Kinetic *trans* Effect of Phosphine Ligands in Anation Reactions of Aquocobaloximes

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Abstract

Both electronic and steric effects concur to determine the *trans* effect of the P ligands in the anation reactions of phosphino aquocobaloximes, electronic effects being prevailing.

The anation reactions and the pK_a values of these complexes vary in a rather restricted range with variation of the phosphine ligands.

A fairly linear relationship is observed between pK_a and log k_1, suggesting that the labilizing effect of the phosphine mainly acts through a weakening of the *trans* bond in the ground state.

Introduction

Most of the kinetic studies concerning the substitution reactions of the bis(dimethylglyoximato)-Co(III) complexes containing phosphine ligands concern the ligand exchange reactions in non-coordinating solvents

$$XCo(DH)_2L + L' \rightleftharpoons XCo(DH)_2L' + L \quad (1)$$

where the phosphine is the exchanging ligand [1]. These reactions proceed through a D mechanism and the dissociation rate is determined both by the basicity and by the steric size of the phosphine.

The importance of the steric bulk of the P ligands in determining their behavior as leaving groups is evident also in the anation reactions of the phosphino aquocobaloximes in water [2], where only complexes containing bulky P donor groups undergo phosphine dissociation in a slower step following water substitution.

Less information is available on the *trans* effect of the phosphine ligands in the bis(dimethylglyoximato)Co(III) complexes although they constitute an interesting class of non-labile ligands, because their electronic and steric properties may be systematically varied.

The solvolysis of $PR_3Co(DH)_2Cl$ in methanol (30%)/water [3]

$$PR_3Co(DH)_2Cl + H_2O \longrightarrow PR_3Co(DH)_2H_2O^+ + Cl^- \quad (2)$$

is about one order of magnitude faster than that of complexes containing N donor ligands and the dissociation rate decreases tenfold in the sequence

$$(n\text{-}C_4H_9)_3P > (C_2H_5)_3P > (C_6H_5)_2C_2H_5P > (C_6H_5)_3P$$

The solvolysis of $(c\text{-}C_6H_{11})_3P$ derivative was too fast to be measured by the technique used. It was suggested that the change in the reaction rates could be attributed mainly to changes in the inductive effect of the phosphine ligand and that steric effects were probably responsible for the high aquation rate of the $(c\text{-}C_6H_{11})_3P$ derivative.

In the present work we examine the anation reactions of a series of phosphino aquocobaloximes containing phosphine ligands with widely different electronic and steric properties in order to test the effect of these variations on the substitution rate.

Experimental

Materials

The phosphino aquocobaloximes were prepared as previously reported [4].

All other chemicals were analytical grade and used without further purification.

Equilibrium Measurements

The pK_a values relative to the deprotonation of the axial water

$$LCo(DH)_2H_2O^+ \rightleftharpoons LCo(DH)_2OH + H^+ \quad (3)$$

were determined by potentiometric titrations with NaOH in methanol(30%)/water at 25 °C.

The pK_a values were calculated by the relation

$$pH = pK_a + \log b/(a - b) \quad (4)$$

where a is the initial concentration of aquocomplex and b is the concentration of added base.

Kinetics

Solutions of $NaHSO_3$ were prepared by addition of HNO_3 to a solution containing an equivalent amount of analytical grade sulphite. The sulphite concentration was determined by titration with iodine. The solutions were prepared fresh each day.

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The solutions of NaN_3, NaI and thiourea (TU) were prepared from a known weight of reagents.

The pH was adjusted with HNO_3 at pH < 3.0, with acetate buffers in the range 5.0–7.0 and with phosphate buffers in the range 7.0–8.0.

Instruments

For pH measurements a pH meter Radiometer pH M4 was used.

The faster kinetics were followed with use of a Hi-Tech SF3 series stopped flow spectrophotometer. The slower kinetics were followed by a Perkin-Elmer Lambda 5 spectrophotometer.

Results

The anation reactions

$$LCo(DH)_2H_2O^+ + HSO_3^- \rightleftharpoons LCo(DH)_2SO_3^- + H_3O^+ \quad (5)$$

(L = $(n\text{-}C_4H_9)_3P$, $(C_2H_5)_3P$, $(C_2H_5)_2C_6H_5P$, $C_2H_5(C_6H_5)_2P$, $CH_3(C_6H_5)_2P$)

were studied in water solution, at I = 1 M ($NaNO_3$), t = 35 °C.

