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Kinetics of Disubstitution Reactions with the Substrate Ligands of Monosubstituted Derivatives of $Co(CO)_3NO$ [1]

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The disubstitution reaction $Co(NO)(CO)_2L + L = Co(CO)(NO)L_2 + CO$ has been investigated for a series of phosphine and phosphite ligands, in toluene solution up to about 65°C. Dissociative and associative reaction paths are generally competitive, their relative weights being strongly dependent on the properties of the ligand L.

Introduction

Known examples of kinetically studied disubstitution reactions with the substrate ligand of tetra- and penta-coordinated carbonyl complexes, are those of (a) $Mn(NO)(CO)_3L$,[2] (b) $C_5H_5Rh(CO)L$,[3] (c) $Co(NO)(CO)_2L$.[4]

The reaction mechanisms for cases (a) and (b) were sufficiently clarified, while for case (c) the available data did not allow elucidation of the reaction path; later, it was generally assumed[5] to be an associative one.

The absence of reliable data for the third reaction above mainly reflects the fact that the low reaction rates to be evaluated required the experiments to be carried out at temperatures (around 60°C) where the complexes might decompose to a large extent. Previous kinetic work in this laboratory[6-8] indicated that these complexes, when dissolved in sufficiently non-interacting solvents (*e.g.*, benzene or toluene) and with a low residual content of dissolved oxygen, are sufficiently stable for kinetic studies up to about 70°C.

Data are presently reported on the above disubstitution reaction (c) for a series of phosphine and phosphite ligands. The results suggest that the relative importance of the associative and dissociative paths involved in the reaction is determined by the properties of the ligand L, even when similar ligands are used.

Experimental Section

(a) *Materials.* The starting and final mono- and disubstituted cobalt complexes were prepared following literature methods.[9,10] The solid compounds were purified by crystallization from methanol solution and the liquids by column chromatography on Al_2O_3 and elution with a methylene chloride-pentane mixture, followed by vacuum evaporation of the solvent. The purity of each complex was checked throughout by analysis and spectra.

The $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ disubstituted cobalt complexes were prepared by treating the monosubstituted compounds with a slight excess of ligand, at a temperature slightly higher than the melting point of the ligand, in the absence of solvent. For $Co(NO)(CO)[P(C_6H_5)_3]_2$ at 80°C the reaction was complete in less than 10 hours and the product was washed with methanol and crystallized from n-buthanol. For $Co(NO)(CO)[As(C_6H_5)_3]_2$, working at 70°C with a ligand/complex ratio of 2:1 the reaction did not go to completion within ten days. A slight decomposition of the starting and/or final complexes was observed and the disubstituted complex was recovered from the reaction mixture, like the phosphorus derivative. For $Co(NO)(CO)[Sb(C_6H_5)_3]_2$, at 70°C and under the same conditions as above, the reaction was slower and was accompanied by an even greater extent of decomposition. In all three cases, working under vacuum reduced decomposition and, by CO evolution, shifted the equilibrium to disubstitution. For the three complexes, the melting points, analyses, νCO and νNO values (cm^{-1}, CCl_4 soln.) and λ_{max} values for the visible band (Å, cyclohexane soln.) were as follows (see also ref. 7): (a) $Co(NO)(CO)[P(C_6H_5)_3]_2$, m.p. 175-178°C, *anal.* found: C, 68.72 and H, 4.76% (theor. C, 69.32 and H, 4.72), νCO 1959, νNO 1714, λ_{max} 4380; (b) $Co(NO)(CO)[As(C_6H_5)_3]_2$, m.p. 128-130°C, *anal.* found: C, 59.23, H, 3.78, N, 2.00% (theor. C, 60.95, H, 4.15, N, 1.92), νCO 1960, νNO 1725, λ_{max} 4600; (c) $Co(NO)(CO)[Sb(C_6H_5)_3]_2$, m.p. 120°C, analysis not reported owing to impurities, νCO 1953, νNO 1725, λ_{max} 4580.

The ligands employed throughout were commercial products not further purified.

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(b) *Conditions of the kinetic work.* The kinetic runs were performed in toluene solution. The solvent (Erba reagent grade) was dried by distillation over sodium metal and de-aerated by prolonged flushing with nitrogen. A low content of residual oxygen in the solvent was necessary (see also above) to ensure sufficient stability of the complexes at the working temperatures. The absence of decomposition was checked by parallel runs without ligand, in the temperature range 50-70°C. The kinetic runs were performed in dark ampoules sealed under flushing nitrogen. The final products of the kinetics runs were identified by comparing their IR spectra with those of the separately prepared disubstituted complexes.

