

Kinetics and Mechanism of the Isotopic NO_2^- Exchange with *Trans*-dinitrobis-(2-amino-2-methyl-3-butanoneoximato)cobalt(III), $[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)]^0$, in Aqueous Media

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The rate of isotopic NO_2^- exchange of $[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)]^0$ with free NO_2^- in water solution has been shown to be first order with respect to the complex, independent of $[\text{NO}_2^-]$ and essentially pH independent. The half-life being about 16 hr at 40.0 °C. Both nitro groups are equivalent. The rate constant is unchanged over the pH range 5–8 and is without major ionic strength effects. Likewise $k_{(\text{exchange})}$ was unchanged in D_2O or pure methanol and visible light has no effect. With free Co^{2+} or amineoxime ligand present during exchange no change in rate was observed. The activation parameters for exchange are $\Delta H^\ddagger = 29.4 \text{ kcal mol}^{-1} \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = +13.0 \pm 0.1 \text{ cal K}^{-1} \text{ mol}^{-1}$. The results indicate that the mechanism of isotopic exchange is probably intramolecular and utilizes a reactive nitrito intermediate.

Introduction

Anion substitution for a nitro group on a cobalt(III) complex is usually quite slow and often requires exceedingly high acidities or high anion concentrations in order to obtain appreciable product concentration at equilibrium [1–7] in a reasonable length of time. Perhaps it is for these reasons that the mechanistic interpretation of the available kinetic studies is difficult and often ambiguous. The nitrito (M-ONO) complex may be an intermediate in the substitution process under certain circumstances since it is generally a relatively stable intermediate in the formation of nitro complexes from the aquo [8, 9]. It has been known for some time that both steric and electronic effects can cause increased anion lability of Co(III) complexes and perhaps also make mechanistic changes [10]. Both of these effects contribute to the ease of replacement of NO_2^- from the title complex. In this complex the less tightly held nitro groups allow more closely controlled experimental conditions and higher precision and accuracy in the kinetic results.

This study, an extension of some previous preliminary results [11], was initiated to gain an understanding of the mechanism of $-\text{NO}_2$ substitution on this Co(III) center in near neutral media. The complex is non-ionic, (Fig. 1), thus alleviating the difficulties with ion-pair effects, has convenient rates at moderate temperatures and has no tendency toward side reactions; *i.e.* substitution at the equatorial positions, *cis-trans* isomerism or oxidation–reduction. The *trans*-dinitro complex is known to rearrange very slowly, if at all, to the *cis*-form and that change can easily be detected due to the change in ionic charge resulting from the loss of the intramolecular hydrogen bond. Isotopic $^{15}\text{NO}_2^-$ substitution kinetics was studied because no net chemical change occurs, and the rate of substitution on the second nitro group would not be modified by the presence of a new *trans*-ligand.

Experimental

The non-ionic complex, *trans*- $[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)]^0$ was prepared by two independent methods; air oxidation of mixtures of NO_2^- , Co(II) and AO at a pH of 7 and from the *trans*-dichloro complex and excess NO_2^- . After recrystallization, the samples gave identical IR spectra, analysis and showed the same kinetic behavior as previous preparations.

Isotopic labeling with both ^{15}N or ^{18}O was accomplished by equilibration for 2–4 days at slightly elevated temperatures with labeled NO_2^- at a pH of about 6 followed by isolation and recrystallization from methanol–water solution. The NaNO_2 , normal and enriched, was recrystallized from methanol, dried under vacuum and weighed in the preparation of standard solutions. Water was double deionized utilizing a double-bed resin and buffering of reactant solutions was accomplished with reagent grade acetic acid, ammonia or redistilled 2,6-lutidine and appropriate acids.

TABLE I. Rate Constants for Exchange of NO_2^- with $[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)_2]^0$.