The kinetics were carried out under pseudo first order conditions, using a large excess of incoming ligand. The plots of $\log(A_t - A_\infty)$ *versus* time are linear and allow calculation of k_{obs}. For all these complexes k_{obs} show a linear dependence on $[HSO_3^-]$ in the range of examined concentrations

$$k_{obs} = k_1[HSO_3^-] + k_{-1} \quad (6)$$

The k_1 and k_{-1} values are reported in Table I.

The reactions were usually carried out at pH 4.0. The pK_a values reported in Table I indicate that at this pH value the complexes are present in solution as aquocomplexes, and the sulphito ligand is present almost entirely as HSO_3^- (pK_{a1} for H_2SO_3 is 1.89 and pK_{a2} is 7.21 [5]).

For L = $(C_2H_5)_3P$ the anation reactions with different ligands were also studied

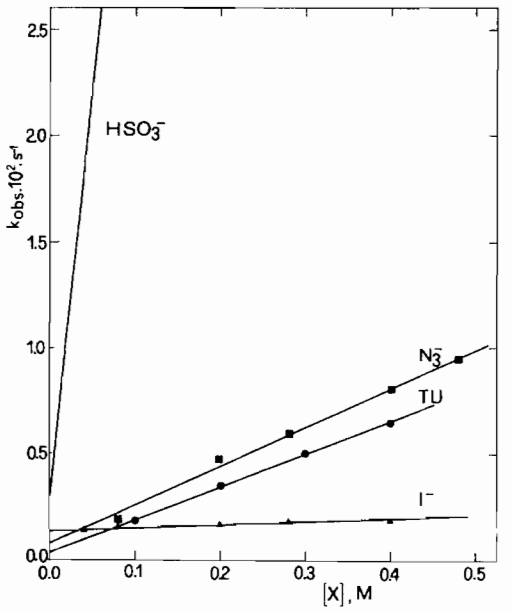

Fig. 1. Dependence of k_{obs} on [X] for the anation reactions of $(C_2H_5)_3P$–$Co(DH)_2H_2O^+$ at 35 °C, pH 4.0 and I = 1 M ($NaNO_3$).

$$(C_2H_5)_3P\text{–}Co(DH)_2H_2O^+ + X^{0,-} \rightleftharpoons (C_2H_5)_3P\text{–}Co(DH)_2X^{+,0} + H_2O \quad (7)$$

(X = N_3^-, I^-, $CS(NH_2)_2$)

in the same experimental conditions. The k_{obs} values obtained from the linear pseudo first order plots still show a linear dependence on [X], according to eqn. (6) (Fig. 1).

The k_1 and k_{-1} values are reported in Table II.

The reactions of $(C_2H_5)_3PCo(DH)_2H_2O^+$ with thiourea were examined in the pH range 0.6–8.3. The k_{obs} values were independent of $[H^+]$ until pH 7 (Fig. 2); above this pH value the reaction rate slows down owing to the formation of the hydroxo complex.

The same reaction was also examined at pH 4.0 at various temperatures (Table III).

TABLE I. Rate Constants for the Reaction of $LCo(DH)_2H_2O^+$ with HSO_3^-, pK_a Values of the Complexes and Physical Parameters for L

Compound	L	$\log k_1$	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	pK_a	$\Sigma\chi$[a]	pK_a(L)[b]	*TCA*[a]
A	$(c\text{-}C_6H_{11})_3P$	0.53	$(33.70 \pm 0.07)10^{-1}$ [c]		8.10 ± 0.03[c]	0.3	9.70	170
B	$(i\text{-}C_3H_7)_3P$	0.21	$(16.10 \pm 0.04)10^{-1}$ [c]	$(6.2 \pm 0.5)10^{-3}$ [c]	8.26 ± 0.01[c]	3.0		160
C	$(n\text{-}C_4H_9)_3P$	−0.23	$(5.87 \pm 0.08)10^{-1}$	$(1.4 \pm 1.4)10^{-3}$	8.30 ± 0.01	4.2	8.43	132
D	$(C_2H_5)_3P$	−0.41	$(3.92 \pm 0.11)10^{-1}$	$(3.0 \pm 2.1)10^{-3}$	8.32 ± 0.02	5.4	8.69	132
E	$(C_2H_5)_2C_6H_5P$	−0.48	$(3.29 \pm 0.09)10^{-1}$	$(2.9 \pm 1.2)10^{-3}$	8.12 ± 0.01	7.9	6.25	136
F	$(C_6H_5)_2C_2H_5P$	−0.56	$(2.76 \pm 0.07)10^{-1}$		7.94 ± 0.01	10.4		140
G	$(C_6H_5)_3P$	−0.84	$(1.44 \pm 0.03)10^{-1}$ [c]	$(4.1 \pm 0.9)10^{-3}$ [c]	7.53 ± 0.01[c]	12.9	2.73	170
H	$(C_6H_5)_2CH_3P$	−1.2	$(0.61 \pm 0.02)10^{-1}$	$(2.2 \pm 0.3)10^{-3}$	7.94 ± 0.02	11.2		136

