

## Kinetics and Mechanism of the Reaction between Hydrogen Chromate and Dihydrogen Phosphite

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The kinetics of the condensation of hydrogen chromate with dihydrogen phosphite have been investigated by a stopped-flow technique with spectrophotometric detection. All data refer to a sodium perchlorate medium at an ionic strength of 3.0 M and a temperature of 25°C. The reaction is first order in each reactant and hydrogen-ion catalyzed. Catalysis by added bases (pyridine and acetate ion) has been observed. The catalysis by the phosphite reactant itself causes the appearance of a second-order term in phosphorus(III) at high concentrations. The reverse reaction gives rise to additional terms in the rate law. The mechanism postulated involves a pre-equilibrium step in which an addition intermediate with a 5-coordinated chromium(VI) atom is formed. A water molecule is proposed to be the leaving group from this intermediate. Any base present may effect the necessary transfer of a proton from the OH group on phosphorus(III) to the chromium(VI) center. The equilibrium constant for the formation of hydrogen chromatophosphite(2-),  $[\text{O}_3\text{Cr}-\text{O}-\text{PHO}_2]^{2-}$ , was found to be about  $8 \text{ M}^{-1}$  both from kinetic data and by spectrophotometric equilibrium measurements.

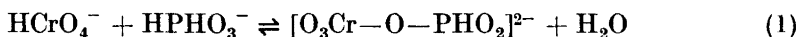
Chromium(VI) is known to form weak complexes with various molecules and ions in aqueous solution.<sup>1</sup> The formation of these complexes is related to the formation of dinuclear oxo- (or hydroxo-) bridged species occurring in many redox reactions.<sup>2</sup> Apart from the hydrolysis of dichromate ion,<sup>3</sup> the kinetics of the formation or decomposition of the chromium(VI) complexes have not been extensively investigated. Often succeeding oxidation-reduction processes cause complications. Difficulties also arise from the protolytic equilibria involving the reacting species. The tendency of hydrogen chromate ion to condense with itself (to form dichromate) is another limiting factor, as is the usually low value of the equilibrium constant for the formation of the complex.

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Furthermore, several of these condensations are too rapid to be followed by conventional or flow techniques, *e.g.*, the reaction between hydrogen chromate and hydrochloric acid.

Wilkins *et al.*<sup>4</sup> studied the reaction between hydrogen chromate and hydrogen peroxide in weakly acidic medium, Baldea and Niac<sup>5</sup> made a preliminary study of the formation of the chromatophosphate intermediate, and in a previous paper<sup>6</sup> we reported on the kinetics and mechanism for the formation of hydrogen chromatophosphate (2—).

In the present work the studies of the formation of chromato complexes with other oxoanions have been continued by an examination of the kinetics of the formation of the corresponding phosphorus (III) complex with chromium(VI). In the pH range (pH > 4) where the equilibrium given by eqn. 1 is the only important condensation equilibrium in the system, the reaction is sufficiently slow so that it can be investigated by the stopped-flow method, and no redox reaction occurs within an appreciable time.<sup>7</sup>



## EXPERIMENTAL

*Chemicals.* Disodium phosphite of analytical grade was used. All other chemicals were the same as used before.<sup>8</sup>

*Procedure.* The Sutin stopped-flow apparatus used has been described.<sup>6</sup> The progress of reaction was followed at wavelength 350 nm, where the absorption peak of hydrogen chromate is higher than that of the complex formed. The change in absorbance was so small in all the experiments that the oscilloscope pattern could be treated as an ordinary concentration *vs.* time curve. Pseudo first-order rate constants, evaluated from conventional semilogarithmic linear plots over 2 to 3 half-lives, were generally reproducible to  $\pm 5\%$ . Each experimental point is the average from 5 runs.

The hydrogen-ion concentration was obtained in the same way as described before.<sup>6</sup> The value of the equilibrium constant ( $K_1$ ; eqn. 1) was determined by the spectrophotometric technique used previously.<sup>6,9</sup> For a fixed concentration of Cr(VI), a plot of  $[\text{HPO}_3^-]/(A_1 - A)$  *vs.*  $[\text{HPO}_3^-]$  gives a straight line of slope  $1/(A_1 - A_0)$  and an intercept of  $1/K_1(A_1 - A_0)$ , where  $A_1$  is the absorbance if Cr(VI) is all  $\text{HCrO}_4^-$ ,  $A_0$  would be the absorbance if Cr(VI) were all  $[\text{CrPHO}_3]^{2-}$ , and  $A$  is the observed absorbance.

