The Kinetics of the Rapid Reactions of the Cobalt(II)–Triethylenetetramine System with Oxygen

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Abstract: The spectra of anaerobic solutions of the (1:1) cobalt(II)–trien complex have been measured in aqueous solution from pH 7.5 to 12.6. The (reversible) change from a pink to a striking grape-colored solution in the more basic media is ascribed to the transformation of $Co(trien)(H_2O)_2^{2+}$ (**1A**), ϵ_{484}^{max} 8.0, ϵ_{460}^{sh} 6.6, into a monohydroxylated species (**1B**), ϵ_{545}^{max} 30.2 and ϵ_{510}^{sh} 25.0. For this process K_1 = [**1B**][H$^+$]/[**1A**] = 6.3×10^{-12} *M* at 25°. Reaction of basic solutions of these species with molecular O_2 (I = 0.2 *M*) occurs in *two stages* which can be characterized as: (1) second-order reaction of **1A** (k_{1A}) and **1B** (k_{1B}) with O_2 to give intermediates **2A** and **2B**, which are believed to be single bridged species $(trien)Co(H_2O)O_2Co(trien)(OH)^{3+}$ and $(trien)Co(OH)O_2Co(trien)(OH)^{2+}$, respectively. (2) These bridged species then undergo first-order transformation to the dibridged species **3**, $(trien)Co(O_2,OH)Co(trien)^{3+}$, the product at all pH's. These structures are assigned on the basis of the extent and rate of pH changes accompanying these stages, and by determining the point at which O_2 uptake is completed. For reaction 1, d/dt ([**2A**] + [**2B**]) = $(k_{1A}[H^+] + k_{1B}K_1)([H^+] + K_1)^{-1}$([**1A**] + [**1B**])[$O_2$] where $k_{1A} = 2.5 \times 10^4\ M^{-1}\ sec^{-1}$ at 25°, $\Delta H_{1A}^* = 7.1$ kcal mol^{-1}, and $\Delta S_{1A}^* = -15$ eu; and $k_{1B} = 2.8 \times 10^5\ M^{-1}\ sec^{-1}$ at 25°, $\Delta H_{1B}^* = 7.9$ kcal mol^{-1}, and $\Delta S_{1B}^* = -7$ eu. For stage 2, d/dt (**3**) = $(k_{2A}[H^+] + k_{2B}K_2)([H^+] + K_2)^{-1}$([**2A**] + [**2B**]) with $k_{2A} = 2.0\ sec^{-1}$ at 25°, $\Delta H_{2A}^* = 11.0$ kcal mol^{-1}, and $\Delta S_{2A}^* = -21$ eu, $k_{2B} \approx 0.012\ sec^{-1}$ at 25°, and K_2 = [**2B**]·[H$^+$]/[**2A**] = 1.2×10^{-11} *M* at 25°.

We have previously examined the ability of cobalt(II) complexes with ammonia[1] and a variety of polyamine ligands[2] to take up molecular oxygen in aqueous solution and have investigated the mechanistic aspects of this process. With certain complexes, it was observed that the rapid oxygenation process was followed by an only slightly slower reaction.[2] The rate of this slower change was qualitatively insensitive to metal, ligand, and (over a narrow pH range) hydroxide concentrations. It thus appeared to be an interesting intramolecular change in which the O_2 bridge, a structural feature of oxygenated products, was retained, but in which perhaps a second bridge was formed between the two cobalt centers. Work being carried out at the same time as ours[3,4] indicated, from pH changes, that the product of the O_2 reaction with certain cobalt(II) complexes was a dibridged (O_2, OH) species.

In order to study these processes in more detail, we chose to examine the reaction of O_2 with the cobalt complex of 1,4,7,10-tetraazadecane (triethylenetetramine, trien). The use of a tetradentate ligand would avoid the multiplicity of species present with complexes of simpler ligands, and thus facilitate the interpretation of results. In addition, Fallab has investigated the uptake of O_2 by the cobalt(II)–trien system and showed in solution that there is a 2 Co:2 trien:1 O_2 brown product which could be made to give up its oxygen completely by acidifying to pH ~2.[5] Further work[3] indicated that the brown product was a dibridged species containing the $(trien)Co(O_2,OH)Co(trien)^{3+}$ ion. We have therefore examined (spectrally) the cobalt(II)–trien system in the absence of O_2 and then studied the kinetics of O_2 uptake by this system over a wide pH range, where two processes are easily discerned.

