TABLE III

EFFECT OF TEMPERATURE ON ISOPRENE POLYMERIZATION INITIATED BY PHENYLLITHIUM IN ETHER

Temp., °C.	Structure of polymer, % 1,2	3,4	*trans*-1,4	*cis*-1,4
−78	9	69	22	..
0	9	68	23	..
25	7	61	32	..
38	5	47	48	..

In Table IV the structure of various aryllithium initiated polyisoprenes is shown. The data are quite definite in showing a very minor effect on structure as produced by different organic anions.

TABLE IV

STRUCTURE OF ARYLLITHIUM INITIATED POLYISOPRENES

Aryl group	Solvent	Temp., °C.	Polymer structure, % 1,2	3,4	1,4 (*trans*)
p-Tolyl	Ether	0	6	61	33
p-Tolyl	Ether	25	7	46	47
o-Tolyl	Ether	25	3	65	32
o-Tolyl	Tetrahydrofuran	25	26	69	5
α-Naphthyl	Tetrahydrofuran	25	28	65	7

Finally, it is worth mentioning that in cationic polymerization of isoprene and butadiene, concurrent work going on in this Laboratory shows relatively slight changes of structure with initiator and solvent.[6] Perhaps the carbonium ion is less affected by its counterion than the carbanion.

In conclusion, we have observed the following results using organometallic initiators in isoprene polymerization. These are consistent with the anionic mechanism.

1. Extremely large variations in structure with changing positive counter ion in homogeneous solutions.
2. Extremely large differences in structure in certain cases depending on whether the reaction is homogeneous or heterogeneous. Perhaps the surface is to be regarded as a large counterion of a special nature. On the other hand, we may here have an extreme case of a solvent effect.
3. Large effects of solvent on the structure of the polymer produced in homogeneous solution. The solvent can certainly influence the electrical forces between the components of the ion-pair.
4. Very small effect of temperature in one solvent; a fairly important effect of temperature in another.
5. Relatively small effect of negative ion (the organic moiety).

The support of the Goodyear Tire & Rubber Company is gratefully acknowledged.

(6) T. Ferington and A. V. Tobolsky (in preparation).

PRINCETON, N. J.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Kinetics and Mechanism of the Reactions between Chloroaquochromium(III) Ions and Silver Ion

BY PHILIP J. ELVING AND BERNARD ZEMEL

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The reaction of the dichlorotetraaquochromium(III) ion with Ag(I) was studied in high hydrogen ion activity (3 to 6 *M* perchloric acid) so that the contributions due to basic and polymeric species were negligible; the only ligands available for complexing chromium were chloride ions and solvent water. Rates were followed by titrimetric determination of Ag(I) concentration; reaction products in terms of chromium species were verified by spectra. The reaction consists of two well-defined steps: conversion of the dichlorotetraaquo ion to chloropentaaquochromium(III) ion and AgCl, followed by conversion of the chloropentaaquo ion to the hexaaquo species. Rates for both reactions are second order, proportional to both Ag(I) and Cr(III) concentrations; rate constants in 6.0 *M* perchloric acid at 25° are 132 ± 45 l. mole^{-1} hr.^{-1} for the first reaction and 0.41 ± 0.01 l. mole^{-1} hr.^{-1} for the second. The rates increase with decrease in perchloric acid concentration. The energy of activation for the second reaction in 3 *M* perchloric acid is 25 kcal./mole; the entropy of activation is +1.6 e.u. The aquation rate of the dichlorotetraaquochromium(III) ion is many times as rapid in the presence of silver as in its absence. The kinetics indicate a reaction mechanism involving formation of a chloride bridge between Cr(III) and Ag(I); this is then followed by the loss of silver chloride and the addition of the water to the residual pentacoördinate chromium species.

