# The Oxidation of Water by Cobaltic Aquo Ions

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**Abstract:** The oxidation of water to oxygen by $Co(III)_{aq}$ has been investigated using $O^{18}$ as tracer. It has been shown that the oxidation reaction, which proceeds by inner-sphere ligand to metal electron transfer, involves the oxidation of a $Co(III)_{aq}$ dimer by a $Co_{aq}^{3+}$ ion. The $HO_2$ radical, which is being formed in the rate-determining step, is therefore the immediate precursor of molecular oxygen. $Co(III)_{aq}$ was shown to contain substantial amounts of dimers even in strongly acid solutions.

Cobaltic aquo ions in aqueous solution are known to oxidize water to oxygen. The kinetics of this reaction have been studied by several investigators;[1-3] however, the mechanism of this reaction has not been hitherto unequivocally elucidated.[4] Mechanisms proposed for this reaction have been based solely on kinetic evidence, on which conflicting information is available.[4] On thermodynamic grounds it may be inferred that the primary step of oxidation of water to oxygen by $Co(III)_{aq}$ does not involve a single electron transfer, as the reaction $Co(III)_{aq} + H_2O \rightarrow Co(II)_{aq} + OH + H^+$ has a positive free energy of about 24 kcal/mole.[5,6] An alternative primary product is hydrogen peroxide formed by the concerted reduction of two $Co(III)_{aq}$ ions. The kinetics of reduction of $Co(III)_{aq}$ by water as interpreted by Bawn and White[2] support a bimolecular pathway; however, no experimental evidence for the formation of $H_2O_2$ as a primary product of oxidation of water is available. A third possibility suggested by Baxendale in his interpretation of the kinetic data[3] is the formation of $HO_2$ as primary product by the oxidation of a $Co(III)_{aq}$ dimer by $Co_{aq}^{3+}$. This mechanism is thermodynamically more favorable than the former one by a $\Delta F$ of about 3 kcal/mole.[5,6]

Another open question is whether hydrogen peroxide or $HO_2$, if formed, are produced by an inner-sphere electron transfer from the ligand[7-9] or by an outer-sphere oxidation of the solvent molecules. By the use of $^{18}O$ as tracer, we were able to show that $HO_2$ is formed as primary product in the oxidation of water by $Co(III)_{aq}$ and that this reaction proceeds by an inner-sphere oxidation of water bound to the metal.

## Experimental Section

**Materials.** Oxygen-18 enriched water was supplied by the isotope separation plant of the Weizmann Institute of Science. It was distilled several times over alkaline permanganate in an all-glass still. $Co(ClO_4)_2$ (reagent grade, G. F. Smith Chemical Co., Columbus, Ohio) and hydrogen peroxide 50% (Analar grade, B.D.H.) were used. Triply distilled water was used throughout this study.

$Co(III)_{aq}$ solutions were prepared by electrolytic oxidation of 0.6 *M* $Co(ClO_4)_2$ in 6 *M* $HClO_4$ at 0°. The electrolysis (current density of 300 ma/cm²) was carried out in a cell consisting of a platinum anode inside a nonglazed ceramic vessel surrounded by a copper foil cathode. The solution was electrolyzed for 2 hr, *i.e.*, considerable time after the oxidation of Co(II) was complete. As soon as the electrolytic oxidation was stopped, the $Co(III)_{aq}$ solution was frozen in liquid nitrogen and kept as such until used. The Co(II) content of the Co(III) solutions prepared by this method is negligible.

$Co(III)_{aq}$ labeled with $^{18}O$ was prepared by the same method using $H_2{}^{18}O$ (~70 atom % $^{18}O$) as solvent.

