

## KINETICS AND EQUILIBRIA IN THE REPLACEMENT BY CARBON MONOXIDE OF THE LIGANDS OF $\text{Co}(\text{CO})_2(\text{NO})\text{L}$ COMPLEXES

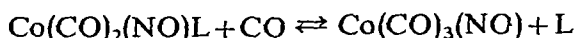
G. INNORTA, G. REICHENBACH AND A. FOFFANI

*Institute of Physical Chemistry, University of Perugia (Italy)*

(Received December 8th, 1969)

### SUMMARY

Equilibrium and rate data have been estimated for the reverse ligand substitution reaction



with  $\text{L} = \text{Sb}(\text{C}_6\text{H}_5)_3$ ,  $\text{As}(\text{C}_6\text{H}_5)_3$  and  $\text{P}(\text{C}_6\text{H}_5)_3$  in toluene solution. The kinetics follow a two-term rate law  $v = k_{-1} \cdot [\text{C}] + k_{-2} \cdot [\text{C}] \cdot [\text{CO}]$ . Variations in the equilibrium and rate constants appear to be mainly associated with the  $\sigma$ -donor abilities of the substrate ligands. The results are discussed in terms of the possible reaction mechanism.

### INTRODUCTION

The monosubstitution reactions between  $\text{Co}(\text{CO})_3\text{NO}$  and  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{As}(\text{C}_6\text{H}_5)_3$  and  $\text{Sb}(\text{C}_6\text{H}_5)_3$  were studied by Thorsteinson and Basolo<sup>1</sup> and by us<sup>2</sup>; the reaction follows a two-term rate law  $v = (k_1 + k_2 \cdot [\text{L}]) \cdot [\text{Co}(\text{CO})_3\text{NO}]$ . Later, we studied the exchange reaction between the monosubstituted complex  $\text{Co}(\text{CO})_2(\text{NO})\text{L}$  [ $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{Sb}(\text{C}_6\text{H}_5)_3$ ] and  $^{14}\text{CO}$ <sup>3</sup>; we confirmed that while  $\text{Co}(\text{CO})_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]$  was chemically stable,  $\text{Co}(\text{CO})_2(\text{NO})[\text{As}(\text{C}_6\text{H}_5)_3]$  and  $\text{Co}(\text{CO})_2(\text{NO})[\text{Sb}(\text{C}_6\text{H}_5)_3]$  reacted with CO to give back the parent complex and we now report kinetic data for reactions of type (1), where  $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{Sb}(\text{C}_6\text{H}_5)_3$ .



In some cases equilibrium constants are also given; it is noteworthy that in contrast with the substantial body of kinetic data, there is little information about equilibria such as those under study here<sup>4,5</sup>.

### EXPERIMENTAL

#### (a). Materials

The parent complex  $\text{Co}(\text{CO})_3\text{NO}$  was prepared as previously described<sup>6</sup> and was purified by vacuum sublimation at room temperature; it was stored under argon

at  $-25^{\circ}$ . The ligands were reagent grade Fluka products, used without further treatment.

The monosubstituted complexes were prepared in tetrahydrofuran under argon with an excess of  $\text{Co}(\text{CO})_3\text{NO}$  as previously described<sup>3</sup>; they were crystallized twice from acetone/methanol and dried under vacuum.  $\text{Co}(\text{CO})_2(\text{NO})[\text{Sb}(\text{C}_6\text{H}_5)_3]$ , m.p.  $102-105^{\circ}$ ;  $\text{Co}(\text{CO})_2(\text{NO})[\text{AsC}_6\text{H}_5_3]$ , m.p.  $112-115^{\circ}$ ;  $\text{Co}(\text{CO})_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]$ , m.p.  $130^{\circ}$ . Carbon monoxide was prepared by Gilliland and Blanchard's method<sup>7</sup> and purified by bubbling through Fieser's solution<sup>8</sup> and then through concentrated sulphuric acid. The gases employed were analysed with an Atlas mass spectrometer; they were found pure to about 99.9%, with a residual oxygen content  $< 0.01\%$ . The solvent employed throughout was Erba reagent grade toluene purified according to Vogel<sup>9</sup>. Argon was supplied by SIO.

