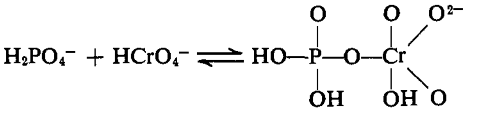
Rate-Determining Proton Transfer in Substitution on Tetrahedral Hydrogen Chromate(VI) Ion

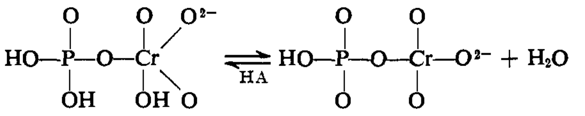
Chin-tung Lin and James K. Beattie[1]

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received July 20, 1971*

Abstract: A general mechanism is proposed for substitution on the tetrahedral hydrogen chromate ion in acidic aqueous solution. Rate-determining proton transfer occurs from a weakly associated HX nucleophile or by a proton in solution to the hydroxo ligand on chromium to form the departing water molecule. The rates of the uncatalyzed reactions depend directly on the acidity of HX, but the rates of catalysis by H^+ are independent of the identity of HX. The formation and hydrolysis of thiocyanatochromate ion was studied by temperature-jump relaxation spectroscopy at 25° and 0.3 *M* ionic strength. The observed rate law is $d[(NCS)CrO_3^-]/dt = ((5.4 \pm 0.4) \times 10^5\ M^{-2}\ sec^{-1})[H^+][NCS^-][HCrO_4^-] - ((2.4 \pm 0.1) \times 10^3\ sec^{-1})[(NCS)CrO_3^-]$.

Although the kinetics of the hydrolysis of dichromate ion has been investigated since 1928,[2-6] the mechanism of the condensation of hydrogen chromate with other oxo anions has been examined only recently.[7,8] General acid catalysis is observed which requires the participation of the acid catalyst in the transition state. A mechanism proposed[7,8] to account for these observations involves the formation of a five-coordinate chromium(VI) intermediate in an equilibrium step followed by rate-determining proton transfer and subsequent loss of a water molecule from the chromium(VI). For example, formation of hydrogen phosphatochromate anion is catalyzed by acetic acid and dihydrogen phosphate ion (HA).[7]


(1)


(2)

The formation of dichromate by the dimerization of hydrogen chromate may proceed by a similar mechanism.[7] If so, the hydrolysis of dichromate must also involve proton transfer in the rate-determining step, in accord with the principle of microscopic reversibility. Our suggestion of rate-determining proton transfer was strengthened by the recent observation that the hydrolysis of dichromate is catalyzed by acids according to the Brønsted catalysis law.[9]

An alternative mechanism involves nucleophilic catalysis of the hydrolysis of dichromate by attack of a nucleophile with displacement of a chromate ion, followed by rapid hydrolysis of the intermediate formed.[10]

$$B + Cr_2O_7^{2-} \longrightarrow BCrO_3 + CrO_4^{2-} \tag{3}$$

$$BCrO_3 + H_2O \xrightarrow[\text{fast}]{} HCrO_4^- + B + H^+ \tag{4}$$

We have recently demonstrated that this mechanism occurs in the catalysis by thiosulfate ion in neutral solution.[11] In this case, the hydrolysis of the thiosulfatochromate intermediate according to eq 4 can be observed.

To investigate further the mechanisms of these reactions, we have examined the kinetics of the rapid formation of thiocyanatochromate(VI) by temperature-jump relaxation spectroscopy. In this reaction, the substitution on chromium(VI) does not involve the formation of a chromium–oxygen bond, although it is not certain whether the thiocyanate is N-bonded or S-bonded.

$$NCS^- + HCrO_4^- + H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (NCS)CrO_3^- + H_2O \tag{5}$$

Experimental Section

Chemicals. Analytical grade reagents were obtained as follows: anhydrous sodium perchlorate and perchloric acid from G. F. Smith Chemical Co., sodium thiocyanate from Allied Chemical Corp., and potassium dichromate from Baker Chemical Co.

Kinetics Experiments. Solutions containing $NaClO_4$, $HClO_4$, and NaNCS were freshly prepared and thermostated at 21° before each experiment. The ionic strength was maintained at 0.3 *M* with sodium perchlorate. Potassium dichromate was added to the solution just before beginning the temperature-jump experiment.

