

for the "bell-clapper" effect suggested by Gleiter and Hoffmann.⁸

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Supplementary Material Available. The important distances and amplitudes for models A, B, and C (Table II), the correlation matrix for model A (Table III), and a listing of the experimental intensity data (Table IV) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-289.

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Quang Shen, Kenneth Hedberg*

Department of Chemistry, Oregon State University
Corvallis, Oregon 97331

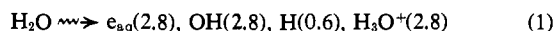
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Kinetics of Ammonia Detachment from Reduced Cobalt(III) Complexes Based on Conductometric Pulse Radiolysis¹

Sir:

Pulse radiolysis of aqueous solutions has been increasingly exploited in the study of fast reduction processes^{2,3} because (a) it conveniently produces a strong reducing agent, the hydrated electron, e_{aq} , and (b) quantitative reduction can be achieved in less than 1 μ sec (depending on the pulse length, rate constant, and the concentration of the reactant) which is a few orders of magnitude faster than in the conventional stopped-flow techniques. We wish to report some observations regarding the kinetics of ammonia detachment from a rapidly reduced cobalt(III)hexamine and some $Co^{III}(NH_3)_5X$ complexes as well as to demonstrate a research potential of a recently developed alternating current (ac) kinetic conductivity technique coupled to pulse radiolysis in the study of coordination complexes.

The radiolysis of aqueous solutions leads to formation of free radicals and ions² with G values (number/100 eV



absorbed, after neutralization of the OH^- also formed) indicated in parentheses. The formation of e_{aq} and H_3O^+ generates an increase in conductivity of the solution with specific conductance (e_{aq}) = 198 $\Omega^{-1} \text{equiv}^{-1} \text{cm}^2$ and (H_3O^+) = 350 $\Omega^{-1} \text{equiv}^{-1} \text{cm}^2$ (all at 25°). These and other conductivity changes can be easily followed by kinetic conductivity as a function of time.⁴

(1) Supported in part by NIH Grant GM 13 557 and AEC contract AT-(40-1)-3408.

(2) See, e.g., E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York, N. Y., 1970; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968.

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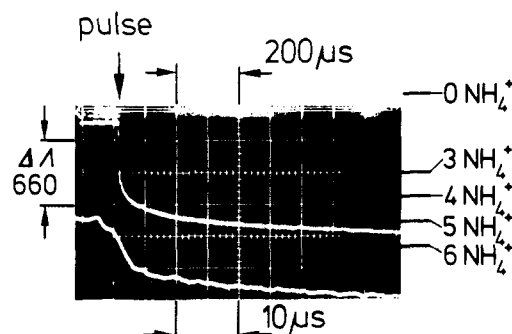
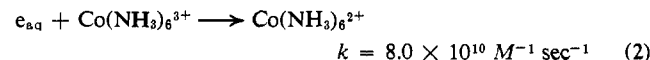


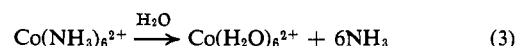
Figure 1. Pulse radiolysis of $5 \times 10^{-4} M Co(NH_3)_6^{3+}$, $0.1 M t\text{-BuOH}$, pH 4.0, Ar purged. Conductivity changes due to the following reactions: (a) $Co(NH_3)_6^{3+} + (e_{aq}, H^+) \rightleftharpoons Co(NH_3)_6^{2+} + H^+$; $\Delta\Lambda = 290 \Omega^{-1} \text{cm}^2$; (b) $Co(NH_3)_6^{2+} + H^+ \rightarrow Co^{2+} + 6NH_4^+$ ($-5H^+$); $\Delta\Lambda = -1360 \Omega^{-1} \text{cm}^2$. Reaction b takes place stepwise.

Briefly, a cell with two pairs of platinum electrodes (one pair for compensation) is irradiated with 1- μ sec pulses of 1.6 MeV electrons from a Van de Graaff generator. The radiation induced changes (reaction 1 and subsequent reactions of the primary species) can be followed simultaneously by optical absorption and conductivity measurements. The 10-MHz input allows response in the 1 μ sec region. Conductivity changes induced by the formation or loss of $10^{-7} M$ ions can be quantitatively followed in solutions of up to $10^{-2} M$ ions. Tetranitromethane was used as a dosimeter. The output signals are recorded on a tape and the kinetic data are evaluated by a computer. All experiments were performed at the Hahn-Meitner-Institute.

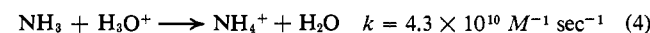
Many Co(III) complexes react with e_{aq} at a diffusion controlled rate,² e.g.



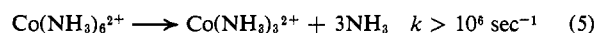
Since the resulting Co(II) complex is unstable, it decomposes with an overall stoichiometry



Under our experimental conditions (pH 4.0–4.5) the ammonia molecules are rapidly protonated⁵ ($\tau < 1 \mu$ sec)



and a decrease in conductance results since H_3O^+ ($\Lambda = 350 \Omega^{-1} \text{equiv}^{-1} \text{cm}^2$) is replaced by NH_4^+ ($\Lambda = 75 \Omega^{-1} \text{equiv}^{-1} \text{cm}^2$). Hence, the overall time resolution for the detection of the ligand detachment was about 1 μ sec. In Figure 1 conductivity changes resulting from reaction 2 are presented as a function of time. It is clear that reaction 3 takes place in four distinguishable steps. The first step is a very fast elimination of the first three ammonia ligands.