The concentration of the starting monosubstituted complexes was kept throughout around 2×10^{-2} moles/liter and that of the entering ligand was varied in the range $0.2\div1$ moles/liter. An extension of the kinetic work to lower ligand concentrations was prevented by the excessive slowness of the reactions and by the occurrence, under these conditions, of appreciable decomposition. In every case pseudo-first order conditions with respect to the entering ligand were used. For the evaluation of the thermal kinetic parameters reactions were carried out for every ligand (except $P[OCH(CH_3)_2]_3$) at two or more temperatures.

The kinetic runs were followed analytically with a Perkin-Elmer 337 IR spectrophotometer, using NaCl 0.1 mm cells. Whenever possible, both the disappearance of the CO and NO bands of the starting monosubstituted complex, and the appearance of the corresponding ones of the final disubstituted complex, were followed. In contrast to a previous study,[7] no difference was found here in the kinetic results obtained from the two sets of measurements. The high ligand concentrations employed and the fact that some ligands, particularly the phosphite, absorbed rather strongly in the carbonylic stretching region of the complexes studied, required the use of reference solutions containing the same ligand concentration as for the reacting solutions. The kinetic parameters were deduced from the experimental data as dscribed in ref. 6.

Results and Discussion

Tables I to III give the experimental kinetic results for the reactions $Co(NO)(CO)_2L+L=Co(NO)(CO)L_2+CO$ with $L = P(C_6H_5)_3$, $P(n\text{—}C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OC_4H_9)_3$ and $P[OCH(CH_3)_2]_3$; in Table IV dissociative first-order and associative second-order rate constants at different temperatures, and thermal parameters are collected. No reliable kinetic data could be obtained with $P(OC_6H_5)_3$, owing to the slowness of the reaction. For the same reason, and because the reactions were incomplete (see above), the disubstitution processes with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ could not be studied.

Table I shows for $P(C_6H_5)_3$ the invariance of the experimental first-order rate constant k_{Iobs} (see ref. 6) in the ligand concentration range considered. From Table II it is apparent, on the other hand that, for $P(n\text{—}C_4H_9)_3$, both k_{Iobs} and k_{IIobs} are functions of the ligand concentration. The first changes linearly with ligand concentration, as shown in Figure 1. The other limiting situation is found for the phosphites $P(OCH_3)_3$, $P(OC_2H_5)_3$ and $P(OC_4H_9)_3$, where the k_{IIobs} values are invariant and also rather similar in magnitude. A different behaviour is shown by the last phosphite examined, $P[OCH(CH_3)_2]_3$, for which k_{IIobs} is a function of ligand concentration and is in addition, about ten times smaller than the values found for the other phosphites.

Table I. Experimental pseudo first-order rate constants (k_{Iobs}) for the reaction $Co(CO)_2NOP(C_6H_5)_3+P(C_6H_5)_3 = Co(CO)(NO)\ [P(C_6H_5)_3]_2+CO$ at different temperatures.

Temp. °C	$10^2\times[C]$ [a] moles/liter	$10\times[L]$ [b] moles/liter	$10^6\times k_{Iobs}$ sec^{-1}
60.0	1.987	10.060	2.26
60.0	1.992	4.995	2.28
60.0	1.992	2.005	2.35
60.0	3.000	9.986	2.15
60.0	3.011	7.496	2.07
60.0	2.995	5.038	2.12
60.0	3.000	3.038	2.10
67.0	2.005	10.000	5.52
67.0	2.008	7.498	5.59
67.0	2.005	5.037	5.47
67.0	1.996	3.053	5.32

[a] [C] = complex concentration; [b] [L] = ligand concentration.

