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Kinetics of Exchange Reactions of ^{14}CO with Monosubstituted Derivatives of $Co(CO)_3NO$ and with the Parent Complex [1]

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The ^{14}CO exchange kinetics with $Co(CO)_3NO$ and derivatives of the type $Co(CO)_2NOPX_3$ ($X = C_6H_5$, $n-C_4H_9$, OC_6H_5 and OCH_3) have been studied in toluene solution. The monosubstituted complexes follow a two-term rate law $v = k_1[C]+k_2[C][CO]$. For the first-order term, the variations of k_1 and of the thermal parameters have been interpreted as arising from the size of the substrate ligand and the coordinating intervention of the solvent in the transition state. For the second order term, the high values of k_2 with respect to the corresponding ligand disubstitution reactions have been mainly attributed to the π-accepting ability of the entering CO ligand. The parent complex follows a first-order rate law, whose rate constants and thermal parameters differ remarkably from those for the corresponding ligand monosubstitution reactions; possible explanations of this behaviour have been presented.

Introduction

The kinetic study of ^{14}CO exchange reactions on carbonyl complexes of transition metals has recently been the subject of much work.[2] As yet limited information is available[3] concerning the effect of the presence in the substrate complexes of ligands other than CO, *e.g.* PX_3, and concerning the thermal parameters of the kinetics. An investigation of the ^{14}CO exchange kinetics on complexes of the type $Co(CO)_2NOL$ ($L = CO$, $P(C_6H_5)_3$, $P(n-C_4H_9)_3$, $P(OC_6H_5)_3$, $P(OCH_3)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$) has been undertaken in order also to evaluate the thermal parameters of the reactions. Related studies have been carried out in this laboratory using infrared, mass-spectrometric, and electrochemical methods.[4] It has been observed that the possible action of the solvent as a nucleophile in the transition state for these exchange reactions is strongly affected by the steric requirements of the ligand L; furthermore, the behaviour of the unsubstituted complex has appeared singular when compared to the substitution reactions.

Experimental Section

(*a*) *Materials.* $Co(CO)_3NO$ was prepared following Seel,[5] and was purified by vacuum sublimation at room temperature; it was stored under nitrogen or argon at −25°C. The ligands were reagent grade Fluka products; they were used without further purification. Carbon monoxide was prepared following Gilliland and Blanchard[6] and purified by bubbling through a Fieser solution[7] and then through conc. H_2SO_4. 0.5 mc Amersham radioactive CO (30.5 mc/m*M*) was diluted to about 500 ml with non-radioactive CO. Argon was a SIO product. All the gases employed were analyzed with an Atlas CH4 mass spectrometer; they were found pure to about 99.9%, with an oxygen content $<0.01\%$.

The solvent employed throughout was Erba reagent grade toluene, purified following Vogel.[8] The monosubstituted complexes were prepared by literature methods (see, *e.g.*,[4b,9]); they were identified by IR and UV spectra, m.p. and analysis. $Co(CO)_2NOP(OC_6H_5)_3$ was prepared following ref. 9 and was purified by low temperature crystallization from methanol. *Anal.* Calcd. C, 52.76; H, 3.32; N, 3.08; m.p. 50°C. Found: C, 52.3; H, 3.2; N, 3.35, m.p. 62-63°C.

(*b*) *Conditions of the Kinetic Work.* The reactor for the exchanges was similar to that described by Basolo and Wojcicki;[10] its geometry was modified in view of the somewhat low rates of the exchange reactions reported here. In this regard, high values of $k_{app.}$ and sufficiently high rates of change of activity in the gaseous phase could be obtained (see eq. (1) below) by lowering the factor y by reducing as much as possible the ratio (volume of gas)/(volume of liquid). The reactor adopted had a total volume of about 100 ml with about two thirds of its volume occupied by the gas. In this way the factor y was

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(1) This investigation was supported in part by a research grant from the Italian National Research Council.

(2) For recent reviews on the matter see R. J. Angelici, *Organometal. Chem. Rev.*, *3*, 173 (1968); F. Basolo and R. G. Pearson, « Mechanisms of Inorganic Reactions », 2nd ed., J. Wiley and Sons, Inc., New York, N. Y., 1967, Chapt. 7; D. A. Brown, *Inorg. Chim. Acta Rev.*, *1*, 35 (1967).

