

result for expt 9 is rejected as deviating too markedly from the others, we find for  $k_3$  a value of approximately  $1.0 M^{-1} \text{ sec}^{-1}$ . This value, though not accurate, does show that  $\text{Cr}^{2+}$  reacts very much more rapidly with the  $\text{Co}^{\text{III}}$  complex when the ligand is in the carbonyl form than when it is in the hydrate form.

In Figure 2 the values of  $k_1$ , as they are determined by the slopes of the lines in Figure 1, are shown plotted against  $(\text{H}^+)$ . From this graph we find  $k_1 = 0.075 + 0.64(\text{H}^+)$ . The rate of dehydration of pyruvic acid has also been shown to depend on  $(\text{H}^+)$ , and the rate law in this case has the corresponding terms  $0.22 + 1.25(\text{H}^+)$  where these terms are to be multiplied by (pyruvic acid) to yield the actual rate.<sup>5</sup> The close correspondence between the function we have deter-

mined by indirect means and that obtained by Strehlow provides strong support for our interpretation of the data. It should be mentioned also that Strehlow reports that glyoxylic acid dehydrates at about one-half the rate of pyruvic acid.

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## Anation, Water Exchange, and Ion-Pair Formation of Aquopentaamminechromium(III) Ion in Acidic Aqueous Solutions Containing Chloride or Thiocyanate Ions<sup>1</sup>

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**Abstract:** The kinetics of the formation of  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{+2}$  and  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{+2}$  from  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  in dilute acidic aqueous media have been studied. The rate of water exchange of  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  and ion-pair formation have also been investigated under similar conditions.  $\text{NCS}^-$  forms a more stable ion pair and reacts more rapidly than does  $\text{Cl}^-$ . Both anations are slow with respect to water exchange. The results are interpreted on the basis of a rate-limiting loss of coordinated water followed by collapse of the solvation shell to fill the vacancy created.

The rate of entry of anions into the coordination sphere of dipositive aquo ions of first transition series metals is determined by two factors: the rate of water exchange of the aquo ions and the tendency for ion-pair formation between the cation and the entering anion.<sup>2</sup> The same two factors have been found to dominate substitutions on  $\text{Co}(\text{III})$  in nonaqueous solvents.<sup>3</sup> The rate of water exchange establishes a limiting rate for substitutions on  $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{-2}$  in aqueous solutions, although anions differ in the concentration necessary to approach the limiting rate.<sup>4</sup> There is evidence that ion-pair formation and the rate of water exchange also are important in determining rates of slow substitution on tripositive aquo ions in aqueous media; however, most studies of these systems have been principally concerned with the thermodynamically favored aquation reactions.<sup>5</sup> For most trivalent transition metal ions, one or more of the

three relevant quantities (rate of anation, rate of water exchange, ion-pair formation constant) is missing or must be estimated from fragmentary information generated as a by-product in an unrelated investigation. We now report a study of the rate of the reaction by which two anions replace water in  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$ . We have studied the rate of water exchange of the aquo ion and its ion-pair formation with the same anions under closely similar conditions.

### Experimental Section

**Reagents.** Deionized distilled water and analytical reagent grade chemicals were employed. Chromium complexes were prepared from  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3\text{NH}_4\text{NO}_3$  by standard methods<sup>6</sup> or modifications of these methods. Analyses were carried out in three to five replicates by standard methods.<sup>7</sup>

**Anal.** Calcd for  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ : Cr, 11.5;  $\text{NH}_3$ , 18.8. Found: Cr, 11.4;  $\text{NH}_3$ , 18.4. Calcd for  $[\text{Cr}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ :

(1) Taken, in part, from a Ph.D. thesis presented at Georgetown University in 1966 by N. V. Duffy.

(2) R. G. Wilkins in "Mechanisms of Inorganic Reactions," R. K. Murmann, Ed. American Chemical Society, Washington, D. C., 1965, p 55.

(3) M. L. Tobe, ref 2, p 7.

(4) A. Haim, R. J. Grassi, and W. K. Wilmarth, ref 2, p 31.

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(6) T. Moeller, *Inorg. Syn.*, 5, 132 (1951).

(7) H. F. Walton, "Principles and Methods of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1952, p 348; B. Harrow, E. Borek, A. Mazur, G. C. H. Stone, and H. Wagreich, "Laboratory Manual of Biochemistry," 4th ed, W. B. Saunders Co., Philadelphia, Pa., 1955, p 29.

Cr, 14.0; NH<sub>3</sub>, 22.9; Cl, 9.5. Found: Cr, 13.6; NH<sub>3</sub>, 22.7; Cl, 9.5. Calcd for [Cr(NH<sub>3</sub>)<sub>5</sub>NCS](ClO<sub>4</sub>)<sub>2</sub>: Cr, 13.2; SCN, 14.7. Found: Cr, 13.3; SCN, 15.2. Calcd for [Cr(NH<sub>3</sub>)<sub>5</sub>NCS]Br<sub>2</sub>·<sup>8</sup>N, 23.67; Br, 45.01; C, 3.38; H, 4.26. Found: N, 23.49; Br, 42.53; C, 3.65; H, 4.28.

[Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]<sup>+3</sup> labeled with H<sub>2</sub>O<sup>18</sup> was prepared by precipitating the perchlorate from water enriched in O<sup>18</sup>. Absorbance measurements were made using 0.1, 1, and 10-cm silica cells in Cary 14 and Beckman DU spectrophotometers. A Beckman Model G pH meter, with glass and calomel electrodes standardized with buffers of known temperature coefficients, was used to measure the apparent pH of the acidic reaction mixtures.