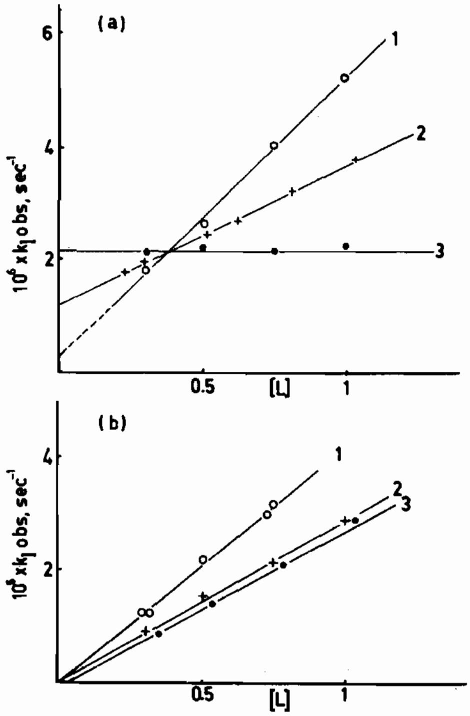

Figure 1. $k_{Iobs}/[L]$ plots for the reaction $Co(NO)(CO)_2$-$L+L = Co(NO)(CO)L_2+CO$ in toluene sol. at 60.0°C. (a), $L = P[OCH(CH_3)_2]_3$ (curve 1), $L = P(n\text{—}C_4H_9)_3$ (curve 2), $L = P(C_6H_5)_3$ (curve 3); (b), $L = P(OCH_3)_3$ (curve 1), $L = P(OC_4H_9)_3$ (curve 2), $L = P(OC_2H_5)_3$ (curve 3). $[L]=$ ligand conc. in moles/liter.

Table II. Experimental pseudo first-order (k_{Iobs}) and second-order (k_{IIobs}) rate constants for the reaction $Co(CO)_2NOP(nC_4H_9)_3 + P(n{-}C_4H_9) = Co(CO)(NO)[P(n{-}C_4H_9)_3]_2 + CO$ at different temperatures.

Temp. °C	$10^2 \times [C]$ [a] moles/liter	$10 \times [L]$ [b] moles/liter	$10^6 \times k_{Iobs}$ sec^{-1}	$10^6 \times k_{IIobs}$ l.mole^{-1} sec^{-1}
60.0	2.060	10.261	3.75	3.65
60.0	2.060	8.115	3.19	3.93
60.0	2.060	6.165	2.66	4.31
60.0	2.060	5.144	2.44	4.74
60.0	2.060	2.952	1.95	6.60
60.0	2.060	2.300	1.76	7.65
54.7	1.950	10.250	2.00	1.95
54.7	1.950	8.092	1.69	2.09
54.7	1.950	6.180	1.64	2.65
54.7	1.950	5.120	1.23	2.40
54.7	1.950	2.977	1.03	3.46
54.7	1.950	2.294	0.84	3.66

[a] [C] = complex concentration; [b] [L] = ligand concentration.

Table III. Experimental pseudo first-order (k_{Iobs}) and second-order (k_{IIobs}) rate constants for the reaction $Co(CO)_2NOL + L = Co(CO)(NO)L_2 + CO$ at different temperatures, for phosphite ligands