Experimental Section

Materials. All chemicals used were reagent grade; trien (Fisher) was used as the recrystallized tetrahydrochloride salt, which had a satisfactory chloride content. Solutions of cobalt(II) nitrate were standardized by titration with EDTA using murexide indicator.

Oxygen Uptake and Rate Measurements. These were carried out as described previously.[1,2] All experiments were performed in solutions of ionic strength 0.2 *M*, using KNO_3 as added electrolyte. A collidine buffer (pK = 7.5) was used where necessary.[6] It was shown using the oxygen probe that oxygen uptake was complete in the conditions of the kinetic experiments. Since, in addition, the cobalt(II) complex concentration (0.5–3.0 m*M*) was in ⩾tenfold excess of [O_2], the formation kinetics were simple, irreversible, and first order (rate constant = k_{obsd}). The formation of oxygenated products was followed directly at 360–460 mμ, usually at 420 mμ, and in a few experiments also at 600 mμ, using thymol blue indicator. The solitary temperature-jump experiment was carried out, in the absence of oxygen, on a 10^{-2} *M* cobalt(II)–trien solution at pH 10.8 (I = 0.1 *M*) using an apparatus purchased from Messanlagen Studiengesellschaft, Göttingen, West Germany. The results are given in Table I and the kinetic parameters are collected in Table II.

Determination of pK of Cobalt(II)–trien Species. Spectra were measured with a Cary-14 spectrophotometer using a 1-cm quartz flow-through cell with stopcocks at either end of the cell. This allowed the complete exclusion of O_2 in the process of filling the cell and during the spectral measurements. Determinations of pH were also made in the absence of O_2 using either a Beckman 76005 Expandomatic or a Leeds and Northrup 7401 pH meter. Beckman-certified buffer solutions were used below pH 10. Above this pH both meters were calibrated with standard KOH solutions, and these calibrations were used to convert meter readings to pH values. The spectra of a cobalt(II)–trien mixture (1:1.05) at different pH's are shown in Figure 1. If in the equilibrium 1 the spectrum at pH 8.0 represents **1A**, and that at pH 12.6 is **1B**, then at any specific wavelength $\epsilon_{1A}[\mathbf{1A}] + \epsilon_{1B}[\mathbf{1B}] = \epsilon_{obsd}([\mathbf{1A}] + [\mathbf{1B}])$, where ϵ_{1A}, ϵ_{1B},

$$\underset{\mathbf{1A}}{Co(trien)(H_2O)_2^{2+}} \rightleftharpoons \underset{\mathbf{1B}}{Co(trien)(OH)(H_2O)^+} + H^+ \qquad K_1 \quad (1)$$

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[1] J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **91**, 1325 (1969).

[2] F. Miller, J. Simplicio, and R. G. Wilkins, *ibid.*, **91**, 1962 (1969).

[3] S. Fallab, *Chimia*, **23**, 177 (1969).

[4] M. S. Michailidis and R. B. Martin, *J. Amer. Chem. Soc.*, **91**, 4683 (1969).

[5] S. Fallab, *Chimia*, **21**, 538 (1967).

[6] J. G. Pritchard and F. A. Long, *J. Amer. Chem. Soc.*, **79**, 2365 (1957).

