Contribution from the Institute of Physical Chemistry, University of Perugia, Italy

Kinetics of Monosubstitution Reactions of Phosphine-, Arsine- and Stibine-Ligands with $Co(CO)_3NO$.[1]

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The kinetics of the ligand substitution reactions between $Co(CO)_3NO$ *and* $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, *1,2-bis(diphenylphosphino)ethane has been studied. For the first three ligands it was found active a kinetic two-term rate law for the monosubstitution reaction of the type* $v = (k_1 + k'[L])[Co(CO)_3NO]$, *coming from a comparable contribution of a first- and a second-order path. There is evidence, also from activation enthalphy and entropy data, that the first-order path be a dissociative one; the* k_1 *values for all three ligands are almost coincident in a reasonably wide range of temperature. The second-order path is assigned as an associative one, the value of its overall rate constant* k' *being affected by ligand variation in the order* $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2 > P(C_6H_5)_3 \gg As(C_6H_5)_3 > Sb(C_6H_5)_3$; *consequently, the relative contribution of the first-order path to the overall reaction rate increases for the last three ligands in the reversed order, mean figures for a ligand concentration of* 10^{-1}M *being 0.8, 36 and 85% resp. with* $P(C_6H_5)_3$, $As(C_6H_5)_3$ *and* $Sb(C_6H_5)_3$. *Such a behaviour has been interpreted as a function of the basicity, π-acceptor ability and polarizability of the ligands concerned, the first two factors appearing in these cases to prevail. Also the first-order chelation process with 1,2-bis(diphenylphosphino)ethane, following monosubstitution, appears from thermal data to be an associative one.*

Introduction

In connection with recent measurements by R. F. Heck[2] on the monosubstitution kinetics of $Co(CO)_3NO$ with triphenylphosphine in ether and tetrahydrofuran, and to parallel mass-spectrometric, infrared (solvent effect data) and electrochemical work in progress in this laboratory[3] on this and related complexes, the kinetic study has been now enlarged to other V group ligands like triphenylarsine, triphenylstibine and 1,2-bis-(diphenylphosphino) ethane, for a better elucidation of the reaction mechanism. In the case of triphenylphosphine, -arsine and -stibine a rate-law for monosubstitution has been observed, where the experimental first order rate constant $k_1$obs varies linearly with ligand concentration, according to $k_1\text{obs} = k_1 + k'[L]$. It was also possible to explain why for 1,2-bis(diphenylphoshino)ethane this kinetic behaviour is not observed. Following these results a kinetic mechanism has been proposed involving two competitive processes, first- and second-order respectively, the relative contribution of the second-order process appearing to decrease in the order triphenylphosphine > triphenylarsine > triphenylstibine. The thermal parameters of enthalpy and entropy of activation favour a dissociative mechanism for the first-order process. After completion of the present measurements[4] there is appeared a paper by E.M. Thorsteinson and F. Basolo,[5] where the interest is mainly centered on the effect of the entering ligand on the monosubstitution kinetics of $Co(CO)_3NO$ in toluene. The reaction with $P(C_6H_5)_3$ and $As(C_6H_5)_3$ has been followed also by Thorsteinson and Basolo,[5] but while for $As(C_6H_5)_3$ the rate law observed by these authors agrees with the one presently suggested, for $P(C_6H_5)_3$ the experimental conditions adopted did not allow a direct observation of the first-order contribution (see below). The reaction with $Sb(C_6H_5)_3$ has not been studied by Thorsteinson and Basolo.[5]

Experimental Section

Preparation of the complexes. The parent complex $Co(CO)_3NO$ has been prepared following Seel.[6] The ligands triphenyl-phosphine, -arsine and -stibine were commercial products, used without further purification. 1,2-bis(diphenylphosphino)ethane was prepared and purified according to Chatt and Hart.[7] The monosubstituted complexes of $Co(CO)_3NO$ with triphenylphosphine, -arsine and -stibine and the disubstituted chelate complex with 1,2-bis(diphenylphosphino)-ethane had been described in the literature.[8] The complexes examined have been identified by their melting points and elementary analysis, and by the frequencies of their CO and NO stretching bonds as follows (IR frequencies in cm^{-1}, for spectra in CCl_4 registered with a Perkin-Elmer mod. 337 spectrophotometer. In some cases there is also reported the λ_{max} value in Å for the UV band of kinetic interest, for

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

(2) R. F. Heck, *J. Am. Chem. Soc.*, *85*, 657 (1963).

(3) A. Foffani, S. Pignataro, G. Distefano and G. Innorta, *J. Organometal. Chem.*, *7*, 473 (1967); A. Foffani, A. Poletti and R. Cataliotti, in press; G. Piazza, A. Foffani and G. Paliani, submitted for publication.