Ligand	Temp. °C	$10^2 \times [C]$ [a] moles/liter	$10 \times [L]$ [b] moles/liter	$10^6 \times k_{Iobs}$ sec^{-1}	$10^5 \times k_{IIobs}$ l.mole^{-1} sec^{-1}
$P(OCH_3)_3$	60.0	1.993	7.474	—	4.27
$P(OCH_3)_3$	60.0	1.510	7.230	—	4.04
$P(OCH_3)_3$	60.0	2.003	4.968	—	4.40
$P(OCH_3)_3$	60.0	1.908	3.131	—	3.87
$P(OCH_3)_3$	60.0	2.077	2.995	—	4.11
$P(OCH_3)_3$	55.0	1.975	9.998	—	2.74
$P(OCH_3)_3$	55.0	1.949	7.494	—	2.67
$P(OCH_3)_3$	55.0	1.961	5.000	—	2.64
$P(OCH_3)_3$	55.0	1.983	3.025	—	2.79
$P(OCH_3)_3$	50.0	1.890	10.020	—	1.73
$P(OCH_3)_3$	50.0	1.967	7.496	—	1.65
$P(OCH_3)_3$	50.0	1.978	4.985	—	1.89
$P(OCH_3)_3$	50.0	2.034	3.003	—	1.58
$P(OC_2H_5)_3$	60.0	1.966	10.370	—	2.78
$P(OC_2H_5)_3$	60.0	1.960	7.813	—	2.68
$P(OC_2H_5)_3$	60.0	2.081	5.323	—	2.55
$P(OC_2H_5)_3$	60.0	2.105	3.404	—	2.58
$P(OC_2H_5)_3$	55.0	2.067	10.961	—	1.93
$P(OC_2H_5)_3$	55.0	1.936	7.867	—	1.87
$P(OC_2H_5)_3$	55.0	2.122	9.998	—	1.98
$P(OC_2H_5)_3$	55.0	2.253	7.506	—	2.04
$P(OC_2H_5)_3$	50.0	1.995	10.381	—	1.20
$P(OC_2H_5)_3$	50.0	2.129	7.725	—	1.22
$P(OC_2H_5)_3$	50.0	2.170	5.005	—	1.20
$P(OC_2H_5)_3$	50.0	2.875	2.947	—	1.12
$P(OC_4H_9)_3$	60.0	1.957	10.015	—	2.90
$P(OC_4H_9)_3$	60.0	1.961	7.486	—	2.82
$P(OC_4H_9)_3$	60.0	2.010	5.004	—	3.10
$P(OC_4H_9)_3$	60.0	2.030	3.016	—	3.00
$P(OC_4H_9)_3$	55.0	2.000	10.190	—	2.26
$P(OC_4H_9)_3$	55.0	1.692	7.661	—	2.15
$P(OC_4H_9)_3$	55.0	1.948	9.984	—	2.14
$P(OC_4H_9)_3$	55.0	2.011	7.478	—	2.08
$P(OC_4H_9)_3$	50.0	1.970	10.018	—	1.48
$P(OC_4H_9)_3$	50.0	2.010	7.485	—	1.38
$P(OC_4H_9)_3$	50.0	2.012	5.018	—	1.53
$P(OC_4H_9)_3$	50.0	1.971	7.501	—	1.47
$P[OCH(CH_3)_2]_3$	60.0	2.390	9.976	5.00	0.50
$P[OCH(CH_3)_2]_3$	60.0	2.213	7.490	4.13	0.55
$P[OCH(CH_3)_2]_3$	60.0	2.163	5.049	2.74	0.54
$P[OCH(CH_3)_2]_3$	60.0	2.455	3.000	1.86	0.62
$P[OCH(CH_3)_2]_3$	60.0	1.961	9.981	5.38	0.54
$P[OCH(CH_3)_2]_3$	60.0	2.091	7.513	3.89	0.52
$P[OCH(CH_3)_2]_3$	60.0	1.990	5.003	2.46	0.49
$P[OCH(CH_3)_2]_3$	60.0	1.926	3.004	1.75	0.59

[a] [C] = complex concentration; [b] [L] = ligand concentration.

The results in Table I indicate that, for the ligand $P(C_6H_5)_3$, the disubstitution kinetics follow a dissociative path. This involves in its rate-determining step a metal-carbon bond rupture and a tricoordinated planar transition complex, which is in the best situation to stabilize the system of metal-ligand

Table IV. Dissociative (k_1) and associative (k') rate constants at different temperatures, and thermal parameters for the reaction $Co(CO)_2NOL + L = Co(CO)NOL_2 + CO$.

Ligand	Temp. °C	$10^6 \times k_1$ sec^{-1}	$10^5 \times k'$ l.mole^{-1} sec^{-1}	ΔE^* kcal/mole I ord.	ΔE^* kcal/mole II ord.	ΔS^* e.u. I ord.	ΔS^* e.u. II ord.
$P(C_6H_5)_3$	60.0	2.19	—	29.0		+1	
$P(C_6H_5)_3$	67.0	5.47	—				
$P(n\text{—}C_4H_9)_3$	60.0	1.20	0.25	36.0		+21	
$P(n\text{—}C_4H_9)_3$	54.7	0.5	0.15		20.0		—24
$P(OCH_3)_3$	60.0	—	4.14				
$P(OCH_3)_3$	55.0	—	2.71		19.5		—22
$P(OCH_3)_3$	50.0	—	1.71				
$P(OC_2H_5)_3$	60.0	—	2.59				
$P(OC_2H_5)_3$	55.0	—	1.95		17.5		—29
$P(OC_2H_5)_3$	50.0	—	1.18				
$P(OC_4H_9)_3$	60.0	—	2.95				
$P(OC_4H_9)_3$	55.0	—	2.16		15.0		—36
$P(OC_4H_9)_3$	50.0	—	1.46				
$P[OCH(CH_3)_2]_3$	60.0	0.45	0.53		—		—

π bonds.[11] The values of the energy and entropy of activation rule out, in this case, an associative intervention of the solvent in the transition complex.[5,6,12,13]

