an acid such as $[(NC)_5CoNCCo(CN)_4OH_2]^{-4}$ is very much weaker than $(NC)_5CoOH_2^{--}$ with a pK of 11.

In an earlier and incorrect interpretation[3] of parts of the present work, it was reported that the acid hydrolysis of $[(NC)_5Co^{III}OOCo^{III}(CN)_5]^{-6}$ produced the polymeric Co(III) pentacyanide discussed above. The error arose because at that time it was thought that rehydration of Ag_2Co-

$(CN)_5$ produced the ion $(NC)_5CoOH_2^{--}$, a circumstance which resulted in the mistaken identification of the polymeric Co(III) pentacyanide as $(NC)_5CoOH_2^{--}$ and *vice versa*. In addition, the species which was shown later to be $[(NC)_5Co^{III}-OOCo^{IV}(CN)_5]^{-5}$ had then been isolated in only trace quantities and tentatively identified, again incorrectly, as an isomer of the polymeric Co(III) pentacyanide.

Binuclear Complex Ions. IV. An Investigation of the Mechanism of Oxygenation of the Chromium(II) Ion in Ammoniacal Solution Using O18 Labelled Oxygen[1]

BY T. B. JOYNER[2] AND W. K. WILMARTH

A study has been made of the extent of the labelling of the bridging oxygen atom of the $[(H_3N)_5Cr-O-Cr(NH_3)_5]^{+4}$ ion, formed by oxygenation of the Cr(II) ion in ammoniacal solution. Under all conditions the labelling was extensive but never complete. The percentage labelling varied only over the range 40–70% despite an 80° variation in reaction temperature and a considerable variation in pH and Cr(II) concentration. On the basis of these results and other available information, it is possible to deduce a plausible path for the oxygenation process. In this mechanism the binuclear $[(H_3N)_5Cr-O_2-Cr(NH_3)_5]^{+4}$ ion and a Cr(IV) complex, the $[(H_3N)_5Cr(OH)]^{+3}$ ion, both play important roles as transient intermediates in the over-all reaction.

Introduction

It was first reported by Jorgensen in 1882 that oxygenation of the Cr(II) ion in ammoniacal solution produced the interesting binuclear $[(H_2N)_5-Cr-O-Cr(NH_3)_5]^{+4}$ ion, a species which he named the rhodo ion.[3] Although the rhodo ion is a major product of the reaction under favorable circumstances, all experience indicates that other unidentified substances are always formed in rather appreciable amounts. In these circumstances, product analysis alone does not yield any very definite information about the reaction mechanism. The present study represents an attempt to devise an experimental approach that would identify the reaction paths producing the rhodo ion, despite the presence of the troublesome and uncontrolled side reactions. In brief, the procedure involves a tracer study using O18 labelled molecular oxygen in the oxygenation, followed by analysis of the O18 content of the oxygen atoms in the bridging position of the rhodo ion.

Experimental

Oxygenation Techniques.—The Cr(III) solutions were prepared either by dissolving the common green, reagent grade $CrCl_3 \cdot 6H_2O$ in water or by treating a solution of reagent grade ammonium dichromate with a slight excess of hydrogen peroxide, with the excess hydrogen peroxide being destroyed by boiling after the reaction was complete. The reduction of the Cr(III) ion to the Cr(II) oxidation state was carried out by adjusting the acidity to 2.0 M with hydrochloric acid and then adding an excess of amalgamated zinc. This and subsequent operations were carried out in a nitrogen atmosphere using an all glass apparatus designed to protect the Cr(II) solutions from air oxygenation. After reduction to the Cr(II) state was complete, the solutions were separated from the zinc by transfer through a stopcock into a

portion of the apparatus containing either ammonium chloride or ammonium bromide dissolved in concentrated aqueous ammonia. In this operation, the large excess of ammonia served to neutralize the hydrochloric acid and to convert the Cr(II) ion to the ammonia complex, while the presence of the ammonium salt decreased the basicity, thus preventing the precipitation of basic Cr(II) compounds except in a few experiments carried out at −50° and referred to below.

