Association of Silver Ion and Chloride Ion in Molten Lithium Nitrate–Potassium Nitrate

Sir:

In a recent paper,[1] Tien and Harrington reported formation constants of silver(I) chloro complexes in fused lithium nitrate–potassium nitrate eutectic at 225° which appeared to be inconsistent with measurements made in this laboratory of similar systems but at 391°.[2] They subsequently reported an error in their original calculations which, when corrected,[3] led to better agreement with the results from this laboratory.

We report here the results of additional measurements[4] at 240° in 70–30 mole % potassium nitrate–lithium nitrate which confirm the corrected results of Tien and Harrington and our previous results. The data were obtained potentiometrically and analyzed graphically by methods described previously.[5] The association constant for the formation of AgCl was found to be $K_1 = 860 \pm 40$ moles of solvent (nitrate)/mole, corresponding to a specific Helmholtz free energy of association[6] $\Delta A = -5.1$ kcal./mole with an assumed coordination number $Z = 6$. The corrected result reported by Harrington and Tien was $\beta_1 = 96 \pm 11$ kg./mole or $K_1 = 1090 \pm 130$ moles of solvent/mole, corresponding also to $\Delta A = -5.1$ kcal./mole. In our experiments, the solubility of silver chloride was found to be too low to permit reliable measurement of K_2 (the association constant for the formation of $AgCl_2^-$); *i.e.*, it was not possible to prepare solutions with high chloride concentrations and also with silver concentrations high enough to yield a satisfactory Nernst slope for the silver electrode. This is reflected in the large uncertainty reported by Harrington and Tien for β_2.

Tien and Harrington assert[1] that "smoothness of the data at low chloride concentrations" demonstrates the absence of binuclear complexes. As a matter of fact, their eq. 6 and 7[1] combined with our eq. 6 and 9[5] lead to the expression

$$\frac{C_m - [M]}{[M]} = \beta_1 C_x + \beta_2 C_x^2 - \beta_1^2 C_m C_x + \dots$$

in the absence of polynuclear species; hence, combining with their eq. 21,[1] the limiting slope of Fig. 1 will be $(\beta_1 - \beta_1^2 C_m)$ in the absence of polynuclear species. On the other hand, a limiting slope independent of the metal ion concentration corresponds to a value of the binuclear association constant $\beta_{12} = \frac{1}{2}\beta_1^2$, as demonstrated by eq. 9 and 16 of ref. 5. The concentration

dependence of the limiting slopes of our data indicated that β_{12} was not zero, although scatter prevented a reliable calculation. The function $(C_m - [M])/[M]$ is, in the notation of ref. 5, $(1/\gamma_{AgNO_3} - 1)$. The magnitudes of the association constants in this system, however, are such that the function $\log 1/\gamma_{AgNO_3}$ (which is proportional to $\Delta(e.m.f.)$) leads to a more linear and hence a more reliable extrapolation, with equal statistical weight for all points.

The use of molarity units in fused salt systems makes comparisons between different solvents difficult (particularly in the absence of complete density–temperature data) unless the association constants are to be analyzed in terms of a Debye–Hückel-type theory. To correlate the association constants in different solvents in terms of ionic radii and charges, ionic mole fractions or mole ratios should be used.

Finally, as Tien and Harrington state, the quasi-lattice model cannot be expected to apply to systems in which the sizes of the ions are quite different; however, the perhaps fortuitous near-constancy of ΔA over appreciable ranges of temperature for several solutes in mixtures of $LiNO_3$ and KNO_3,[7] and even in mixtures of $Ca(NO_3)_2$ with KNO_3 (results to be published shortly), indicate that the equations are useful, in the absence of additional information, for the extrapolation of association constants, at least over small ranges of temperature.

(7) J. Braunstein and A. S. Minano, *Inorg. Chem.*, **3**, 218 (1964).

DEPARTMENT OF CHEMISTRY   J. BRAUNSTEIN
UNIVERSITY OF MAINE   H. BRAUNSTEIN
ORONO, MAINE   A. S. MINANO

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(1) H. T. Tien and G. W. Harrington, *Inorg. Chem.*, **3**, 215 (1964).
(2) C. Thomas and J. Braunstein, *J. Phys. Chem.*, **68**, 957 (1964). (This note was in press but not yet published at the time ref. 1 appeared.)
(3) G. W. Harrington and H. T. Tien, *Inorg. Chem.*, **3**, 1333 (1964).
(4) The data have been deposited as Document No. 7995 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
(5) J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).
(6) (a) M. Blander and J. Braunstein, *Ann. N. Y. Acad. Sci.*, **79**, 838 (1960); (b) M. Blander, *J. Chem. Phys.*, **34**, 432 (1961).

