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The Kinetics of Ligand Detachment from Labile Cobalt(II)-Amine Complexes in Aqueous Solution

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Abstract: The e_{aq}^- reduction of some Co(III)-amine complexes and the kinetics of ligand detachment of the resulting Co(II) complexes have been examined by pulse radiolysis with kinetic conductivity detection (time resolution $\sim 1 \mu s$). The halide ligands in $Co(NH_3)_5Cl^+$, $Co(en)_2Cl_2$, and $Co(trien)Cl_2$ are lost very rapidly ($< 1 \mu s$). Similarly all but three NH_3 ligands from $Co(NH_3)_6^{2+}$ and other amine complexes are lost in $< 1 \mu s$. The last three NH_3 ligands from all monodentate complexes are replaced by water with half lives of 11, 81, and 630 μs , independent of pH (3-4.5). Ethylenediamine ligands in $Co(en)_3^{2+}$ and $Co(en)_2Cl_2$ are detached in well-defined consecutive steps. The detachment rates of ethylenediamines are much slower than for ammonia ligands ($t_{1/2} = 0.5, 3, \text{ and } 10 \text{ ms}$ at pH 3.5) and are pH dependent. In $Co(trien)Cl_2$ the elimination of trien proceeds by a single observable pH-dependent step in the ms range. No detachment from $CoEDTA^-$ was observed as expected for stable complexes.

The alternating current (ac) kinetic conductivity technique has been coupled successfully with pulse radiolysis² and exploited in the study of charged free radicals over a wide pH range (2-12). This combination, referred to as "conductometric pulse radiolysis" (CPR), was subsequently demonstrated to be useful for studying the kinetics of ammonia detachment from some simple Co(II) ammine complexes³ and was suggested as a powerful method for the study of the fast kinetics (time resolution of $\sim 1 \mu s$) of basic-ligand detachment from labile Co(II) complexes. More recently, CPR was successfully exploited in the study of ammonia detachment from Rh(II) complexes.⁴ This technique can also be used to monitor intramolecular electron transfer processes³ as in the case of (*p*-nitrobenzoate)Co(III)(NH₃)₅²⁺, where initial addition of an electron to the nitro group is followed by the intramolecular electron transfer to the metal center.⁵

We present here kinetic data concerning the detachment of ammonia and some polyamines from labile Co(II) complexes that are generated by rapid ($\tau < 1 \mu s$) reduction of stable

Co(III) complexes in aqueous solutions. These kinetic data provide also an insight into the mechanism of detachment of polydentates from Co(II) and all partially aquated intermediates. In addition, the significance of the participation of those intermediates in the chemical reactions can be assessed from their lifetimes and reactivities as in the case of the $Rh^{II}-(NH_3)_4^{2+} + O_2 \rightarrow O_2Rh^{II}(NH_3)_4^{2+}$ reaction.⁴

Experimental Section

A 10-MHz ac conductivity cell with two pairs of platinum electrodes, one serving as a compensatory pair, was irradiated using 0.5 μs pulses of 1.6 MeV electrons from a Van de Graaff generator. The cell can be used for simultaneous conductivity and optical measurements with 1- μs resolution. Since the intermediates in the systems examined have very small absorbances, only induced conductivity changes were recorded. The associated optical and electronic equipment have been described elsewhere.⁶ The ac kinetic conductivity cannot be used above 10^{-2} M ionic concentration, i.e., below pH 2.

The solutions were made up from ultrapure water generated by a millipore system. All chemicals were of highest commercial grade

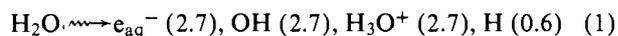
available. The amine complexes were prepared by standard methods. Oxygen was eliminated from solutions by purging with O₂-free argon. Perchloric acid was used for pH adjustment. The complexes were added to purged solutions and investigated within 15 min.