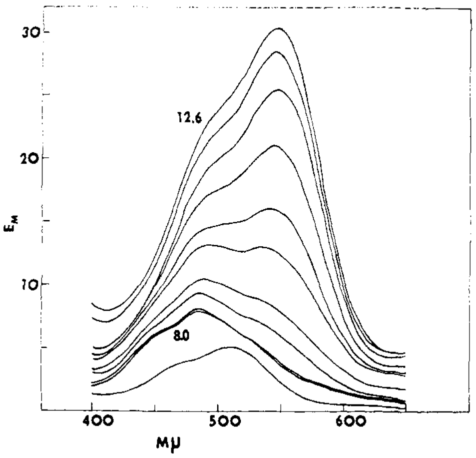

Figure 1. Spectra of Co(II)–trien (1:1.05) mixture at various pH: 12.6, 12.3, 11.7, 11.5, 11.2, 10.9, 10.3, 10.2, 8.0, and 6.8, 2.5.

and ϵ_{obsd} represent the molar absorbancy indices of **1A**, **1B**, and the mixture at any [H$^+$]. Thus $K_1 = (\epsilon_{1A} - \epsilon_{obsd})(\epsilon_{obsd} - \epsilon_{1B})^{-1}[H^+]$. K_1 was determined using the region 480–570 mμ and ten combinations of data sets for each wavelength (not all spectra are shown in Figure 1).

The pH change associated with the reactants proceeding to the final product (**3**) was measured directly with a pH meter in a closed system. The pH at the intermediate stage could only be measured spectrally by using thymol blue indicator and the stopped-flow apparatus. The agreement between pH measured directly and indirectly with indicators was within 10%. The proton equivalence associated with a specific pH change was then determined by titrating, with standard acid, a solution identical in all respects with the reacting solution except for the exclusion of O_2. Changes of pH values could then be equated with [H$^+$] changes for a specific concentration of O_2.

Results and Discussion

Cobalt(II)–trien System in Anaerobic Conditions. Cobalt(II) ion (10^{-2} *M*) is completely complexed by trien (1.05×10^{-2} *M*) at pH 7.5, with the formation of a pink-colored solution in the absence of oxygen. As the pH is raised the color changes to a raspberry red (pH ~10) and finally becomes a striking grape color at pH $\geqslant 11.5$. At pH >12.6, some precipitation occurs. The spectra of such solutions at various pH from 8.0 to 12.6 are shown in Figure 1. The presence of only slight absorption at 360 mμ indicated only traces of oxygenated product ($<5 \times 10^{-6}$ *M*) which do not interfere with the observations in the region of interest, 400–600 mμ. The series of spectra can be interpreted satisfactorily in terms of equilibrium 1, between two species only.[7] Species **1A** (pH 6.8–8.0) appears to be an unprotonated complex ion,[8] $Co(trien)(H_2O)_2^{2+}$, with normal extinction coefficients for an octahedral complex, ϵ_{484}^{max} 8.0 and ϵ_{460}^{sh} 6.6.[9] On the other hand, the relatively large extinction coefficients for the alkaline species (**1B**, pH ~12.6) of ϵ_{545}^{max} 30.2 and ϵ_{510}^{sh} 25.0 suggest that such solutions may contain significant amounts of a five-coordinated species. A five-coordinated structure has been suggested, from spectral and thermodynamic considerations, for the cobalt(II)–trien complex $CoN(CH_2CH_2NH_2)_3(H_2O)^{2+}$ in aqueous solution.[9] The band positions ϵ_{574}^{max} 37 and ϵ_{481}^{max} 45 (values of ϵ of 42 and 47, respectively, have been reported[9]) are similar to those of [CoN-

Table I. Kinetic Data for Formation of Oxygen Adducts at 25°[a]

