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The Kinectis of the Chromium(II)-Catalyzed Aquation of the Pentaaquopyridinechromium(III) Ion

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The kinetics of the chromium(II)-catalyzed aquation of pentaaquopyridinechromium(III) ion has been studied as a function of Cr^{2+} *and* H^+ *concentrations in the temperature range 25-55° at ionic strength 1.0* M *(*$HClO_4+NaClO_4$*). The rate law is of the form* $-d[Cr(py)^{3+}]/dt = k_{-1}[Cr(py)^{3+}][Cr^{2+}][H^+]^{-1}$ *with* $k_{-1} = 1.40\times10^{-4}$ *sec*$^{-1}$ *at 25° and the activation parameters* $\Delta H^{*}_{-1} = 20.6\pm0.2$ *kcal mole*$^{-1}$ *and* $\Delta S^{*}_{-1} = -6.9 \pm 0.6$ *cal mole*$^{-1}$ *deg*$^{-1}$*. A hydroxy-bridged mechanism for the electron transfer is proposed and the role of the non-bridging pyridine ligand is discussed.*

Introduction

Pyridine shows no activity as a bridging ligand in electron transfer reactions involving chromium(II) as the reducing agent[1,2] and is expected to behave as a non-bridging ligand in pentaaquopyridinechromium(III) ion, $Cr(py)^{3+}$, as the oxidizing agent. The non-bridging ligand effect on the electron transfer reaction between monosubstituted chromium(III) complex ions, $(H_2O)_5CrX^{n+}$, and chromium(II) ion has been studied for a number of ligands X[3-7]. We report here on the kinetic studies of the chromium(II)-catalyzed aquation of pyridinechromium(III) ion which accompanies electron transfer:

$$Cr(py)^{3+} + Cr^{2+} \xrightarrow{H^+} Cr^{2+} + H(py)^{+} + Cr^{3+} \qquad (1)$$

The kinetics was studied as a function of acidity and temperature. The pyridinechromium(III) ion was recently prepared and kinetics of its spontaneous aquation measured[8].

Experimental Section

Materials. Pyridinechromium(III) ion in solution was prepared and analyzed as previously described[8]. Hexaaquochromium(III) perchlorate was prepared by reduction of chromium trioxide with formic acid in excess perchloric acid[9]. Solutions of chromium(II) perchlorate were prepared by zinc amalgam reduction of chromium(III) perchlorate under nitrogen atmosphere. The concentration of chromium(II) was determined spectrophotometrically by conversion of total chromium to chromate ion with alkaline peroxide.[10] An allowance was made for the chromium(III) content which was checked at 408 nm.[11]

The acid concentration of chromium(II) solutions was determined by titration with standard sodium hydroxide, after oxidizing aliquots of stock solution by air and absorbing the chromium(III) dimer and zinc ions on a cation-exchange column. Sodium perchlorate was prepared by neutralizing sodium carbonate with perchloric acid. Sodium carbonate was recrystalized three times from water. All chemicals used (Merck) were analytical grade. All solutions were prepared with doubly-distilled water.

Kinetics and Stoichiometry. The reaction was initiated by an addition of a thermostated and deoxygenated pyridine chromium(III) solution to a thermostated solution containing all the other components under nitrogen atmosphere. Aliquots were taken at known times, cooled to 0° and the chromium(II) was oxidized by air. The mixture was absorbed on a cation-exchange column and the pyridinium ion separated from chromium(III) species by elution with 1 *M* $HClO_4$. Analyses of the oxidized chromium showed that under the condition employed no chromate ion and 0-5% of hexaaquochromium(III) was formed, the rest being the chromium(III) dimer.[12] An extent of the reaction corresponding to the amount of the liberated pyridinium ion was determined at 255.6 nm on a Beckman DU-2 spectrophotometer. The pseudo first order rate constants were calculated from the slopes of the straight lines obtained by plotting $\log(D_\infty - D_t)$ *vs.* time, where D_t and D_∞ are the optical densities at time t and 10 half lives of the reaction, respectively. The initial concentrations of pyridinechromium(III) ion were in the range 4.22×10^{-4} to 6.16×10^{-4} *M* and those of chromium(II) ion in the range 2.89×10^{-3}

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[1] F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, *90*, 1162 (1968).

