# Mechanism of Formation of Hydrogen Chromatophosphate(2−)[1]

**Sven-Åke Frennesson, James K. Beattie, and G. P. Haight, Jr.**

*Contribution from the Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801. Received May 17, 1968*

**Abstract**: The kinetics of the formation of $[HO_3P\text{–}O\text{–}CrO_3]^{2-}$ from $HCrO_4^-$ and $H_2PO_4^-$ were examined by the spectrophotometric stopped-flow method at 25° in aqueous solution of ionic strength 3.0 $M$ ($NaClO_4$) in the pH range 3.5–6.5. A spectrophotometric study of the equilibrium was also carried out ($K = 6 \pm 2\ M^{-1}$). Similar condensations have been proposed earlier as a first step in many Cr(VI) oxidations. A postulated reaction mechanism involves a five-coordinated intermediate, $[H_2O_3P\text{–}O\text{–}CrO_4H]^{2-}$, to which the steady-state approximation can be applied. The transient complex is proposed to lose water by the catalytic action of $H_3O^+$, $H_3PO_4$, and $H_2PO_4^-$. General acid–base catalysis is confirmed by rate studies with added buffers. An alternative mechanism, involving a direct formation of the product, is ruled out on the basis of the kinetic data.

The system of dichromate ion and mononuclear chromium(VI) species has been investigated extensively both by thermodynamic and kinetic methods.[2] Several related reactions, involving dinuclear oxo or hydroxo species, have been reported recently.[3]

Spectrophotometric studies have been performed on equilibria involving complex formation between $HCrO_4^-$ and other oxoanions or acids.[4,5] Evidently, similar condensations occur between Cr(VI) and hydrated metal ions.[6] Complexes between molybdate and oxo ions have also been proposed.[7]

The formation of such simple heteropolyanions has been postulated as a first step in several chromium(VI) oxidations of alcohols[8,9] and oxo ions.[10–12] However, these condensations have not been previously studied kinetically without the complication of succeeding redox processes. Therefore, this investigation was undertaken with the aim of obtaining information, by the stopped-flow technique, on the mechanism of the reaction

$$HCrO_4^- + H_2PO_4^- \rightleftharpoons [HO_3P\text{–}O\text{–}CrO_3]^{2-} + H_2O \qquad (1)$$

The most reliable measurements for the reaction given by eq 1 may be made around pH 4,[4,13] where $H_2PO_4^-$ is the predominant P(V) species and $HCrO_4^-$ the predominant mononuclear chromium(VI) species.

## Experimental Section

**Chemicals.** The source of chromium(VI) was potassium dichromate, analytical grade. Sodium perchlorate, sodium acetate, and sodium phosphates were of analytical grade, as was the perchloric acid (G. Frederick Smith Chemical Co.), the acetic acid (Baker and Adamson), and the pyridine (Baker and Adamson).

**Apparatus.** A stopped-flow technique was used for kinetic measurements. The apparatus, based on a design by Dulz and Sutin,[14] was supplied by the Atom-Mech Machine Co., Patchogue, N. Y. It has an eight-jet Teflon mixing chamber.

The detector system was composed of a Beckman DU monochromator with a tungsten lamp, an EMI-6256B photomultiplier, and a Tektronix Type 564 storage oscilloscope with a Polaroid camera. The power supply for the tungsten lamp consisted of four 6-V batteries, connected in parallel and maintained on trickle charge. An additional lens of 25-mm focal length was mounted between the monochromator slit and the observation tube, which improved the signal-to-noise ratio by at least a factor of 2. A Fluka high-voltage dc power supply (Model 412 B) was used to bias the photomultiplier tube. The slit being fully open (2.0 mm), the photomultiplier voltage was about 460 V. The trigger circuit and the variable filter were similar to the ones described by Dulz,[15] but the zero-suppression unit was modified; in this study a balancing potential circuit, containing a 1.35-V mercury battery, was employed.

The performance of the apparatus was tested by a study of the reaction between hydrochloric acid and hydrogen carbonate according to the method described by Dalziel.[16] The rate constant obtained for the dehydration of $H_2CO_3$, 24 ± 1 $sec^{-1}$ at 25.0°, is in agreement with previous results,[17] which range from 10 to 17 $sec^{-1}$ at 18°, corresponding to about 27 ± 7 $sec^{-1}$ at 25° according to the value of the activation energy given by Dalziel.