**Spectrophotometric Kinetic Runs.** The following is typical of the procedure employed. A 100-ml volume of a solution  $1.07 \times 10^{-2}$  M in the aquo ion Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>+3</sup> was prepared by dissolving a weighed sample of the perchlorate in  $8.76 \times 10^{-2}$  M HClO<sub>4</sub>. This solution was placed in an amber bottle in a  $45.0 \pm 0.1^\circ$  water bath. To 25 - *x* ml of 3.31 M NaClO<sub>4</sub> solution in a second thermostated amber bottle was added *x* ml of 3.31 M NaCl. At zero time 25 ml of the substrate solution was added to the perchlorate-chloride solution. A spectrophotometric cell held at  $45 \pm 2^\circ$  in a second bath was rinsed and filled with the reaction mixture and transferred to the cell compartment of the DU, thermostated at  $45.0 \pm 0.1^\circ$ . The absorbance was followed for 10-15 half-times.

**O<sup>18</sup> Determinations.** An aliquot of the reaction mixture (90 ml) was cooled in an acetone-Dry Ice bath to the freezing point and brought to pH 1-2 if necessary. A solution (50 ml) of 53 wt % HgCl<sub>2</sub>, 11 wt % NaCl, and 36 wt % H<sub>2</sub>O was added in small portions with swirling. The orange precipitate ([Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]Cl<sub>3</sub>·*p*HgCl<sub>2</sub>·*q*H<sub>2</sub>O) was filtered off and rinsed with alcohol and then ether. The precipitate was transferred to a Urey tube and dried at 1-5 μ for 12 to 18 hr. The tube was closed, removed from the vacuum line, and heated in an oil bath at 125 to 130° or 113 to 115° for 2 hr, the color of the precipitate changing from orange to pink. Oxygen contained in the water liberated in this change was converted to CO<sub>2</sub> by a modification of Anbar's method.<sup>9</sup> The isotopic composition of the CO<sub>2</sub> was measured mass spectrometrically (Consolidated 21-602A). Replicate aliquots agreed to  $\pm 3\%$ . Rates were calculated from McKay plots (see Figure 3).

## Preliminary Results

Jorgensen and Bjerrum<sup>10</sup> report that aquopentamminechromium(III) ion rather rapidly changes to the *trans*-diaquo ion in acidic nitrate solution. They also report that this reaction, unlike most similar reactions, proceeds more rapidly in solutions of higher acidity. Hashimoto,<sup>11</sup> however, has observed that solutions of the aquopentammine ion in dilute perchloric acid persist without noticeable change for much longer periods than these results indicate. Furthermore, he reports that decomposition is base catalyzed rather than acid catalyzed. As a preliminary experiment, we studied the relative rates of decomposition of aquopentamminechromium(III) ion in nitrate, perchlorate, bromide, and sulfate media.

Solutions containing 1.5 mM Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>+3</sup>, 44 mM HClO<sub>4</sub>, and 1.5 M NaX were placed in amber bottles and kept at 45° for several days. Absorbance measurements (10-cm cells) were made on aliquots which had been cooled to room temperature. Figure 1 shows the change in absorbance at 480 mμ of various reaction mixtures over long time intervals.

The change in absorbance is presumably due to loss of ammonia from the pentaammine ion. Jorgensen and Bjerrum have presented evidence that this occurs

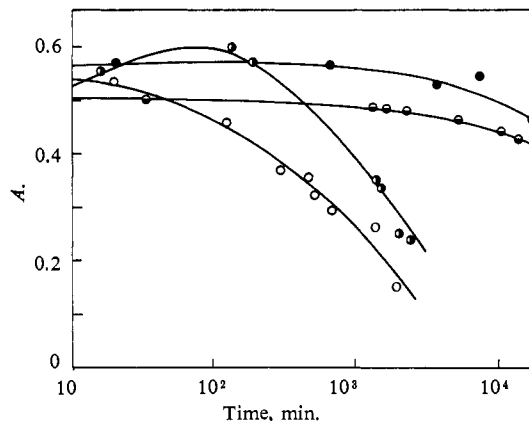
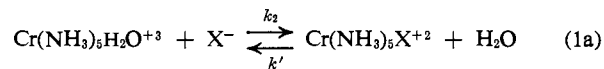


Figure 1. Change in absorbance at 480 mμ and 45° of  $ca. 1 \times 10^{-3}$  M Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>+3</sup> (added HClO<sub>4</sub>,  $4.4 \times 10^{-2}$  M; added salt, 1.5 M): ●, NaBr<sup>-</sup>; ○, NaClO<sub>4</sub>; ○, Na<sub>2</sub>SO<sub>4</sub> (pH 2.5); ○, NaNO<sub>3</sub>.

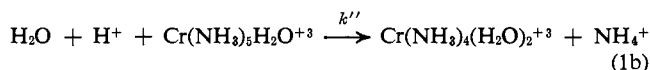
through the *trans*-diaquo isomer in nitrate media. Figure 1 demonstrates that this process occurs more rapidly in nitrate and sulfate media than in perchlorate or bromide media. Figure 1 also indicates that the initial change of absorbance is different for the sulfate (pH 2.5) than for the other systems studied. This may indicate that a different product is formed in this medium than in the other media studied.<sup>10</sup>

Further preliminary experiments indicated that no significant slow spectral change in Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>+3</sup> solutions was caused by the presence of acetate or iodide ions, or thiourea under conditions similar to those of the experiments reported below. In 1 M NaBr the bromo complex could not be detected polarographically.<sup>12</sup> Reaction with F<sup>-</sup> appears<sup>13</sup> to be more complicated than simple substitution. Spectral changes on the addition of iodate ion to acidic solutions of Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>+3</sup> take place so rapidly as to indicate that the iodato complex may be formed without rupture of the Cr-O bond.

