

being more effective in keeping the free end near this site. This also would explain the larger value of  $\Delta S^\ddagger$  in  $\text{CDCl}_3$  since this solvent, in its attempt to coordinate to the "vacant" sixth position, would force the free end away from its original site, thus leading to an increase in  $\Delta S^\ddagger$ .

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**Registry No.**  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2$ , 17099-71-7;  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ , 16925-15-8.

Contribution from the Institute "Ruder Boskovic," Zagreb, Croatia, Yugoslavia

## Pentaaquo(3-chloropyridine)chromium(III) and Pentaaquo(3-cyanopyridine)chromium(III) Ions. The Preparation, Characterization, and Kinetics of the Aquation<sup>1</sup>

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The pentaaquo(3-chloropyridine)chromium(III) and pentaaquo(3-cyanopyridine)chromium(III) ions were prepared by the reduction of the corresponding pyridine adducts of diperoxychromium(VI) species with acidic ferrous perchlorate followed by the separation on a cation-exchange column. These pyridinyl nitrogen-bonded complexes aquate according to the rate law  $-\text{d} \ln [\text{Cr}(3\text{-Xpy})^{3+}]/\text{d}t = k_0 + k_{-1}/(\text{H}^+)$  at different temperatures studied. In 1 M ionic strength ( $\text{HClO}_4 + \text{NaClO}_4$ ) the activation parameters for the 3-chloropyridine complex and 3-cyanopyridine complex have the values:  $\Delta H_0^\ddagger$  (kcal mol<sup>-1</sup>)  $26.3 \pm 0.5$  and  $23.9 \pm 0.6$ ,  $\Delta S_0^\ddagger$  (cal mol<sup>-1</sup> deg<sup>-1</sup>)  $-1.6 \pm 1.3$  and  $-5.2 \pm 1.7$ ,  $\Delta H_{-1}^\ddagger$  (kcal mol<sup>-1</sup>)  $33.5 \pm 0.1$  and  $31.7 \pm 0.2$ ,  $\Delta S_{-1}^\ddagger$  (cal mol<sup>-1</sup> deg<sup>-1</sup>)  $13.7 \pm 0.4$  and  $11.3 \pm 0.6$ . The corresponding specific rates extrapolated to 25° are  $k_0$  (sec<sup>-1</sup>)  $1.6 \times 10^{-7}$  and  $1.3 \times 10^{-6}$  and  $k_{-1}$  (M sec<sup>-1</sup>)  $1.6 \times 10^{-9}$  and  $1.1 \times 10^{-8}$ . A linear correlation between  $\log k_0$  or  $\log k_{-1}$  and  $\text{p}K_a$ 's of a series of the substituted pyridine ligands is found. A comparison with the similar finding for a series of uninegative ligands is made and the mechanistic implications discussed.

### Introduction

The linear relationship between the logarithm of rate of aquation and the logarithm of stability constant has revealed useful insights on modes of spontaneous<sup>2-5</sup> and assisted<sup>6,7</sup> aquation of transition metal complexes. A particular linear free energy relationship (LFER) is the one involving reactivity and basicity.<sup>8</sup> Linear correlations between the free energy of activation for the aquation<sup>9-16</sup> or another octahedral substitution reaction<sup>17-19</sup> and the  $\text{p}K_a$  of the

leaving<sup>9-15,19</sup> or nonleaving<sup>16-18</sup> ligand is often found. This kind of LFER offers less direct insight into mechanism of substitution reactions; however, comparisons of the correlations obtained for different series of ligands related to the same moiety might prove more useful.

This paper deals with 3-chloropyridine and 3-cyanopyridine complexes of monosubstituted chromium(III), aquation of which was studied as a function of acidity and temperature. Acquisition of these data together with those previously published on analogous pyridine<sup>20</sup> and 3-picoline<sup>21</sup> complexes enabled us to make a correlation between the reactivity and the basicity of the leaving pyridine ligands. A comparison with the similar analysis of the reactivity of the complexes with uninegative ligands<sup>14</sup> is made.