The temperature-jump relaxation spectrometer was purchased from Messanlagen Studiengesellschaft, Göttingen, Germany. A 4° temperature rise was obtained by a discharge of 35 kV from the high-voltage condensor. The reaction was observed spectrophotometrically at 380 nm.

The kinetics experiments were completed within 5 min to avoid interference from the oxidation of thiocyanate by chromium(VI).[12] Because of the redox reaction, the hydrogen ion concentration was not increased above 0.13 *M*. No redox reaction occurs within a reasonable time at low acid concentrations of pH 3 even at the highest thiocyanate concentrations employed of 0.3 *M*.

Blank solutions containing chromium(VI) in the absence of thiocyanate at an ionic strength of 0.3 *M* and a hydrogen ion concentration of 0.03 *M* were examined. These solutions were found to

---

[1] Fellow of the Alfred P. Sloan Foundation, 1971–1973.

[2] R. N. J. Saal, *Recl. Trav. Chim. Pays-Bas*, **47**, 264 (1928).

[3] B. Chance, *J. Franklin Inst.*, **229**, 758 (1940).

[4] A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, **65**, 2098 (1961).

[5] P. Moore, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 220 (1966).

[6] B. Perlmutter-Hayman and M. A. Wolff, *J. Phys. Chem.*, **71**, 1416 (1967).

[7] S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *J. Amer. Chem. Soc.*, **90**, 6018 (1968).

[8] S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *Acta Chem. Scand.*, **23**, 3277 (1969).

[9] R. Baharad, B. Perlmutter-Hayman, and M. A. Wolff, *J. Phys. Chem.*, **73**, 4391 (1969).

[10] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 437.

[11] K. A. Muirhead, G. P. Haight, Jr., and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 3006 (1972).

[12] K. A. Muirhead, Ph.D. Thesis, University of Illinois, 1971.

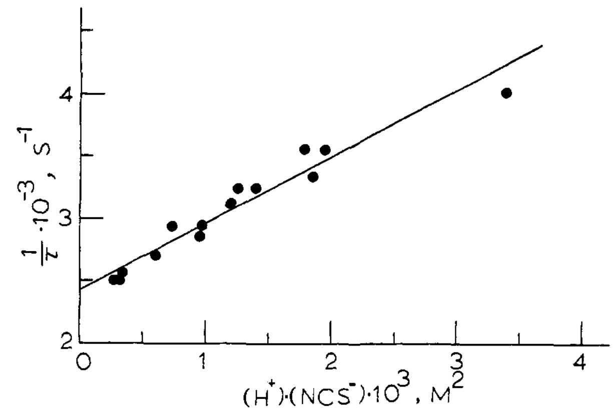


Figure 1. A plot of the reciprocal of the observed relaxation times against the product $[H^+][NCS^-]$.

be free of any observable reaction involving dichromate in an appropriate time range whenever the chromium(VI) concentration was less than 2×10^{-4} M. The dimerization reaction is relatively slow in solutions of low acid concentrations;[13] for example, a relaxation time of 18 msec was observed for a solution of 5×10^{-3} M H^+ and 5×10^{-4} M chromium(VI) at 25° and an ionic strength of 0.3 M. Therefore, higher chromium(VI) concentrations were used in some experiments to increase the relaxation effects when the rate of formation of thiocyanatochromate is much faster than the dichromate–hydrogen chromate reaction.

The equilibrium constant for the formation of thiocyanatochromate ion, eq 5, was determined spectrophotometrically at 25° and 0.3 M ionic strength. The initial concentrations of hydrogen ion and hydrogen chromate ion were maintained at 0.01 M and 2×10^{-4} M, respectively, and the thiocyanate ion concentration varied from 0.1 to 0.3 M. The redox reaction did not interfere with the spectrophotometric observations in the time necessary to measure the absorbance. The equilibrium constant, K_{eq}, was obtained from a five point plot of the equation

$$\frac{1}{A - \epsilon_{Cr}[Cr(VI)]} = \frac{1}{\Delta\epsilon[Cr(VI)]} + \frac{1}{K_{eq}\Delta\epsilon[Cr(VI)][H^+]}\frac{1}{[NCS^-]} \qquad (6)$$

where [Cr(VI)] and $[H^+]$ are the initial concentrations, ϵ_{Cr} is the extinction coefficient of $HCrO_4^-$, $\Delta\epsilon$ is the difference in the extinction coefficients of $HCrO_4^-$ and $(NCS)CrO_3^-$, and A is the measured absorbance at 380 nm.

