rationalization of the H–D isotope effect on K_{diss}, since $K_{\text{diss}} = K_w \cdot K_2$ (it being assumed that the isotope effect on K_w is understood).

Sutin and Dodson[11] have found that the association quotient for $FeCl^{++}$ ($\equiv K_3$) increases by a factor of 2.6 when the solvent change from H_2O to D_2O is made. The large difference between the $(NH_3)_5CoCl^{++}$ and $FeCl^{++}$ systems is surprising, although it must be admitted that there is no substantial basis for preconceived ideas as to the magnitudes of the effects which are to be expected when differences in the nature of the reactants are introduced. It has been pointed out[12] that the differences between the Co(III) and Fe(III) systems are caused largely by differences in the aquo ions. This can be seen by comparing the H–D isotope effects for the reactions

$$(NH_3)_5CoCl^{++} + OH^- = (NH_3)_5CoOH^{++} + Cl^- \quad (k_4)$$

$$FeCl^{++} + OH^- = FeOH^{++} + Cl^- \quad (k_5)$$

$K_4^{D_2O}/K_4^{H_2O} \times K_5^{H_2O}/K_5^{D_2O}$ is calculated as 1.2; *i.e.*, the difference between the systems almost disappears for a comparison not involving the aquo ions.

From the variation of K_1 with temperature, ΔH_1 for the interval 25 to 51° is calculated as 3.4 kcal., and for the interval 51 to 80° as 3.9 kcal. Using the mean of these values as ΔH_1, ΔS_1, at 25° and $\mu = 0.31$ is calculated as 13 e.u. This value can be compared with those reported by Gates and King[13] for the association of Cr^{+++} with Cl^-: 10.6 e.u. at 4.4 *M* Cl^- and 17.2 e.u. at 0 *M* Cl^-, both with total anion normality at 4.44. From the data reported by Rabinowitch and Stockmayer for the association of Fe^{+++} with Cl^-, ΔS at $\mu = 0.61$ and 25° is calculated as 32 e.u. The reliability of the latter value, which depends on the assumption that ϵ for $FeCl^{++}$ does not change with temperature, is questioned by Gates and King.[13]

Some rough observations were made during the course of the present work on the rate of hydrogen exchange between $Co(NH_3)_5OH_2^{+++}$ and the solvent H_2O. The differences in ϵ for the isotopically different species can be used as a measure of the rate of exchange but they are hardly an accurate or sensitive measure. Infrared analysis of the ion, after precipitation as a salt, provides a better measure. The results we obtained using this method suggest that the rate of exchange is inverse in concentration of acid,[14] even when this is present at the 0.1 *M* level; they are not accurate enough however to exclude some contribution by an acid independent term. Under the conditions of the equilibrium measurements it was not possible to measure the association constant for $(NH_3)_5CoOD_2^{+++} + Cl^-$ in D_2O. At 1 *M* acid, however, such measurements may be possible, and are of interest in assessing the magnitude of the effect caused by hydrogen isotopic substitution in the first sphere of coördination.

Acknowledgment.—This study was undertaken as the result of a discussion with R. W. Dodson. The author wishes to thank him for his interest and for the benefit of later helpful discussion, and also to thank J. Bigeleisen and N. Sutin for their interest in and contributions to this work.

NEW YORK, N. Y.
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[11] N. Sutin and R. W. Dodson, private communication.

[12] N. Sutin, private communication.

[13] H. S. Gates and E. L. King, THIS JOURNAL, **80**, 5011 (1958).

[14] J. S. Anderson, H. V. A. Briscoe and N. L. Spoor, *ibid.*, 361 (1943).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

The Transfer of Oxygen in Some Oxidation–Reduction Reactions of Aquo Complexes

BY WALTER KRUSE AND HENRY TAUBE

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Oxygen tracer experiments have been done which show that transfer of oxygen from $(NH_3)_5CoOH_2^{+++}$ to Cr^{++} in the oxidation–reduction reaction is quantitative. The reaction media included solutions acidic enough so that at least 50% of the reaction proceeds by the aquo path. Thus a bridged activated complex is demonstrated also for the aquo path. When *cis*-$(NH_3)_4Co(H_2O)_2^{+++}$ or *cis*-$en_2Co(H_2O)_2^{+++}$ is the oxidizing agent, also one and only one oxygen is transferred to the reducing agent. Thus there is no evidence in these systems for a double oxygen bridge in the activated complexes for electron transfer.

