Volume 28
Number 14
July 12, 1989

Inorganic Chemistry

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Communications

Base Hydrolysis of $[Co(NO_2)_3(NH_3)_3]^0$

This is the first report, to the best of our knowledge, on the base hydrolysis of a nonelectrolyte complex, $[Co(NH_3)_3(NO_2)_3]^0$ (I), which avoids the complications arising out of ion-pair formation (and the "unreactive blind alley"[1]) and follows saturation kinetics.

Almost all Co(III) complexes follow first-order dependence on hydroxide ion concentration in their base hydrolyses.[1,2] There are, however, a few instances where departures from first-order dependence on hydroxide ion concentration have been observed[1,2] and where the dependence is given by the expression[3]

$$k_{obs} = a[OH^-]/(1 + b[OH^-]) \qquad (A)$$

as in Scheme I.

Scheme I

$$[L_4M(HNR_2)X]^{n+} + OH^- \overset{K_{hy} = k_1/k_{-1}}{\rightleftharpoons} [L_4M(NR_2)X]^{(n-1)+} + H_2O \qquad (1)$$

$$[L_4M(NR_2)X]^{(n-1)+} \xrightarrow{k_2} [L_4M(NR_2)]^{n+} + X^- \qquad (2)$$

$$[L_4M(NR_2)]^{n+} + H_2O \xrightarrow{\text{fast}} [L_4M(HNR_2)OH]^{n+} \qquad (3)$$

This rate expression is further complicated by the formation of an ion pair between the complex (mostly always cationic) and the hydroxide ion. The hydroxide ion can also abstract a proton from the complex (forming a conjugate base) while remaining associated with the complex in the ion pair (I_d cb).

An attempt to evaluate ion-pair and acidity constants was made by Buckingham et al.[5] in the base hydrolysis of $[Co(tren)(NH_3)_2]^{3+}$ (II), *S*-$[Co(Me(tren))(NH_3)_2]^{3+}$ (III), and *anti-p*-$[Co(Me(tren))(NH_3)_2]^{3+}$ (IV) (tren = 2,2′,2″-triaminotriethylamine Me(tren) = 2-methylamino-2′,2″-diaminotriethylamine).[6] These authors observed a departure from first-order dependence of k_{obs} on $[OH^-]$ and obtained a rate expression

$$k_{obs} = k_{OH}K_{ip}K_{-H}[OH^-]/\{1 + K_{ip}[OH^-](1 + K_{-H})\} \qquad (B)$$

conforming to Scheme II, where Co^{3+} represents these complexes and CoH^{2+} represents their conjugate bases.

Scheme II

$$Co^{3+} + OH^- \overset{K_{ip}}{\rightleftharpoons} Co^{3+}, OH^- \overset{K_{-H}}{\rightleftharpoons} Co\text{-}H^{2+} \xrightarrow{K_{OH}} \text{products}$$

Table I. Variation of Rate for Base Hydrolysis of Trinitrotriamminecobalt(III) with the Concentration of Sodium Hydroxide[a]

10^3[NaOH], M	10^5k_{obs}, s^{-1}	10^3[NaOH], M	10^5k_{obs}, s^{-1}
1.0	2.25	8.0	7.00
2.0	3.70	10.0	7.60
4.0	5.30	15.0	8.33
6.0	6.10	18.0	8.70

[a] [complex] = 2×10^{-4} M; temp = 50 °C.

Estimates of the values of K_{hy} from proton exchange data suggest that only in the case of IV could the kinetics be due to the saturation of the amido conjugate base. In II and III, this was shown to be complicated by the ion-association formation constant. This work points out the danger of taking a too naive view of these saturation kinetics. It, however, does not point out that there is a further ambiguity.[7] The same kinetics would be observed if ion-pair formation was an "unreactive blind alley" and the rate law still required a second-order interaction between the free substrate cation and hydroxide.[7] Similar behavior was observed in the base hydrolysis of the $Ru(NH_3)_6^{3+}$ complex.[8]

We are, therefore, prompted to present our findings on the base hydrolysis of a nonelectrolyte cobalt(III) complex, I, where this "blind alley" does not complicate matters with alternative interpretations conforming to the observed rate law.