Labelled oxygen used in the oxygenation was prepared by electrolysis of water obtained from the Stuart Oxygen Co. which contained approximately 1.4% H_2O^{18}. The electrolysis was carried out in a simple H-cell, using platinum electrodes and added sodium sulfate electrolyte. At a current of 0.5 ampere it was necessary to cool the cell by immersing it in a bath. The oxygen was collected at the anode by water displacement in storage bulbs which could be attached by ground joints to the reaction vessel containing the ammoniacal Cr(II) solutions.

In a typical oxygenation experiment the initial concentrations of the reagents were: ammonia, 19.0 molal; ammonium bromide, 3.3 molal; chloride ion arising from the added hydrochloric acid, 0.7 molal; Cr(II), 0.01–0.18 molal; zinc ion formed in the reduction, about one half the concentration of the Cr(II). Other reagents added in some experiments were present at the concentrations indicated. Before oxygenation, each solution was frozen by cooling to −80°, the nitrogen removed by evacuation first at −80° and then for a short period (approximately 10 sec.) after the solid had been melted. The solution then was adjusted to any desired temperature with a liquid bath and the labelled oxygen admitted by opening the stopcock to the oxygen storage vessel. To increase the rate of solution of the oxygen, the solution was stirred by manual agitation of the entire reaction vessel. As the oxygenation proceeded, the basic rhodo bromide precipitated. After reaction was complete the color of the solution indicated that only very minor amounts of the rhodo ion could have remained unprecipitated.

To be sure that the oxygenation was complete before exposure to laboratory air, two methods of procedure were developed, with the duplication of results in the two procedures indicating the absence of errors in each. In the first method, the oxygenation was carried out for fifteen minutes, a period which should have been more than sufficient to complete the reaction.[4] At this point, a small amount of

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(1) This work was supported in part by the Office of Naval Research.
(2) Based on a dissertation submitted by Taylor B. Joyner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.
(3) S. M. Jorgensen, *J. prakt. Chem.*, **25**, 321, 308 (1882).

(4) In experiments where efficient agitation is achieved by bubbling air through the solution, the reactions seem to be complete within one minute at 0°.

hydrogen peroxide was added without exposing the solution to air, the hydrogen peroxide serving to destroy any remaining traces of Cr(II) in a reaction known not to produce the rhodo acid. In the second method of procedure, the addition of hydrogen peroxide was omitted, but the oxygenation was carried out for periods from 45–60 minutes, the extra time insuring the removal of even the last traces of Cr(II).

After completion of the oxygenation, the basic rhodo bromide was removed by filtration with exposure to air and immediately converted to its conjugate acid by washing with 1.0 M hydrobromic acid. Purification was achieved by dissolving the solid $[(H_3N)_5Cr-OH-Cr(NH_3)_5]Br_5 \cdot H_2O$ in water at $0°$ and reprecipitating it by addition of concentrated hydrobromic acid. A single precipitation proved to be adequate, since tests indicated that a second reprecipitation did not change the % labelling.

After purification the samples were washed with alcohol and ether and dried over sulfuric acid in a vacuum desiccator. Although this generally removes water of crystallization, dehydration was further assured by heating 2 to 3 hr. at $100°$ under vacuum just prior to decomposing the compounds. Purity was usually checked by nitrogen analysis only. A typical more complete analysis is included below.

Anal. Calcd. for $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Br_5$: N, 20.3; H, 4.52; Br, 57.8. Found: N, 19.9; H, 4.51; Br, 57.7.

Dehydration Procedure.—The over-all procedure for determining the percentage labelling of the rhodo bromide involved thermal decomposition of the solid complex, isolation of the labelled water which was evolved, equilibration of the labelled water with carbon dioxide for at least one week and mass spectrometer analysis of the carbon dioxide. Since the amount of labelled water produced in the thermal decomposition was small, ranging from 9–30 mg., it was necessary to take precautions to avoid contamination from unlabelled water absorbed on the inner walls of the all glass dehydration apparatus. In test experiments, it was found that this contamination could be avoided if the entire apparatus except for the ground joints and stopcock was flamed under vacuum before use. After flaming and cooling the solid complex was introduced rapidly, with the entire apparatus being reevacuated within one minute.