"Five-Coordinated Intermediates" in the Substitution Reactions of Acidopentaamminecobalt(III) Complexes

Sir:

Recently, Haim and Taube[1] have postulated that substitution reactions of ions $Co(NH_3)_5Y^{2+}$ go by a dissociation mechanism in which the five-coordinated intermediate $Co(NH_3)_5^{3+}$ lasts long enough to discriminate between possible nucleophiles.

$$Co(NH_3)_5Y^{2+} \xrightarrow{k_d} Co(NH_3)_5^{3+} + Y^- \quad (1)$$

$$Co(NH_3)_5^{3+} + X^- \xrightarrow{k_x} Co(NH_3)_5X^{2+} \quad (2)$$

$$Co(NH_3)_5^{3+} + H_2O \underset{k_{ex}}{\overset{k_w}{\rightleftharpoons}} Co(NH_3)_5H_2O^{3+} \quad (3)$$
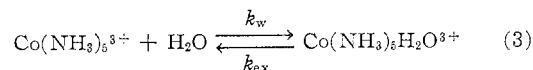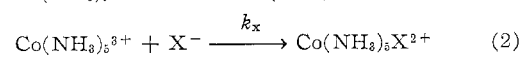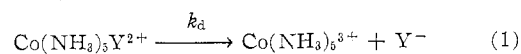
From a study of aquation–anation equilibria and from separate competition experiments, ratios of rate constants, k_x/k_w, have been reported for several anions.[1]

(1) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

$Co(NH_3)_5{}^{3+}$ was supposedly generated by the action of HNO_2 on $Co(NH_3)_5N_3{}^{2+}$.

The existence of $Co(NH_3)_5{}^{3+}$ for even several molecular collisions seems very unlikely to us, first, for energetic reasons,[2] and second, because several attempts on our part have failed to demonstrate nucleophilic discrimination for the, presumably, more stable intermediate $Co(NH_3)_4NH_2{}^{2+}$ involved in base hydrolysis.[3]

We report here experiments which show conclusively that when Y^- is nitrate ion and X^- is thiocyanate ion, the mechanism shown in eq. 1–3 does not account for the rate of formation of isothiocyanato complex.

The data of Haim and Taube[1] predict that when $Co(NH_3)_5{}^{3+}$ is formed in the presence of 0.5 M thiocyanate ion at 25° the immediate product obtained will consist of 14.5% $Co(NH_3)_5NCS^{2+}$ and 85.5% $Co(NH_3)_5-H_2O^{3+}$. Thus, if the aquation proceeds *via* the formation of $Co(NH_3)_5{}^{3+}$, one would expect the above product distribution when $Co(NH_3)_5NO_3{}^{2+}$ undergoes acid hydrolysis in the presence of 0.5 M thiocyanate. Further, since appreciable anation of the product aquo complex occurs during the time required for completion of the hydrolysis, one would expect to find an even larger fraction of $Co(NH_3)_5NCS^{2+}$ than is predicted above.

We have performed several experiments in which $[Co(NH_3)_5NO_3](NO_3)_2$ is made to undergo acid hydrolysis in the presence of excess thiocyanate ion. The absorbancy of the reaction mixture is observed as a function of time at 500 mμ. As shown in Fig. 1 the absorbancy of the solution decreases at first and then slowly increases.

On the basis of the molar absorptivities of the species involved (ϵ_{RNCS} 174,[4a] ϵ_{RH_2O} 47.0,[4b] ϵ_{RNO_3} 57.4[4c] at 500 mμ, R = $Co(NH_3)_5$) one can easily see that the absorbancy of the solution will increase on going from the nitrato complex to the product mixture predicted by Haim and Taube. Since further formation of $Co(NH_3)_5NCS^{2+}$ can only increase the absorbancy of the solution, the observed decrease in absorbancy indicates that $Co(NH_3)_5NCS^{2+}$ is not being formed as rapidly as would be predicted on the basis of their mechanism.

Alternatively, if one assumes that the nitrato complex reacts to give only aquo complex, which subsequently reacts to form isothiocyanato product, then a calculation of the amount of each species present at a given time during the reaction can be made using the equations for successive first-order reactions.[5] The values of the successive rate constants are as follows:

Fig. 1.—Plot of absorbancy *vs.* time for aquation of [Co-$(NH_3)_5NO_3](NO_3)_2$ (0.01 M) in the presence of 0.50 M NaSCN; [H^+] = 0.02 M. Upper curve calculated for mechanism involving a five-coordinate intermediate. Lower curve calculated for mechanism involving conversion to $Co(NH_3)_5H_2O^{3+}$ which subsequently reacts to form $Co(NH_3)_5NCS^{2+}$. Points are experimental.

