Catalytic and Solvent Effects on Substitution Reactions of Dinitrosyldicarbonyliron(0)

Donald E. Morris and Fred Basolo

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received October 21, 1967*

Abstract: Dinitrosyldicarbonyliron(0) undergoes carbon monoxide substitution reactions in tetrahydrofuran or methanol according to a two-term rate law. The second-order rate constant for each reagent is similar to those found in toluene and dichloromethane. The first-order rate constants at 25° are 1.0×10^{-3} and 3.7×10^{-3} sec^{-1} in tetrahydrofuran and methanol, respectively. The reaction of dinitrosyldicarbonyliron(0) with a poor reagent such as triphenylarsine can be catalyzed by carrying out the reaction in the presence of a tetrabutylammonium halide or an amine. The mechanism of these reactions is discussed in terms of nucleophilic attack by the solvent or catalyst on a carbon atom of the dinitrosyldicarbonyliron(0).

Dinitrosyldicarbonyliron(0), $Fe(NO)_2(CO)_2$, undergoes CO substitution reactions with many reagents. Recently, kinetic studies made on reaction 1 in

$$Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO \qquad (1)$$

L = phosphines, phosphites, triphenylarsine

toluene and dichloromethane have been reported.[1] The rate of this reaction was found to be dependent on the nature and concentration of L, and the kinetics conformed to the rate law in eq 2. Previous to this work, Keeley and Johnson[2] had reported that the half-life for ^{14}CO exchange of $Fe(NO)_2(CO)_2$ was approximately 400 hr in benzene at 25°.

$$\text{rate} = k_2[Fe(NO)_2(CO)_2][L] \qquad (2)$$

This paper reports the results obtained from kinetic studies of reaction 1 in tetrahydrofuran and methanol. Also included are results of ^{14}CO exchange experiments of $Fe(NO)_2(CO)_2$ in tetrahydrofuran.

In addition to a large solvent effect, it was also found that various reagents catalyze the CO substitution reactions of $Fe(NO)_2(CO)_2$ in dichloromethane. This paper, therefore, also reports the results from kinetic studies of reactions 3 and 4. Two possible mechanisms will be discussed for these catalytic reactions as well as for the solvent reactions.

$$2Fe(NO)_2(CO)_2 + 3(C_6H_5)_3P \xrightarrow{Y} Fe(NO)_2(CO)[(C_6H_5)_3P] + Fe(NO)_2[(C_6H_5)_3P]_2 + 3CO \qquad (3)$$

Y = $(n\text{-}C_4H_9)_4NX$, where X = Cl, Br, I, N_3
Y = $NaOCH_3$

$$Fe(NO)_2(CO)_2 + (C_6H_5)_3As \xrightarrow{Y} Fe(NO)_2(CO)[(C_6H_5)_3As] + CO \qquad (4)$$

Y = $(n\text{-}C_4H_9)_4NX$, where X = Br, N_3
Y = imidazole, pyrrolidine, $NaOCH_3$

Results are also given from the kinetic studies of reaction 5.

$$Fe(NO)_2(CO)_2 + Y \longrightarrow Fe(NO)_2(CO)Y + CO \qquad (5)$$

Y = Cl^-, Br^-, I^-, $C_6H_{11}NH_2$, pyridine, imidazole, pyrrolidine, triphenylphosphine oxide, triphenylphosphine sulfide.

Experimental Section

Dinitrosyldicarbonyliron(0). The dinitrosyldicarbonyliron(0) was prepared according to the method of Hieber and Beutner[3] with some minor modifications.

Reagents. The reagents $(C_6H_5)_3P$, $(C_6H_5)_3P{=}O$, $(C_6H_5)_3P{=}S$, $(n\text{-}C_4H_9)_4NI$, $(n\text{-}C_4H_9)_4NBr$, pyrrolidine, and imidazole were all obtained commercially and used without further purification. $C_6H_{11}NH_2$ and pyridine were obtained commercially but were distilled under nitrogen before use. $(n\text{-}C_4H_9O)_3P$ and $(C_6H_5O)_3P$ were obtained commercially. Before use they were each dissolved in a suspension of sodium in ether, allowed to stand overnight, and then fractionally distilled under nitrogen. $(C_6H_5)_3As$, which was obtained commercially, was recrystallized from methanol before use. $(n\text{-}C_4H_9)_4NCl$ was obtained commercially. Before use it was recrystallized from a benzene–pentane mixture. It was then dried in an oil pump vacuum and stored in a Schlenk tube under dry nitrogen. The carbon monoxide used was obtained from Matheson Coleman and Bell and used without further purification. Carbon-14 monoxide (1.0 mCi, 54.3 ml) was purchased from Tracerlab, Inc. It was diluted to 1 atm with inactive carbon monoxide and used in this form. $(n\text{-}C_4H_9)_4NN_3$ was prepared by the method described in the literature.[4] $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$, diphos, was prepared by the method of Chatt and Hart[5] but was purified by chromatography on silica gel. The $[(C_6H_5)_4As]SnCl_3$ was kindly supplied by Dr. M. P. Johnson.

Solvents. All of the solvents were distilled in an atmosphere of nitrogen. Hexane was refluxed over and distilled from sodium. Dichloromethane was refluxed over and distilled from $Mg(OH)_2$ and $Mg(OCH_3)_2$. All of these solvents were stored under nitrogen. Tetrahydrofuran was refluxed over and distilled from sodium and benzophenone. This solvent had to be used immediately after distillation for kinetic purposes. If it was stored under nitrogen and then used later the kinetic data were not reproducible.

Stock Solutions. Stock solutions containing known concentrations of $Fe(NO)_2(CO)_2$ in an appropriate solvent were prepared as described earlier.[1,6]

Preparation of Complexes. Several of the monosubstituted derivatives of $Fe(NO)_2(CO)_2$ obtained in this kinetic study had previously been prepared and reported in the literature. Therefore, when studying the kinetics of a reaction which led to one of these known products, the infrared spectrum of the final reaction mixture was compared to the published spectrum for the product. Thus the following products have been reported elsewhere: $Fe(NO)_2(CO)[(C_6H_5)_3P]$,[7] $Fe(NO)_2(CO)[(C_6H_5)_3As]$,[8] $Fe(NO)_2(CO)[(C_6H_5O)_3P]$,[8] and $Fe(NO)_2(CO)[(n\text{-}C_4H_9O)_3P]$.[1]

All complexes prepared during this work were prepared in an atmosphere of nitrogen.

---

[1] D. E. Morris and F. Basolo, *J. Am. Chem. Soc.*, **90**, 2531 (1968).

[2] D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).

[3] W. Hieber and H. Beutner, *Z. Anorg. Allgem. Chem.*, **320**, 101 (1963).

[4] V. Gutmann, G. Hampel, and O. Lietmann, *Monatsh. Chem.*, **95**, 1034 (1964).

[5] J. Chatt and F. Hart, *J. Chem. Soc.*, 1378 (1960).

[6] E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, **88**, 3929 (1966).

[7] D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, **1**, 386 (1962).

[8] M. Malatesta and A. Araneo, *J. Chem. Soc.*, 3803 (1957).

$Fe(NO)_2(CO)[(C_6H_5)_3P]$ and $Fe(NO)_2[(C_6H_5)_3P]_2$ Prepared from $Fe(NO)_2(CO)_2$ and $(C_6H_5)_3P$ in the Presence of $(n\text{-}C_4H_9)_4NCl$. A dichloromethane solution (10 ml) containing 0.34 g (2 mmoles) of $Fe(NO)_2(CO)_2$, 0.79 g (3 mmoles) of $(C_6H_5)_3P$, and 0.29 g (1 mmole) of $(n\text{-}C_4H_9)_4NCl$ was allowed to stand at room temperature for 3 hr. The solvent was removed under reduced pressure (25 mm) at 25°. The residue was chromatographed. Two bands separated on the column. The faster moving band was eluted with a 1:4 mixture of dichloromethane and hexane. As the solvent was being removed from the effluent containing the first band, a red-brown solid crystallized. It was recrystallized from hexane and dried overnight under vacuum (10^{-1} mm).

Anal. Calcd for $Fe(NO)_2(CO)[(C_6H_5)_3P]$: C, 56.19; H, 3.72; N, 6.90. Found: C, 55.68; H, 3.59; N, 6.73.