An initial rapid change, followed by slow further changes in the absorption spectrum, occurred when solutions of Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>+3</sup> were mixed with solutions containing either Cl<sup>-</sup> or NCS<sup>-</sup>. In the case of reactions involving Cl<sup>-</sup>, steady absorbance values (*A*) were reached and maintained for extended periods although eventually a small further change occurred. In the case of NCS<sup>-</sup>, a slow decrease in *A* after the maximum value was observed. This effect was relatively smaller at higher anion concentrations. The reaction responsible for the major slow change is taken as



This interpretation is consistent with independent measurements of the spectra of the species involved. The competing reaction is taken as



(8) Analyses performed by Schwarzkopf Microanalytical Laboratory; one analysis for each determination.

(9) M. Anbar, *Intern. J. Appl. Radiation Isotopes*, **3**, 131 (1958).

(10) E. Jorgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958); J. Bjerrum and E. Jorgensen, *J. Inorg. Nucl. Chem.*, **8**, 313 (1958).

(11) S. Hashimoto, *Bull. Chem. Soc. Japan*, **32**, 945 (1959).

(12) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).

(13) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **278**, 24 (1955).

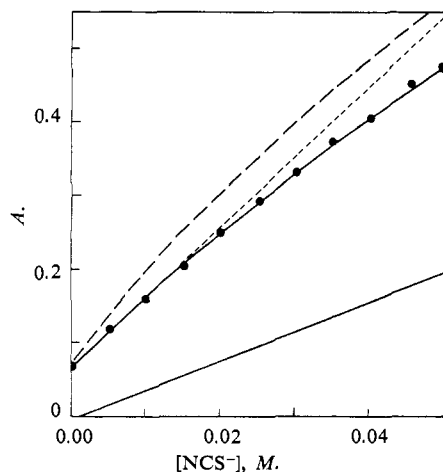


Figure 2. Variation of initial absorbance (●) of  $1 \times 10^{-2} M$   $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  as a function of  $[\text{NCS}^-]$  at  $260 \text{ m}\mu$  and  $23.27^\circ$  (ionic strength,  $0.158 M$  ( $\text{NaClO}_4$ ); added  $\text{HClO}_4$ ,  $4.8 \times 10^{-2} M$ ): lower solid curve, correction for absorbance of  $\text{NCS}^-$  and cell; upper solid curve, fitted, parameters in Table V; lower dashed curve, best straight line for four points at lowest  $[\text{NCS}^-]$ ; upper dashed curve, absorbance after 10 min.

This is supported by the decrease of the effect at higher anion concentration.

#### Treatment of Data

Colmar and Schwartz<sup>14</sup> have reported the visible absorption spectrum of  $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+3}$  and, on the basis of their results, we assign a value of 29 for the molar absorptivity of this complex at  $474 \text{ m}\mu$ . In order to estimate the relative importance of the decomposition of  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  to the anation and hydrolysis reactions, absorbance *vs.* time data for reactions between  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  and  $\text{NCS}^-$  were examined on the basis of the set of reactions (1a, 1b), using an IBM 1620-II computer to calculate absorbance *vs.* time curves for various values of the rate constants on the basis of equations presented by Rodiguin and Rodiguina.<sup>15</sup> Initial values of  $k$  and  $k'$  were those which gave best fit for  $k'' = 0$ . The initial value of  $k''$  was that which gave best fit for independent experiments in the absence of  $\text{NCS}^-$  ( $k'' = 7 \times 10^{-6} \text{ min}^{-1}$ ). These results indicated that the values of  $k$  calculated on the basis of assuming that  $A_{\text{max}} = A_\infty$  were close to those calculated on the basis of eq 1a. The correction for the decomposition of the substrate more seriously affected the values of  $k'$ , which differed by as much as a factor of 3 from those calculated on the basis of  $A_{\text{max}} = A_\infty$  (see Table IB).

The data for all kinetic runs were treated according to

$$-2.303 \log \frac{A_\infty - A_t}{A_\infty - A_0} = (k + k')t$$

where  $k = k_2[\text{X}^-]$  and

$$k \left[ \frac{A_\infty}{[\text{RH}_2\text{O}^{+3}]_0} - A'_m \right] = k' \left[ A_m - \frac{A_\infty}{[\text{RH}_2\text{O}^{+3}]_0} \right]$$

(14) R. I. Colmar and F. W. Schwartz, *J. Am. Chem. Soc.*, **54**, 3204 (1932).

(15) N. M. Rodiguin and E. N. Rodiguina, "Consecutive Chemical Reactions," D. Van Nostrand Co., Inc., Princeton, N. J., 1964.

where the molar absorptivities  $A_m$  and  $A_m'$  corresponding to  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  and  $\text{Cr}(\text{NH}_3)_5\text{NCS}^{+2}$  were measured using solutions of the appropriate perchlorate (or bromide) salts. The subscripts 0,  $\infty$ , and  $t$  refer to initial, final, and intermediate conditions. The equilibrium constant  $K$  was computed from the measured  $D_\infty$  and molar absorptivities.

#### Ion-Pair Formation

Rapid intensification of the ultraviolet absorbance of aquo ions on the addition of simple anions has been interpreted in terms of outer-sphere complex formation.<sup>16</sup> The extent of this change was studied for mixtures containing  $\text{RH}_2\text{O}^{+3}$  and  $\text{Cl}^-$  between 216 and  $220 \text{ m}\mu$  and for mixtures of  $\text{RH}_2\text{O}^{+3}$  and  $\text{NCS}^-$  between 255 and  $265 \text{ m}\mu$  (R denotes  $\text{Cr}(\text{NH}_3)_5$ ).

With  $\text{Cl}^-$  as counterion, essentially linear plots were obtained. Under suitable conditions, real, but slight, curvature was observed in plots of initial absorbance *vs.*  $[\text{NCS}^-]$ .

Figure 2 shows the variation of initial absorbance at  $260 \text{ m}\mu$  with total  $[\text{NCS}^-]$  as well as the absorbance of  $[\text{NCS}^-]$  under the same conditions. Under the conditions of these experiments,  $\text{NCS}^-$  in the absence of substrate did not change in absorbance at  $260 \text{ m}\mu$  during a 15-min period, although marked changes occur at higher temperature.<sup>17</sup> The absorbance of the  $\text{NCS}^-$ -substrate mixture slowly increases because of the anation reaction. The extent of this change in 10 min is also shown in Figure 2.