**Methods.** One milliliter of the concentrated stock solution of $Co(III)_{aq}$ (0.6 *M*) enriched in $^{18}O$ was mixed under vacuum at room temperature (22-24°) with 20 ml of degassed, triply distilled water of natural $^{18}O$ content. Any oxygen dissolved, or formed in the $Co(III)_{aq}$ solution, was quantitatively removed before mixing by continuous pumping from the two solutions until the moment of mixing. The oxygen formed after mixing was completely pumped off by a Toepler pump at predetermined time intervals (3, 6, 10, 30, 120, and 360 min following time of mixing), and its isotopic composition was mass-spectrometrically analyzed. Masses 28 and 40 were also measured to check on air contamination. The experiments were repeated using $Co(III)_{aq}$ of natural $^{18}O$ content mixed with water enriched in $^{18}O$.

The experiments designed for detection of the intermediary formation of hydrogen peroxide were carried out as follows: 50 µl of 0.6 *M* $Co(III)_{aq}$ stock solution were injected through a serological cap into 250 ml of $10^{-4}$ *M* $H_2O_2$ solution, thoroughly degassed, and vigorously stirred. The isotopic composition of the solvent water was different from that of the coordination sphere of $Co(III)_{aq}$; the $H_2O_2$ was of natural isotopic composition. The acidity of the reaction mixture was preadjusted by NaOH to give a final pH of ~4. After the reaction was complete the molecular oxygen formed was pumped off for isotopic analysis. The solution was then thoroughly degassed, and the residual hydrogen peroxide was decomposed by injecting either a suspension of platinum black in water or a solution of ceric ions. The $O_2$ produced from the residual $H_2O_2$ was then analyzed for its isotopic composition.

## Results and Discussion

The working hypothesis of this study was that the oxidation of water by $Co(III)_{aq}$ proceeds by an inner-sphere electron transfer from the coordinated ligand water to the central ion. This hypothesis could be proven by demonstrating that the molecular oxygen formed originates from water molecules bound to the metal ion in the inner coordination sphere. Cobaltic ions are known to form substitution inert complexes.[10] The $Co(III)_{aq}$–$H_2O$ isotopic exchange has been estimated to be a relatively slow process[10] unless $Co(II)_{aq}$ ions are present; these may catalyze the water exchange by $Co(III)_{aq}$–$Co(II)_{aq}$ electron exchange.[11] It seemed plausible therefore that when the aquo complex of Co(III) labeled with $^{18}O$ reacts with $H_2{}^{16}O$, the rate of

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(1) A. A. Noyes and T. J. Dahl, *J. Am. Chem. Soc.*, **59**, 1337 (1937).

(2) C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 331 (1951).

(3) J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, **53**, 800 (1957).

(4) H. Taube, *J. Gen. Physiol.*, 49, 29 (1965).

(5) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1952, p 211.

(6) P. George in "Oxidases and Related Redox Systems," Vol. I, T. E. King, H. S. Mason, and M. Morrison, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, p 5.

(7) M. Anbar in "Mechanisms of Inorganic Reactions," Advances in Chemical Series, No. 49, American Chemical Society, Washington, D. C., 1966, p 126.

(8) F. P. Gortsema and J. W. Cobble, *J. Am. Chem. Soc.*, **81**, 5516 (1959).

(9) D. D. Thusius and H. Taube, *ibid.*, **88**, 850 (1966).

(10) H. Taube, *Chem. Rev.*, 50, 69 (1952).

(11) H. L. Friedman, H. Taube, and J. P. Hunt, *J. Am. Chem. Soc.*, 73, 4028 (1951).

**Table I.** Calculated and Experimental Values of the Isotopic Distribution of Oxygen in $O_2$ Evolved from $Co(III)_{aq}$ and Water