To dehydrate the rhodo acid, it was necessary to heat the solid to $200°$ for a period of 2 hr., conditions which resulted in extensive decomposition and evolution of gaseous ammonia as well as water. The separation of water and ammonia involved a preliminary fractionation with the bulk of the ammonia being separated by distillation at $-30°$. Following this the water containing traces of ammonia was condensed on a sample of benzoic acid which previously had been dried by evacuation for several hours. A final distillation then transferred the water to the sample tubes for carbon dioxide equilibration, the ammonia remaining behind as the poorly volatile ammonium salt. In most instances the water introduced in the sample tubes represented approximately 40% of the oxygen in the sample of the rhodo acid.

While decomposing the rhodo bromide in the manner outlined above, traces of hydrogen bromide must be formed as a few milligrams of this material collects as a sublimate a few centimeters above the portion of the apparatus surrounded by the heating mantle. Recently, it has been reported that at temperatures above $300°$ detectible amounts of water and sodium chloride are formed by the reaction of hydrogen chloride with Pyrex glass.[5] Since the conditions in our thermal decomposition reaction are much milder than those employed by Boggs, there was only a minor possibility that the labelled water in our experiments was contaminated by water formed in the reaction of hydrogen bromide with Pyrex glass. In a single test experiment carried out some time after the completion of the tracer experiments, ammonium bromide and water were heated in a container at $200°$ for 90 minutes. Unfortunately, the apparatus used in this experiment was of such a design that it could not be flamed before use. However, the 14% loss of labelling which was observed corresponded only to that which was found in early, exploratory measurements using unflamed apparatus.

Mass Spectrometer Analysis.—The percentage labelling is defined as the percentage of the oxygen atoms in the rhodo ion arising from the molecular oxygen used in the oxygenation.

(5) J. E. Boggs, *Chem. and Eng. News*, **34**, 126 (1956).

$$\% \text{ labelling} = 100 \frac{N_{\text{obsd.}} - N_w}{N_w{}^* - N_w}$$

N_w, $N_w{}^*$ and $N_{\text{obsd.}}$ are the mole fractions of H_2O^{18} in normal water, the enriched water and the water obtained from the decomposition of the rhodo bromide respectively. Numerical values for the required mole fractions of H_2O^{18} are calculated from the mass spectrometer data using the formula developed by Hunt and Taube.[6]

$$N_{\text{obsd.}} = \frac{R}{K + R} + \frac{R}{Q(1 + R)} - \frac{R_0}{Q}$$

R is the ratio of the mass spectrometer readings for peak 46 to peak 44 obtained in analysis of carbon dioxide after equilibration with the enriched water obtained from dehydration of the rhodo bromide; R_0 refers to the same ratio for tank CO_2. Q is the mole ratio of water to carbon dioxide used in the O^{18} equilibration. K, the equilibrium constant for the equilibration reaction, has the numerical value of 2.078 at $25°$.

$$H_2O^{18} + Co^{16}O^{16} \rightleftarrows H_2O^{16} + CO^{16}O^{18}$$
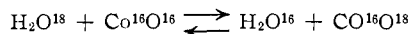
Evaluation of Experimental Error.—The present work is not of a high order of accuracy, since there are various reasons to believe that the experimental error may be as large as $\pm 5\%$. The major source of error, discovered only after the measurements were complete, arose from our failure to realize that the particular mass spectrometer employed apparently required daily calibration using carbon dioxide samples of known enrichment. The analysis of a given sample of carbon dioxide, when carried out on successive days, usually did not vary by more than $\pm 2-3\%$, but in one instance the result deviated by 5% from the expected value. Errors in measurement of Q were usually unimportant, but in a few experiments may have reached $\pm 2\%$. A less well defined source of error, which is rather difficult to evaluate, may have been introduced by the rather inefficient manual shaking of the solutions during oxygenation. In a reaction as fast as the present one, the rate of solution of the gas may well have been rate determining, with the reaction occurring mainly at the interface between the gas and solution phases. In these circumstances, the Cr(II) concentration at the interface would be different in experiments which were identical except for accidental variation in the rate of agitation. As the data prescribed in Fig. 1 indicates, gross changes in the initial Cr(II) concentration do influence the % labelling, but the dependence upon initial Cr(II) concentration is not very pronounced. Isotopic fractionation arising from differences in rate of reaction of O_2^{16} and $O^{18}O^{16}$ would be small, compared to the other sources of error, and can be neglected.