pH	[Co(trien)$_T$],[b] m*M*	k_{obsd}, sec^{-1}	$10^{-4}k_2$,[c] M^{-1} sec^{-1}
		Stage 1	
7.4	1.0	19	1.9
7.4	3.0	61	2.0
7.5	0.50	10	2.0
8.1[d]	1.06	15	1.4
8.1[e]	1.06	8.2	0.78
8.2	1.0	20[f]	2.0
8.4[g]	1.07	29	2.7
8.5	1.0	23	2.3
9.0[h]	1.06	24	2.3
9.0[h]	2.1	58	2.7
9.1	1.1	23	2.2
9.1[i]	1.06	26	2.5
9.1[j]	1.06	23	2.2
9.3	3.0	89	3.0
9.5	1.0	35	3.5
9.8	1.0	44	4.4
10.7[g]	1.06	91	8.5
10.9	1.0	106	10.6
11.2	1.0	106	10.6
11.2[i]	1.06	113	10.6
11.2[j]	1.06	59	5.9
11.7	0.53	118	22
11.9	0.50	119	24
12.3[e]	1.0	95	9.5
12.6	0.50	140	28
		Stage 2	
7.5		2.0	
7.6[k]		2.0	
8.1[d]		1.1	
8.1[e]		0.45	
8.2		2.0	
8.4[g]		2.1	
9.1[i]		2.0	
9.1[j]		1.8	
9.1[h]		2.9	
9.3		1.8	
9.5[h]		2.1	
10.5		1.4	
10.5[g]		1.4	
10.9		1.1	
11.1[j]		0.88	
11.2		0.56	
11.2[i]		0.56	
11.3		0.41	
12.3[d]		0.037	
12.3[e]		0.014	
12.4		0.081	
12.6		0.054	

[a] *I* = 0.2 *M*, with added KNO_3. [b] Total concentration of Co(II)–trien species. Ratio trien:Co = 1.05. [c] k_{obsd}/[Co(trien)$_T$]. [d] 15.0°. [e] 4.0°. [f] Similar results at 360, 390, 450, and 540 mμ. Most observations at 420 mμ. [g] *I* = 0.2 *M*, with added $NaClO_4$. [h] With added thymol blue, λ 600 mμ. [i] trien:Co = 3.20. [j] trien:Co = 10.5. [k] Starting concentration of Co(trien)$^{2+}$ is 15 m*M*; in the majority of the experiments it is 1.0 m*M*.

Table II. Kinetic Data for Second-Order Cobalt(II) Complex–O_2 Interaction at 25°

Reactant	k_2, M^{-1} sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
$Co(trien)(H_2O)_2^{2+}$	2.5×10^4	7	−15
$Co(trien)(OH)(H_2O)^+$	2.8×10^5	8	−7
$Co(tetraen)(H_2O)^{2+}$	~10^5 [a]		
$Co(histamine)_2(H_2O)_2^{2+}$	1.8×10^4 [a]	5	−23
$Co(en)_2(H_2O)_2^{2+}$	4.7×10^5 [a]	15	+19

[a] From ref 2.

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[7] With the analogous Co(II)–tren system (tren = $N(CH_2 \cdot CH_2 \cdot NH_2)_3$) at different pH, isosbestic points at 493 mμ and 582 mμ are actually observed: F. Miller and R. G. Wilkins, unpublished.

[8] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).

[9] P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

$(CH_2CH_2NMe_2)_3Br]Br$ in nitroethane, the solid structure of the cation in the latter being trigonal bipyramidal,[10] although absorption coefficients are only about one-third, suggesting an equilibrium in aqueous solution. With the cobalt(II)–trien–hydroxy species **1B** the values of extinction coefficients indicate, very tentatively, that only about 20% of the complex may be present as the five-coordinated species, presumably Co(trien)(OH)$^+$.

The pK_1 value for equilibrium 1 is 11.2 ± 0.1 at 25°, and interestingly it is close to that found for the corresponding aquohydroxy equilibrium involving the cobalt(II)–$N(CH_2CH_2CH_2NH_2)_3$ complexes (11.0).[11] Since equilibrium 1 may differ from a normal acid–base equilibrium in incorporating slower configurational changes, we attempted to measure the rate of reaction 1 by the temperature-jump relaxation method. A reasonable optical density increase was observed for a 5° jump in temperature, but the relaxation time was $\leqslant 10\ \mu$sec.