**Measurements.** One of the two reactant solutions contained dihydrogen phosphate and, to obtain the desired pH value, perchloric acid or hydrogen phosphate; the ionic strength was adjusted to 3.0 $M$ by addition of sodium perchlorate. The other solution consisted of (1–3) × $10^{-4}$ $M$ chromium(VI) in 3.0 $M$ $NaClO_4$. In some experiments the background salt of the latter solution was partly replaced by a buffer of the pyridine system or by an acetic acid–acetate buffer. At high buffer concentrations efficient mixing was obtained only when this buffer was present in both the solutions. In a few experiments equilibrium was approached from the opposite direction; *i.e.*, an equilibrium solution containing the complex was diluted with 3.0 $M$ $NaClO_4$ at the moment of mixing.

In the formation experiments a decrease in absorbance was observed at wavelength 350 nm, where both $HCrO_4^-$ and the complex have an absorption maximum. The internal cell breadth was 0.2 cm, and the change in absorbance was generally less than 0.010. Therefore, the recorded trace could be treated as a concentration *vs.* time curve without significant error.

The hydrogen-ion concentrations were determined with a Radiometer pH meter (Type PHM26c), equipped with a calomel electrode (Type K401), in which 4 $M$ NaCl had been substituted for the potassium chloride to prevent precipitation of $KClO_4$. Solutions

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[1] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. Supported by Public Health Service Research Grant No. 14348 from the National Institute of General Medical Sciences.

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[3] N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 160 (1966).

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[6] J. C. Sullivan and J. E. French, *ibid.*, 3, 832 (1964).

[7] G. P. Haight, Jr., and W. F. Sager, *J. Amer. Chem. Soc.*, 74, 6056 (1952).

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[12] G. P. Haight, Jr., M. Rose, and J. Preer, *ibid.*, **90**, 4809 (1968).

[13] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, pp 89, 180.

[14] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[15] G. E. H. Dulz, Ph.D. Dissertation, Columbia University, 1963, pp 90, 92.

[16] K. Dalziel, *Biochem. J.*, **55**, 79 (1953).

[17] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **5**, 1523 (1966), and references therein.

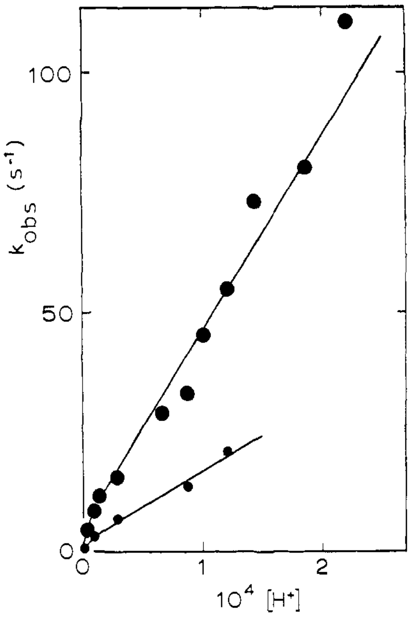

Figure 1. Observed pseudo-first-order rate constant, $k_{obsd}$, as a function of $[H^+]$ for the reaction between $HCrO_4^-$ and $H_2PO_4^-$ at 25° and ionic strength 3.0 *M*. The total concentration of phosphate species, which are in large excess over chromium(VI), is 1.00 *M* (big circles) and 0.50 *M* (small circles), respectively.

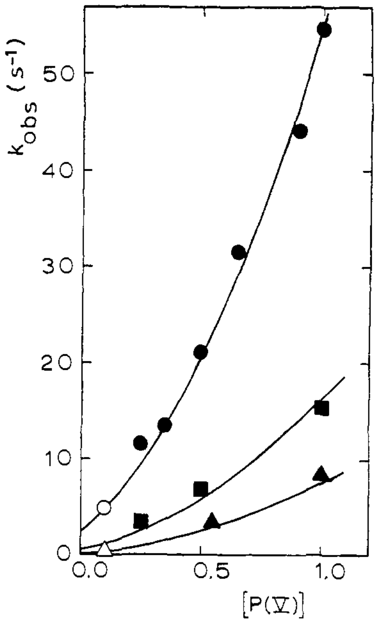

Figure 2. Variation of $k_{obsd}$ with total phosphate concentration, [P(V)]. The open symbols refer to experiments of dilution type: $[H^+] \times 10^4$ = 1.20 *M*, ●; 0.29 *M*, ■; 0.10 *M*, ▲. The curves represent values calculated from eq 6 with rate constants evaluated from Figure 1, the upper intercept of this figure, and the directly determined equilibrium constant of eq 1.

of various concentrations of $HClO_4$ in 3.0 *M* $NaClO_4$ were used for calibration.