$k_1 = 2.7 \times 10^{-5}$ sec.$^{-1}$,[6a] $k_2 = 5 \times 10^{-7}$ sec.$^{-1}$.[6b] The results of this calculation are given by the lower, solid curve in Fig. 1. A similar calculation was carried out assuming that the dissociative mechanism was being followed. This is represented by the upper, dashed curve in Fig. 1.

From the above analysis of the data we conclude that no more than 2% of the $Co(NH_3)_5NO_3{}^{2+}$ is converted directly to the isothiocyanato product.

Another treatment of the data was carried out in which it was assumed that no direct formation of $Co(NH_3)_5NCS^{2+}$ occurred, and the value of k_1 was varied until the best fit to the data was obtained. (Since the pseudo-first-order constant, k_2, for the anation was measured using the same conditions given in Fig. 1, this constant was not allowed to vary.) A value of $k_1 = 1.8 \times 10^{-5}$ sec.$^{-1}$ gives good agreement with the experimental data.

An additional experiment was carried out in which the aquo complex was trapped as soon as it was formed by the addition of nitrite ion. This is possible since the nitrito complex is rapidly formed.[7] Under the conditions employed (0.50 M NaSCN, 0.04 M NaNO$_2$, 0.01 M HClO$_4$, 0.01 M [Co(NH$_3$)$_5$NO$_3$](NO$_3$)$_2$) the rate of formation of $Co(NH_3)_5ONO^{2+}$ from $Co(NH_3)_5-H_2O^{3+}$ is much greater than the rate of aquation of $Co(NH_3)_5NO_3{}^{2+}$. The nitrito complex isomerizes intramolecularly to the nitro form, which has an absorption peak at 358 mμ. Analysis of the spectrum obtained upon completion of the reaction shows that only 4% of the $Co(NH_3)_5NO_3{}^{2+}$ has been converted to $Co(NH_3)_5NCS^{2+}$. The remainder has been converted to the nitro species.

Separate experiments show that over the period of time required for complete aquation of $Co(NH_3)_5-$

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 76–79, 98–100.

(3) See M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963). For example, base hydrolysis of $Co(NH_3)_5Cl^{2+}$ in the presence of 0.1 M oxalate ion, where strong ion pairing would be expected, does not produce more than 4% of an oxalato complex. In 0.5 M thiocyanate ion solution base hydrolysis gives less than 2% isothiocyanato complex.

(4) (a) W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Am. Chem. Soc.*, **81**, 2960 (1959); (b) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955); (c) this work.

(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, N. Y., 1961, p. 166.
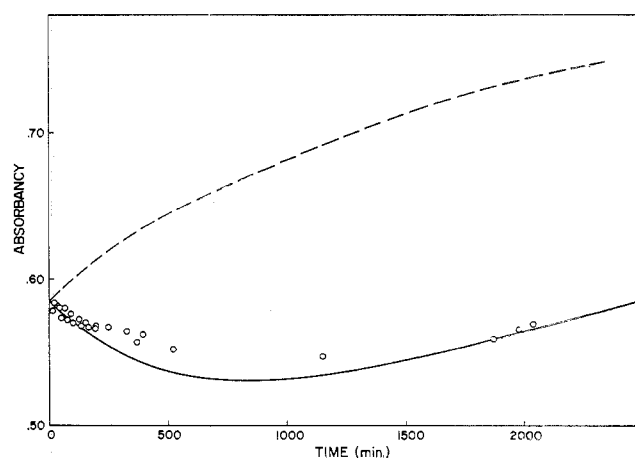
(6) (a) J. N. Brønsted, *Z. physik. Chem.*, **122**, 383 (1926); (b) this work.
(7) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954).

NO_3^{2+} (36 hr.) both the isothiocyanato and nitro species are stable under the reaction conditions. In addition, when $Co(NH_3)_5N_3^{2+}$ is allowed to react under these conditions one finds 13.5% $Co(NH_3)_5NCS^{2+}$, in good agreement with Haim and Taube, so that it is apparent that the nitrite ion is not present in a large enough quantity to compete successfully with thiocyanate. Thus, the nitro complex must be formed from $Co(NH_3)_5H_2O^{3+}$.

