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Kinetics and Mechanism of the Anation Reactions of Aquocobaloximes Containing Bulky Phosphine Ligands

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Abstract

The anation reactions of phosphino–aquocobaloximes containing bulky P donor ligands with HSO_3^- lead through a multistep mechanism to the formation of $SO_3Co(DH)_2SO_3^{3-}$; the first step leads to the water substitution. The successive steps involve the hydrolysis of the phosphine and the ligation of HSO_3^-, the dissociation of phosphine being the rate determining step.

The steric bulk of the P ligand appears to be the factor determining the phosphine lability.

Introduction

The kinetics of the water substitution reactions of the organoaquocobaloximes have been exhaustively studied [1]. Less attention has been paid to the anation reactions of the non-organometallic cobaloximes, but detailed kinetic studies have been reported for the iodo– and nitro– [2] and for the sulphito–aquocobaloximes [3].

For all these complexes only the water substitution occurs, even if the incoming ligand has a higher *trans* effect and a higher *trans* influence than the non-labile group, as in the reaction of nitro–aquocobaloxime with HSO_3^- [2].

An indication that the substitution of the ligand *trans* to the water molecule may occur in a successive step arises from a preparative work, in which it was demonstrated that addition of an excess of phosphine to chloro–aquocobaloxime leads to the formation of the 1:1 electrolyte $PR_3Co(DH)_2PR_3^+$-$ClCo(DH)_2Cl^-$ [4].

In the present work we report a kinetic study of the anation reactions of some phosphino–aquocobaloximes containing bulky P ligands, which in the presence of an excess of incoming ligand undergo phosphine substitution.

Experimental

The $(c\text{-}C_6H_{11})_3P$–, $(i\text{-}C_3H_7)_3P$– and $(C_6H_5)_3P$–$Co(DH)_2H_2O^+NO_3^-$ complexes were prepared as previously reported [4].

Solutions of $NaHSO_3$ were prepared by addition of HNO_3 to a solution containing an equivalent amount of analytical grade Na_2SO_3. The sulphite concentration was determined by titration with iodine. The solutions were prepared fresh each day. Thiourea solutions were prepared from a known weight of reagent. Generally 1×10^{-4} M solutions of complexes were used.

The pH was maintained with acetic acid/sodium acetate buffers in the range 3.0–5.0 and with HNO_3 at pH lower than 3. For pH measurements a pH-meter Radiometer pH M4 was used.

The slower kinetic runs were performed by a Perkin-Elmer Lambda 5 UV visible spectrophotometer; the faster kinetic runs were followed by a Hi-Tech SF 3 series stopped flow apparatus.

Results

Equilibrium Studies

The ionization constants of the phosphino–aquo complexes $(LCo(DH)_2H_2O^+$, where $L = (c\text{-}C_6H_{11})_3P$, $(i\text{-}C_3H_7)_3P$, $(C_6H_5)_3P)$, were determined by potentiometric titration with NaOH in methanol (30%)–water at 25 °C. The pK_a values were calculated by the relation

$$pH = pK_a + \log b/(a - b) \quad (1)$$

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

Both $(c\text{-}C_6H_{11})_3P$– and $(C_6H_5)_3P$–$Co(DH)_2H_2O^+$ easily lose the phosphine in basic solution. In order to obtain a sufficient accuracy the titrations were performed as fast as possible. Furthermore for $(c\text{-}C_6H_{11})_3PCo(DH)_2H_2O^+$ the pK_a was calculated from the first points of the titration curve (in the acid range). The pK_a values are reported in Table I.

Kinetic Results

The reactions between $LCo(DH)_2H_2O^+$ complexes and HSO_3^- were studied at 35 °C, $I = 1$ M ($NaNO_3$) in the pH range 3.0–5.0. In this pH range, the complexes are present in solutions as aquocomplexes.