Results

The formation of thiocyanotochromate(VI) ion acording to eq 5 obeys the following equilibrium expression

$$K_{eq} = \frac{k_f}{k_r} = \frac{[(NCS)CrO_3^-]}{[H^+][NCS^-][HCrO_4^-]} \qquad (7)$$

From the rate law 8 and the usual conservation relations, expression 9 for the observed relaxation time is obtained.

$$\frac{d[(NCS)CrO_3^-]}{dt} = k_f[H^+][NCS^-][HCrO_4^-] - k_r[(NCS)CrO_3^-] \qquad (8)$$

$$\frac{1}{\tau} = k_f([H^+][NCS^-] + [H^+][HCrO_4^-] + [NCS^-][HCrO_4^-]) + k_r \qquad (9)$$

Table I. Experimental Conditions and Results at 25° and 0.3 M Ionic Strength

$[NaNCS] \times 10^3$ M	$[HClO_4] \times 10^3$ M	$[K_2Cr_2O_7] \times 10^4$ M	$\tau^a \times 10^6$ sec
300	11.3	1.5	250
300	6.0	2.5	280
200	9.3	1.5	300
200	6.0	2.5	320
150	8.3	1.5	310
120	8.0	2.5	350
100	7.4	2.0	340
50	6.4	2.0	400
30	10.0	2.5	400
15	130	1.0	280
14	100	1.0	310
13	75	1.0	340
12	50	1.0	370
12	30	2.0	390[b]

[a] Average of at least three determinations. The average deviation was about 7%. This deviation was not included in the least-squares treatment. [b] Two relaxation times were observed. The longer time of 3.1 msec arises from the dimerization of $HCrO_4^-$, a conclusion which was confirmed with a blank solution containing $HCrO_4^-$ in the absence of NCS^-.

Under the experimental conditions, which are given in Table I, $[H^+][NCS^-] \gg [H^+][HCrO_4^-]$, $[NCS^-][HCrO_4^-]$, and eq 9 can be simplified to

$$1/\tau = k_f[H^+][NCS^-] + k_r \qquad (10)$$

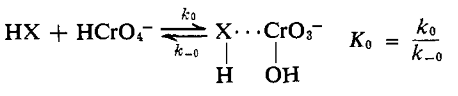
A plot of the reciprocal of the observed relaxation times against the product $[H^+][NCS^-]$ is presented in Figure 1. A least-squares treatment of these data with inverse squared weights yields the rate constants $k_f = (5.4 \pm 0.4) \times 10^5$ M^{-2} sec^{-1} and $k_r = (2.4 \pm 0.1) \times 10^3$ sec^{-1} at 25° and ionic strength 0.3 M.

An equilibrium constant of 225 ± 25 M^{-2} is calculated from the experimentally determined rate constants, with the error residing principally in the forward rate constant. From the direct spectrophotometric method an equilibrium constant of 150 ± 50 M^{-2} is obtained, with the error due largely to the small difference in absorbance between $HCrO_4^-$ and $(NCS)CrO_3^-$. The extinction coefficient of $(NCS)CrO_3^-$ at 380 nm is simultaneously determined to be 2000 ± 400 M^{-1} cm^{-1}.

Discussion

A general mechanism has been advanced for the condensation of $HCrO_4^-$ with various acidic species and consequently for the reverse hydrolysis reactions as well.[8] The present results on the formation of thiocyanatochromate and a parallel study on the formation of thiosulfatochromate[11] substantiate and elaborate this mechanism. They demonstrate that the uncatalyzed rates of formation depend strongly on the acidity of the substrate condensing with $HCrO_4^-$. The rates are virtually independent of the overall stability of the condensed product. In addition, the rates of the hydrogen ion catalyzed condensation reactions are nearly the same for all of the species, independent of their acidity and of the stability of the complex formed.