The classic establishment of the formulas of the differently colored isomeric chromic chloride hydrates which provided one of the foundations for Werner's theory of coördination compounds and our contemporary views on inorganic complex species, was largely based upon the evidence presented by the reaction of these salts in aqueous solution with Ag(I). The salts were shown to be the violet $[Cr(H_2O)_6]^{+3}$, the light green $[Cr(H_2O)_5Cl]^{+2}$ and the dark green $[Cr(H_2O)_4Cl_2]^+$. However, in titration of their chlorides with silver, many investigators reported precipitation of varying amounts of chloride ion in excess of that predicted by Werner's coördination theory. Such discrepancy was ascribed to chloride produced by dissociation of the complex during titration.

Meanwhile, data, accumulated on the rates of interconversion of the three Cr(III) species, indicated (a) a very slow aquation (replacement of ligand Cl by H_2O), (b) the strong *p*H-dependence of the process (inhibition by increasing hydrogen ion concentration), and (c) the reversible formation of hydroxo and polynuclear species on aging a Cr(III) solution. The rates of exchange of solvent H_2O and Cl^- with complexed H_2O and Cl^- were shown to be very slow. The slow rates of equilibration permit the first three members of the series to be separated from non-equilibrium mixtures as crystalline chlorides, and recrystallized without cross-contamination.

The present study, which is part of an investigation[1] of the chloroaquochromium(III) ions under such circumstances that the nature of the Cr(III) species being observed is well-defined, concerns their reaction with a common reagent. Reaction of a successive series of complex species with a common reagent presents a useful method for comparing the series. By establishing the reaction mechanism, one can interrelate the species through a specific reaction path. In the case of the halo Cr(III) species, Ag(I), Hg(II) and Tl(I) present suitable reagents for this purpose.

At room temperature a solution of the green dichlorotetraaquo ion eventually releases most of its chloride ion and turns violet. Qualitative experiments indicated that removal of chloride from the chromic chlorides in the presence of Ag(I) proceeded much faster than the normal aquation process; this higher aquation rate permits study of the kinetics at high hydrogen ion concentration. Since chloride ion is removed as fast as it is released by the complex, there is no complication due to back reactions. In addition, the reaction can be followed by a sensitive experimental method over wide ranges of concentrations.

After the present study was completed, the excellent study[2] was located in which the reaction between $[Co(NH_3)_5Br]^{++}$ and Hg(II) to form the aquopentammine ion and $HgBr_2$ was found to be bimolecular.

Discussion

Possible Paths for the Reaction of Silver with the Chloroaquochromium(III) Ions.—In principle, the aquation of the Cr(III) chlorides may proceed by a silver-independent path; the evidence to be presented shows that the reactions proceed at a rate proportional to Ag(I) concentration as well as to that of the complex

$$[Cr(H_2O)_{6-n}Cl_n]^{3-n} + Ag^+ \xrightarrow{[H_2O]} [Cr(H_2O)_{6-(n+1)}Cl_{n+1}]^{3-(n+1)} + AgCl \quad (1)$$

While analysis of a second-order parent–daughter relationship is difficult, the problem is solved easily if the rate constants of the two successive reactions are relatively far apart. The amount of AgCl formed in each reaction is proportional to the concentration of Cr(III) species which has reacted; consequently, a relationship exists between the concentrations of Cr(III) complexes and Ag(I) in solution. Since Ag(I) can be determined with good precision and accuracy by differential potentiometric titration, the latter may be used to follow the aquation rate over a wide range of Ag concentrations. In addition, the consecutive aquation of the individual complexes may be verified spectrophotometrically.[1] The low molar absorptivities and the overlapping of the absorption bands restrict the use of spectra for quantitative analysis to relatively high concentrations; furthermore, the difficulties of analyzing the spectrum of the three-component mixture make this method considerably less convenient for obtaining rate data.

Separation of the Reactions.—Since the data (Fig. 1) indicate a relatively sharp division of the course of reaction into two parts, it is assumed that, regardless of the order or orders of the reactions, the latter occur in two consecutive steps: the first, complete in a matter of minutes, is due to the reaction of the dichlorotetraaquochromium(III) ion and the second, which then goes on for many hours, is due to the subsequent reaction of the chloropentaaquo ion formed in the first reaction. The rates of the two reactions are sufficiently different that only a negligible amount of the second ion reacts in the time necessary for the first ion to react. It is thus possible to isolate the second reaction by merely considering the data after the first reaction is essentially complete. As shown in the subsequent discussion of the manner of handling the experimental data, the assumptions made in this paragraph are valid when judged on the basis of the consistency of the results and the reasonableness of the conclusions drawn.