The dose per pulse and the conductivity cell constant were always determined before each series of experiments using 10⁻⁴ M tetranitromethane solutions in the presence of 10⁻² M 2-propanol.⁶ The dose was calculated⁷ from $G(\text{C}(\text{NO}_2)_3^-) = 6.0$ and $\epsilon(\text{C}(\text{NO}_2)_3^-) = 14\,000\text{ M}^{-1}\text{ cm}^{-1}$. The cell constant was calculated from equivalent conductivities:⁸ $\Lambda(\text{H}_3\text{O}^+) = 350\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ and $\Lambda(\text{C}(\text{NO}_2)_3^-) = 40\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ all at 25 °C. The equivalent conductivities of intermediates were calculated from the dose/pulse and $G(e_{\text{aq}}^-) = 2.7$. In most of the experiments between 0.5 and 1 krad/pulse was used which corresponded to $1.3\text{--}2.6 \times 10^{-6}\text{ M}$ hydrated electrons.

The time dependent conductivity signals were digitized and stored in a Biomation 8100 transient recorder, the digital data then transferred to paper tape and later evaluated on a PDP 11 computer for the best kinetic fit. Because of the overlapping kinetics of ligand detachment, the k values have an estimated error of about 20–30%.

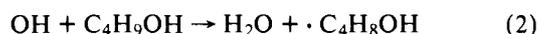
Results

Pulses of high-energy electrons produce in aqueous solutions two main reactive species—hydrated electrons, e_{aq}^- , and hydroxyl radicals, OH. The overall reaction is given below



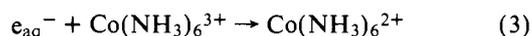
with G values (number/100 eV absorbed) indicated in parentheses.

The OH radicals, which are strong oxidizing agents, are usually removed in the reaction with *tert*-butyl alcohol (0.1 M solutions were sufficient for complete scavenging).



The resulting *tert*-butyl alcohol radicals do not show any acid–base properties in the pH region investigated⁹ and were unreactive towards Co complexes as expected for β -hydroxy radicals.¹⁰ H atoms disappeared by reaction with *tert*-butyl alcohol or radicals from *tert*-butyl alcohol, since the rates with the complexes used were relatively low.¹¹

The rapid reduction of Co(III) complexes was accomplished using hydrated electrons which are unreactive towards *tert*-butyl alcohol,¹¹ e.g.



The reaction rate of the above reaction and of e_{aq}^- with other complexes used in this work is extremely high,¹¹ $k \sim 8 \times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$. Hence, with the concentrations of complexes used, $>10^{-4}\text{ M}$, the reduction reactions were over in a time shorter than the time resolution of kinetic conductivity ($\sim 2\ \mu\text{s}$).

Formation of charged species on irradiation of aqueous solutions, reaction 1, results in a transient change in conductivity after the pulse that is determined by $\Lambda(e_{\text{aq}}^-) = 180\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ and $\Lambda(\text{H}_3\text{O}^+) = 350\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$, i.e., $\Delta\Lambda = 530\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$. If an electron acceptor is present, the conductivity due to e_{aq}^- reaction will be lost after the completion of the e_{aq}^- reaction. The exact level of the remaining conductivity will depend on the nature of the electron acceptor. For example, if one starts with a neutral solute, S, the overall conductivity change at the end of the e_{aq}^- reaction will be $\Delta\Lambda = \Lambda(\text{H}_3\text{O}^+) + \Lambda(\cdot\text{S}^-)$; in case of a positively charged metal or a metal complex, it will be $\Delta\Lambda = \Lambda(\text{H}_3\text{O}^+) + \Lambda(\text{M}^{(n-1)+}) - \Lambda(\text{M}^{n+})$. In some cases the exact values of $\Lambda(\cdot\text{S}^-)$ and $\Lambda(\text{metal complex})$ are not known, e.g., for unstable complexes, and have to be approximated with those for similar species. Those Λ values associated with change in charge of metal ions are much smaller than $\Lambda(\text{H}_3\text{O}^+)$; hence only a small error may result from these approximations. For instance, for reactions 1 and 3 $\Delta\Lambda = 350 - 60 = 290\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ is expected and a small error in $\Delta\Lambda = \Lambda(\text{Co}(\text{NH}_3)_6^{3+}) - \Lambda(\text{Co}(\text{NH}_3)_6^{2+}) = 60\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ can be neglected.