### Experimental Section

**Preparation of Pentaaquo(3-chloropyridine)chromium(III) and Pentaaquo(3-cyanopyridine)chromium(III) Ions.** These complex ions were prepared by the reduction of the respective pyridine adducts of diperoxychromium(VI) species with acidic ferrous perchlorate solution, followed by the separation on a cation-exchange resin. The procedure was analogous to the one reported for the preparation of pentaaquo(3-picoline)chromium(III) ion.<sup>21</sup> The concentration of pentaaquo(3-chloropyridine)chromium(III) ion<sup>22</sup> or pentaaquo(3-cyanopyridine)chromium(III) ion<sup>22</sup> in 3 M perchloric acid solution obtained in this way was  $1-3 \times 10^{-2}$  M. The solution stored at  $-5^\circ$  did not change for an extended period of time. Aquation of the complex ions to a certain degree was observed when, for the purpose of kinetic studies at low acidity, cooled (0°) stock solutions were reduced to 0.1 M  $\text{HClO}_4$  by titration with cooled 3 or 1 M potassium hydroxide.

**Other Materials.** Laboratory grade 3-chloropyridine (Fluka) was distilled and a middle fraction with bp 146-147° was used. Labora-

(1) (a) Presented at the Meeting of Croatian Chemist, Zagreb, Feb 1973. (b) Taken from the theses submitted by A. Bakac and R. Marcec in partial fulfillment of the requirements for the Master of Science degree at the University of Zagreb, 1972.

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(22) Hereafter: (3-chloropyridine)chromium(III) and (3-cyanopyridine)chromium(III).

tory grade 3-cyanopyridine (Fluka) was recrystallized from ethanol. All other chemicals,<sup>20</sup> analytical grade (Merck), were used without further purification. All solutions were prepared with double-distilled water.

**Analytical Methods.** Qualitative and quantitative determination of 3-chloropyridine and 3-cyanopyridine was made by uv spectrophotometry in aqueous perchloric acid solutions after the decomposition of the complex ions in an alkaline media or after aqutation of the complexes for 10 or more half-lives. Absorption maxima in 0.1 M HClO<sub>4</sub> at 271 ( $\epsilon$  4.71  $\times$  10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) and 215 nm ( $\epsilon$  3.76  $\times$  10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) for 3-chloropyridine and at 264 ( $\epsilon$  4.33  $\times$  10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) and 216.5 nm ( $\epsilon$  6.98  $\times$  10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) for 3-cyanopyridine were used. Interference from Cr<sup>3+</sup> absorption was negligible. Chromium(III) was determined spectrophotometrically as chromate ion ( $\epsilon$  4.83  $\times$  10<sup>3</sup> at 372 nm) after decomposition of the complexes and oxidation with alkaline peroxide.<sup>23</sup> Interference from 3-chloropyridine or 3-cyanopyridine absorption was negligible. The concentration of free perchloric acid in solutions of the complexes was determined by the method of King and Neptune.<sup>24</sup>

All absorbance measurements were performed on Cary 16 or Beckman DU-2 spectrophotometers.<sup>25</sup>

**Kinetic Measurements.** Kinetics of the aqutation was followed spectrophotometrically. First-order rate constants were calculated from the slopes of the straight lines obtained by plotting log ( $D_{\infty} - D_t$ ) or log ( $D_t - D_{\infty}$ ) vs. time, where  $D_t$  and  $D_{\infty}$  are the optical densities at time  $t$  and 10 half-lives of the reaction, respectively. The kinetics was followed for three or more half-lives of the reaction. For (3-chloropyridine)chromium(III) a decrease in optical density at 271 or 260 nm and an increase at 205, 215, or 225 nm was measured, depending on the acidity used. At 205 nm, for example, the  $\epsilon$  value (M<sup>-1</sup> cm<sup>-1</sup>) of the complex ion is about 1.3  $\times$  10<sup>4</sup>, that of the Cr<sup>3+</sup> ion about 80, and that of the 3-chloropyridinium ion comparable to the unprotonated species about 4  $\times$  10<sup>3</sup>. For (3-cyanopyridine)chromium(III) a decrease in optical density at 205 nm and for higher acidities an increase at 265 nm was measured. At 205 nm the  $\epsilon$  value of the complex ion is about 1.4  $\times$  10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, while 3-cyanopyridinium ion and the unprotonated species show here an isosbestic point with  $\epsilon$  about 5.4  $\times$  10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>. Similar results at different wavelengths were obtained.

For runs with half-lives longer than 15 min the technique using ampoules was employed as previously described.<sup>20</sup> For faster runs the reaction was initiated by an addition of the complex ion solution from a thermostated piston-pipette to a thermostated solution containing all the other components. Aliquots of the reaction mixture were withdrawn at known times with a fast running pipette surrounded by a jacket through which cooled (0°) water was circulated.