*(b). Conditions of the kinetic work*

The apparatus used, similar to that described by Calderazzo and Cotton<sup>5</sup>, differed from it as follows. It consisted of a 50 or 100 ml three-necked Erlenmeyer flask connected to a constant pressure gas burette. The burette had a 25 ml total capacity in 0.05 ml divisions. During the spectrophotometric measurements the central neck was kept closed with a serum cap. The solutions were rapidly stirred with a magnetic stirrer, and the temperature was controlled by a water jacket around the burette and the reaction flask. It was checked gas-volumetrically that these conditions ensured complete equilibration between the gaseous and liquid phases within about 5 min (see also ref. 3).

In a typical kinetic run, the apparatus was evacuated to 40 mm and filled with gas of the required composition (carbon monoxide or carbon monoxide/argon mixtures); the operations were repeated 6 to 7 times until the reactor's residual oxygen content was  $< 0.01\%$ , as checked mass-spectrometrically. Then 2/3 of the CO-saturated solvent were introduced into the reaction flask and stirred; after 10 min a concentrated solution of the complex was added and the clock started. The volume of carbon monoxide absorbed was then recorded as a function of time. The observed volumes were corrected for temperature, atmospheric pressure and vapour pressure of the solvent<sup>10</sup>; the volume of carbon monoxide absorbed at a given time was converted to moles, and used to calculate the  $\text{Co}(\text{CO})_2(\text{NO})\text{L}$  concentration at that time.

The reactions were carried out under pseudo-first-order conditions, the CO concentration being constant. The rate constants were determined from the initial slope of the kinetic plots; they were reproducible to within 20%. The substrate concentration was varied over about a 4-fold range, without change in the pseudo-first-order rate constant. The reaction order in carbon monoxide was determined by varying the gaseous CO concentration from the saturation value to 1/13 of that value, diluting the pure CO in a gasometer with increasing amounts of argon. The CO solubility in toluene had been determined previously<sup>3</sup>.

The rates of some reactions were also measured by changes in IR spectra, the disappearance of the lowest-frequency carbonyl-stretching absorption of the substrate and the appearance of the highest-frequency carbonyl-stretching absorption of  $\text{Co}(\text{CO})_3\text{NO}$  being recorded. Aliquots of the solutions were withdrawn from the flask through a serum cap, and transferred to 0.1 mm NaCl cells; the reference cells contained CO-saturated toluene. A Perkin-Elmer Model 337 IR spectrometer was

used. The rate constants obtained by the CO-evolution and the IR methods were in good agreement. The kinetic data of Table 2 are those by the first method.

(c). *Equilibrium measurements*

The equilibrium concentrations required for the determination of the equilibrium constant  $K = [\text{Co}(\text{CO})_3\text{NO}] \cdot [\text{L}] / [\text{Co}(\text{CO})_2(\text{NO})\text{L}] \cdot [\text{CO}]$  were obtained after allowing the system to react until no further change was detectable by IR measurement of the concentrations of the complexes. The measurements were repeated starting from one side or the other of the equilibrium.

The phosphine derivative did not react appreciably with CO at 52° and 70°, even after 30 h. CO at atmospheric pressure was reacted at 60° with a solution  $2.3 \times 10^{-3} M$  in  $\text{Co}(\text{CO})_3\text{NO}$ ,  $10^{-3} M$  in  $\text{P}(\text{C}_6\text{H}_5)_3$  and  $2.4 \times 10^{-2} M$  in  $\text{Co}(\text{CO})_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]$ ; after 2 h the  $\text{Co}(\text{CO})_3\text{NO}$  IR peak (see above) decreased significantly, and that of the monosubstituted complex increased correspondingly, indicating that the equilibrium constant is less than 0.02 (see Table 1).

The pyridine derivative was found to be easily oxidized under the conditions used, so that even semi-quantitative equilibria and/or rate measurements could not be attempted. The figures reported in Tables 1 and 3 were estimated from the qualitative observations of Thorsteinson and Basolo<sup>1</sup>.