The slower moving band on the column was eluted with a 1:1 mixture of dichloromethane and hexane. As the solvent was removed from the effluent containing this band a green-brown solid crystallized. It was recrystallized from a dichloromethane–hexane mixture and dried overnight under vacuum (10^{-1} mm).

Anal. Calcd for $Fe(NO)_2[(C_6H_5)_3P]_2$: C, 67.51; H, 4.72; N, 4.37. Found: C, 67.76; H, 4.74; N, 4.22.

$Fe(NO)_2(CO)[(C_6H_5)_3As]$ Prepared from $Fe(NO)_2(CO)_2$ and $(C_6H_5)_3As$ in the Presence of $(n\text{-}C_4H_9)_4NCl$. This compound was prepared and purified in a manner very similar to that used for $Fe(NO)_2(CO)[(C_6H_5)_3P]$ above. There was only one noticeable band on the chromatography column. The product was a red-brown crystalline solid.

Anal. Calcd for $Fe(NO)_2(CO)[(C_6H_5)_3As]$: C, 50.70; H, 3.36; N, 6.23. Found: C, 50.93; H, 3.39; N, 5.84.

$Fe(NO)_2[(C_6H_5)_3P]_2$ Prepared from $Fe(NO)_2(CO)_2$ and $(C_6H_5)_3P$ in the Presence of $NaOCH_3$. A methanol solution (15 ml) containing 0.02 g (0.13 mmole) of $Fe(NO)_2(CO)_2$, 0.262 g (1 mmole) of $(C_6H_5)_3P$, and 0.054 g (1 mmole) of $NaOCH_3$ was allowed to stand at room temperature. After 15 min a precipitate had formed. The solution was filtered after sitting overnight and the precipitate collected. It was not analyzed. The infrared spectrum of a dichloromethane solution of this precipitate in the C–O and N–O stretching regions showed nitrosyl bands at 1714 and 1669 cm^{-1}. This agrees well with the published spectrum[7] for $Fe(NO)_2[(C_6H_5)_3P]_2$.

$Fe(NO)_2(CO)[(C_6H_5)_3As]$ Prepared from $Fe(NO)_2(CO)_2$ and $(C_6H_5)_3As$ in the Presence of $NaOCH_3$. This compound was prepared in a manner very similar to that described in the previous paragraph for the preparation of $Fe(NO)_2[(C_6H_5)_3P]_2$. An infrared spectrum of the reaction solution was taken in the C–O and N–O stretching regions immediately after the reaction was started. It showed a carbonyl band at 2019 cm^{-1} and nitrosyl bands at 1771 and 1729 cm^{-1}. This spectrum agrees well with the published spectrum[7] for $Fe(NO)_2(CO)[(C_6H_5)_3As]$. After 3 hr the infrared spectrum of the reaction mixture had not changed. The bands all had the same position and intensity. However, after 1 day a precipitate had separated from the solution. This precipitate was collected and its infrared spectrum (in dichloromethane) showed only two nitrosyl bands at 1725 and 1677 cm^{-1}. This final spectrum agrees well with the published spectrum[7] of $Fe(NO)_2[(C_6H_5)_3As]_2$.

Attempts to isolate products from the reactions of $Fe(NO)_2(CO)_2$ with $(n\text{-}C_4H_9)_4NCl$, $(C_6H_5)_4AsCl$, and $NaOCH_3$ are described elsewhere.[9]

The monosubstituted products $Fe(NO)_2(CO)L$, where L is cyclohexylamine, pyridine, pyrrolidine, imidazole, triphenylphosphine oxide, and triphenylphosphine sulfide, were not isolated because of their instability. They were presumed to be the monosubstituted $Fe(NO)_2(CO)L$ products on the basis of the similarity of their infrared spectra to that of known $Fe(NO)_2(CO)L$ compounds. The infrared spectra of these presumed products as well as those of some known $Fe(NO)_2(CO)L$ compounds are given in Table I.

Analyses. Analyses were performed by Miss H. Beck of Northwestern University.

Mass Spectra. Mass spectra were recorded by Mr. R. M. Sherrill of Northwestern University. They were taken at 70-eV electron energies using a Consolidated Electrodynamics 21-130 mass spectrometer.

Infrared Spectra. Infrared spectra were recorded using a Perkin-Elmer Model 337 spectrophotometer equipped with an external recorder.

Table I. Infrared C–O and N–O Stretching Frequencies for Some $Fe(NO)_2(CO)L$ Compounds[a]

L	Solvent[b]	ν(C–O), cm^{-1}	ν(N–O), cm^{-1}
CO	T	2090, 2040	1810, 1766
$(n\text{-}C_4H_9O)_3P$	D	2039	1779, 1727
$(C_6H_5O)_3P$	T	2029	1782, 1739
$(C_6H_5)_3As$	D	2019	1768, 1723
$(C_6H_5)_3P{=}S$[c]	D	2017	1763, 1718
$(C_6H_5)_3P{=}O$[c]	D	2016	1758, . . .[d]
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$[c]	T	2012	1759, 1716
$(C_6H_5)_3P$	T	2010	1766, 1725
Pyridine[c]	T	2007	1754, 1709
Pyrrolidine[c]	D	2002	1748, 1700
Imidazole[c]	D	2002	1741, 1694
$(n\text{-}C_4H_9)_4NBr$[c]	D	2000	. . . ,[d] 1677
$C_6H_{11}NH_2$	T	1996	1748, 1702
$(n\text{-}C_4H_9)_4NI$[c]	D	1992	1732, 1683
$(n\text{-}C_4H_9)_4NCl$[c]	D	1989	. . . ,[d] 1674

[a] All spectra were calibrated with polystyrene film using the peaks at 1946 and 1602 cm^{-1}. [b] T = toluene, D = dichloromethane. [c] Compound has not been isolated. [d] Band was not detected because compound was not present in sufficient quantity.

Kinetic Studies. The rates of the various reactions were followed by monitoring changes in the infrared spectrum of the reaction mixture. The method used has been described.[1]

The pseudo-first-order rate constants obtained from duplicate runs of the same reaction were reproducible to 5% or better. The second-order rate constants obtained from reactions with the same reagent but at different reagent concentrations were reproducible to 10% or better in most cases. The values of $\Delta H^{\ddagger}$ are estimated to be accurate to ± 0.9 kcal/mole and $\Delta S^{\ddagger}$ to ± 3 eu.

The method used to investigate the rate of ^{14}CO exchange with $Fe(NO)_2(CO)_2$ was similar to that described earlier.[6,10] However, because of the volatility of tetrahydrofuran and its tendency to foam when being vigorously pumped, several minor modifications needed to be made in the method. Briefly these modifications were: (1) running the condenser at −25° or lower, (2) allowing part of the incoming gas phase to by-pass the reaction mixture, and (3) injecting the metal carbonyl solution into the solution phase rather than into the gas phase above the solution as had previously been done.

Voltage readings (voltage is proportional to radioactivity) at infinite time could be calculated from

$$V_\infty = \frac{(\text{mmoles of CO}_g)}{(\text{mmoles of CO}_g) + (\text{mmoles of CO}_M)}\,V_0 \qquad (6)$$

where V_∞ is the voltage at infinite time, V_0 is the initial voltage, (mmoles of CO_g) is the number of millimoles of gaseous carbon monoxide added to the system ($^{14}CO + {}^{12}CO$), and (mmoles of CO_M) is the number of mmoles of exchangeable carbon monoxide on the metal carbonyl.

In the exchange experiments with $Fe(NO)_2(CO)_2$ in tetrahydrofuran, the experimental V_∞ values were always somewhat higher than the calculated V_∞ values. This was thought to be due to some decomposition of the $Fe(NO)_2(CO)_2$ during the exchange experiment. The infrared spectrum did show a decrease in the absorbance of the 2090-cm^{-1} C–O stretching band of the solution at the completion of exchange as compared to the initial solution. In addition, a small amount of brown film was often seen on the inside of the reaction chamber after the exchange was complete. The decomposition could be eliminated by going to lower temperatures and/or running the exchange reactions in a complete CO atmosphere.

