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REACTIONS OF SOLVATED IONS

FINAL REPORT

Submitted by

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REACTIONS OF SOLVATED IONS

Contract No. AT(11-1)-378

Final Report

The final report covering the work done under Contract No. AT(11-1)-378 consists of (A) reprints of journal articles describing work done under the contract, and (B) brief summaries of work which has been completed and is being prepared for publication. The work begun on the contract and not yet completed is being continued at Stanford University (Contract AT(04-3)-326). This work is not described in this report but will be described in due course in connection with the administration of the current AEC contract.

A. The titles of the papers published on work done on the contract are listed below.

1. The Uncatalyzed Exchange of Cl^- and $AuCl_4^-$. J. Phys. Chem., $\underline{58}$, (1954). (With Ronald L. Rich.)

2. The Induced Exchange of Cl^- and $AuCl_4^-$. Evidence for Au(II). J. Phys. Chem., $\underline{58}$, 6 (1954). (With Ronald L. Rich.)

3. Use of Oxygen Isotope Effects in the Study of Hydration of Ions. J. Phys. Chem., $\underline{58}$, 523 (1954).

4. Tracer Studies on the Decomposition of Ozone in Water. J. Am. Chem. Soc., $\underline{76}$, 2099 (1954). (With Otto L. Forchheimer.)

5. Oxygen Tracer Experiments in the Reaction of NO_2 in Water. J. Am. Chem. Soc., $\underline{77}$, 2993 (1955). (With M. Anbar.)

6. Oxygen Isotope Effects at Anodes. J. Am. Chem. Soc., $\underline{78}$, 3252 (1956). (With M. Anbar.)

*7. The Mechanism of Formation and Rearrangement of Nitrito-cobalt-(III) Ammonia. J. Am. Chem. Soc., $\underline{78}$, 4886 (1956). (With R. K. Murmann.)

*Reprint supply depleted.

*8. The Mechanism of Substitution Reaction of Octahedral Complexes. J. Am. Chem. Soc., 79, 255 (1957). (With F. A. Posey.)

*9. Mechanism of Electron Transfer in Aquo Cations: The Reaction of $(NH_3)_5Co(OH_2)^{+++}$ with Cr^{++}. J. Am. Chem. Soc., 79, 262 (1957). (With R. K. Murmann and F. A. Posey.)

10. The Exchange of Hypochlorite and Hypobromite Ions with Water. J. Am. Chem. Soc., 80, 1073 (1958). (With M. Anbar:)

11. Halides as Bridging Groups for Electron Transfer in the Systems $Cr^{++} + (NH_3)_5CrX^{++}$. J. Am. Chem. Soc., 80, 1084 (1958). (With A. E. Ogard.)

12. Lability of Cr(IV) to Substitution. J. Phys. Chem., 62, 357 (1958). (With A. E. Ogard.)

13. The Deuterium Isotope Effect for an Oxidation-Reduction Reaction between Aquo Ions. J. Am. Chem. Soc., 81, 1288 (1959). (With A. M. Zwickel.)

14. Substitution Coupled to Electron Transfer. J. Am. Chem. Soc., 81, 2906 (1959). (With R. T. M. Fraser and D. K. Sebera.)

15. The Outer Sphere Activated Complex in the Reduction of Co(III) Species. J. Am. Chem. Soc., 81, 2915 (1959). (With A. M. Zwickel.)

16. Tracer Experiments on the Oxidation of Oxalic Acid. J. Am. Chem. Soc., 81, 3515 (1959). (With R. M. Milburn.)

17. Activation of Bridging Groups in Electron Transfer. II. Position of Bond Breaking in Ester Hydrolysis. J. Am. Chem. Soc., 81, 5000 (1959). (With R. T. M. Fraser.)

18. Activation by Electron Transfer - Induced Cis-trans Isomerism. J. Am. Chem. Soc., 81, 5514 (1959). (With R. T. M. Fraser.)

19. Nuclear Magnetic Resonance Studies on Hydration of Cations. J. Chem. Phys., 32, No. 2, 553 (1960). (With J. A. Jackson and J. F. Lemons.)

20. Flow Adaptation of the Isotopic Dilution Method for the Study of Ionic Hydration. J. Chem. Phys., 33, No. 1, 206 (1960). (With H. W. Baldwin.)

21. The Oxidation of Captive Oxalate. J. Am. Chem. Soc., 82, 13 (1960). (With Patricia Saffir.)

*Reprint supply depleted.

22. The Transfer of Oxygen in Some Oxidation-Reduction Reactions of Aquo Complexes. J. Am. Chem. Soc., $\underline{82}$, 526 (1960). (With Walter Kruse.)

23. The Reduction of Oxalate by Chromium (II). J. Phys. Chem., $\underline{64}$, 1776 (1960). (With Ronald M. Milburn.)

24. The Oxidation of Captive p-Aldehydobenzoate. J. Am. Chem. Soc., $\underline{82}$, 4152 (1960). (With R. T. M. Fraser.)

