concentrations of L and $Mn_2(CO)_{10}$. Although the values of $k_{init.}$ are higher than k_{obs} of Table I, it is reasonable to assume that their constancy within the accuracy of these experiments again reflects a rate determining dissociation of CO and that the deviation to higher values is due to some contribution of the catalytic reaction to the overall rate of disappearance of $Mn_2(CO)_{10}$.

Hence, the experimental evidence is in good agreement with the dissociation mechanism represented by eqs. (6) and (7). Furthermore, the constancy of the rate constants for various ligands of such different nucleophilicity and over such a wide range of concentrations also suggests that this is the only path by which these reactions proceed. Although species such as $Mn(CO)_5$ and $(OC)_5MnCOMn(CO)_4$ may form due to the low Mn-Mn bond energy,[20] it appears unlikely that these contribute to the overall rate of substitution. This would allow for the constancy of k_{obs} that is found, only if at all experimental conditions all of the species were substituted before they recombine to form $Mn_2(CO)_{10}$.

Reaction of $Mn_2(CO)_9L$. Compounds of the type $Mn_2(CO)_9L$ (L= $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$ were prepared to investigate the second substitution step, eq. (2).

All pseudo-first-order rate constants were independent of the concentration of L (Tables III and IV), the activation entropies were positive and the activation enthalpies were of the same order of magnitude as for reaction (1). Again, we suggest that the reaction proceeds by a rate determining dissociation of CO.

$$Mn_2(CO)_9L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Mn_2(CO)_8L+CO \qquad (11)$$

$$Mn_2(CO)_8L+L \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Mn_2(CO)_8L_2 \qquad (12)$$

With L= $P(n\text{-}C_4H_9)_3$ and $P(OC_6H_5)_3$ the reactions went to completion at all concentrations of the experiment.

Table VI. C–O Stretching Frequencies (cm^{-1}) of $Mn_2(CO)_{10}$ and its Derivatives in p-Xylene

$Mn_2(CO)_{10}$	2052 s	2016 ss	1984 m		
$Mn_2(CO)_9P(n\text{-}C_4H_9)_3$	2096 m	2009 s	1993 ss	1971 sh	1933 s
$Mn_2(CO)_9P(C_6H_5)_3$	2098 s	2015 s	1997 ss	1969 w	1937 s
$Mn_2(CO)_9P(OC_6H_5)_3$	2103 w	2026 s	2001 ss	1977 sh	1957 w
$Mn_2(CO)_8[P(n\text{-}C_4H_9)_3]_2$			1974 w	1949 ss	
$Mn_2(CO)_8[P(C_6H_5)_3]_2$			1980 w	1959 ss	
$Mn_2(CO)_8[P(OC_6H_5)_3]_2$			2005 sh	1983 ss	

However, with $P(C_6H_5)_3$ the reaction approached an equilibrium (Figure 1); when CO was removed from the reaction flask (at x in Figure 1), a new equilibrium was reached by the further reaction of $Mn_2(CO)_9P(C_6H_5)_3$. The equilibrium constant K ($[Mn_2(CO)_8L_2][CO]/[CO]/[Mn(CO)_9L][L]$) for $L=P(C_6H_5)_3$ was calculated to be $<10^{-2}$ at 80°C (a more precise value would not be justified since [CO] can only roughly be estimated), indicating a greater thermodynamic stability of $Mn_2(CO)_9P(C_6H_5)_3$ compared to $Mn_2(CO)_8[P(C_6H_5)_3]_2$.

The first-order rate constants for reaction (2) are surprising in two respects. They are considerably higher than k_1 of reaction (1), which is in contrast to the usual experience that higher substitution of metal carbonyl phosphines becomes increasingly difficult.[1,2] Secondly, the relative magnitude of the rates for various complexes $Mn_2(CO)_9L$ was unexpected.

$Mn_2(CO)_9L$	$L=P(C_6H_5)_3$ >	$P(n\text{-}C_4H_9)_3$ >	$P(OC_6H_5)_3$ >	CO
k, sec^{1-} (100°)	8.2×10^{-4}	2.4×10^{-4}	3.1×10^{-5}	1.8×10^{-5}

If one takes the C–O stretching frequencies as an indication of th metal-carbon bond strength, then the Mn–C bond strength for the various compounds should decrease in the order $P(n\text{-}C_4H_9)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$ (Table VI), and the expected order of the first order rate constants would be ($P(OC_6H_5)_3 > P(C_6H_5)_3 > P(n\text{-}C_4H_9)_3$. This same discrepancy was previously found for mononuclear carbonyls and steric factors were used to explain the results.[25] Clearly the molecule $Mn_2(CO)_9L$, in which a carbonyl group trans to L is replaced, rules out steric considerations in this case. Other examples have been found where steric factors are not important but also the rates of CO dissociation do not correlate the metal-carbon bond strength estimated from ir spectra.[26] Either these estimates of bond strengths are not correct or otherwise the effect of these ligands on the transition states is more important than that on the ground states of the substrates. The important point is that L has an influence on the rate of release of the *trans* CO in $Mn_2(CO)_9L$, although these two groups in axial positions are separated by two atoms of manganese.