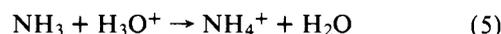
If H_3O^+ does not enter into any subsequent reaction, $\Delta\Lambda = 290\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ is the conductance, Λ_{in} , that one would observe at $2\ \mu\text{s}$. On the other hand, if protonation reactions take place, a corresponding decrease in conductivity occurs. In most cases the protonation reactions are too fast to be followed, $\tau < 1\ \mu\text{s}$, by the equipment used.

In the Co(III) hexaamine example, the reduction reaction (eq 3) leads to a labile Co(II) complex that under our conditions quantitatively loses all ammonia ligands:



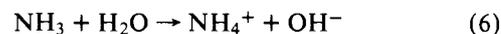
In order to simplify the presentation, as is customary, the coordinated water molecules replacing the detached ligands are hereafter omitted.

Under our experimental conditions, the pH of the solutions was kept below 4.5 and the released ammonia ligands would be protonated in less than $2\ \mu\text{s}$ or even faster or lower pH since:¹²

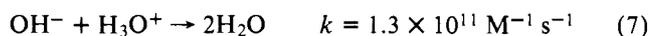


$$k = 4.3 \times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$$

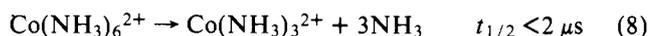
For every ammonia released a decrease in conductance $\Delta\Lambda = \Lambda(\text{H}_3\text{O}^+) - \Lambda(\text{NH}_4^+) = 350 - 75 = 275\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ takes place. For hexaammine complex a total conductivity change of $\Delta\Lambda = -1350\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$ should be reached when all six ammonias are detached; while for pentaammine complexes, $\Delta\Lambda = -1075\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$. In most cases about 90% of those values are observed which is within the experimental error of the technique (10–20%). Protonation of ammonia by water can also be achieved; however, the results would not be changed inasmuch as



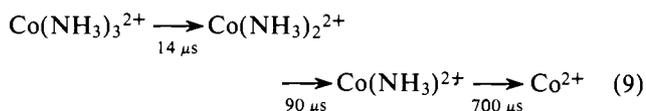
is followed by a very fast ($t_{1/2} < 1\ \mu\text{s}$) consumption of a proton¹² at pH < 4.5



The first three ligands of the generated Co(II) complex are released too rapidly to be resolved.³

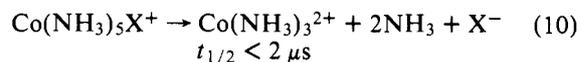


On the other hand, the last three ammonias are detached at considerably slower rates and their corresponding kinetics, although overlapping to a certain extent, can be resolved by a computer treatment. Hence, the following half-lives are observed:



The above half-lives and the corresponding ones for some other Co complexes are given in Table I.

Elimination kinetics of halide ligands is considerably more difficult to assess when associated with detachment of large number of ammonias. This is mainly due to a relatively large error in the measurements of $\Delta\Lambda$ values, which are of the same order as Λ for halides. It appears, from all the considerations taken into account, that the following reaction takes place



where $\text{X} = \text{Cl}^-$ or F^- . For the above reaction one expects $\Lambda_{\text{in}} = -120\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ at $2\ \mu\text{s}$ since at that time the two detached ammonias will be fully protonated. The observed Λ_{in} for the F^- complex is in a much better agreement with the expected value than in the case of the Cl^- complex (see Table

Table I. Equivalent Conductance, Λ_{in} , 2 μ s after the Pulse due to the Reduction of Co(III) Complexes by Hydrated Electrons^a and Half-Lives for Detachment of the Last Three Ammonias from Generated Labile Co(II) Complexes