(4) Privately communicated, on August 18, 1966, to prof. F. Basolo, to whom the authors are indebted for helpful criticism.

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

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

(7) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(8) (a) L. Malatesta and A. Araneo, *J. Chem. Soc.*, 3803 (1957); W. Hieber and J. Ellermann, *Chem. Ber.*, 96, 1643 (1963); (b) R. J. Mawby, D. Morris, E. M. Thorsteinson and F. Basolo, *Inorg. Chem.*, 5, 27 (1966).

spectra performed in cyclohexane; see also Figure 1):

(a) $Co(CO)_3NO$, $\nu CO(A_1)$ 2100, $\nu CO(E)$ 2034, νNO 1803, λ_{max} 3760; (b) $Co(CO)_2NOP(C_6H_5)_3)$, $\nu CO(A')$ 2039, $\nu CO(A'')$ 1981, νNO 1762, λ_{max} 3900; (c) $Co(CO)_2NOAs(C_6H_5)_3$, $\nu CO(A')$ 2036, $\nu CO(A'')$ 1979, νNO 1765, λ_{max} 4000; (d) $Co(CO)_2NOSb(C_6H_5)_3$, $\nu CO(A')$ 2035, $\nu CO(A'')$ 1979, νNO 1762, λ_{max} 4000; (e) $Co(CO)NOP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, νCO 1958, νNO 1714.

Conditions of the kinetic work. The kinetics of the substitution reactions have been folowed through the variation of the absorbance of the examined solutions in UV and visible, using an Hitachi Perkin-Elmer mod. 139 UV-Vis spectrophotometer with 0.5 cm quartz cells. The kinetic runs have been performed under nitrogen in dark ampoules, to avoid possible photochemical effects;[9] such a protection turned out sufficient to eliminate any influence on the rate constant values. The solvent employed was benzene, distilled over Na and collected under flushing nitrogen in order to reduce the oxygen concentration to values sufficiently low not to affect appreciably the kinetic runs (see below).

The equations used throughout for the plots in dependance on the absorbances, for the experimentally first-order and resp. second-order kinetic runs, are as follows:

$$k_{I}\text{obs} = \frac{2.3}{t} \lg \frac{D_\infty - D_o}{D_\infty - D}$$

and resp. $$k_{II}\text{obs} = \frac{2.3}{t(b-a)} \lg \frac{[b/a(D_\infty - D_o) + D_o - D]}{b/a(D_\infty - D)}$$

where *b* and *a* are initial concentrations resp. of the excess and defect components.

The zero-time absorbance value normally has been taken by measuring the absorbance immediately after the room temperature mixing of the solutions. In such conditions the graphical plot of the above kinetic equations gave a small non-zero intercept on the time-axis. To test that this fact should be due only to the time elapsed before thermostating of the solutions and on sealing the ampoules, and not to secundary kinetic effects, some kinetic runs were performed by pre-thermostating separately the complex and ligand solutions and taking experimentally as zero-time that of their mixing; so working, any rate constant value did not vary appreciably, only going to zero the time-axis intercept.

The infinite-time absorbance has been evaluated from linear plots of the Beer's law for the different components absorbing at the wavelengths chosen for the kinetic runs, knowing the initial composition of the solutions and considering that the reaction goes to completion, *i.e.*, up to disappearance of at least one of the two reactive species. The correctness of this assumption was tested by observing in some cases the correspondence between experimental and calculated values of absorbance.

Two frequency ranges have been used in the kinetic work, depending on the reagent concentrations: for high ligand concentrations ($[L] > 5 \cdot 10^{-3}$ moles/liter) the reaction was studied around 4500 Å, for lower concentrations around 3100 Å. The choise is evident from the spectra of Figure 1 for $Co(CO)_3NO$, $Co(CO)_2NOP(C_6H_5)_3)$ and $P(C_6H_5)_3$; the situation was quite similar for the monosubstituted complexes of $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$. For the limiting cases where it was possible to work at both wavelength ranges, the rate constant values were coincident within the limits of the experimental error. Some of the kinetics were also followed, for reasons of control, in infrared with a Perkin-Elmer mod. 337 spectrophotometer and 0.1 mm NaCl cells, observing the disappearance of the high frequency CO stretching band; the rate constant values from IR and UV data coincided within experimental error. The kinetics with 1,2-bis(diphenylphosphino)-ethane have been performed with a Perkin-Elmer mod. 521 IR spectrophotometer and 0.5 mm NaCl cells, observing the disappearance of the high-frequency CO stretching band of $Co(CO)_3NO$ for the process of mono-substitution, and the appearance of the chelate NO band for the process of chelation.