Thermal stability tests were performed on the monosubstituted and parent complexes in the temperature ranges used (see also ref. 3). For this purpose the gas-volumetric device was used as described for the IR kinetic experiments; in some cases the complex was sealed in ampoules, thermostatted to the working temperature and analyzed at different times.  $\text{Co}(\text{CO})_3\text{NO}$ , in CO-saturated toluene solution appeared to be thermally stable for at least 6 h under a CO atmosphere at 60° and 70°.  $\text{Co}(\text{CO})_2(\text{NO})[\text{Sb}(\text{C}_6\text{H}_5)_3]$  was thermally stable in toluene solution under argon at 52° and 60° for at least 5 h.  $\text{Co}(\text{CO})_2(\text{NO})[\text{As}(\text{C}_6\text{H}_5)_3]$ , in the same solution and atmosphere underwent about 20% decomposition in 8 h at 70°, and after that there was little further reaction; in air the decomposition was much faster and went to completion.

## RESULTS AND DISCUSSION

Table 1 reports mean values of the equilibrium constants and the corresponding analytical data. They show that the phosphine derivative is more stable than the arsine and stibine derivatives, and much more stable than the pyridine derivative. These differences are as expected for a substrate metal of the Class B or soft type. Stability data for complexes of Class B metals show that within group V elements the phosphorus derivatives give the stablest complexes, and the stabilities vary in the order  $\text{N} \ll \text{P} > \text{As} > \text{Sb}$ <sup>11,4a</sup>. A similar order would be expected for the Co-L bond strengths and for the relative rates of the second-order reaction (see below); it shows that the  $\sigma$ -donor ability of the substrate ligand is the main factor governing the position of equilibrium. It follows that for the series examined an increased kinetic reactivity of the complexes for the entering ligand CO corresponds to a decreased thermodynamic stability of the monosubstituted complexes.

Table 2 gives the observed pseudo-first-order rate constants for reaction (1). Plotting  $k_{\text{obs}}$  vs.  $[\text{CO}]$  gives a straight line with a non-zero intercept at every temperature (see Fig. 1); this indicates that, as already found for the CO replacement reaction<sup>1,2</sup>,

TABLE 1

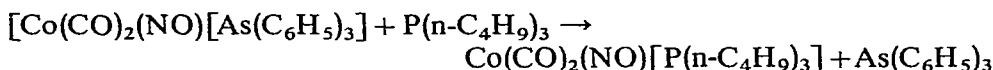
EQUILIBRIUM CONSTANTS FOR THE REACTION  $\text{Co}(\text{CO})_2(\text{NO})\text{L} + \text{CO} \rightleftharpoons \text{Co}(\text{CO})_3\text{NO} + \text{L}$  IN TOLUENE AT DIFFERENT TEMPERATURES

L	K at (°C)			
	39.4	52	60	70
$\text{Sb}(\text{C}_6\text{H}_5)_3$	2.5	6.2	14.1	
	2.4	6.7	14.1	
	av. 2.45 <sup>a</sup>	av. 6.5 <sup>a</sup>	av. 14.1 <sup>a</sup>	
$\text{As}(\text{C}_6\text{H}_5)_3$			1.50	
			2.50	
			2.45	2.20
			1.20	2.26
			1.90	2.45
		av. 1.91 <sup>b</sup>	av. 2.3 <sup>b</sup>	
$\text{P}(\text{C}_6\text{H}_5)_3$				< 0.02 <sup>c</sup>
Pyridine	> 170 <sup>d</sup>			

<sup>a</sup> These data allow an estimate of  $\Delta H^\circ = 15.7$  kcal/mole;  $\Delta S^\circ = 42$  e.u. <sup>b</sup> These data allow an estimate of  $\Delta H^\circ = 8.1$  kcal/mole;  $\Delta S^\circ = 23$  e.u. <sup>c</sup> See experimental section. <sup>d</sup> In nitromethane; see ref. 1.

the reaction (1) follows two parallel pathways with a rate-law  $v = k_{-1} \cdot [\text{Co}(\text{CO})_2(\text{NO})\text{L}] + k_{-2} \cdot [\text{Co}(\text{CO})_2(\text{NO})\text{L}] \cdot [\text{CO}]$ . The  $k_{-1}$  and  $k_{-2}$  values are given respectively by the intercept and by the slope of the above plots. Table 3 lists these rate constants.