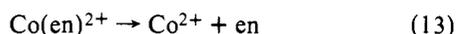
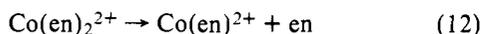
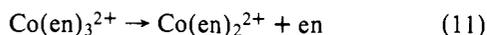
Labile Co(II) complex	Λ_{in} at 2 μ s ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Ligand, $t_{1/2}$		
		4th	5th	6th
$\text{Co}(\text{NH}_3)_6^{2+}$	-460	14	90	700
$\text{Co}(\text{NH}_3)_5\text{Cl}^+$	+10	10	65	540
$\text{Co}(\text{NH}_3)_5\text{F}^+$	-95	8	92	740
$\text{Co}(\text{NH}_3)_4\text{Cl}_2$	+225	14	84	640
$\text{Co}(\text{NH}_3)_4\text{Cl}(\text{OH})_2^+$	+120	7	75	550
Average		11 ± 4	81 ± 16	630 ± 110

^a Complexes 4×10^{-4} M, pH 4.1 with 10^{-1} M *tert*-butyl alcohol.

I). At present, these differences cannot be accepted as critical and instrumentation with better accuracy and time resolution has to be developed. With the reduction of ammonia ligands as in $\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^+$ and $\text{Co}(\text{NH}_3)_4\text{Cl}_2$ the error should be reduced and in fact the observed Λ_{in} values (+120 and +225) are in a better agreement with the expected values (+150 and +285). Fast detachment of Cl^- ligands from Co(II) is more evident and unequivocal in the case of $\text{Co}(\text{en})_2\text{Cl}_2$ and $\text{Co}(\text{trien})\text{Cl}_2$ as described below where the detachment of the amino ligands is much slower than the detachment of Cl^- ligands.

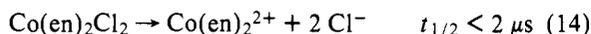
Hence the detachment rates of the last three ammonia ligands for all the complexes investigated (Table I) are considered to be derived from the same species as in the case of cobalt hexamine, i.e., $\text{Co}(\text{NH}_3)_3^{2+}$. These last three aquation steps are shown in Figure 1 for the $\text{Co}(\text{NH}_3)_5\text{Cl}^+$ complex. No pH effect has been observed in the pH range 3–4.5.

In contrast to the halide and NH_3 complexes, ethylenediamine, en, a well-known bidentate ligand, is eliminated at a considerably slower rate and, despite overlapping to a certain extent, all individual steps can be resolved by the computer (see Figure 2 for oscilloscope traces):



Since en protonates to give enH_2^{2+} ($\text{p}K_a = 7.31$ and 10.05),¹³ six H_3O^+ are consumed. The half-lives of these steps are pH dependent and are presented in Figure 3 for all three steps and Table II for the first one.

For $\text{Co}(\text{en})_2\text{Cl}_2$, two Cl^- are detached prior to detachment of en:



as the high initial conductivity indicates (observed $\Lambda_{in} = 600 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ against the expected value of 560). The next two steps follow the pattern of reactions (12 and 13), see Figure 3.

The $\text{Co}(\text{trien})\text{Cl}_2^+$ complex, where trien is the tetradentate ligand triethylenetetramine, on reduction by the hydrated electron shows a uniform decay that can be characterized only by a single half-life. The initial conductance immediately after the pulse is $\Lambda_{in} = 550 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (as in the $\text{Co}(\text{en})_2\text{Cl}_2^+$ case the expected value is 560) while the final is $\Lambda_{\infty} = -350 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at pH 3.4. This final value is pH dependent ($\Lambda_{\infty} = -120$ at pH 4.7). The total change corresponds to the consumption of four H_3O^+ at pH < 3.4 and three protons at pH > 4.7. This change is explained by the fact that trien has a $\text{p}K_a = 4.0$ for the fourth protonation. The rate of the aquation of the $\text{Co}(\text{trien})^{2+}$ intermediate is pH dependent as in the case