Results

The most conclusive experiments are those presented in Fig. 1 in a plot of % labelling *versus* the initial Cr(II) concentration. For the reasons outlined above the degree of reproducibility is difficult to estimate, but to the best of our knowledge it is represented by the size of the "points" in Fig. 1. Considering the internal consistency of the four results represented by the points connected by the solid line, it must be concluded that there is an appreciable increase in labelling with increasing initial Cr(II) concentration. In two separate experiments the addition of hydrazine produced a detectable increase in labelling. The conclusion that there is an increase in labelling with decreasing temperature, illustrated by the single result at $0°$, is supported by further results presented in Table I. Table I contains the results of scattered experiments carried out under conditions somewhat different from those employed in the work presented in Fig. 1. Under most conditions only a single experiment was performed, as the results indicated that no very striking change in labelling had been obtained. In the absence of duplicate experiments

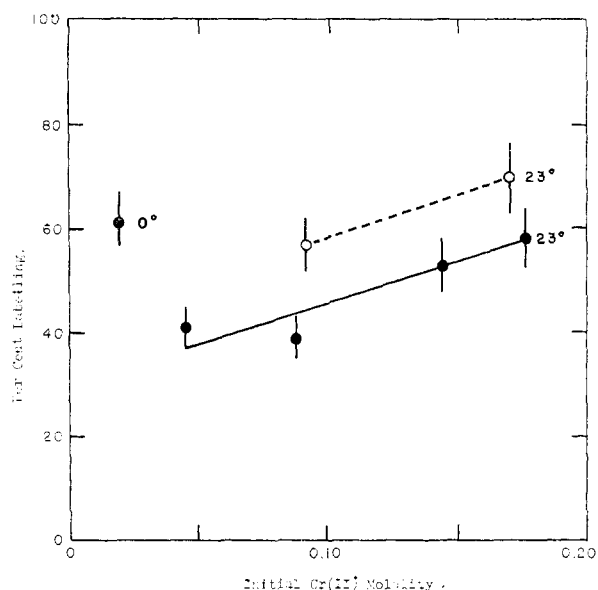(6) J. P. Hunt and H. Taube, *J. Phys. Chem.*, **19**, 602 (1951).

Fig. 1.—Per cent. labelling at various Cr(II) concentrations, with all experiments in solutions containing 19.0 molal ammonia and 3.3 molal ammonium bromide. In the two experiments represented by open circles, the hydrazine concentrations of 0.94 molal and 0.20 molal correspond to initial Cr(II) concentrations of 0.09 and 0.17, respectively. In the experiments represented by darkened circles, the solutions contained no added scavenger. All experiments were at 23 ± 2°, except the one at 0°, as indicated by the figures in the graph.

