*Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201, U.S.A.*

The Kinetics and Mechanism of the Carbon Monoxide Exchange Reaction with Cobalt Nitrosyl Tricarbonyl and Mercury *Bis*(Tetracarbonylcobaltate)

J. P. Day, D. Diemente, and F. Basolo

Received May 26, 1969

The exchange of carbon monoxide with $CoNO(CO)_3$ *has been determined by an infrared tecnique using* $C^{18}O$*. The results differ from the reported exchange studies on this system, but are in agreement with the first-order rates of substitution. The rates of carbon monoxide exchange with* $Hg[Co(CO_4)]_2$ *were also determined by this tecnique and the results are in accord with those reported earlier.*

Introduction

The kinetics of the exchange reactions of carbon monoxide with various metal carbonyls, in solution, have been reported previously (L = CO, in reactions (1),[1,2,3] (2)[4,5] and (3)).[6]

$$Ni(CO)_4+L = Ni(CO)_3L+CO \quad (1)$$

$$Co(NO)(CO)_3+L = Co(NO)(CO)_2L+CO \quad (2)$$

$$Hg[Co(CO)_4]_2+L = Hg[Co(CO)_4][Co(CO)_3L]+CO \quad (3)$$

In the case of $Ni(CO)_4$, the earlier results[1,2] seemed inconsistent with the kinetic observations of substitution reactions,[7] in which L was a variety of nucleophiles, *e.g.* Ph_3P. More recently,[3] we have remeasured the CO exchange, using $C^{18}O$ and infrared spectrophotometry as against the earlier radioactive-tracer method,[1,2] using ^{14}CO. The two sets of exchange results do not agree, but the $C^{18}O$ measurements are consistent with those for substitution reactions, and for the thermal decomposition[8] of $Ni(CO)_4$, all of which appear to have the first step in common. Furthermore, studies of the rate of $C^{18}O$ exchange in the gas phase[3] confirm that the earlier ^{14}CO measurements could be in error due to the intervention of gas phase reactions. As a corollary, it was suggested[3] that many of the earlier exchange measurements with volatile carbonyls could be in error.

We now report kinetic studies of $C^{18}O$ exchange with $Co(NO)(CO)_3$ and $Hg[Co(CO)_4]_2$, using the infrared technique. The former compound is similar in volatility to $Ni(CO)_4$, while the latter is comparatively involatile. In both cases, ^{14}CO exchange has previously been carried out.

In the case of $Co(NO)(CO)_3$, we do not confirm the previous work,[4,5] However, as with $Ni(CO)_4$, our findings seem reasonable as they are consistent with observations on substitution reactions of this compound with N–, P–, As–, and Sb–donor ligands.[4,9] For $Hg[Co(CO)_4]_2$, however, we obtain reasonable agreement with the earlier work,[6] which would seem to confirm the hypothesis that the ^{14}CO method can give erroneous results with volatile carbonyls.

Experimental Section

General. We have assumed that $Co(NO)(CO)_3$ is potentially as dangerous as $Ni(CO)_4$, and we have followed the strict safety precautions described previously.[3]

$Co(NO)(CO)_4$ was obtained from Alfa Inorganics, Inc., and distilled twice (under CO, at *ca.* 1 cm Hg pressure to reduce decomposition). The $Hg[Co(CO)_4]_2$ was prepared as described by Hieber[10] and purified by recrystallization from aqueous acetone. Benzene and *n*-hexane («Spectro» grade, from Eastman Organic Chemicals) were dried by distillation from potassium, under nitrogen. Carbonyl solutions were made up gravimetrically, under nitrogen. Due to the possibility of photodecomposition, these solutions were handled in subdued lighting (photographic safelight during kinetic measurements). $C^{18}O$ (*ca.* 90% ^{18}O) was obtained from Miles Laboratories, Inc.