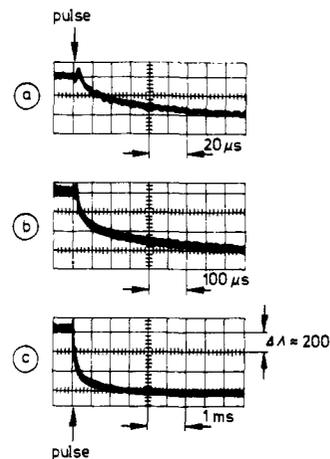


Figure 1. Oscilloscope traces of conductivity vs. time for aquation of $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}^+$ at pH 4.1.

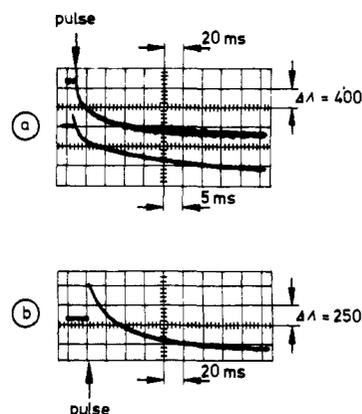


Figure 2. Oscilloscope traces of conductivity vs. time for aquation of (a) $\text{Co}^{\text{III}}(\text{en})_3^{2+}$ and (b) $\text{Co}^{\text{III}}(\text{en})_2\text{Cl}_2$ at pH 4.1.

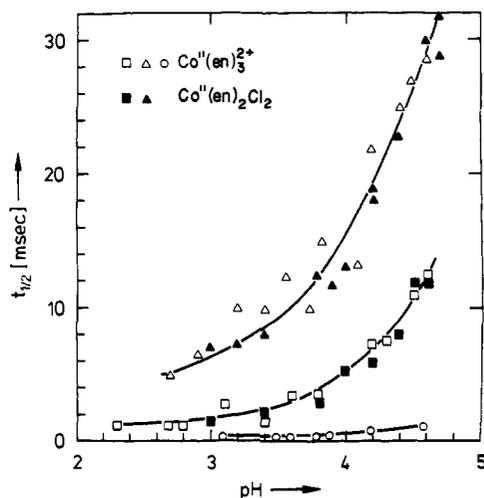
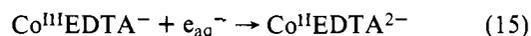


Figure 3. Half-lives vs. pH for the consecutive elimination of ethylenediamine ligands from $\text{Co}^{\text{III}}(\text{en})_3^{2+}$ (○, 1st; □, 2d; △, 3d) and $\text{Co}^{\text{III}}(\text{en})_2\text{Cl}_2$ (■, 1st; ▲, 2d) Co(II) complexes generated on pulse radiolytic reduction of corresponding Co(III) complexes by hydrated electron.

of the en complexes. Figure 4 shows the half-lives as a function of pH.

When reduction leads to a relatively stable complex as in reaction 15



involving ethylenediaminetetraacetate, a strong hexadentate

Table II. $\text{Co(en)}_3^{2+} \rightarrow \text{Co(en)}_2^{2+} + \text{enH}^+$

pH	$t_{1/2}, \mu\text{s}$	pH	$t_{1/2}, \mu\text{s}$
2.5	320	4.2	690
3.1	360	4.4	780
3.6	400	4.6	910
3.9	510		

ligand, the conductivity change observed at pH 3.5–5 is due only to the radiation produced H_3O^+ , reaction 1, and the change in the charge of the complex.