The experiments reported here demonstrate conclusively that the aquation of $Co(NH_3)_5NO_3^{2+}$ does not proceed *via* the same intermediate which is formed when $Co(NH_3)_5N_3^{2+}$ is treated with nitrous acid, contrary to the assumptions of Haim and Taube. The virtually total formation of aquopentaammine as an intermediate and the independence of the rate of aquation on the presence of 0.50 M thiocyanate ion are in good agreement with the solvent-assisted dissociation mechanism proposed earlier.[2,8,8a]

(8) T. P. Jones, W. E. Harris, and W. J. Wallace, *Can. J. Chem.*, **39**, 2371 (1961); R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964).

(8a) NOTE ADDED IN PROOF.—Repetition of the hydrolysis experiment in 0.5 M NaSCN with [Co(NH₃)₅Br]Br₂ gave the same result as for [Cr(NH₃)₅NO₂](NO₃)₂.

(9) NSF predoctoral fellow, 1961–1964.

CHEMICAL LABORATORIES   RALPH G. PEARSON
NORTHWESTERN UNIVERSITY   JOHN W. MOORE[9]
EVANSTON, ILLINOIS

Transition Metal Acetylides

Sir:

The only well-characterized transition metal acetylides are those of yttrium and lanthanum, on the one hand, and of the copper and zinc group elements on the other, all of which form acetylides in at least one of their oxidation states. The only report on acetylides of other transition elements is Durand's claim that manganese, iron, cobalt, and nickel acetylides can be prepared by the reaction of calcium carbide with aqueous solutions of the respective metal salts.[1] Evidence for the proposed constitution of these compounds was based entirely on the evolution of acetylene on treatment with dilute hydrochloric acid, and no elemental analyses were recorded.

Terry[2] patented a method for recovering copper by the passage of acetylene through aqueous solutions of its salts, and the process was apparently also applicable to silver, mercury, nickel, osmium, and palladium.

Since copper, silver, and mercury are known to form acetylides under such conditions, it seemed possible that the other elements might also be precipitated as acetylides, although this was not specifically claimed.

We have been unable to confirm the work of Durand with respect to the preparation of the acetylides of manganese, iron, cobalt, and nickel and conclude that his products were almost certainly unreacted calcium carbide, possibly coated with difficultly-soluble material. Moreover, all attempts to precipitate nickel, in any form, by the passage of acetylene through aqueous solutions of its salts have failed, although cuprous acetylide was produced when copper(I) solutions were so treated. Similar negative results were obtained from copper(II), manganese(II), iron(II), and cobalt(II) solutions.

Following Durand,[1] finely-ground calcium carbide (90% purity) was added to a solution of nickel chloride in water contained in a conical flask. The stopper was fitted quickly and the reaction allowed to proceed for 15 min. At the end of this time, the contents of the flask were filtered and the residue was washed repeatedly with 2 M acetic acid. Eventually, only a minute amount of material was left and this dissolved in 2 M hydrochloric acid, except for a trace of black material, probably free carbon, which floated on the solution. No nickel was detected in the hydrochloric acid solution.

In a more sophisticated experiment, a weighed amount of calcium carbide was added to a solution of known nickel content, in an evacuated system, and the evolved acetylene was quantitatively determined by its infrared spectrum. The volume of acetylene recovered was identical with that obtained by a straightforward water hydrolysis of calcium carbide. The small amount of residue after filtration was rinsed thoroughly with 2 M acetic acid, and the washings were added to the original filtrate. The filtrate and the residue were analyzed for nickel using both the dimethylglyoxime and pyridine–thiocyanate methods. No nickel was found in the residue, and this was confirmed by the excellent agreement between the values for the nickel content of the solutions before and after reaction. However, the residue was shown by qualitative analysis to contain calcium and it evolved a trace of acetylene when dissolved in 2 M hydrochloric acid. As before, a trace of free carbon was observed. In similar experiments with salts of manganese, iron, and cobalt, no transition elements were detected in the residues.

In a final series of experiments acetylene gas from a cylinder was passed through a trap at $-80°$ to remove most of the acetone vapor and then successively through a flask containing a standard aqueous nickel(II) solution and a similar flask containing a copper(I) solution. After 24 hr. all the copper had been precipitated, presumably as the acetylide, but no precipitate was visible in the nickel solution. Repetition of the experiment with 2 M hydrochloric acid, 2 M sodium hydroxide, or aqueous ammonia in the nickel solution did not affect the result, though cuprous acetylide

(1) J. F. Durand, *Compt. rend.*, **177**, 693 (1923).

(2) J. T. Terry, U. S. Patent 1,544,197 (June 30, 1925).