The data were analyzed using a nonlinear least-squares program, to be described elsewhere,<sup>18</sup> and the equation

$$A = A_m M_t + \frac{X_e M_t K_{ip} (A_m'' - A_m)}{K_{ip} X_e + 1}$$

where  $A$  is the observed absorbance (corrected for blank absorbance in the case of  $\text{NCS}^-$ ),  $A_m$  is the molar absorptivity of  $\text{RH}_2\text{O}^{+3}$ ,  $M_t$  is total concentration of  $\text{Cr}(\text{III})$ ,  $X_e$  is equilibrium concentration of the anion  $\text{X}^-$ ,  $A_m''$  is the molar absorptivity of the ion pair, and  $K_{ip}$  is the formation constant of the 1:1 ion pair assumed to be responsible for the enhancement of the absorbance.

As King has pointed out,<sup>19</sup> it is not always possible to obtain independent estimates of the parameters  $K_{ip}$  and  $A_m''$  from  $A$  *vs.*  $X_e$  plots for weak complexes. The separation of these parameters depends on the curvature of the  $A$  *vs.*  $X_e$  plots. In the absence of curvature, only the quantity  $K_{ip}(A_m - A_m'')$  can be evaluated.

For those cases in which linear  $A$  *vs.*  $[\text{X}^-]$  plots were obtained, the slope, intercept, and root-mean-square deviation of the data were determined for each line. Values of  $K_{ip}$  and  $A_m''$  which would generate a curve with the same intercept and initial slope and an  $A_m''$  at maximum  $[\text{X}^-]$ , two rms deviations below the straight line, were computed. Since greater curvature should

(16) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

(17) A. L. Phipps and R. A. Plane, *J. Am. Chem. Soc.*, **79**, 2458 (1957).

(18) W. Alexander and J. E. Earley, to be published.

(19) E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

**Table I.** Kinetic Data for the Reaction  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3} + \text{X}^- \xrightleftharpoons[k']{k_2} \text{Cr}(\text{NH}_3)_5\text{X}^{+2}$

$[\text{X}^-]$ , $M$	Temp, <sup>a</sup> $^{\circ}\text{C}$	pH	$k + k'$ $\times 10^3,^b \text{min}^{-1}$	$k \times 10^5$ , $\text{min}^{-1}$	$k_2 \times 10^3$ , $M^{-1}\text{min}^{-1}$	$k' \times 10^3$ , $\text{min}^{-1}$	$K$ , $M^{-1}$
(A) $\text{X}^- = \text{Cl}^-$							
(i) $[\text{RH}_2\text{O}^{+3}]_0 = 1.46 \times 10^{-3} M$ , $\mu = 0.106 M$ (NaClO <sub>4</sub> ), $\lambda$ 216 m $\mu$							
0.01	45.0	1.30	$3.8 \pm 0.9$	3.8	3.8	3.8	1.0
0.02	45.0	1.30	$4.1 \pm 0.8$	8.2	4.1	4.0	1.0
0.03	45.0	1.30	$4.1 \pm 0.7$	11	3.7	4.0	0.92
0.04	45.0	1.30	$3.7 \pm 0.4$	13	3.4	3.5	0.97
0.05	45.0	1.30	$4.4 \pm 0.2$	19	3.9	4.3	0.91
0.05	29.7	...	$0.84 \pm 0.02$	2.3	0.46	0.81	0.57
0.05	40.09	1.45	$3.3 \pm 0.2$	9.3	1.9	3.2	0.59
0.05	60.16	1.34	$24 \pm 2$	150	30	23	1.3
(ii) $[\text{RH}_2\text{O}^{+3}]_0 = 5.34 \times 10^{-3} M$ , Total Salt = 1.71 M (NaClO <sub>4</sub> ), $\lambda$ 235 m $\mu$							
0.331	45.0	1.20	$4.6 \pm 0.1$	47	1.4	4.1	0.34
0.663	45.0	1.20	$5.7 \pm 0.1$	94	1.4	4.8	0.29
0.994	45.0	1.20	$6.3 \pm 0.1$	130	1.3	5.0	0.26
1.33	45.0	1.20	$7.6 \pm 0.6$	170	1.3	5.9	0.22
1.66	45.0	1.20	$9.2 \pm 0.1$	210	1.3	7.1	0.18
0.994	30.0	1.18	$0.96 \pm 0.01$	16	0.16	0.80	0.20
1.66	60.52	1.35	$38 \pm 2$	1400	8.3	25	0.34
(B) $\text{X}^- = \text{NCS}^-$							
(i) $[\text{RH}_2\text{O}^{+3}]_0 = 1.46 \times 10^{-3} M$ , $\mu = 0.106 M$ (NaClO <sub>4</sub> ), $\lambda$ 474 m $\mu^c$							
0.01	45.0	1.33	$0.49 \pm 0.02$	23	23	0.26	88
0.02	45.0	1.33	$0.65 \pm 0.02$	40	20	0.25	80
0.03	45.0	1.33	$0.90 \pm 0.02$	63	21	0.28	75
0.04	45.0	1.33	$1.07 \pm 0.04$	74	18	0.30	60
0.05	45.0	Varied <sup>d</sup>	$1.28 \pm 0.04$	96	19	0.32	59
0.05	45.0	1.33	...	85	17	0.26	65 <sup>e</sup>
0.05	29.9	1.40	$0.20 \pm 0.01$	14	2.9	0.057	50
0.05	29.9	1.40	...	15	3.0	0.020	150 <sup>e</sup>
0.05	60.9	...	$9.6 \pm 0.2$	690	140	2.7	52
0.05	60.9	...	...	700	140	2.1	67 <sup>e</sup>
0.05	60.9 <sup>f</sup>	...	9.9	640	130	3.5	37
0.05	60.9 <sup>f</sup>	...	...	600	120	2.5	48 <sup>e</sup>
(ii) $[\text{RH}_2\text{O}^{+3}]_0 = 5.34 \times 10^{-3} M$ , Total Salt = 1.71 M (NaBr), $\lambda$ 474 m $\mu$							
0.994	45.0	1.22	$6.6 \pm 0.5$	660	6.7	...	...
1.33	45.0	1.22	$9.6 \pm 0.2$	960	7.2	...	...
1.66	45.0	1.22	$12 \pm 1$	1200	7.0	...	...
1.66	30.0	1.22	$2.3 \pm 0.2$	200	1.2	...	...
1.66	60.0	1.45	$61 \pm 1$	5300	32	8	4