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

L	X	$a = k_1$ (M^{-1} s^{-1})	$b = k_{-1}$ (s^{-1})	$c = k_2$ (s^{-1})	pK_a	*TCA*[c]	$\Sigma\chi$[c]	$pK_a(L)$[d]
$(c\text{-}C_6H_{11})_3P$	HSO_3^-	3.37 ± 0.07		$(2.03 \pm 0.05)10^{-3}$	8.10 ± 0.03	170	0.3	9.70
$(i\text{-}C_3H_7)_3P$	HSO_3^-	1.61 ± 0.04	$(6.2 \pm 0.5)10^{-3}$	$(1.31 \pm 0.04)10^{-3}$	8.26 ± 0.01	160	3.0	
$(C_6H_5)_3P$	HSO_3^-	$(1.44 \pm 0.03)10^{-1}$	$(4.1 \pm 0.9)10^{-3}$	$(1.38 \pm 0.12)10^{-3}$	7.53 ± 0.01	170	12.9	2.73
	$CS(NH_2)_2$	$(5.21 \pm 0.15)10^{-3}$ [a]	$(1.7 \pm 0.4)10^{-4}$ [a]					
		$(5.47 \pm 0.52)10^{-3}$ [b]	$(1.8 \pm 0.2)10^{-4}$ [b]					

[a] Value determined at pH 1.7. [b] Value determined at pH 4.0. [c] From ref. 9. [d] From ref. 10.

The reactions were carried out under pseudo first order conditions, in presence of a large excess of HSO_3^-. The free HSO_3^- concentration was calculated using a value of 1.89 for the pK_a relative to the first ionization of H_2SO_3 [5]. The second ionization (pK_a = 7.21 [5]) is negligible at the examined pH values. It was assumed that only HSO_3^- and not H_2SO_3 was the associating form of the ligand.

Two consecutive well separated reactions were observed. The pseudo first order rate constants relative to the faster reactions, $k_{obs}(I)$, were obtained from the linear plots of log $(A_t - A_\infty)$ *versus* time and show a linear dependence on $[HSO_3^-]$ in the range of examined concentrations (Fig. 1)

$$k_{obs}(I) = a[HSO_3^-] + b \qquad (2)$$

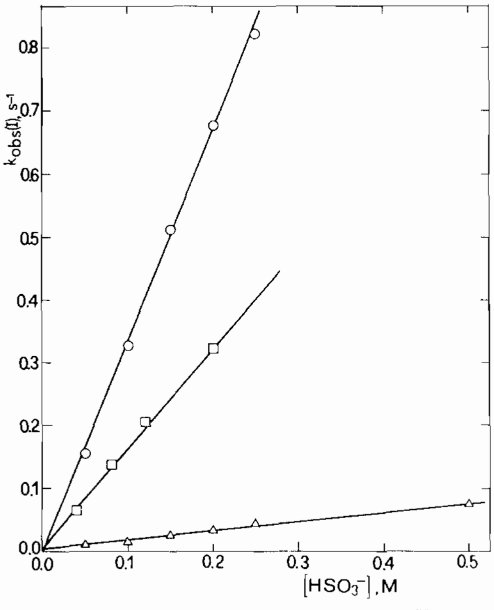

Fig. 1. Dependence of $k_{obs}(I)$ on $[HSO_3^-]$ for L = $(c\text{-}C_6H_{11})_3P$ (○), $(i\text{-}C_3H_7)_3P$ (□) and $(C_6H_5)_3P$ (△).

The *a* and *b* values are collected in Table I. The $k_{obs}(I)$ values are independent of pH in the examined pH range. The final spectra of the faster reaction could not be obtained for L = $(c\text{-}C_6H_{11})_3P$ and $(i\text{-}C_3H_7)_3P$, because the reactions, followed by stopped flow technique, are too fast, so that during the running of the spectrum the second reaction starts. For L = $(C_6H_5)_3P$ the UV–Vis spectrum shows a maximum at 350 nm.

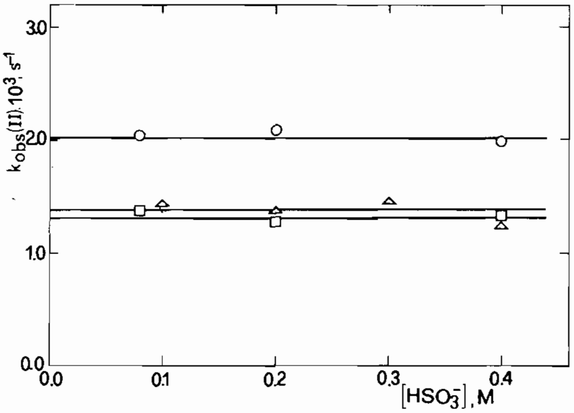

Fig. 2. Dependence of $k_{obs}(II)$ on $[HSO_3^-]$ for L = $(c\text{-}C_6H_{11})_3P$ (○), $(i\text{-}C_3H_7)_3P$ (□) and $(C_8H_5)_3P$ (△).