[a]From ref. 14. [b]From ref. 15. [c]From ref. 2.

TABLE II. Rate Constants for the Anation Reactions of $(C_2H_5)_3P$–$Co(DH)_2H_2O^+$ [a]

X	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})
HSO_3^-	$(3.92 \pm 0.11)10^{-1}$	$(3.0 \pm 2.1)10^{-3}$
N_3^-	$(1.84 \pm 0.09)10^{-2}$	$(7.4 \pm 2.9)10^{-4}$
$CS(NH_2)_2$	$(1.53 \pm 0.05)10^{-2}$	$(3.5 \pm 1.4)10^{-4}$
I^-	$(1.39 \pm 0.06)10^{-3}$	$(1.5 \pm 0.1)10^{-4}$

[a]Conditions: at 35 °C, pH = 4 and I = 1 M ($NaNO_3$).

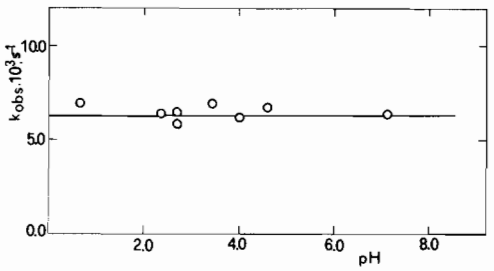

Fig. 2. Dependence of k_{obs} on pH for the reaction between $(C_2H_5)_3P$–$Co(DH)_2H_2O^+$ and thiourea at 35 °C and I = 1 M ($NaNO_3$).

TABLE III. Rate Constants and Activation Parameters for the Anation Reaction of $(C_2H_5)_3P$–$Co(DH)_2H_2O^+$ with $CS(NH_2)_2$ [a]

$k_1 \times 10^3$ (M^{-1} s^{-1})	t (°C)
1.57	14.0
1.55	14.2
2.55	17.6
6.47	25.0
9.97	29.0
16.2	35.0
29.5	41.1

$\Delta H^* = 19.1 \pm 0.3$ Kcal/mol
$\Delta S^* = -4.9 \pm 1.0$ e.u.

[a]Conditions: at pH 4.0 and I = 1 M ($NaNO_3$).

The activation parameters ΔH^* and ΔS^* were calculated by fitting the $k_1 - T$ data to the Eyring equation in the exponential form

$$k_1 = (kT/h) \exp(-\Delta H^*/RT) \exp(\Delta S^*/R) \quad (8)$$

by a non-linear least-squares analysis, each value of k_1 being weighted as $1/\sigma k_1^2$.

Discussion

It is well established that the substitution reactions of the cobaloximes proceed through a dissociative mechanism, so that the reaction rate is rather insensitive to the nature of the incoming ligand. In the present case the spread of the k_1 values with the variation of the entering group is somewhat larger than that for the organo– [6] or sulphito–aquocobaloximes [7]. A comparable variation has been previously found for the iodo– and nitro–aquocobaloxime [8].

As far as the lability of the aquocobaloximes containing a *trans* phosphine group towards the anation reactions is regarded, they are only a little more labile than the inert iodo– and nitro–aquo-complexes. The k_1 values for the reactions of the latter complexes with HSO_3^-, calculated at 35 °C on the basis of the activation parameters of ref. 8, are 2.8×10^{-2} M^{-1} s^{-1} for $X = NO_2^-$ and 1.01×10^{-2} M^{-1} s^{-1} for $X = I^-$; the corresponding values for the phosphino derivatives are reported in Table I.