Although reaction (2) is first-order, it is seen that the rate of reaction of $P(C_6H_5)_3$ with $Mn_2(CO)_9P(C_6H_5)_3$ is slightly slower than its reaction with either $P(n\text{-}C_4H_9)_3$ or $P(OC_6H_5)_3$ (Table III). This is because for such a case where the entering group differs from that present, the observed experimental rate constants for the disappearance of $Mn_2(CO)_9L$ are the sum of the first-order rate constants of reactions (13) and (14).

$$Mn_2(CO)_9L + L' \rightarrow Mn_2(CO)_8LL + CO \qquad (13)$$

$$Mn_2(CO)_9L + L \rightarrow Mn_2(CO)_9L' + L \qquad (14)$$

That reaction (14) takes place at a rate which would make a small contribution to the total rate was confirmed by the use of CO as L′ with the formation of $Mn_2(CO)_{10}$.

Reaction of $Mn_2(CO)_8[P(C_6H_5)_3]_2$. The rates of reaction (15) were followed by monitoring the rate of

$$Mn_2(CO)_8[P(C_6H_5)_3]_2 + L \rightarrow Mn_2(CO)_8P(C_6H_5)_3L + P(C_6H_5)_3 \qquad (15)$$

disappearance of starting material. Unlike the reactions of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9L$, the rates of reaction of $Mn_2(CO)_8[P(C_6H_5)_3]_2$ depend on the nature of L and on its concentration.

The kinetic data (Table V) of this reaction lead to rate law (16) where the rate constants are defined

$$-\frac{d[Mn_2(CO)_8\{P(C_6H_5)_3\}_2]}{dt} = \frac{k_5k_6[Mn_2(CO)_8\{P(C_6H_5)_3\}_2][L]}{k_{-5}+k_6[L]} \qquad (16)$$

by equation (17)

$$Mn_2(CO)_8[P(C_6H_5)_3]_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [Mn_2(CO)_8P(C_6H_5)_3 + P(C_6H_5)_3] \xrightarrow[+L]{k_6} Mn_2(CO)_8P(C_6H_5)_3L + P(C_6H_5)_3 \qquad (17)$$

At low concentrations of L, $k_{-5} \gg k_6[L]$, the rate of reaction is proportional to [L], at high concentration, $k_6[L] \gg k_{-5}$, a limiting rate is approached, which is independent of [L]. This limiting rate was realized for $L=P(n\text{-}C_4H_9)_3$, it was also approached for L= CO with increasing CO pressure, where $Mn_2(CO)_9P(C_6H_5)_3$ was formed.

The experimentally measured pseudo-first-order rate constants, k_{obs}, correspond to eqs. (18) and (19).

$$k_{obs} = \frac{k_5k_6[L]}{k_{-5}+k_6[L]} \qquad (18)$$

$$\frac{1}{k_{obs}} = \frac{k_{-5}}{k_5k_6} \times \frac{1}{[L]} + \frac{1}{k_5} \qquad (19)$$

Thus $1/k_{obs}$ changes lineary with $1/[L]$ (Figure 2).

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(25) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, *81*, 4200 (1959); R. J. Angelici and F. Basolo, *Inorg. Chem.*, *2*, 728 (1963); H. Wawersik and F. Basolo, *J. Am. Chem. Soc.*, *89*, 4626 (1967).

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The following data were calculated: $k_5 = 2.5 \times 10^{-3}$ sec^{-1}, $k_6/k_{-5} = 8.3$ for $L = P(OC_6H_5)_3$ and $k_6/k_{-5} \sim 180$ for $L = P(n\text{—}C_4H_9)_3$.

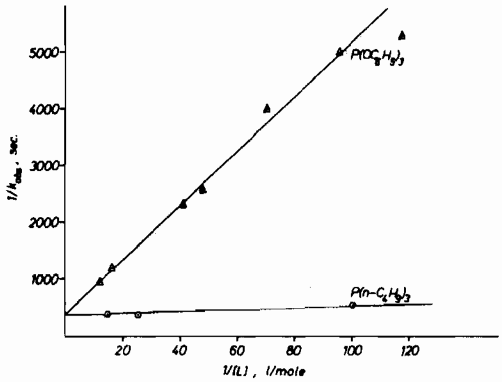

Figure 2. Plot of the reciprocal of the observed rate constants *vs.* the reciprocal of the concentration of L for reaction (15).

A reasonable possibility for the identity of the intermediate of the reaction is $Mn_2(CO)_8P(C_6H_5)_3$. However, if this molecule and $P(C_6H_5)_3$ would dissociate as to give completely isolated species, the concentration of $P(C_6H_5)_3$ would multiply k_{-5} in (16) and would therefore result in a rate law not rigorously pseudo-first-order. At rates below the limiting rate this would demand non-linear first-order rate plots. That this was not observed may be due to the fact, that overlap of the ir bands of reactants and products introduced some uncertainty in the evaluation of the experimental results. Alternatively, the released $P(C_6H_5)_3$ may be held in a solvent cage with $Mn_2(CO)_8P(C_6H_5)_3$ or ligand migration may take place to form $P(C_6H_5)_3(CO)_4$-$MnCOMn(CO_3P(C_6H_5)_3$. Neither of these alternatives seem very likely. If the solvent cage process is involved it would require that $P(n\text{—}C_4H_9)_3$ outside the cage react 180 times faster than $P(C_6H_5)_3$ which is inside the cage. If the carbonyl bridged species is formed, then it is difficult to account for the reaction of $Mn_2(CO)_8[P(C_6H_5)_3]_2$ with NO to yield equivalent amounts[12b] of $MnNO(CO)_4$ and $MnNO(CO)_3P(C_5H_5)_3$. The bridged compound would be expected to react with NO to yield only the more stable $MnNO(CO)_3$-$P(C_6H_5)_3$ product.

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