In an earlier paper,[1] the results of some tracer experiments bearing on the question of oxygen transfer from $(NH_3)_5CoOH_2^{++}$ to Cr^{++} aq. were reported. These experiments showed that the transfer is essentially complete by the path for the oxidation–reduction reaction which makes use of the activated complex implied by the rate function $((NH_3)_5CoOH_2^{+++})(Cr^{++})/(H^+)$. The work indicated that at least some transfer takes place by the path having the activated complex of composition $(NH_3)_5CoOH_2^{+++}.Cr^{++}$, but the evidence was weakened by a later revision of the kinetic data.[2]

With the development of the subject of the mechanism of oxidation–reduction reactions of complex ions, the question of oxygen transfer from an aquo ion oxidizing agent to the reducing agent has taken on increasing importance—obviously the views concerning the mechanisms of these reactions would be greatly affected if in a system in which a definitive test of this feature of mechanism can be made, no evidence for water transfer is found. Accordingly we have returned to the problem, taking advantage of the experience gained since the early results were obtained, and applying a new analytical technique, in the hope of obtaining a definite answer to the question posed. The experiments have also been extended to oxidizing agents of the *cis*-

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[1] R. K. Murmann, H. Taube and F. A. Posey, THIS JOURNAL, **79**, 262 (1957).

[2] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

diaquoamminecobalt(III) type, the point of interest here being to learn whether evidence can be found for a double oxygen bridge.

Procedure

The tracer experiments were done using the oxidant cation enriched in O^{18}, this being the only source of O^{18} enriched oxygen in the system throughout the entire procedure.

To ensure that a substantial fraction of the reaction takes place by the aquo rather than by the hydroxo path the temperature must be kept low and the concentration of $HClO_4$ high. Under these conditions the concentration of $Co(NH_3)_5H_2O^{+++}$ which is tolerated in solution is small, and a large reaction volume must be used (this volume was 500 ml. in all experiments). The solution after reaction contains aquoamminecobalt(III), $Cr(H_2O)_6^{+++}$, Co^{++}, NH_4^+, H^+ and ClO_4^-. It was poured through a column of Dowex 50 cation-exchange resin. In this process all the Co(III), $Cr(H_2O)_6^{+++}$ and Co^{++} is held back by the resin. The Co^{++} was eluted using 2 *M* $HClO_4$, and the $Cr(H_2O)_6^{+++}$ with 4 *M* NH_4Cl. Complete separation of the $Cr(H_2O)_6^{+++}$ from Co^{++} and aquoamminecobalt(III) can be achieved in this way. The processes of charging the resin and of eluting were done in a refrigerator at 2°.

The $Cr(H_2O)_6^{+++}$ in the NH_4Cl solution is at about the 0.02 *M* level of concentration. The precipitation of $Cr(H_2O)_6PO_4$ followed the procedure of Plane and Hunt.[3] The solid material was collected, washed and dried, then heated at 160° to expel water. Not all the water was liberated at this temperature, but the exchange of the oxygen of the hydrate water with phosphate which sets in at a more elevated temperature[4] is avoided. The oxygen isotope composition of the water is then determined in the usual way.

Cr^{++} aq. in perchloric acid solution was prepared by electrolytic reduction of $Cr(H_2O)_6^{+++}$ using a mercury cathode.[5] The preparation of the O^{18} enriched $Co(NH_3)_5H_2O^{+++}$ has been described elsewhere.[6] *cis*-$(NH_3)_4Co(H_2O)_2(ClO_4)_3$ was prepared from $[(NH_3)_4CoCO_3]ClO_4$ which in turn was prepared following a procedure similar to that described for $[(NH_3)_4CoCO_3]_2SO_4$.[7] *cis*-$en_2Co(H_2O)_2(ClO_4)_3$ was prepared from *cis*-$en_2CoH_2OOH(ClO_4)_2$. This latter salt was prepared making the necessary modifications in the procedure described for the bromide salt.[8]

Both $(NH_3)_4Co(H_2O)_2^{+++}$ and $en_2Co(H_2O)_2^{+++}$ reacted largely in the *cis*-form. According to the data of Bjerrum and Rasmussen,[9] not only is the *cis–trans* change slow in acid solution, but the *cis*-form predominates at equilibrium. The equilibrium is less favorable to the *cis*-form in the case of the tetrammine complex (17% *cis* at 25°)[10] but the rate of the transformation at 2° is slow ($t = {}^1/_2 \sim 23$ hr.) compared to the rate of the oxidation–reduction process.

Results

The results of the experiments with three different oxidizing agents are given in Table I.