Kinetic Measurements. $C^{18}O$ exchange reaction were carried out on $Co(NO)(CO)_3$ in solution in benzene (40.0 to 60.0°) and in the gas phase (60.0 to 90.0°), and on $Hg[Co(CO)_4]_2$ in solution in *n*-hexane (−18.4 to 14.8°). In solution reactions, the starting concentr-

---

[1] F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, *83*, 520 (1961).
[2] L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *J. Am. Chem. Soc.*, *88*, 2334 (1966).
[3] J. P. Day, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, *90*, 6927 (1968).
[4] E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, *88*, 3929 (1966).
[5] G. Innorta, G. Reichenbach, and A. Foffani, *Inorg. Chim. Acta*, *3*, 139 (1969).
[6] S. Breitschaft and F. Basolo, *J. Am. Chem. Soc.*, *88*, 2702 (1966).
[7] F. Basolo and R. G. Pearson, « Mechanisms of Inorganic Reactions », 2nd ed. Wiley, New York, 1967, p. 543, and references therein.
[8] J. P. Day, R. G. Pearson, and F. Basolo, *J. Am. Chem. Soc.*, *90*, 6933 (1968).
[9] G. Cardaci, A. Foffani, G. Distefano, and G. Innorta, *Inorg. Chimica Acta*, *1*, 340 (1967).
[10] Von W. Hieber, E. O. Fischer and E. Böckly, *Z. anorg. allgem. Chem.*, *269*, 308 (1952).

ation of $C^{18}O$ relative to metal carbonyl was varied from 1 : 1 to 3 : 1, and in the gas phase from 1 : 1 to 10 : 1. Reactions were followed by infrared spectrophotometry in the C—O stretching region (*ca.* 2000 cm^{-1}), using the apparatus and techniques described for $Ni(CO)_4/C^{18}O$ exchange.[3] In both cases, rate constants were obtained from the decay in intensity of an infrared band of the starting material, namely 2101 cm^{-1} (A_1 mode[11]) for $Co(CO)(CO)_3$, and 2072 cm^{-1} (A_{2u} mode[12]) for $Hg[Co(CO)_4]_2$ (the spectral assignments are discussed in a later section).

In calculating results, reasonable linearity was obtained for the initial stages of standard first-order plots, *i.e.* ln(obsorbance) against time. However, the problem arises that the proportion of $C^{18}O$ in the *free* CO (initially *ca.* 90%) falls during reaction; thus the slope of a first-order plot decreases as the reaction proceeds, even if first-order kinetics ase obeyed. To take this into account, we used the method of calculation described for $Ni(CO)_4/C^{18}O$ exchange.[3] This method assumes first-order knetics, but this assumption was later justified by the constancy of the rate constants obtained over the range of $C^{18}O$ starting concentrations used.

Table I. Rate Constants and Activation Parameters for the Exchange of $C^{18}O$ with $Co(NO)(C^{16}O)_3$, in Benzene Solution and in the Gas Phase

	10^5 k_1,[a] sec^{-1}	
Temp., °C	Solution	Gas Phase
40.0	0.096	—
50.0	0.421	—
60.0	1.68	2.07
70.0	—	8.97
80.0	—	35.6
90.0	—	131.
ΔH^*, kcal/mole^{-1}	29.0±1	32.4±1
ΔS^*, eu.	7 ±3	17 ±3

[a] Defined by equation (4) with k_2 = 0.

The final rate constants are given in Tables I and III, for $Co(NO)(CO)_3$ and $Hg[Co(CO)_4]_2$ respectively, and are the mean of at least three measurements at each temperature. Probable errors in k_1 are two and five percent, in ΔH^*, 1 and 2 kcal/mole, and in ΔS^*, 3 and 6 eu, in Tables I and III, respectively.

Results and Discussion

Cobalt Nitrosyl Tricarbonyl. The infrared spectra of $Co(NO)(CO)_3$ species with various degrees of ^{13}CO isotopic substitution have been discussed recently.[11]

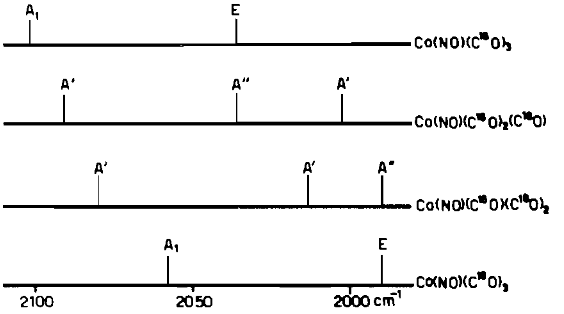

Figure 1. Spectra of $Co(NO)(C^{16}O)_n(C^{18}O)_{3-n}$ species

The spectral changes in the C—O stretching region produced by $C^{18}O$ substitution are very similar to these. The all—^{16}O species shows two bands, at 2101 and 2035 cm^{-1} (hexane solution), assigned to A_1 and E modes, respectively (point group C_{3v}). The situation during progressive $C^{18}O$ exchange is shown in Figure 1. The mono—$C^{18}O$ species is predicted to have three infrared-active modes (A′, A′, and A″, in C_s), but one of these (A″, essentially the anti-symmetric vibration of the two remaining $C^{16}O$ groups) would be expected at the same frequency as the E mode of the all—$C^{16}O$ species. Experimentally, *two* new bands were observed in the initial stages of $C^{18}O$ exchange, at *ca.* 2090 and 1997 cm^{-1}. These are assigned to the two A′ modes, and it is assumed that a third band (A″) is appearing at *ca.* 2035 cm^{-1}, and is unobservable as a new band. Confirming this, it was found that the rate of decay of the 2035 cm^{-1} band during exchange was (initially) about half that of the 2101 cm^{-1} band.