The ^{14}CO exchange reaction of $Fe(NO)_2(CO)_2$ in tetrahydrofuran was found to follow the McKay[11] equation and gave satisfactory linear plots of log $(V_t - V_\infty)$ *vs.* time, where V_t is the voltage of the gas phase recorded at time t and V_∞ is the voltage at infinite time. From these plots the apparent rate constants, k_{app}, were determined and used to estimate the values of the true rate constants, k_{true}, by

$$k_{\text{true}} = k_{\text{app}}\frac{xa^{1-\alpha}\sigma}{xa + \sigma} \qquad (7)$$

---

(9) D. E. Morris, Doctoral Dissertation, Northwestern University, 1967.

(10) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961).

(11) H. A. C. McKay, *Nature*, **142**, 997 (1938).

where a is the concentration of metal carbonyl, α is the order in a, x is the number of exchangeable CO's in the metal carbonyl, and σ is the number of millimoles of CO in the enclosed system divided by the number of milliliters of solvent used. If $\alpha = 1$, then the rate of exchange is first order and the specific rate constant, k_{true}, is designated by k_1 (sec^{-1}). If k_1 is divided by the concentration of CO, the rate constant is second order and is represented by k_2 (M^{-1} sec^{-1}). The solubility of CO in tetrahydrofuran at 25° was determined during this work.

The rate constants obtained from the ^{14}CO exchange experiments were reproducible to within 10%. Because of some decomposition, the data are not as accurate as the data obtained from the substitution reactions.

Determination of the Solubility of Carbon Monoxide in Tetrahydrofuran. The solubility of carbon monoxide in tetrahydrofuran was needed in order to calculate the true second-order rate constants for the ^{14}CO exchange reactions.

The determination was made using the same gas-evolution apparatus which has been described.[12] The method was to measure the number of millimoles of gaseous CO in the enclosed system before and after the solvent was added. The difference divided by the volume of solvent used is the solubility at that temperature. The method was checked first using toluene since the solubility of CO in toluene is known.[10,13]

The solubility of CO in tetrahydrofuran at 25° was found to be 30.4 ± 1.6 mmoles/l. This was the average of four determinations.

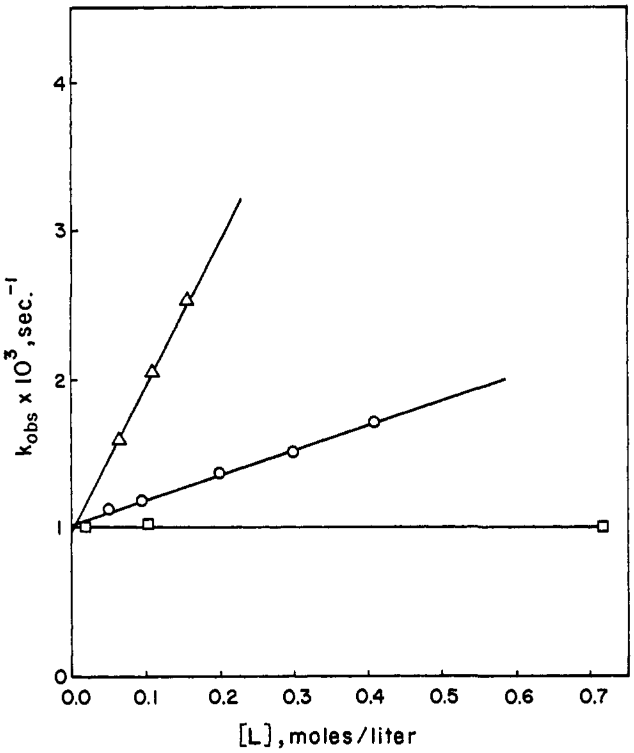


Figure 1. Plot of k_{obsd} *vs.* [L] for reactions of $Fe(NO)_2(CO)_2$ with L in tetrahydrofuran at 25°: △, L = $(n\text{-}C_4H_9O)_3P$; ○, L = $(C_6H_5)_3P$; □, L = $(C_6H_5)_3As$.

Results

All rate constants were determined from the disappearance of the highest energy C–O stretching band of $Fe(NO)_2(CO)_2$ (2090 cm^{-1}) unless otherwise noted. After each kinetic run the infrared spectrum of the reaction mixture in the C–O and N–O stretching regions was compared to the corresponding spectrum of the isolated product. The agreement was always good.

Phosphines, Phosphites, and Triphenylarsine. The data collected from kinetic studies of reaction 1 in tetrahydrofuran are shown in Table II. From these data one can see a definite dependence of the pseudo-first-order rate constants on the concentration and type of reagent L, if L is a good reagent. This is illustrated in Figure 1. These data are consistent with the two-term rate law given by

$$\text{rate} = k_1[Fe(NO)_2(CO)_2] + k_2[Fe(NO)_2(CO)_2][L] \quad (8)$$

Table II. Pseudo-First-Order Rate Constants[a] for the Reactions $Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO$ in Tetrahydrofuran

L	[L], *M*	Temp, °C	k_{obsd}, sec^{-1}
$(C_6H_5)_3P$	0.050	25	1.1×10^{-3}
$(C_6H_5)_3P$	0.098	25	1.2×10^{-3}
$(C_6H_5)_3P$	0.199	25	1.4×10^{-3}
$(C_6H_5)_3P$	0.300	25	1.5×10^{-3}
$(C_6H_5)_3P$	0.412	25	1.7×10^{-3}
$(C_6H_5)_3P$	0.059	15	3.7×10^{-4}
$(C_6H_5)_3P$	0.099	15	4.0×10^{-4}
$(C_6H_5)_3P$	0.059	35	3.2×10^{-3}
$(C_6H_5)_3P$	0.099	35	3.4×10^{-3}
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$[b]	0.066	25	1.7×10^{-3}
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$[b]	0.198	25	2.9×10^{-3}
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$[b]	0.296	25	3.9×10^{-3}
$(n\text{-}C_4H_9O)_3P$	0.064	25	1.6×10^{-3}
$(n\text{-}C_4H_9O)_3P$	0.110	25	2.0×10^{-3}
$(n\text{-}C_4H_9O)_3P$	0.157	25	2.5×10^{-3}
$(C_6H_5)_3As$	0.021	25	1.0×10^{-3}
$(C_6H_5)_3As$	0.108	25	1.0×10^{-3}
$(C_6H_5)_3As$	0.720	25	1.0×10^{-3}
$(C_6H_5)_3As$	0.102	15	3.4×10^{-4}
$(C_6H_5)_3As$	0.101	35	2.9×10^{-3}

[a] All rate constants were obtained by following the disappearance of the $Fe(NO)_2(CO)_2$ in the C–O and/or N–O stretching regions of the infrared. The initial concentration of $Fe(NO)_2(CO)_2$ was approximately 3×10^{-3} *M*. [b] The initial product was the monodentate $Fe(NO)_2(CO)[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$.

Figure 1 shows a nonzero intercept which is required by this rate law. Table III summarizes the second-order rate constants k_2 for reaction 1 in tetrahydrofuran and methanol and also gives the second-order rate constants reported for the corresponding reaction in toluene and dichloromethane.[1] The activation parameters of reaction 1 are presented in Table IV.

The first-order rate constant k_1 in tetrahydrofuran was obtained from the intercept in Figure 1 and is 1.0×10^{-3} sec^{-1}. The activation parameters for this first-order path are represented by those obtained with $(C_6H_5)_3As$ in tetrahydrofuran given in Table IV.

Although a complete kinetic study was not made in methanol, the data which were obtained indicate an adherence of reaction 1 in this solvent to the rate law given by eq 8 with a first-order rate constant of 3.7×10^{-3} sec^{-1}.

In tetrahydrofuran the rate of reaction 1 involving poor reagents shows no dependence on the reagent concentration at the reagent concentrations used (see Figure 1). Thus the second-order term of eq 8 becomes inoperative, and poor reagents such as triphenylarsine show only first-order kinetics. This occurs because the first-order rate constant k_1 is much larger than the second-order rate constant k_2 for these reagents. As

---

(12) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1, 30 (1962); I. A. Cohen, Doctoral Dissertation, Northwestern University, 1964.

(13) E. W. Washburn, Ed., "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 265.