(3) For a summary of the available data see R. J. Angelici, ref. 2.

(4) (a) A. Foffani, A. Poletti, and R. Cataliotti, *Spectrochim. Acta*, *24A* (1968) in press; *Inorg. Chim. Acta*, *2*, 157 (1968); G. Distefano, G. Innorta, S. Pignataro, and A. Foffani, *J. Organometal. Chem.*, *7*, 473 (1967); *13* (1968) in press; G. Piazza, A. Foffani, and G. Paliani, *Z. Phys. Chem.* (Frankfurt), *60*, (1968) in press; (b) G. Cardaci, A. Foffani, G. Distefano, and G. Innorta, *Inorg. Chim. Acta*, *1*, 340 (1967); *2*, (1968) in press.

(5) F. Seel, *Z. Anorg. Allgem. Chem.*, *269*, 40 (1952).

(6) W. L. Gilliland and A. A. Blanchard, in W. C. Fernelius, Ed. « Inorganic Syntheses » 2, Mc Graw-Hill Book Company, Inc. New York, N. Y., 1946, pg. 81.

(7) A. I. Vogel, ed. « A Textbook of Practical Organic Chemistry », 3rd ed. Longmans Green and Co., Inc.; London, 1957, pg. 186.

(8) ibid. pg. 173.

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

reduced to about 16, compared with figures ranging from 35 to 50 for the reactor described by Basolo and Wojcicki;[10] the $k_{app.}$ values were increased by about 50%. The vessel was thermostated by circulating water; particular care was taken, considering the somewhat high working temperatures and the possibility of partial exchange of the parent molecule in the gaseous phase (see below), to provide for efficient refrigeration before the counting window. For this purpose, a 10 cm Vigreux column cooled by circulating water was inserted. The gas circulation within the vessel was obtained with a Sigmamotor mod. T65 peristaltic pump.

After having checked that the apparatus was air-tight and having flushed it for about 60 minutes with argon or carbon monoxide, the toluene solution of the carbonyl saturated with argon (about 35 ml) was introduced. It had been verified radiochemically that 30 minutes sufficed to renew the atmosphere of the reactor. The reactor's residual oxygen content was $<0.01\%$, as determined by mass-spectrometry. From a gas buret a known amount of radioactive CO was added, the circulatory pump was turned on and the activity counting was begun; the activity was found to decrease uniformly and to become steady after abount 5 minutes. At that time the initial activity A_o was measured. The equilibrium activity A_∞ was in each case evaluated from the actual amounts of carbon monoxide and of complex, assuming that all CO ligands exchanged at the same rate; this was done because the reactions studied were too slow to reach equilibrium without appreciable decomposition of the complex. The activities were measured with a SELO model GP4 Geiger tube connected to a SELO model DCS-415-AU counter; they were corrected for the deadtime of the Geiger.

The stability of each of the complexes was checked under the experimental conditions by measuring IR and UV spectra of the solutions before and after the kinetic runs; no appreciable thermal decomposition was found throughout, nor any concentration change due to solute or solvent volatility. In view of the possibility of a contribution from gaseous phase exchange,[11] for $Co(CO)_3NO$ the complex concentration in that phase was measured mass-spectrometrically; only small amounts were found (see below). The exchange fraction ranged from 13 to 80% for $Co(CO)_3NO$, from 5 to 40% for the derivatives. The kinetic runs follow the McKay law[12] with good linear plots of $\lg \frac{A_o - A_\infty}{A - A_\infty}$ *vs.* t; the slopes of these plots give a $k_{app.}$ figure which is related to the true rate constant k by the equation

$$k = k_{app} \frac{xa^{1-\alpha}\, yb^{1-\beta}}{xa + yb} \qquad (1)$$

where a = [complex], b = [CO] in the solution, x = number of CO ligands in the complex which exchange, y = ratio between the total number of CO molecules in the system and their number in the solution, α = reaction order with respect to the complex, β = reaction order with respect to CO. The reproducibility of the rate constants was within 10% for the parent complex and within 15% for its monosubstituted derivatives. All the kinetic runs were performed in the dark. Within the above limits of uncertainty the rate constants for the present reactions did not appear to be influenced by (i) changes of the reactor volume, (ii) changes of the ratio (volume of gas)/(volume of liquid), (iii) changes of the volume/surface ratio of the reactor.