All data refer to a temperature of 25°C and a medium the ionic strength of which was held constant at 3.0 M with sodium perchlorate as the inert salt. An attempt to study the temperature dependence and evaluate  $\Delta S^*$  values would probably not be very informative, for the result would be composed of effects from various equilibria involved in the overall reaction.

## RESULTS

*Effect of pH.* The results of the rate measurements are presented in Fig. 1 in the form of plots of the observed rate constant against the hydrogen-ion concentration for two different values of the total phosphorus(III) concentration,  $[\text{P(III)}] = 0.25 \text{ M}$  and  $0.10 \text{ M}$ , respectively. The chromium(VI) concentration was generally  $2.5 \times 10^{-4} \text{ M}$ . The pseudo-first-order rate constant,  $k_{\text{obs}}$ , is defined by eqn. 2 which expresses the rate of increase of the

$$\frac{dx}{dt} = k_{\text{obs}}(x_{\infty} - x) \quad (2)$$

concentration of hydrogen chromatophosphate(2—);  $x$  represents this concentration at the time  $t$ , whereas  $x_{\infty}$  is the equilibrium value.

In the range  $1 \times 10^{-5} < [\text{H}^+] < 1 \times 10^{-4}$  M, where  $\text{HCrO}_4^-$  and  $\text{HPO}_3^-$  are the predominant reactant species, the observed pH dependence is given by eqn. 3, where  $\alpha$  and  $\beta$  are constants

$$k_{\text{obs}} = \alpha[\text{H}^+] + \beta \quad ([\text{P(III)}] \text{ constant}) \quad (3)$$

provided that the total phosphorus(III) concentration is kept constant. For  $[\text{P(III)}] = 0.25$  M the upper graph of Fig. 1 gives:  $\alpha = (18 \pm 2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  and  $\beta = 1.1 \pm 0.5 \text{ s}^{-1}$ . The corresponding results for  $[\text{P(III)}] = 0.10$  M are  $\alpha = (11 \pm 2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  and  $\beta = 0.5 \pm 0.2 \text{ s}^{-1}$ .

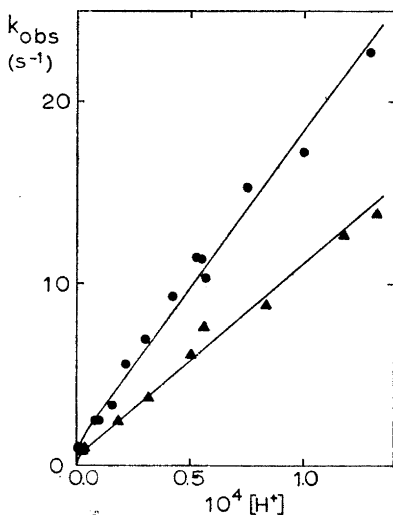


Fig. 1. Observed pseudo-first-order rate constant,  $k_{\text{obs}}$ , as a function of  $[\text{H}^+]$  for the reaction between  $\text{HCrO}_4^-$  and  $\text{HPO}_3^-$  (see eqn. 1) at  $25^\circ\text{C}$ . Reaction followed at 350 nm.  $[\text{Cr(VI)}] = 2.5 \times 10^{-4}$  M;  $[\text{P(III)}] = 0.25$  M (●) and 0.10 M (▲), respectively;  $I = 3.0$  M ( $\text{NaClO}_4$ ).

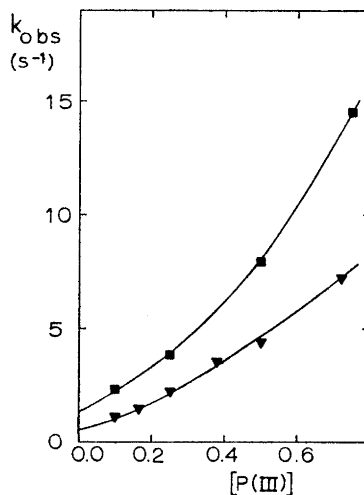


Fig. 2. Variation of  $k_{\text{obs}}$  with the total concentration of phosphate species,  $[\text{P(III)}]$ , for  $[\text{H}^+] = 2.0 \times 10^{-5}$  M (■) and  $[\text{H}^+] = 0.6 \times 10^{-5}$  M (▼), respectively.

When the hydrogen-ion concentration was lowered to  $1 \times 10^{-7}$  M no useful kinetic trace could be observed.