The $k_{obs}(II)$ values, relative to the slower reactions, are also obtained from the linear plots of log $(A_t - A_\infty)$ *versus* time and results are independent of both $[HSO_3^-]$ (Fig. 2) and $[H^+]$.

$$k_{obs}(II) = c \qquad (3)$$

The *c* values are collected in Table I. Good isosbestic points are observed during the second reactions, at 334 nm for $(c\text{-}C_6H_{11})_3P$ and $(i\text{-}C_3H_7)_3P$ derivatives and at 350 nm for the $(C_6H_5)_3P$ derivative. The final spectrum, showing a maximum at 348 nm, is the same for all the examined complexes and is independent of pH in the examined pH range.

In an attempt to isolate the reaction products, a solution of $(C_6H_5)_3PCo(DH)_2H_2O^+$ in methanol was reacted with HSO_3^- in water in the ratio 1:1; the isolated product was $SO_3Co(DH)_2H_2O^-Na^+ \cdot 2H_2O$ (Calc.: C, 21.5, H, 4.5; N, 12.5. Found: C, 21.4; H, 4.5; N, 11.7%).

For L = $(C_6H_5)_3P$ the reaction with thiourea was also examined in the pH range 1.7–5.0. At low pH values ($\leqslant$3.0) only one reaction is observed. The k_{obs}(I) values for this reaction, obtained at pH 1.7, are linearly dependent on [$CS(NH_2)_2$] according to eqn. (2). The *a* and *b* values are reported in Table I. At higher pH values two sufficiently well separated reactions are observed and the second reaction becomes faster as pH increases.

The faster reaction, which shows a spectral variation analogous to that of the reaction at pH 1.7, can be easily followed at 354 nm, where the product of the first reaction shows a maximum and the second reaction an isosbestic point. The k_{obs}(I) values obtained at pH 4.0 are still linearly dependent on [$Cs(NH_2)_2$] according to eqn. (2). Comparison of the *a* and *b* values obtained at pH 1.7 and 4.0 (Table I) demonstrates that the first reaction is independent of pH.

A kinetic study of the second reaction is hindered by the low solubility in water of the reaction products; however the spectral variations are very similar to that observed for the slower reaction with HSO_3^- and good isosbestic points are observed until precipitation begins. The final spectrum shows a maximum at 340 nm.

The low solubility allowed us to isolate the product of the faster reaction by reacting $(C_6H_5)_3PCo(DH)_2H_2O^+$ with a tenfold excess of thiourea in methanol (50%)/water at [H^+] = 0.05 M (HNO_3). The resulting product was $(C_6H_5)_3PCo(DH)_2CS(NH_2)_2NO_3^-\cdot H_2O$(Calc.: C, 45.8; H, 4.9; N, 13.8. Found: C, 45.4; H, 4.9; N, 13.3%). If the reaction is carried out in the same experimental conditions, but without adding HNO_3, the isolated product is $CS(NH_2)_2Co(DH)_2CS(NH_2)_2^+NO_3^-$ (Calc.: C, 23.8; H, 4.4; N, 25.0. Found: C, 23.2; H, 4.5; N, 22.5%). The same product can be directly recovered from the solutions used in the kinetic runs (C, 24.1; H, 4.1; N, 22.0%).

Discussion

On the basis of the above kinetic results the following reaction scheme can be proposed

$$L(DH)_2H_2O + X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} LCo(DH)_2X + H_2O \qquad \text{(Step 1)}$$

$$LCo(DH)_2X \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} XCo(DH)_2H_2O + L \qquad \text{(Step 2)}$$

$$XCo(DH)_2H_2O + X \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} XCo(DH)_2X + H_2O \text{ (Step 3)}$$

If the first step is so fast that it does not overlap with successive steps, k_{obs}(I) becomes

$$k_{obs}(I) = k_1[X] + k_{-1} \qquad (4)$$

This actually occurs for the examined complexes, so that by comparison with eqn. (2) the result, both for X = HSO_3^- and X = thiourea, is

$$a = k_1$$

$$b = k_{-1} \qquad (5)$$

The *trans* effect of the P ligands in the anation reactions of the phosphino aquo derivatives using a more complete series of phosphines will be discussed in a following paper.