Kinetic Data.[3]—The data, considered in terms of both first- and second-order reactions, fitted second-order kinetics with the rate being proportional to both Ag(I) and chloroaquochromium(III) ion concentrations.

Rate data for reactions 2 and 3, based on observations such as Fig. 1

$$[Cr(H_2O)_4Cl_2]^+ + Ag^+ + H_2O \xrightarrow{k_1} [Cr(H_2O)_5Cl]^{+2} + AgCl \quad (2)$$

$$[Cr(H_2O)_5Cl]^{+2} + Ag + H_2O \xrightarrow{k_2} [Cr(H_2O)_6]^{+3} + AgCl \quad (3)$$

are summarized in Tables I and II; the method of computation is described in the Experimental section. In some experiments it was possible to determine both rate constants and in others only one. In all cases, values for the initial conditions could be obtained by suitable evaluation of the intercept

TABLE I

KINETICS OF THE REACTION BETWEEN DICHLOROTETRAAQUOCHROMIUM(III) AND SILVER IONS IN 6 *M* PERCHLORIC ACID AT 25°[a]

	Initial concn.		State at time t		
	Ag(I)	Cr(III)		$[Ag]_t$,	Rate constant
No.	$[Ag]_0 = a$ *M*	$[CrCl_x] = b$ *M*	Time, hr.	$a - x$ *M*	k_1, l. mole^{-1} hr.$^{-1}$
1	0.071	0.071	0.10	0.038	122
2	.036	.070	7/60	.021	76
3	.075	.0142	7/60	.0647	158
4[c]	.0738[b]	.0139[b]	7/60	.0647	133[b]
5	.0422	.0153	7.5/60	.0354	127
6[c]	.0419[b]	.0152[b]	7.5/60	.0354	125[b]
7	.0235	.0156	7/60	.021	65
8[c]	.0354[b]	.0277[b]	7/60	.021	230[b]
9	.0727	.0362	7/60	.0513	128
10	.0192	.0383	7.5/60	.0103	153

k_1 in 6 *M* $HClO_4$ at 25° $(\overline{X} \pm \sigma) = 132 \pm 45$ l. mole^{-1} hr.$^{-1}$ = $(36.7 \pm 12.5) \times 10^{-3}$ l. mole sec.$^{-1}$

[a] Concentration terms used are defined in the Experimental section. [b] Values of initial concentrations obtained from extrapolated data for reaction of chloropentaaquo ion. [c] Runs 4, 6 and 8 are, respectively, part of the same experiments as no. 11, 12 and 15 of Table II.

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(1) P. J. Elving and B. Zemel, THIS JOURNAL, **79**, 1281 (1957).

(2) J. N. Brönsted and R. Livingston, *ibid.*, **49**, 435 (1927).

(3) Detailed tables of data may be obtained from the senior author.

TABLE II

SUMMARY OF RATE DATA FOR THE REACTION BETWEEN CHLOROPENTAAQUOCHROMIUM(III) ION AND SILVER ION

No.	Initial concn. Ag(I)	Initial concn. Cr(III)	$HClO_4$, M	Temp., °C.	Rate constant k_2, l. mole^{-1} hr.$^{-1}$
11	0.060	0.014	6	25	0.41
12	.0267	.015	6	25	.42
13	.063	.015	6	25	.41
14	.028	.016	6	25	.40
15	.008	.028	6	25	.40
16	.034	.051	6	25	.40
17	.097	.112	6	25	.41
18	.118	.008	4[a]	25	.70
19	.094	.016	4	25	.80
20	.048	.036	3	25	1.14
21	.035	.027	3	30	2.28

k_2 in 6 M $HClO_4$ at 25° $(\overline{X} \pm \sigma) = 0.41 \pm 0.01$ l. mole^{-1} hr.$^{-1}$
$= (0.113 \pm 0.002) \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$

[a] Ionic strength equalled 6 due to addition of sodium perchlorate.

at zero time. In experiments where both k_1 and k_2 were determined, it was possible to determine initial conditions both from titration of the original solution and from extrapolating to zero time the proper function for the second reaction.