Table III. Second-Order Rate Constants[a] for the Reactions $Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO$

L	Solvent[b]	k_2, M^{-1} sec^{-1}
	25°	
$(n\text{-}C_4H_9O)_3P$	THF	1.0×10^{-2} [c]
$(n\text{-}C_4H_9O)_3P$	T	6.6×10^{-3} [e]
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	THF	9.7×10^{-3} [c,f]
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	T	5.1×10^{-3} [e,f]
$(C_6H_5)_3P$	THF	1.6×10^{-3} [c]
$(C_6H_5)_3P$	M	...[d]
$(C_6H_5)_3P$	T	1.0×10^{-3} [e]
$(C_6H_5)_3P$	D	1.0×10^{-3} [e]
$(C_6H_5O)_3P$	THF	...
$(C_6H_5O)_3P$	T	1.3×10^{-5} [e]
$(C_6H_5)_3As$	THF	...[c]
$(C_6H_5)_3As$	M	...[d]
$(C_6H_5)_3As$	T	1.5×10^{-5} [e]
$(C_6H_5)_3As$	D	2.0×10^{-5} [e]
Pyrrolidine	D	2.0×10^{-2} [f]
Imidazole	D	1.1×10^{-2} [f,g]
$C_6H_{11}NH_2$	T	8.7×10^{-3} [f,g]
Pyridine	T	5.6×10^{-3} [f,g]
$(C_6H_5)_3P{=}O$	D	3.7×10^{-5} [f,g]
$(C_6H_5)_3P{=}S$	D	2.7×10^{-5} [f,g]
$(n\text{-}C_4H_9)_4NCl$	D	2.7×10^{-2} [f]
$(n\text{-}C_4H_9)_4NBr$	D	7.6×10^{-3} [f]
$(n\text{-}C_4H_9)_4NI$	D	1.9×10^{-3} [f]
$[(C_6H_5)_4As]SnCl_3$	D	0
	At 15°	
$(C_6H_5)_3P$	THF	5.7×10^{-4} [h]
$(C_6H_5)_3As$	THF	...[h]
	At 35°	
$(C_6H_5)_3P$	THF	5.0×10^{-3} [i]
$(C_6H_5)_3As$	THF	...[i]

[a] All of the second-order rate constants were determined from the slopes of plots of the pseudo-first-order rate constants *vs.* the reagent concentrations unless otherwise noted. [b] T = toluene, THF = tetrahydrofuran, D = dichloromethane, M = methanol. [c] The first-order rate constant is 1.0×10^{-3} sec^{-1}. [d] The first-order rate constant is 3.7×10^{-3} sec^{-1}. [e] From ref 1. [f] The product $Fe(NO)_2(CO)L$ was not stable. [g] Second-order rate constant was determined by dividing the pseudo-first-order rate constant by the reagent concentration. [h] The first-order rate constant is 3.4×10^{-4} sec^{-1}. [i] The first-order rate constant is 2.9×10^{-3} sec^{-1}.

Table IV. Activation Parameters for the Reactions $Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO$ in Tetrahydrofuran

L	Order in L	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}(298°)$, eu
$(C_6H_5)_3P$	First	19	−9
$(C_6H_5)_3As$	Zero	18	−11
CO	Zero	19	−8

a matter of fact, in methanol where k_1 is even larger than in tetrahydrofuran, the rate of reaction of triphenylphosphine, a reagent which is considered to be a good nucleophile, shows little dependence on the reagent concentration

Carbon-14 Monoxide. The data collected from kinetic studies of reaction 1 when L is ^{14}CO are shown in Table V. The true first-order rate constants were calculated using eq 7. The true second-order rate constants were calculated by dividing the true first-order rate constants by the concentration of carbon monoxide in tetrahydrofuran. From Table V it can be seen that the first-order rate constants at various carbon monoxide concentrations remain constant, whereas the second-order rate constants do not. Thus the rate constant for ^{14}CO exchange in tetrahydrofuran at 25° is 1.1×10^{-3} sec^{-1} which agrees very well with the first-order rate constant for the substitution reactions of $Fe(NO)_2(CO)_2$ in tetrahydrofuran at 25°.

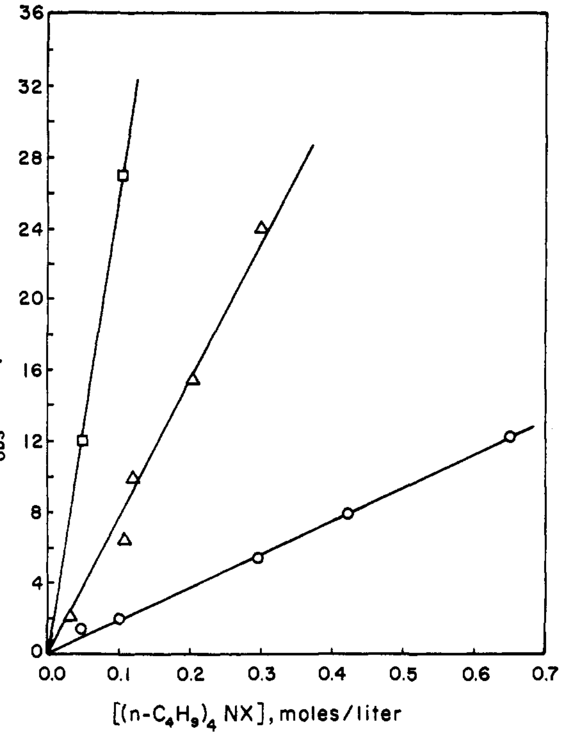


Figure 2. Plot of k_{obsd} *vs.* $[(n\text{-}C_4H_9)_4NX]$ for reactions of $Fe(NO)_2(CO)_2$ with $(n\text{-}C_4H_9)_4NX$ in dichloromethane at 25°: □, X = Cl; △, X = Br; ○, X = I.

The activation parameters for the ^{14}CO exchange of $Fe(NO)_2(CO)_2$ are given in Table IV.

Amines, Tetrabutylammonium Halides, Triphenylphosphine Oxide, and Triphenylphosphine Sulfide. The data collected from kinetic studies of reaction 5 in dichloromethane solution are in accordance with rate law 2. Figure 2 shows the dependence of the pseudo-first-order rate constants on the concentration and type of reagent used when the reagents are three different tetrabutylammonium halides. From these plots one can see that the rates of reaction of $Fe(NO)_2(CO)_2$ with these halides decreases in the order Cl > Br > I. The second-order rate constants k_2 for all of these reagents are given in Table III.

When pyridine or cyclohexylamine were used as reagents in toluene, C–O and N–O stretching bands characteristic of monosubstituted $Fe(NO)_2(CO)_2$ products appeared. These bands remained unchanged at the completion of the reaction for several hours, but disappeared completely after 24 hr with no new bands forming.

When pyrrolidine, imidazole, tetrabutylammonium chloride, bromide, or iodide, triphenylphosphine oxide, or triphenylphosphine sulfide were used as reagents in dichloromethane, C–O and N–O stretching bands characteristic of monosubstituted $Fe(NO)_2(CO)_2$ products appeared. However, when using these reagents, a second group of bands also appeared: a medium N–O stretching band at ≈1790 cm^{-1} and a strong N–O stretching band at ≈1720 cm^{-1} (see Table VI). It was not clear whether the species responsible for these final spectra were coming directly from $Fe(NO)_2(CO)_2$ or if the $Fe(NO)_2(CO)L$ species were precursors.

Table V. Rate Data for the ^{14}CO Exchange with $Fe(NO)_2(CO)_2$ in Tetrahydrofuran[a]

Temp, °C	$[Fe(NO)_2(CO)_2]$, *M*	$[CO]_t$[b]	$[CO]_s$[b]	10^4k_{app}, sec^{-1}	10^4k_1, sec^{-1} [c]	k_2, M^{-1} sec^{-1}
25	3.9×10^{-2}	1.50	4.2×10^{-3}	14	11	0.26
25	3.9×10^{-2}	2.88	8.0×10^{-3}	9.8	11	0.14
25	3.9×10^{-2}	8.52	2.4×10^{-3}	6.4	10	0.042
25	1.95×10^{-2}	1.65	4.6×10^{-3}	9.8	11	0.24
25	3.1×10^{-2}	1.07	3.0×10^{-3}	15	11	0.36
15	3.9×10^{-4}	2.91	. .	3.1	3.4	...
5	3.9×10^{-2}	2.89	...	0.85	0.94	...
0	3.1×10^{-2}	0.193	...	2.6	0.50	...
0	3.1×10^{-2}	0.193	...	2.8	0.53	...
0	3.1×10^{-2}	2.46	...	0.48	0.55	...