The general mechanism is an extension of that previously proposed[7,8] for the formation of phosphato- and phosphitochromium(VI) complexes



$$HX + HCrO_4^- \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} \underset{\substack{| \\ H}}{X}\cdots\underset{\substack{| \\ OH}}{CrO_3^-} \qquad K_0 = \frac{k_0}{k_{-0}} \qquad (11)$$

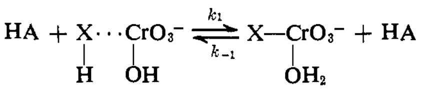
---

[13] J. R. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, 10, 634 (1971).

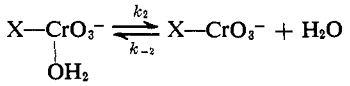
Table II. Rate Constants for the Condensation of $HCrO_4^-$ with Acidic Substrates at 25°

Reaction	K_{eq}, M^{-1}	k_f, M^{-1} sec^{-1}	$k_f^{H^+}$, M^{-2} sec^{-1}	$k_f^{HA^+}$, M^{-2} sec^{-1}	pK_a	Ionic strength, M	Ref
$H^+ + NCS^- + HCrO_4^- = CrO_3(CNS)^- + H_2O$	220 ± 25[g]		5.4×10^5		<0[h] (HCNS)	0.3	This work
$HS_2O_3^- + HCrO_4^- = CrO_3S_2O_3^{2-} + H_2O$	$(1.1 \pm 0.2) \times 10^4$	2.0×10^4			1.2 ($HS_2O_3^-$)	0.11	*a*
$HCrO_4^- + HCrO_4^- = Cr_2O_7^{2-} + H_2O$	98		6.2×10^5		6.0	1.0	*b*
	60		6.6×10^5		($HCrO_4^-$)	0.2	*c*
	50	2				0.1	*d*
$H_2PO_4^- + HCrO_4^- = CrO_3PO_3(OH)^{2-} + H_2O$	6		1.2×10^5	5 ($H_2PO_4^-$)	6.0 ($H_2PO_4^-$)	3.0	*e*
$H_2PO_3^- + HCrO_4^- = CrO_3PHO_3^{2-} + H_2O$	8		5×10^5	12 ($H_2PO_3^-$)	6.3 ($H_2PO_3^-$)	3.0	*f*

[a] Reference 11. [b] Reference 13. [c] B. Perlmutter-Hayman, *J. Phys. Chem.*, **69**, 1736 (1965). [d] J. H. Swinehart and G. W. Castellan, *Inorg. Chem.*, **3**, 278 (1964). [e] Reference 7. [f] Reference 8. [g] The units are M^{-2}. [h] T. D. B. Morgan, G. Stedman, and P. A. E. Whincup, *J. Chem. Soc.*, 4813 (1965); S. Tribalat and J. M. Caldero, *Bull. Soc. Chim. Fr.*, 774 (1966).



$$\underset{\displaystyle H}{\overset{|}{X}}\cdots\underset{\displaystyle OH}{\overset{|}{CrO_3^-}} + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X{-}\underset{\displaystyle OH_2}{\overset{|}{CrO_3^-}} + HA \qquad (12)$$



$$X{-}\underset{\displaystyle OH_2}{\overset{|}{CrO_3^-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X{-}CrO_3^- + H_2O \qquad (13)$$

where HX is the acidic substrate and HA is an acid or base catalyst, or solvent.

The first step is the diffusion-controlled encounter of the acidic substrate and hydrogen chromate ion to form a weak, possibly five-coordinate chromium(VI) complex (eq 11). The second step involves proton transfer from HX or from an acid catalyst to $HCrO_4^-$ with formation of a second five-coordinate intermediate with a stronger X-Cr bond and a coordinated water molecule. The final step involves loss of water from the five-coordinate chromium(VI) intermediate to form the substituted tetrahedral chromate product.

That proton transfer occurs in the rate-determining step is indicated by the observation of general acid catalysis in the condensation of hydrogen chromate ion with dihydrogen phosphate,[7] dihydrogen phosphite,[8] and hydrogen chromate ions.[9] The proton transfer can occur directly from the acidic substrate to hydrogen chromate, most likely with the participation of solvent molecules, or indirectly with the participation of a catalyst (hydrogen ion or other acidic or basic species).