*Phosphorus(III) dependence at constant pH.* Rate measurements were carried out at several phosphorus(III) concentrations in the range 0.10–0.75 M, while the acidity was kept constant. These data are depicted in Fig. 2 for two different values of the hydrogen-ion concentration. The shape of the curves indicate a relation of the following type.

$$k_{\text{obs}} = a[\text{P(III)}]^2 + b[\text{P(III)}] + c([\text{H}^+] \text{ constant}) \quad (4)$$

The third constant,  $c$ , can be evaluated easily from the intercept on the  $k$  axis. Extrapolation of the upper curve gives  $c = 1.3 \pm 0.4 \text{ s}^{-1}$  at  $[\text{H}^+] = 2.0 \times 10^{-5}$ .

*Effect of added acid-base pairs.* Figs. 3 and 4 show that straight lines are obtained when at constant pH the observed rate constant is plotted against the total concentration of an added buffer (pyridinium ion plus pyridine or acetic acid plus acetate ion). The total concentration of phosphite is the same in all these experiments,  $[P(III)] = 0.25$  M. The straight lines are extrapolated to the  $k$  axis to give values of  $k_{\text{obs}}$  that are in agreement with those read from Fig. 1 for the same conditions of chromium(VI), phosphorus(III) and hydrogen-ion concentrations.

When the hydrogen-ion concentration was as high as  $5 \times 10^{-5}$  M, no increase in reaction rate with increasing pyridine concentration could be observed. From the different slopes at the two different pH values in Fig. 3 it can be shown that added pyridine increases the reaction rate substantially, whereas no appreciable effect can be attributed to the pyridinium ion. The interpretation of Fig. 4 is less certain. The decreased slope at the highest pH ( $[H^+] = 0.3 \times 10^{-5}$  M) can be partly attributed to the decreased concentrations of the reactive species  $HCrO_4^-$  and  $H_2PO_3^-$ , but our data are not sufficiently accurate to exclude catalysis by acetic acid as well as acetate ion.

*Equilibrium measurements.* The equilibrium of eqn. 1 has been studied earlier by a spectrophotometric technique.<sup>8</sup> In the present work the equilibrium constant referring to a medium of ionic strength 3.0 M ( $NaClO_4$ ) was determined by the same method. The value of  $K_1$  (25°C) was found to be  $8 \pm 2$  M<sup>-1</sup>, which agrees well with the value reported by Haight *et al.*<sup>8</sup> ( $K_1 = 7$  M<sup>-1</sup>) for a somewhat lower ionic strength.

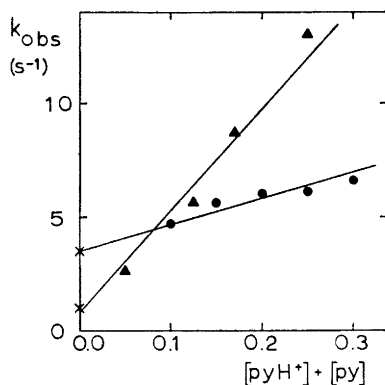


Fig. 3. Plots of  $k_{\text{obs}}$  vs. the total concentration of added pyridine buffer at  $[H^+] = 1.3 \times 10^{-5}$  M (●) and  $[H^+] = 1.3 \times 10^{-6}$  M (▲), respectively. Conditions are the same as for the upper graph of Fig. 1, from which the  $k$  values for  $[pyH^+] + [py] = 0$  are obtained for the two different pH values.

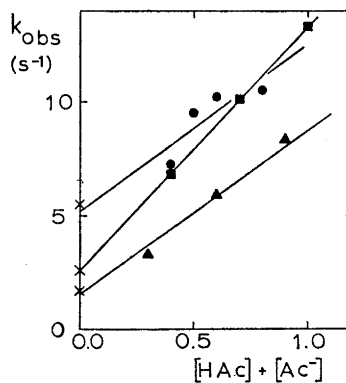
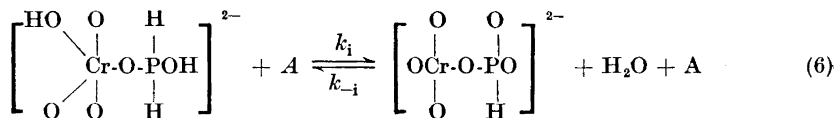
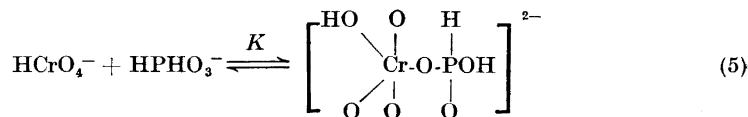


Fig. 4. Dependence of  $k_{\text{obs}}$  on the total concentration of acetic acid-acetate buffer. Apart from this added acid-base pair, conditions are the same as those represented by the upper curve of Fig. 1. Symbol,  $10^5[H^+]$ : ●, 2.5; ■, 0.8; ▲, 0.3. The data plotted on the  $k$  axis are obtained from Fig. 1.