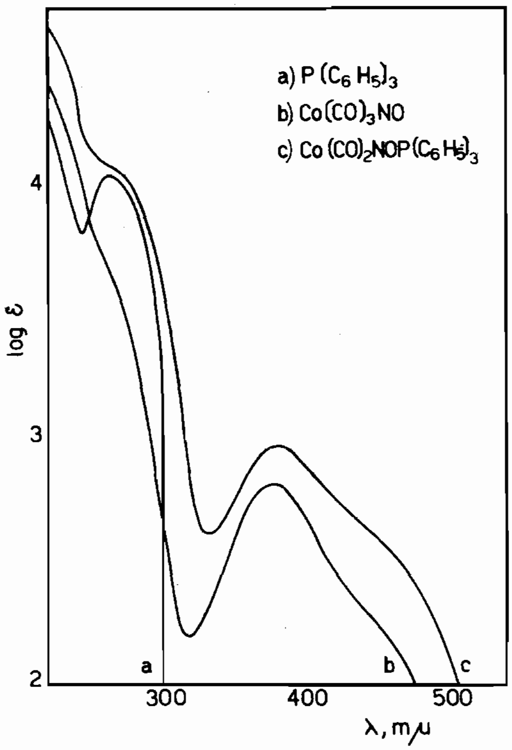

Figure 1. Representative UV spectra of the components interested to the monosubstitution reaction $Co(CO)_3NO + P(C_6H_5)_3$.

The largest part in the kinetic runs have been done at 46.4°C; in these conditions the volatility of $Co(CO)_3NO$ in solution is sufficiently high so that its concentration might be appreciably different from that obtained by weighing. However, by working in ampoules with a small free volume, the change of concentration is within the limits of the experimental error. This was tested by doing, as mentioned before, some kinetic runs so as to prethermostate separately the

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

complex and ligand solutions, and measuring the absorbance also immediately after mixing. From this absorbance value there was obtained, thorugh Beer's law, the correct value of the initial concentration of $Co(CO)_3NO$. A series measurements in these conditions gave rate constant values coincident to those obtained by operating in ampoules.

In the presence of atmopheric oxygen there was noticed a slight decomposition of $Co(CO)_3NO$ to give slowly a light precipitate, presumably due to partial oxidation of the complex. Its stability was improved, as tested from UV spectra, by working in the absence of oxygen, so that in the kinetic experiments there were employed desaerated solutions under nitrogen atmosphere (see above). Besides it was noticed that, with the ligands here used the decomposition of the complex was apparently inhibited by the ligand itself; this could be seen among others from the good agreement between the experimental absorbance of the products by completed reaction and those calculated through Beer's law.

The reactions with $P(C_6H_5)_3$ went completely to monosubstitution, differently from $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$; however, in these last two cases the kinetics were followed for a percent of reaction of 5-15% and the D_∞ figures employed were the calculated ones, so that the rate constant values obtained refer to the beginning of the reaction.

Results and Discussion

The experimental results of the kinetics with $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ are reported respectively in Tables I, II and III, which give the observed first- and second-order rate constant values. From them it may be observed first of all the systematic increase of the k_{II}obs values, and correspondingly the decrease of the $k_I$obs ones, by decreasing the ligand concentration. Besides it may be noted from Table I that the value of the observed rate constants does not depend on the concentration of the complex, at least in the range here investigated ($5 \cdot 10^{-4} + 10^{-2}$ moles/liter). Tables II and III give for $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ the $k_I$obs values, since sufficient excess of ligand was always used to get first-order representations. It may be noted that for the case of $Sb(C_6H_5)_3$ in Table III the value of the first-order rate constant varies much less than for $As(C_6H_5)_3$ of Table II, the direction of variation being anyway the same as for $As(C_6H_5)_3$ and $P(C_6H_5)_3$.

The experimental data can be well represented through a linear dependence from concentration parameters, as from the plots of Figure 2. In Figure 2a there are reported the k_{II}obs values (liter mole^{-1} sec^{-1}) vs 1/[L] for $P(C_6H_5)_3$, where [L] is the ligand concentration; a satisfactory linear trend is obtained in a wide range of concentrations. Figure 2b gives as a function of [L] the $k_I$obs values (sec^{-1}) for $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$; also in this case a good linear trend is observed with non-zero intercept.