[2] R.G. Gaunder and H. Taube, *Inorg. Chem.*, *9*, 2627 (1970).

[3] D.E. Pennington and A. Haim, *J. Amer. Chem. Soc.*, *88*, 3450 (1966): *Inorg. Chem.*, *6*, 2138 (1967).

[4] J.H. Espenson and D.W. Carlyle, *Inorg. Chem.*, *5*, 586 (1966).

[5] (a) A. Adin and A.G. Sykes, *J. Chem. Soc.* (*A*), *1966*, 1518. (b) A. Adin, J. Doyle, and A.G. Sykes, *ibid.*, *1967*, 1504.

[6] J.P. Birk and J.H. Espenson, *Inorg. Chem.*, *7*, 991 (1968).

[7] J. Doyle, A.G. Sykes, and A. Adin, *J. Chem. Soc.* (*A*), *1968*, 1314.

[8] A. Bakač and M. Orhanović, *Inorg. Chem.*, *10*, 2443 (1971).

[9] J.B. Kirwin, P.J. Proll, and L.H. Sutcliffe, *Trans. Faraday Soc.*, *60*, 119 (1964).

[10] G.W. Haupt, *J. Res. Natl. Bur. Stand.*, *48*, 2331 (1952).

[11] J.P. Fackler, Jr., and D.G. Holah, *Inorg. Chem.*, *4*, 954 (1965).

[12] A.C. Adams, J.R. Crook, F. Bockhoff, and E.L. King, *J. Amer. Chem. Soc.*, *90*, 5761 (1968).

Table I. The rate constants for the chromium(II)-catalyzed aquation of pentaaquopyridinechromium(III) ion at 1.0 M ionic strength ($NaClO_4$).

T(°)	$10^2H^+(M)$	$10^2Cr^{2+}(M)$	$10^4k_{obs}(sec^{-1})$	$10^3k_{II}(M^{-1}sec^{-1})$	$10k_{-1}(sec^{-1})$
24.9	50.0	16.6	0.48	0.29	1.45
24.9	5.00	4.91	1.43	2.90	1.45
24.9	3.30	2.84	1.34	4.74	1.57
24.9	2.50	1.86	1.07	5.72	1.43
24.9	2.00	2.26	1.81	8.00	1.60
24.9	1.66	1.51	1.33	8.82	1.46
24.9	1.39	0.91	0.96	10.6	1.47
34.9	50.0	13.9	1.22	0.87	4.35
34.9	10.0	4.03	1.61	3.98	3.98
34.9	10.0	5.56	2.43	4.36	4.36
34.9	10.0	7.07	2.96	4.19	4.19
34.9	10.0	7.54	3.21	4.26	4.26
34.9	10.0	8.00	3.35	4.19	4.19
34.9	10.0	9.22	3.94	4.27	4.27
34.9	10.0	10.73	4.58	4.26	4.26
34.9	10.0	11.96	4.78	4.01	4.01
34.9	10.0	12.38	5.37	4.34	4.34
34.9	10.0	13.79	6.00	4.36	4.36
34.9	10.0	15.48	6.78	4.38	4.38
34.9	5.0	5.92	5.21	8.79	4.39
34.9	3.30	3.14	3.90	12.4	4.09
34.9	2.50	2.25	3.69	16.5	4.12
34.9	2.00	1.51	3.08	20.4	4.08
34.9	1.66	0.79	2.10	26.7	4.43
34.9	1.39	0.47	1.47	31.0	4.31
45.0	50.0	16.6	4.53	2.73	13.7
45.0	10.0	3.81	5.83	15.3	15.3
45.0	5.0	1.70	5.14	30.2	15.1
45.0	3.30	1.35	5.50	40.7	13.4
45.0	2.50	0.64	3.61	56.2	14.1
45.0	2.00	0.43	3.10	71.4	14.3
45.0	1.66	0.29	2.46	85.0	14.1
45.0	1.39	0.52	5.13	98.9	13.8
55.0	50.0	10.4	7.40	6.85	34.3
55.0	10.0	5.07	18.6	36.7	36.7
55.0	5.0	2.79	21.4	76.8	38.4
55.0	3.30	1.74	20.7	119.	39.2
55.0	2.50	1.57	23.8	152.	38.0
55.0	2.00	1.23	23.5	191.	38.2
55.0	1.66	0.82	18.6	228.	37.8
55.0	1.39	0.50	13.4	271.	37.7

to 0.165 M. The ionic strength was maintained at 1.0 M with sodium perchlorate. The change of perchloric acid concentration during a run due to the protonation of the liberated pyridine was negligible. The contribution of the spontaneous aquation to the rate of the aquation reaction was negligible.