| % of Co(III) decomposed | Atom % $^{18}O$ | | | % mole fraction | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | $B$ | $C$ | $P$ | $x$ | $y$ | $z$ | $k$ | $l$ | $m$ | $\alpha$ | $f$ | $\beta$ | $g$ |
| 0–100 | 65 | 2.6 | 6.65 | 0.0677 | 0.829 | 3.08 | 2.86 | 88.81 | 4.37 | 0.053 | 12.03 | 11.27 | 0.39 | 0.34 |
| 0–20 | 63 | 2.6 | 16.5 | 0.229 | 3.14 | 10.69 | 9.10 | 73.10 | 3.90 | 0.051 | 5.22 | 5.14 | 0.63 | 0.60 |
| 20–39 | 63 | 2.6 | 6.49 | 0.0640 | 0.88 | 3.00 | 2.56 | 88.76 | 4.74 | 0.062 | 11.60 | 10.96 | 0.33 | 0.29 |
| 39–59 | 63 | 2.6 | 3.26 | 0.0109 | 0.149 | 0.508 | 0.433 | 93.83 | 5.01 | 0.066 | 17.03 | 16.32 | 0.091 | 0.065 |
| 59–89 | 63 | 2.6 | 2.77 | 0.0027 | 0.033 | 0.123 | 0.114 | 94.61 | 5.05 | 0.067 | 18.30 | 18.00 | 0.035 | 0.015 |
| 0–9 | 63 | 2.6 | 32.0 | 0.487 | 6.66 | 22.69 | 19.3 | 48.70 | 2.60 | 0.034 | 2.19 | 1.95 | 0.76 | 0.61 |
| 9–31 | 63 | 2.6 | 5.50 | 0.048 | 0.657 | 2.24 | 1.90 | 90.30 | 4.82 | 0.063 | 12.88 | 11.98 | 0.25 | 0.23 |
| 31–79 | 63 | 2.6 | 2.70 | 0.001 | 0.013 | 0.045 | 0.039 | 94.77 | 5.06 | 0.066 | 18.56 | 18.60 | 0.021 | 0.022 |
| 0–16 | 63 | 2.6 | 22.8 | 0.336 | 4.60 | 15.68 | 13.35 | 62.96 | 3.10 | 0.037 | 3.59 | 3.37 | 0.71 | 0.54 |
| 16–40 | 63 | 2.6 | 3.85 | 0.0239 | 0.327 | 1.11 | 0.95 | 92.60 | 4.56 | 0.055 | 16.39 | 16.04 | 0.18 | 0.16 |
| 40–72 | 63 | 2.6 | 2.47 | 0.0012 | 0.015 | 0.053 | 0.045 | 94.76 | 4.54 | 0.056 | 20.60 | 20.22 | 0.022 | 0.024 |
| 0–10 | 65 | 2.6 | 31.4 | 0.463 | 5.67 | 21.08 | 19.57 | 51.13 | 2.51 | 0.030 | 2.40 | 1.98 | 0.83 | 0.53 |
| 10–22 | 65 | 2.6 | 5.51 | 0.0497 | 0.608 | 2.26 | 2.098 | 90.52 | 4.45 | 0.054 | 13.58 | 19.41 | 0.32 | 0.053 |
| 22–78 | 65 | 2.6 | 2.52 | 0.0019 | 0.023 | 0.086 | 0.080 | 95.08 | 4.68 | 0.057 | 19.95 | 19.55 | 0.0003 | 0.018 |
| 0–8 | 33 | 2.0 | 17.8 | 0.509 | 22.83 | 22.49 | 5.54 | 47.18 | 1.93 | 0.019 | 2.87 | 2.72 | 0.22 | 0.20 |
| 8–13 | 33 | 2.0 | 11.0 | 0.291 | 13.08 | 12.88 | 3.17 | 68.10 | 2.78 | 0.028 | 5.18 | 5.00 | 0.20 | 0.18 |
| 13–63 | 33 | 2.0 | 2.20 | 0.0071 | 0.318 | 0.312 | 0.077 | 95.36 | 3.89 | 0.039 | 22.77 | 24.65 | 0.028 | 0.072 |
| 0–17 | 33 | 1.4 | 11.54 | 0.321 | 14.40 | 14.19 | 3.49 | 66.02 | 1.87 | 0.013 | 5.01 | 5.12 | 0.21 | 0.16 |
| 17–29 | 33 | 1.4 | 5.80 | 0.139 | 6.28 | 6.18 | 1.52 | 83.62 | 2.37 | 0.016 | 10.51 | 9.86 | 0.18 | 0.13 |
| 29–42 | 33 | 1.4 | 3.12 | 0.0535 | 2.40 | 2.36 | 0.582 | 92.00 | 2.61 | 0.017 | 18.90 | 18.20 | 0.12 | 0.092 |
| 42–77 | 33 | 1.4 | 1.51 | 0.0035 | 0.156 | 0.153 | 0.037 | 96.88 | 2.75 | 0.019 | 22.67 | 22.67 | 0.10 | 0.075 |
| 0–8 | 33 | 1.4 | 16.2 | 0.469 | 21.07 | 20.75 | 5.11 | 51.59 | 1.46 | 0.011 | 3.27 | 2.95 | 0.23 | 0.050 |
| 8–14 | 33 | 1.4 | 11.5 | 0.321 | 14.40 | 14.19 | 3.49 | 66.02 | 1.87 | 0.013 | 5.00 | 8.11 | 0.21 | 0.14 |