#	$10^3 [\text{Complex}]M$	$[\text{NO}_2^-]M$	pH	I	T °C	$10^5 k(\text{sec}^{-1})$	Special Conditions
1	2.06	0.100	6.8	0.100	40.0	1.16	
2	2.10	0.090	6.2	0.100	40.0	1.18	0.01 M NaOAc
3	2.11	0.086	7.3	0.097	40.0	1.15	0.01 M NaOAc
4	2.06	0.090	6.8	0.090	40.0	1.16	10^{-5} M in Co(II)
5	2.06	0.090	7.6	0.190	40.0	1.19	0.1 M NaOAc
6	2.05	0.050	6.4	0.050	40.0	1.18	
7	1.98	0.100	7.1	0.125	25.2	0.122	0.025 NaOAc
8	1.04	0.050	7.2	0.050	40.0	1.15	
9	2.10	0.100	8.0	0.110	40.0	1.19	0.01 M 2,6,-Lutidine
10	2.21	0.100	7.3	0.103	40.0	1.12	0.003 M AO•HCl
11	2.29	0.105	—	0.105	40.0	1.22	99.9% MeOH
12	2.35	0.106	—	0.106	40.0	1.13	99.5% D ₂ O
13	2.04	0.106	—	0.106	40.0	1.08	99.5% D ₂ O
14	2.61	0.102	6.9	0.102	40.0	1.11	Excess Light
15	3.02	0.125	6.8	0.125	60.0	21.6	
16	3.00	0.085	5.2	0.085	40.0	1.05	HClO ₄ added
17	2.45	0.090	9.0	0.101	40.0	1.39	0.017 M $\text{NH}_4^+\text{-NH}_3$
18	1.98	0.0051	6.9	0.0051	40.0	1.14	Low Ionic Strength
19	2.85	0.097	9.8	0.142	40.0	1.84	0.2 M $\text{NH}_4^+\text{-NH}_3$
20	2.12	0.103	6.1	0.603	40.0	1.20	0.50 M NaCl
21	4.08	0.120	5.0	0.141	40.0	1.23	0.028 HOAc Buffer

All reactions were carried out in closed containers in a water bath, (constant to 0.05°), under an inert atmosphere. The rates of NO_2^- exchange were followed with either ^{15}N or ^{18}O with the enrichment being either in the complex or in the free NO_2^- . The results were identical for all four situations. For practical reasons the majority of work was done with the excess isotope ^{15}N in the complex ion.

Isotope Exchange Kinetics

The required amount of ^{15}N enriched complex was dissolved in the appropriate temperature controlled solvent-buffer system and at time zero, NaNO_2 , either solid or in concentrated solution, added. Aliquots were removed at timed intervals and passed over a purified Dowex 1-X4 resin column in the chloride form. For those reactions which were relatively fast, the column was cooled during use. On the column, the NO_2^- (free) was replaced from solution with Cl^- and the complex passed through without holdup. This solution was reduced in volume to about 0.2 ml by roto-evaporation and the complexed NO_2^- group completely replaced by OH^- by the addition of NaOH solution with slight warming. The free NO_2^- which resulted was reacted with PO_4^{3-} -buffered N_3^- in an evacuated (10^{-5} mm) Y tube at pH 2 (^{15}N), 4 (^{18}O), the resulting N_2 removed and the N_2O (of the same ^{15}N content as the NO_2^-) purified and stored until measured on a NUCLIDE RMS mass spectrometer. The higher pH for the ^{18}O measurements prevented NO_2^- - H_2O exchange during