or the test of internal consistency, the rather small changes in labelling which generally were observed should perhaps be regarded as less certainly established than those of Fig. 1, although the observed changes would seem to be somewhat outside the assigned limit of reproducibility. Many of the results of Table I were obtained in an effort to investigate the influence of temperature upon labelling. In the first three experiments at 0–11° an appreciable increase in labelling was observed, but unfortunately at this lower temperature part of the Cr(II) had precipitated before oxygenation, a factor which later experiments indicate may have produced a new heterogeneous reaction path capable of producing very efficient labelling. To avoid the complication of the solid phase present only in these three experiments, the ammonium bromide component of the buffer was replaced with ammonium chloride, a change which prevented the precipitation, presumably because the chloride or basic chloride salts of Cr(II) are more soluble than the corresponding bromide containing compounds. In a single experiment at 0° in the ammonium chloride solutions a 50% labelling was obtained, a result to be compared with the 61% given in Fig. 1, which was observed in the presence of ammonium bromide. In an effort to obtain quantitative labelling the next experiments were carried out at −50°, but to our surprise the labelling increased only to 61–65%, a value comparable to that obtained in the presence of the solid phase at 0–11°. These results may mean that the presence of a solid phase at 0–11° did introduce a new reaction path, as sug-

gested above, but an alternate explanation is also possible. At −50° the solution became very viscous, a factor which must markedly influence the rate of solution of the molecular oxygen and the rate of diffusion of the reactants. Quite possibly under these conditions the reaction becomes entirely diffusion controlled and the observed labelling may be less than it would have been in the absence of such complications. Perhaps even at 0° diffusion is important enough so that the change in viscosity produced by replacing the 3.3 M ammonium bromide by 6.6 M ammonium chloride is reflected in the rather poor agreement afforded by the two results, 50% versus 61%, which were cited above. In an effort to explore the dependence of labelling upon pH, the ammonium bromide was replaced by sodium bromide, a change which should have increased appreciably the alkalinity of the ammoniacal solution, but a comparison of the result with that presented in Fig. 1 indicates that there was no major change in labelling. In the single experiment designed to test the scavenger action of iodide ion, a detectable decrease in labelling was observed.

Attempts were made to prepare the rhodo ion by oxidation of Cr(II) in ammoniacal solution using hypochlorite ion, hypobromite ion and hydrogen peroxide. No observable amount of rhodo ion was formed with any of these oxidants, despite the fact that it would have been detected readily, even if produced in a yield as small as 5%.

The stoichiometric yield of rhodo ion, measured in many but not all experiments, has not been recorded here, since it is not of major interest in the discussion below. As a general statement it can be said that the yield varied over the range 30 to 60%, except when hydrazine was added. In the single experiment at 0.09 M Cr(II) and 0.94 M hydrazine the yield dropped to 16%, perhaps because of the formation of hydrazine complexes in the Cr(II) solution.

TABLE I

LABELLING EXPERIMENTS PERFORMED UNDER VARIOUS CONDITIONS IN 19.3 MOLAL AMMONIACAL SOLUTION

T, °C.	Cr(II), M	Labelling, %	Medium[a]
11	0.044	70[b]	3.3 molal NH$_4$Br
5	.044	68[b]	3.3 molal NH$_4$Br
0	.028	67[b]	3.3 molal NH$_4$Br
0	.044	50	6.6 molal NH$_4$Cl
−50	.045	65	3.3 molal NH$_4$Cl
−50	.045	61	3.3 molal NH$_4$Cl
23	.044	55	3.3 molal NaBr
23	.174	41	3.3 molal NH$_4$Br, 0.43 molal NH$_4$I

[a] All solutions were 19.3 molal in NH$_3$. [b] Partial precipitation of Cr(II) occurred before oxygenation at 0 and 11°. Solution at 5° was supersaturated and precipitation of Cr(II) may have occurred during oxygenation.
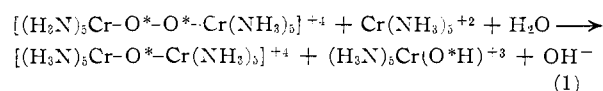
Discussion

Various observations greatly restrict the number of otherwise plausible mechanisms for the formation of the rhodo ion. First it may be noted that the rate of oxygenation[5] is much faster than the dimerization of Cr(NH$_3$)$_5$(H$_2$O)$^{+3}$, or of other