ligand oxidation might compete with that of ligand exchange resulting in the formation of molecular oxygen partly labeled with $^{18}O$. To check on these assumptions we have treated $^{18}O$ labeled $Co(III)_{aq}$ with $H_2{}^{16}O$ and determined the $^{18}O$ content of the oxygen formed. As there are no reliable data available on the rate of the $Co(III)_{aq}$–$H_2O$ isotopic exchange, it was impossible to predict the relative rates of isotopic exchange *vs.* oxidation of water *a priori.*

It has been found that $(6.65 - 2.6)/65 = 6.2\%$ of the oxygen evolved originates from the inner coordination sphere of $Co(III)_{aq}$. This result could be interpreted in two ways: either that 6.2% of the reaction proceeds by an inner-sphere oxidation mechanism and the rest by an outer-sphere process, or that all the oxygen formed originates from the ligand water but that an over-all average of 93.8% of the ligand $H_2{}^{18}O$ has exchanged with the solvent before oxidation. The second interpretation seems to be much more plausible in view of the $^{18}O$ content of $O_2$ collected in successive fractions during the reaction of $Co(III)_{aq}$ with water (Table I). It may be seen that, whereas the first fraction collected contains up to half of the oxygen originating from the inner sphere, the last fractions collected have an isotopic composition identical with that of the solvent. These findings show that the relatively low yield of $^{18}O$ in the molecular oxygen formed is due to $H_2O_{solvent}$–$H_2O_{ligand}$ isotopic exchange, and that it is very likely that all the oxygen evolved originates from the inner sphere of hydration. It is experimentally hard to sample oxygen at the very early stages of $Co(III)_{aq}$ decomposition, which could allow the isotopic composition of the evolved oxygen at time zero to be obtained. Thus a small contribution (<5%) of an outer-sphere mechanism cannot be completely excluded.