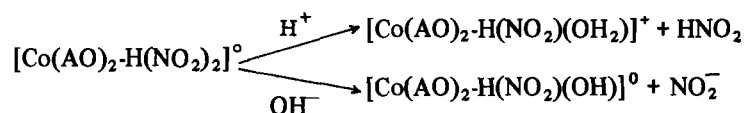
the conversion to N_2O . For ^{15}N measurement the 45/44 + 46 ratio was determined while for ^{18}O measurement, the 46/44 + 45 ratio was measured. Since the enrichments were quite low, (never greater than 2X normal abundance), these ratios were directly proportional to the atom mol-fraction. The loss or gain of the isotope as a function of time was mathematically evaluated by a weighted linear least-squares analysis giving the best fit to $-\ln(1 - F)$ vs. time data points. The observed first order rate constant was converted to the true rate constant [12] of exchange, k, by:

$$k = k_{\text{obs}} \cdot 2 [\text{NO}_2^-] / 2 [\text{complex}] + [\text{NO}_2^-]$$

An average of six points in addition to the origin and infinity value were used in the evaluation of k_{obs} and the standard deviation of it was about 1%. Replicate runs duplicated to $\pm 2\%$ at 40 °C.

Results

Unlike the simple, (*i.e.* NH_3 or en), *trans*-dinitroamine complexes of cobalt(III), this *trans*-complex (and some others of this series) has relatively labile nitro groups, and outside of a narrow pH range, come to equilibrium with a significant amount of free NO_2^- on either the acid or base side.



Experimental studies have established that less than 0.1% of the complex exists as a hydrolyzed species in the pH range 5–8 at 40 °C in the concentrations used. Obviously, the presence of excess NO_2^- used in these studies represses this dissociation, but it would be experimentally apparent as a zero-time exchange in a pH range much outside that given. The experimental zero-time exchange was consistently less than 1%.

The first main observation is that the McKay graphs were all highly linear for over 85% of the exchange. Thus within the estimate of error, the two nitro groups must have equivalent rates of exchange to within about 5% at 40 °C. This is in agreement with our preliminary results and different from the analogous PnAO^{11} complex where two widely differing rates are observed. A summary of the results of this study are given in Table I.

At 40 °C, in water, the rate constant for isotopic exchange is identical when measured by ^{18}O or ^{15}N transfer, thus the NO_2 group is transferred intact. This is in agreement with the ^{18}O transfer experiments on the reaction $[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)(\text{OH}_2)]^+ + \text{NO}_2^- \rightarrow [\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)_2]^0$ which show no incorporation of the Co-oxygen water into the coordinated nitro group. The rate constant is independent of $[\text{NO}_2^-]$ over a factor of 25 in concentration and is independent of $[\text{complex}]$ over a factor of four. It is independent of pH in the region 6–8, the mean value being $1.16 \pm 0.28 \times 10^{-5} \text{ sec}^{-1}$ with a range of $1.11\text{--}1.20 \times 10^{-5} \text{ sec}^{-1}$. No specific ionic atmosphere effects were found using HOAc , 2,6-lutidine, AO, or NH_3 with their conjugate salts as buffers. Ionic strength changes with NaCl showed no appreciable effect from $I = 0.005$ to 0.60 and visible light (intensity equivalent to 200 watt bulb at 12'') did not show an enhancement in the rate constant.

In D_2O , with no buffer, the rate constants found were within the range expected on the basis of experimental error alone. Even in 99.9% MeOH , the rate constant did not change appreciably. Finally, the presence of added $\text{Co}(\text{II})_{\text{aq}}$ or free AO ligand caused no change. It was not possible to check the kinetics in the presence of both $\text{Co}(\text{II})$ and AO and the resulting complex because NO_2^- oxidizes the metal ion to the parent complex. Isotopic exchange measurement in anhydrous DMSO was not possible due to simultaneous replacement of coordinated NO_2^- by DMSO .

In the high and low pH regions (Runs 16, 21, 17, 19) the complex was equilibrated at the appropriate temperature in the presence of NO_2^- for about a day before the exchange was initiated by the addition

of trace amounts of highly enriched NO_2^- or complex. Only the dinitro complex was isolated for ^{15}N content. Thus the exchange studied was between NO_2^- and all complex species present at equilibrium giving the dinitrocomplex. It is estimated that 1–2% of the aquonitro complex is present at pH 5 and as high as 5% of the hydroxonitro complex at pH 9.8 based on the estimates of the equilibrium constants from the PnAO system [11]. The average of the 16 and 20 values shows no enhancement of exchange rate in the more acidic region. However, runs 17 and 19 are consistent in indicating a significant enhancement in the rate constant in basic media.