25. The Rates and Mechanisms of Reactions of $Cr(bip)_3^{2+}$ with Co(III) Complexes. Faraday Society Discussions, No. 29 (1960). (With A. M. Zwickel.)

26. Kinetics of Some Electron Transfer Reactions of Cobalt(III). J. Am. Chem. Soc., $\underline{83}$, 793 (1961). (With Allan Zwickel.)

27. Organic Anions as Bridging Groups in Oxidation-Reduction Reactions. J. Am. Chem. Soc., $\underline{83}$, 1785 (1961). (With D. K. Sebera.)

28. Remote Attack and Ester Hydrolysis on Electron Transfer. J. Am. Chem. Soc., $\underline{83}$, 2239 (1961). (With R. T. M. Fraser.)

29. Activation Effects and Rates of Electron Transfer. J. Am. Chem. Soc., $\underline{83}$, 2242 (1961). (With R. T. M. Fraser.)

30. Malonate as a Bridging Group for Electron Transfer. J. Am. Chem. Soc., $\underline{83}$, 4172 (1961). (With George Svatos.)

31. The Exchange of Methanol between Solvated Cations and Solvent. I. Accepted for publication in the Journal of Chemical Physics. (With J. H. Swinehart and T. E. Rogers.)


Part B

1. Isotopic dilution studies on salts dissolved in CH_3OH (J. H. Swinehart and T. E. Rogers). --At low temperatures substitution in the first coordination sphere of many metal cations becomes slow enough so that the hold-back of solvent molecules by the cations can be measured using the isotopic dilution technique. To give the maximum yield in the research, most of the work has been done close to the lowest temperatures possible for liquid CH_3OH.

Under the conditions found practicable for the work, some water is inevitably present in the solutions, and even small amounts of water have a dramatic effect on the results.

A hold-back by Mg^{++} has been demonstrated at -97° and -83°, and the rate of exchange has been measured as a function of temperature. The hold-back is less than the value of 6.0 expected for Mg^{++} in CH_3OH (see paragraph following) and the defect is attributed to the circumstance that in species such as $Mg(CH_3OH)_5H_2O^{++}$, $Mg(CH_3OH)_4(H_2O)_2^{++}$ etc. the bound methanol is so labile that exchange for it is complete by the time the first sample is taken (ca. 1 min.).

At -65°C and at lower temperatures, the nmr absorption of the hydroxyl-hydrogen of bound methanol is displayed separately from that of solvent methanol, and this is true also of the hydrogen of the dissolved water. By comparing peak intensities, the total coordination number of Mg^{++} in the solutions is shown to be 5.9 $\pm$ 0.2, and the equilibrium quotient for the reaction

$$Mg(CH_3OH)_6^{++} + H_2O = Mg(CH_3OH)_5H_2O^{++} + CH_3OH$$
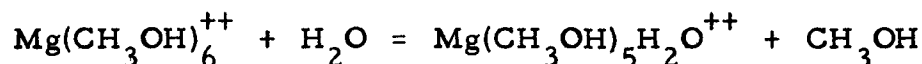
has been measured.

(c) The observations with methanolic solutions of $Co(ClO_4)_2$ are also strongly affected by the water content of the solutions. Again the results can be interpreted on the assumption that hold-back for $Co(CH_3OH)_6^{++}$ can be measured, but the lability of CH_3OH in the mixed aquo-methanolo complexes is so great that exchange is complete by the time the first sample is taken.

(d) In solutions of $NiCl_2$ in CH_3OH, the results seem straightforward. A coordination number of 6.0 is indicated and the slight defect from this which is occasionally observed can be attributed to displacement of CH_3OH from the cation complex by H_2O. Rates of exchange are perhaps 10 fold slower than they are for Co^{++} or Mg^{++} complexes. When $Ni(ClO_4)_2$ is used the results are erratic and often display marked curvature in the McKay plots as well as values for total hold-back well in excess of 6.0.

(e) Cd^{++}-CH_3OH solvate complexes are so labile that exchange is complete in 1 minute even at -97°; for Li^+, exchange is complete in 1 minute even at -110° (supercooled solutions).

(f) Solutions of $Fe(ClO_4)_3$ show behavior like those of $Ni(ClO_4)_2$ except in more exaggerated form. The initial hold-back indicated for Fe^{+++} in certain experiments comprises almost the total alcohol contained in the solution before the O^{18} enriched CH_3OH is added. Yet in no case is there evidence for a solid phase. It should be mentioned that solutions of $Co(ClO_4)_2$ also show anomalously high values of initial hold-back if they are aged for long periods of time. The explanation of the hold-back, whether real or apparent is not known; if it is real, and it is difficult to see how it can be an artifact, it points to the conclusion that electrolyte solutions can adopt superstructures which limit the rate of diffusion of solvent molecules, even though the systems remain liquid.

2. <u>Studies on metals and metal salts in solvents of the amine type</u> (Arlen Viste). --(a) It has been shown that the catalysis of the reaction

$$R_3SiH + H_2NR' = R_3SiNHR' + H_2$$
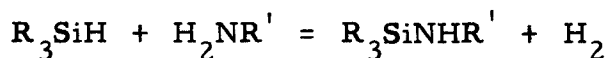
by solutions of Li in the amine $R'NH_2$ is caused by the amide present, and catalysis by solvated electrons is very slight indeed.