(*c*) *Measurements of CO Solubility.* Scattered values of CO solubility are reported,[10,13] but measurements were needed in the temperature range of the present kinetic work. These were performd radiochemically in the thermostated vessel of Figure 1. In A, toluene is saturated with CO by bubbling. Space B is filled with about 50 ml Hg with a known amount of radioactive CO. Saturated toluene is transferred from A to B by extracting an equivalent amount of mercury. The radioactive CO in the gaseous phase is equilibrated with that dissolved in toluene by means of a circulatory pump; the activity decreases steadily in the gaseous phase and equilibrium is reached within about 5 minutes.[14] The carbon monoxide solubility is evaluated from a knowledge of the volumes of the toluene solution and of the gaseous phase, and of the initial and equilibrium activities. At 25°C the Bunsen coefficient, α, was found to be 0.166 (literature values 0.167 and 0.165[13]). The other values obtained are 0.146, 0.136 and 0.125 resp. at 35°, 45° and 55°C.

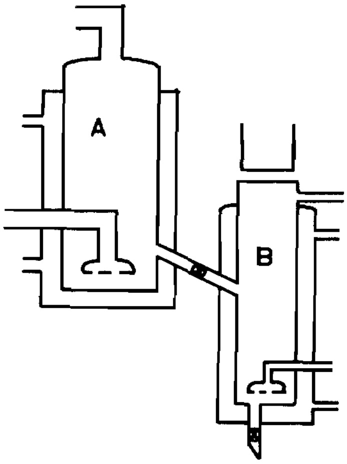

Figure 1. Sketch of the vessel for CO solubility measurements.

Results and Discussion

(*a*) *Phosphine- and Phosphite-monosubstituted Complexes.* Table I gives the kinetic results for Co-

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

[12] A. C. Wahl and N. A. Bonner, Ed., « Radioactivity Applied to Chemistry » J. Wiley and Sons, Inc., New York, N. Y., 1951, pg. 11.

[13] « International Critical Tables », E .W. Washburn, Ed., Mc Graw-Hill Book Co., Inc., New York, N. Y., Vol. III, 1926, pg. 265.

[14] It may be remarked that for both the exchange measurements (normally performed with a 2/1 ratio vol. of gas/vol. of liquid) and for the solubility ones (with a 1.4/1 ratio vol. of gas/vol. of liquid) the times required for equilibration were about the same.

Table I. Rate data for the ^{14}CO exchange with $Co(CO)_2NOL$ in toluene soln.