The activation energy for the reaction of chloropentaaquochromium(III) ion with silver ion in 3.0 M perchloric acid is 25 kcal./mole; the corresponding frequency factor is about 10^{14}. The latter corresponds to an entropy of activation of +1.6 e.u.

It is apparent that the variable results reported in the older literature for the reaction of Cr(III) chloride species and Ag(I) were merely reflections of a rate-controlled process, and it is of interest to consider the aquation of the complex chromic chlorides by a path different from the normal reactions previously postulated.

Mechanism of the Reaction.—The over-all reaction in perchloric acid solution between the dichlorotetraaquo ion and Ag(I) proceeds in two well-defined stages, the second stage representing the reaction between Ag(I) and the chloropentaaquochromium(III) ion produced by the first reaction; in 6.0 M $HClO_4$ the rate of the first reaction is approximately 300 times that of the second. The formation of the chloropentaaquo ion and the subsequent formation of the hexaaquo ion were confirmed by absorption spectra.

It has been demonstrated that the reaction of silver with chloroaquochromium(III) ions is an aquation reaction, and that the chloride elimination step cannot precede the reaction with silver since the reaction rate is proportional to the concentration of Ag(I) as well as that of the chloroaquochromium ion. Since water exists in great excess over the other components in the reactions, the effect it may have on the reaction rates does not appear in the data, but the reaction must proceed at least through a bimolecular collision intermediate involving both Ag(I) and Cr(III) ions. In the presence of Ag(I) the aquation rate of the dichlorotetraaquo ion is many times greater than the rate in the absence of Ag(I), *e.g.*, *ca.* 10^5 at the Ag(I) concentrations used in the present study.

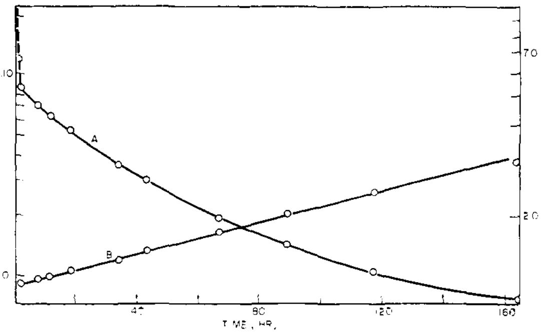


Fig. 1.—Rate of reaction of Ag(I) with dichlorotetraaquochromium(III) ion in 6 M perchloric acid at 25°. Initial concentration of Ag(I) = 0.209 M; initial concentration of Cr(III) = 0.112 M; (A) log $[Ag]_t$ *vs.* time; (B) log $\{([Ag]_t + U)/[Ag]_t\}$ *vs.* time.

In the total absence of silver ion there are two possible rate-determining steps in the aquation of chromic chloride

$$[Cr(H_2O)_5Cl]^{++} + H_2O \rightleftharpoons [Cr(H_2O)_6Cl]^{++} \quad (4)$$

$$[Cr(H_2O)_5Cl]^{++} \rightleftharpoons [Cr(H_2O)_5]^{+3} + Cl^- \quad (5)$$

In order to account for the slow substitution rates of such complexes in solution, the argument[4] has been advanced that the former (equation 4) is more probable than the latter on the grounds that the electronic structure of the inner orbital type can stabilize the required heptacoördinate complex; the second case is presumed to require a higher activation energy, since there is no way to compensate adequately for the energy required to remove the chloride ion.