These linear trends suggest a kinetic mechanism involving competitive first- and second-order processes, with a relative weight variable according to the type of the ligand and giving both anyway the same final product. A possible scheme is a follows :

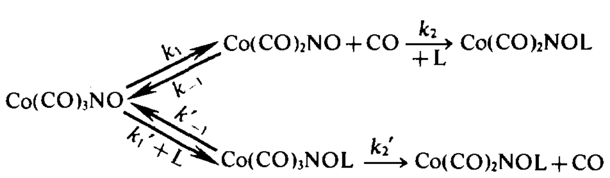

Table I. Experimental second-order rate constants k_{II}obs for the monosubstitution reaction $Co(CO)_3NO + P(C_6H_5)_3$, as a function of ligand L and complex C concentrations. T=46.4°C

$10^2 \times [C]$ moles/liter	$10^3 \times [L]$ moles/liter	$10^3 \times k_{II}$obs l mole^{-1} sec^{-1}
0.957	1.063	8.53
1.220	1.180	7.80
0.992	2.042	6.80
»	2.182	6.84
0.994	2.517	6.95
0.996	4.031	6.23
0.972	4.034	6.40
0.995	5.031	6.28
1.010	5.000	6.35
0.976	5.954	5.84
0.962	6.999	5.97
0.980	7.949	5.88
0.956	12.47	5.76
0.984	19.88	5.85
0.991	20.02	5.62
0.992	49.26	5.35
1.060	50.08	5.51
0.904	50.24	5.66
0.976	50.48	5.46
1.010	50.64	5.36
0.976	100.5	5.55
0.957	101.0	5.47
0.507	0.756	8.58
0.502	1.000	8.25
0.505	4.940	6.4
0.521	15.02	5.56
0.489	30.39	5.61
0.486	40.01	5.66
»	»	5.44
0.499	49.60	5.34
0.492	49.95	5.34
0.520	50.05	5.46
0.128	2:43	6.49
0.225	51.50	5.65
0.048	3.450	6.27
0.047	3.510	6.07
0.049	3.980	6.11
0.049	4.608	6.23

$$k' = \frac{k_2' \, k_1'}{k'_{-1} + k_2'} = 5.45 \times 10^{-3} \text{ l mole}^{-1} \text{ sec}^{-1} \text{ (see text).}$$

Table II. Experimental first-order rate constants $k_I$obs for the monosubstitution reaction $Co(CO)_3NO + As(C_6H_5)_3$, as a function of ligand L concentrations. T=46.4°C

$10^2 \times [C]$ moles/liter	$10^2 \times [L]$ moles/liter	$10^6 \times k_I$obs sec^{-1}
0.920	5.01	4.42
0.976	7.00	4.64
»	7.51	4.96
0.966	7.96	5.57
1.004	10.00	5.57
0.976	10.01	5.14
0.920	14.99	7.01
0.976	19.96	9.11
»	30.01	12.20
»	35.05	13.80

Table III. Experimental first-order rate constants $k_I$obs for the monosubstitution reaction $Co(CO)_3NO+Sb(C_6H_5)_3$, as a function of ligand L concentration. T = 46.4°C

$10^2\times$[C] moles/liter	$10^2\times$[L] moles/liter	$10^6\times k_I$obs sec^{-1}
0.968	5.01	3.09
»	5.98	3.13
»	7.01	3.35
0.966	8.00	3.22
0.968	9.01	3.31
1.004	10.00	3.56
0.984	11.01	3.41
»	11.99	3.37
»	13.01	3.52
»	14.00	3.50
0.920	25.16	4.19

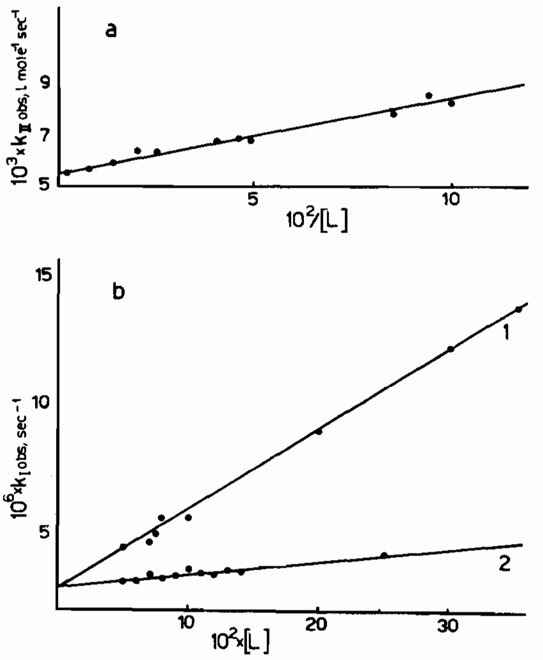

Figure 2. Experimental plots (a) of k_{II}obs vs 1/[L], with L = $P(C_6H_5)_3$, and (b) of $k_I$obs vs [L], with L = $As(C_6H_5)_3$ (curve 1) or $Sb(C_6H_5)_3$ (curve 2), for the monosubstitution reaction $Co(CO)_3NO+L$; [L] is ligand conc. in moles/liter.