Discussion

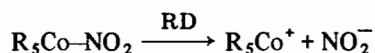
According to numerous X-ray crystal structures [13] of $\text{Co}(\text{III})$, $\text{Ni}(\text{II})$, and $\text{Cu}(\text{II})$ complexes of the AO s, the two *trans*-positions are not equivalent in the solid state. This was confirmed in solution by H-nmr studies of planar $\text{Ni}(\text{II})$ and octahedral $\text{Co}(\text{III})$ complexes. The present observation that the nitro groups have the same isotopic exchange rate ($\pm 5\%$) can be explained by either a rapid intramolecular inversion around the AO-amine nitrogen or by the insensitivity of the kinetic method to small differences between the nitro groups. At present, there is no means of distinguishing between these two alternatives.

For this complex, which has more labile NO_2 groups than the usual $\text{Co}(\text{III})$ complexes, the most important kinetic feature is the lack of any important ionic or solvent involvement. Neither acidity (over a moderate range), ionic strength, specific salts, visible light or a change in solvent from H_2O to D_2O or MeOH changes the intrinsic rate of exchange appreciably. One is inclined to suggest that this results primarily from the zero charge of the molecule. Very few kinetic studies on neutral complexes of $\text{Co}(\text{III})$ are available for comparison and to our knowledge none involve NO_2^- replacement. However, it is generally true that the effects of 'solution atmosphere' increase with the charge on the ion (other things being roughly equal).

A reasonable mechanistic possibility for facile exchange would be electron transfer between the $\text{Co}(\text{III})$ complex and $\text{Co}(\text{II})$ -AO complexes. Only traces of the latter need be present. However, since the exchange rate constant is not modified by excess $\text{Co}(\text{II})_{\text{aq}}$ or free AO we believe the $\text{Co}(\text{III})$ - $\text{Co}(\text{II})$ electron exchange is not responsible for the isotopic NO_2^- exchange observed.

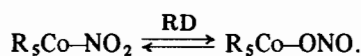
The results presented in this study are consistent with mechanisms where the molecule reaches the activated complex without substantial interaction with its 'solvent atmosphere'.

A reasonable suggestion is simple dissociation to a five coordinated intermediate which rapidly reacts with either solvent and then NO_2^- or with NO_2^- alone to complete exchange. However, the separation of charges,



would be expected to be strongly affected by the nature of the solvent and solvation energies of the ions and the simple breaking of the Co-N bond, without the compensating solvent interactions would require an extremely large activation energy.

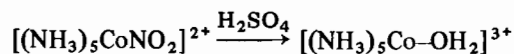
An alternate suggestion is that the rate determining step involves an intramolecular rearrangement to the nitrito species:



Such a reaction would require little separation of charges and a minimum of solvent involvement in reaching the activated state. To complete the exchange, the highly reactive nitrito complex would rapidly be replaced by solvent and then NO_2^- or by NO_2^- directly. Such steps would be expected to be quite rapid in the presence of free NO_2^- on the basis of the rapid water exchange rate of the Nitro-Aquo complex and the relative rapidity of its reaction [10] with NO_2^- . The inability to detect the nitrito complex is no doubt due to the thermodynamic weakness of the Co-O bond and its kinetic lability. These lead only to very low concentrations at any time during the exchange. The activation enthalpy and entropy changes are consistent with nitrito formation, but both values are somewhat higher than expected for such a rearrangement.

In a report on $[\text{Co}(\text{tetraMeen})_2(\text{NO}_2)_2]^+$, almost identical kinetic behavior was observed in roughly the same pH range. It is likely that the same mechanism for exchange is occurring, *i.e.* intramolecular rearrangement to the nitrito complex followed by rapid replacement by NO_2^- or solvent.