<sup>a</sup> Normally  $\pm 0.1^{\circ}$ ;  $\pm 0.02^{\circ}$  when four significant figures listed. <sup>b</sup> Average of two to five determinations. <sup>c</sup> Results reported calculated on the basis of  $A_{\text{max}} = A_{\infty}$ . <sup>d</sup> Runs at apparent pH of 1.33, 1.45, 1.58, 1.76, and 2.07 gave results within error listed, no change in  $K$ . <sup>e</sup> Same data as preceding entry, computed including correction for substrate decomposition. <sup>f</sup> HBr-HClO<sub>4</sub> medium, single experiment. <sup>g</sup> Reaction went to completion.

be detectable, these were taken as an upper limit for  $K_{\text{ip}}$  and a lower limit for  $A_{\text{m}}''$ .

## Results

Table I gives results of spectrophotometric kinetic runs. The reaction between  $\text{Cl}^-$  and  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  is first order in  $[\text{Cl}^-]$  within the precision of the data, with a rate constant in agreement with those previously reported.<sup>11</sup> The corresponding reaction with  $\text{NCS}^-$  is more rapid<sup>20</sup> by a factor of 5. There is some tendency for a decrease in  $k_2$  at higher  $[\text{NCS}^-]$ , but no limiting rate is approached.

Rate constants for aquation are consistent with other studies,<sup>12,21,22</sup> but less precise since we are principally

interested in anations and have chosen conditions to drive the reaction toward completion. The variation of the equilibrium constant  $K$  with anion concentration is primarily due to variation in rate of aquation. The  $\text{NCS}^-$  complex is more stable than the  $\text{Cl}^-$  complex. Table IB presents a comparison of rate constants for the reaction of  $\text{RH}_2\text{O}^{+3}$  with  $\text{NCS}^-$  calculated on the basis of  $A_{\text{max}} = A_{\infty}$  and corrected for the decomposition of the substrate as discussed above.

Table II and Figure 3 present  $\text{H}_2\text{O}^{18}$  exchange data. The rate of water exchange is more rapid than the anation reactions and is unaffected by the presence of  $\text{Cl}^-$  or  $\text{NCS}^-$ . Increase in pH (1-3) increases the rate of water exchange but does not affect the rates of anation.

Tables III and IV present activation and thermodynamic parameters calculated from the data of Tables

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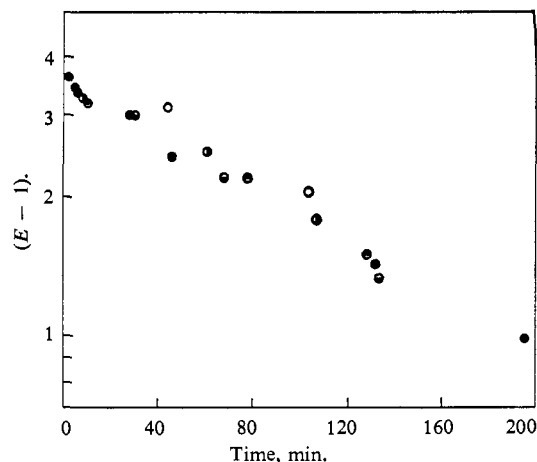


Figure 3. Water exchange of  $1.46 \times 10^{-3} M$   $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  at  $29.72^\circ$  (ionic strength,  $0.106 M$ ; added  $\text{HClO}_4$ ,  $4.8 \times 10^{-2} M$ ; added salts ( $5 \times 10^{-2} M$ ):  $\bullet$ ,  $\text{NaClO}_4$ ;  $\circ$ ,  $\text{NaNCS}$ ;  $\ominus$ ,  $\text{NaCl-NaClO}_4$ ;  $\oplus$ ,  $\text{NaCl}$ ;  $\odot$ ,  $\text{NaClO}_4$  (ionic strength,  $0.204 M$ ). The enrichment,  $E$ , is obtained by dividing the 46/44 isotope abundance ratio of  $\text{CO}_2$  prepared from the aquo ion by the 46/44 ratio of  $\text{CO}_2$  prepared from normal water.

I and II. The greater stability of the inner-sphere thiocyanato complex, relative to the chloro complex, is a result of more negative enthalpy. A similar effect is suggested in the activation parameters, particularly at high ionic strength.