The scheme implies that the process leading to the monosubstituted complex may take place through parallel dissociative and associative paths. The first-order dissociative mechanism might be replaced by an associative one, involving the solvent and going through a pentacoordinate intermediate structurally similar to that considered for the associative mechanism with the ligand; this should be followed by fast steps of CO detachment and of substitution of the solvent with the ligand, so that the step of solvent associatiom should turn out rate-determining. Using the stationary-state approximation for the above written mechanism there is obtained, for $k_{-1}[CO]\ll k_2[L]$, a rate equation as follows: $v = (\frac{k_1}{[L]} + k')[Co(CO)_3NO][L]$ where $k' = k_1' \frac{k_2'}{k'_{-1}+k_2'}$. The experimental second-order rate constant k_{II}obs is therefore equal to $(k_1/[L]+k')$, so that its representation vs 1/[L] should give a linear plot with an intercept equal to the overall rate constant k' of the second-order associative mechanism, and a slope corresponding to the rate constant k_1 of the first-order dissociative one. The experimental first-order rate constant $k_I$obs results equal, on the basis of the overall rate equation above given, to $k_1+k'[L]$, so that in this case the intercept of the $k_I$obs vs [L] plot gives the rate constant k_1 of the dissociative mechanism while the slope gives the overall rate constant k' of the associative one.

Being not generally for $P(C_6H_5)_3$ in a first-order experimental situation (see Table I), and having therefore at disposal only experimental k_{II}obs values, there was employed a representation as from Figure 2a. In this case the k_{II}obs values have been obtained from the initial stage of the kinetic runs, owing to the dependance of k_{II}obs on the ligand concentration. The values obtained for $P(C_6H_5)_3$ at 46.4°C are $k' = 5.45\times10^{-3}$ liter mole^{-1} sec^{-1}, $k_1 = 2.95\times10^{-6}$ sec^{-1}. Given the large difference of these two rate constant values, in order that both mechanisms be detectable at the same time it should be necessary to go to ligand concentrations at least lower than about 10^{-2} mole/liter. This explains why Heck[2] and Thorsteinson and Basolo,[5] working the first one gasvolumetrically and the second ones in IR, for the too high ligand concentrations employed were unable to observe the first-order process.

In the case of $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ the overall second-order rate constants k' turned out to be much lower than for $P(C_6H_5)_3$ (see below), so that in order to get rates of reaction well measurable it was worked in a range of ligand concentrations remarkably higher. This implied first-order kinetic runs and so, the experimental $k_I$obs values have been plotted as from Figure 2b. In both cases the linear diagrams of Figures 2a and 2b allow of a sufficiently accurate evaluation of the slopes. The values obtained for $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ at 46.4°C are: $As(C_6H_5)_3$ $k' = 2.8\times10^{-5}$ liter mole^{1-} sec^{-1}, $k_1 = 2.9\times10^{-6}$ sec^{-1}; $Sb(C_6H_5)_3$ $k' = 4.6\times10^{-6}$ liter mole^{-1} sec^{-1}, $k_1 = 2.9\times10^{-6}$ sec^{-1}. The figures obtained for $As(C_6H_5)_3$ are in good agreement with those by Thorsteinson and Basolo,[5] taking into account the difference in the solvent used and in the experimental conditions of the measurements.

It may be noted that the k_1 values are concident within the experimental uncertainty for all three ligands. This fact confirms the intervetion (as from the above given scheme) of a kinetic process parallel to the associative one with the ligand, and shows besides that this process should retain its nature by changing the ligand. Such a comparison was not possible on the basis of the experimental results by:[5] in fact these authors only for $As(C_6H_5)_3$ had at disposal a two-term experimental rate law, because (as above discussed) for $P(C_6H_5)_3$ they could not observe a possible first-order process. By varying the type of the ligand, the remarkable decrease of the k' values on going from $P(C_6H_5)_3$ to $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$, causes correspondingly an increase in the order $P(C_6H_5)_3 \ll As(C_6H_5)_3 < Sb(C_6H_5)_3$ of the relative contribution of the first-order process to the overall reaction rate. This is illustrated by the following representative values for the percent

Table IV. Rate constants for the first-and second-order processes at different temperatures

