of $RhCl_3(C_3H_5NH_2)_2$ in ethanol at 50°. The bands at 930 cm^{-1} (δ_{CH}), 990 cm^{-1} (δ_{CH}), and 1648 cm^{-1} ($\nu_{C=C}$) decreased with the reaction time, and the carbonyl stretching band (ν_{CO} 1720 cm^{-1}) appeared. This suggests that a carbonyl compound which is derived from allylamine coordinates to rhodium(III). The bands at 1630 and 3200 cm^{-1} indicate the coordinated ammonia. This compound is insoluble in solvents and further characterization was unsuccessful.

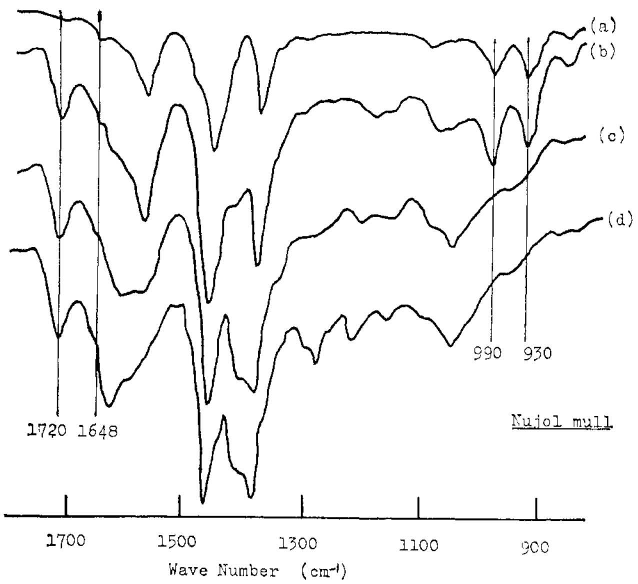

Figure 1.—Infrared spectra of the reaction product from bis(allylamine)rhodium(III) chloride at 50° in ethanol. Reaction time: (a) zero, (b) 10 min, (c) 30 min, (d) 60 min.

The coordination of the double bond to rhodium(III) in an intermediate state may be necessary for the reaction of coordinated allylamine. In the complexes $RhCl_3(C_3H_5NH_2)(H_2O)$ and $RhCl_3(C_3H_5NH_2)_2$, the coordination of the double bond to rhodium(III) after the breakdown of the bridging of chloride ion is considered to occur in an intermediate state. After π-complex formation, hydride transfer and amino group transfer occur. A hydride-transfer reaction with subsequent hydrolysis gives acrolein and propionaldehyde. An amino group transfer reaction causes the formation of propylene (Scheme I). In case of the rearrangement of allyl alcohol catalyzed by rhodium trichloride, a similar hydride transfer and hydroxide transfer have been reported.[8,9] *N*-Propylideneallylamine is obtained from propionaldehyde and allylamine.[10]

The complexes $RhCl_3(C_3H_5NH_2)_3$ and $[RhCl(C_3H_5NH_2)_5]Cl_2$, in which chloride ion and amino groups occupy all of the coordination sites and prevent the double bond from coordination, do not react under the above conditions. However, hydrochloric acid reacts with coordinated allylamine to give allylammonium ion and the coordination of the double bond becomes possible in an intermediate state and reaction occurs

$$L_5RhNH_2CH_2CH{=}CH_2 \xrightarrow{+H^+} L_5Rh(CH_2{=}CHCH_2NH_3^+) \rightsquigarrow \text{propionaldehyde, acrolein, propylene}$$

(L = Cl and allylamine)

---

[8] J. K. Nicholson and B. L. Shaw, *Proc. Chem. Soc., London,* 282 (1963).

[9] R. I. Rinehart and R. E. Fuest, *Chem. Eng. News,* **43**, No. 7, 40 (1965).

[10] R. Tiollais, *Bull. Soc. Chim. Fr.,* **14**, 708 (1947).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MISSOURI, COLUMBIA, MISSOURI 65201

On the Existence of Binuclear Aquocobalt(III) Perchlorates. Oxygen-18 Studies

BY R. KENT MURMANN

Received July 22, 1970

Several lines of conflicting evidence appear in the literature concerning the species present in acidic aqueous cobalt(III) perchlorate solutions. The main questions are as follows. (a) What is the value of the first hydrolysis constant ($\sim10^{-3}$ or 10^{-1})? (b) What is the thermodynamic stability and the composition of binuclear, hydroxy-bridged species? (c) What is the magnitude of the velocity of reaction relating these ions?