Table II. Kinetics of the Reaction

$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{18}]^{+3} + \text{H}_2\text{O}^{16} \xrightarrow{k_{\text{ex}}} [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{16}]^{+3} + \text{H}_2\text{O}^{18}$		
Temp, $^\circ\text{C}$	pH	$k_{\text{ex}} \times 10^3, \text{min}^{-1}$
(A) $[\text{RH}_2\text{O}^{+3}] = 1.47 \times 10^{-3} M, \mu = 0.106 M$ ( $\text{NaClO}_4$ )		
29.72	1.25	$6.9 \pm 0.2$
29.72	1.29 <sup>a</sup>	$7.1 \pm 0.4$
29.72	1.28 <sup>b</sup>	$5.9 \pm 0.7$
29.72	1.28 <sup>c</sup>	$6.6 \pm 0.6$
29.72	2.19	$17 \pm 2$
29.72	4.08	$36 \pm 5$
14.96	1.31	$1.6 \pm 0.6$
45.11 <sup>i</sup>	1.43	$63 \pm 7$
(B) $[\text{RH}_2\text{O}^{+3}] = 5.1\text{--}5.2 \times 10^{-3} M$ ; Total Salt = $1.71 M$		
14.96	1.2 <sup>d,e</sup>	$1.5 \pm 0.6$
29.72	1.2 <sup>d,e</sup>	$5.4 \pm 1.0$
29.72	1.29 <sup>d,f</sup>	$6.3 \pm 1.2$
45.11 <sup>i</sup>	1.25 <sup>d</sup>	$61 \pm 3$
14.96	1.08 <sup>g</sup>	$2.0 \pm 0.2$
14.96	1.08 <sup>g</sup>	$1.8 \pm 0.4$
29.72	1.09 <sup>g</sup>	$6.9 \pm 2.5$
29.72	0.97 <sup>g,h</sup>	$7.2 \pm 0.7$
45.11 <sup>i</sup>	1.15 <sup>g</sup>	$51 \pm 8$

<sup>a</sup>  $1.7 \times 10^{-2} M \text{Cl}^-$ . <sup>b</sup>  $5 \times 10^{-2} M \text{Cl}^-$ . <sup>c</sup>  $5 \times 10^{-2} M \text{SCN}^-$  (substituted for  $\text{ClO}_4^-$ ). <sup>d</sup>  $\text{NaClO}_4$ . <sup>e</sup> Calculated, not measured. <sup>f</sup>  $0.829 M \text{NaCl}$ . <sup>g</sup>  $\text{NaBr}$ . <sup>h</sup>  $0.331 M \text{NaSCN}$ . <sup>i</sup> Samples dehydrated at  $113\text{--}115^\circ$ ; other samples dehydrated at  $125\text{--}130^\circ$ .

Table V presents formation constants calculated for the 1:1 ion pairs assumed responsible for the rapid change in the ultraviolet spectrum on mixing. Although association of both anions is small,<sup>23</sup> the  $\text{NCS}^-$

(23) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **78**, 15 (1956).

Table III. Activation Parameters for  $\text{Cr}(\text{NH}_3)_5\text{A} + \text{B} \rightleftharpoons \text{Cr}(\text{NH}_3)_5\text{B} + \text{A}$

A	B	$\mu = 0.106 M$		Total salt = $1.71 M$	
		$E_a, \text{kcal/mole}$	$S^*, \text{eu}$	$E_a, \text{kcal/mole}$	$S^*, \text{eu}$
$\text{H}_2\text{O}$	$\text{Cl}^-$	$27.2 \pm 1.1$	+7	$26.2 \pm 0.4$	+2
$\text{Cl}^-$	$\text{H}_2\text{O}$	$21.3 \pm 1.1$	-11	$20.1 \pm 3.3$	-15
$\text{H}_2\text{O}$	$\text{NCS}^-$	$24.8 \pm 2.1^a$	+3 <sup>a</sup>	$21.8 \pm 0.3$	-9
$\text{NCS}^-$	$\text{H}_2\text{O}$	$30.2 \pm 1.6^a$	+11 <sup>a</sup>	...	...
$\text{H}_2\text{O}^{18}$	$\text{H}_2\text{O}$	$22 \pm 4$	-4	$23 \pm 5$	-4
$\text{H}_2\text{O}^{18}$	$\text{H}_2\text{O}^b$			$20 \pm 4$	-10

<sup>a</sup> With correction for substrate decomposition. <sup>b</sup>  $\text{NaBr}$  medium.

Table IV. Thermodynamic Parameters for  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3} + \text{X}^- \rightleftharpoons \text{Cr}(\text{NH}_3)_5\text{X}^{+2} + \text{H}_2\text{O}$

X	$\mu = 0.106 M$		Total salt = $1.71 M$	
	$\Delta H, \text{kcal/mole}$	$\Delta S, \text{eu (45}^\circ)$	$\Delta H, \text{kcal/mole}$	$\Delta S, \text{eu (45}^\circ)$
$\text{Cl}^-$	+6	+19	+6	+16
$\text{NCS}^-$	-5	-6 <sup>a</sup>		

<sup>a</sup> With correction for substrate decomposition.

ion pair appears more stable than the corresponding  $\text{Cl}^-$  species. The approximate values, 10 for  $\text{NCS}^-$  and 3 for  $\text{Cl}^-$ , are estimated for the formation constants under the conditions of the low ionic strength kinetic experiments.

Table V. Formation Parameters for the  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3} \cdot \text{X}^-$  Ion Pair<sup>a</sup>

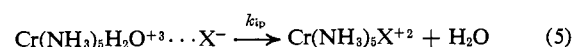
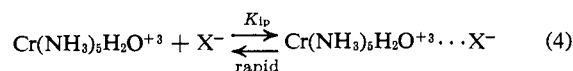
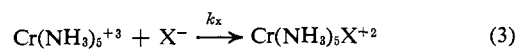
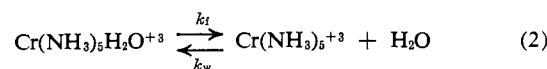
$\text{X}^-$	$\lambda$	$A_m$	$A_m''$	$K, M^{-1}$
$\text{NCS}^-$	265	$6.3 \pm 0.6$	$51 \pm 19$	$9.6 \pm 5.6$
	260	$7.4 \pm 0.4$	$68 \pm 9$	$11.5 \pm 2.6$
	255	$9.7 \pm 0.7$	$104 \pm 26$	$9.3 \pm 3.5$
$\text{Cl}^-$	220	66	>166	<2.2
	218	$81.1 \pm 0.4$	$366 \pm 447$	$1.3 \pm 2.1$
	216	$123.1 \pm 0.5$	$252 \pm 31$	$5.9 \pm 1.8$

<sup>a</sup>  $\mu = 0.158 M$  ( $\text{NaClO}_4$ ),  $[\text{RH}_2\text{O}^{+3}]_0 = 1.00 \times 10^{-2} M$ ,  $23.27^\circ$ ,  $[\text{X}^-]$  varied 0 to  $0.05 M$  at constant  $\mu$ .