Ligand	Temp. °C	k_1 [a] sec^{-1}	k' [a] l mole^{-1} sec^{-1}	Ligand	Temp. °C	k_2 [b] sec^{-1}	k_1 [b] l mole^{-1} sec^{-1}
$P(C_6H_5)_3$	27.1	5.5×10^{-8}	1.19×10^{-3}	diphos. [b]	19.8		4.02×10^{-3}
»	40.4	6.8×10^{-7}	3.68×10^{-3}	»	25		5.8×10^{-3}
»	46.4	2.9×10^{-6}	5.45×10^{-3}	»	33.5		11.0×10^{-3}
»	52.3	8.4×10^{-6}	9.14×10^{-3}	»	35.0	1.96×10^{-4}	
$As(C_6H_5)_3$	39.4	1.2×10^{-6}	1.4×10^{-5}	»	39.7	3.15×10^{-4}	
»	46.4	2.9×10^{-6}	2.7×10^{-5}	»	46.4	5.52×10^{-4}	
»	52.3	7.5×10^{-6}	4.1×10^{-5}				

[a] The rate constants k_1 and k' refer resp. to the first- and second-order monosubstitution paths. [b] k_1 is the second-order rate constant for the first attack of monosubstitution, k_2 the first-order one for the process of chelation, with the bidentate ligand diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

first-order contribution: (a) at [L] = 1.5×10^{-1} mole/liter, 0.3% for $P(C_6H_5)_3$ (extrapolated from the kinetic data of Table I), 27% for $As(C_6H_5)_3$ and 77% for $Sb(C_6H_5)_3$; (b) at [L] = 5×10^{-2} mole/liter, 1.3% for $P(C_6H_5)_3$, 45.5% for $As(C_6H_5)_3$ and 92.3% for $Sb(C_6H_5)_3$.

Kinetic runs have been performed (see Table IV) with 1,2-bis(diphenylphosphino)ethane, to see whether such a ligand might also participate in two competitive mechanisms. In this case, two consecutive reactions give, a monosubstituted compound, and then a chelate complex,[8b] and it was not possible to follow the kinetics in UV, so that the IR method had to be employed. This did not allow to drop to ligand concentrations such as to permit of the direct experimental observation of the first-order process contribution. It is under way in this lab. a kinetic study on the reactions of ligand substitution and of chelation for the attack of the present bidentate ligand on monosubstituted complexes of $Co(CO)_3NO$.[10]

Considering that the thermal decomposition of $Co(CO)_3NO$ takes place at a rate of the same order of magnitude as for the first-order ligand substitution process,[11] one might think that parallel—to the first-order substitution reaction a first-order decomposition of the complex should occur. That this be not the case in the present situation can be inferred first of all from the kinetic data with $Sb(C_6H_5)_3$, where the first-order mechanism takes a prevailing role (about 85%) in the overall kinetics; therefore, should a decomposition path contribute appreciably to it, one would not observe the formation of the monosubstituted complex for an amount corresponding to what is found experimentally. Further support to this view is gained from the comparison, for the same reaction with $Sb(C_6H_5)_3$, between the absorbance values calculated through Beer's law at different times during the reaction—considering valid the above outlined mechanism and using for it the integrated expression of the rate law—and the experimental absorbance values. It was worked at 4500 Å; at this wavelength both $Co(CO)_3NO$ and the monosubstituted complex contributed comparatively to the total absorbance. The comparison was quite satisfactory.

It must be noted anyway that the kinetics of the thermal dissociation process, implying (as mentioned above) rate constants of the same order of magnitude as for the first-order substitution path, suggests that the rate-determining step should be the same for both processes. This seems to support the view, also considering the non polar solvent medium adopted, that a dissociative mechanism be active for the first-order process, and justifies the inhibition of the decomposition itself by ligand excess.

Useful informations as to te kinetic mechanism discussed here can be obtained from the activation enthalpy and entropy data. The rate constant values at different temperatures for the ligands now studied, are given in Table IV, while Table V reports the corresponding enthalpies and entropies of activation. For purposes of comparison in Table V are given, together with the present values, the enthalpy and entropy of activation values Thorsteinson and Basolo[5] for the processes there studied.

The most relevant data are those for the first-order processes,[12] which can give positive indications as to the type of mechanism interested. From Table V it is seen that for $As(C_6H_5)_3$ there is good agreement betwen the present values and the indicative ones by Thorsteinson and Basolo;[5] besides, these values are reasonably near, considering the not too high accuracy, to those now obtained for the first-order process with $P(C_6H_5)_3$. This shows that the agreement among the first-order rate constant values is not limited to the temp. of 46.4°C, but is valid at least in the range of temperatures now examined. The values of activation enthalphy for the first-order process—35 kcal/mole for $P(C_6H_5)_3$ and 31 kcal/mole for $As(C_6H_5)_3$—are very high and typical, for carbonylic complexes, of dissociative processes, as it may be inferred from literature data.[13] The positive values of activation entropy—for $P(C_6H_5)_3$ $\Delta S^* = +26$ eu/mole, for

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(10) G. Cardaci and A. Foffani, in preparation.

