$HgCl^+$ reaction does not contribute significantly to the aquation rate.

The temperature dependences of the rate constants k_0 and k_1 were described in terms of the activation parameters ΔH^* and ΔS^* in the absolute rate theory equation, $k = (k_BT/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R}$. The values of k_0 and k_1 listed in Tables I and III were fit to this equation with a nonlinear least-squares program[10] with the following results. For Hg^{2+}, $\Delta H^* = 14.9 \pm 0.2$ kcal mole^{-1} and $\Delta S^* = -13.4 \pm 0.7$ cal mole^{-1} deg^{-1} with the indicated uncertainties representing standard deviations. In the case of $HgCl^+$, the calculation used values of k_1 based on different estimates for Q_4 in the range 0.25–1.0. The activation parameters are not especially sensitive to the choice of Q_4; for the values 0.25, 0.38, and 1.0, ΔH^* is 14.3 ± 0.6, 14.4 ± 0.5, and 14.1 ± 0.6 kcal mole^{-1}, respectively. The corresponding values of ΔS^* all lie within 2 eu of -15 eu.

Discussion

The observed lack of dependence of the rate of reaction 1 on hydrogen ion appears significant, especially in view of the importance, in the analogous reaction of $Cr(OH_2)_5Cl^{2+}$, of a rate law term k_{-1} $[Cr(OH_2)_5Cl^{2+}]\cdot[Hg^{2+}]/[H^+]$ in a region of $[H^+]$ where no appreciable acid ionization of the reactants takes place.[2] Two mechanisms which are consistent with the kinetics for this pathway both involve a very slight extent of an acid dissociation of one reactant, followed by the rate-determining bimolecular reaction of its basic form with the second reactant. The question of whether this path corresponds to reaction of $Cr(OH_2)_4(OH)Cl^+$ and Hg^{2+} or of $Cr(OH_2)_5Cl^{2+}$ and $HgOH^+$ necessarily remains unsettled from the earlier work.

These results suggest rather strongly, but do not establish beyond question, that the reaction of the species $Cr(OH_2)_4(OH)Cl^+$ with Hg^{2+} rather than that of $HgOH^+$ with $Cr(OH_2)_5Cl^{2+}$ is responsible for the rate law term inversely dependent upon hydrogen ion. The ion $Cr(NH_3)_5Cl^{2+}$ in the present study is a very much weaker acid than is $Cr(OH_2)_5Cl^{2+}$, whereas it is difficult to see how $HgOH^{2+}$, comparably abundant in both studies, could discriminate drastically between the two acidic forms. It should be pointed out also that analogous hydrogen ion dependences are observed in the case of spontaneous aquation of chloroaquo and chloroammine complexes of chromium(III) and cobalt(III).

Although attempts have been made[2,9] at correlation of the rates and activation parameters of similar halide-transfer reactions with data on systems in which chloride ion transfer accompanies electron exchange, the earlier comparisons invariably involved rates or activation parameters for which complete experimental data were not available, and estimates based on analogy were employed. The present study provides data permitting a comparison of the activated complexes $[(NH_3)_5Cr\cdots Cl\cdots Hg(aq)^{4+}]^*$ and $[(NH_3)_5Cr\cdots Cl\cdots Cr(aq)^{4+}]^*$. The values of ΔS^* for formation of these activated complexes from the component ions are -13 and -27 eu,[9] respectively. Two changes affecting the first coordination spheres of the reactant complexes are impending in the transition state for the electron-exchange reaction: five ammonias are to be released by one chromium, and five water molecules are bound more strongly and more closely to the chromium which will become chromium(III). The entropy of activation will reflect the extent to which the coordination spheres of the ions, in forming the transition state, are readjusted to equalize energies for electron transfer. The former change would act to produce a more positive ΔS^*, and the latter, a more negative value. Assuming these two factors provide the main contribution to ΔS^* in the reaction of $Cr(NH_3)_5Cl^{2+}$ with Cr^{2+}, beyond those factors common to each, one concludes the increasingly tight hold of water molecules by chromium is the more important. The 14 eu by which the ΔS^* values of the two reactions differ does not appear unreasonably large to be interpreted as the net effect of such changes.

The reactions of Hg^{2+} with $Cr(NH_3)_5Cl^{2+}$ and $Cr(OH_2)_5Cl^{2+}$, considering for the latter only the rate law term independent of hydrogen ion, proceed with remarkably similar specific rates, 0.087 and 0.048 M^{-1} sec^{-1} at 25.0°. The spontaneous aquation reactions, however, differ in rate[9,11] by a factor of $\sim$70 at the same temperature, again considering only the path independent of hydrogen ion in the case of $Cr(OH_2)_5Cl^{2+}$. In the Hg^{2+}-catalyzed aquation reactions, five of the ligands on chromium(III) exert only minor effects relative to their roles in spontaneous aquation.

(10) This program is based on a report from the Los Alamos Scientific Laboratory, LA2367 plus addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for supplying us with the computer programs and to Mr. J. P. Birk for adapting them to the IBM 7074 computer facilities.