Conversion of one-third of the  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  to the thiocyanate ion pair does not sensibly change the rate of water exchange.

## Discussion

For discussion purposes, the following possible mechanistic steps may be considered.



Process 5 should involve steps similar to eq 2 and 3. Steps 2 and 3 together provide a dissociative path

(SN1); steps 4 and 5 together provide a path in which association is more prominent (SN1 IP).

The ultraviolet spectra clearly demonstrate ion-pair formation. The rate of anation is a small fraction of the rate of water exchange. The observed rate of anation ( $k$ ), but not the rate of water exchange, is sensitive to the concentration and nature of the entering anions.

If the loss of the coordinated water molecule ( $k_t$  and the corresponding term in the  $k_{ip}$  path) is considered to proceed by a (solvent-assisted) dissociative mechanism, leading to an intermediate of reduced coordination number and at least transitory existence, the primary point of interest becomes the origin and significance of the difference in rate of reaction of  $\text{Cl}^-$ ,  $\text{NCS}^-$ , and solvent water with this intermediate. Any information which can be gained with respect to the detailed influence of ion pairing should have significance with respect to discussion of the nature and lifetime of the intermediate.

Haim and Taube<sup>24</sup> have discussed the reactivity of the pentacoordinate intermediates  $\text{Co}(\text{NH}_3)_5^{+3}$ ,  $\text{Co}(\text{CN})_5^{-2}$ , and  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  with various entering groups using the ratio of the second-order anation rate constant ( $k_x$ ) and pseudo-first-order solvation rate constant ( $k_w$ ) as an index of reactivity. Neglecting, for the moment, the presence of ion pairs, and assuming the transitory existence of  $\text{Cr}(\text{NH}_3)_5^{+3}$ , one may compute values of  $k_x/k_w$  for our systems as the ratio of experimental parameters  $k_2/k_{ex}$ . These are listed in Table VI. These ratios are roughly comparable with those for the reactive species discussed by Haim and Taube. By multiplying by an appropriate factor to convert the pseudo-first-order exchange rate to a second-order constant for attack of water, values of the order of 20 for  $\text{NCS}^-$  and 4 for  $\text{Cl}^-$  are obtained for the ratio of rate of reaction of  $\text{Cr}(\text{NH}_3)_5^{+3}$  with an anion to its rate of reaction with a water molecule. These ratios may be compared with the corresponding ratios published by Swain, Scott, and Lohmann<sup>25</sup> for the reaction of trityl ion: for  $\text{NCS}^-$ ,  $1.3 \times 10^4$ , and for  $\text{Cl}^-$ ,  $3.1 \times 10^3$ . If such discrimination factors may be taken as an index of the lifetime of the intermediate,  $\text{Cr}(\text{NH}_3)_5^{+3}$  would be similar in this respect to the other inorganic species but would have a much shorter lifetime than the well-characterized organic intermediate.

Table VI. Ratios  $k_2/k_{ex}$  for  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3} + \text{X}^-$

X <sup>-</sup>	$\mu = 0.106 M$		$\mu = 1.7$	
	30°	45°	30°	45°
Cl <sup>-</sup>	0.04	0.06	0.03	0.02
NCS <sup>-</sup>	0.4	0.3	0.2	0.1

In both  $\text{Cl}^-$  and  $\text{NCS}^-$  cases the presence of a  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3} \cdots \text{X}^-$  ion pair is demonstrated by the variation of the charge-transfer spectra with anion con-

centration. In this particular system, the thiocyanate ion pair is more stable than the chloride ion pair.<sup>26</sup> On the basis of steps 4 and 5,  $k_{ip}$  may be computed as the ratio of experimental parameters  $k_2/K_{ip}$ . At  $\mu = 0.11 M$  (30°), the lower limit for  $k_{ip}$  for  $\text{Cl}^-$  is  $2 \times 10^{-4}$ . For  $\text{NCS}^-$ ,  $k_{ip}$  is  $3 \times 10^{-4}$ . These are the same within the experimental limits and about 3% of the rate of exchange of water. On the basis of these values, some curvature in the plot of the pseudo-first-order anation constant  $k$  vs.  $[\text{NCS}^-]$  would be expected. In fact, the second-order constant  $k_2$  does tend to lower values at higher  $[\text{NCS}^-]$ .<sup>27</sup>

The relatively large difference between  $k_{ip}$  and  $k_{ex}$  requires comment. Postmus and King have explained the lower values of  $K_{ip}$  for association of anions with  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  relative to  $\text{Co}(\text{NH}_3)_6^{+3}$  in terms of repulsion of the anion by spare electron pairs on bound water molecules.<sup>28</sup> On this basis, the anion in an ion pair with  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  would be somewhat more likely to be located on the sides of the coordination sphere away from the coordinated water molecule. This would result in a low ratio of  $k_{ip}$  to  $k_{ex}$ . Langford and Gray<sup>29</sup> have pointed out that the estimated values of  $k_{ip}$  for  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  are larger, relative to the rate of water exchange, than are corresponding  $k_{ip}$  values for  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$ . They discuss this in terms of a statistical factor. Preferred location<sup>30</sup> of the weakly associated anion away from the site of the loss of water from the pentaammine substrates could cause this effect. There is no evidence that the presence of a counterion in the outer sphere speeds or slows loss of water. The symmetry of  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  would cause all ion-pairing sites to be equally effective for anation. On this basis, the expected increase in anion concentration close to the substrate due to ion-pair formation may be more than offset by preferred location remote from the site of the loss of the water molecule. Thus the correction for ion-pair formation which should be applied to  $k_x/k_w$  values for pentaammine substrates, for comparison with aquo ions or for evaluation of precise discrimination factors for pentaammine intermediates, may not be straightforward.