## Results and Discussion

**Characterization of (3-Chloropyridine)chromium(III) and (3-Cyanopyridine)chromium(III) Ions.** (H<sub>2</sub>O)<sub>5</sub>Cr(3-Clpy)<sup>3+</sup> and (H<sub>2</sub>O)<sub>5</sub>Cr(3-CNpy)<sup>3+</sup> like (H<sub>2</sub>O)<sub>5</sub>Cr(py)<sup>3+</sup> and (H<sub>2</sub>O)<sub>5</sub>Cr(3-pic)<sup>3+</sup> are eluted from a Dowex 50W-X8 ion-exchange column somewhat less readily than Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ion. This behavior is compatible with a 3+ charge and with the size of the ions.<sup>26</sup> The chromium-to-ligand ratio in both complex ions was found to be 1:1 within an average deviation of 2%. The uv-visible spectrum in 1 and 3 M perchloric acid shows absorption (nm) at (molar absorption index follows in parenthesis): 561, max (18.5); 471, min (4.3); 402, max (20.6); 366, min (12.0); 273, max (3.43  $\times$  10<sup>3</sup>); 242, min (3.51  $\times$  10<sup>2</sup>) for (3-chloropyridine)chromium(III) ion; and 561, max (19.0); 471, min (4.6); 402, max (20.5); 346, min (7.0); 271, max (2.90  $\times$  10<sup>3</sup>); 265, max (3.38  $\times$  10<sup>3</sup>); 241, min (6.9  $\times$  10<sup>2</sup>) for (3-cyanopyridine)chromium(III) ion. Table I summarizes the visible absorption maxima of (H<sub>2</sub>O)<sub>5</sub>Cr<sup>III</sup>X ions for X being different pyridine ligands and their neighbors in the spectrochemical series, with NCS<sup>-</sup> representing the N-bonded isomer.

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(25) We thank the Faculty of Pharmacy and Biochemistry, University of Zagreb, for making the Cary 16 instrument available.

(26) Abbreviations: 3-Clpy = 3-chloropyridine, 3-CNpy = 3-cyanopyridine, py = pyridine, 3-pic = 3-picoline, 4-NH<sub>2</sub>COPY = isonicotinamide.

**Table I.** Visible Absorption Maxima of Some Pentaquo(ligand)chromium(III) Ions

Ligand	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	
NCS <sup>-a</sup>	570 (31.4)	410 (33.5)
3-CNpy <sup>b</sup>	561 (19.0)	402 (20.5)
3-Clpy <sup>b</sup>	561 (18.5)	402 (20.6)
4-NH <sub>2</sub> COPY <sup>c</sup>	555 (18.6)	401 (20.9)
py <sup>d</sup>	560 (18.2)	402 (20.8)
3-pic <sup>e</sup>	558 (18.6)	402 (20.8)
NH <sub>3</sub> <sup>f</sup>	545 (22.1)	397 (21.8)

<sup>a</sup> A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966).

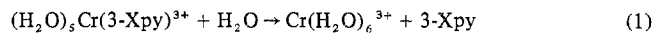
<sup>b</sup> This work. <sup>c</sup> Reference 29. <sup>d</sup> Reference 20. <sup>e</sup> Reference 21.

<sup>f</sup> M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

The wavelengths of the d-d transition bands for the four pyridine complexes in Table I are very similar, the fact leading to the conclusion that the 3-chloropyridine is nitrogen bonded in the complex. It is reasonable to conclude that the 3-cyanopyridine is also pyridinyl nitrogen bonded. If it were nitrile nitrogen bonded a behavior on the cation-exchange column different from that of the three other pyridine complexes and compatible with a 4+ charge would have been observed, due to the very probable protonation of the pyridinyl nitrogen in 3 M HClO<sub>4</sub>. This conclusion is also supported by the report that the isocyanochromium(III) ion, (H<sub>2</sub>O)<sub>5</sub>CrNC<sup>2+</sup>, which was found to be a rather unstable species, has visible absorption maxima at 535 and 396 nm.<sup>27</sup>

The uv spectra of the two complexes, given in Figure 1, are unaffected by change of ionic strength over the range 3.0 to 0.1 M and by change of acid concentration in the range from 1 to 10<sup>-2</sup> M HClO<sub>4</sub> at 1.0 M ionic strength.