## DISCUSSION

*Derivation of a rate law from a proposed mechanism.* The dependence of the observed pseudo-first-order rate constant (eqn. 2) on the acidity (Fig. 1) and on the total concentration of phosphorus(III) species (Fig. 2), together with the pronounced effect by added Brønsted bases (Figs. 3 and 4), suggests a mechanism similar to the one proposed for the reaction between hydrogen chromate and dihydrogen phosphate.<sup>6</sup> The mechanism involves the formation of a 5-coordinated addition intermediate (eqn. 5). In eqn. 6, A is any active catalyst present.



We believe that water is the most likely leaving group. The water is proposed to be lost from the chromium(VI) center rather than from phosphorus(III), since oxygen-18 exchange on phosphorus(III)<sup>9</sup> is much slower than the rapid <sup>18</sup>O exchange on chromium(VI).

Although the sodium ion concentration is practically constant, the curvature of the graphs in Fig. 2 might possibly be due to a medium effect. However, the proposal of a catalytic effect by phosphite species is supported by the strong effect of the added buffers in this system and in the phosphate system.<sup>6</sup> Furthermore, the statement of Baldea and Niac<sup>5</sup> that the reaction between hydrogen chromate and hydrogen thiosulfate is faster in an excess of thiosulfate also implies a second-order term in the species reacting with hydrogen chromate. If catalysis by hydrogen ion (subscript *i*=1) and by the main phosphite species,  $\text{HPO}_3^{2-}$ , (*i*=2) are considered, eqns. 5 and 6 give the following rate law, where *K* is the equilibrium constant for the pre-equilibrium step (eqn. 5), and where  $K_p''$  and  $K_{Cr}''$  are acidity constants.<sup>6</sup>

$$k_{\text{obs}} = \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_p''} \right)^2 \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_{Cr}''} \right) K k_2 [\text{P(III)}]^2 \\ + \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_p''} \right) \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_{Cr}''} \right) (K k_1 [\text{H}^+] + k_{-2} [\text{P(III)}] + k_{-1} [\text{H}^+]) \quad (7)$$

*Comparison of rate law with observed kinetics.* Comparing eqns. 4 and 7 we obtain the relation  $c = k_{-1} [\text{H}^+]$ . The extrapolation to  $[\text{P(III)}] = 0$  (Fig. 2) gives  $k_{-1} = (6 \pm 2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

Knowing  $k_{-1}$  we can now calculate a value of the equilibrium constant  $K_1$  (eqn. 1) from the slope of the plot of  $k_{\text{obs}}$  vs.  $[\text{H}^+]$  (Fig. 1). According to eqns. 3 and 7 and the equilibrium conditions,  $k_{-1}$  and  $\alpha$  are related as shown by eqn. 8. The factors in eqn. 7 that include the acidity constants are approximately equal to 1 in the pH range where  $\alpha$  is obtained. The

$$\alpha = Kk_1[\text{P(III)}] + k_{-1} = K_1k_{-1}[\text{P(III)}] + k_{-1} \quad (8)$$

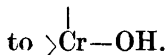
two straight lines of Fig. 1 both give  $K_1 = 8 \text{ M}^{-1}$ . This is identical with the value determined by the spectrophotometric equilibrium measurements, but because of the experimental errors the agreement is fortuitous.

The value of  $k_{-2}$  can be evaluated, by means of eqn. 9, from the

$$\beta = Kk_2[\text{P(III)}]^2 + k_{-2}[\text{P(III)}] = K_{-1}k_2[\text{P(III)}]^2 + k_{-2}[\text{P(III)}] \quad (9)$$

intercept on the  $k$  axis of Fig. 1. The data for  $[\text{P(III)}] = 0.25 \text{ M}$  give  $k_{-2} = 1.5 \pm 0.5 \text{ M}^{-1}\text{s}^{-1}$ . Therefore  $k_2K = k_{-2}K_1 = 12 \text{ M}^{-2}\text{s}^{-1}$ . Similarly, we obtain  $k_1K = k_{-1}K_1 = 5 \times 10^5 \text{ M}^{-2}\text{s}^{-1}$ . The values of the rate constants seem to be somewhat higher than those reported for the reaction between chromium(VI) and phosphorus(V), but this might well be an effect of experimental uncertainties.