All rate and pH measurements were carried out at 25.0°.

**Equilibrium Studies.** The equilibrium of eq 1 was studied directly by a spectrophotometric technique previously described.[5] Differential absorption measurements were made at 350, 370, and 380 nm with a Beckman Model DU-2 spectrophotometer (with scale expander).

**Tracer Experiment.** The rate of oxygen exchange between $HCrO_4^-$ and water is rapid,[2] whereas $H_2PO_4^-$ exchanges $^{18}O$ very slowly with water.[18] In order to determine if there was any induced exchange between $H_2PO_4^-$ and water in the presence of $HCrO_4^-$, the two reactants were mixed in oxygen-18-labeled water (obtained from YEDA). The phosphate was then precipitated as the calcium salt, and the isotopic oxygen composition of the precipitate was determined by the silver cyanide method of Shakhashiri and Gordon.[19] No enrichment of $^{18}O$ was found in the phosphate.

## Results

**Effect of $[H^+]$ upon Reaction.** The pH–rate profile shows a rapid increase in rate with increasing acidity. At pH <3.5 the reaction becomes too fast to be studied by the stopped-flow technique. This causes a great uncertainty in the high acid experiments. In Figure 1 the observed pseudo-first-order rate constant, $k_{obsd}$, is plotted against $[H^+]$ for two different values of the total phosphate concentration, [P(V)].

In most experiments the total concentration of Cr(VI) was $1.2 \times 10^{-4}$ *M*. Under this condition only 2% of the chromium is present as dichromate, as the equilibrium constant for the formation of $Cr_2O_7^{2-}$ from $HCrO_4^-$ is 155 $M^{-1}$ (in 3 *M* $NaClO_4$).[20] Variation of the Cr(VI) concentration in the range $(0.8\text{–}3.2) \times 10^{-4}$ *M* did not cause any discrepancies in $k_{obsd}$.

This necessarily low concentration of hydrogen chromate ion together with the rather low value of the equilibrium constant for eq 1 (*vide infra*) limited the concentration range for dihydrogen phosphate ion to 0.1–1 *M*.

Around pH 4 $k_{obsd}$ is a linear function of $[H^+]$ at a constant value of [P(V)]. At pH >5 $k_{obsd}$ decreases more rapidly with decreasing $[H^+]$ owing to the conversion of $HCrO_4^-$ and $H_2PO_4^-$ into their corresponding bases.

The relation between $k_{obsd}$ and $[H^+]$ in the linear region being represented by eq 2, the following values

$$k_{obsd} = \alpha[H^+] + \beta \quad ([P(V)] = \text{constant}) \qquad (2)$$

of $\alpha$ and $\beta$ can be evaluated from Figure 1.

$$\alpha = 4.0 \times 10^5\ M^{-1}\ \text{sec}^{-1} \text{ and}$$
$$\beta = 5.6\ \text{sec}^{-1} \text{ at } [P(V)] = 1.00\ M$$
$$\alpha = 1.5 \times 10^5\ M^{-1}\ \text{sec}^{-1} \text{ and}$$
$$\beta = 2.0\ \text{sec}^{-1} \text{ at } [P(V)] = 0.50\ M$$

**Dependence on Phosphate Concentration.** Figure 2 shows the variation of $k_{obsd}$ with [P(V)] for three different pH values. The experiments at the lowest value of [P(V)] were performed by dilution of an equilibrium solution rather than mixing of the two reactants. The form of the curves suggests that the rate law contains a $[P(V)]^2$ term. Extrapolation of the upper curve gives an intercept on the $k_{obsd}$ axis of 2.5 ± 0.5 $\text{sec}^{-1}$.

**Catalysis by Added Acid–Base Pairs.** The linear dependence of $k_{obsd}$ on the total concentration of acetic acid–acetate buffer was observed for three different buffer compositions (see Figure 3). The middle line represents a 1:1 buffer, and the pH measured, 5.0 ± 0.1, was in accord with the value of the acidity constant reported for a medium of 3 *M* $NaClO_4$[21] and was not much affected by the dimerization equilibria in the acetic acid system.