**Aqutation of (H<sub>2</sub>O)<sub>5</sub>Cr(3-Clpy)<sup>3+</sup> and (H<sub>2</sub>O)<sub>5</sub>Cr(3-CNpy)<sup>3+</sup> Ions.** The stoichiometry of the aqutation, reaction 1, was



routinely observed by identifying the ligand product as 3-chloropyridinium ion or 3-cyanopyridinium ion from their uv spectra given in Figure 1. For this purpose "infinite time" samples acidified to 1.0 M were used, since in the acidity range studied the extent of protonation of the ligand products, eq 2, varied substantially.



The initial concentration of (3-chloropyridine)chromium(III) was in the range 1.85  $\times$  10<sup>-5</sup> to 4.58  $\times$  10<sup>-4</sup> M and that of (3-cyanopyridine)chromium(III) in the range 2.66  $\times$  10<sup>-5</sup> to 3.12  $\times$  10<sup>-4</sup> M. At a particular hydrogen ion concentration the reactions obeyed first-order rate law

$$-d[Cr(3-Xpy)^{3+}]/dt = k_{\text{obsd}}[Cr(3-Xpy)^{3+}]$$

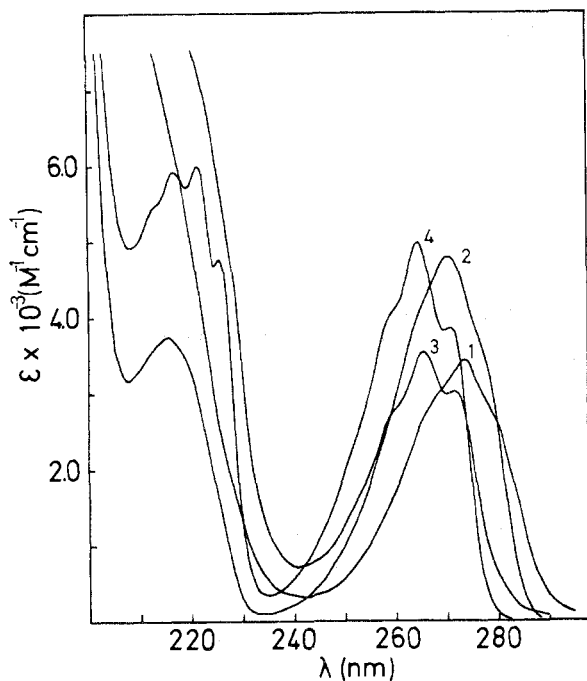
The rate constants observed at different hydrogen ion concentrations and different temperatures are given in Tables II and III. The ionic strength was maintained constant at 1.0 M with sodium perchlorate.

A least-squares treatment of the data at a particular temperature according to the equation

$$k_{\text{obsd}} = k_0 + k_{-1}/(H^+) \quad (4)$$

shows that the experimental values of  $k_{\text{obsd}}$  deviate from the fitted straight line within an average deviation of 0.6 to 1.8% for (3-chloropyridine)chromium(III) and within 1.1 to 3.0% for (3-cyanopyridine)chromium(III). No deviation trend is observed when NaClO<sub>4</sub> almost completely replaces HClO<sub>4</sub>.

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**Figure 1.** Ultraviolet spectra in 1.0 M HClO<sub>4</sub>: (1) pentaquo(3-chloropyridine)chromium(III) ion, (2) 3-chloropyridinium ion, (3) pentaquo(3-cyanopyridine)chromium(III) ion, (4) 3-cyanopyridinium ion.

**Table II.** First-Order Rate Constants for the Aquation of Cr(H<sub>2</sub>O)<sub>5</sub>(3-Clpy)<sup>3+</sup> Ion at 1.0 M Ionic Strength (HClO<sub>4</sub> + NaClO<sub>4</sub>)<sup>a</sup>