In view of the competition between the ligand exchange and ligand oxidation it was of interest to examine the exact isotopic distribution of $^{18}O$ in the oxygen molecules produced. We have examined therefore the isotopic distribution of $^{18}O$ between $^{18,18}O_2$ and $^{16,18}O_2$ and found it to be far from the statistical: $[^{16,18}O_2]^2/[^{18,18}O_2][^{16,16}O_2] = 4.$[12] If the $O_2$ formed originated from *two* $Co(III)_{aq}$ ions labeled with $^{18}O$, the oxygen should contain $^{18,18}O_2$. However, in view of the extensive isotopic exchange, it seemed improbable that $^{18,18}O_2$ would be formed in any appreciable amount if the oxygen originated from the reaction between two separate $Co(H_2O)_6{}^{3+}$ ions. On the other hand, if the $^{18,18}O_2$ would originate from $H_2{}^{18}O$ labeled $Co(III)_{aq}$ in a chemical form which does not readily undergo isotopic exchange with the solvent, one could calculate the isotopic distribution of $^{16,16}O_2$, $^{16,18}O_2$, and $^{18,18}O_2$ assuming that the evolved $O_2$ originates from *two* sources: $O_2$ labeled with $^{18}O$ formed from the labeled $Co(III)_{aq}$ exclusively and the rest of the $O_2$ from the water exclusively. Following this assumption the mole fractions of $^{16,16}O_2$ ($x$), $^{16,18}O_2$ ($y$), and $^{18,18}O_2$ ($z$) originating from the $Co(III)_{aq}$ containing an atom fraction $A = (0.5y + z)/(x + y + z)$ of $^{18}O$ are in isotopic equilibrium, *i.e.*, $y^2/xz = 4$. Analogously the molar fractions $^{16,16}O_2$ ($k$), $^{16,18}O_2$ ($l$), and $^{18,18}O_2$ ($m$) of oxygen originating from solvent contain an atom fraction $B$ of $^{18}O$ ($B = (0.5l + m)/(k + l + m)$ and $l^2/mk = 4$). The oxygen formed is a mixture of molecules originating from the two sources and contains an atom fraction $C$ of $^{18}O$: $C = (0.5y + 0.5l + z + m)/(x + y + z + k + l + m)$, and, as $x + y + z + k + l + m = 1$, $C = 0.5(y + l) + z + m$. If one defines the mole fraction of $O_2$ originating from the $Co(III)_{aq}$ as $P = x + y + z$, then $C = AP + B(1 - P)$ or $P = (C - B)/(A - B)$. From these equations one may derive that $x = P(1 - A)^2$; $y = 2AP\cdot(1 - A)$; $z = PA^2$; $k = (1 - P)(1 - B)^2$; $l = 2B(1 - B)(1 - P)$; $m = (1 - P)B^2$. Thus the values of the ratios $\alpha = {}^{16,16}O_2/{}^{16,18}O_2 = (x + k)/(y + l)$ and $\beta = {}^{18,18}O_2/{}^{16,18}O_2 = (z + m)/(y + l)$ could be calculated on basis of the measured values of $A$, $B$, and $C$ and

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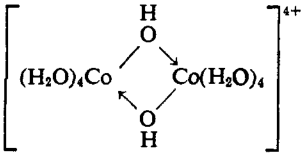
(12) F. Z. Roginsky, "Theoretical Principles of Isotope Methods for Investigating Chemical Reactions," Academy of Sciences, U.S.S.R. Press, Moscow, 1956.

compared with the ratios between the masses ${}^{16,16}O_2$ ($\overline{32}$), ${}^{16,18}O_2$ ($\overline{34}$), and ${}^{18,18}O_2$ ($\overline{36}$) experimentally determined by the mass spectrometric analysis of the evolved gas. $f = (\overline{32})/(\overline{34})$ and $g = (\overline{36})/(\overline{34})$. The results presented in Table I show a satisfactory agreement between the calculated values of $\alpha$ and $\beta$ and the experimental values of $f$ and $g$, respectively. Thus the assumption that the oxygen formed is a mixture of two types of oxygen molecules with practically no isotopic equilibrium between them has been verified. As the value of $\overline{36}$ was much smaller than $\overline{32}$ and $\overline{34}$, the accuracy of $g$ is smaller than that of $f$. Consequently the agreement between $\alpha$ and $f$ is evidently better than between $\beta$ and $g$.