The above experimental evidence for the ligand $P(n\text{—}C_4H_9)_3$, as from Table II and Figure 1, suggests in this case a competitive participation in the overall kinetics of a dissociative and an associative path with the entering ligand. In the second instance the its trigonal bipyramidal structure, again well stabilizes,[14] the π-bond system. A similar situation has been encountered[6,12,15] for the monosubstitution reactions with the present and/or similar ligands on the substrate $Co(CO)_3NO$. As discussed in ref. 6, the plot shown in Figure 1 for $P(n\text{—}C_4H_9)_3$ gives both the k_1 and k' values (Table IV). The competitive occurrence of both reaction paths is also clearly supported by the typical values of the thermal parameters for the ligand concerned (see Table IV). On the other hand, the associative path with the enetering ligand is predominant for the three phosphite ligands $P(OCH_3)_3$, $P(OC_2H_5)_3$ and $P(OC_4H_9)_3$, as is apparent from Table III and from the plots of Figure 1, in which the intercepts on the k_{1obs} axis are zero within the limits of experimental uncertainty. The thermal parameters in these cases change remarkably with the ligand, as seen in Table IV. In particular, the decrease of activation energy in the order $P(OCH_3)_3 > P(OC_2H_5)_3 > P(OC_4H_9)_3$ apparently reflects the reverse order of π-bonding capacity of the ligands (see[16] and references therein), and should therefore correspond to an increased stabilization of the pentacoordinated transition complex.[14,15]

The rate constant values in Table III for the ligand $P[OCH(CH_3)_2]_3$ are somewhat less reproducible than for the other three phosphites. Within these limits of uncertainty, the non-zero intercept on the k_{1obs} axis (see Figure 1) should be significant. It points to an appreciable dissociative contribution to the overall kinetics, resembling the situation above reported for the $P(n\text{—}C_4H_9)_3$ ligand. Further possible support for the suggested mechanism from thermal parameters could not be obtained for this ligand.

The influence of the ligand L on the first- and present cases in a simple way. In fact, the ligand properties which are likely to be of importance in this regard, *i.e.*, basicity, polarizability, π-bonding capacity and steric requirement, play different and often opposing roles as far as the substrate or the entering ligand are concerned. It is therefore difficult, particularly for the associative path, to identify the separate effects of these different properties.

The order of reactivity for the associative path is $P(OCH_3)_3 > P(OC_4H_9)_3 > P(OC_2H_5)_3 > P[OCH(CH_3)_2]_3 > P(n\text{—}C_4H_9)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$. The ligand $P(OC_6H_5)_3$ is inserted tentatively in the series, in the absence of reliable kinetic information.

The rate constants with the phosphite ligands are about ten times higher than with the phospines, apart from $P[OCH(CH_3)_2]_3$ the reactivity of which approaches that of the phosphines. The high reactivity with the phosphites should reflect a synergic influence of substrate and as entering ligands; this influence weathe high π-bonding capacity of these ligands[16] both as ken the Co—C bonds and stabilize the pentacoordinated transition complex. The singular behaviour of the $P[OCH(CH_3)_2]_3$ ligand might arise from some kind of steric influence. The particularly low reactivity with the phosphite ligand $P(OC_6H_5)_3$ is contrary to its remarkable π-bonding capacity,[16] and could possibly reflect a prevailing influence of its low basicity.[6,15,17]

The higher reactivity of $P(C_6H_5)_3$ with respect to $P(n\text{—}C_4H_9)_3$ probably reflects the greater steric requi-

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rement of the first ligand, which is likely to affect negatively the reaction rate both as substrate and entering ligand. On the other hand, π-bonding capacity and basicity should be less important factors in this case, owing to the small difference in π-bonding capacity of the two ligands[16] and to the opposing influence of their basicity[18] on the rate when they are acting at the same time as substrate and entering ligand. The result is a reduced relative influence of these ligands on disubstitution, with respect to monosubstitution rates.[15]

The order of reactivity for the dissociative path is $P(C_6H_5)_3 > P(n-C_4H_9)_3 > P[OCH(CH_3)_2]_3 > P(OC_6H_5)_3$, again the last ligand being inserted tentatively.

Considering also the small dissociative reactivity shown by the three other phosphite substrate ligands examined, this order agrees (with the exception of the $P(OC_6H_5)_3$ ligand) with that generally effective for dissociative processes in octahedral complexes[19] and for dissociative disubstitution on substrates like $Mn(NO)(CO)_3L$[2] and $Ni(CO)_3L$.[20] On the other hand, the order is essentially that of the steric requirements of the ligands concerned.[19] It should therefore be inferred that the bulkiness of the substrate ligands is a main factor determining the rate of dissociative processes, even in the case of the less compact tetrahedral substrates.

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