Further $C^{18}O$ exchange produces the bands indicated and assigned in Figure 1. It can be seen that absorbance measurements on the 2101 cm^{-1} band, but not the 2035 cm^{-1} band, can be used as a measure of the concentration of the all—$C^{16}O$ species, and thus to follow the reaction kinetics.

The results are given in Table I. We find, in agreement with the earlier work,[4] that the reaction is

Table II. Collected Activation Parameters[a] for Substitution Reactions in $Ni(CO)_4$ and $Co(NO)(CO)_3$

		First-Order Process		Second-Order Process	
	Solvent	ΔH_1^*	ΔS_1^*	ΔH_2^*	ΔS_2^*
$Ni(CO)_4+C^{18}O$ [b]	hexane	24.0	13.1	not observed	
$Ni(CO)_4+Ph_3P$ [b]	hexane	24.2	13.5	not observed [c]	
$Ni(CO)_4+Ph_3P$ [b]	toluene	22.3	8.4	not observed [c]	
$Co(NO)(CO)_3+C^{18}O$ [d]	benzene	29.0	7	not observed	
$Co(NO)(CO)_3+Ph_3P$ [e]	benzene	35 [f]	26 [f]	16.3	−20
$Co(NO)(CO)_3+Ph_3As$ [e]	benzene	31	14	17.0	−28
$Co(NO)(CO)_3+Ph_3P$ [g]	toluene	not observed		15	−24
$Co(NO)(CO)_3+Ph_3As$ [g]	toluene	30	10	21	−13

[a] ΔH^*, kcal/mole^{-1}; ΔS^*, eu. [b] Reference 3. [c] Possibility of small second-order contribution; see text. [d] This work, Table I. [e] Reference 9. [f] These values have a large experimental uncertainty, and are essentially the the same as those for Ph_3As substitution in benzene. [g] Reference 4.

Table III. Rate Constants and Activation Parameters for the Exchange of $C^{18}O$ with $Hg[Co(CO)_4]_2$ in *n*—Hexane Solution

Temp., °C	$C^{18}O$ Method [a]	^{14}CO Method [b]
−21.0	—	5.90
−18.4	7.53	—
−4.0	21.4	—
0.0	—	43.5
5.1	53.9	—
14.8	129.	—
20.0	—	295.
ΔH*, kcal/mole^{-1}	12.1±2	−19
ΔS*, eu	−25 ±6	13.6

[a] This work. [b] Reference 6.

first-order (*i.e.* equation (4), with $k_2=0$), but our numerical results differ considerably from the earlier ones. However, we find that the activation parameters for exchange in solution and in the gas phase are similar, even though the experimental techniques are necessarily rather different (reducing the chances of a systematic error). Furthermore, the present results seem to be consistent with those for other substitution reactions, as will now be described.

Previous knetic studies[4,9] of the substitution reaction (2) (L=N–, P–, As–, and Sb–donor nucleophiles) has shown, that, in general, the two-term rate law (4) is obeyed.

$$\text{Rate} = -d[Co(NO)(CO)_3]/dt = k_1[Co(NO)(CO)_3]+k_2[Co(NO)(CO)_3][L] \qquad (4)$$

With the better reagents the second-order term is of over-riding importance.[4] However, for the weaker nucleophiles (Ph_3P, Ph_3As, Ph_3Sb), the second-order term can be made small enough for both k_1 and k_2 to be obtained experimentally.[9] It seems reasonable to interpret this in terms of two simultaneous reaction pathways; a bimolecular path, with the formation of a five-coordinate intermediate, giving rise to the second order term, and a unimolecular dissociative process, such as (5), giving rise to the second order term, and a unimolecular dissociaetive process, such as (5), giving rise to the first-order term.