Temp, °C	(HClO <sub>4</sub> ), mM	10 <sup>5</sup> × k <sub>obsd</sub> , sec <sup>-1</sup>	Temp, °C	(HClO <sub>4</sub> ), mM	10 <sup>5</sup> × k <sub>obsd</sub> , sec <sup>-1</sup>
80.0	986	19.8	60.0	6.67	12.1
80.0	303	23.1	60.0	4.92	15.2
80.0	79.6	35.7	60.0	4.12	18.3
80.0	19.9	87.5	60.0	2.51	28.5
80.0	10.0	152	60.0	1.89	36.7
80.0	6.69	222	60.0	1.74	40.2
80.0	5.10	282	60.0	1.39	51.3
70.0	1000	6.5	60.0	1.25	56.3
70.0	79.6	10.2	60.0	1.06	64.2
70.0	30.0	16.7	60.0	0.870	79.7
70.0	19.9	22.5	50.1	10.4	1.87
70.0	10.2	37.3	50.1	3.48	4.62
70.0	3.59	92.5	50.1	2.09	7.30
70.0	2.14	149	50.1	1.54	9.87
70.0	1.55	201	50.1	1.25	12.3
70.0	1.16	288	50.1	1.01	14.8
70.0	0.998	327	50.1	0.870	17.2
70.0	0.870	380	45.0	2.50	2.80
60.0	100	2.65	45.0	1.54	4.40
60.0	23.0	4.93	45.0	1.11	6.13
60.0	19.9	5.30	45.0	0.870	7.65
60.0	9.85	8.62			

<sup>a</sup> Concentration of Cr(H<sub>2</sub>O)<sub>5</sub>(3-Clpy)<sup>3+</sup> varied in the range 1.85 × 10<sup>-5</sup> to 4.58 × 10<sup>-4</sup> M.

The acid-independent rate terms have definite values, and for the temperatures at which acidity was extended to higher than 10<sup>-2</sup> M the calculated k<sub>0</sub> values have standard deviation within 2.2% for Cr(3-Clpy)<sup>3+</sup> and within 3.5% for Cr(3-CNpy)<sup>3+</sup>.

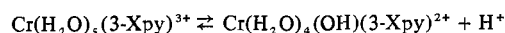
The rate law thus has two terms in the acidity range studied, as previously observed for a number of monosubstituted chromium(III) complexes,<sup>21</sup> and it is consistent with k<sub>0</sub> in expression 4 being the rate constant for aquation of (H<sub>2</sub>O)<sub>5</sub>Cr(3-Xpy)<sup>3+</sup> ion and k<sub>-1</sub>/K<sub>h</sub> = k<sub>-1</sub>' the rate constant for the aquation of the conjugate base ion, (H<sub>2</sub>O)<sub>4</sub>(OH)Cr(3-Xpy)<sup>2+</sup>.

**Table III.** First-Order Rate Constants for the Aquation of Cr(H<sub>2</sub>O)<sub>5</sub>(3-CNpy)<sup>3+</sup> Ion at 1.0 M Ionic Strength (HClO<sub>4</sub> + NaClO<sub>4</sub>)<sup>a</sup>

Temp, °C	(HClO <sub>4</sub> ), mM	10 <sup>5</sup> × k <sub>obsd</sub> , sec <sup>-1</sup>	Temp, °C	(HClO <sub>4</sub> ), mM	10 <sup>5</sup> × k <sub>obsd</sub> , sec <sup>-1</sup>
70.0	1000	29.6	50.0	5.09	16.5
70.0	90.0	45.3	50.0	2.90	29.6
70.0	10.0	173	50.0	2.00	39.8
70.0	5.10	321	50.0	1.37	59.2
70.0	3.30	472	50.0	1.10	69.6
60.0	1000	10.1	50.0	0.910	85.5
60.0	100	13.9	50.0	0.830	91.7
60.0	15.0	31.6	40.0	10.0	2.33
60.0	8.31	47.2	40.0	4.93	3.96
60.0	5.00	77.0	40.0	2.94	6.02
60.0	3.33	109	40.0	2.14	8.13
60.0	2.00	170	40.0	1.32	12.8
60.0	1.60	210	40.0	1.24	14.0
60.0	1.25	275	40.0	0.982	17.8
60.0	1.00	321	40.0	0.856	19.2
50.0	1000	3.34	35.0	1.32	4.90
50.0	90.1	3.82	35.0	1.02	6.48
50.0	13.9	8.37	35.0	0.815	7.87

<sup>a</sup> Concentration of Cr(H<sub>2</sub>O)<sub>5</sub>(3-CNpy)<sup>3+</sup> varied in the range 2.66 × 10<sup>-5</sup> to 3.12 × 10<sup>-4</sup> M.