The comparison of the k_1 values for the reaction with thiourea shows that the phosphino derivatives are considerably less reactive than $SO_3Co(DH)_2H_2O^-$ complex (k_1 at 25 °C is 8.34×10^{-1} M^{-1} s^{-1} for the sulphito complexes [7] and 6.47×10^{-3} M^{-1} s^{-1} for the triethylphosphinato complex).

All these results suggest that the phosphine ligands do not exert a large *trans* effect in the cobaloximes, and the trend of the *trans* labilizing ability appears to be $NO_2^- < PR_3 < SO_3^{2-} < R$.

The comparison of the ΔH^* and of the ΔS^* values obtained for the reactions with thiourea of the organoaquocobaloximes [9] and of $(C_2H_5)_3P$-$Co(DH)_2H_2O^+$ (Table III) evidences that the inertness of the latter compound is mainly due to the higher ΔH^* value, whereas the ΔS^* values, which are highly scattered, do not differ considerably.

The kinetic *trans* effect, as assessed by the k_1 values, strictly parallels the *trans* influence, as assessed by the pK_a values relative to the deprotonation of the axial water (6.87 for $X = I^-$ [10], 7.28 for $X = NO_2^-$ [10], 10.23 for $X = SO_3^{2-}$ [7]). Since the acidity of the axial water reflects the Co–O bond strength, this result clearly suggests that the *trans* group labilizes the water molecule by weakening the $Co-H_2O$ in the ground state.

Unfortunately, few $Co-H_2O$ distances are available, but the lengthening of the $Co-H_2O$ bond from 1.98 Å for $NO_2Co(DH)_2H_2O$ [11] to 2.055 Å for $CH_3Co(DH)_2H_2O$ [12] agrees with the above conclusion.

Obviously, the variation of the electron donor properties in going from $NO_2Co(DH)_2H_2O$ to CH_3-$Co(DH)_2H_2O$ is so overwhelming that steric effects, if present, cannot be easily detected.

When the electronic and the steric properties of the group *trans* to the aquo ligand are more systematically varied along a series, as for the organocobaloximes [13], the relevance of the steric effects becomes immediately apparent.

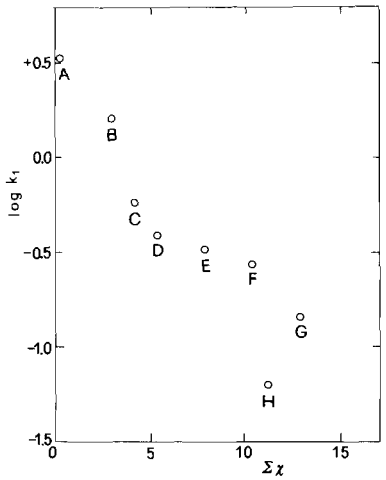

Fig. 3. Plot of log k_1 *vs.* Tolman's $\Sigma\chi$ for the reaction LCo-$(DH)_2H_2O^+$ + HSO_3^- ⇌ $LCo(DH)_2SO_3^-$ + H_3O^+. Letters correspond to complexes as given in Table I.

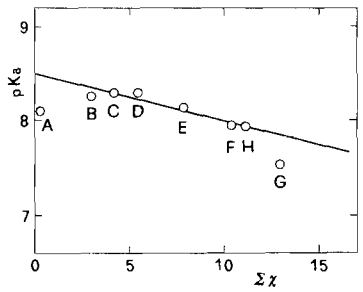

Fig. 4. Plot of pK_a of $LCo(DH)_2H_2O^+$ *vs.* Tolman's $\Sigma\chi$. Letters correspond to complexes as given in Table I.

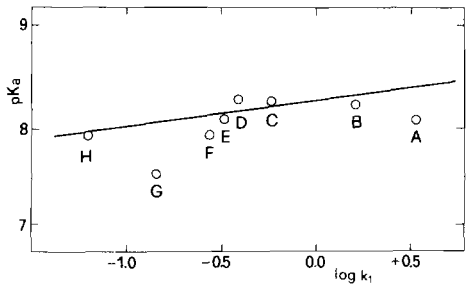

Fig. 5. Plot of pK_a of $LCo(DH)_2H_2O^+$ *vs.* log k_1 for the reactions with HSO_3^-. Letters correspond to complexes as given in Table I.

For the phosphino derivatives a qualitatively good relationship is observed between the k_1 rate constants and the Tolman's $\Sigma\chi$ values [14] (Fig. 3) or the pK_a of the phosphine [15], when available (Table I). Both these parameters reflect the electronic properties of the P donor ligand. No correlation is found between k_1 and the ligand bulk, as assessed using Tolman's cone angle (*TCA*) [14]. This seems to indicate that the lability trend along this series is still determined by electronic effects, although steric effects cannot be neglected.