Temp. °C	$10^2 x [C]$ *M*	$10^4 x [CO]$ *M*	$10^7 x k_I obs$ sec^{-1}	$10^4 x k_{II} obs$ $M^{-1} sec^{-1}$
		$L = P(C_6H_5)_3$		
43.5	5	0.49	0.76	15.3
43.5	5	0.59	1.02	17.3
43.5	5	0.75	1.0	13.5
43.5	5	0.78	1.26	16.2
43.5	5	0.78	0.92	11.7
43.5	5	4.04	1.17	2.9
43.5	5	4.06	2.02	4.97
43.5	5	4.90	2.09	4.27
43.5	5	5.15	3.14	6.14
43.5	5	13.9	4.87	3.50
43.5	5	49.4	19.7	3.98
43.5	5	50.0	7.5	1.37
43.5	9.8	49.0	8.2	2.90
52.8	5	0.71	3.82	53.2
52.8	5	0.73	4.12	56.5
52.8	5	1.18	4.31	36.4
52.8	5	3.0	6.23	21.0
52.8	5	2.98	6.07	21.0
52.8	5	3.78	6.03	15.9
52.8	5	44.8	31.20	6.96
52.8	20.0	2.50	5.33	21.3
52.8	10.0	2.73	3.78	19.1
52.8	1	0.77	4.18	85.5
		$L = P(C_4H_9)_3$		
43.5	5	0.54	0.82	15.1
43.5	5	0.82	0.99	12.0
43.5	5	1.48	1.14	7.7
43.5	5	3.67	3.45	9.42
43.5	5	4.72	2.34	4.96
43.5	5	50.6	16.3	3.22
43.5	5	50.6	15.5	3.06
52.8	5	0.61	2.87	47.2
52.8	5	0.78	2.96	38.4
52.8	5	0.78	3.07	39.8
52.8	5	1.40	3.72	26.6
52.8	5	3.00	4.32	14.4
52.8	5	3.02	3.74	12.4
52.8	5	3.02	4.97	16.4
52.8	5	44.8	22.5	5.02
		$L = P(OC_6H_5)_3$		
43.5	4.8	0.54	0.74	13.7
43.5	4.8	0.67	0.82	12.3
43.5	4.8	0.76	0.84	11.1
43.5	4.8	1.48	1.08	7.25
43.5	4.8	1.75	1.00	5.7
43.5	4.8	3.76	1.27	3.08
43.5	4.8	4.67	1.9	4.27
43.5	4.8	14.6	3.4	2.24
43.5	4.8	14.8	4.15	2.76
43.5	4.8	49.0	14.2	3.14
43.5	4.8	50.0	13.1	2.6
43.5	9.7	15.7	5.3	3.4
52.8	4.8	0.62	1.74	28.2
52.8	4.8	1.44	2.28	15.9
52.8	4.8	2.92	3.6	12.4
52.8	4.8	3.0	3.07	10.2
52.8	4.8	7.6	5.78	7.66
52.8	4.8	14.2	8.3	5.84
52.8	4.8	44.6	27.0	6.05
		$L = P(OCH_3)_3$		
43.5	5	0.58	0.94	16.4
43.5	5	0.77	0.94	12.2
43.5	5	1.09	1.15	10.6
43.5	5	4.05	3.22	7.95
43.5	5	50.0	36.0	7.2
43.5	5	50.0	7.5	1.5
52.8	5	0.45	1.42	31.7
52.8	5	0.46	1.45	31.5
52.8	5	0.53	1.18	22.3
52.8	5	0.67	0.79	11.8
52.8	5	1.31	1.50	11.5
52.8	5	2.98	2.56	8.6
52.8	5	2.90	4.38	15.1
52.8	5	42.0	78.96	18.8
52.8	5	44.0	18.04	4.1
52.8	5	44.0	19.8	4.5
60.0	5.2	0.6	2.16	36.0
60.0	5	0.63	2.04	32.4
60.0	5	0.96	3.0	31.3
60.0	5	2.73	3.9	14.3
60.0	5	3.70	6.77	18.3
60.0	5	52.0	43.2	8.3

$(CO)_2NOP(C_6H_5)_3$, $Co(CO)_2NOP(n{-}C_4H_9)_3$, $Co(CO)_2NOP(OC_6H_5)_3$ and $Co(CO)_2NOP(OCH_3)_3$. In all cases the CO concentration in the solution was varied in the range 4.5×10^{-3}–4.5×10^{-5} moles/liter, while the complex concentration was approximately 5×10^{-2} moles/liter. For $Co(CO)_2NOP(OC_6H_5)_3$, kinetic runs were also performed at a complex concentration of 9×10^{-2}, and for $Co(CO)_2NOP(C_6H_5)_3$ of 1×10^{-2}, 10^{-1} and 2×10^{-1} moles/liter.

The exchanges for all the monosubstituted complexes examined follow a two-term rate law, $v = k_1[C] + k_2[C][CO]$. Plotting the experimental second-order rate constants $k_{II}obs = k_1/[CO] + k_2$ *vs.* $1/[CO]$, or the experimental first-order rate constant $k_I obs = k_1 + k_2[CO]$ *vs.* $[CO]$ good linear plots were generally obtained (see Figure 2) from which the rate constants k_1 and k_2 of the first- and second-order reaction paths were evaluated. They are given, with the corresponding thermal parameters, in Table II. The two reaction paths involved here are analogous to those described in ref. 4b and 26 for the corresponding ligand monosubstitution reactions; an intervention of the solvent in the first-order path might also be possible (see below).

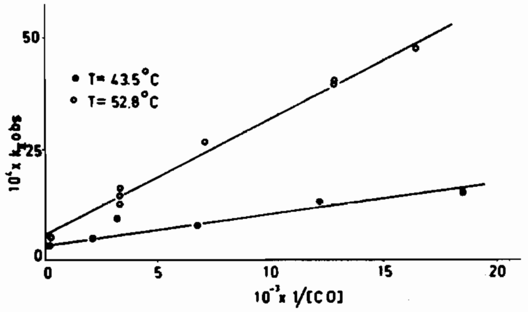

Figure 2. Experimental plots of $k_{II}obs$ *vs.* $1/[CO]$ at different temperatures for the process $Co(CO)_2NOP(n\text{-}C_4H_9)_3 + {}^{14}CO$.