If one accepts this argument, then since in the presence of silver ion, the reaction proceeds more rapidly than in its absence, it is not reasonable to expect the rate-determining path to reside in the reaction of Ag(I) with the heptacoördinate intermediate

$$[Cr(H_2O)_6Cl]^{++} + Ag^+ = [Cr(H_2O)_6]^{+3} + AgCl \quad (6)$$

In order to fit the kinetic data, the reaction must proceed along the rate-determining path

$$[Cr(H_2O)_5Cl]^{++} + Ag^+ = [Cr(H_2O)_5Cl \cdots Ag]^{+3} \quad (7)$$

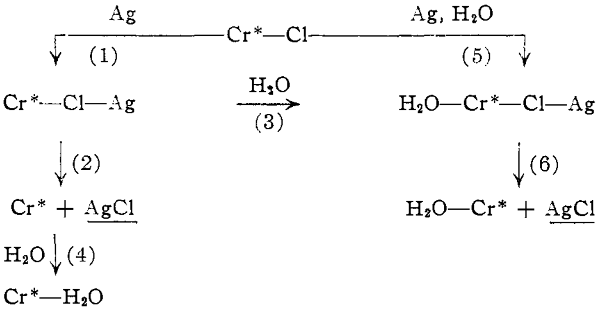
This then can be followed by a dissociation step, which would be equivalent to the case of equation 5 in the absence of silver, the polarization of the chloride by the silver ion providing the driving force necessary for the reaction, or it may be followed by a direct substitution step. As a special case under substitution, if the rate were sufficiently slow, the reaction would appear to be termolecular, if one could measure the effect of the water.

On the basis of the foregoing discussion and of available knowledge on the reactions of complex ions, the following paths may then be considered, where Cr* represents the complex species fraction $[Cr(H_2O)_4Cl]^{++}$ or $[Cr(H_2O)_5]^{+3}$.

Reaction 1 represents a bimolecular collision followed by either a pentacoördinate (*via* 2) or a heptacoördinate (*via* 3) chromium transition state. Reaction 5 represents a termolecular reaction resulting in the formation of a heptacoördinate transi-

[4] H. Taube, *Chem. Revs.*, **50**, 91 (1952).

tion state. On the basis of the previous argument concerning rate-determining steps and the well-known paucity of verified termolecular mechanisms, path 5 appears unlikely. Assuming that the reaction proceeds along path 1, as the rate-determining step, then paths 2 or 3 are equally possible



from the rate data available; however, the reaction between Ag(I) and Cr*Cl goes on in solvents containing very little water, and, while no rate studies have been made, the reaction rates in ether and in 95% alcohol appear qualitatively at least to be of the same order of magnitude as that in aqueous solution. On this very slight evidence one may choose path 2 over path 3, and consider that the decomposition of the transition state formed by path 1 is independent of the concentration of water, but proceeds along path 2 to form a pentacoördinate aquochromium(III) complex, which then adds water (reaction 4) to reform a hexacoördinate complex.

Heterogeneous catalysis by the precipitated silver chloride can be excluded as a significant factor on the basis of the consistency of the data when calculated for second-order reactions. In view of the tremendous silver chloride surface and the fivefold variation in the amount of AgCl produced involved in the experiments described, the observed variation in k_1 would be unexpectedly small for heterogeneous catalysis; actually, there is no correlation between the amount of silver chloride formed and the deviation in k_1. The values of k_2 show no significant variation.

Experimental

Preparation, purification and analysis of the Cr(III) salts used have been described.[1] Since dichlorotetraaquochromium(III) chloride is quite hygroscopic, perchloric acid solutions of this salt were made to approximate concentrations and the exact concentrations then determined by analysis in terms of free chloride ion at 0°; the free chloride concentration has been shown to be equivalent to the $[Cr(H_2O)_4Cl_2]^+$ concentration under the given conditions of chloride analysis.[1] Perchloric acid solutions were prepared by dilution of the 72% acid and adjustment after titration against standard 2 *M* sodium hydroxide solution (carbonate-free); the concentration of perchloric acid is assumed not to be appreciably altered by the volume change due to addition of the solid Cr(III) chloride.