Steric effects may account for the apparently anomalous rate sequence

$$(C_6H_5)_2C_2H_5 > (C_6H_5)_3P > (C_6H_5)_2CH_3P$$

The substitution of a phenyl group with an ethyl group enhances the lability, as the accelerating effect of the increase of the σ donor power prevails on the decelerating effect of the reduction of the steric bulk. The lower increase of the σ donor power and the further reduction of bulkiness arising from the substitution of a phenyl group with a methyl group leads to the opposite result, and the reaction of the $(C_6H_5)_2CH_3P$ complex is slower than that of the $(C_6H_5)_3P$ complex.

Steric effects may also account for the relatively high lability of $(c\text{-}C_6H_{11})_3P$ and $(i\text{-}C_3H_7)_3P$ derivatives. In fact only for these complexes both steric and electronic effects concur to accelerate the reactions, whereas in all the other cases a good donor power corresponds to a reduced steric bulk, so that a compensating effect results.

On the whole, reaction rates vary in a rather restricted range with variation of the phosphine ligand. This result may be only partially attributed to the just discussed compensating effect, since ligands with similar *TCA* but widely different electronic properties, such as $(i\text{-}C_3H_7)_3P$ and $(C_6H_5)_3P$, show only a tenfold variation in reaction rates.

It should be noted also that the pK_a values relative to the deprotonation of the axial water are not very sensitive to the variation of the phosphine ligand. In fact, a good correlation exists between the pK_a of the complexes and the Tolman's $\Sigma\chi$ values (Fig. 4) or the pK_a of the free phosphine, but the obtained slope of the latter plot (not shown) is about 0.1, whereas in the analogous plot for $X\text{–}C_5H_4NCo(DH)_2H_2O^+$ complexes a slope of 0.2 was obtained [1].

A fairly linear relationship is observed between log k_1 and pK_a relative to the deprotonation of the axial water in the phosphine aquocobaloximes, with the only remarkable exception of the $(C_6H_5)_3PCo(DH)_2H_2O^+$ and, in a lesser degree, of $(c\text{-}C_6H_{11})_3PCo(DH)_2H_2O^+$ (Fig. 5). For the latter compound, however, the determination of the pK_a is rather uncertain [2]. Hence the increase of lability for the phosphino derivatives generally parallels the weakening of the Co–O bond in the ground state, but the relatively high lability of $(C_6H_5)_3PCo(DH)_2H_2O^+$, arising from steric effects, cannot be explained in this way and should be a transition state effect, likely related to a higher degree of relief of steric strain. This hypothesis is supported by structural data, which show that when L is a bulky P donor ligand, as in this case, the displacement of the Co

out of the plane of the four nitrogen equatorial donors towards the phosphorous ligand and the bending angle between the two (DH) units away from it are the largest observed in the cobaloximes [1].

Structural data relative to the bond lengths between the cobalt atom and the ligand *trans* to the phosphine group do not confirm the hypothesis that the labilizing effect of the phosphine mainly acts through a weakening of the *trans* bond in the ground state. The Co–Cl and the Co–CH_3 distances do not vary greatly as the phosphine ligand varies (CoCl bond length is 2.294 Å for $(n\text{-}C_4H_9)_3P$ and $(c\text{-}C_6H_{11})_3P$ and 2.277 Å for $(C_6H_5)_3P$ [1]). No structural data relative to the Co–OH_2 bond in phosphino derivatives are available, but a very similar behavior should be expected. However it should be noted that to a variation in anation rate of about 10^5 times in going from NO_2–$Co(DH)_2H_2O$ to CH_3–$Co(DH)_2H_2O$ corresponds a lengthening of the Co–OH_2 bond of 0.075 Å [1] and to a variation of about 10^2 times in the anation rates from CH_3– to $i\text{-}C_3H_7$–$Co(DH)_2H_2O$ corresponds a lengthening of the Co–N bond in the corresponding pyridinato derivatives of 0.031 Å [1]. Hence the 6 fold variation in lability from $(c\text{-}C_6H_{11})P$- to $(n\text{-}C_4H_9)_3$-$PCo(DH)_2H_2O^+$ may be too tenuous to reflect in a lengthening of the Co–Cl bond.

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