Of considerable interest is how this study relates to the usual amine type, *i.e.* $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$, complex. Insofar as NO_2^- isotopic exchange is concerned, only its relative slowness has been demonstrated. In substitution studies [4] however,



a large acid independent range was found with $k = 6 \pm 2 \times 10^{-7} \text{ sec}^{-1}$ at 25°C and above $\approx 50 \text{ wt.}\%$ H_2SO_4 a term first order in H^+ was observed. The mechanism postulated, based in part on ^{18}O transfer

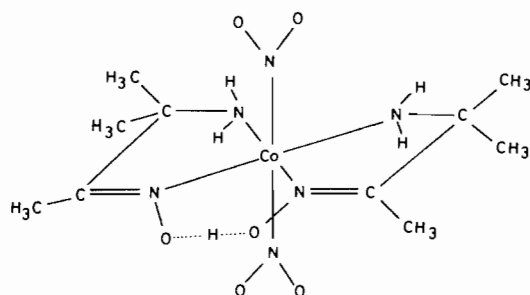


Fig. 1. Structure of $[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)_2]^0$.

studies, involved rearrangement to a protonated nitro complex as the rate determining step of the acid catalyzed term. It is not a long extension to visualize the acid independent term consisting of an internal rearrangement to the nitrito complex as we have suggested.

Other molecules showing similar behavior are the Co(III) dinitro complexes of EnAO and BnAO*. A comparison of the relative rates of NO_2^- exchange for these *trans*-complexes at 40°C is:

Complex	$k (\text{sec}^{-1}) (40^\circ)$
$[\text{Co}(\text{PnAO-H})(\text{NO}_2)_2]^0$	$1.2 \times 10^{-3}, 2.4 \times 10^{-5}$
$[\text{Co}(\text{EnAO-H})(\text{NO}_2)_2]^0$	9.1×10^{-3} (est.) (1.3×10^{-5} at 0° , 50% MeOH)
$[\text{Co}(\text{BnAO-H})(\text{NO}_2)_2]^0$	3.7×10^{-6} (30% MeOH)
$[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)_2]^0$	1.17×10^{-5}
$[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$	6×10^{-7}
$[\text{Co}(\text{tetraMeen})_2(\text{NO}_2)_2]^+$	9.8×10^{-5}

There appears to be a direct relationship between the bond distances between the metal and the 4-planar nitrogens and the isotopic NO_2^- exchange rate [14]. A study of the rates of NO_2^- exchange with *trans*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ as a function of 'solvent atmosphere' would seem highly desirable in order to understand the importance of the charge on the ion.

Summary

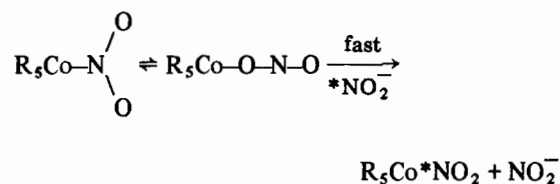
The kinetics of NO_2^- exchange with $[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)_2]^0$ in water or methanol follows the rate law:

*The abbreviations stand for: $\text{AO} = \text{HON}=\text{C}(\text{CH}_3)_2\text{-N}-$

EnAO = $\text{AO}-\text{CH}_2-\text{CH}_2-\text{AO}$, PnAO = $\text{AO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AO}$,

BnAO = $\text{AO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AO}$, tetra Meen = $\text{NH}_2-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-\text{NH}_2$.

$R = k[\text{Co}(\text{AO})_2\text{-H}(\text{NO}_2)_2]^0$. The rate is insensitive to 'solvent atmosphere'. It is suggested that the mechanism involves a slow intramolecular rearrangement to the nitrito complex followed by rapid replacement by solution NO_2^- .



The mechanism may be the major one operating with most Co(III) nitro complexes in the neutral region.

Acknowledgement

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