[a] All reactions carried out in the absence of light with the gas phase partially bubbling through the solution phase and partially by-passing the solution phase. [b] $[CO]_t$ = total CO in millimoles in the enclosed system. $[CO]_s$ = concentration of CO in moles in solution. [c] True first- and second-order rate constants calculated from eq 7. Note the variation in k_2 with changes in the CO concentration, whereas the values of k_1 are reasonably constant supporting a first-order exchange.

Table VI. Infrared Spectral Changes in the C–O and N–O Stretching Regions of the Reaction Sequence[a]
$Fe(NO)_2(CO)_2 + L \longrightarrow \text{Intermediate} \longrightarrow \text{Final}$

L	Intermediate, cm^{-1}	Final, cm^{-1}
$(n\text{-}C_4H_9)_4NI$	1992, 1732, 1683	1781, 1711
$(n\text{-}C_4H_9)_4NBr$	2000, . . . ,[b] 1677	1786, 1717
$(n\text{-}C_4H_9)_4NCl$	1989, . . . ,[b] 1674	1780, 1708
Pyrrolidine	2002, 1748, 1700	1801, 1733
Imidazole	2002, 1741, 1694	1806, 1741
$(C_6H_5)_3P{=}S$	2017, 1763, 1718	1799, 1732
$(C_6H_5)_3P{=}O$	2016, 1758, . . .[b]	1802, 1717

[a] In dichloromethane. [b] Band not detected because the intermediate was not present in sufficient quantity.

The compounds responsible for the spectra having two N–O stretching frequencies were not isolated. Attempts made to isolate these final products from the reactions of $Fe(NO)_2(CO)_2$ with $(n\text{-}C_4H_9)_4NCl$ and $(C_6H_5)_4AsCl$ were unsuccessful.[9] It is certain that these final species are not disubstituted compounds, since the N–O stretching bands for known $Fe(NO)_2L_2$ compounds are generally 40 cm^{-1} lower than those of the corresponding $Fe(NO)_2(CO)L$ compounds. It is felt at the present time that these final species are disproportionation products similar to those reported by Hieber and coworkers[14] for the reactions of $Fe(CO)_5$ with the same or similar reagents.

A mass spectrum run on the gas evolved from the reaction of $Fe(NO)_2(CO)_2$ with pyrrolidine in toluene showed an intense peak at *m/e* 28. Thus no nitric oxide was evolved, substantiating the statement that the two infrared bands are N–O and not very low C–O stretching frequencies.

Competition Reactions. The data collected from kinetic studies of reaction 3 are shown in Table VII. From these data one can see a definite dependence of the observed first-order rate constants on the concentration and type of catalyst Y used as well as the concentration of triphenylphosphine. The dependence on the catalyst is illustrated in Figure 3. The data collected from reaction 3 are in accord with the two-term rate law given by eq 9. The second-order rate

$$\text{rate} = k_2[Fe(NO)_2(CO)_2][(C_6H_5)_3P] + k_Y[Fe(NO)_2(CO)_2][Y] \quad (9)$$

Table VII. Observed Rate Constants[a] for the Reactions

$$2Fe(NO)_2(CO)_2 + 3(C_6H_5)_3P \xrightarrow{Y} Fe(NO)_2(CO)[(C_6H_5)_3P] + Fe(NO)_2[(C_6H_5)_3P]_2 + 3CO$$

and

$$Fe(NO_2)(CO)_2 + (C_6H_5)_3As \xrightarrow{Y} Fe(NO)_2(CO)[(C_6H_5)_3As] + CO$$

at 25° in Dichloromethane

Y	[Y], *M*	k_{obsd}, sec^{-1}
	$[(C_6H_5)_3P] = 0.201$ *M*	
...	0.0000	2.1×10^{-4}
$(n\text{-}C_4H_9)_4NCl$	0.0064	3.7×10^{-4}
$(n\text{-}C_4H_9)_4NCl$	0.0266	9.5×10^{-4}
$(n\text{-}C_4H_9)_4NCl$	0.0578	15.7×10^{-4}
$(n\text{-}C_4H_9)_4NBr$	0.0268	4.0×10^{-4}
$(n\text{-}C_4H_9)_4NBr$	0.0482	5.6×10^{-4}
$(n\text{-}C_4H_9)_4NI$	0.0495	3.1×10^{-4}
$(n\text{-}C_4H_9)_4NI$	0.0495	3.1×10^{-4} [b]
$(n\text{-}C_4H_9)_4NI$	0.0495	3.1×10^{-4} [c]
$(n\text{-}C_4H_9)_4NI$	0.101	4.1×10^{-4}
$(n\text{-}C_4H_9)_4NI$	0.101	4.2×10^{-4} [b]
$(n\text{-}C_4H_9)_4NI$	0.101	3.9×10^{-4} [c]
$(n\text{-}C_4H_9)_4NI$	0.209	6.7×10^{-4}
$(n\text{-}C_4H_9)_4NI$	0.483	12.3×10^{-4}
$(n\text{-}C_4H_9)_4NN_3$	0.010	15.0×10^{-4}
	$[(C_6H_5)_3As] = 0.201$ *M*	
...	0.0000	4.0×10^{-6}
$(n\text{-}C_4H_9)_4NBr$	0.0547	3.9×10^{-4}
$(n\text{-}C_4H_9)_4NBr$	0.0547	4.0×10^{-4} [b]
$(n\text{-}C_4H_9)_4NBr$	0.0970	7.0×10^{-4}
$(n\text{-}C_4H_9)_4NN_3$	0.010	15.0×10^{-4}
Imidazole[d]	0.044	5.9×10^{-4}
Imidazole[d]	0.097	13.0×10^{-4}
Pyrrolidine[d]	0.108	24.0×10^{-4}
	Y = $(n\text{-}C_4H_9)_4NCl$, [Y] = 0.0266 *M*	
$[(C_6H_5)_3P]$, *M*		
0.0000		7.0×10^{-4} [e]
0.0265		7.9×10^{-4}
0.114		8.7×10^{-4}
0.201		9.5×10^{-4}
0.486		11.6×10^{-4}
	Y = $(n\text{-}C_4H_9)_4NBr$, [Y] = 0.097 *M*	
$[(C_6H_5)_3As]$, *M*		
0.000		7.3×10^{-4} [e]
0.101		7.0×10^{-4}
0.201		7.0×10^{-4}
0.549		7.1×10^{-4}

[a] All rate constants were obtained by following the disappearance of the $Fe(NO)_2(CO)_2$ in the C–O and/or N–O stretching regions of the infrared unless otherwise noted. [b] This rate constant was obtained by following the appearance of the C–O stretching band of the $Fe(NO)_2(CO)L$ product in the infrared. [c] This rate constant was obtained by following the appearance of the N–O stretching band of the $Fe(NO)_2L_2$ product in the infrared. [d] In addition to the major product $Fe(NO)_2(CO)[(C_6H_5)_3As]$, there was another product (see text). [e] Estimated from Figure 2.

---

(14) W. Hieber and J. G. Floss, *Chem. Ber.*, **90**, 1617 (1957); W. Hieber and R. Werner, *ibid.*, **90**, 286, 1116 (1957); W. Hieber and N. Kahlen, *ibid.*, **91**, 2223, 2234 (1958); W. Hieber and A. Lipp, *ibid.*, **92**, 2075, 2085 (1959).

constants k_Y were determined from the slopes of the plots in Figure 3 and are presented in Table VIII. The second-order rate constant k_2 was determined from the slope of a similar plot not shown here. These second-order rate constants agree very well with those obtained from reactions 1 and 5, *i.e.*, when only $(C_6H_5)_3P$ or Y are present.