The proof of this conclusion was possible taking advantage of the discovery that R_3SiF reacts rapidly with amide, but that it does not oxidize the dissolved metal rapidly. Disappointing as the conclusion was to us, it does bring out the point that NH_2^- is a much more potent base catalyst than are solvated electrons. Under the conditions of our experiments the ratio of $LiNH_2/Li$ was as low as 10^{-5} or 10^{-6}, yet no catalysis by Li was detected.

(b) The equilibrium nitrogen isotopic fractionation brought about by some salts and by some metals dissolved in liquid NH_3 were measured. As is observed for the corresponding measurements in water, the effects depend much more strongly on the nature of the cation than of the anion. The effects for all of the salts measured are positive (i.e. the salt enriches the liquid relative to the vapor with the isotope of higher mass). The effects decrease in the order $Ca^{++} > Pb^{++} > Li^+ > Na^+ > K^+$. A striking effect is the difference observed for a salt such as LiCl compared to Li; for metals the fractionations are very small, and may even be negative for some. The comparison at the least, shows that the electrons cannot be regarded as ordinary negative ions at least in the concentrated solution which we studied.

3. <u>Studies on phosphato complexes of the pentammine Co(III) series</u> (Willfred Schmidt). --(a) A method of preparing $(NH_3)_5CoPO_4 \cdot 2H_2O$ has been worked out and described. None of the methods described in the literature lead to the formation of an inner-sphere phosphate complex of the pentammine cobaltic(III) series. Methods of preparing $(NH_3)_5CoPO_4(CH_3)_3^{+3}$ and of $(NH_3)_5CoPO_4(CH_3)_2^{++}$ in trimethyl phosphate and aqueous solutions respectively have also been developed, but we were unable to prepare pure compounds containing these cations.

(b) The equilibrium quotients governing the addition of 1, 2 and 3 protons to $(NH_3)_5CoPO_4$ have been determined. Comparison with the acid dissociation constants for H_3PO_4 makes it possible to assess the effect which the tripositive residue $(NH_3)_5Co^{+++}$ has on the acidity of the phosphoric acids. The equilibrium quotient for the reaction

$$(NH_3)_5CoPO_4H_2^{++} + H_2O = (NH_3)_5CoOH_2^{+++} + H_2PO_4^{-}$$
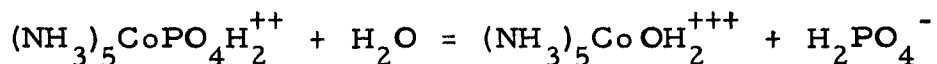
was also measured.

(c) The aquation and hydrolysis of the ion $(NH_3)_5CoPO_4(CH_3)_3^{+++}$ were studied. Aquation is rapid, and $t_{1/2}$ at 25° is approximately 50 minutes. The reaction in basic solution is so rapid that only a lower limit on the specific rate can be set. In neither case is an appreciable amount of methanol formed; in both cases, bond breaking takes place partially at the P-O bond (20% for the aquation reaction and 15% for hydrolysis). Aquation and hydrolysis are much slower for $(NH_3)_5CoPO_4(CH_3)_2^{++}$, and are very slow for $(NH_3)_5CoPO_4$.

(d) The reaction of Cr^{++} with $(NH_3)_5CoPO_4H_2^{++}$ is extremely rapid, and phosphate transfer from Co(III) to Cr(II) accompanies electron transfer. The reaction of Cr^{++} with $(NH_3)_5CoPO_4(CH_3)_3^{+++}$ is much slower and is zero order in (Cr^{++}). The specific rate is the same as for the aquation of $(NH_3)_5CoPO_4(CH_3)_3^{+++}$. The results show that direct electron transfer to the complex is slow, and the reaction waits on the formation of the aquation product $(NH_3)_5CoH_2O^{++}$. The reaction of Cr^{++} with $(NH_3)_5CoPO_4(CH_3)_2^{++}$ is first order in each reagent and takes place at an easily measurable rate.

(e) The experiments on possible activation effects accompanying electron transfer are conclusive only in part. No evidence of oxygen exchange between $PO_4^{\equiv}$ and water was found in the reaction of Cr^{++} with $(NH_3)_5CoPO_4H_2^{++}$ or of Cr^{++} with $Cr(III)-H_2PO_4^{-}$ complex. Erratic results were obtained in the search for production of CH_3OH in the reaction of Cr^{++} with $(NH_3)_5CoPO_4(CH_3)_2^{++}$, yet the conclusion seems definite that no free CH_3OH is produced in the reaction. However, a component may be present in some of the preparations which does form CH_3OH on reaction with Cr^{++}, and this component may be $(NH_3)_5CoPO_4CH_3^{+}$. Further work on this phase of the study is called for.

Twelve graduate students, six post-doctoral research fellows and three undergraduates received training while carrying out the work referred to in this report.