$$\begin{gathered} Co(NO)(CO)_3 \xrightarrow[\text{slow}]{k_1} Co(NO)(CO)_2+CO \\ Co(NO)(CO)_2+L \xrightarrow[\text{fast}]{} Co(NO)(CO)_2L \end{gathered} \qquad (5)$$

The activation parameters for the *first-order* component of the reactions with different nucleophiles are essentially the same (Table II), considering the rather large experimental uncertainty in the obtaining of k_1 by extrapolation in some cases (*e.g.* Ph_3P). Their values, *e.g.* ΔH* = 31 kcal/mole and ΔS* = 14 eu for Ph_3As substitution in benzene, support a dissociative mechanism, and can be compared with the activation parameters for the analogous $Ni(CO)_4$ dissociative process (ΔH* = 24.2 kcal/mole, ΔS* = 13.5 eu, in *n-hexane*).

The $C^{18}O$ exchange results can now be seen to be consistent with those for substitution. The exchange obeys a first-order rate law, and for a nucleophile as weak as CO the absence of a second-order term can be accepted. The activation parameters, ΔH* = 29±1 kcal/mole and ΔS* = 7±3 eu, are in reasonable agreement with these for the first-order component of substitution. By comparison, the ^{14}CO exchange results were anomalous. The exchange rate[4] at 25° was apparently 50 times faster than the (extrapolated) $C^{18}O$ exchange rate. Also, the activation parameters[5] for ^{14}CO exchange (ΔH*±20 kcal/mole, ΔS* = −13 eu) were very different from those for the first order substitution process, and in particular the negative value for ΔS* would not be expected for a dissociative process.

In comparing the behavior of $Co(NO)(CO)_3$ and $Ni(CO)_4$ towards nucleophilic substitution in general (Table II), the most obvious difference is the apparent occurrence of both first and second-order processes for $Co(NO)(CO)_3$, but only a first-order process with $Ni(CO)_4$. However, it should be noted that the first-order process with $Ni(CO)_4$ is very much faster than that with $Co(NO(CO)_3$; *e.g.* at 25°, $k_1=1.07\times10^{-2}$ and $\simeq 8\times10^{-8}$ sec^{-1}, for $C^{18}O$ exchange in solution, for the two compounds respectively. It would seem that $Ni(CO)_4$ could also be undergoing a second-order reaction (say with Ph_3P) at much the same rate as $Co(NO)(CO)_3$, but this would not have been measurable. For example, at 25°, for Ph_3P substitution with $Co(NO)(CO)_3$ in benzene solution,[9] $k_1=5\times10^{-8}$ sec^{-1} and $k_2=1.1\times10^{-3}$ M^{-1} sec^{-1}. In conditions where the concentration of Ph_3P is 0.5 *M*, the first-order component is negligible and $k_{obs}=6\times10^{-4}$ sec^{-1}. For Ph_3P substitution in $Ni(CO)_4$ under the same conditions, k_{obs} $(=k_1)$ $\simeq 10^{-2}$ sec^{-1}. Thus, k_{obs} for $Co(NO)(CO)_3$ is only about 6 percent of k_{obs} for $Ni(CO)_4$, under these conditions. However, it is possible that up to 10 percent of k_{obs} in the $Ni(CO)_4$/Ph_3P substitution, with 0.5 *M* Ph_3P, is due to a second-order term, since it was reported[3] that a change in concentration of Ph_3P from 0.005 to 0.5 *M* increased k_{obs} by *ca.* 10 percent. We conclude that in the $Ni(CO)_4$ substitutions, a second-order reaction could be occurring at a rate comparable to that in $Co(NO)(CO)_3$ substitutions. The appearance of the second-order reactions for $Co(NO)(CO)_3$ in Table II is, therefore, probably the results of the compound's reduced participation in the first-order reaction, and does not necessarily indicate that $Co(NO)(CO)_3$ is a stronger electrophile than $Ni(CO)_4$.

Mercury bis(*tetracarbonylcobaltate*). The structure of $Hg[Co(CO)_4]_2$ has recently been determined,[14] and the essentials are shown in Figure 2. The infrared spectra of the compound in the solid state and in solution are consistent with this structure[12] (point group D_{3d}). Since not all CO groups in the molecule are equivalent, the possibility arises for the two different types of CO («axial» and «radial») to exchange at different rates.

---

(11) G. Bor, *J. Organometallic Chem.*, *10*, 343 (1967).
(12) A. R. Manning, *J. Chem. Soc.* (A) 1968, 1018.
(13) Equations (11) to (15) in reference 3.
(14) G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc.* (A), 1968, 1005.