The introduction of a ligand with a phosphorus donor atom in the parent complex appears to cause a drastic decrease in the exchange rate and also the

Table II. Rate constants and thermal parameters for the first- and second-order processes of the exchange reaction $Co(CO)_2NOL + {}^{14}CO$.

Complex	Temp. °C	$10^6 \times k_1$ sec^{-1}	$10^4 \times k_2$ $M^{-1} sec^{-1}$	ΔH* kcal/mole	ΔS* e.u.
$Co(CO)_2NOP(C_6H_5)_3$	43.5	7.54	3.03	32.8	+10 (I order)
	52.8	34.31	7.28	18.7	−17.4 (II order)
$Co(CO)_2NOP(C_4H_9)_3$	43.5	6.67	3.24	29.3	− 1.4 (I order)
	52.8	25.9	5.71	12.0	−34 (II order)
$Co(CO)_2NOP(OC_6H_5)_3$	43.5	6.39	2.36	16.7	−40 (I order)
	52.8	14.0	5.89	19.6	−15 (II order)
$Co(CO)_2NOP(OCH_3)_3$	43.5	6.3	4.78	11.0	−56.4 (I order)
	52.8	8.89	7.79	10.5	−37.1 (II order)
	60.0	15.28	10.8		
$Co(CO)_3NO$	9.6	227		20.0	−13.4 (I order)
	23.1	1210			
	34.7	4360			

intervention of a second-order contribution in the rate equation which for $Co(CO)_3NO$ is absent or undetectable. That the reaction rate decreases on monosubstitution, as was also found for the isoelectronic complex $Ni(CO)_4$,[10] is mainly attributable to an increased back-bonding effect on the CO ligands; this is caused both by the higher basicity and the lower π-acceptor ability of the phosphorus ligand introduced.

A second-order path for the exchange in carbonyl complexes is somewhat uncommon (for other cases reported see, *e.g.*[15]). A comparison with data[16] obtained at 60°C for disubstitution reactions of the type $Co(CO)_2NOL + L = Co(CO)NOL_2 + CO$, performed on the same complexes is worthwhile. For $L = P(C_6H_5)_3$ the reaction is first-order with $k_1 = 1.95 \times 10^{-6}$ sec^{-1} (ΔH* = 29.2 kcal/mole, ΔS = +1 e.u.); for $L = P(n\text{–}C_4H_9)_3$ parallel first- and second-order mechanisms occur ($k_1 = 1.08 \times 10^{-6}$ sec^{-1}, $k_2 = 3 \times 10^{-6}$ l $mole^{-1}$ sec^{-1}); for $L = P(OCH_3)_3$ the reaction is second-order with $k_2 = 42 \times 10^{-6}$ l $mole^{-1}$ sec^{-1} (ΔH* = 22.0 kcal/mole, ΔS* = −15 e.u.).

The above figures show that the second-order rate constants for the exchange reactions are remarkably higher than for the corresponding disubstitution reactions, at least for the two cases ($L = P(n\text{–}C_4H_9)_3$ and $P(OCH_3)_3$) where comparison is possible. For the other two cases of Table I even more the situation should be the same, considering that for $Co(CO)_2NOP(C_6H_5)_3$ the disubstitution process does not show a second-order path and that for $Co(CO)_2NOP(OC_6H_5)_3$ the disubstitution reaction is in fact too slow to be kinetically followed. There is good evidence[4b,9,17] that for the same substrate the second-order rate constant grows with the basicity and/or polarizability of the entering ligand. In the present case, however, the observed increase of the second-order rate constant on going from disubstitution to exchange reactions cannot be ascribed to a higher basicity and/or polarizability of the CO–ligand lone-pair; instead it could reflect the higher π–acceptor ability of the entering CO–ligand, and the increased electron charge density at the central metal atom for the presence of the phosphorus ligand L in the substrate. The steric requirement of the entering ligand L is also likely to contribute to this effect.