The values in column 4 are the experimental ones corrected for the exchange which $Cr(H_2O)_6^{+++}$ was found to undergo in putting it through the separation procedure. The extent of the exchange in two experiments using enriched $Cr(H_2O)_6^{+++}$ was found to be 7.4 and 5.5%, and the mean value of 6.5% was used in correcting the observed values of *E* for $Cr(H_2O)^{+++}$ to give those shown in column 4. The values of *E* for the aquocobaltammines in column 3 have been corrected for the isotope fractionation in the aquo-oxidizing agent. The differential fractionation factor for the reaction of $(NH_3)_5CoOH_2^{+++}$ with Cr^{++} is 1.03_5%[1] and since ${}^1/_3$ of the oxidant remains it will be enriched in O^{18} by approximately 4%. Thus the initial enrichment ratio of the oxidizing agent was divided by 1.02 to give the average value of the isotopic composition of the material consumed.

TABLE I

RESULTS ON OXYGEN TRANSFER FROM Co(III) TO Cr^{++}

(Temp. 2°, concn. of oxidant, 3.0×10^{-3} *M*, concn. of Cr^{++}, 2.0×10^{-3} *M*)

Oxidant	$(HClO_4)$	E^a for oxidant	E^a for $Cr(H_2O)_6^{+++}$	No. atoms transferred per $Cr(H_2O)_6^{+++}$
$(NH_3)_5CoOH_2^{+++}$	2.0	7.69	2.12	1.00
	2.0	7.69	2.12	1.00
	1.0	7.69	2.15	1.03
	0.25	7.69	2.13	1.01
cis-$(NH_3)_4Co(OH_2)_2^{+++}$	2.0	4.84	1.63	0.98
	0.25	4.84	1.64	0.99
cis-$en_2Co(OH_2)_2^{+++}$	1.0	8.00	2.06	0.91
	0.25	8.00	2.22	1.04
	0.015	8.00	2.18	1.01

[a] O^{18} content of sample compared to that of normal water.

Some miscellaneous observations made in the present work also seem of interest. In the search for a reaction medium which would accommodate a higher concentration of $(NH_3)_5CoOH_2^{+++}$ than does the perchlorate medium, the reactions of Cr^{++} with $(NH_3)_5CoOH_2^{+++}$ in 2 *M* HCl and in 2 *M* HBr also were investigated. The rates do not appear to be markedly different from those in 2 *M* $HClO_4$, but sufficient interference by the anions is noted to make the perchlorate medium preferable for the present work, in spite of the limited solubility of the compound $(NH_3)_5CoOH_2(ClO_4)_3$. With 2 *M* HCl as the reaction medium, in duplicate experiments it was found that 48.5 and 50% of the Cr^{++} is converted to $CrCl^{++}$; in 2 *M* HBr, 10 and 7.7% was found converted to $CrBr^{++}$.

Discussion

The data of Table I justify the conclusion that under all conditions studied, one and only one oxygen is transferred from Co(III) to Cr(II) when the oxidation–reduction reaction takes place. Some values corresponding to substantially less than 100% transfer are recorded, but it must be remembered that since the only source of O^{18}-enriched oxygen is the oxidizing agent, all effects short of gross errors in the mass spectrometer readings, and certain fractionation effects will operate to reduce the apparent extent of transfer. Gross errors in mass spectrometer readings were eliminated. The fractionation effects have been partially allowed for (the fractionations in fixing the coördination spheres about the Cr atoms, and in the partial dehydration of the $Cr(H_2O)_6PO_4$ were not allowed for. These effects will largely compensate and the net effect probably does not exceed 1 or 2%) and in any case will not cause the variability in the extent of apparent transfer which is observed. The low value of apparent transfer in experiment 7 may have been caused by the variability in the extent of exchange on the resin (this is the most likely cause of the fluctuations in extent of transfer near 1.00) and by the exchange of the product $Cr(H_2O)_6^{+++}$ caused by

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(3) J. P. Hunt and R. A. Plane, THIS JOURNAL, **76**, 5960 (1954).

(4) R. A. Plane and J. P. Hunt, *ibid.*, **79**, 3343 (1957).

(5) R. Flatt and F. Sommer, *Helv. Chim. Acta*, **25**, 684 (1942).

(6) A. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952).

(7) L. Vanino, "Handbuch der Präparative Chemie," Verlag von F. Enke, Stuttgart, 1913.

(8) A. Werner, *Ber.*, **40**, 262 (1907).

(9) J. Bjerrum and S. Rasmussen, *Acta. Chem. Scand.*, **6**, 1265 (1952).

(10) R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, **59**, 298 (1955).

Cr^{++}[11,12] (unless this exchange which takes place by Cr^{++}–$Cr(H_2O)_6^{+++}$ electron transfer is itself catalyzed—and this is entirely possible—it will not significantly affect the results).

Published kinetic data[2] when extrapolated to the temperature of the present experiments show that in the 3rd experiment of Table I approximately 52% of the reaction proceeds by the aquo path. The observation that oxygen transfer is substantially 100% proves that not only by the hydroxo path but also by the aquo path electron transfer is accompanied by oxygen transfer, and a bridged activated complex is indicated for both paths. This conclusion is supported by the other data which extend to higher and lower acidity so that the relative contribution of the two paths to the total reaction is changed.