The only explanation of these results we are able to offer is the following. Oxygen is formed from binuclear complexes of $Co(III)_{aq}$ and these oxygen molecules originate exclusively from their inner hydration sphere. The $Co(III)_{aq}$ solution (0.6 $M$ in 6 $M$ $HClO_4$) contains a certain percentage (<3.1%) of dimers having most probably the structure

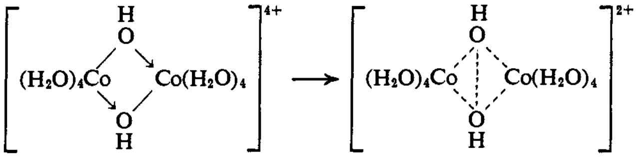


$= [(H_2O)_4CoOH]_2^{4+}$

in addition to monomeric $Co(H_2O)_6^{3+}$ ions. The formation of $O_2$ from $Co(III)_{aq}$ requires 4 equiv of Co(III), two of which have to be in a dimeric form. Thus the finding of 6.2% of nonequilibrated oxygen implies the existence of $\geqslant$3.1% nonequilibrated dimers introduced into the dilute solution. If one assumes that the equilibrium $Co(H_2O)_5OH^{2+} \rightleftharpoons$ dimer is strongly shifted to the right, then the concentration of the dimer will be approximately equal to that of $Co(H_2O)_5OH^{2+}$. The equilibrium constant for $Co(H_2O)_6^{3+} \rightleftharpoons Co(H_2O)_5OH^{2+} + H^+$ has been found to be 0.22 ± 0.05.[13] From this value one may derive the concentration of dimers in 6 $M$ $HClO_4$ to be $\leqslant$3.5%, in good agreement with our findings. These dimers yield oxygen before undergoing isotopic exchange with the solvent. The monomeric $Co(H_2O)_6^{3+}$ has to undergo dimerization before yielding $O_2$. However, the rate of water exchange of $Co(H_2O)_6^{3+}$ is faster than the rate of dimerization; thus the coordination sphere of the newly formed dimers, and consequently the $O_2$ formed from them, will be in isotopic equilibrium with the solvent. If some of the dimers present in the concentrated solution of $Co(III)_{aq}$ undergo cleavage to give monomers, the latter will undergo complete isotopic exchange with the solvent before reacting to give a dimer again. The rapid exchange of the monomers is most probably catalyzed by the Co(II)–Co(III) electron exchange.[11]

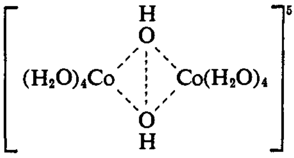
The existence of polynuclear species higher than dimers in our solution cannot be excluded. It is, however, unlikely that these exist in 6 $M$ $HClO_4$, and as their rate of formation is a rather slow process (*cf.* aging processes in Fe(III) or Al(III) solutions), their contribution to the over-all oxidation of water by Co(III) under our experimental conditions may be neglected.

The mechanism of oxidation of the ligand in the dimeric $Co(III)_{aq}$ remained an open question. Two alternative mechanisms are possible. (a) One is the intramolecular conversion of the dimeric complex of Co(III) into a binuclear peroxy complex of Co(II)



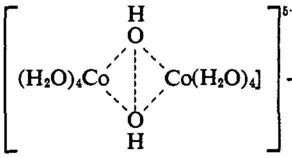
followed by hydrolysis of the cobalto peroxide to $H_2O_2 + 2Co(II)$. The following steps would then be $H_2O_2 + Co(H_2O)_6^{3+} \rightarrow Co(H_2O)_6^{2+} + H^+ + HO_2$ and $HO_2 + Co(H_2O)_6^{3+} \rightarrow Co(H_2O)_6^{2+} + O_2 + H^+$. (b) The other is an attack of $Co(H_2O)_6^{3+}$ on the dimeric aquo cobaltic complex

$[(H_2O)_4CoOH]_2^{4+} + Co(H_2O)_6^{3+} \longrightarrow$



$+ Co(H_2O)_6^{2+}$

followed by the formation of $HO_2$ radical



$\longrightarrow 2Co(H_2O)_6^{2+} + HO_2$

followed by either $HO_2 + Co(H_2O)_6^{3+} \rightarrow O_2 + Co(H_2O)_6^{2+} + H^+$ or $2HO_2 \rightarrow H_2O_2 + O_2$.