The open symbols of Figure 3 refer to similar rate measurements in which pyridine buffers had been

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[18] C. A. Bunton, D. R. Llewellyn, C. A. Vernon, and V. A. Welch, *J. Chem. Soc.*, 1636 (1961).

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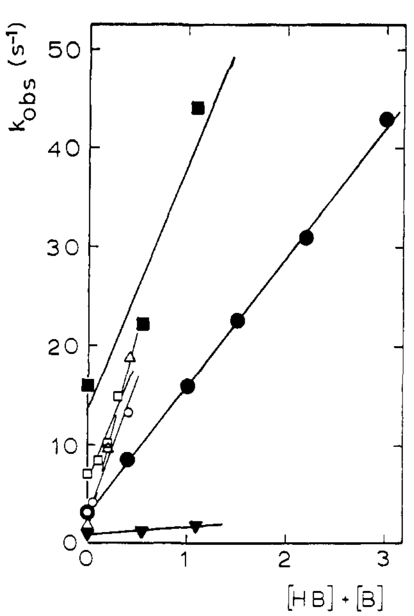

Figure 3. Effect of added acid–base pair (HB–B) on the rate of the reaction. Apart from this added system, conditions are the same as those represented by the lower curve of Figure 1: ■, pH 4.0, HB = acetic acid; □, pH 4.5, HB = pyridinium ion; ● and ○, pH 5.0, HB = acetic acid and pyridinium ion, respectively; △, pH 5.7, HB = pyridinium ion; ▼, pH 6.2, HB = acetic acid.

added to the reactant solutions at three different pH values. The concentration range was limited for solubility reasons.

Addition of a pyridine buffer had no effect on the spectrum of chromium(VI). Acetic acid has been reported to form a weak complex with hydrogen chromate[22] in aqueous solution. However, all our kinetic data are consistent with an interpretation in terms of general acid and base catalysis.

**Equilibrium Studies.** The concentration of Cr(VI) was $1.0 \times 10^{-4}$ $M$. Assuming that the observed decrease in absorbance with increasing concentration of $H_2PO_4^-$ was due to the formation of hydrogen chromatophosphate(2−) according to eq 1, we calculated the equilibrium constant, $K_1$, by the method described by Haight and coworkers.[5] The concentration of dihydrogen phosphate was varied from 0.3 to 3.0 $M$. $K_1$ was found to be $6 \pm 2$ $M^{-1}$ at 25° and ionic strength 3.0 $M$ ($NaClO_4$). This is a reasonable value compared with that reported by Holloway[4] for a lower ionic strength.

## Discussion

**Mechanism.** The apparently rectilinear graph (through the origin) of Figure 1 suggests the possibility of a mechanism involving a preequilibrium, in which $H_2CrO_4$ (or, perhaps, $H_3PO_4$) is formed, as has been proposed for the reaction between $HCrO_4^-$ and $H_2O_2$.[23] This simple scheme is, however, not consistent with all our experimental results. The data of Figure 2 would not be accounted for properly, and the results of the equilibrium measurements would not be in agreement with the kinetic data.

These facts, together with the indication of a term in $[P(V)]^2$ and the confirmation of general acid and base catalysis (Figure 3), led us to postulate a mechanism involving the formation of an addition intermediate (eq 3), which loses water through the catalytic action of the acidic and basic species present (eq 4). This mechanism also justifies the slight curvature and the small intercept of the plot of $k_{obsd}$ *vs.* $[H^+]$ in Figure 1.

$$HCrO_4^- + H_2PO_4^- \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} [H_2O_3P\text{–}O\text{–}CrO_4H]^{2-} \quad (3)$$

$$[H_2O_3P\text{–}O\text{–}CrO_4H]^{2-} + A \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} [HO_3P\text{–}O\text{–}CrO_3]^{2-} + H_2O + A \quad (4)$$

A is an acid catalyst (HB) or a base catalyst (B)

In the kinetic intermediate chromium(VI), rather than phosphorus(V), is described as five-coordinated. Since the tracer experiment shows no induced exchange of oxygen between phosphate and water, we conclude that water is lost from chromium rather than phosphorus.

**Rate Law.** Around pH 4 the important catalytic species are likely to be hydrogen ion, phosphoric acid, and dihydrogen phosphate, provided that no extra acid–base pair has been added. We then put the subscript $i$ (of eq 4) = 1, 2, and 3 for A = $H_3O^+$, $H_3PO_4$, and $H_2PO_4^-$, respectively.