Kinetics of O_2 Uptake. Both the pink and grape-colored forms of the cobalt(II)–trien complex reacted readily with O_2 to form the same brown species. In the whole pH range of study (7.4–12.6) the reaction took place in two stages indicated by a large optical density increase, followed by a smaller decrease in the spectral region 360–450 mμ, where the products would be expected to absorb.[1,2] Both reactions were rapid and required stopped-flow apparatus for their rate measurements. They will be designated as stage 1, in which reactants are converted into an intermediate **2**, and stage 2, in which the intermediate(s) changes to a final (insofar as this study is concerned) product, **3**. The rate constants associated with both stages were pH dependent, and each stage was accompanied by [H$^+$] changes. The half-lives observed with stage 1 were always shorter than those of stage 2 (by at least a factor of 10) and there was thus no problem in obtaining an accurate final reading for the first stage. The kinetic data are shown in Table I.

Stage 1. The concentration of cobalt(II) complex used always exceeded that of O_2 and excellent pseudo-first-order kinetics were observed. Examination of the kinetic data showed that the rate was first-order in cobalt(II) concentration at pH 7.4, 9.5, and 11.2 and so the rate law 2 holds, with [**2**] the concentration of the

$$d/dt\,[\mathbf{2}] = k_2[\text{Co(trien)}_T][O_2] \tag{2}$$

intermediate(s) and [Co(trien)$_T$] the combined concentration of **1A** and **1B**. The value of k_2 was independent of the initial O_2 concentration used from 10 to 100 μM and of the observation wavelength. It was little affected by small changes in ionic strength, or by changing the added electrolyte from KNO_3 to $NaClO_4$. In most of the experiments the initial trien/cobalt(II) molar ratio was maintained at 1.05. Only when this ratio was drastically increased (to around 10) was there any sign of a change in the value of k_2, and then this decreased, presumably due to the formation of a higher cobalt(II)–trien species which would be expected to react much less readily with O_2.[2]

The value of k_2 was independent of pH from 7.4 to 9.0, but in more alkaline solutions it increased, reaching a limit around pH 12.5, above which precipitation of the original reactants occurred. The variation of k_2 with pH suggests that both species **1A** and **1B** react with O_2 with second-order rate constants k_{1A} and k_{1B} and thus relation 3 together with 1 lead to (4) which

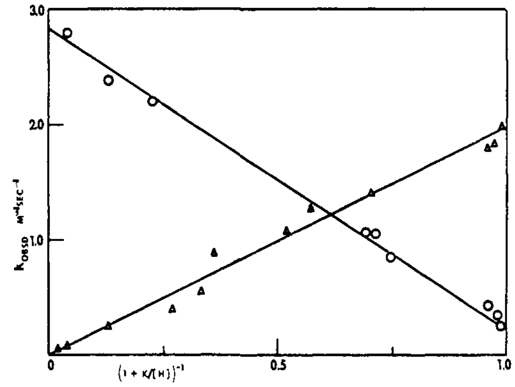

Figure 2. Plots of $10^{-5}k_{obsd}$ (M^{-1} sec^{-1}) against $[1 + (K/[H^+])]^{-1}$ for stage 1 (○) and k_{obsd} (sec^{-1}) against $[1 + (K/[H^+])]^{-1}$ for stage 2 (△).

$$k_2([\mathbf{1A}] + [\mathbf{1B}])[O_2] = k_{1A}[\mathbf{1A}][O_2] + k_{1B}[\mathbf{1B}][O_2] \tag{3}$$

$$k_2 = \frac{k_{1A} + (k_{1B}K_1/[H^+])}{1 + (K_1/[H^+])} = \frac{k_{1A} - k_{1B}}{1 + (K_1/[H^+])} + k_{1B} \tag{4}$$