Since  $\text{NCS}^-$  forms more stable ion pairs and competes more favorably with solvent water than does  $\text{Cl}^-$ , the two processes appear related. The factors which favor ion-pair formation tend to increase the concentration of entering ligand in the region of the departing water molecule. Factors such as preferred location in the ion pair modify this effect.

Changes in solvation certainly play an important role in both anation and the imprecisely defined process called ion-pair formation. Since sufficiently precise thermodynamic data are not available, discussion in these terms is best postponed. This seems especially true of  $\text{NCS}^-$  systems in which specific effects are likely.

The present data indicate that the factors responsible for greater rate of reaction of  $\text{NCS}^-$  with the substrate are related to those which are responsible for more

(26) Earlier studies on this and similar  $\text{NCS}^-$  systems were carried out at higher ionic strength where association constant is smaller.<sup>11,17,20</sup>

(27) The  $k$  vs.  $[\text{X}^-]$  curve (45°) drawn on the basis of  $k_{ip}$  and  $k_{ex}$  gives a standard deviation for five points of  $6 \times 10^{-3}$ ; the deviation of the same points from the straight line of slope  $k_2$  is  $4 \times 10^{-5}$ .

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(24) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963); see also R. G. Pearson, and J. W. Moore, *ibid.*, **3**, 1336 (1964); D. A. Loelinger and H. Taube, *ibid.*, **5**, 1376 (1966).

(25) C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Am. Chem. Soc.*, **75**, 136 (1953); see also "Solvolytic Displacement Reactions," A. Streitwieser, Jr., Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 51 ff.

(29) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

(30) S. Mason and B. Norman, *Proc. Chem. Soc.*, 339 (1964).

stable ion-pair formation between  $\text{NCS}^-$  and the substrate. We conclude that anations of  $\text{Cr}(\text{NH}_3)_5\text{-H}_2\text{O}^{+3}$  are governed by release of the coordinated water molecule, quickly followed by incorporation of an adjacent particle into the resulting vacancy in the  $\text{Cr}(\text{III})$  coordination sphere. Anions in the vicinity of the site vacated by the water molecule, for reasons connected with the formation of ion pairs or otherwise, are trapped into the product. This may be regarded as the collapse of the solvation shell originally associated with the aquo ion.<sup>31</sup>

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(31) We suggest "the solvent shell collapse mechanism" as an appropriate designation for this process.

## Kinetic Studies of the Reactions of Peroxy Compounds of Chromium(VI), Vanadium(V), and Titanium(IV) in Acid Media<sup>1</sup>

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*Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received July 27, 1966*

**Abstract:** The kinetics of formation and decomposition in perchloric and other acids of blue chromium(VI) diperoxy and the formation of red vanadium(V) monoperoxy, yellow vanadium(V) diperoxy, and orange titanium(IV) monoperoxy species have been examined by flow methods. Rate laws have been established, and mechanisms are suggested for these reactions.

There has been a good deal of interest in, and development of flow equipment for, the study of the mechanism of formation, decomposition, and substrate reactions of peroxy species of biologically important iron(III) compounds such as the enzymes catalase and peroxidases.<sup>2</sup> The kinetic behavior of the "simpler" peroxy species of other transition metals have, however, been little investigated. We have reported previously a short study of the formation of blue peroxychromic acid in aqueous solution over a limited range of concentrations of reactants.<sup>3</sup> We have now extended this work to a higher acid region than previously examined, thus enabling us to make some reasonable conclusions about the detailed mechanisms of the formation reaction. We have also investigated the kinetics of formation of the red monoperoxy- and yellow diperoxyvanadium(V) species as well as the orange monoperoxytitanium(IV) complexes. All studies have been confined to acid concentrations above about  $10^{-2} M$ , where, with the notable exception of titanium(IV), both reactant and peroxy species have been reasonably well characterized.<sup>4</sup>

The titanium peroxy species are stable in acid medium, the vanadium complexes only decompose very slowly at room temperatures,<sup>5,6</sup> while  $\text{CrO}_5$  decomposes rapidly, especially at high acid concentrations. These peroxy species are sufficiently stable then to allow the study of their formation rates although in all cases flow methods have to be used, using spectrophotometry to study the strong color changes which accompany these reactions.

### Experimental Section

**Materials.** Sources of transition metal ions were Analar potassium dichromate, ammonium vanadate, and freshly precipitated titanium(IV) oxide from addition of base to  $\text{K}_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$  in solution. Both stabilized (with sodium stannate) and nonstabilized hydrogen peroxide (Fisher Reagent) were used with similar results.

Solutions of the required ionic strength and acid concentration were prepared by treatment of sodium hydroxide solutions with the appropriate amount of perchloric, sulfuric, or nitric acids. Stock solutions of hydrogen peroxide were titrated with standard cerium(IV) sulfate immediately after the completion of runs.

**Kinetic Runs.** A glass-Lucite stopped-flow apparatus was used. The formation and decomposition of  $\text{CrO}_5$  were studied at 580  $\mu$ . The two processes are sufficiently separated on a time scale that both are easily measured, except at the highest acidities investigated where, because of the  $[\text{H}^+]^2$  dependence of decomposition, the latter interferes seriously with the formation. Solutions of chromium(VI) in high nitric acid concentrations were used shortly after prep-

(1) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) B. Chance in "Investigation of Rates and Mechanisms of Reactions," Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 1314.

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(4) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964), for a well-written, critical account of the transition metal peroxy compounds.

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