Stoichiometry of the reaction given by equation 1 was confirmed by determination of chromium(II) ion and pyridinium ion concentrations in kinetic solutions. The amount of chromium(II) ion was checked at the beginning and at the end of the run by oxidation with an excess of iron(III) followed by titration of iron(II) with standard dichromate. Pyridinium ion was determined in the eluate of the «infinite-time» samples by recording UV spectrum on a Unicam SP 700 spectrophotometer.

Determination of pK$_a$. Unsuccessful attempts were made to determine the apparent acid dissociation constant of pyridinechromium(III) ion in 1 M ionic strength ($NaClO_4$) at 25°. A thermostated well stirred pyridinechromium(III) perchlorate solution of known acidity was carefully titrated with carbonate free standard sodium hydroxide under nitrogen atmosphere and pH was measured with a M 26 Radiometer pH meter. Actual hydrogen ion concentration for every addition of sodium hydroxide was determined on the base of pH measurement from the pH–[H^+] calibration curve independently obtained for the similar set of the experimental conditions. However, K_a calculated did not give results consistent enough, most likely because of the partial decomposition of the complex ion due to the high local concentrations of hydroxide ion.

Results

The pseudo first order rate constants (k_{obs}) obtained for chromium(II)-catalyzed aquation of pyridinechromium(III) ion at different chromium(II) ion concentrations, different hydrogen ion concentrations, and four temperatures are given in Table I. The reaction is of the first rate order in chromium(II) as explycitly seen from the data at 34.9° and 0.1 M $HClO_4$. The second order rate constants expressed as $k_{II} = k_{obs}/(Cr^{2+})$ are given in the fifth column of Table I. At a particular temperature k_{II} increase with decreasing perchloric acid concentration and a straight line is obtained when plotting k_{II} *vs.* $1/(H^+)$, with an intercept seemingly equal to zero.

Using the least-squares method the data at a particular temperature were treated accordingto the expression

$$k_{II}=k_0+k_{-1}/(H^+)$$

in order to determine the significance of the numerical value of k_o. The computed k_o values differed from zero within their standard deviations. In addition, for three out of the four temperatures negative values were obtained. We conclude that no contribution of an acid independent path to the rate of the reaction is observed, and that the rate law has the form:

$$-[Cr(py)^{3+}]/dt=k_{-1}[Cr(py)^{3+}][Cr^{3+}][H^+]^{-1} \qquad (2)$$

The experimental k_{-1} values are given in the last column of Table I.

The mixed second order rate constants given in Table I were treated simultaneously for all hydrogen ion concentrations and temperatures according to the expression

$$k_{II}=kT/h(H^+)^{-1}e^{\Delta S^*_{-1}/R}e^{-\Delta H^*_{-1}/RT}$$

A CAE 90-40 computer and a nonlinear least-squares program[13] were used to calculate the best value of the enthalpy and entropy of activation as well as the rate constant at 25°. Each rate constant was weighted according to the inverse of its square. The calculated values of the rate constants agreed with the k_{II} given in Table I with an average deviation of 4.9%. The parameters obtained in this way have the values $\Delta H_{-1}^* = 20.6\pm0.6$ kcal mole^{-1} and $\Delta S_{-1}^* = -6.9\pm 0.6$ cal mole $^{-1}$ deg^{-1}. The mean experimental k_{-1} from Table I having values (in 10^4 sec^{-1}) 1.49, 4.24, 14.2, and 37.4 at temperatures of 24.9, 34.9, 45.0, and 55.0° compare well with the respective values (in 10^4 sec^{-1}) 1.40, 4.49, 13.4, and 37.3 calculated from the activation parameters for temperatures of 25, 35, 45, and 55°