Discussion

On rapid pulse radiolytic reduction ($< 10^{-6}$ s) of relatively inert Co(III) complexes by the hydrated electron, a labile d^7 configuration of Co(II) is formed with a possibility of being in either a high or low spin state¹⁴ depending, of course, on the state of the starting Co(III) complex. For all of the complexes studied, except Co(EDTA), the final products are a high spin aquated Co(II) ion and free ligands in various states of protonation depending on the pH and the pK_a values of the ligands. The lability of Co(II) complexes is a well known fact yet it appeared to be of interest to determine the relevant kinetics data. The rates of ligand detachment (aquation) are fast as expected from water ($9 \times 10^6 \text{ s}^{-1}$)¹⁵ and ammonia ($5 \times 10^6 \text{ s}^{-1}$)¹⁶ exchange rates which may, perhaps, explain a relatively smaller abundance of kinetic information for Co(II) complexes than for some other systems with slower exchange rates.¹⁷ To a certain extent, indirect conclusions can be reached by comparison to a much better studied Ni(II) d^8 configuration.^{17,18}

From the kinetic data obtained here, certain generalizations can be made. As expected, the fastest detachment rates are observed for unidentate ligands while the detachment rates of polydentate ligands can be 3–5 orders of magnitude slower. In addition, the rates are dependent on the nature and the number of the remaining ligands of the Co(II) intermediate. No distinction between displacement and dissociation mechanism can be made from the observed data; hence we tend to use "detachment" to express a loss of ligand.

Elimination of the first three ligands from $\text{Co}(\text{NH}_3)_6^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{X}^+$ (where X is a halide) and related complexes is faster than 10^{-6} s, corresponding to limiting rate constant determinable by our technique; yet the last three steps in spite of some overlap can be resolved (Table I). The rate of detachment of the last ammonia is in good agreement with $k = 1.1 \times 10^3 \text{ s}^{-1}$ (20 °C) as measured by the T-jump method at high ammonia concentration.¹⁹ The rates of all steps are pH independent (pH 3–4.5) in agreement with relaxation measurements for the last step and in contrast to a strong pH dependence of detachment rates of polyamino ligands to be discussed later. A great disparity in detachment rates for the first and the last amonias from $\text{Co}(\text{NH}_3)_6^{2+}$ is not surprising. This can be explained perhaps by the following observations. The effect of different ligands on water replacement from the first coordination sphere has been known for some time. In particular, the exchange rate of water and nitrogen donors increases as the number of coordinated nitrogens is increased, as elegantly demonstrated by ¹⁷O NMR²⁰ and T-jump experiments for Ni(II) amino complexes.²¹ In our case, the labilization of ammonia by remaining ammonia ligands is on the order of $\geq 10^3$ ($t_{1/2} < 10^{-6}$ s and 6×10^{-4} s for the first and the last NH_3) as compared to factor of 10^3 observed by NMR and 10^4 by T-jump for Ni(II) complexes (for a review see ref 17).

The $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{2+}$ intermediate has a rather short lifetime ($t_{1/2} < 2 \mu\text{s}$) under our conditions and it is unlikely that it could participate in any kind of reaction to a significant ex-

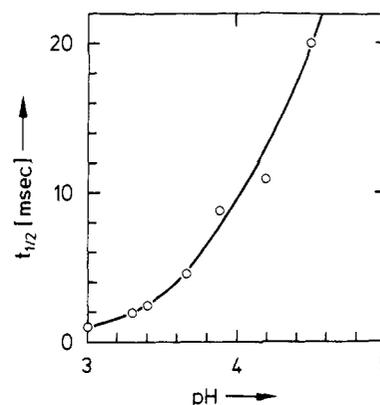
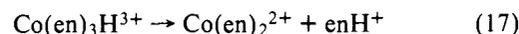
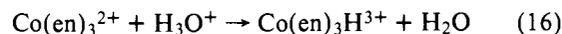


Figure 4. Half-life vs. pH for aquation of $\text{Co}^{\text{II}}(\text{trien})\text{Cl}_2$ generated on pulse radiolytic reduction of $\text{Co}^{\text{III}}(\text{trien})\text{Cl}_2$ by hydrated electron.