Table VIII. Second-Order Rate Constants[a] for the Reactions

$$2Fe(NO)_2(CO)_2 + 3(C_6H_5)_3P \xrightarrow{Y} Fe(NO)_2(CO)[(C_6H_5)_3P] + Fe(NO)_2[(C_6H_5)_3P]_2 + 3CO$$

and

$$Fe(NO)_2(CO)_2 + (C_6H_5)_3As \xrightarrow{Y} Fe(NO)_2(CO)[(C_6H_5)_3As] + CO$$

at 25° in Dichloromethane

L	Y	k_2, M^{-1} sec^{-1} [b]	k_Y, M^{-1} sec^{-1} [b]
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NCl$	8.2×10^{-4}	2.9×10^{-2}
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NBr$	. . .	7.5×10^{-3}
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NI$	. . .	2.0×10^{-3}
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NN_3$	. . .	1.3×10^{-1} [c]
$(C_6H_5)_3As$	$(n\text{-}C_4H_9)_4NBr$	Very small	7.2×10^{-3}
$(C_6H_5)_3As$	$(n\text{-}C_4H_9)_4NN_3$	. . .	1.5×10^{-1} [c]
$(C_6H_5)_3As$	Imidazole	. . .	1.3×10^{-2}
$(C_6H_5)_3As$	Pyrrolidine	. . .	2.2×10^{-2} [c]

[a] All of the second-order rate constants were determined from the slopes of plots of the observed first-order rate constants *vs.* the appropriate reagent concentration while keeping the other reagent at a constant concentration unless otherwise noted. [b] The second-order rate constant k_2 is for the $(C_6H_5)_3P$ or $(C_6H_5)_3As$ path. The second-order rate constant k_Y is for the Y path. [c] Second-order rate constant was determined by dividing the observed first-order rate constant by the concentration of Y.

The $Fe(NO)_2[(C_6H_5)_3P]_2$ that is formed in reaction 3 does *not* come by way of $Fe(NO)_2(CO)[(C_6H_5)_3P]$ as an intermediate. This was shown by the fact that a dichloromethane solution containing 0.2 *M* $(C_6H_5)_3P$, 0.027 *M* $(n\text{-}C_4H_9)_4NBr$, and 0.002 *M* $Fe(NO)_2(CO)[(C_6H_5)_3P]$ showed little or no change in the C–O and N–O stretching regions of the infrared after 30 hr at 25°.

$$Fe(NO)_2(CO)[(C_6H_5)_3P] + (C_6H_5)_3P \xrightarrow{(n\text{-}C_4H_9)_4NBr} \text{no reaction} \quad (10)$$

In another experiment $Fe(NO)_2(CO)_2$ and $(n\text{-}C_4H_9)_4NCl$ were allowed to react until no $Fe(NO)_2(CO)_2$ remained. When a $(C_6H_5)_3P$ solution was added to this reaction mixture, there was no indication of the formation of $Fe(NO)_2(CO)[(C_6H_5)_3P]$ or $Fe(NO)_2[(C_6H_5)_3P]_2$ for 2 days at 25°.

The data collected from kinetic studies of reaction 4 in dichloromethane are also shown in Table VII. From these data one can see a definite dependence of the observed first-order rate constants on the concentration and type of catalyst Y used but not on the concentration of triphenylarsine. These data are in accord with the rate law given by eq 11. Thus, even though

$$\text{rate} = k_Y[Fe(NO)_2(CO)_2][Y] \quad (11)$$

the product of reaction 4 is $Fe(NO)_2(CO)[(C_6H_5)_3As]$, the rate of formation of this product is dependent on the nature and concentration of Y. The second-order rate constants k_Y were determined from the slopes of plots of the observed first-order rate constants *vs.* the concentrations of Y and are given in Table VIII. These second-order rate constants agree very well with those obtained from reaction 5, *i.e.*, when only the reagent Y is present. They also agree well with those obtained from reaction 3.

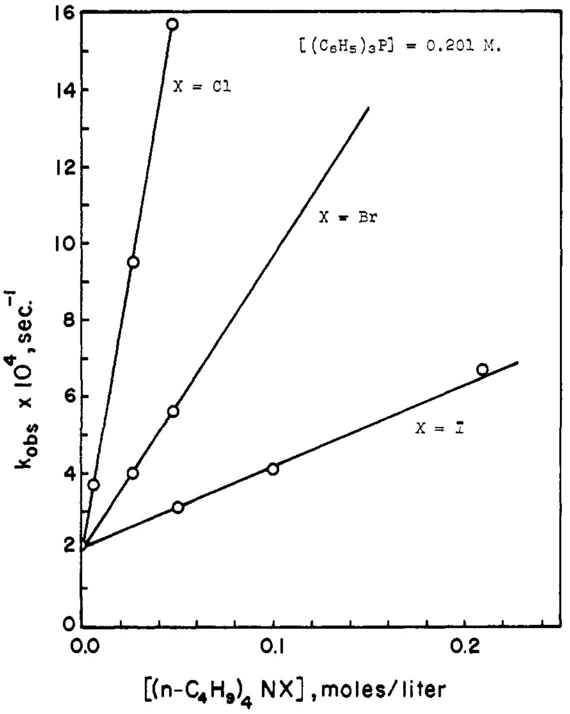


Figure 3. Plot of k_{obsd} *vs.* $[(n\text{-}C_4H_9)_4NX]$ for the reaction of $Fe(NO)_2(CO)_2$ with $(C_6H_5)_3P$ in the presence of $(n\text{-}C_4H_9)_4NX$ in dichloromethane at 25°.

The $Fe(NO)_2(CO)[(C_6H_5)_3As]$ product obtained from reaction 4 is not stable in the presence of Y. For example, on standing with $(n\text{-}C_4H_9)_4NBr$ the $Fe(NO)_2(CO)[(C_6H_5)_3As]$ decomposes to a species which has an infrared spectrum (1786 and 1717 cm^{-1}) identical with that obtained from the infinite time reaction mixture of $Fe(NO)_2(CO)_2$ and $(n\text{-}C_4H_9)_4NBr$. This decomposition takes about 24 hr at 25°.

If pyrrolidine or imidazole is used to catalyze reaction 4, the major product is $Fe(NO)_2(CO)[(C_6H_5)_3As]$. However, the infrared spectra of the final reaction solutions (*ca.* 1 hr after the start of the reaction) also show bands which are characteristic of the final species observed from the reactions of $Fe(NO)_2(CO)_2$ with pyrrolidine or imidazole in the absence of triphenylarsine (see Table VI). The second-order rate constants using these two reagents are shown in Table VIII and agree well with those from reaction 5, *i.e.*, when only the reagent Y is present.

Kinetic studies were not performed on reactions 3 and 4 when Y was $NaOCH_3$ because the reactions were too fast to follow. However, the products obtained from these reactions were identified and are summarized in Table IX along with products from some of the other competition reactions for comparison. The $Fe(NO)_2[(C_6H_5)_3P]_2$ which is formed from reaction 3, when Y is $NaOCH_3$, does not come by way of $Fe(NO)_2(CO)[(C_6H_5)_3P]$. This was shown by the fact that there was no noticeable change in the infrared spectrum of a methanol solution of $Fe(NO)_2(CO)[(C_6H_5)_3P]$, $(C_6H_5)_3P$, and $NaOCH_3$ after 16 hr at 25°. In contrast to this the $Fe(NO)_2(CO)[(C_6H_5)_3As]$ formed by reaction 4

Table IX. Products Obtained from the Reaction of $Fe(NO)_2(CO)_2$ with $(C_6H_5)_3P$ or $(C_6H_5)_3As$ in the Presence of Various Catalysts and in Various Solvents

L	Y	Solvent[a]	Products[b]
$(C_6H_5)_3P$	...	D	Mono
$(C_6H_5)_3P$	...	M	Mono
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NCl$	D	Mono and di
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NBr$	D	Mono and di
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NI$	D	Mono and di
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NN_3$	D	Mono and di
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NCl$	M	Mono[c]
$(C_6H_5)_3P$	$(n\text{-}C_4H_9)_4NCl$	M	Mono and di[d]
$(C_6H_5)_3P$	$NaOCH_3$	M	Di
$(C_6H_5)_3As$	...	D	Mono
$(C_6H_5)_3As$	...	M	Mono
$(C_6H_5)_3As$	$(n\text{-}C_4H_9)_4NBr$	D	Mono
$(C_6H_5)_3As$	$(n\text{-}C_4H_9)_4NN_3$	D	Mono
$(C_6H_5)_3As$	$NaOCH_3$	M	Mono[e]

[a] D = dichloromethane. M = methanol. [b] Mono = $Fe(NO)_2(CO)L$; di = $Fe(NO)_2L_2$. It has been pointed out in the text that any disubstituted product formed does not come by way of the monosubstituted product. [c] Mono formed in 10–20 min. However, after 4 days some mono had gone to di. [d] Nitrogen gas was bubbled through the solution of $Fe(NO)_2(CO)_2$ and $(n\text{-}C_4H_9)_4NCl$ before the $(C_6H_5)_3P$ was added. After the solution turned dark green (*ca.* 10 min), $(C_6H_5)_3P$ was added. Both mono and di products were formed within 2 or 3 min. [e] Mono formed within 5 min; however, it went to di after sitting overnight at 25°.

slowly goes to $Fe(NO)_2[(C_6H_5)_3As]_2$ in the presence of excess $NaOCH_3$ and $(C_6H_5)_3As$.