As far as the slower reaction with HSO_3^- is concerned, the presence of good isosbestic points ensures that only two absorbing species are present in solution. One of these is the product of the faster reaction, $PR_3Co(DH)_2SO_3^-$; the other, as demonstrated by comparison of the final spectra with that of an authentic sample, is $SO_3Co(DH)_2SO_3^{3-}$. Therefore, the intermediate $SO_3Co(DH)_2H_2O^-$ never accumulates in solution. If the steady state approximation is applied to $SO_3Co(DH)_2H_2O^-$ and if the reverse reaction of step 3 is neglected (at the used concentration of incoming ligand this reaction proceeds to completion [3]), k_{obs}(II) becomes

$$k_{obs}(II) = k_2k_3[X]/\{k_3[X] + k_{-2}[L]\} \qquad (6)$$

If $k_3[X] \gg k_{-2}[L]$, k_{obs}(II) becomes

$$k_{obs}(II) = k_2 \qquad (7)$$

In this case, the kinetics are of first order and the reaction rate is independent of [X], as was actually found.

An indirect proof of the validity of the assumption $k_3[X] \gg k_{-2}[L]$ in this case arises from consideration of the anation reactions of $SO_3Co(DH)_2H_2O^-$ with various ligands. The reactions rate constants for the examined nucleophiles vary in a very restricted range (from 1.45 M^{-1} s^{-1} for $S_2O_3^{2-}$ to 8.43 M^{-1} s^{-1} for thiourea), according to the dissociative activation process. Thus it is probable that k_3 and k_{-2} have comparable values. In this hypothesis $k_3[X] \gg k_{-2}[L]$, because HSO_3^- is present in solution in large excess (0.1–0.5 M) whereas L reaches a concentration of about 10^{-4} M at the end of the reaction.

Furthermore the condition $k_3[X] \gg k_{-2}[L]$ is always satisfied when L = $(c\text{-}C_6H_{11})_3P$ or $(i\text{-}C_3H_7)_3P$ because in the pH range 3.0–5.0 protonation of free phosphine makes the reverse reaction of step 2 negligible.

From comparison of eqn. (3) with eqn. (7) it follows

$$c = k_2 \qquad (8)$$

Obviously an expression of k_{obs}(II) formally analogous is obtained if the steady state intermediate is the pentacoordinated species $SO_3Co(DH)_2^-$. In the ligand exchange reactions of the organocobaloximes

$$XCo(DH)_2L + L' \rightleftarrows XCo(DH)_2L' + L \qquad (9)$$

in non-coordinating solvent, the formation of five coordinated species is well established [6], but this hypothesis does not seem very probable in water and in the presence of an X group having a lower *trans* effect.

The fact that $SO_3Co(DH)_2H_2O^-Na^+\cdot 2H_2O$ was isolated by reacting $(C_6H_5)_3PCo(DH)_2H_2O^+$ and HSO_3^- in a 1:1 ratio and the small variation of *c* with the nature of the phosphine ligand could suggest that the faster reaction corresponds to step 1 and 2, step 1 being the rate determining step. In this hypothesis, if $LCo(DH)_2SO_3^-$ is a steady state intermediate and the reverse reaction of step 2 is neglected, k_{obs}(I) becomes

$$k_{obs}(I) = k_1 k_2 [X] \{k_{-1} + k_2\} \qquad (10)$$

which still agrees with eqn. (2), the *b* values being in the limits of experimental errors.

A comparison of the final spectra of the faster reaction for the various complexes, which should be identical in this hypothesis, cannot be made (see 'Results'). However, in this case, the second reaction should correspond to the anation of the sulphito derivative

$$SO_3Co(DH)_2H_2O^- + HSO_3^- \longrightarrow SO_3Co(DH)_2SO_3^{3-} + H_3O^+ \qquad (11)$$

which has previously been studied. The k_{obs} values for this reaction show a linear dependence on $[HSO_3^-]$ until 0.5 M [3], whereas the k_{obs}(II) values are independent of it and are much lower than the values found for the anation of the sulphito complex. Furthermore in this hypothesis the spectral variations during step 3 should be identical for all the examined complexes, which does not occur.