Applying the steady-state approximation to the intermediate, we obtain, under the conditions described in the Results section, the following rate expression, identical for the forward and the reverse directions.

$$dx/dt = k(x_\infty - x) \quad (5)$$

$$k = \left(\frac{[H^+]}{[H^+] + K_P''}\right)^2\left(\frac{[H^+]}{[H^+] + K_{Cr}''}\right)\left(\frac{k_0k_2}{k_{-0}K_P'}[H^+] + \frac{k_0k_3}{k_{-0}}\right)[P(V)]^2 + \left(\frac{[H^+]}{[H^+] + K_P''}\right)\left[\left(\frac{[H^+]}{[H^+] + K_{Cr}''} \times \frac{k_0k_1}{k_{-0}} + \frac{k_{-2}}{K_P'}\right)[H^+] + k_{-3}\right][P(V)] + k_{-1}[H^+] \quad (6)$$

In eq 5 $x$ is the concentration of the hydrogen chromatophosphate(2−) ion at the time $t$, and $x_\infty$ is this concentration when equilibrium is reached. $K_{Cr}''$, $K_P''$, and $K_P'$ in eq 6 are the acidity constants for $HCrO_4^-$, $H_2PO_4^-$, and $H_3PO_4$, respectively. In the derivation of the expression for $k$, the following approximation has been made: $1 \gg k_1[H^+]/k_{-0} + (k_2[H^+]/k_{-0}K_P' + k_3/k_{-0})[P(V)]$. This is equivalent to assuming that eq 3 is a rapid preequilibrium step. This seems to be a reasonable assumption, for the reverse rate constant of eq 3, $k_{-0}$, is probably very large. Then the equilibrium constant, $K$, for the preequilibrium (eq 3) may be substituted for $k_0/k_{-0}$.

When a catalytic buffer is added to the solution, additional terms will be included in the expression for $k$. For each effective acid–base pair (HB–B, charges omitted), the following term will be added. $K_{HB}$ is the acidity constant for the acid HB.

$$\Delta k = \left(\frac{(k_{HB}[H^+] + k_BK_{HB})K[H^+]^2[P(V)]}{([H^+] + K_P'')([H^+] + K_{Cr}'')([H^+] + K_{HB})} + \frac{k_{-HB}[H^+] + k_{-B}K_{HB}}{[H^+] + K_{HB}}\right)([HB] + [B]) \quad (7)$$

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[22] U. Kläning and M. C. R. Symons, *J. Chem. Soc.*, 3204 (1961).

[23] M. Orhanović and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 278 (1967).

**Comparison with Observed Kinetics.** The above-mentioned result of the extrapolation to [P(V)] = 0 (Figure 2) gives, according to eq 6, $k_{-1} = (2.0 \pm 0.5) \times 10^4\ M^{-1}\ \text{sec}^{-1}$. This value is similar to the rate constant reported for the hydrogen-ion catalyzed path of the hydrolysis of dichromate ion.[24] Since, according to our equilibrium measurements, $K_1 = k_iK/k_{-i}$ ($i$ = 1, 2, 3, HB, and B) = $6 \pm 2\ M^{-1}$, we obtain $k_1K = (1.2 \pm 0.7) \times 10^5\ M^{-2}\ \text{sec}^{-1}$.

Between pH 4 and 5 the rate law reduces to the simple form given by eq 2 with

$$\alpha = (k_2K/K_P')[P(V)]^2 + (k_1K + k_{-2}/K_P')[P(V)] + k_{-1}$$

and

$$\beta = k_3K[P(V)]^2 + k_{-3}[P(V)]$$

Using our experimentally determined values of $\alpha$, $\beta$, and $K_1$, we evaluated the following constants: $k_2K/K_P' = (2.3 \pm 0.5) \times 10^5\ M^{-3}\ \text{sec}^{-1}$, $k_{-2}/K_P' = (4 \pm 1) \times 10^4\ M^{-2}\ \text{sec}^{-1}$, $k_3K = 5 \pm 2\ M^{-2}\ \text{sec}^{-1}$, and $k_{-3} = 0.9 \pm 0.2\ M^{-1}\ \text{sec}^{-1}$. Since $K_P' = (1.5 \pm 0.2) \times 10^{-2}\ M$ (estimated from our pH measurements), $k_{-2} = (6 \pm 2) \times 10^2\ M^{-1}\ \text{sec}^{-1}$.