Cr(III) mononuclear ions.[7]   Secondly, the reaction is highly specific with molecular oxygen being the only oxidant known to produce detectable amounts of the rhodo ion. Of special importance here is the observation that the rhodo ion is not formed by the oxidant hydrogen peroxide, a possible reduction product of molecular oxygen. Evidently the oxygen molecule is incorporated in a chromium containing transient intermediate in the initial stages of the reaction. In view of the known existence of binuclear peroxides in other oxygenation systems, it seems plausible to assume that this transient intermediate is the binuclear ion $[(H_3N)_5Cr-O*-O*-Cr(NH_3)_5]^{+4}$, formed by reaction of molecular oxygen and two Cr(II)-ammonia complex ions. In the formula above, the asterisks are used to indicate not merely the labelled O^{18} atoms, but all of the atoms present originally in the oxygen molecule.
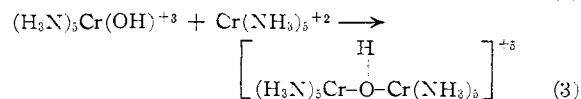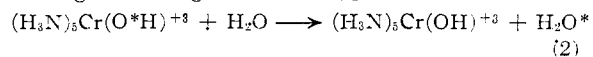
The labelling results further restrict the choice of possible reaction mechanisms. For any mechanism to be acceptable, it must explain the observation that the labelling always roughly approximates 50%, with so extreme a change as 80° in reaction temperature yielding results, all of which fall in the interval of 40–70% labelling. The failure to obtain complete oxygen retention even at −50° seems to require an exchange between solvent and coordinately bound oxygen atoms much too rapid to be attributed to a Cr(III) complex but entirely compatible with the expected behavior of a Cr(IV) complex.[8] Accordingly, a mechanism will be adopted which involves two transient intermediates, the binuclear peroxide mentioned above and a Cr(IV) complex having the formula $Cr(NH_3)_5OH^{+3}$.

In more detail, the mechanism involves formation of the binuclear peroxide and its subsequent rapid reduction by the Cr(II) complex ion in the reaction

$$[(H_3N)_5Cr-O*-O*-Cr(NH_3)_5]^{+4} + Cr(NH_3)_5^{+2} + H_2O \longrightarrow$$
$$[(H_3N)_5Cr-O*-Cr(NH_3)_5]^{+4} + (H_3N)_5Cr(O*H)^{+3} + OH^- \quad (1)$$

In this equation, the formulas $Cr(NH_3)_5^{+2}$ and $Cr(NH_3)_5(OH)^{+3}$ are assumed in part for convenience in balancing the equation and in part because present evidence would suggest that this was the most reasonable formulation.[9]

Reaction 1 would produce only completely labelled rhodo ion. Reactions 2 and 3 constitute the major path for production of unlabelled rhodo ion, with the reaction sequence 1, 2 and 3 yielding an average labelling value of 50%.

$$(H_3N)_5Cr(O*H)^{+3} + H_2O \longrightarrow (H_3N)_5Cr(OH)^{+3} + H_2O* \quad (2)$$

$$(H_3N)_5Cr(OH)^{+3} + Cr(NH_3)_5^{+2} \longrightarrow$$
$$\left[(H_3N)_5Cr-\overset{H}{\underset{|}{O}}-Cr(NH_3)_5\right]^{+5} \quad (3)$$

(7) For a recent study of the aqueous solutions, see the paper by J. A. Laswick and R. A. Plane, THIS JOURNAL, 81, 3564 (1959).

(8) A. E. Ogard and H. Taube, J. Phys. Chem., 62, 357 (1958).

(9) In the ammoniacal solution, the ion $Cr^{IV}(NH_3)_5(OH_2)^{+4}$ would presumably be acidic enough to lose one proton in a neutralization reaction. Stability constants for the ammonia complexes of Cr(II) have not been reported, but the measurements of R. L. Pecsok and J. Bjerrum, Acta. Chem. Scand., 11, 1419 (1957), suggest that Cr(II) resembles Cu(II) in that a fifth ammine ligand is introduced only incompletely and at very high ammonia concentrations.