As regards the first-order contribution to the exchange process, it may be noted that the kinetic data for the exchange and disubstitution reactions agree reasonably well (both for the rate constants and for the thermal parameters), at least in the two cases ($L = P(C_6H_5)_3$ and $P(n\text{–}C_4H_9)_3$) where a comparison is possible (a similar situation was found with $Ni(CO)_3P(C_6H_5)_3$;[10,18] see also R. J. Angelici ref. 2, pg 192). It may therefore be inferred that the rate-determining step of the process is the same for both reactions.

The sequence now observed of the first-order rate constants, valid both at 43.5° and at 52.8°C:

$$P(C_6H_5)_3 > P(C_4H_9)_3 > P(OC_6H_5) > P(OCH_3)_3 \qquad (2)$$

agrees with previous results for first-order disubstitution reactions in carbonyl and nitrosyl-carbonyl complexes of the types $Mn(CO)_4LBr$,[19] $Mn(CO)_3NOL$,[20] $Fe(CO)_3LBr_2$,[21] and $Ni(CO)_3L$,[18] where L is a phosphorus donor-atom ligand. This behaviour is not easily explained only by the donor and/or acceptor abilities of the substrate ligand L (although the rate constants k_1 seem to increase with the decreased π-acceptor ability[22] of the substrate ligand): it appears rather to be influenced by the size of that ligand. In fact, a bulkier substrate ligand makes the dissociation of the complex easier, since intermediate with a lower coordination number and a lower size is formed.

It can also be seen that both ΔH* and ΔS vary on changing L, with the same relative order as the k_1 's. This suggests a remarkable intervention of the solvent in these reactions, both in the form of a difference in solvation of the transition intermediate, relative to the reacting complex, and of a direct coordination by the solvent itself. An active participation of the solvent in substitution reactions of $Ni(CO)_4$ has been suggested[23] to explain the remarkable decrease both of ΔH* and ΔS* on increasing the solvent coordinating ability. The data available here seem to indi-

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[15] A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, *17*, 77 (1961).
[16] Unpublished results from this lab.
[17] H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, *88*, 1657 (1966).
[18] L. S. Meriwheter and M. L. Fiene, *J. Am. Chem. Soc.*, *81*, 4200 (1959).
[19] R. J. Angelici and F. Basolo, *Inorg. Chem.*, *2*, 728 (1963).
[20] G. Wawersik and F. Basolo, *J. Am. Chem. Soc.*, *89*, 4626 (1967).
[21] I. A. Cohen and F. Basolo, *J. Inorg. Nucl. Chem.*, *28*, 511 (1966).
[22] W. A. Graham, *Inorg. Chem.*, *7*, 315 (1968).
[23] R. J. Angelici and B. E. Leach, *J. Organometal. Chem.*, *11*, 203 (1968).

cate that a bulkier substrate ligand decreases the possibility of a coordinating intervention of the solvent in the transition state. Therefore ΔH^* decreases along the above series reflecting a decrease in the relative energy of the transition complex, while the parallel decrease of ΔS^* indicates a reduction in the freedom of complex and solvent in the transition state. The variations of ΔH^* and ΔS^* are indeed very remarkable, so that the coordinating effect of the solvent, which gives rise to an associative reaction path, seems to play an important and increasing role along the series. A similar coordinating intervention of the solvent may take place (see below) for the parent complex $Co(CO)_3NO$. At present, we are examining the effect of different solvents on these exchange reactions and on the corresponding ligand substitution processes.

(b) *Arsine- and Stibine-monosubstituted Complexes.* The ^{14}CO exchange has also been attempted with $Co(CO)_2NO\ As(C_6H_5)_3$ and $Co(CO)_2NOSb(C_6H_5)_3$ at 52.8 °C. These complexes, however, undergo a substitutive attack by CO with formation of $Co(CO)_3NO$, as inferred by the IR and UV spectra and by the very rapid decrease of ^{14}CO concentration in the gaseous phase. These measurements show that after 6 hours reaction, the $Co(CO)_2NOAs(C_6H_5)_3$ concentration is decreased by more than 14%, while after 4 hours that of $Co(CO)_2NOSb(C_6H_5)_3$ is decreased by more than 30%. These inverse substitution reactions are now being studied gasvolumetrically. The present qualitative information on the equilibrium conditions indicates that the exchange kinetics might be studied in the presence of a sufficient excess of arsine or stibine.