The first order rate constants vary in the order:  $\text{Sb}(\text{C}_6\text{H}_5)_3 > \text{As}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3$ ; this order parallels that of the  $\sigma$ -donor and  $\pi$ -acceptor abilities of the ligands<sup>12</sup>. It would be of particular interest to compare these rate constants with the corresponding values for the ligand L exchange reactions on the same monosubstituted substrates; the same active intermediate should be involved in both reactions if the formation of the tricoordinated species is determining for the kinetics. The relevant information comes from the work of Thorsteinson and Basolo<sup>13</sup> who reported only a second-order kinetic path for the reaction



This is probably because the entering ligand concentration used was 20–100 times greater than that employed in the present work, so that any possible first-order reaction would not contribute appreciably to the overall rate.

The  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values of Table 3 for the first-order path are remarkably high. Even if they are regarded with some caution, it is not unreasonable to find the values of  $\Delta H^\ddagger$  higher than that for the isotopic exchange on  $\text{Co}(\text{CO})_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]$  [ $\Delta H^\ddagger = 32.8$  kcal/mole (ref. 3)]. In the isotopic exchange the ligand CO lost in the formation of the tricoordinated intermediate is much less basic than the ligands replaced in the present study; if the ligand  $\sigma$ -donor ability is the governing factor in the

TABLE 2

RATE DATA FOR THE REACTION  $\text{Co}(\text{CO})_2(\text{NO})\text{L} + \text{CO}$  IN TOLUENE SOLUTION

$10^3 \times [\text{C}]$ (M)	$10^4 \times [\text{CO}]$ (M)	$10^6 \times k_{\text{obs}}$ ( $\text{sec}^{-1}$ )	$10^3 \times [\text{C}]$ (M)	$10^4 \times [\text{CO}]$ (M)	$10^6 \times k_{\text{obs}}$ ( $\text{sec}^{-1}$ )
$L = \text{Sb}(\text{C}_6\text{H}_5)_3, \text{temp.} = 39.4^\circ$			$L = \text{As}(\text{C}_6\text{H}_5)_3, \text{temp.} = 60.0^\circ$		
24.1	57.0	19.6	20.0	41.7	44.0
24.0	57.0	18.6	20.0	41.7	42.0
40.0	39.0	10.5	5.0	42.5	44.0
40.0	39.0	11.4	20.0	20.8	23.0
40.0	28.4	6.0	10.0	10.6	16.0
40.0	28.4	10.9	10.0	10.6	14.0
40.0	28.4	7.2	8.3	3.2	5.2
11.5	13.9	7.5	8.3	3.2	4.2
$L = \text{Sb}(\text{C}_6\text{H}_5)_3, \text{temp.} = 52.0^\circ$			$L = \text{As}(\text{C}_6\text{H}_5)_3, \text{temp.} = 70.0^\circ$		
47.4	49.0	112.0	10.0	32.5	120.0
23.2	49.0	90.0	20.0	17.3	80.0
11.6	49.0	105.0	20.0	17.3	76.0
23.2	34.5	54.7	10.0	2.7	34.0
23.2	24.4	64.0	10.0	2.7	38.0
17.4	24.3	44.0			
23.0	16.0	35.8			
44.5	3.7	11.8			
44.7	3.7	5.6			
$L = \text{Sb}(\text{C}_6\text{H}_5)_3, \text{temp.} = 60.0^\circ$					
29.6	42.0	181.0			
15.5	42.0	172.0			
18.1	30.0	104.5			
15.4	21.0	103.0			
16.3	21.0	130.5			
16.3	14.0	70.0			
16.3	14.0	92.0			
45.2	3.0	25.2			