The minor dependence of labelling upon temperature would require that reactions 2 and 4 have comparable activation energies, a not implausible coincidence since both reactions must be very rapid.

$$(H_3N)_5Cr(O*H)^{+3} + Cr(NH_3)_5^{+2}$$
$$\left[(H_3N)_5Cr-\overset{H}{\underset{|}{O}}-Cr(NH_3)_5\right]^{+5} \quad (4)$$
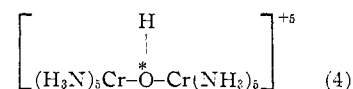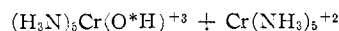
For the moment we will defer discussion of an alternate reaction path which must also produce unlabelled rhodo ion, at least in those experiments at very low Cr(II) concentration where the labelling seems to drop slightly below 50%.

In principle the above mechanism predicts that an increase in labelling might be obtained in at least two different ways. The first and most obvious approach involved increasing the Cr(II) concentration, thus favoring reaction 4, a Cr(II) dependent process, over reaction 2. As Fig. 1 demonstrates, an increase in the Cr(II) concentration does increase the labelling, with the increase perhaps being as large as might be anticipated under the circumstances. Unfortunately, an increase in initial Cr(II) concentration favors reaction 4 only in the initial stages of the oxygenation, since the concentration decreases continuously during the reaction and ultimately drops to zero. As we have indicated, inadequate stirring may also have limited the labelling at the higher concentrations of Cr(II), the concentrations at the interface between the gas and solution phases being less than that in the body of the solution.

A second and less straight-forward method of increasing the labelling involved the addition of reducing scavengers, the hope being that they would destroy the $Cr(NH_3)_5(OH)^{+3}$ ion before reactions 3 and 4 could occur, thus limiting the formation of rhodo ion to the completely labelled product formed in reaction 1. Unfortunately there are relatively few scavengers which are soluble in alkaline solution, and there is no sound basis for selecting one which would react with $Cr(NH_3)_5(OH)^{+3}$ in preference to the binuclear peroxide, molecular oxygen or Cr(II). Hydrazine, one of the two substances employed, did appreciably increase the labelling, but not to the limiting value of 100%, possibly because the scavenger action was incomplete at the concentrations employed. In a single experiment the scavenger action of iodide ion actually seemed to decrease the labelling, a result to be anticipated if the iodide ion reacted preferentially with the binuclear peroxide, thus competing with reaction 1, a process which yields completely labelled rhodo ion.

The mechanism presented above must be oversimplified in that it does not provide an explanation for the labelling values below 50%, obtained at low Cr(II) concentrations. Labelling below 50% may perhaps be plausibly explained in terms of a second parallel reaction path initiated by reaction 5 and followed by reaction 3.

$$Cr(NH_3)_5^{+2} + O_2* + 2H_2O \longrightarrow$$
$$(H_3N)_5Cr(OH)^{+3} + H-O*-O*-H + OH^- \quad (5)$$
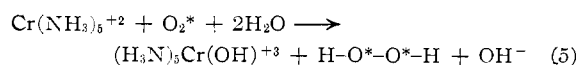
In their discussion of the oxidation of Cr(II) in acid solution, Ardon and Plane have proposed an analogous mechanism to explain the formation of binuclear aquo complexes, by molecular oxygen and a variety of other strong "two-electron" oxidants.[10] Most of the oxidants they employed may indeed operate entirely through this mechanism but, with molecular oxygen, a path through a binuclear peroxide might be favored. Tracer experiments using labelled molecular oxygen would test this possibility. It is possible that reaction 5 proceeds stepwise with the intermediate formation of a mononuclear peroxide having the formula $(H_3N)_5Cr-O^*-O^{*+2}$. The idea is attractive because reaction 5 then becomes an integral part of an over-all mechanism, the mononuclear peroxide decomposing to give the products indicated in equation 5 at very low Cr(II) concentrations, but being converted increasingly to the binuclear peroxide at higher Cr(II) concentrations.