(11) As from a private communication of F. Basolo, confirmed by UV measurements done in this lab. on the thermal stability of $Co(CO)_3NO$ in the absence of ligands and with or without oxygen.

(12) These values, having been obtained extrapolating from rate constant data, are to be considered as somewhat more uncertain than these obtained directly from experimental rate constants.

(13) For example (ΔS^* (298°) figures; for other similar cases see [14]): (a) for the reaction between $Mo(CO)_6$ and 1,2-bis(diphenylphosphino)-ethane [15] in decane/cyclohexane, $\Delta E^* = 30.1$ kcal/mole, $\Delta S^* = -6.3$ eu/mole (value inferred from [15]); (b) for $Mo(CO)_4$ (dipy) and $P(OCH_2)_3$-CCH_3 [16] in clorobenzene, $\Delta H^* = 28.9$ kcal/mole, $\Delta S^* = +12.5$ eu/mole; (c) for $Ni(CO)_4$ and $P(C_6H_5)_3$ in toluene [17], $\Delta H^* = 21 \pm 1$ kcal/mole, $\Delta S^* = +2$ eu/mole; (d) for $Mn(CO)_5I$ and $As(C_6H_5)_3$ in chloroform [18], $\Delta E^* = 32.2$ kcal/mole, $\Delta S^* = +20.7$ eu/mole.

(14) (a) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, *87*, 5586 (1965); R. J. Angelici and F. Basolo, *Inorg. Chem.*, *2*, 728 (1963); E. E. Siefert and R. . Angelici, *J. Organometal. Chem.*, *8*, 374 (1967); (b) F. Zingales, F. Canziani and F. Basolo, *J. Organometal. Chem.*, *7*, 461 (1967).

(15) H. Werner, *J. Organometal. Chem.*, *5*, 100 (1966).

(16) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, *87*, 5590 (1965).

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

(18) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, *84*, 2495 (1962).

Table V. Enthalpies and entropies of activation for the first- and second-order processes

Ligand	Order of reaction	ΔH^* kcal/mole		ΔS^* (298°) eu/mole	
		present work	ref.[3]	present work	ref.[3]
$P(C_6H_5)_3$	I order	35		+26	
	II order	16.3	15	−20	−24
$As(C_6H_5)_3$	I order	31	30	+14	+10
	II order	17	21	−28	−13
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$	II attack (I order)	18		−19	
	I attack (II order)	13		−27	

$As(C_6H_5)_3$ $\Delta S^* = +14$ eu/mole – point to an increase of freedom in the formation of the activated complex. Since effects coming from differences in solvation between starting molecule and activated complex, being these both neutral, should not be important, these positive values support a kinetic mechanism whose rate be determined by the dissociation of the Co-CO bond, followed by a fast reaction with the ligand of the tricoordinate dissociation intermediate. In order to get more accurate and selective informations as to the reaction mechanism, a study is under way of the solvent effect on the reaction kinetics between $Co(CO)_3NO$ and 1,2-bis(diphenylarsino)ethane; this ligand was chosen to reach a favourable experimental compromise beween reaction times not too long and possibly to evaluate with sufficient accuracy the first-order contribution to the overall reaction.

Also for the second-order paths Table V gise, together with the present values of activation enthalpy and entropy, those by Thorsteinson and Basolo.[5] The agreement is good for $P(C_6H_5)_3$ while for $As(C_6H_5)_3$, owing to the greater uncertainty coming from the use of extrapolated constants to evaluate the thermal data, the comparison is less accurate particularly for the activation entropy; anyway, any difference of activation enthalpy from $P(C_6H_5)_3$ to $As(C_6H_5)_3$ ligand does not sem to be significant.[19] The negative activation entropy values for all these processes agree with an associative mechanism; associative appear to be also the monosubstitution and chelation processes with 1,2-bis-(diphenylphosphino)ethane.[8b] For this last ligand the rate of monosubstitution is almost the same[20] as for $P(C_6H_5)_2C_2H_5$.[5] Also the thermal parameters are almost equal: $P(C_6H_5)_2C_2H_5$, $\Delta H^* = 15$ kcal/mole, $\Delta S^* = -19$ eu/mole ;[5] 1,2-bis(diphenylphosphino)ethane, $\Delta H^* = 13$ kcal/mole, $\Delta S^* = -27$ eu/mole (see Table V).