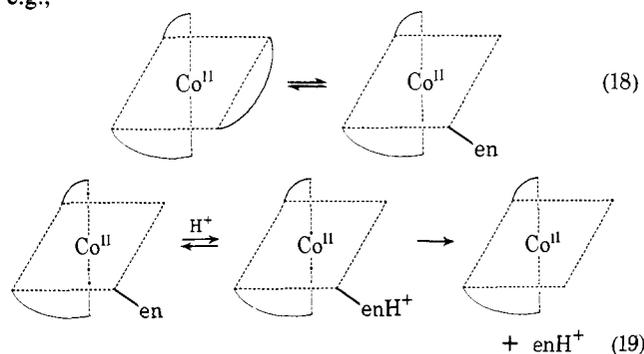
tent. The $\text{Co}(\text{NH}_3)_3(\text{OH}_2)_3^{2+}$ intermediate, on the other hand, could participate in some fast reactions in view of its much longer lifetime ($t_{1/2} = 14 \mu\text{s}$). These considerations apply, of course, only in the absence of added ammonia ions. For instance, the lifetime of $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{2+}$ can be sufficiently increased in the presence of 2 M NH_4^+ to observe formation of $\text{O}_2\text{Co}(\text{NH}_3)_5^{2+}$ ($k = 2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).²² One should point out that our technique is more accurate at lower salt concentrations than at $c > 10^{-2}$ M where the distortions of the signal are high; hence, we are not in a position to compare data at high salt concentrations.

It is of interest to note differences in detachment kinetics of high spin and low spin Co(II) complexes based on a few data available at present.²³ For instance, the first three NH_3 ligands are detached in less than 2 μs from a presumably high spin $\text{Co}(\text{NH}_3)_6^{2+}$. On the other hand, only the first NH_3 ligand is detached at less than 2 μs from low spin $\text{Co}(\text{Me}_6[14]4,11\text{-dieneN}_4)(\text{NH}_3)_2^{2+}$ ²⁴ while the second ammonia ligand comes off much slower, $t_{1/2} = 20 \mu\text{s}$. The effect of the spin state on the detachment rates of ligands can be also inferred from data obtained for low spin $\text{Co}(\text{CN})_6^{4-}$ where the first CN^- is detached in less than 2 μs while the second one comes off at a much slower rate ($t_{1/2} = 84 \mu\text{s}$). This interesting phenomenon can be studied in detail using the pulse radiolytic approach and development of kinetic ESR should be particularly useful.²⁵

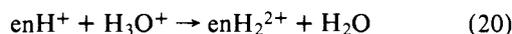
For bidentate amino ligands such as ethylenediamine, the strong pH dependence of ligand elimination rates suggests reaction of a proton with the labile complex.



The initial conductivity change is the same in the pH range from 3 to 5, showing that only a very small fraction of the reduced complex can be in the protonated form. Hence, a relatively long-lived singly protonated intermediate is excluded. These processes can be envisaged in a more detailed manner, e.g.,

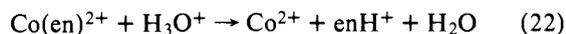
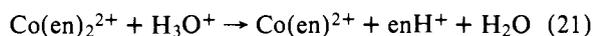


The detached enH^+ intermediate is then rapidly protonated in the bulk



This step is relatively fast in comparison to reactions 16, 17, 21, and 22. From these considerations it appears that the detachment rate is mainly governed by the equilibrium constant K_{18} and the protonation rate in reaction 19. Hence, the proton consumption rates are associated with two protons. The above set of detachment reactions (18 and 19) for bidentate ligands is encountered in various complexes of less labile nature.²⁶ A particularly useful comparison can be made to the well-studied Ni(II) complexes where dissociation rate constants are relatively slower. Despite the more favorable kinetic conditions, the $\text{M}(\text{en})_2(\text{OH}_2)\text{en}$ intermediates (protonated or deprotonated) still could not be isolated, indicating a short life of these species in general. At low pH where the H_3O^+ concentration is excessive, the detachment rate of en in Co(II) complexes appears to be reaching a limiting value and is probably governed by the forward rate of reaction 18.