The equilibrium constants, K<sub>h</sub>, for the acid dissociation reaction



are not known, but on the basis of the good fitting of the experimental data to expression 4 it is assumed that K<sub>h</sub>/(H<sup>+</sup>) ≪ 1 at the conditions employed.

The activation parameters for the two reaction paths were computed by treatment of the 43 rate constants from Table II or the 36 rate constants from Table III simultaneously for all hydrogen ion concentrations and temperatures according to the expression

$$k_{\text{obsd}} = (kT/h) \sum_i (\text{H}^+)^i e^{\Delta S_i^\ddagger/R} / R e^{-\Delta H_i^\ddagger/RT}$$

with *i* = 0 and -1, using a nonlinear least-squares program.<sup>28</sup> Each k<sub>obsd</sub> was weighted according to the inverse of its square. The fitted values of k<sub>obsd</sub> agreed with the experimental ones with an average deviation of 2.5% for Cr(3-Clpy)<sup>3+</sup> and 3.7% for Cr(3-CNpy)<sup>3+</sup>. The activation parameters obtained in this way have the values ΔH<sub>0</sub><sup>‡</sup> = 26.3 ± 0.5 kcal mol<sup>-1</sup>, ΔS<sub>0</sub><sup>‡</sup> = -1.6 ± 1.3 cal mol<sup>-1</sup> deg<sup>-1</sup>, ΔH<sub>-1</sub><sup>‡</sup> = 33.5 ± 0.1 kcal mol<sup>-1</sup>, and ΔS<sub>-1</sub><sup>‡</sup> = 13.7 ± 0.4 cal mol<sup>-1</sup> deg<sup>-1</sup> for (3-chloropyridine)chromium(III) and ΔH<sub>0</sub><sup>‡</sup> = 23.9 ± 0.6 kcal mol<sup>-1</sup>, ΔS<sub>0</sub><sup>‡</sup> = -5.2 ± 1.7 cal mol<sup>-1</sup> deg<sup>-1</sup>, ΔH<sub>-1</sub><sup>‡</sup> = 31.7 ± 0.2 kcal mol<sup>-1</sup>, and ΔS<sub>-1</sub><sup>‡</sup> = 11.3 ± 0.6 cal mol<sup>-1</sup> deg<sup>-1</sup> for (3-cyanopyridine)chromium(III). The uncertainties quoted are standard deviations.

Table IV summarizes the activation parameters and the specific rates at 70 and 25° for the aquation of different pyridine complexes of monosubstituted chromium(III) thus far studied. The rate constants decrease with the decrease of conjugate acid dissociation constant, K<sub>a</sub>, of the free ligands, and a fair linearity is obtained by plotting -log k<sub>0</sub> or -log k<sub>-1</sub> = -log(k<sub>-1</sub>'/K<sub>h</sub>) against pK<sub>a</sub>. Though the differences in the aquation rate are both enthalpy and entropy controlled, a trend of an increase in the enthalpy of activation with the increased basicity of the ligands is noted in Table IV.

Electronically unsaturated pyridine and 3-picoline ligands were found to deviate substantially toward slower reactivity

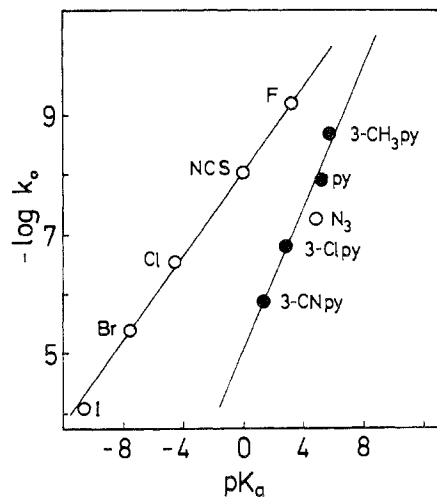
**Table IV.** Activation Parameters and Specific Rates for the Aquation of Pentaquo(X-pyridine)chromium(III) Ions at Ionic Strength 1.0 M (HClO<sub>4</sub> + NaClO<sub>4</sub>)