A recent review[1] summarized the lines of evidence on these topics. The strongest evidence for the existence of di-μ-hydroxy-bridged cobalt(III) dimers in 1–6 *M* $HClO_4$ comes from ^{18}O experiments[2] where the molecular oxygen derived from the oxidation of water by Co^{3+} apparently comes partially from the inner, nonsolvent-equilibrated coordination sphere of the metal ion. In the initial part of the reaction it approaches 50% and overall comprises about 6% of the oxygen contained. It is known, however, that the Co^{2+}–Co^{3+} electron exchange is rapid,[3] that the Co^{2+} water exchange is very rapid,[4] and that Co^{3+} solutions invariably contain significant quantities of Co^{2+}.[4,5]

Thus, one expects the apparent water-exchange rate to be rapid, faster than the relatively slow rate of water oxidation under the usual concentration conditions. An early study[4] of the water-exchange rate of $Co(H_2O)_6^{3+}$ showed complete exchange in about 2 min at 0°. However, only *ca.* 50% of the cobalt was in the higher oxidation state and, as was pointed out, the presence of Co^{2+} would be expected to increase the apparent rate. It is significant, however, that no oxygen holdback was observed in this study.

The explanation of the ^{18}O data[2] from the oxidation of water by Co(III) assumed the presence of di-μ-hydroxy-bridged species in which the OH groups are relatively nonlabile, that K_{eq} for the formation of the bridged species from the hydroxy monomer is large, and that molecular oxygen is derived from the bridging groups. Further it was suggested on the basis of the nonstatistical distribution of ^{18}O in the molecular oxygen that both oxygens came from the same ion.

While qualitatively consistent with several types of data, the suggestion that appreciable concentrations of dimers exist in 0.6 *M* Co^{3+} and 6 *M* $HClO_4$ requires an abnormally large K_{eq} of hydrolysis and/or a very favorable dimerization constant. Evidence has been mounting that these dimers do not have such a high thermodynamic stability.[6] However, the isotopic experiments, if correct, are so definitive that they cannot

---

[1] G. Davies and B. Warnquist, *Coord. Chem. Rev.,* in press.

[2] M. Anbar and I. Pecht, *J. Amer. Chem. Soc.,* **89**, 2553 (1967).

[3] S. A. Hoshowsky, O. G. Holmes, and K. J. McCallum, *Can. J. Res.,* **27** (4), 254 (1949).

[4] H. L. Friedman, H. Taube, and J. P. Hunt, *J. Chem. Phys.,* **18**, 759 (1950).

[5] D. W. Weiser, Ph.D. Thesis, The University of Chicago, 1956.

[6] B. Warnquist, *Inorg. Chem.,* **9**, 682 (1970).

TABLE I

$4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + O_2 + 4H^+$

Run no.	% decompn	$[Co^{3+}]_0$, M	$[H^+]_0$,[e] M	$[Co^{3+}]$,[a] %	$[Co^{3+}]$, M	$[H^+]$,[b,e] M	$R_N(O_2)$[c]	$R_N(H_2O)$[c]	$[O_2]/[H_2O]$	$[O_2]/[H_2O]$[i]
2	100	0.11	2.3	97	0.083	1.72	0.013801	0.013880	0.9943	0.9581
3	100	0.11	2.3	97	0.073	1.53	0.016809	0.016881	0.9957	0.9540
4	100	0.34	4.62	99	0.23	3.08	0.017144	0.017000	1.0085	0.9548
5[f]	100	0.34	4.62	99	0.23	3.08	0.016980	0.016895	0.0050	0.9549
6[d]	100	0.34	4.62	99	0.17	2.31	0.004225	0.004270	0.9895	...
7	100	0.67	5.21	94	0.45	3.48	0.023900	0.023960	0.9975	0.9505
8	100	0.67	5.21	94	0.45	3.48	0.023922	0.023942	0.9992	0.9505
9	50	0.052	2.35	95	0.039	1.76	0.013715	0.013670	1.0033	0.9584
10[j]	95	0.243	2.97	93	0.162	1.98	0.015785	0.015740	1.0029	0.9559
11	51	0.255	3.30	98	0.170	2.20	0.015832	0.015815	1.0011	0.9559
12[g]	61	0.262	3.41	98	0.175	2.26	0.015607	0.015655	0.9969	0.9561
13[h]	100	0.732	5.81	65	0.49	3.87	0.017190	0.016910	1.0166	0.9548
14[d]	100	0.27	5.01	100	0.14	2.50	0.004234	0.004293	0.9863	...
15[h]	100	0.703	4.21	99	0.466	2.80	0.016921	0.016941	0.9988	0.9548
16[h]	100	0.685	5.10	100	0.456	3.40	0.016224	0.016344	0.9927	0.9554