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Oxidation of Cuprous Chloride by Oxygen in Glacial Acetic Acid

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Cuprous chloride has long been known to be oxidized readily by oxygen to copper(II) in aqueous solutions, but, because of the speeds of the reaction, attempts to define the kinetics have been unsuccessful.[1-3] The oxidation of slurries of cuprous chloride in solvents such as acetic acid is much slower than in water. This decrease in rate is presumably at least partially due

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to the low solubility of cuprous chloride in organic solvents. We have found that the rate of oxidation of a slurry of cuprous chloride in acetic acid containing excess chloride is constant with time to the point where the formation of cupric chloride has appreciably altered the chloride ion concentration. This constancy no doubt results from the rapid dissolution of cuprous chloride maintaining a constant equilibrium concentration of dissolved cuprous copper. Since the concentration of cuprous copper can be varied over a wide range by varying the chloride ion concentration, we have a convenient means of measuring the kinetics of the oxidation of cuprous copper in acetic acid.

Experimental Section

Reagents.—The cuprous chloride, acetic acid, and lithium chloride were of reagent grade. They were used without further purification. The oxygen was Air Reduction Co, U.S.P. grade.

Kinetic Runs.—The majority of runs were made using creased flasks connected to thermostated gas burets. This technique has been described.[4] A 2.45-g portion of the cuprous chloride was mixed with 25 ml of a glacial acetic solution of lithium chloride of a known molarity in the reaction flask. The solution was put under an oxygen atmosphere and the stirrer started. The rate was followed by measuring oxygen uptake. A solution identical with the reaction mixture was agitated under a nitrogen atmosphere for a few minutes and the supernatant analyzed for Cu(I). The Cu(I) was determined by difference between Cu(II) and total copper. The Cu(II) was first determined by adding KI to an aliquot of the supernatant and titrating the I_2 released with standard thiosulfate. Another portion was evaporated to dryness, all the copper oxidized to Cu(II) with nitric acid, and the Cu(II) then determined in the same fashion.

Two of the runs, one at 1 atm and one at 3 atm, were made in a modified Sutherland reactor.[5] The pressure was maintained by means of a large mercury manometer equipped with thermowatch controller. Gas from a thermostated reservoir was fed automatically following a pressure drop of 1 mm. The reaction was followed by the pressure drop of the thermostated reservoir.

Results

The plot of oxygen uptake *vs.* time was linear until the chloride concentration was changed appreciably by the oxidation of cuprous chloride to cupric chloride. The time during which a constant rate was observed varied with the original [Cl^-] but, in general, the curvature was detectable when the moles of Cu(I) oxidized was equal to 5% of the moles of total soluble chloride originally present. Results are given in Table I.

The value of k_3 in the last column of Table I is calculated from the relationship

$$-\frac{d[\mathrm{Cu(I)}]}{dt} = k_3[\mathrm{Cu(I)}]^2[P_{\mathrm{O}_2}] \qquad (1)$$

The soluble Cu(I) is probably present as $LiCuCl_2$ since $CuCl_2$ is the predominant species of soluble Cu(I) in aqueous chloride solutions[6] and this is the most likely form in acetic acid containing chloride.

Discussion

Although the variation in k_3 is almost a factor of 2, the range of rates measured was a factor of over 1000, so there is little doubt that eq 1 is the correct kinetic expression.

TABLE I

RATE DATA FOR THE OXIDATION OF CUPROUS CHLORIDE IN ACETIC ACID AND AT 25° AND VARIOUS CHLORIDE ION CONCENTRATIONS

[LiCl], M	[Cu(I)], M	[H^+],[a] M	Oxygen pressure, atm	Rate, M $sec^{-1} \times 10^6$	$k_3 \times 10^3$, M^{-1} atm^{-1} sec^{-1}
0.1	0.0118	...	1	0.58	4.2
0.25	0.044	...	1	8.9	4.6
0.5	0.090	...	1	64.5	8.0
1.0[b]	0.211	...	1	283.0	6.3
1.0	0.211	...	1	220.0	4.9
1.0[b]	0.211	...	3	880.0	6.6
2.0	0.299	...	1	655.0	7.3
1.0	0.211	0.1	1	230.5	5.2
1.0	0.211	0.2	1	231.0	5.2
1.0	0.211	0.5	1	202.0	4.5

[a] Added as CH_3SO_3H. [b] Run in Sutherland reactor.

The third-order reaction path has also been shown to be operative for the air oxidation of Fe(II) in aqueous sulfate and perchlorate medium[7] and of Pu(III) in sulfate solutions.[8] As suggested for the Fe(II) oxidation,[7] this order implies that the rate-determining step is the addition of O_2 to 2Cu(I).

$$O_2 + 2LiCuCl_2 \xrightarrow{\text{slow}} LiCl_2CuOOCuCl_2Li \qquad (2)$$

$$I + 2HOAc \xrightarrow{\text{fast}} 2LiOAc + 2CuCl_2 + H_2O_2 \qquad (3)$$

$$H_2O_2 + 2LiCuCl_2 + 2HOAc \xrightarrow{\text{fast}} 2LiOAc + 2CuCl_2 + 2H_2O \qquad (4)$$

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Metal Complexes of N,N,N′,N′-Tetramethylmalonamide

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Recent studies[2-5] of amides as ligands have involved various substituted monoamides which function as monodentate ligands. A search of the literature

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