Assuming a rapid equilibrium for the formation of the first intermediate (eq 11) and a steady-state treatment for the small concentration of the second intermediate, the following expressions for the overall rate constants are obtained.

$$\begin{aligned} k_f &= K_0k_1k_2/(k_{-1}[HA] + k_2) \\ k_r &= k_{-1}k_{-2}/(k_{-1}[HA] + k_2) \end{aligned} \qquad (14)$$

If the departure of the coordinated water molecule from the second intermediate is rapid, $k_2 \gg k_{-1}[HA]$, and the observed rate constants become

$$k_f = K_0k_1[HA] \qquad k_r = (k_{-1}/K_2)[HA] \qquad (15)$$

There is no evidence for the accumulation of a second intermediate, so the rate constants given in (15) will suffice for the present discussion.

The various rate constants which have been determined for the condensation of different acidic substrates with $HCrO_4^-$ are collected in Table II. If the reaction is uncatalyzed, HA is the solvent and k_f is a second-order rate constant. Catalysis by the hydrogen ion is described by $k_f^{H^+}$ and catalysis by general acids as k_f^{HA}, both third-order rate constants. In the formation of thiocyanatochromate(VI), hydrogen ion is consumed, and the reaction is not strictly hydrogen ion catalyzed, but the kinetic characteristics of the complex formation reaction are similar to the hydrogen ion catalyzed reactions, and they will be discussed together.

The Hydrogen Ion Dependent Rate Terms. All four of the condensation reactions which have been examined kinetically have hydrogen ion dependent rate terms with third-order rate constants in the narrow range (1–7) × 10^5 M^{-2} sec^{-1}. If $k_1^{H^+}$ is assumed to be equal to a diffusion-controlled proton transfer to the hydroxy ligand of $X\cdots CrO_3(OH)$ to form the leaving water molecule, with a rate constant of approximately 10^{10} M^{-1} sec^{-1}, then K_0 is calculated to be 10^{-4}–10^{-5} M^{-1} for the weak association between each of the acidic substrates and $HCrO_4^-$ (eq 11). This implies that the release of a proton from the acidic substrate occurs after the transition state in the hydrogen ion catalyzed mechanism, since the rate constants are independent of the acid strength of these species.

The Uncatalyzed Rate Constants. The second-order rate constants k_f for the uncatalyzed reaction between the acidic species HX and $HCrO_4^-$ depend on the acidity of HX. A rate constant of 2.0×10^4 M^{-1} sec^{-1} is observed for the strong acid $HS_2O_3^-$ which has a pK_a value of 1.2. A much smaller rate constant of 2 is observed for the condensation of $HCrO_4^-$ with itself to form dichromate; $HCrO_4^-$ is a much weaker acid, with a pK_a of 6.0. Uncatalyzed second-order rates were not observed for $H_2PO_4^-$ and $H_2PO_3^-$ with pK_a values of 6.0 and 6.3, respectively.

The rate law for the formation of thiocyanatochromate does not distinguish, of course, a mechanism involving the uncatalyzed substitution by HNCS from the hydrogen ion dependent substitution by NCS^-. In Table II, the rate constant is interpreted by the latter mechanism with a value of 5.4×10^5 M^{-2} sec^{-1}. If the mechanism were substitution by HNCS, the constant should be related to the acid dissociation constant of HNCS[14,15] to give a value of k_f comparable

---

(14) T. D. B. Morgan, G. Stedman, and P. A. E. Whincup, *J. Chem. Soc.*, 4813 (1965).

(15) S. Tribalat and J. M. Caldero, *Bull. Soc. Chim. Fr.*, 774 (1966).

with $k_f^{H^+}$, again consistent with the strongly acidic character of HNCS.

The Intimate Mechanism. An estimate can be made of the rate of proton transfer k_1 within the complex $HX\cdots CrO_3(OH)$ if it is assumed that the acidity of the weakly complexed HX is the same as that of the free acid. Since the rate of recombination of the proton with its conjugate base X^- is usually diffusion controlled,[16] the rate of proton dissociation can be estimated as

$$\begin{gathered} HX \rightleftharpoons H^+ + X^- \\ K_a = k_d/k_{-d} \\ k_d = k_{-d}K_a = 10^{10}K_a \end{gathered} \qquad (16)$$

For the strong acid $HS_2O_3^-$, this implies a value of k_1 of approximately 10^9 sec^{-1}, which in turn leads to an estimate of K_0 of 2×10^{-5} M^{-1}, in excellent agreement with the values of K_0 estimated from the hydrogen ion catalyzed rate constants.