Solutions were stored in two constant-temperature baths. Samples and starting solutions were immersed for temperature equilibration in a 50-gal. high inertia bath, maintained at 25 ± 0.1°. The other bath was an insulated 3-gal. tank containing a circulating pump rated at 3.5 gal./min., from which constant-temperature water (25 or 30 ± 0.1°) was pumped through a jacketed vessel within which sample solutions were placed. This reaction vessel contained provisions for stirring and for introducing or removing sample solution through the stopper.

The spectra of the chloroaquochromium(III) ions have been described.[1] The spectra obtained in the present study were reproducible and constant, indicating that under the experimental conditions involved, the effect of ultraviolet radiant energy on the rate of aquation of the chloro complexes[5] was negligible.

Procedure.—The approximate weight of dry dichlorotetraaquochromium chloride was dissolved with rapid stirring in a perchloric acid solution, which was diluted to volume in a volumetric flask. An aliquot was taken, cooled to 0°, and titrated potentiometrically with a standard $AgClO_4$ solution, using a Ag/AgCl indicating electrode and a glass reference electrode. Both the $AgClO_4$ solution and the aliquot were maintained at the same perchloric acid concentration as the original chromic chloride solution. The $AgClO_4$ necessary to react with the free chloride ion in solution was then calculated, and this amount plus a calculated excess of silver perchlorate was added with stirring to the chromic chloride in the reaction vessel.

Addition of $AgClO_4$ to the chromic chloride solution caused an initial curdy precipitate of AgCl which settled quite rapidly; however, the solution soon became cloudy and a slow post-precipitation went on throughout the course of the experiment. All samples pipetted out within the first hour after silver was added, visibly precipitated out some AgCl during the sampling process. After this initial period, the rate of precipitation was sufficiently low so that no sampling errors were involved. The solutions did, however, show a Tyndall beam effect at all times.

Analysis during a run was accomplished by transferring 1.00- to 5.00-ml. aliquots with volumetric pipets to a solution of 6 *M* $HClO_4$ and immediately titrating the excess Ag(I) with a standard NaCl solution. In the samples taken during the first hour of a run, this procedure was slightly modified by transferring the sample to a solution containing a known chloride ion excess in order to quench the reaction, and back-titrating the excess chloride with standard $AgClO_4$ solution. The transfer process could be completed within 1 to 2 min.; except at the beginning of the experiment, the time of transfer did not introduce any appreciable error. Occasional check runs were made in which larger samples were withdrawn. In such cases, the excess silver was removed by the addition of chloride ion, and the absorption spectrum of the filtered solution measured in order to observe the species present in solution.

The raw experimental results were expressed in terms of the molar concentration of silver ion in solution as a function of time.

Calculations.—The handling of the data is described for the two types of experimental situations encountered with respect to the ratio of the concentration of Ag(I) to that of Cr(III) species. The reaction of Ag(I) with dichlorotetraaquochromium(III) is considered on the basis of two separate consecutive reactions as previously discussed.

Case I.—The Ag(I) molarity is greater than that of the particular Cr(III) species under consideration; the following relationships hold

$[Ag]_0$ = initial concn. of Ag(I) in soln.
$[Ag]_t$ = concn. of Ag(I) at any time, *t*
$[Ag]_f$ = concn. of Ag(I) at end of reaction ($t = \infty$)
$[Ag]_0 - [Ag]_f$ = initial concn. of the particular $[Cr(H_2O)_{6-n}Cl_n]^{3-n}$ species
$[Ag]_0 - [Ag]_t$ = concn. of Cr species which has reacted in time, *t*
$[Ag]_t - [Ag]_f$ = concn. of Cr species present at time, *t*

For second-order kinetics, where the rate is proportional to both silver and chloroaquochromium ion concentrations

$$kt = \frac{2.3}{[Ag]_f} \log \frac{([Ag]_0 - [Ag]_f)[Ag]_t}{([Ag]_t - [Ag]_f)[Ag]_0} \qquad (4)$$

Since $[Ag]_0$ and $[Ag]_f$ are constants for a given experimental run

$$kt = \frac{2.3}{[Ag]_f} \log \frac{[Ag]_0 - [Ag]_f}{[Ag]_0} + \frac{2.3}{[Ag]_f} \log \frac{[Ag]_t}{[Ag]_t - [Ag]_f} \qquad (5)$$

which has the form

$$kt = A + B \log \frac{[Ag]_t}{[Ag]_t - [Ag]_f} \qquad (6)$$

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(5) D. S. Datar and M. Quershi, *J. Osmania Univ.*, **8**, 6 (1940); *C. A.*, **35**, 5392 (1941).