In considering the validity of our over-all mechanism, some brief comments may be made regarding the procedure of ignoring reaction paths not yielding the rhodo ion, a course of action which is valid only if these latter reactions do not involve transient intermediates which considerably influence the rhodo-producing reactions. In support of this procedure, it may be noted that the nature of the side reactions is not entirely unknown. Various observations not presented here suggest that these side reactions yield highly soluble

(10) M. A. Ardon and R. A. Plane, THIS JOURNAL, 81, 3197 (1959).

binuclear ions, perhaps entirely analogous in structure to the rhodo ion, but containing a smaller number of ammonia ligands. In terms of the mechanism which has been adopted, such products would not be unanticipated, since they naturally would arise from oxygenation of Cr(II) complexes containing less than five ammonia molecules.[9] Occurrence of such reactions would decrease the stoichiometric yield of rhodo ion but should not cause major changes in the % labelling. One further reason for low yields of rhodo ion might also be mentioned explicitly, since it has bearing on the question of lability of the Cr(IV) oxidation state, a problem of considerable current interest. In our mechanism, it is assumed that the ion $Cr(NH_3)_5-$ $(OH)^{+3}$ may exchange oxygen with the water solvent in reaction 2 before reaction 4 occurs, but possible replacement of ammonia by water in the ligand sphere has been ignored. Increase or decrease of ammonia content in $Cr(NH_3)_5(OH)^{+3}$ presumably would eliminate the rhodo ion formed in both reactions 3 and 4, thus decreasing the yield of rhodo ion. Since reaction 3 is the only source of unlabelled rhodo ion, a product of major importance in most experiments, it must be concluded that no major change in ammonia content occurs during the brief period of existence of the $Cr(NH_3)_5(OH)^{+3}$ ion. However, it is possible that the increase in labelling observed in the more alkaline medium employed in experiment 7 of Table I represents a detectable hydrolytic destruction of the $Cr(NH_3)_5-$ $(OH)^{+3}$ ion.

Metal Carbonyls. I. Carbon Monoxide Exchange with Nickel Tetracarbonyl and Dicobalt Octacarbonyl[1,2]

BY FRED BASOLO AND ANDREW WOJCICKI[3]

An experimental technique for the investigation of radiocarbon monoxide exchange with metal carbonyls in solution is described. The activation energy for exchange in the system $^{14}CO-Ni(CO)_4$ in toluene is 13 kcal. and the rate of exchange does not depend on the concentration of CO. A dissociation mechanism was therefore assigned to this process. The rates of CO exchange decrease in the order $Ni(CO)_4 > Ni(CO)_3PR_3 > Ni(CO)_2(PR_3)_2$. In $Co_2(CO)_8$ all eight CO's exchange at the same rate via a dissociation mechanism with $E_a = 16$ kcal. Essentially the same results were obtained for the lactone derivative $Co_2(CO)_7(C_7H_8O_2)$, suggesting that only one bridged Co–CO–Co bond need rupture for exchange.

This paper is the first in a series on the investigation of the kinetics and mechanisms of reactions of metal carbonyls and metal carbonyl derivatives. Relatively little quantitative work has been done on these systems.[4-7] Yet they are of considerable importance because of the role that some play as catalysts[8] and because of their relation to the transition metal organometallics and hydrogen compounds.[9] Furthermore, these compounds afford a study of analogous systems having a variety of different coördination numbers and structures. Often with such compounds it is possible to study the reactivity of non-equivalent carbon monoxides in the same compound.

(1) This research was supported in part by a Research Corporation Grant-in-Aid.

(2) Presented in part as paper No. 139 at the XVIIth Congress of the International Union of Pure and Applied Chemistry, Munich, Germany, 1959.

(3) Based upon a portion of a thesis submitted by A. W. to Northwestern University in June 1960, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) M. R. Tirpak, J. H. Wotiz and C. A. Hollingsworth, THIS JOURNAL, 80, 4265 (1958).

(5) L. S. Meriwether and M. L. Fiene, ibid., 81, 4200 (1959).

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