is applicable at any hydrogen ion concentration, [H$^+$]. The plot of k_2 against $[1 + (K_1/[H^+])]^{-1}$ was linear (Figure 2), the intercepts being k_{1B} (when the x coordinate = 0) and k_{1A} (when the x coordinate = 1). These values are close to k_2 values found at pH 12.6 and 8.0, respectively, and so k_2 at these pH's was measured at different temperatures to obtain the Arrhenius parameters. It was found that $k_{1A} = 10^{9.9}$ exp($-7700/RT$) and $k_{1B} = 10^{11.6}$ exp($-8500/RT$) and that at 25° $k_{1A} = 2.5 \times 10^4$ and $k_{1B} = 2.8 \times 10^5$ M^{-1} sec^{-1}. These rate parameters refer to the formation of the 1:1 Co(trien)–O_2 species which then rapidly reacts with another Co–trien species to give the intermediate **2**.[12] Comparison with the values obtained in similar polyamine systems (Table II) shows a remarkable constancy for $k_2 = 2 \times 10^4$–2×10^5 M^{-1} sec^{-1} at 25° and ΔH^* in the range of 5–8 kcal/mole^{-1}, except for the puzzling case of the bis(ethylenediamine) complex. We have interpreted this constancy as arising from a similar process of H_2O replacement by O_2 in all these complexes, dominated by the H_2O exchange.[2] The enhanced rate constant associated with the hydroxy species **1B** may arise from (a) the known ability of an OH group to labilize coordinated H_2O molecules or (b) an enhanced sensitivity of a five-coordinated species to attack by O_2.

It was found that stage 1 was accompanied by a sizable pH decrease (*vide infra*). In the presence of a buffer (to reduce the magnitude of the pH change) and an indicator, the pH change could be monitored spectrally and used to follow the kinetics. The rate constant at pH ~9 agreed well with that measured directly.

Stage 2. The slower of the two reactions was first order, and the rate constant k_{obsd} was independent of

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(10) M. DiVaira and P. L. Orioli, *Inorg. Chem.*, **6**, 955 (1967).

(11) A. Dei, P. Paoletti, and A. Vacca, *ibid.*, 7, 865 (1968).

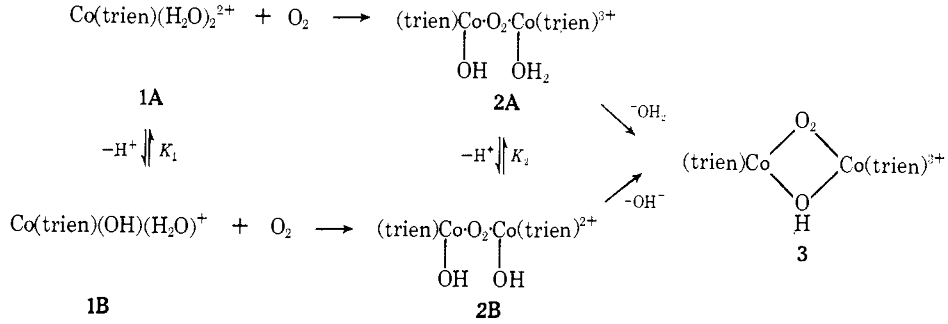
(12) J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 6092 (1967).

the initial concentrations of cobalt(II), trien, and O_2, and ionic strength medium. The simple rate law (5)

$$\mathrm{d}/\mathrm{d}t\,(\mathbf{3}) = k_{\mathrm{obsd}}[\mathbf{2}] \qquad (5)$$

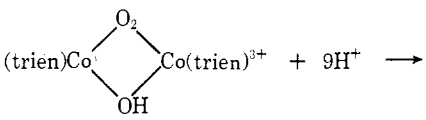
holds. Some type of intramolecular reaction is obviously involved. Once again the rate constant was dependent on pH but this time there was a decrease with increasing base and because of this it was difficult to measure the lower limiting rate constant. It is apparent that at pH around 12, because of the opposing effects of $[OH^-]$, stage 1 was very much faster than stage 2. It is reasonable to ascribe the rate constant/pH behavior to two forms of intermediate **2A** and **2B**, interrelated by pH, and even though it was difficult to assess the limiting rate constant at higher alkalinity, examination of the data shows that K_2 $(=[\mathbf{2B}][H^+]/[\mathbf{2A}])$ must be close to 10^{-11}. This and other near values were used to construct a series of k_{obsd} against $[1 + (K_2/[H^+])]^{-1}$ plots based on eq 4. The best plot (Figure 2) gave k_{2A} and k_{2B} values of 2.0 and ~0.012 $\sec^{-1}$ and $K_2 = 1.2 \times 10^{-11}$ M at 25°. Temperature coefficients are only meaningful for the reaction of **2A**, and for this $k_{2A} = 10^{8.7} \exp(-11{,}600/RT)$, using the rate constant values, at different temperatures, at pH 8.0. Stage 2 is accompanied by a very small pH increase and there is a fair agreement between the rate constant measured directly and that from indicator experiments at pH ~9. These rate constants will be considered after a discussion of the possible species involved.