I was prepared by the reported method[9] and analyzed chemically for Co and NO_2^-. Anal. Calcd: Co, 23.8; NO_2^-, 55.6. Found: Co, 23.6; NO_2^-, 55.3. It has λ_{max} at 254, 348, and 440 nm with ϵ (molar extinction coefficient values) of 1.7×10^4, 4.93×10^3, and 28.5 L mol^{-1}/cm^{-1} respectively.[10] The reaction was followed at 348 nm on a Bausch & Lomb Spectronic 21 UVD spectrophotometer fitted with a thermostating jacket and using cuvettes of 1-cm path length. The determination of the effect of $[OH^-]$ on the reaction was carried out at 50 °C and at constant ionic strength of 0.1 M using $NaClO_4$–NaOH mixtures. The results of an average of three runs are collected in Table I.

The data clearly points to a deviation of k_{obs} from first-order dependence on $[OH^-]$ and show saturation kinetics (Figure 1). A plot of $1/k_{obs}$ v/s $1/[OH^-]$ gives a straight line with least-squares slope ($=k_2K_{hy}$) and definite positive intercept on the $1/k_{obs}$ axis ($=1/k_2$) (cf. Figure 2). The values of k_2 and K_{hy} so obtained (using a linear least-squares program on an IBM compatible PC XT) are $(1.0 \pm 0.02) \times 10^{-4}$ s^{-1} and 288 ± 20 M^{-1}.

The value of K_{hy} ($=K_a/K_w$) derived kinetically can be due to the ability of nitro group to vacate a p orbital on its nitrogen and form a pd π bond with d electrons of cobalt. The presence of a

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(3) Since we are interested in only this form of rate expression, the dependence on $[OH^-]$ as given by the expression[4] $k_{obs} = k_{OH}[OH^-] + k'_{OH}[OH^-]^2$ is not being considered.

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(7) Reference 1, pp 45, 84.

(8) Waysbort, D.; Navon, G. *Inorg. Chem.* **1979**, *18*, 9.

(9) Schlessinger, G. *Inorg. Synth.* **1960**, *6*, 189.

(10) The two isomers, meridional and facial, could not be isolated by ion-exchange chromatography.[11] Attempts to use gel filtration, too, failed.

(11) Kanazawa, S.; Shibata, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2424.

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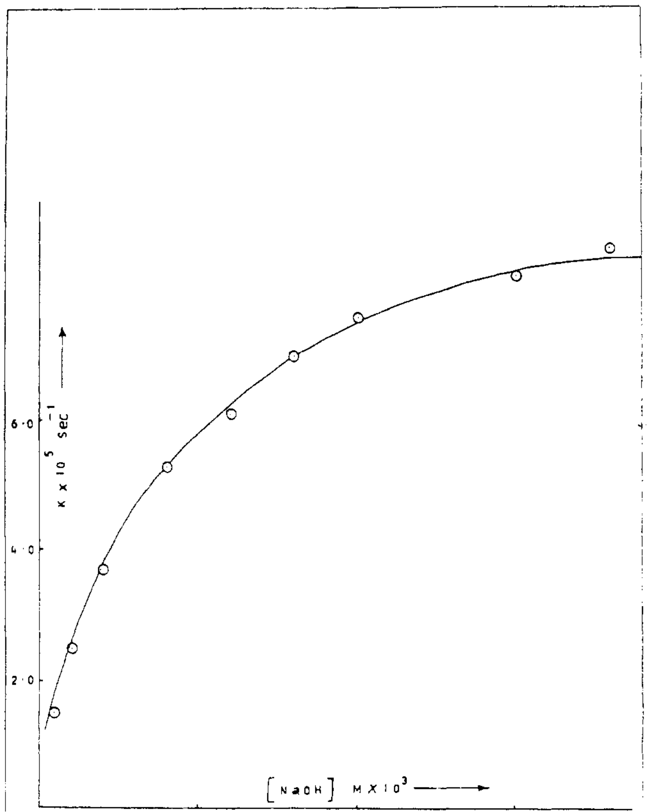

Figure 1. Plot of k_{obs} vs [NaOH] for base hydrolysis of $[Co(NH_3)_3(NO_2)_3]$. [complex] = 2.0×10^{-4} M at 50 °C.