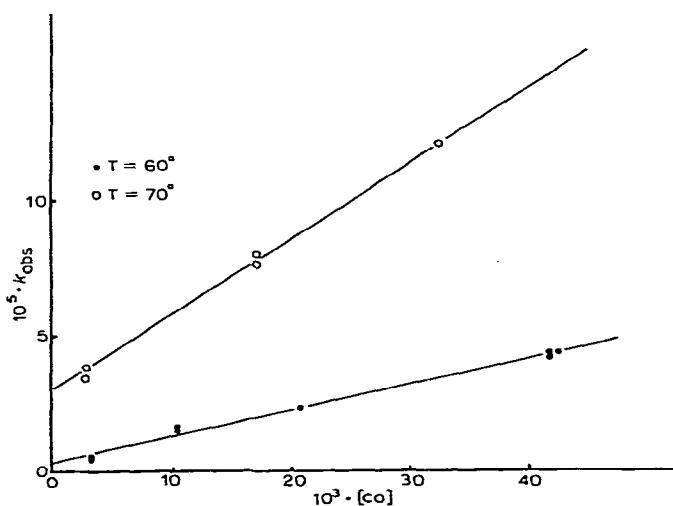
Fig. 1. Plots of  $k_{\text{obs}}$  vs.  $[\text{CO}]$  at different temperatures for the reaction  $\text{Co}(\text{CO})_2(\text{NO})[\text{As}(\text{C}_6\text{H}_5)_3] + \text{CO}$ .

TABLE 3

RATE CONSTANTS AND THERMAL PARAMETERS FOR THE FIRST- AND SECOND-ORDER PROCESSES OF THE REACTION  $\text{Co}(\text{CO})_2(\text{NO})\text{L} + \text{CO}$ 

L	Temp. (°C)	$10^6 \times k_{-1}$ ( $\text{sec}^{-1}$ )	$10^3 \times k_{-2}$ ( $M^{-1} \cdot \text{sec}^{-1}$ )	$\Delta H^\ddagger$ ( $\text{kcal} \cdot \text{mole}^{-1}$ )	$\Delta S^\ddagger$ (333°) (e.u.)
$\text{Sb}(\text{C}_6\text{H}_5)_3$	39.4	0.19	3.1	47.4	63.0 (1st order)
	52.0	1.90	19.4	23.4	5.2 (2nd order)
	60.0	26.70	35.2		
$\text{As}(\text{C}_6\text{H}_5)_3$	60.0	3.00	9.4	43.3	46.0 (1st order)
	70.0	30.00	27.0	20.3	-6.9 (2nd order)
$\text{P}(\text{C}_6\text{H}_5)_3$	52.0	Undetectable in 30 h			
	70.0				
Pyridine	20	Fast <sup>a</sup>			

<sup>a</sup> In nitromethane; see ref. 1.

strength of the metal–ligand bond, the bond energy involved in the exchange reaction should be substantially lower. Similarly the high  $\Delta S^\ddagger$  values when compared with those in the  $^{14}\text{CO}$  exchanges<sup>3</sup> suggest that the solvent has no significant role.

It is noteworthy that on adding algebraically the  $\Delta F^\circ$  for the reaction (obtained from equilibrium data) to the  $\Delta F^\ddagger$  for the first-order path at 60°, one obtains 26.5 – (–1.7) = 28.2 kcal/mole for the stibine derivative, and 27.9 – (–0.4) = 28.3 kcal/mole for the arsine derivative. Since the transition state must be the same for both processes, the agreement gives further support to the validity of the present kinetic and equilibrium data even though their limits of uncertainty are of the same order as the differences in the overall  $\Delta F^\circ$ 's. The second-order rate constants  $k_{-2}$  decrease in the order  $\text{Sb}(\text{C}_6\text{H}_5)_3 > \text{As}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3$ . It was not possible to measure the rate constant for the phosphine derivative, owing to the slowness of the reaction. However, we know that the rate constant for the isotopic exchange reaction between  $\text{Co}(\text{CO})_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]$  and  $^{14}\text{CO}$  is  $0.73 \times 10^{-3} M^{-1} \cdot \text{sec}^{-1}$  at 52.8°<sup>3</sup>; this can be taken as an upper limit for the substitution process if we assume the same activated complex to be involved in the two reactions.