Species Involved. A number of experiments were carried out to characterize the species observed during and at the conclusion of the rapid spectral changes. The pH changes which accompany these reactions and which could be used to follow the kinetics (*vide supra*) were measured directly (pH meter) as well as indirectly with the use of indicators. In the pH range 8.5–9.5, it was shown that there was released one equivalent of proton per mole of oxygen used in forming the final species, that is, after the two stages of reaction. This is in agreement with the results of Fallab,[3] and is expected from those of Michailidis and Martin,[4] although the latter workers never actually investigated the cobalt(II)–trien–O_2 system. It was very difficult to measure directly the $[H^+]$ change accompanying the first stage, because of the fleeting existence of the intermediate, so that the less accurate indicator method and the flow apparatus had to be used. It was clear from an examination of the kinetic traces in which indicators had been used, that at pH ~9, slightly more than one proton was released in reaching the intermediate, and that this transformed into the final product with the consumption of a small fraction of one proton. From a number of experiments we concluded that, per O_2 taken up, 1.15 ± 0.05 protons were released and 0.15 ± 0.05 proton consumed, respectively, during the two stages of the reaction at pH 9.0–8.6. It was difficult to extend these experiments to much lower pH because of problems of dissociation of the cobalt(II) complex. At much higher pH, the $[H^+]$ changes were relatively smaller and less easily measurable accurately, and in addition the interpretation of the experiments would be complicated by the hydroxo–aquo equilibrium present with the original cobalt(II)–trien complex.



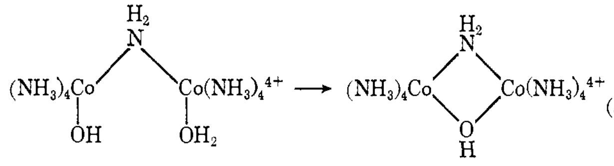
(6)

It was of some interest also to determine at what stage the oxygen uptake was completed. This could be easily answered only at the highest pH, where the first rate was very fast and the second stage relatively slow, with $t_{1/2} = 49$ sec at 4° at pH 12.3. The oxygen probe thus had a sufficiently rapid response (90% within 10 sec) to resolve this question. It was shown (using a mixture of 2.1×10^{-3} M Co(II), 2.2×10^{-3} M trien, and 2.6×10^{-4} M O_2, pH 12.4 and 4°) that ≥95% oxygen was taken up in the first stage with the production of the deep brown color of the intermediate. This then appears to already have the O_2 bridge feature. The intermediate then slowly changed to a much lighter brown, which no longer completely masked the grape-colored Co(II)-trien species which was present in excess. The spectrum of this final product ($\epsilon_{\max}$ (355 mμ) 1.93×10^4) was identical, whether the reaction was carried out at pH 9.6, 10.6, or 12.0. These observations lead us to suggest the scheme of eq 6 to explain our results. The dibridged (O_2, OH) nature of the product had already been indicated previously from $[H^+]$ changes in solution.[3] This structure is supported by our observation that oxygen can be completely recovered from the final solutions only by the addition of acid, when reaction 7 occurred.[5] Addition of EDTA to the alkaline solution and/or flushing such solutions with N_2 produced no breakdown of brown solution over long periods of time, a procedure that is effective with a few single O_2-bridged materials.[12]



$$(\text{trien})\text{Co}(O_2)(OH)\text{Co}(\text{trien})^{3+} + 9H^+ \longrightarrow 2\,\text{trien}\,H_4^{4+} + H_2O + 2Co^{2+} + O_2 \qquad (7)$$