(c) *Parent Complex.* Table III gives the kinetic results of the ^{14}CO exchange reactions with $Co(CO)_3NO$ at 9.6°, 23.1° and 34.7 °C; the corresponding thermal parameters are reported in TableII. Our measurements support those previously reported[9] on showing that the process is first-order with respect to the complex and zero-order with respect to CO. The rate constant value obtained here ($k_1 = 12.1 \times 10^{-6}$ sec^{-1} at 23.1 °C) is however remarkably higher than that reported previously ($k_1 = 3.5 \times 10^{-6}$ sec^{-1} at 25°C). The present value is a mean from 15 kinetic runs, where the CO concentration was varied from 7×10^{-3} to 0.29×10^{-3}, and that of the complex from 5.4×10^{-2} to 0.54×10^{-2} moles/liter.

The kinetic results of Table III have been repeatedly checked to exclude the possible influence on them of different experimental factors. The reactor was changed more than once, varying its volume from about 72 to 292 ml. The factor y of eq. (1) was varied from 7 to 65 on varying the ratio (volume of gas) (volume of liquid) from about1.1 to 10.7. None of this affected the kinetic results within the limits of their uncertainty (see Table III). Also the repeated sublimation of the complex and the use of different stocks of toluene did not influence the rate constants. Particular care was taken to determine if the complex had undergone decomposition in solution during the kinetic runs; IR and UV spectra of both the fresh and the exchanged solutions did not show appreciable qualitative or quantitative differences.

Table III. Rate data for the ^{14}CO exchange with $Co(CO)_3NO$ in toluene soln.

Temp. °C	$10^2 x[C]$ M	$10^4 x[CO]$ M	$10^7 x k_1$ sec^{-1}	y [a]
9.6	4.5	4.56	20.6	22.1
9.6	4.5	4.83	22.9	22.5
9.6	5.0	4.38	21.1	22.2
9.6	5.0	6.26	25.0	22.7
9.6	8.2	4.47	24.0	22.6
23.1	0.54	3.24	110	26.0
23.1	5.30	2.89	139	28.8
23.1	5.0	3.25	115	26.5
23.1	5.4	3.97	124	26.7
23.1	4.7	4.06	116	26.4
23.1	4.7	23.5	125	28.6
23.1	5.4	70.0	143	26.6
23.1	5.4	70.0	123	27.4
23.1	4.0	2.09	146	65 [b]
23.1	4.8	4.0	125	15.8 [b]
23.1	2.1	14.2	122	13 [b]
23.1	4.2	69.5	105	7.2 [b]
23.1	4.2	69.5	122	7.0 [b]
34.7	4.6	4.12	448	29.7
34.7	4.6	5.13	425	30.3
34.7	7.4	3.72	454	29.7
34.7	7.4	4.02	416	30.3

[a] See eq. (1) text. [b] Runs done to check the influence of the ratio (volume of gas)/(volume of liquid) (see text).

The results indicate a remarkable difference between the kinetics of the exchange and of the first-order monosubstitution processes:[4b] not only the rate constants ($k_1 = 12.1 \times 10^{-6}$ sec^{-1} for the exchange at 23.1 °C and 5.5×10^{-8} for the substitution with $P(C_6H_5)_3$ at 27.1 °C), but also the thermal parameters ($\Delta H^* =$ 19.9 kcal/mole and ΔS^* (298°)$\Delta -13.4$ e.u. for the exchange, $\Delta H^* = 35.0$ kcal/mole and ΔS^* (298°)$=$ $+26$ e.u. for the substitution) differ.

