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Nitrite Substitution on *cis*-Tetraamminediaquacobalt(III) Ion in HNO_2-NO_2^- Buffer Media

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Synopsis. The anation of the title complex by NO_2^- was followed spectrophotometrically. The anation proceeds in two steps. A simple second-order rate law applies to each step. No evidence has been furnished for the formation of any nitrito intermeidates.

Studies previously reported by Pearson *et al.*[1] showed that nitrite substitution reactions for pentaammineaquacobalt(III) and *cis*-aquabis(ethylenediamine)nitrocobalt(III) ions involve a nitrosation step followed by an intramolecular rearrangement to give stable nitro derivatives. Rates of the rearrangement reaction were found independent of the concentration of added nitrite. We report here some results from kinetic studies on reactions of *cis*-tetraamminediaquacobalt(III) ion with NO_2^-, which however has provided no evidence for *O*-nitrosation.

The formation of the dinitro complex was followed with a Pye-Unicam spectrophotometer SP8-150 by measuring the growth of its absorption maximum at 440 nm. Spectra of solutions which had ceased reacting were identical at nitrite concentrations exceeding *ca.* 0.04 M (1 M=1 mol dm^{-3}) at a given complex concentration (10^{-3} M) and agreed well with the spectrum of *cis*-tetraamminedinitrocobalt(III),[2] ensuring complete conversion to the product. Conventional pseudo-first-order plots of log $(A_\infty - A_t)$ *vs.* time (where A_t and A_∞ denote the absorbances at time$=t$ and ∞ respectively) gave curved plots, suggestive of a biphasic nature of the reaction (Fig. 1) based on replacement of two coordinated water molecules, and were resolved following Weyh and Hamm.[3] At a constant pH the reaction was first-order dependent on $[NO_2^-]$ in each of the steps (Table 1). Variation of pH in the region 4.0—6.04 had no measurable effect on the first-step reaction rate ($k^{I}_{obsd}=(1.43\pm0.04)\times10^{-3}\ s^{-1}$ at $[NO_2^-]=0.1$ M, temp $=40$ °C, and $I=0.2$ M). The rate of the second-step reaction also remained constant upto pH *ca.* 5.6 ($k^{II}_{obsd}=(1.17\pm0.02)\times10^{-4}\ s^{-1}$ under the identical conditions), but on going above this pH, k^{II}_{obsd} dropped by as much as 30%. Experimental runs above pH 6.04 could not be conducted since the complex was found to decompose to form a brown precipitate.

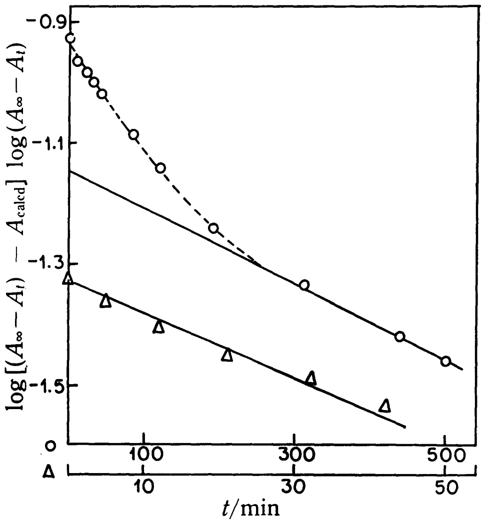

Fig. 1. A typical kinetic plot for the nitrite substitution of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$·[complex], 10^{-3} M; $[NO_2^-]$, 0.1 M; pH, (5.07±0.03); temp, 20 °C; *I*, 0.2 M ($NaClO_4$).
A_{calcd} at different times are extracted from the linear portion of the curve after extrapolation to zero time.