A plot of log $\{[\mathrm{Ag}]_t/([\mathrm{Ag}]_t - [\mathrm{Ag}]_f\}$ against t should give a straight line with a slope of $2.3/(k[\mathrm{Ag}]_f)$, whose intercept at $t = 0$ gives the initial concentration $[\mathrm{Ag}]_0$ for the reaction step under consideration.

Case II.—The Ag(I) molarity is less than that of the particular Cr(III) species under consideration. Since the concentration of complexed chromic chloride species can now no longer be defined by the Ag(I) concentrations, a slightly different approach is used than in Case I, based on the following relations with $[\mathrm{Ag}]_0$, $[\mathrm{Ag}]_t$ and $([\mathrm{Ag}]_0 - [\mathrm{Ag}]_t)$ defined as in case I

$[\mathrm{CrCl}_x]$ = initial concn. of the particular $[\mathrm{Cr(H_2O)}_{6-n}\mathrm{Cl}_n]^{(3-n)}$species

$[\mathrm{CrCl}_x] - [\mathrm{Ag}]_0 + [\mathrm{Ag}]_t$ = concn. of Cr species present at time, t

The equation for a second-order reaction for constant $[\mathrm{Ag}]_0$ and $[\mathrm{CrCl}_x]$ can then be written as

$$\log \frac{[\mathrm{CrCl}_x]}{[\mathrm{Ag}]_0} + \log \frac{[\mathrm{Ag}]_t}{[\mathrm{Ag}]_t + [\mathrm{CrCl}_x] - [\mathrm{Ag}]_0} = \frac{[\mathrm{Ag}]_0 - [\mathrm{CrCl}_x]}{2.3}\, kt \quad (7)$$

If the quantity $[\mathrm{CrCl}_x] - [\mathrm{Ag}]_0$ is written as U

$$\log \frac{[\mathrm{CrCl}_x]}{[\mathrm{Ag}]_0} + \frac{U}{2.3}\, kt = \log \frac{[\mathrm{Ag}]_t + U}{[\mathrm{Ag}]_t} \quad (8)$$

The plot of log $\{([\mathrm{Ag}]_t + U)/[\mathrm{Ag}]_t\}$ against time should give a straight line with a slope of $(-U/2.3)k$ and an intercept at $t = 0$ of log $([\mathrm{CrCl}_x]/[\mathrm{Ag}]_0)$.

The data of Tables I and II are expressed in the above terms. In cases where the silver concentration was in excess, the values of $[\mathrm{Ag}]_t$ and of $([\mathrm{Ag}]_t - [\mathrm{Ag}]_f)$ were used; where the silver concentration was insufficient, values of $([\mathrm{Ag}]_t + U)$ and of $([\mathrm{Ag}]_t + U)/[\mathrm{Ag}]_t$ were used. The data are presented in terms of either the first or the second of the two reaction steps; the very rapid rate of the first reaction precludes the detailed analysis possible for the second step.

Values of the rate constant k_2 were obtained graphically from the slopes of plots of either of two functions, log $\{[\mathrm{Ag}]_t/([\mathrm{Ag}]_t - [\mathrm{Ag}]_f)\}$ or log $\{([\mathrm{Ag}]_t + U)/[\mathrm{Ag}]_t\}$ against time in accordance with the previous discussion. Although k_2 values could be obtained from the individual points, use of a graphical procedure served to smooth out variations in the data and gave more realistic values.

Values of k_1 were obtained by substituting the measured data into equation 7. The short time available for sampling did not permit more than one value for $[\mathrm{Ag}]_t$ to be determined in each run, so that the graphical procedure could not be used. Sampling time was held to 30 sec. or less, this being the time required to drain completely the sampling pipet into a known sodium chloride solution which served to quench the reaction. All of the samples withdrawn had precipitated silver chloride present; the effect of this on the results obtained could not be ascertained, but is believed to be minor.