As we know from the kinetic behavior of the $Co(III)_{aq}$ oxidation of water, the rate of this reaction is proportional to $[H_3O^+]^{2-}$ which is implied in the preequilibrium: $2Co(H_2O)_6^{3+} \rightleftarrows [(H_2O)_4CoOH]_2^{4+} + 2H^+$.[14] As we have shown, $Co(III)_{aq}$ dimers exist even in 6 $M$ $HClO_4$ solution; consequently, in less acid solution, *e.g.*, <0.01 $N$ $H^+$, practically all $Co(III)_{aq}$ will be in the dimeric form.

In order to decide between the two mechanisms, we have carried out a series of experiments in which $Co(III)_{aq}$ reacted with water in the presence of $H_2O_2$. We had to choose conditions where the rate of the $Co(III)_{aq}$–$H_2O$ reaction competes with the Co(III)–$H_2O_2$ oxidation reaction. The kinetic information available for both reactions[3] indicates that only at low acidities and high dilutions of $Co(III)_{aq}$ has the ligand oxidation a chance to compete with the $H_2O_2$ reaction. Accordingly we chose pH 4 and $[(Co(III)_{aq}] = 10^{-4}$ $M$ as the appropriate experimental conditions. Using $Co(III)_{aq}$ and $H_2O$ of different isotopic composition from that of $H_2O_2$, it was possible to examine by isotope dilution the amount of hydrogen peroxide formed as intermediate in the oxidation of water. The results presented in Table II show that under the experimental conditions some oxidation of water by $Co(III)_{aq}$ took place in spite of the efficient competitive reaction of $Co(III)_{aq}$ with $H_2O_2$; moreover, some hydrogen peroxide produced from the $Co(III)_{aq}$ and from water could be detected in the residual $H_2O_2$. From a quantitative evaluation of the results, one could determine

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(13) T. J. Conocchioli, G. N. Nancollas, and N. Sutin, *Inorg. Chem.*, 5, 1 (1966).

(14) An $OH^-$ induced $S_N2$ hydrolysis of the cobalto peroxide formed according to the first mechanism or of the complex formed by the second mechanism may be excluded in view of the measured rates and the steady-state concentration of $OH^-$ ions in the range of acidities investigated.

**Table II.** The Isotopic Composition of Oxygen and Hydrogen Peroxide Formed from $Co(III)_{aq}$ in the Presence of Hydrogen Peroxide[a]

| Atom % $^{18}O$ in | | | |
|---|---|---|---|
| $H_2O$ | $Co(III)_{aq}$ | Evolved $O_2$ | Residual $H_2O_2$ |
| 0.213 | 63.0 | 1.71 ± 0.30 | 0.402 ± 0.03 |
| 25.2 | 0.200 | 0.54 ± 0.06 | 0.311 ± 0.04 |
| 25.2 | 63.0 | 2.48 ± 0.42 | 0.432 ± 0.04 |

[a] $[Co(III)_{aq}] = 1.10^{-4}$ *M*; $[H_2O_2] = 2.10^{-4}$ *M*; $^{18}O$ content of $H_2O_2$ = 0.2 atom %.

the mole fractions of $O_2$ and $H_2O_2$ which originate from the $Co(III)_{aq}$ and from water, respectively.

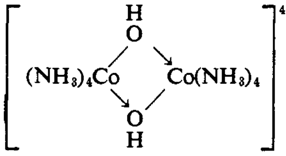
As we have carried out these experiments with $Co(III)_{aq}$ and $H_2O$ of different isotopic composition (Table II), the contribution of each pathway could be determined by solving three simultaneous linear equations with three unknowns. From the composition of the evolved oxygen, it was calculated that under the experimental conditions 2.3 ± 0.4% of the oxygen is formed from the $Co(III)_{aq}$ (*i.e.*, from the dimers present in the original $Co(III)_{aq}$ solution; see above), and 1.4 ± 0.3% originates from the water. This means that in the presence of $H_2O_2$ about 60% of the oxygen originates from the isotopically (nonequilibrated) dimers and only 40% from secondary dimers, compared with 16.2 *vs.* 93.2% in pure water. This result is not surprising if one assumes that the rate of reaction of $Co(H_2O)_6^{3+}$ with $H_2O_2$ is considerably faster than that of the $Co(III)_{aq}$ dimer, which may undergo ligand oxidation before being reduced by $H_2O_2$ in solution.