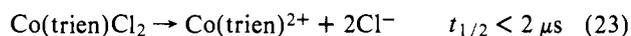
The $\text{Co}(\text{en})_2^{2+}$ intermediate loses its remaining two ethylenediamine ligands by the same proton catalyzed mechanism. The overall reactions are:



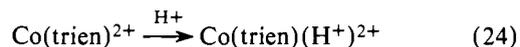
Mechanistic considerations for these two steps are the same as for the first step discussed above. Differences in detachment rates of the three en ligands can be rationalized, in this case too, on the basis of the ligand labilization effect.^{17,18,20,21}

The $\text{Co}(\text{en})_2^{2+}$ intermediate with $t_{1/2} > 1$ ms can be generated easily in less than $1 \mu\text{s}$ from $\text{Co}(\text{en})_2\text{Cl}_2^+$ and, because of its long lifetime, is a potential reactant as observed, e.g., in the reaction with O_2 .²⁷ The above mechanism for generating $\text{Co}(\text{en})_2^{2+}$ is preferred to the one via $\text{Co}(\text{en})_3^{3+}$, since in the latter case the detachment of the first en is much slower (see Table II) than the detachment of the two Cl^- ligands from $\text{Co}(\text{en})_2\text{Cl}_2$.

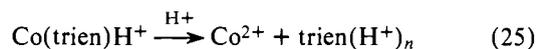
Detachment of trien, a tetradentate ligand, from Co(II) proceeds with a pH dependent rate in the 10^{-3} s region. The Co(II) complex is produced in the usual way by e_{aq}^- reduction of $\text{Co}^{\text{III}}(\text{trien})\text{Cl}_2^+$. The first step in aqution of the labile Co(II) complex is pH independent and relatively fast



The next step is pH dependent and shows only a single half-life



This reaction is then followed by a fast protonation of $\text{trien}(\text{H}^+)$. Interpretation of our data reveals that after detachment and protonation of one of the nitrogens all subsequent detachments proceed rapidly, i.e., "unzipping" of the whole ligand:



At which particular state of protonation trien detaches itself fully from Co cannot be determined. The final protonation of $\text{trien}(\text{H}^+)_3$ or $\text{trien}(\text{H}^+)_4$, depending on pH, can take place either at a free or a coordinated ligand, but one has to keep in mind that the overall protonation kinetics is governed by the kinetics of the first proton attachment. Hence, the $\text{Co}(\text{trien})$ -

$(\text{H}^+)_n$ intermediates could not be isolated as was possible in the case of Cr(III).²⁸ Coulombic repulsion may play a considerable role in fast detachment of a singly semiprotonated ligand from Co(II), perhaps to a much larger extent than in Ni(II) complexes where a 30-fold change in rate constants on protonation of trienH^+ to $\text{trien}(\text{H}^+)_2$ is observed.²⁹

The elimination of halide ligands (Cl^- and F^-) from Co(II) complexes appears to be very fast ($t_{1/2} < 2 \mu\text{s}$). The conclusions are somewhat ambiguous for $\text{Co}(\text{NH}_3)_5\text{Cl}^+$ because of the overlapping detachment of two NH_3 , while more convincing for $\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}^+$. Without any doubt the Cl^- ligands are eliminated in that fast time regime from $\text{Co}(\text{en})_2\text{Cl}_2$ and $\text{Co}(\text{trien})\text{Cl}_2$. These conclusions are in agreement with higher lability of Cl^- in numerous Co(III) amine complexes^{14,26} and labilization of Cl^- by amines.¹⁷

In conclusion, it is hoped that development of conductometric pulse radiolysis with better time resolution and its application to some special complexes will make it possible to determine directly the kinetics and mechanism of ligand detachment from labile complexes without interferences of complicating reverse reactions. The Co(II) complexes can be produced under nonequilibrium conditions at a relatively low ionic strength ($\mu \sim 10^{-3}$) and examined on a time scale not currently approachable by other methods.

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