The infrared spectrum of $Hg[Co(CO)_4]_2$ in benzene solution has three principal bands in the C–O stretching region, which have been assigned as follows: 2072 cm^{-1} (strong), A_{2u} mode consisting primarily of axial-CO vibration; 2021 cm^{-1} (weak), A_{2u} mode, and 2007 cm^{-1} (very strong), E_u mode, both consisting primarily of radial-CO vibrations. The distinction between axial-CO and radial-CO modes is not exact, since (a) the radial CO groups are not exactly at 90° to the axial, and (b) the two A_{2u} modes, being of the same symmetry class, are presumably mixed to some degree. However, the axial-radial distinction is perhaps good enough to be useful in determining the relative exchangeabilities of axial and radial groups.

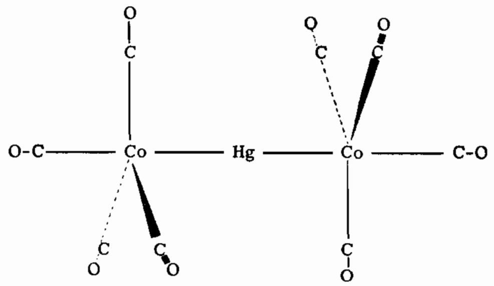

Figure 2. The molecular geometry of $Hg[Co(CO)_4]_2$

During C^{18}O exchange, it was observed that all the original bands diminished in intensity, and many new bands appeared, corresponding to the formation of intermediate species. Ultimately, the fully exchanged product showed a three-band spectrum similar in appearance to that of the starting material, but shifted by *ca.* 45 cm^{-1} to lower wavenumbers. It was not possible to resolve all the intermediate bands in the 2000 to 2020 cm^{-1} region, and the spectra of the different species were, therefore, not determined. Also, it was not possible to obtain accurate kinetic data from the disappearance of the 2007 and 2021 cm^{-1} bands, due to the appearance of overlapping bands. However, good kinetic data could be obtained from the 2072 cm^{-1} band (A_{2u}, axial CO) as no new bands appeared in this position. It was found that the initial rate of decay of the 2007 cm^{-1} band was rather less (0.4 to 0.8 times) than the rate of decay of the 2072 cm^{-1} band. (This difference can perhaps be ascribed to the simultaneous growth of a band at the same position, rather than to a genuine difference in axial and radial reaction rate).

The kinetic results are in Table III, together with the previous ones for ^{14}CO exchange. We find, as before,[6] that the exchange follows a rate law first order in metal carbonyl, and zero order in CO; numerical agreement with the earlier results is also within experimental error. It was concluded from the ^{14}CO exchange results that all CO groups exchanged at the same rate. We now conclude that: (a) all CO groups exchange, and (b) that the distribution of C^{18}O in the exchanged species is probably random between axial and radial positions. One possibility is that axial and radial groups are equally reactive; however, on chemical grounds this does not seem very likely. Alternatively, there could be a mechanism by which axial and radial CO groups interchange in $Hg[Co(CO)_4]_2$ (*i.e.* in the ground state), either by an intra- or an inter-molecular mechanism at a rate rapid compared to CO exchange. Axial-radial interchange could also occur in the transition state for CO exchange, although care must be taken, in postulating a mechanism of this type, not to contravene the principle of microscopic reversibility, as has recently been pointed out in a discussion of CO exchange in $Mn(CO)_5X$ compounds.[15]

The actual mechanism for CO exchange is still obscure. The rather large negative entropy of activation, –25 eu, would seem to rule out a simple dissociative process analogous to (5) for $Co(NO)(CO)_3$. We now confirm the earlier observations[6] that phosphine substitution reactions (*e.g.* L = Bu_3P in (3)) proceed much more rapidly than CO exchange, to produce disubstituted products, $Hg[Co(CO)_3L]_2$. If CO exchange does not proceed by a dissociative process, then, since Bu_3P substitution is a *faste*r reaction, this mechanism is ruled out for substitution also (by the application of the principle of microscopic reversibility). However, neither of the alternative possibilities suggested earlier[6] can yet be eliminated.

Acknowledgment. We wish to thank Professor R. G. Pearson for stimulating and valuable discussions. We thank the National Science Foundation for an award of a predoctoral Fellowship to D. D. This research was supported in part by a grant from the National Science Foundation.

---

(15) T. L. Brown, *Inorg. Chem.*, 7, 2673 (1968).