Since $HCrO_4^-$ is much weaker acid, the rate of proton transfer, k_1, is much slower, estimated as 10^4 sec^{-1}, which together with the observed value of $k_f = 2$ M^{-1} sec^{-1} implies that K_0 for $HCrO_4^-$ is 2×10^{-4} M^{-1}, again in agreement with the estimate obtained from the hydrogen ion catalyzed reaction.

These results imply that the rate-determining step in these condensation reactions is proton transfer either from a proton in solution or from the weakly associated acidic species to the hydroxy ligand on chromium(VI) to form the departing water molecule. From the principle of microscopic reversibility, it follows that the rate-determining step in the reverse hydrolysis reactions is the deprotonation of the entering water molecule to form the Cr–OH bond.

Independent support for this mechanism can be obtained from consideration of the entropy of activation for the formation of dichromate from two monohydrogen chromate anions. The experimental entropy of activation for the formation of dichromate is -52.7 eu, obtained from the entropy of activation for the hydrolysis of dichromate at 0.1 M ionic strength (-44.2 eu)[5] and the entropy change for the formation of dichromate at zero ionic strength (-8.5 eu).[17]

The entropy of activation can be calculated from the proposed mechanism as

$$\Delta S_f^* = \Delta S_0 + \Delta S_1^* \qquad (17)$$

For the formation of the weakly associated complex between two $HCrO_4^-$ ions (eq 11), ΔS_0 is estimated as -14 eu, equivalent to the loss of one degree of translational freedom.[18] For the proton-transfer reaction, ΔS_f^* is taken as the entropy of activation for the ionization of $HCrO_4^-$, corresponding to ΔS_d^* in eq 16. This may be estimated from the known entropy of ionization of $HCrO_4^-$ ($\Delta S_a = -32$ eu)[17] and the entropy of activation for the diffusion-controlled recombination of a proton and its conjugate base

$$\Delta S_d^* - \Delta S_{-d}^* = \Delta S_a \qquad (18)$$

A representative value of the frequency factor for a diffusion-controlled proton transfer reaction[19] is 10^{12} M^{-1} sec^{-1}, which from absolute rate theory leads to a value of ΔS_{-d}^* of -4 eu. Thus, ΔS_d^* is approximately -36 eu, which, together with the value of -14 eu for ΔS_0 leads to an estimate for ΔS_f^* of -50 eu, in good agreement with the observed value of -53 eu.

Similarly, the calculated value of the entropy of activation for the formation of dichromate ion catalyzed by hydrogen ion, $\Delta S_0 + \Delta S_{-d}^* = -18$ eu, is again in excellent agreement with the experimental value obtained recently (-17.7 ± 1.5 eu).[13]

Conclusions

The rapid substitution by NCS^- on $HCrO_4^-$ requires proton transfer to form the departing water molecule on chromium(VI). The forward rate constant of 5.4×10^5 M^{-2} sec^{-1} is nearly identical with those of other substitution reactions on chromium(VI) catalyzed by H^+, suggesting a common mechanism involving rate-determining proton transfer. In the absence of catalysis by H^+, the rate of substitution on $HCrO_4^-$ depends on the acidity of the substituting species, a further indication of rate-determining proton transfer.

Acknowledgments. The authors acknowledge with pleasure many stimulating discussions with Dr. Katharine Muirhead and Professor G. P. Haight, Jr. This work was supported in part by a grant from the National Institutes of Health, No. GM 16168, and in part by a Du Pont Young Faculty Grant to J. K. B.

---

(16) M. Eigen, *Discuss. Faraday Soc.*, No. **39**, 7 (1965); *Pure Appl. Chem.*, 6, 97 (1963); "Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Interscience, New York, N. Y., 1967, p 245.

(17) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(18) R. E. Powell, *J. Phys. Chem.*, 58, 528 (1954).

(19) E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964, p 242.