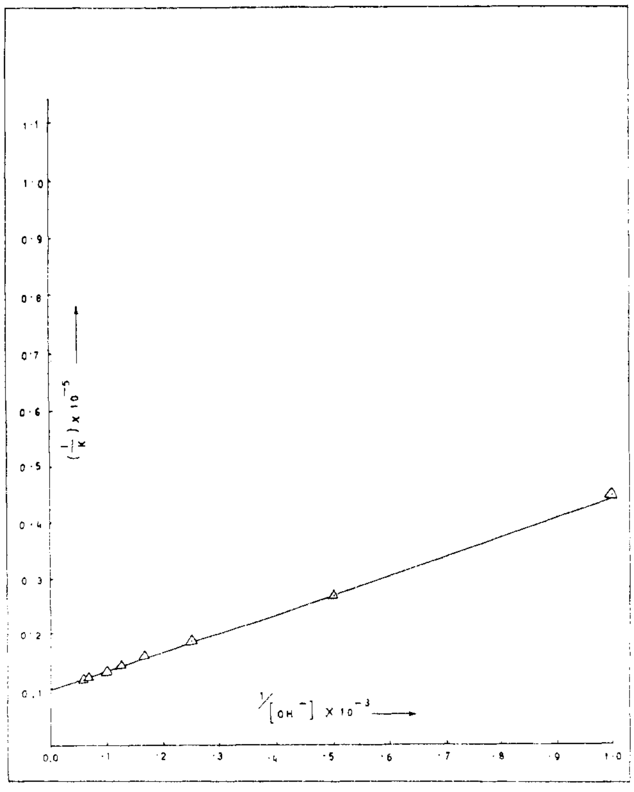

Figure 2. Base hydrolysis of $[Co(NH_3)_3(NO_2)_3]$ by NaOH presented as $1/k_{obs}$ vs $1/[OH^-]$. [complex] = 2.0×10^{-4} M at 50 °C.

π-bonding ligand in the complex would tend to stabilize the transition state $Co-NH_2\cdots H\cdots OH^-$ by enhancing the delocalization of the p electrons on the amido nitrogen.[12]

This clearly demonstrates the D_{cb} nature of the mechanism. Whether it is D(ish)cb or D_{cb} (or even Id(ish)cb) mechanism (in the purist's sense)[13] will be subject of detailed report on the base hydrolyses of other nonelectrolyte complexes of types $[Co(SCN)_3(NH_3)_3]$, $[Co(N_3)_3(NH_3)_3]$, and I.

Acknowledgment. Financial support from the University Grants Commission, New Delhi, is gratefully acknowledged.

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Received December 6, 1988

Stability Range of Heterometal Cubane-Type Clusters MFe_3S_4: Assembly of Double-Cubane Clusters with the $ReFe_3S_4$ Core

It is now apparent that the heterometal cubane-type clusters $[MFe_3S_4L_n]^z$ with anionic terminal ligands L (n = 3–5) and overall negative charge z = 1– to 4– exhibit a stability plateau at the 50–52e cores $[MFe_3S_4]^q$ (q = 1+ to 4+). Under the conditions of cluster assembly systems, which contain an Fe(II) or Fe(III) salt, $[VS_4]^{3-}$ or $[MS_4]^{2-}$ (M = Mo, W), and L = RS^- or halide, the heterometal is reduced, a portion of the iron reactant is reduced or oxidized, and the *isoelectronic* (51e) core oxidation levels $[VFe_3S_4]^{2+}$ [1,2] and $[MFe_3S_4]^{3+}$ [2-5] are formed without exception.[6] Oxidation levels differing by one electron are recoverable from these by redox reactions. Since the initial syntheses of $MoFe_3S_4$ and WFe_3S_4 clusters in 1978–80,[3,4] the stability range of MFe_3S_4 clusters has been tested only by the synthesis of those with M = V.[1,2] We report here a significant extension of this range, with implications for the stabilities of as yet unrealized clusters.

The findings that $[ReS_4]^-$ [9-11] in acetonitrile undergoes a chemically reversible one-electron reduction[12] at $E_{1/2} = -1.12$ V

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[6] When L = $R_2NCS_2^-$, a more highly oxidized core ($[MoFe_3S_4]^{5+}$) has been obtained;[7] this result is another manifestation of the stabilization of high oxidation states by dithiocarbamates. The compound $[(OC)_3MoFe_3S_4(SEt)_3]^{3-}$ [8] contains a more reduced core ($[MoFe_3S_4]^0$) but was not made by an assembly reaction of the above type. On a structural basis, this cluster is a weak complex between $[Fe_3S_4(SEt)_4]^{3-}$ and the $Mo(CO)_3$ fragment, whereas in other $MoFe_3S_4$ cubanes the Mo atom is tightly integrated into the core.[2-5]

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