[a] Apparent per cent Co(III) based on ϵ_{602} 35.3 and ϵ_{480} 3.68. [b] H_2O enriched 8.3 times was used except where noted. [c] 34/(32 + 33) standard oxygen gave a value of 0.004181. [d] Normal water used. [e] As $HClO_4$. [f] Solutions degassed separate. [g] Degassed by pumping not by freezing. [h] Degassed but O_3 not removed. [i] Calculated—see text. [j] Copper anode used in preparation as in ref 2.

be discounted. Thus, reinvestigation of the ^{18}O-transfer studies occurring on oxidation of water by Co(III) seemed necessary.

It was noted that ozone was generated in appreciable quantities when Co^{3+} was prepared electrolytically at high $[Co^{3+}]$ and $[HClO_4]$. Potentially its presence could be responsible for the effects seen by Anbar and Pecht and attributed to binuclear species. However, as seen later, the amount of O_3 as estimated from its solubility and determined by direct measurement is too small to be responsible for the previously reported effects. This paper reports the results of work designed to determine if ^{18}O results from the oxidation of water by Co_{aq}^{3+} demand binuclear complexes in ~1-6 M $HClO_4$ solution. It, therefore, also has a bearing on the validity of the mechanism proposed[7] for water oxidation by Co(III).

Experimental Section

Stock solutions of cobalt(II) perchlorate were prepared from the hydrated solid which was recrystallized three times from about 2 M $HClO_4$. Two sources were used: $CoCO_3 + HClO_4$ and $CoCl_2 \cdot 6H_2O$ exhaustively boiled with concentrated $HClO_4$ until all Cl^- was gone. Both sources showed identical properties before and after conversion to Co(III). Solutions of Co(III) were prepared electrolytically with large-gauze platinum electrodes (except where noted) in a cooled glass container with two concentric compartments separated by a large fine glass frit. The anode compartment was stirred with a magnetic Teflon bar and with a stream of H_2SO_4–CrO_3-scrubbed N_2 or CO_2. The highest internal temperature during electrolysis (0.5–1.5 A) was 1.5°. The compartments contained initially (anode) cobalt(II) perchlorate + $HClO_4$ and (cathode) $HClO_4$ at approximately the same ionic strength. Triply distilled water, once each from acid CrO_3 and MnO_4^-, was employed. Since some mixing between compartments occurred, each anode solution was analyzed for total cobalt, $[H^+]$, and [Co(III)] by one or more of the following methods. Total cobalt was determined by EDTA titration (±1%) and by a gravimetric procedure weighing $CoSO_4$ (dehydrated at 400°) (±0.2%). $[H^+]$ was determined by OH^- titration to a pH of 5 (±1%) and by an ion exchange–base titration sequence (±2%) using the known total cobalt concentration. [Co(III)] was determined by absorption measurements at 480 and 602 mμ on dilute solutions in 2.0 M $HClO_4$ (±1%) and by reaction with standard $Fe(NH_4)_2(SO_4)_2$ solution and back-titration with standard Ce(IV) using $Fe(o\text{-phen})_3^{2+}$ indicator (±0.1%). The ± values given above refer to the average reproducibility of the method. The different methods used gave the same results within the average reproducibility except for the determination of [Co(III)]. Using the molar absorbancies[5] at 602 and 480 mμ of Co(II) and Co(III) of 0.352 and 3.72 and 34.78 and 3.8, respectively, gave high values (4–5%) by the spectrophotometric method. Changing to 35.3[1] and 3.68 for the molar absorbancies of Co(III) gave consistent values for the two methods. When the oxidation–reduction method was used to determine [Co(III)], the ozone was removed with a stream of purified N_2 during the preparation. Except where noted, the Co(III) solutions were analyzed and used within 5 min of the completion of their preparation.