X	$\Delta H_0^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S_0^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	$\Delta H_{-1}^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S_{-1}^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	70° <sup>a</sup>		25° <sup>a</sup>		pK <sub>a</sub> (free ligand)
					10 <sup>5</sup> k <sub>0</sub> , sec <sup>-1</sup>	10 <sup>6</sup> k <sub>-1</sub> , M sec <sup>-1</sup>	10 <sup>8</sup> k <sub>0</sub> , sec <sup>-1</sup>	10 <sup>10</sup> k <sub>-1</sub> , M sec <sup>-1</sup>	
3-Cyano <sup>b</sup>	23.9	-5.2	31.7	11.3	29	14	130	110	1.35 <sup>f</sup>
3-Chloro <sup>b</sup>	26.3	-1.6	33.5	13.7	6.2	3.1	16	16	2.81 <sup>f</sup>
4-Amido					4.3 <sup>c</sup>				3.61 <sup>g</sup>
H <sup>d</sup>	27.2	-3.5	35.6	15.2	0.55	0.3	1.2	0.99	5.21 <sup>f</sup>
3-Methyl <sup>e</sup>	31.3	6.9	34.7	11.8	0.25	0.22	0.21	0.9	5.67 <sup>f</sup>

<sup>a</sup> Calculated from the activation parameters. <sup>b</sup> This work. <sup>c</sup> The value in 1 M HClO<sub>4</sub>: F. Nordmayer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968). <sup>d</sup> Reference 20. <sup>e</sup> Reference 21. <sup>f</sup> Thermodynamic values at 25°: F. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591 (1964). <sup>g</sup> Thermodynamic value at 20°: H. H. G. Jellinek and J. R. Urwin, *J. Phys. Chem.*, **58**, 548 (1954).

from the linear dependence observed between  $-\log k$  and pK<sub>a</sub> for the dissociation of saturated amine ligands from the soft Cr(CO)<sub>5</sub> moiety in hexane.<sup>19</sup> This strengthening of the metal-amine bond was attributed to some degree to metal-nitrogen bonding. No relevant data exist on kinetics of the aquation of Cr<sup>III</sup>(H<sub>2</sub>O)<sub>5</sub>-saturated amine complexes to allow an analogous comparison. The aquation of Cr(H<sub>2</sub>O)<sub>5</sub>NH<sub>3</sub><sup>3+</sup> cation was studied in nitrate media,<sup>29</sup> but rough estimates of rates in perchlorate media showed that the nitrate media catalyzed the reaction.<sup>30</sup>

In Figure 2 the aquation rate data extrapolated to 25° for the substituted pyridine complexes are given as the function of ligand basicity together with the plot presented by Monacelli<sup>14</sup> for the analogous complexes with a series of uninegative ligands. Assuming the other factors being constant including the substrate constant of Cr(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup> moiety, the aquation rates of the two series of complexes given in Figure 2 can be compared on the basis of ligand basicity. At the pK<sub>a</sub> of a particular ligand, the 3+ charged complex aquates substantially faster than the 2+ charged one. There is an increasing amount of data indicating that a degree of the bond making in the transition state plays a role in substitution reactions involving Cr(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup> and Cr(NH<sub>3</sub>)<sub>5</sub><sup>3+</sup> moieties,<sup>31-37</sup> and the enhanced rates of 3+ charged complexes in Figure 2 could be associated with a higher degree of bond making in the transition state. However, a higher

**Figure 2.** Plot of  $\log k_0$  for the aquation at 25° of monosubstituted chromium(III) complexes with a series of neutral and a series of uninegative ligands against pK<sub>a</sub> of the free ligands at 25°.

sensitivity of the aquation rates of 3+ charged species to the basicity of the leaving ligands, as revealed by the slopes of the linear correlation (slope = 0.35 for the 2+ species<sup>14</sup> and 0.59 for the 3+ species), points to a higher degree of bond breaking<sup>8</sup> in the transition states formed by the 3+ species over those formed by 2+ species, *i.e.*, points to an increased dissociative character in the aquation process of the 3+ charged complexes. The implication, if any, might be that a higher degree of bond making or a greater "assistance" by the incoming water ligand is present in the transition state during electrostatically more difficult and slower dissociation of uninegative ligands from Cr(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup> moiety than during electrostatically easier and faster dissociation of neutral ligands.

**Registry No.** (H<sub>2</sub>O)<sub>5</sub>Cr(3-Clpy)<sup>3+</sup>, 42476-27-7; (H<sub>2</sub>O)<sub>5</sub>Cr(3-CNpy)<sup>3+</sup>, 42422-49-1.

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