Conclusions

The rate law for the chromium(II)-catalyzed aquation of pyridinechromium(III) ion is consistent with a transition state of the composition $\{Cr(OH)Cr(py)^{4+}\}^*$. The lack of an acid-independent path for the catalyzed aquation is a strong indication that the preceding electron transfer proceeds by a hydroxy-bridged inner-sphere mechanism.[14,15]

Hydrogen ion independent path makes no or little contribution in the analogous reaction of the other monosubstituted chromium(III) ions, $(H_2O)_5CrX^{n+}$, thus far studied and an operation of the hydroxy-bridged mechanism was proposed.[3-7] The non-bridging ligands X are assumed to operate from the position *trans* to hydroxy bridge in the halide ligands series,[3,5] causing a reactivity decrease in the order I>Br>Cl (10_4k_{-1} in sec^{-1} at 25°: 213, 17.4, and 3.2, respectively) in accordance with the Orgel's hypothesis.[16] The complexes with a stronger crystal field ligand, including pyridine, react slower than the chloro complex but only roughly enter the picture. For the oxidants having a 3+ charge the ligand field sequence H_2O–py–NH_3, which is the same as the sequence of the spontaneous aquation rates,[17,8,4] is not strictly followed by the reactivity toward Cr^{2+} (10^4k_{-1} in sec^{-1} at 25°: $\sim$1 or $\sim$0.2, 1.40 and 0.72, respectively).[18,5b,19,4] Similar observation was made for the complexes having azide,[7] fluoride,[5a] and cyanide[6] as the non-bridging ligands (10^4k_{-1} in sec^{-1} at 25°: $\sim$0.06, $\sim$0.016, and $\sim$1, respectively).

The rate constants for the reduction of the latter six monosubstituted chromium(III) ions by chromium(II) have not very different values, however. For the ligands having stronger crystal field than H_2O it is likely that the *cis* isomers (with H_2O *trans* to the hydroxy group) are more reactive than the *trans* isomers, as previously suggested,[4,6] and that *cis* non-bridging ligands show specific but minor effects on the rate. The rate of chloride-bridged electron transfer between Cr^{2+} and $Cr(NH_3)_5Cl^{2+}$, for example, is enhanced for a factor of $\sim$15 by substituting water for ammonia in position *trans* to chloride ligand.[20]

If $Cr(OH)(py)^{2+}$ and Cr^{2+} species form the precursor complex in reaction 1 then a second order rate constant $k_2 = k_{-1}/K_a$ could be calculated were the acid dissociation constant (K_a) known. K_a for the $Cr(H_2O)_6^{3+}$ and a $Cr(H_2O)_4(py)_2^{3+}$ species at 25° and $\mu = 1.0$ *M* have the values 4.0×10^{-5} *M*[21] and 6.0×10^{-5} *M*[22], respectively. It appears reasonable to assume $K_a\sim5\times10^{-5}$ *M* for $Cr(py)^{3+}$ giving $k_2\sim3M^{-1}$. However the latter value would be meaningless if $Cr(py)^{3+}$ and Cr^{2+} form the precursor complex which deprotonates in a step faster than the electron transfer. Evidence or indications for deprotonation of precursor complexes for some reactions have been observed[23,24].

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(13) The computer program is based on the Los Alamos Scientific Laboratory Reports LA-2367 and Addenda.

(14) A. Zwickel and H. Taube, *Discuss. Faraday Soc.*, *29*, 42 (1960).

(15) N. Sutin, *Accounts Chem. Res.*, *1*. 225 (1968).

(16) L. Orgel, « Report of the Tenth Solvay Conference », Brussels, *1956*, p. 289.

(17) J.P. Hunt and R.A. Plane, *J. Amer. Chem. Soc.*, 76, 5960 (1960).

(18) A. Anderson and N.A. Bonner. *ibid.*, 76, 3826 (1954).

(19) This work.

(20) T.J. Williams and C.S. Garner, *Inorg. Chem.*, 9, 2058 (1970).

(21) E. Deutsch and H. Taube, *ibid.*, 7, 1532 (1968).

(22) A. Bakač and M. Orhanović, unpublished results.

(23) D. Seewald, N. Sutin, and K.O. Watkins, *J. Amer. Chem. Soc.*, *91*, 7307 (1969).

(24) M.P. Liteplo and J.F. Endicott, *ibid.*, *91*, 3982 (1969).