The equilibrium concentration of O_3 in a 5.0 M $HClO_4$ solution being electrolyzed at 1° with a current of 3.0 A was $(5 \pm 1) \times 10^{-4}$ M as determined by reaction with Fe^{2+}. This is in approximate agreement with the data of Taube[8] for a saturated solution. Portions of the concentrated Co(III) solutions were, in certain cases, flushed with purified N_2 or CO_2 until all O_3 was gone,[9] degassed in a vacuum apparatus, and mixed with ^{18}O-enriched water (distilled from $KMnO_4$ and degassed). After careful mixing the solution was again degassed at 0 to −5° and allowed to warm to 23–27°. The evolved O_2 was collected using a Toepler pump and purified, and the 34/(32 + 33) ratio was measured on a Nuclide double-collector mass spectrometer. In certain cases the reaction was stopped before completion by cooling, the O_2 was collected, and a sample of the remaining solution was analyzed for the Co(III)/Co(II) ratio using the spectral method. The ^{18}O content of the final solvent water as well as normal water was determined on a mixture of 2:1 H_2–O_2 from the electrolysis of the water in a vacuum apparatus. It was shown that the presence of H_2 did not alter (±0.5%) the 34/(32 + 33) ratio when compared to the $Hg(CN)_2$–$HgCl_2$ method[10] of analyzing for ^{18}O in water using CO_2. Further, the apparent fractionation was constant under the conditions used.

Results and Discussion

Table I summarizes the results obtained when a large fraction (50–100%) of the Co(III) is reduced by water. The average value of $R_N(O_2/H_2O)$ for 13 runs utilizing enriched water is 1.0010 ± 0.0049 (average deviation). This is to be compared with the two runs using only normal water providing the effective fractionation under these conditions; $R_N(O_2/H_2O) = 0.9879 \pm 0.0014$. These values cover the ranges $[Co(III)] = 0.083$–0.490 M and $[H^+] = 1.53$–3.48 M with the initial Co(III) usually being 95–98% of the total cobalt. The results appear to be independent of the method of mixing and the procedure used in degassing. The last column in Table I gives the $R_N(O_2/H_2O)$ assuming 6%

---

[7] M. Anbar and I. Pecht, *Trans. Faraday Soc.*, **64**, 744 (1968).

[8] H. Taube, *ibid.*, **53**, 656 (1957).

[9] The presence of O_3 was demonstrated by its odor, by its reaction with aqueous I^-, and by the "rubber band" test. Its absence was considered demonstrated when a stream of purified CO_2 (about 200 cm³) did not give I_2 in an aqueous I^- solution.

[10] M. Anbar and S. Guttman, *Int. J. Appl. Radiat. Isotop.*, **4**, 233 (1959).

of the O_2 comes from the inner, unexchanged coordination sphere of Co(III) as suggested by the previous study at 0.6 *M* Co(III) and 6 *M* $HClO_4$ (initial concentrations). This calculated value is the maximum expected assuming the same degree of polymerization and 100% decomposition. These results are clearly not consistent with the previous data[2] and suggest either that the coordination sphere of Co(III) is in complete equilibrium with the solvent before appreciable oxidation takes place or that the molecular oxygen comes entirely from the solvent.

Table II gives the results of one of two runs carried out to find a change in the ^{18}O content of O_2 as the reaction proceeded. The second run gave equivalent results. It had been previously observed[2] that the initial O_2 (0–8% reaction) was composed of nearly 50% of oxygen from the unexchanged Co(III) coordination sphere. Thus this type of experiment should be a much more sensitive test of oxygen holdback by polymeric Co(III) ions. The calculated values for $R_N(O_2/H_2O)$ are as follows: (a) O_2 completely from unexchanged Co(III) sphere, 0.27; (b) O_2 equally from the Co(III) sphere and the solvent, 0.63; (c) O_2 completely from the solvent, 1.00. These results show that the O_2 evolved has the same ^{18}O content as the final solvent and do not support the suggestion that Co(III) solutions in 1–5 *M* acid contain hydroxy polymers which give O_2 with the composition of the hydroxy groups when Co(III) is reduced in water. The last column in Table II gives the approximate maximum O_2 contamination from air as measured by the $^{28}N_2$ peak. Appreciable air contamination would lower the $R_N(O_2/H_2O)$ ratio and is not significant in this work. Runs 13, 15, and 16 show the results of purposely not flushing the O_3 out of the solution being electrolyzed. After transfer to the vacuum apparatus, however, it was degassed as usual. The effect was very small suggesting that the initial $[O_3]$ was very small or that its concentration is quite easily lowered to a small value by the degassing method employed. This result is in agreement with the measured O_3 concentration and suggests the presence of O_3 cannot account for the previous ^{18}O results.