The individual steps are too fast ($< 2 \mu$ sec) and cannot be separated by the present technique. Such high values for the NH_3 elimination are expected from measurements of the ammonia exchange rate of concentrated aqueous ammonia solutions of Co^{II} where a value of $k = 5 \times 10^6 \text{sec}^{-1}$ has been measured for the exchange of one NH_3 by another.⁶

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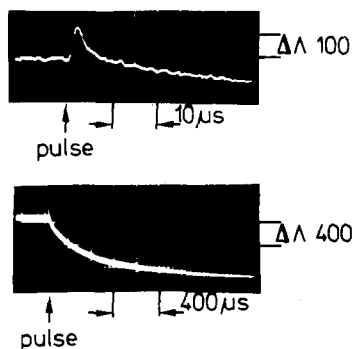
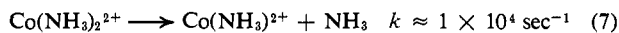


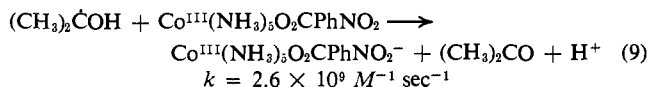
Figure 2. Pulse radiolysis of $5 \times 10^{-4} M$ $\text{Co}(\text{NH}_3)_5\text{O}_2\text{CPhNO}_2^{2+}$ (PNAP): $0.1 M$ *t*-BuOH, pH 4.3, Ar purged. Conductivity changes following the reduction of PNAP by e_{aq} and subsequent decomposition of reduced intermediates.

The next three steps are considerably slower



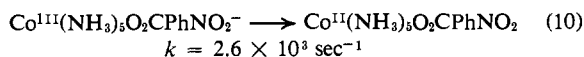
The last rate constant (8) agrees very well with the value $k = 1.1 \times 10^3 \text{ sec}^{-1}$ (for 20°) measured by the temperature jump method.⁷ (In all the equations the H_2O ligands that replace the NH_3 are omitted for getting easier formulas.) Similar kinetics were observed for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, where the elimination of Cl^- and 2NH_3 was very fast, followed by the reactions 6–8.

Using the ac conductivity technique we have also examined the reduction of the cobalt(III) *p*-nitrobenzoatopentaamine, PNAP, complex which exhibits an interesting primary reduction step of the *p*-nitrobenzoate ligand.^{8–10} With isopropyl alcohol radicals as the sole reducing agents (N_2O saturated aqueous solutions of $0.2 M$ $(\text{CH}_3)_2\text{CHOH}$ and $5 \times 10^{-4} M$ PNAP, at pH 4.5) the following reaction takes place quantitatively⁸



(For the sake of clarity the charge on the metal center and the carboxylate group are not indicated.) At this stage elimination of ammonia cannot be observed in accordance with the stability of the Co(III) complexes.

At pH >4 the extra electron is subsequently transferred intramolecularly from the *p*-nitrobenzoate ligand to the metal center.⁸



The reduced complex is labile and swiftly decomposes. Since the detachment of ammonia is faster than reaction 10, the latter reaction is the rate determining step, and the decrease in conductivity (reaction 4) closely follows the optical decay at 330 nm (reaction 10). Certain lag is present due to the slow elimination of the last ammonia ligand.

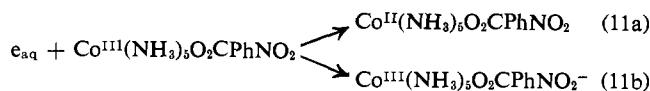
When the hydrated electron is used as the reducing agent the reduction mechanism is somewhat different.

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The product of reaction 11a is unstable and decays rapidly (similar to the decay of $\text{Co}(\text{NH}_3)_6^{2+}$, Figure 1). This initial decay is evident in Figure 2 and is clearly distinguishable from the much slower one. The intermediate from reaction 11b behaves as described above with reaction 10 as the rate determining step. It is of interest to note the difference in reducing mechanism between e_{aq} and other reducing radicals such as $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and CO_2^- . Reactions 11a and b have a 0.3 and 0.7 probability, respectively, as determined by the optical method¹¹ and the present experiments are a direct proof of that observation.

In conclusion, the described technique is particularly sensitive and can be exploited for the measurements of decay rates of various unstable metal complexes (produced on rapid reduction by hydrated electrons) which are associated with the change in the state of protonation of the freed ligands.

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(11) M. Simic and M. Z. Hoffman, submitted for publication.

M. Simic

Laboratory of Radiation Biology
Zoology Department, University of Texas
Austin, Texas 78712

J. Lilie*

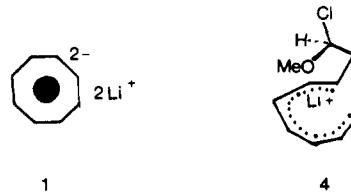
Bereich Strahlenchemie
Hahn-Meitner-Institut für Kernforschung, Berlin GmbH
1 Berlin 39, Germany

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Relative Ease of Epimerization of *syn*-9-Fluoro-, *syn*-9-Methoxy-, and *syn*-9-Dimethylaminobicyclo[6.1.0]nonatriene

Sir:

In contrast to the stereoselective formation of anti-9-substituted bicyclo[6.1.0]nonatrienes in the reaction of dipotassium cyclooctatetraenide with *gem*-dihalo compounds,¹ we have found that the dilithium salt (**1**) may direct reaction to preferential production of *syn* isomer. For example, addition of 1,1-dichlorodimethyl ether to a solution of **1** in Me_2O at -80° gave rise to 73% *syn* isomer (**2a**) and 27% anti isomer (**3a**). The trends in product ratio (less *syn* isomer with a more basic ether solvent or at higher temperatures) serve to suggest that the reversal of stereochemistry is brought about by intramolecular coordination of methoxyl to the small, hard lithium cation in intermediate **4**. There are precedents for expecting sub-



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