Values of $[\mathrm{Ag}]_t$ were obtained by differential potentiometric titration, which method is capable of good accuracy; the results obtained were quite reproducible. To calculate k, it was also necessary to have values for either $[\mathrm{Ag}]_f$ or $([\mathrm{CrCl}_x] - [\mathrm{Ag}]_0)$. Of these two, $[\mathrm{Ag}]_f$ values are obviously available with greater accuracy for the second reaction. Since the latter approaches the final equilibrium value asymptotically, by waiting a sufficiently long time the difference between the final measured Ag(I) concentration and the true $[\mathrm{Ag}]_f$ value can be made as small as desired. Values of log $\{[\mathrm{Ag}_t/([\mathrm{Ag}]_t - [\mathrm{Ag}]_f)\}$, when plotted against time, gave a straight line only when the $[\mathrm{Ag}]_f$ values used were essentially those of final equilibrium. If the experimental value of $[\mathrm{Ag}]_f$ used was higher than the true value, the curve sloped upward with increasing time; if it was too low, the curve sloped downward. Consequently, an internal check is available for the deviation of $[\mathrm{Ag}]_f$ from equilibrium. The latter is particularly useful in experiments involving very dilute silver solutions where the values of $[\mathrm{Ag}]_f$ are difficult to measure accurately.

For cases where the silver was insufficient to react with all of the complexed chloride ion, it was necessary to know U. For the first reaction, U can be computed from the known initial concentrations of dichlorotetraaquochromium(III) and silver ions. The chromic species concentration was determined, immediately before adding the silver, by titration of the ionizable chloride with standard silver solution. In some cases the desired silver for $[\mathrm{Ag}]_0$ was added to the titrated solution. In other cases, an amount of silver sufficient to precipitate the ionizable chloride and to furnish $[\mathrm{Ag}]_0$ was added to a fresh sample of the analyzed chromium solution.

The value of U for the second reaction must be derived from that of U for the first reaction, and involves a small uncertainty due to two factors: the tendency for some of the dichlorotetraaquo complex to react with the silver when titrating the uncomplexed chloride, and the uncertainty in the "zero" time of the second reaction due to the mother-daughter relationship. It was found, when the quantity log $\{([\mathrm{Ag}]_t + U)/[\mathrm{Ag}]_t\}$ is plotted against time, that, as in the previous case, a straight line is obtained only when the value of U used had one particular value; otherwise, the line curved upwards or downwards with time depending on whether the value of U is too high or too low.

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[CONTRIBUTION FROM DUQUESNE UNIVERSITY AND CHRISTIAN BROTHERS COLLEGE]

Some Metal Complexes of Glycine Peptides, Histidine and Related Substances[1]

BY NORMAN C. LI, BROTHER EDWARD DOODY AND JAMES M. WHITE

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An ion-exchange method was developed for obtaining the successive formation constants of the Co(II) complexes of glycylglycine, glycylglycylglycine and tetraglycine, and the results are in agreement with those obtained by the pH method. It is shown that the coördination sites of the glycine peptides toward Co(II) are probably the terminal amino group and the immediately adjacent peptide oxygen. The formation constants of Cu(II), Ni(II) and uranyl complexes of glycylglycine, glycine amide, histidine and histidine ester have been measured and compared. The predominant coördination sites of histidine toward Cu(II), Ni(II) and uranyl ions are probably the "pyridine" nitrogen of the imidazole group and the amino group. The rates of alkaline hydrolysis of histidine methyl ester have been determined in the presence and absence of metal ions and it was found that an increase in the stability of metal-ester complex is accompanied by an increase in the bimolecular rate constant.

Introduction

In glycine peptides the following functional groups must be considered as potential sites of coördination to metal ions: the terminal carboxyl group in its charged form, the terminal amino group, the peptide oxygen atom and the peptide nitrogen atom. The formulation of the metal

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