Discussion

In toluene the rates of reaction of phosphines, phosphites, and triphenylarsine with $Fe(NO)_2(CO)_2$[1] (reaction 1) were found to be very similar to the corresponding reactions of $Co(NO)(CO)_3$.[6] Thus the results obtained from studies of CO substitution reactions of these two isoelectronic and isostructural metal nitrosyl carbonyls conformed to a rate law similar to that given by eq 2. In both cases the mechanism was presumed to involve a nucleophilic attack by the entering reagent on the respective metal atom.

In contrast to the similarities in the kinetic behavior of $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$, there are some very noticeable differences which are summarized in Table X.

Table X. Comparison of the Kinetic Behavior of $Fe(NO)_2(CO)_2$[a] and $Co(NO)(CO)_3$[b]

$$\mathrm{M{-}CO} + \mathrm{L} \xrightarrow{25^\circ} \mathrm{M{-}L} + \mathrm{CO}$$

M-CO = $Fe(NO)_2(CO)_2$				M-CO = $Co(NO)(CO)_3$	
k_1, sec^{-1}	k_2, M^{-1} sec^{-1}	L	Solvent	k_1, sec^{-1}	k_2, M^{-1} sec^{-1}
0	6.0×10^{-3}	$(C_2H_5)(C_6H_5)_2P$	Toluene	0	5.9×10^{-3}
0	1.0×10^{-3}	$(C_6H_5)_3P$	Toluene	0	1.0×10^{-3}
0	1.0×10^{-3}	$(C_6H_5)_3P$	Dichloromethane	...	...
1.0×10^{-3}	1.6×10^{-3}	$(C_6H_5)_3P$	Tetrahydrofuran	0	1.3×10^{-3}
3.7×10^{-3}		$(C_6H_5)_3P$	Methanol	...	...
0	5.6×10^{-3}	Pyridine	Toluene	0	4×10^{-5}
0	2.7×10^{-3}	$(n\text{-}C_4H_9)_4NCl$	Dichloromethane	0	0[c]

[a] This work and ref 1. [b] Reference 6. [c] Reference 18.

The first difference in the kinetic behavior of $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ is the large solvent effect exhibited by the former as is shown in Table X. The results from kinetic studies carried out on reaction 1 in tetrahydrofuran are summarized in Tables II and III. In this solvent the results are in accord with the two-term rate law given by eq 8. Figure 1 demonstrates the dependence of the pseudo-first-order rate constants on the reagent concentrations and also shows the large nonzero intercept. The two different reaction paths are depicted by eq 12. The path represented by k_2 is

$$\begin{tikzcd}
\mathrm{Fe(NO)_2(CO)_2} + \mathrm{L} \arrow[r, "k_2"] \arrow[d, shift right, "\substack{+\mathrm{THF} \\ \mathrm{slow} \\ k_1}"'] & \mathrm{Fe(NO)_2(CO)L} \\
\text{intermediate} \arrow[u, shift right, "k_{-1}"'] \arrow[ur, "\substack{+\mathrm{L} \\ \mathrm{fast}}"'] &
\end{tikzcd} \tag{12}$$

exactly like that described earlier[1] for the same reactions in toluene or dichloromethane. This is substantiated by the fact that the second-order rate constants for the same reagent in toluene, dichloromethane, and tetrahydrofuran are all approximately the same (see Table III).

The path represented by k_1 seems to be one in which the solvent itself is acting as a nucleophile. Support for this associative rather than dissociative mechanism comes from the sign and magnitude of the activation parameters, as well as the fact that only when the reactions are carried out in coordinating solvents are first-order kinetics observed.

Of the reagents used in tetrahydrofuran, the most interesting one was $(C_6H_5)_3As$. In toluene or dichloromethane, this reagent was one of the poorest nucleophiles toward $Fe(NO)_2(CO)_2$. At a 0.1 *M* $(C_5H_5)_3As$ concentration, the pseudo-first-order rate constant is 1.5×10^{-6} sec^{-1}. At the same $(C_6H_5)_3As$ concentration in tetrahydrofuran, the pseudo-first-order rate constant is over 600 times faster as shown in Table XI.

Carbon monoxide was another reagent which was considered to be a poor nucleophile. This was because Keeley and Johnson[2] found the half-life for ^{14}CO exchange of $Fe(NO)_2(CO)_2$ in benzene to be 400 hr at 25°. However, in tetrahydrofuran we found the half-life for ^{14}CO exchange to be approximately 10 min at 25°. There is no dependence on the carbon monoxide concentration (see Table V) and the true first-order rate constant is 1.1×10^{-3} sec^{-1}. This number agrees very well with the first-order rate constant obtained from the substitution reactions in this solvent. There is also good agreement between the activation parameters obtained from the substitution reactions and those obtained from the ^{14}CO exchange reactions. These results indicate that both substitution and exchange proceed by the same mechanism. This is in accord with the recent

Table XI. Some Pseudo-First-Order Rate Constants for the Reaction

$$Fe(NO)_2(CO)_2 + (C_6H_5)_3As \xrightarrow{25°} Fe(NO)_2(CO)[(C_6H_5)_3As] + CO$$

$[(C_6H_5)_3As]$, *M*	Solvent	k_{obsd}, sec^{-1}
0.1	Toluene	1.5×10^{-6}
0.1	Dichloromethane	2.0×10^{-6}
0.1	Tetrahydrofuran	1.0×10^{-3}

observations on the exchange and substitution reactions of $Ni(CO)_4$.[15]

The second difference in the kinetic behavior of $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ is the order of reactivity of the group V donor atom reagents. Since both the iron and cobalt atoms of these complexes are in low oxidation states, they are considered to be class b[16a] or soft[16b] metals. Therefore, the order of reactivity of the group V donor atom reagents toward both of these substrates should be $N \ll P > As$;[16] *i.e.*, phosphines should be better reagents toward the soft-metal atoms than amines. This was found to be the case using $Co(NO)(CO)_3$[6] and $(C_5H_5)Rh(CO)_2$[17] as substrates. However, the results in Table III show that the amines used are as good or better reagents toward $Fe(NO)_2(CO)_2$ than most phosphines or phosphites. Triphenylarsine is still much slower than the corresponding phosphine. Thus, the order $N \geq P > As$ seems to be the correct one for the reactivities of the group V donor atom reagents toward $Fe(NO)_2(CO)_2$.

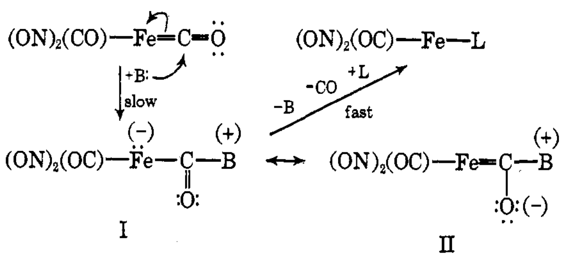
The third difference in the kinetic behavior of $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ is that the tetrabutylammonium halides react very rapidly with $Fe(NO)_2(CO)_2$, whereas they do not react with $Co(NO)(CO)_3$[18] (see Table X). The rates of reaction of $Fe(NO)_2(CO)_2$ with these halides decrease in the following order: $Cl > Br > I$. This means that the harder base chloride ion is more reactive toward $Fe(NO)_2(CO)_2$ than the softer base iodide ion.

The variations in the kinetic behavior of $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ which have been described were completely unexpected in light of the similarities of these substrates in reactions with the phosphorus reagents.[1] Several of the results for the reactions of $Fe(NO)_2(CO)_2$ seem to be inconsistent with nucleophilic attack at a soft-metal center.