TABLE II[a]

$$4Co(H_2O)_6^{3+} + 2H_2O^* \rightarrow O_2 + 4Co_{aq}^{2+} + 4H^+$$

Run no.[b]	% decompn[c]	$10^3R_N(O_2)$	$R_N(O_2)/R_N(H_2O)$	% atm O_2 (max)
1	0–12	1.5550	1.0016	2.0
2	12–26	1.5565	1.0025	1.2
3	26–45	1.5600	1.0048	1.1
4	45–66	1.5585	1.0039	0.6
5	66–75	1.5610	1.0055	1.3
6	75–95	1.5590	1.0042	0.7

[a] Conditions: 10.00 ml of stock to 4.4 ml of H_2O enriched 8.4 times; stock solution $[Co^{3+}] = 0.929$ *M*, $[H^+] = 3.32$ *M*, % $Co^{3+} = 98$; after dilution $[Co^{3+}] = 0.645$ *M*, $[H^+] = 2.31$ *M*; $R_N(H_2O \text{ and } Co^{3+}) = 4.18 \times 10^{-3}$, $R_N(H_2O \text{ enriched}) = 3.48 \times 10^{-2}$, $R_N(\text{final } H_2O) = 1.5525 \times 10^{-2}$. [b] Some O_3 present. Degassed 4 times before H_2O was added; then degassed 3 times. [c] Decomposed at 20–25° in diffuse light. Determined spectrally (±1%).

It was noted by a referee that the final total $[Co^{3+}]$ was greater than that used previously and a reasonable explanation of the discrepancy between laboratories could be made on this basis. Thus a few measurements were made at high dilution and are reported in Table III. These results are consistent with the others reported in this paper.

TABLE III

^{18}O TRANSFER DURING H_2O OXIDATION BY Co(III)[a]

$[Co(III)]_i$, *M*	$[HClO_4]_i$, *M*	% Co(III)[b]	$R(O_2)/R(H_2O)$
0.32[c]	2.86	94	0.9901
0.74[c]	5.33	93	0.9936
0.62[c]	5.50	100	0.9982
0.62[d]	5.50	100	0.9816
0.73[e]	4.85	99	1.0026

[a] Conditions: 1 ml of Co(III) stock + 20 ml of H_2O of differing ^{18}O content. Complete decomposition. [b] As determined spectrophotometrically. [c] Co(III) in normal water; enriched water (3.49 times) added. [d] Co(III) in normal water; normal water added. [e] Co(III) in enriched water (4.54 times); normal water added.

The values in Tables I and III using normal water are slightly low. The reason for this observation is uncertain since many factors could contribute including experimental problems and cobalt(III) water holdback with the O_2 having the composition of the resulting solvent.

For future comparisons an analysis of the stock cobalt(II) perchlorate solution (from $CoCl_2$) was made by arc spectra: Mn, Ca, Mg, Pb, Sn, Ag, Ti, Mo, V, Cr, Al < 10 ppm, Zn < 300 ppm, Cu < 20 ppm, Fe < 1 ppm, Ni (flame photometry) 3000 ppm based on cobalt. This represents a relatively pure cobalt with the nickel content unmodified by the purification procedure.[11]

Summary

On the basis of these measurements, the molecular oxygen obtained from the oxidation of water by Co(III) has the composition of the solvent. No evidence was found for oxygen "holdback" by 3–6 *M* Co(III) in 1.5–6 *M* $HClO_4$, when diluted with ^{18}O-labeled water, in the time necessitated by the rate of water oxidation (∼5 min). The ozone often present in Co(III) solutions prepared electrochemically cannot account for the differences observed in the two studies. The much higher ^{18}O enrichment used in the first study seems to be the only experimental change, but it is difficult to explain the differing results on this basis. An additional study of this reaction is indicated.

Acknowledgment.—The arc-spectra analysis was the courtesy of E. E. Pickett and R. Koirtyohann and is appreciated.

---

[11] NOTE ADDED IN PROOF.—A highly purified $Co(ClO_4)_2$ solution with the observable impurities being Cu, Fe, Mg, and Ni (all below 10 ppm) gave essentially the same results as in Table I.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
GENEVA COLLEGE, BEAVER FALLS, PENNSYLVANIA 15010

Dimethyl Sulfide–Borane as a Borane Carrier

BY JOHN BERES, ALAN DODDS, ALFRED J. MORABITO,
AND ROY M. ADAMS*

Received August 6, 1970

Since diborane is not stable at room temperature, the preparation of borane adducts of Lewis bases has generally involved *in situ* preparation of borane or