Except a few runs above pH 5.6, the anion and pH variation results are consistent with the rate law: rate$=k$[complex]$[NO_2^-]$. This simple rate law for the replacement of H_2O by NO_2^- is of some significance. In many $R_5\ Co(OH_2)^{3+}$–NO_2^- reactions[1,4] where R is an ammine, a nitrito intermediate is observed and the rate law assumes the form $-d[R_5Co(OH_2)^{3+}]/dt=k[\text{complex}][NO_2^-]^2[H^+]$. This is generally the case when the water exchange rate is low and the second-order rate dependence on $[NO_2^-]$ arises from the involvement of N_2O_3. In the present system no nitrito intermediate could be detected and the NO_2^- dependence caused no measurable deviation from the first-order dependence. It may be that under the conditions adopted no formation of nitrito intermediate actually occurs. This points to a different mechanism operating here which involves rupture of the cobalt-oxygen bond. The pK_1[5] of the diaqua species under investigation is 5.69 at 20 °C. On going above pH 4.4, formation of aquahydroxo species starts. The absence of any pH effect on the first-step reaction suggests that both the

TABLE 1. RATE CONSTANTS IN THE NITRITE SUBSTITUTION REACTION OF *cis*-TETRAAMMINEDIAQUACOBALT(III) ION AT 20 °C

$10^2[NO_2^-]$/M[a)]	$10^4\ k^{I}_{obsd}$/s^{-1}	$10^3\ k^{I}$/$M^{-1}\ s^{-1}$ [b)]	$10^5\ k^{II}_{(obsd)}$/s^{-1}	$10^4\ k^{II}$/$M^{-1}\ s^{-1}$
5	1.08	2.16	1.23	2.46
7	1.53	2.19	1.70	2.43
9	1.92	2.13	2.07	2.30
10	2.12	2.12	2.30	2.30
12.5	2.77	2.22	2.90	2.32
15	3.27	2.18	3.30	2.20
17.5	3.77	2.15	3.92	2.24
20	4.13	2.06	4.60	2.30

a) pH=(5.07±0.03) held constant with $[NaNO_2]/[HClO_4]=100$; [complex]$=1\times10^{-3}$ M; ionic strength$=$0.2 M ($NaClO_4$). b) Under the identical conditions, the second-order rate constants evaluated at 40 °C are $k^{I}=(1.35\pm0.10)\times10^{-2}\ M^{-1}\ s^{-1}$ and $k^{II}=(1.19\pm0.04)\times10^{-3}\ M^{-1}\ s^{-1}$.

diaqua and aquahydroxo species are kinetically indistinguishable with respect to the NO_2^- substitution. In the anation reaction of *trans*-$[Co(dmgH)_2(NO_2)(OH_2)]$ by NO_2^- ($dmgH^-$=dimethylglyoximate ion), Hague and Halpern[6] have shown two paths, one of which is pH independent (predominant at high pH) and the other pH dependent. The pH-independent path was shown to be first-order in $[NO_2^-]$. The pH-dependent path, though not studied in detail by the authors, has been presumed to be arising from attack of HNO_2 which apparently has stronger nucleophilicity than NO_2^-. The pH dependence on rate obtained for the mononitro species above pH 5.6 in our study may be attributed to the lower reactivity of the corresponding hydroxo species. The pK[5] (25 °C) of the second coordinated water in *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ is 8.0 and coordinated NO_2^- could have some effect for lowering this value significantly. This view is supported by known pK values[7] (25 °C) for closely comparable systems: 8.19 as the pK_2 of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ and 6.34 as the pK of *cis*-$[Co(en)_2(NO_2)(H_2O)]^{2+}$ (en=ethylenediamine).

Experimental

cis-Tetraamminediaquacobalt(III) perchlorate was prepared by the method described in the literature[8] and spectra of this compound matched well with those reported. Recrystallized sodium nitrite (AR grade) was used. Ionic strength was maintained with sodium perchlorate. Buffering was achieved by adding perchloric acid to sodium nitrite to a constant ratio.

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References

1) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954).

2) G. B. Kauffman, S. F. Abbott, S. E. Clark, J. M. Gibson, and R. D. Meyers, *Inorg. Synth.*, **18**, 69 (1978).

3) J. A. Weyn and R. E. Hamm, *Inorg. Chem.*, **8**, 2298 (1969).

4) R. K. Murmann and H. Taube, *J. Am. Chem. Soc.*, **78**, 4886 (1956).

5) G. Schwarzenbach, J. Boesch, and H. Egli, *J. Inorg. Nucl. Chem.*, **33**, 2141 (1971).

6) D. N. Hague and J. Halpern, *Inorg. Chem.*, **6**, 2059 (1967).

7) "Stability Constants of Metal-ion Complexes," ed by L. G. Sillen and A. E. Martell, The Chemical Society, London (1964), Special Publication No. 17, pp. 55, 56.

8) J. Springborg and C. E. Schaffer, *Inorg. Synth.*, **18**, 83 (1978).