*Catalysis by added acid-base pairs.* The result than only added bases, but not their corresponding acids, have appreciable effect on the reaction rate to form  $[\text{O}_3\text{Cr}-\text{O}-\text{PHO}_2]^{2-}$  is similar to the observations reported by Perlmutter-Hayman<sup>10</sup> for the hydrolysis of dichromate. Recently Perlmutter-Hayman found evidence for some general acid catalysis in addition to base catalysis in the dissociation of dichromate.<sup>11</sup> In our previous work,<sup>6</sup> both acids and bases were postulated to effect proton transfer from an OH group on P(V)



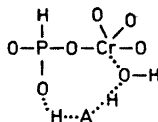
Assuming that an added base provides another path for the formation and/or removal of a water molecule from the 5-coordinated intermediate (A = pyridine or acetate ion; see eqn. 6), we can evaluate the rate constants  $k_{-\text{py}}$  and  $k_{-\text{Ac}^-}$  from Figs. 3 and 4, respectively. The catalysis by the base A leads to the following increase in the value of  $k_{\text{obs}}$ . (Charges of A and HA are omitted.)

$$\Delta k = \left( \frac{k_A K K_{\text{HA}} [\text{H}^+]^2 [\text{P(III)}]}{([\text{H}^+] + K_{\text{P}''})([\text{H}^+] + K_{\text{Cr}''})([\text{H}^+] + K_{\text{HA}})} + \frac{k_{-\text{A}} K_{\text{HA}}}{[\text{H}^+] + K_{\text{HA}}} \right) ([\text{HA}] + [\text{A}]) \quad (10)$$

$K_{\text{HA}}$  is the acidity constant for the conjugate acid of the base A.<sup>6</sup> The acidity constant of the phosphite reactant,  $\text{HPO}_3^-$ , was found to be  $5.5 \times 10^{-7} \text{ M}$  in the medium used. The experimental material gives:  $k_{-\text{Ac}^-} = 7 \pm 3 \text{ M}^{-1}\text{s}^{-1}$  and  $k_{-\text{py}} = 90 \pm 10 \text{ M}^{-1}\text{s}^{-1}$ . The  $k_A$  term and the  $k_{-\text{A}}$  term as given in eqn. 10 are enough to account for the change in slope with changing pH for the pyridine system very well (Fig. 3), so the observed kinetic behavior gives no indication of a detectable contribution from the corresponding acid ( $\text{pyH}^+$ ). For the acetate system the relatively large experimental errors do not permit

us to rule out catalysis by acetic acid, in addition to the predominant catalysis by acetate ion. Since catalysis by bases appears to be dominant, no reaction involving  $\text{H}_2\text{PHO}_3$  has been included in the derivation of the rate expression ( $\text{A}=\text{H}_2\text{PHO}_3$ , eqn. 6).

*Possible detailed mechanisms.* The formation of both the P(V) complex,  $[\text{HCrPO}_7]^{2-}$ , and the P(III) compound,  $[\text{CrPHO}_6]^{2-}$ , are catalyzed by hydrogen ion but in the former general acid catalysis is observed while in the latter general base catalysis is dominant. Since specific hydrogen ion catalysis is observed in all systems, the  $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$  acid-base pair in apparently especially effective in catalysis. Where general acid catalysis is effective, the conjugate base A of the acid HA may be acting in concert with  $\text{H}_3\text{O}^+$ , since terms in the rate law proportional to  $[\text{HA}]$  are also proportional to  $[\text{H}^+][\text{A}]$ . Where general base catalysis is observed the acid HA may be acting in concert with  $\text{OH}^-$ , since terms proportional to  $[\text{A}]$  are also proportional to  $[\text{HA}][\text{OH}^-]$ . In each case an internal proton transfer can be effected to form an  $\text{H}_2\text{O}$  leaving group on Cr(VI).



It is not possible from the kinetic data to distinguish a protolytic effect as described above from a nucleophilic attack on chromium by the catalyst as has been suggested for the simpler case of the base hydrolysis of dichromate ion.<sup>12,13</sup> The latter mechanism would involve two displacements one after the other in order to form the product *via* the catalytic path. Because of this additional bond making and bond breaking we prefer the protolytic mechanism. The hypothesis that various acid-base pairs can effect the proton transfer is an attractive one and accounts for the subtle differences between general acid and general base catalysis observed in the various systems.

*Acknowledgement.* This investigation was supported by *United States Public Health Service*, Research Grant No. 14348 from the *National Institute of General Medical Sciences*.

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Received April 26, 1969.