Cases of first-order substitution and exchange reactions with negative entropies of activation are known,[24] and different mechanisms have been proposed to explain this behaviour; moreover, for $Hg[Co(CO)_4]_2$ a difference of behaviour of the exchange and substitution processes has been claimed.[24] The same difference seemed to occur for $Ni(CO)_4$;[25] however, additional IR kinetic work of $C^{18}O$ exchange with the same substrate[11] has led to coincidence of the rate constants and thermal parameters for exchange and monosubstitution in this case. The singular behaviour of the previous results of ^{14}CO exchange has been attributed to the volatility of $Ni(CO)_4$, and it has been suggested that a similar effect might influence the ^{14}CO exchange data for $Co(CO)_3NO$.[9,26]

We deem that the present results for $Co(CO)_3NO$ are reliable for the following reasons:

(i) mass-spectrometric checks were performed (see also the experimental section) on the gaseous phase in equilibrium with the solution during the kinetic runs. Only small amounts of $Co(CO)_3NO$ were found in

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(24) S. Breitschaft and F. Basolo, *J. Am. Chem. Soc.*, *88*, 2702 (1966); R. F. Heck, *ibid.*, *85*, 657 (1963); D. E. Morris and F. Basolo, *ibid.*, *90*, 2536 (1968).

(25) L. R. Kangas, R. F. Heck, Henry, S. Breitschaft, E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, *88*, 2334 (1966).

(26) $C^{18}O$ exchange measurements with $Co(CO)_3NO$, (J. P. Day, F. Basolo and R. G. Pearson, submitted to Chem. Comm.: private communication from F. Basolo) also appear to give exchange rates and thermal parameters of the same order of magnitude as for the substitution process. The previous ^{14}CO exchange measurements, on the other hard gave rate constants about 50 times higher than for the corresponding monosubstitution processes, *i.e.* a ratio not far from the present one.

that phase: *e.g.*, with 25 ml of solution at 25 °C and with a complex concentration of about 5×10^{-2} moles/liter, which is a mean value employed in the kinetic work, the $Co(CO)_3NO$ content of the gaseous phase was found to be about 5×10^{-4} moles/liter below the refrigerant and 1×10^{-4} moles/liter above it. Assuming the same exchange rate in the gaseous as in the liquid phase, it was calculated that for every molecule which exchanged in the gaseous phase, about 44 exchanged in solution. For a solution temp. of 35°C the $Co(CO)_3NO$ content increased to about 1×10^{-3} moles/liter below the refrigerant, while remaining the same as before above it; for every molecule exchanging in the gaseous phase about 23 were calculated to exchange in solution. Under the limitation of exchange rates of the same order of magnitude in the two phases, the exchange contribution in the gaseous phase would therefore be kinetically almost undetectable for $Co(CO)_3NO$;

(ii) the ^{14}CO exchange data for $Co(CO)_3NO$ in the temperature range investigated show that the rate constant for the exchange is always at least a hundred times higher than for the first-order monosubstitution process: in fact, apart from the above comparison at 23.1° and 27.1°C, k_1 for the exchange is calculated to be 8×10^{-5} sec^{-1}, compared with 6.8×10^{-7} sec^{-1} for the substitution at 40° C.[4b] On the other hand, the rate constants for the ^{14}CO exchange with $Ni(CO)_4$[10] ($k_1 > 60 \times 10^{-4}$ and $= 7 \times 10^{-4}$ sec^{-1} at 25° and 0 °C respectively) do not differ remarkably from those obtained for the corresponding $C^{18}O$ exchange[11] ($k_1 = 52 \times 10^{-4}$ and 2.5×10^{-4} sec^{-1} at the same temperatures) or for the substitutions. The fact that for $Co(CO)_3NO$ the rate constants and the thermal parameters differ so drastically on going from ^{14}CO exchange to monosubstitution, makes it difficult to see how the volatility effect suggested for $Ni(CO)_4$[11] can occur to a greater extent for the much less volatile complex $Co(CO)_3NO$;

(iii) suppose that the exchange rate is much higher in the gas phase than in solution, owing to a catalytic mechanism. Then, in order to justify the observed rate constants, a ratio of the exchange rates, in the two phases, of 10^3—10^4 is required. Under these conditions a tenfold variation of the ratio (volume of gas)/(volume of liquid), as experimentally effected would have changed the rate constant by at least a factor of ten, while the observd variations did not exceed 10-20%.

This apparently anomalous behaviour is difficult to explain. ^{14}CO exchanges with other volatile complexes having a different central metal, and experimental checks as to the possible intervention of catalytic paths in solution, should help to clarify the matter.[26] It should be noted that the thermal parameters of Table II for the parent complex agree with those observed in the ^{14}CO exchanges with the monosubstituted complexes, having a substrate ligand L of low size. This would point again to a coordinating intervention of the solvent in the preferred exchange path.

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