We have also shown that the intermediate formed at high pH (12.3) and quickly plunged into a buffer of lower pH (7.5) decomposes with a rate constant (0.46 $\sec^{-1}$ at 4°) similar to that of the intermediate formed directly at pH 7.5 (0.45 sec^{-1} at 4°). This showed that the intermediates **2A** and **2B** at the two pH's are related by some simple (and scheme 6 indicates an acid–base) equilibrium, and that they are not radically different species. The pK values for the intermediate are 10.9 and <7.0 and these do not seem unreasonable in view of the values for the mononuclear α-*cis*-Co(trien)$(H_2O)_2^{3+}$ ion (7.6 and 5.3).[18] The higher value for the intermediate, however, presents a slightly disturbing feature to our explanation. At pH 9.0 there should be virtually no pH change for the second stage, since only condensation with removal of an H_2O molecule occurs. We observe a small pH increase and can only conclude that this small pH change is a result of some unknown secondary reaction. The rate constant for the transformation **2A** → **3** (2.0 sec^{-1} at 25°) might be considered high for the reaction of a cobalt(III) complex, but for reaction 8 the relatively high value of 0.013 sec^{-1} has been measured.[14] In order to estimate this value it is necessary to use the measured pK of 6.2 for the reactant. The second pK must be much higher and this behavior resembles our system. Reaction 8 shows an anchiomeric effect, the NH_2 bridge holding the two cobalt-coordinated OH and H_2O groups close together for reaction. Such an effect can also be envisaged with reaction 6, one of the Co–O_2 bonds easily rotating from the normal Co–O–O–Co staggered conformation.[15] The low rate constant for **2B** → **3** ($\approx$0.012 sec^{-1}) reflects the difficulty of replacement of an hydroxy group compared with coordinated water.



(8)

The product **3** slowly changes color from brown to strawberry pink. This takes about 2 weeks at room temperature at pH ~12, but very much longer at lower pH's. The spectra of the pink product indicates that it contains the mononuclear cobalt(III) complex *cis*-β-Co(trien)$(OH)_2^+$ ion,[16] the production of which from the bridged species must be base-catalyzed. It is not yet known whether the final β configuration of the trien is also in the double bridged **3**, or whether it results from isomerization processes involving the mononuclear complex. The *cis* is preferred to the *trans* configuration with the tetramine, trien.[19]

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(16) Acidifying the pink solution to pH 3.0 produces an orange-pink colored ion, with a maximum at 493 mμ (ϵ_M 123) to be compared with the *cis*-β-Co(trien)$(H_2O_3)^{3+}$ ϵ_{487}^{max} 122, and the *cis*-α form, ϵ_{500}^{max} 87.[17] The *trans*-Co(trien)$(H_2O)_2^{3+}$ ion has only a shoulder at 495 mμ.[18]

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A Proton Nuclear Magnetic Resonance Investigation of the Kinetics of Tetrahedral $\rightleftharpoons$ Planar Isomerization of Bis(n-alkyldiphenylphosphine)nickel(II) Dihalides

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Abstract: The rates of tetrahedral, paramagnetic $\rightleftharpoons$ planar, diamagnetic isomerization have been determined for a series of bis(n-alkyldiphenylphosphine)nickel(II) dihalides, $(RP(Ph)_2)_2NiX_2$ (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X = Cl, Br, I), by analysis of the proton magnetic resonance line-width dependence on temperature. The first-order kinetics, ~10^5–10^6 sec^{-1} at 25°, depend on both R and X. In the presence of excess ligand, an additional second-order ligand-exchange mechanism also contributes to the rate of isomerization. Although some reproducible trends in rate constants appear to characterize the variables, such as I > Cl > Br for fixed R, and C_2H_5 > n-C_4H_9 $\gtrsim$ n-C_3H_7 > CH_3 for fixed X, no simple relationship between ligand steric and/or electronic properties was found. Though the thermodynamics are more regular, some differences between expected and observed trends are also noted. Some reasons for the complex dependence of the rate of isomerization on R and X are discussed.

It is now well established[1–4] that a number of four-coordinated nickel(II) complexes possess sufficiently similar ground-state free energies for the pseudotetrahedral, paramagnetic, and planar, diamagnetic configurations so that both states are appreciably

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