It is of interest that, for cobalt tetracoordinated complexes the same sequence and also approximately the same relative rate changes are observed in the associative ligand displacement with phosphine ligands<sup>12</sup> on the one hand and in the monosubstitution reaction with the parent complex on the other<sup>2</sup>. (In the second case the sequence is reversed, as the effect of entering ligands is being considered.) Since the  $\sigma$ -donor and  $\pi$ -acceptor effects on the rates act in parallel for entering ligands and in opposition for leaving ones, it follows that the  $\sigma$ -effect is clearly dominant.

The rather high values of the second-order rate constants seem to reflect the high charge density on the central metal, which favours the attachment of the strong  $\pi$ -acceptor entering CO group<sup>3</sup>. The activation parameters for the second-order path are quite normal.

For the second-order path, it would be rather interesting to compare the substitution rates observed in this work with the isotopic exchange rates. Both processes apparently involved in their first step the formation of the same pentacoordinated intermediate; if this step were rate-determining, the exchange and reverse substitution rates would be the same. Unfortunately, the exchange rate for  $\text{Co}(\text{CO})_3\text{NO}$  is about

1000 times greater than that found for the monosubstituted complexes; on the basis of the equilibrium data in Table 1 we estimate that the isotopic exchanges would have to be studied in the presence of very large amounts of  $\text{As}(\text{C}_6\text{H}_5)_3$  or  $\text{Sb}(\text{C}_6\text{H}_5)_3$  in order to reduce to an acceptable minimum the exchange rate of the parent complex. Other monosubstituted substrates (*e.g.*, iron monosubstituted complexes) may possibly prove to be more suitable for this comparison.

## ACKNOWLEDGEMENT

We are indebted to Dr. Santini for his contribution to the experimental work described.

## REFERENCES

- 1 E. M. THORSTEINSON AND F. BASOLO, *J. Amer. Chem. Soc.*, 88 (1966) 3929.
- 2 G. CARDACI, A. FOFFANI, G. DISTEFANO AND G. INNORTA, *Inorg. Chim. Acta*, 1 (1967) 340.
- 3 G. REICHENBACH, G. INNORTA AND A. FOFFANI, *Inorg. Chim. Acta*, 3 (1969) 139.
- 4 (a) R. J. ANGELICI AND C. M. INGEMANSON, *Inorg. Chem.*, 8 (1969) 83; (b) J. R. GRAHAM AND R. J. ANGELICI, unpublished results.
- 5 F. CALDERAZZO AND F. A. COTTON, *Inorg. Chem.*, 1 (1962) 30.
- 6 F. SEEL, *Z. Anorg. Allg. Chem.*, 269 (1952) 40.
- 7 W. L. GILLILAND AND A. A. BLANCHARD, in W. C. FERNELIUS (Ed.), *Inorganic Syntheses*, Vol. 2. McGraw-Hill, New York, N.Y., 1946, p. 81.
- 8 A. I. VOGEL, *A. Textbook of practical Organic Chemistry*, Longmans Green, London, 3rd ed., 1957, p. 186.
- 9 See ref. 8, p. 173.
- 10 C. D. HODGMAN, *Handbook of Chemistry and physics*. The Chemical Rubber Publishing Co., Cleveland 42nd ed., 1960, p. 2385.
- 11 S. AHRLAND, J. CHATT AND N. R. DAVIES, *Quart. Rev. (London)*, 12 (1958) 265; R. G. PEARSON, *J. Amer. Chem. Soc.*, 85 (1963) 3533.
- 12 See *e.g.* G. CARDACI AND A. FOFFANI, *Inorg. Chim. Acta*, 2 (1968) 252 and references therein.
- 13 E. M. THORSTEINSON AND F. BASOLO, *Inorg. Chem.*, 5 (1966) 1691.