An earlier experiment[13] in which evidence for a doubly bridged activated complex was sought in the reaction of *cis*-$Co\text{-}en_2Cl_2^+$ with Cr^{++} was inconclusive owing to the rapid dissociation of $CrCl_2^+$ brought about by Cr^{++}. The reactions described in the present paper are free from a similar difficulty. As has been mentioned, the exchange of $Cr(H_2O)_6^{+++}$ with water brought about by Cr^{++} is so slow as not materially to affect our results. We find that even when *cis* Co(III) ions are oxidizing agents, one and only one atom of oxygen is transferred to the reducing agent. The range of acid covered in the experiment is large enough so that this conclusion can probably be taken to apply to the aquo path and to the hydroxo path. However, the dihydroxy path may not be significantly featured even at our lowest acidities and the question of the extent of transfer by this path is left open.

It should be mentioned explicitly that the present results prove that a seven-coördinated aquochromic ion is not formed as an intermediate product in the reactions studied. Such an intermediate would arise for example if the water molecule from the Co(III) complex were presented to the face of the octahedron about the Cr^{++}. If such an intermediate were formed it would lead to loss to solvent of at least $^1/_7$ of the labelled water. The results thus provide some support for the view that the bridging group occupies one of the normal coördination positions about the chromium, but they by no means constitute proof because alternative formulations remain.

The experiments at high Cl^- and Br^- show that these ions do function as non-bridging ligands, although not very efficiently. Whether oxygen transfer takes place by the paths involving the halide ion is not known, and it will in fact be very difficult to find out because the process $CrX^{++} + Cr^{++}$ [14,15] provides for very rapid exchange of water between $(H_2O)_5CrX^{++}$ and solvent. The participation of Cl^- in the reaction of $Co(NH_3)_6^{+++} + Cr^{++}$ has been demonstrated and this reaction does not involve a bridged activated complex. It is thus possible that the reaction of $(NH_3)_5CoH_2O^{++}$ with $CrCl^+$ takes place by an analogous mechanism. The specific rate coefficient for the term $(Co(NH_3)_6^{+++})(Cr^{++})(Cl^-)$ is 0.7 at 25°, $\mu = 0.4$. From the present results, the coefficient for the rate term $(Co(NH_3)_5H_2O^{+++})(Cr^{++})(Cl^-)$ at $\mu = 1.0$ is estimated as 2×10^1. The rate comparison is consistent with the view that the reaction takes place by similar mechanisms, the Cl^- acting to bring the electron from the Cr^{++} to the exterior of the first coördination shell.

Acknowledgment.—This work was supported by the National Science Foundation under Contract NSF-G-5411.

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[12] A. Anderson and N. A. Bonner, This Journal, **76**, 3826 (1954).

[13] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

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[15] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

[16] A. Zwickel, Ph.D. Dissertation, University of Chicago, 1959.

[Contribution from the W. A. Noyes Laboratory of Chemistry, University of Illinois]

The Phosphonitrilic Isothiocyanates

By G. Tesi, R. J. A. Otto, F. G. Sherif and L. F. Audrieth

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The preparation of the trimeric (I) and tetrameric (II) phosphonitrilic isothiocyanates, $[PN(NCS)_2]_{3,4}$, is best accomplished by reaction between the chlorides and alkali metal (ammonium) thiocyanates in acetone. Derivatives of I and II are obtainable by reaction with compounds containing NH_2, OH and N_2H_3 groups. Both I and II polymerize on heating to rubber-like gels.

Non-metallic inorganic (iso)thiocyanates are usually prepared by allowing the corresponding halides, oxy-halides or thio-halides to react with silver, lead or mercury(II) thiocyanate in some inert organic solvent. Since long refluxing of the components is required due to the fact that the heavy metal thiocyanates are insoluble, extensive decomposition often occurs and yields of the desired (iso)thiocyanates are relatively small. In a communication[1] to the Editor reporting the preparation of the trimeric phosphonitrilic isothiocyanate, $[PN(NCS)_2]_3$, an alternative procedure was disclosed entailing the use of alkali metal thiocyanates. It is necessary, however, to make use of non-aqueous solvents in which the phosphonitrilic chlorides are soluble without reaction, and the alkali (ammonium or substituted ammonium) thiocyanates are also appreciably soluble. Interaction then takes place with the precipitation of the alkali metal (ammonium or substituted ammonium) chloride in accordance with the illustrative equation

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[1] R. J. A. Otto and L. F. Audrieth, This Journal, **80**, 5894 (1958).