When the entering reagent is a soft base such as a phosphine, phosphite, arsine, or sulfide, the electrophilic center of $Fe(NO)_2(CO)_2$ is surely the soft-metal atom. It is unlikely, however, that when the entering reagent is a hard base it should react at this same soft-metal atom at a rate greater than that for the soft bases. Thus in order to explain the experimental findings which show amines to be better reagents than phosphines, the order of halide ion reactivity toward $Fe(NO)_2(CO)_2$ to be $Cl > Br > I$, and tetrahydrofuran to be a good nucleophilic solvent, it is proposed that $Fe(NO)_2(CO)_2$ has a second electrophilic center which is a hard center.

This hard center may be either a carbon atom of a carbonyl or a nitrogen atom of a nitrosyl. Since it appears that an attack on nitrogen will increase the electron density in the system and enhance metal–carbon π bonding, such an attack is expected to retard substitution. For this reason and for the reason that examples of carbonyl attack are known, we shall assume that hard nucleophiles attack the carbon atom. Thus Kruck and Noack[19] have described the reaction of sodium methoxide with the cation $[Mn(CO)_4((C_6H_5)_3P)_2]^+$ to give the ester $Mn(CO)_3[(C_6H_5)_3P]_2CO_2CH_3$. Edgell and coworkers[20,21] have reported that various amines attack a carbon atom of $Fe(CO)_5$. They were able to identify compounds such as pyrrolidine carbamate from their reaction mixtures which support amine attack on a carbon atom. Another example of carbonyl carbon attack is shown by the isolation[22] of $(C_5H_5)Mn(CO)(NO)CO_2CH_3$ from the reaction of sodium methoxide and $[(C_5H_5)Mn(CO)_2(NO)]^+$. This example is especially pertinent to this discussion, since it shows that the methoxide attacked a carbonyl carbon atom rather than a nitrosyl nitrogen atom.

The mechanism proposed for carbonyl attack is shown in eq 13. In this mechanism the hard base attacks an electrophilic carbon atom in the slow rate-determining step to form a transition state or active intermediate which is labeled as structure I. Structure I can be stabilized by resonance hybrid II or by delocalization of the negative charge on the iron into the other nitrosyl and carbonyl groups bonded to the iron. Now the leaving carbon monoxide group has been destabilized (it has been made a better leaving group) and can be quickly displaced by the incoming reagent L to generate the final product $Fe(NO)_2(CO)L$. Using some specific examples, if B is tetrahydrofuran and L is triphenylarsine, then the rate of formation of the product $Fe(NO)_2(CO)[(C_6H_5)_3As]$ will show first-order kinetics since tetrahydrofuran as the solvent is in excess and the triphenylarsine is not involved in the rate-determining step. If B is pyridine and L is also pyridine, then the rate of formation of the product $Fe(NO)_2(CO)$(pyridine) will show a dependence upon the pyridine concentration. The same is true for the halide ions, and chloride would be expected to react the fastest, since it is reacting at a hard electrophilic center.



(13)

An alternative mechanism to that described in eq 13 involves attack of the hard bases on the soft-metal atom. Equation 14 depicts this possible mechanism with regard to the first-order path in tetrahydrofuran. In this

---

[15] J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas, and P. M. Henry, *J. Am. Chem. Soc.*, 90, 1925 (1968).

[16] (a) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), 12, 265 (1958); (b) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[17] H. G. Schuster-Woldan and F. Basolo, *ibid.*, **88**, 1657 (1966).

[18] E. M. Thorsteinson, private communication.

[19] T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

[20] W. F. Edgell and B. J. Bulkin, *J. Am. Chem. Soc.*, **88**, 4839 (1966).

[21] W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *ibid.*, **87**, 3080 (1965).

[22] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.* (Amsterdam), **4**, 256 (1965).

$$\begin{tikzcd}
\mathrm{(ON)_2(OC)Fe{-}CO + THF} \arrow[r, shift left, "k_1"] & \mathrm{(ON)_2(OC)Fe{-}THF + CO} \arrow[l, shift left, "k_{-1}", "\text{slow}"'] \arrow[d, "\text{fast}"', "+\mathrm{L}"] \\
 & \mathrm{(ON)_2(OC)Fe{-}L + THF}
\end{tikzcd} \qquad (14)$$

case the rate-determining step is the attack of the solvent molecule on the metal forming a four-coordinated intermediate in which the solvent occupies one of the coordination positions. It this is correct, the equilibrium for this step must lie almost completely toward the starting material $Fe(NO)_2(CO)_2$, since the infrared spectrum showed no indication of the proposed $Fe(NO)_2(CO)(THF)$ intermediate. The final step involves a fast displacement of the solvent by the reagent L to generate the product $Fe(NO)_2(CO)L$. However, since the slow step was the replacement of carbon monoxide by tetrahydrofuran, then there will be no dependence of the pseudo-first-order rate constant on L for this particular path.

Kinetic studies on reaction 3 have shown that the rate of this reaction is dependent on the nature and concentration of Y as well as the concentration of triphenylphosphine. Thus the two-term rate law given by eq 9 holds for this reaction. The probable reaction paths for reaction 3 are shown in eq 15.

$$\begin{tikzcd}
\mathrm{Fe(NO)_2(CO)_2 + L} \arrow[r, "k_2", "\text{slow}"'] \arrow[d, "+\mathrm{Y}\ \text{slow}"', "k_{\mathrm{Y}}"] & \mathrm{Fe(NO)_2(CO)L} \\
\text{intermediate} \arrow[ur, "+\mathrm{L}", "\text{fast}"'] \arrow[r, "\text{fast}", "+2\mathrm{L}"'] & \mathrm{Fe(NO)_2L_2}
\end{tikzcd} \qquad (15)$$

The observation that the disubstituted product $Fe(NO)_2[(C_6H_5)_3P]_2$ was being formed as a product from reaction 3 was very surprising. It was shown that the monosubstituted product $Fe(NO)_2(CO)[(C_6H_5)_3P]$ was not a precursor, and it was thus concluded that the disubstituted product was coming directly from the intermediate shown in eq 15.

Kinetic studies on reaction 4 have shown that the rates of this reaction are dependent on the nature and concentration of Y but not on the concentration of triphenylarsine. This is in accord with the rate law given by eq 11. The probable pathway for this reaction is the same as that shown in eq 15, except that the direct reagent path represented by the rate constant k_2 is inoperative. In addition the intermediate only gives the monosubstituted triphenylarsine product.

It is obvious from the results that the various Y groups are acting as catalysts in reactions 3 and 4. Thus, even though the products are the phosphine and arsine products, they are beng formed at rates which are faster than they would be in the absence of Y. The mechanism proposed for the catalytic or k_Y pathway is shown in eq 13, where B is the catalyst Y and L is $(C_6H_5)_3As$. Thus the leaving carbon monoxide group has been activated in the slow rate-determining step. A second step involves the elimination of the leaving carbon monoxide group either with or without the assistance of the entering $(C_6H_5)_3As$.

An alternative mechanism is an attack on the metal by the catalyst Y followed by its rapid replacement by $(C_6H_5)_3As$. However, this is not in accord with the observation that, when $Fe(NO)_2(CO)$(imidazole) was allowed to form and then $(C_6H_5)_3As$ added to this "intermediate," approximately one-eighth as much $Fe(NO)_2(CO)[(C_6H_5)_3As]$ was formed as compared to when the $Fe(NO)_2(CO)_2$, $(C_6H_5)_3As$, and imidazole were all present initially. This seems to be good evidence against a mechanism in which the catalyst Y attacks the metal.

Finally, one would like to understand why the second-order rate constants for the reactions of hard[16] reagents (amines, halides, etc.) with $Fe(NO)_2(CO)_2$ are much faster than for the same reactions with $Co(NO)(CO)_3$. This is not understood, but it is possible to speculate that it may be because two NO's and one CO can stabilize active intermediate I (or transition state) of eq 13 better than one NO and two CO's could for a similar intermediate (or transition state) in the cobalt system. This stabilization results from the ability of the CO and NO groups to delocalize the additional negative charge which has been placed upon the metal by attack of the hard reagent on the carbonyl group. Since NO is thought to be a better π acceptor than CO, it follows that the iron system with two NO's would be stabilized to a greater extent than the cobalt system with only one NO.

Acknowledgment. We wish to thank Professor R. G. Pearson for helpful discussions. This research was supported in part by a National Science Foundation Grant, GP-5479.