The analysis of the residual $H_2O_2$ data shows that 0.3 ± 0.1% of the $H_2O_2$ originates from the $Co(III)_{aq}$ and 0.2 ± 0.1% from the water. The latter results indicate that $H_2O_2$ is *not* the precursor of the oxygen evolved. If $H_2O_2$ would be the only intermediate in the formation of $O_2$ as required by mechanism a, one would expect to find much more $H_2O_2$ originating from the $Co(III)_{aq}$-$H_2O$ reaction in the residual $H_2O_2$ than in the evolved oxygen. The small amounts of labeled $H_2O_2$ detected are most probably due to the secondary reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, which is unfavored in the presence of $H_2O_2$ and of $Co(H_2O)_6^{3+}$.

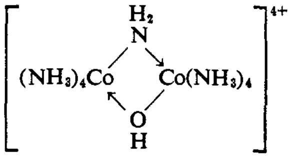
Our results exclude the formation of an O–O bond in the dimer prior to its being attacked by $Co(H_2O)_6^{3+}$. If the cobaltic dimer would undergo spontaneous intramolecular conversion to a cobalto peroxide complex, the latter would undergo rapid hydrolysis, owing to the substitution lability of Co(II), and release $H_2O_2$.

From the tracer experiment described here one may reach the following conclusions. (1) $O_2$ is formed from $Co(III)_{aq}$ and water only *via* dimers. (2) The formation of oxygen involves the reaction of these dimers with $Co(H_2O)_6^{3+}$ resulting in the formation of $HO_2$ as intermediate. If the latter process is the rate-determining step, one would expect the rate at low acidity to be proportional to $[Co(III)_{aq}]^{1/2}$. Such a kinetic behavior has been actually observed,[3] and the results were interpreted by the same mechanism. We have thus corroborated the mechanism suggested by Baxendale and Wells which has been challenged[4] for lack of supporting evidence. (3) $Co(III)_{aq}$ contains substantial amounts of dimers even in concentrated acid solutions. In less acid solution $Co(III)_{aq}$ is predominantly in the dimeric form.

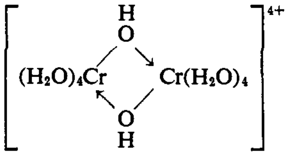
The formation of dimeric aquo or hydroxo complexes of Co(III) should not be surprising in view of the existence of other binuclear Co(III) complexes such as[15,16]



or



or of analogous Cr(III) binuclear complexes[17]



It is interesting to note that the oxidation of substituted Co(II) complexes, *e.g.*, $[Co(NH_3)_5H_2O]^{2+}$ [18] or $[Co(CN)_5H_2O]^{3-}$,[19] by molecular oxygen produces binuclear peroxy complexes of the type $[(NC)_5Co(O_2)Co(CN)_5]^{6-}$ or $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$, which may be further oxidized to $[(NC)_5Co(O_2)Co(CN)_5]^{5-}$ and $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$, respectively.[20] These complexes are most probably closely related with the intermediate postulated in this study.

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[15] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Van Nostrand Co. Inc., Princeton, N. J., 1960, p 164.

[16] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, pp 727-688.

[17] R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, 3, 322 (1964).

[18] E. Fremy, *Ann. Chem.*, 83, 227 (1852).

[19] A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc*, 83, 509 (1961).

[20] For reviews on this subject, *cf.* G. L. Goodman, H. G. Hecht, and J. A. Weil in Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 90; and also J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, 6, 279 (1964).