The precipitation of $SO_3Co(DH)_2H_2O^-Na^+\cdot 2H_2O$ from the water/methanol solution when the reagents are in a 1:1 ratio may be accounted for if step 1 is so fast that formation of $(C_6H_5)_3PCo(DH)_2SO_3^-$ is practically complete before dissociation of $(C_6H_5)_3P$ reaches a considerable extent, so that no free HSO_3^- is available in solution to form $SO_3Co(DH)_2SO_3^{3-}$.

As pointed out in 'Results', quantitative data cannot be obtained for the slower reaction when thiourea was the incoming ligand, owing to the insolubility of the products in water. The close similarity between the spectral variations involved in the slower reaction with thiourea at $pH > 3$ and those of the slower reaction with HSO_3^-, and the fact that, at these pH values $CS(NH_2)_2Co(DH)_2CS(NH_2)_2^+NO_3^-$ was recovered from the reacted solutions, lead to the conclusion that steps 1–3 account also for the reactions with thiourea.

As already outlined, the second reaction is not observed when $(C_6H_5)_3PCo(DH)_2H_2O^+$ reacts with thiourea at $pH < 3.0$, and at these pH values $(C_6H_5)_3PCo(DH)_2CS(NH_2)_2^+NO_3^-$ could be isolated in the presence of a large excess of thiourea. The qualitatively observed increase in the rate of the second reaction with increasing pH, might be explained if dissociation of $(C_6H_5)_3P$ from $(C_6H_5)_3PCo(DH)_2CS(NH_2)_2^+$ occurs through a S_NCB mechanism. The pK_a values relative to the proton dissociation from the equatorial ligand are generally high for organocobaloximes (about 12–13 [7]), but they decrease considerably when the axial ligands become poorer electron donors [8], and show a further decrease in cobaloximes containing two neutral axial ligands (about 7.0–8.0 [8]), probably owing to the resulting positive charge of the complex. Therefore the pK_a relative to the dissociation of the equatorial proton from $(C_6H_5)_3PCo(DH)_2CS(NH_2)_2^+$ could be sufficiently low that small quantitites of the highly reactive equatorially deprotonated form could be present in solution even at relatively low pH values.

The common feature of the complexes examined in the present work is the bulkiness of the phosphine ligands, evidenced by the high Tolman's Cone Angle (TCA) [9], whereas the electronic properties, as assessed by the Tolman's $\Sigma\chi$ [9] or by pK_a of the free phosphine [10], are very different (Table I). Preliminary results evidence that aquocobaloximes containing smaller phosphine groups ($L = (C_6H_5)_2C_2H_5P$, $(C_2H_5)_3P$; for these ligands *TCA* values are 140 and 132, respectively [9]) do not undergo phosphine substitution after the anation reaction with HSO_3^-. Hence the steric bulk of PR_3 is the main factor which determines whether for a given *trans* ligand, phosphine substitution occurs or not.

Structural data show that a lengthening of the Co–P bond is observed with increasing the size of the phosphine (for example, the Co–P bond length in $ClCo(DH)_2PR_3$ is 2.369 Å for $PR_3 = (c\text{-}C_6H_{11})_3P$ and 2.265 Å for $PR_3 = (n\text{-}C_4H_9)_3P$ [11]), so that the lability of the phosphine ligand may be directly related to the Co–P bond length in the ground state.

In general, for $XCo(DH)_2L$ complexes the dissociation rate of L, for a given X group, increases with increasing steric size of L and with decreasing its electron donor power [1]. For $SO_3Co(DH)_2L^-$ the importance of steric effects has been outlined above; the influence of the electron donor properties of the leaving group is more difficult to evaluate. A suggestion that electronic effects also contribute to determining the lability of the phosphine might arise from consideration of the relatively high dissociation rate of $(C_6H_5)_3P$. For this complex the low basicity of the phosphine could compensate for the reduction of the steric bulk.

Finally, it should be noted that $(C_6H_5)_2C_2H_5P$ dissociates from $CH_3Co(DH)_2PC_2H_5(C_6H_5)_2$ in CH_2Cl_2, although at a rate considerably slower than that of $(c\text{-}C_6H_{11})_3P$, $(i\text{-}C_3H_7)_3P$ and $(C_6H_5)_3P$ [1], whereas in the present case it does not dissociate at all. The different behavior is probably due to the weakening of the Co–P bond in the organometallic complex, owing to the higher electron donor power of the CH_3 group relative to the SO_3^{2-} group.

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