For $Ni(CO)_4$ and substituted complexes it has been observed[2,17,21] that the substitution kinetics with phosphinic ligands are first-order, not depending on the ligand concentration, and the mechanism has been assigned as of dissociative type. In such a kind of process the activated complex should acquire a trigonal sp^2 structure, stabilized with respect to the tetrahedral one by the large availability in these conditions of *d* orbitals to form π back-bondings with the ligands.[22,23] The dissociative path is also favoured by the low mean Ni-CO bond energy, as compared to that for other carboylic complexes.[24] In the case of $Co(CO)_3NO$ the central metal gains further availability of negative charge by electronic contribution from NO^+ ligand; this increases the π contribution to the Co-CO bonds disfavouring the disociative path;[26] on the other hand the strong π-backbonding capacity of the NO^+ ligand,[29] decreasing the electron density at the central metal *d* orbitals, allows the attack of the electron pair of the entering ligand to give the pentacoordinated activated complex responsible of the associative path.[5] As it was found in the reaction between $Mo(CO)_4$(dipy) or $W(CO)_4$(dipy) and phosphites,[16] also for $Co(CO)_3NO$ the two mechanisms (associative and dissociative) may well be parallel, without the necessity to consider a possible solvent assisted associative path[5] to explain the experimental rate law;[30] this also taking into account the poor cordinating character of the solvent used.

The values of the overall rate constants *k'* of the associative path for the different ligands vary in the order $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (1000) > $P(C_6H_5)_3$ (200) ⋙ $As(C_6H_5)_3$ (5) > $Sb(C_6H_5)_3$ (1), the figures in parenthesis being relative rate constants referred to $Sb(C_6H_5)_3$ as unity. The factors which are likely to affect the ligand nucleophilicity are their basicity, polarizability and π-acceptor ability. On going from $P(C_6H_5)_3$ to $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ the basicity and π-acceptor ability decrease, while the polarizability increases. Given the observed order of the rates, it seems that the first two factors be the most important ones in these cases on determining the ligand nucleophilicity. This seems to be supported also by the

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(19) For the reaction between $Co(CO)_3NO$ and $P(C_6H_3)_3$ the following thermal parameters in tetrahydrofuran have been given by [2]: $\Delta E^* = 11.7$ kcal/mole and $\Delta S^* = -34$ eu/mole, again in good agreement with the values of Table V, considering the different medium employed.

(20) The values of the second-order rate constants are at 25°C: for $P(C_6H_5)_3$ 1.0×10^{-3} [5], for $P(C_6H_5)_2C_2H_5$ 5.9×10^{-3} [5], for 1,2-bis(diphenylphosphino) ethane 5.8×10^{-3} (see Table IV); the fact that the last two figures are about six fimes higher than that for $P(C_6H_5)_3$, reflects mainly the variation of basicity and/or polarizability due to the substitution of a phenyl group with an ethyl one.

(21) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, *81*, 4200 (1959).

(22) G. E. Kimball, *J. Chem. Phys.*, *8*, 188 (1940).

(23) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, *83*, 525 (1961).

(24) D(M-CO) = 44 kcal for $Ni(CO)_4$ against 57 kcal for $Cr(CO)_6$ and 60 kcal for $Fe(CO)_5$; values inferred from thermal data referred to the corresponding metal valence states.[25]

(25) F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions» Ed. Wiley, p. 63 (1958).

(26) This is shown, e.g., by the force constant values for the Ni-C bond (2.1 md/Å) in $Ni(CO)_4$ [27], as compared to the Co-C bond (2.92 md/Å) in $Co(CO)_3NO$ [28].

(27) L. M. Jones, *J. Chem. Phys.*, *28*, 1215 (1958).

(28) R. S. McDowell, W. H. Horrocks Jr. and J. T. Yates, *J. Chem. Phys.*, *34*, 530 (1961).

(29) E. A. C. Lucken, N. Noak and D. F. Williams, *J. Chem. Soc.*, (*A*), 148 (1967).

(30) It is not yet clear the exchange mechanism of $Co(CO)_3NO$ with ^{14}CO, which seems to be different from that of the first-order substitution (see [5,17] and work in progress in this lab. [31]).

(31) G. Reichenbach, G. Innorta and A. Foffani, unpublished results.

(32) F. I. Vilesov and V. M. Zaitsev, *Dokl. Akad. Nauk. SSSR*, *154*(4), 886 (1964).

available values of ionization potential for $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$,[32] which are resp. 7.36, 7.34 and 7.3 eV (from photoionization), *i.e.*, almost equal; since these ionization potentials are affected both by basicity and polarizability, the three ligands should show almost the same kinetic behaviour if the polarizability factor would play a relevant role on determining the nucleophilicity of these ligands (work is in progress in this lab. to evaluate by electron impact the ionization potentials of ligands of this kind, in order to better clarify the matter). Anyway, it remains the fact ([5] and references therein; see also [14b]) that for the same ligand donor atom, the rates be affected by substitution to this ligand atom in a parallel way by factors of polarizability and basicity.

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