The constants thus obtained are in accord with the rest of the kinetic data, if eq 6 is used in the calculations ($pK_P'' = pK_{Cr}'' = 6.0$). For reasonably high values of [P(V)] the $k_2$ term is the most important one at pH 4, whereas the $k_3$ term is dominating at pH 5. Both of these terms involve two P(V) molecules, one of which is a reactant in the over-all reaction, and the other of which is a general catalyst. A rate equation in which the terms that arise from catalysis by $H_3PO_4$ are excluded is not in agreement with the experimental results.

We cannot rule out the possibility that a direct reaction between $H_2CrO_4$ and $H_2PO_4^-$ (or the kinetically indistinguishable reaction between $HCrO_4^-$ and $H_3PO_4$) contributes to the $k_1$ term of eq 6.

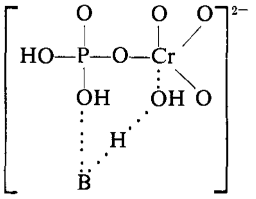
The forward rate constants ($k_i$, $i$ = 1, 2, 3, and A) cannot be evaluated, because the equilibrium constant ($K$) of eq 3 is unknown. If a diffusion-controlled encounter were rate determining for the hydrogen-ion-catalyzed path, $k_1$ would have a value of about $10^{10}\ M^{-1}\ \text{sec}^{-1}$. Knowing the products $k_iK$ ($i$ = 1, 2, and 3), we would then get the following relative values: $\log k_1 = 10.0$, $\log k_2 = 8.5$, and $\log k_3 = 5.7$. These rate constants correspond to an equilibrium concentration of the intermediate of about $1 \times 10^{-9}\ M$ (from $K \approx 1 \times 10^{-5}\ M^{-1}$). Therefore, a lower value of $k_1$—by two or three powers of ten—would still be consistent with a possible order of magnitude for the concentration of the intermediate.

Using the limiting value of $k_1$ and the values 5.0 and 6.2 for the $pK_a$ values for acetic acid and pyridinium ion, respectively, we obtain from eq 7 and Figure 3: $k_{HAc} = (4 \pm 1) \times 10^6\ M^{-1}\ \text{sec}^{-1}$, $k_{-HAc} = 7 \pm 2\ M^{-1}\ \text{sec}^{-1}$, $k_{pyH^+} = (2 \pm 1) \times 10^7\ M^{-1}\ \text{sec}^{-1}$, $k_{-pyH^+} = (4 \pm 2)\ M^{-1}\ \text{sec}^{-1}$, $k_{py} = (4 \pm 2) \times 10^7\ M^{-1}\ \text{sec}^{-1}$, and $k_{-py} = (0.6 \pm 0.2) \times 10^2\ M^{-1}\ \text{sec}^{-1}$. The reverse rate constant for the reaction catalyzed by acetate ion was estimated to be less than $1\ M^{-1}\ \text{sec}^{-1}$.

Acetic acid and pyridinium ion thus produce slightly larger effects than dihydrogen phosphate, which is in accordance with the postulate of general acid catalysis. The relatively great effect by the pyridinium ion, compared to what would be expected from the $pK_a$ values, might be attributed to its higher positive charge as compared to acetic acid and dihydrogen phosphate ion. $H_2PO_4^-$ may be active both as an acid and as a base catalyst. Our data require no term in $HPO_4^{2-}$, but catalysis by this base is probably of some importance in the higher pH region. The charge effect probably also contributes to the relatively high rate constant for pyridine as compared to acetate ion and $HPO_4^{2-}$.

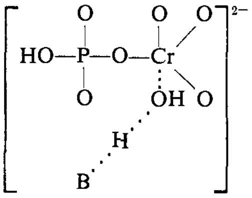
The detailed mechanism of the process indicated by eq 4 can only be tentative. Since the pathways from the five-coordinated intermediate to the products include protonation and deprotonation at two different sites of the same ion, it is tempting to assume that each of these steps proceeds according to a concerted mechanism, *i.e.*, a coupling of several elementary steps, as has been proposed for many proton-transfer processes, particularly with regard to enzyme catalysis.[25]

A solvated hydrogen ion, or any other acid present (HB), has probably partly donated its proton to the OH group on chromium in the transition state, whereby this group is made a good leaving group as water. The conjugate base of the acid catalyst is then left free to interact with the proton of one of the OH groups on phosphorus. The activated complex may then be depicted in the following way.



It is very unlikely that the protonation of the complex is completed through a fast equilibrium step before a rate-determining reaction with the conjugate base occurs, for such a separation into individual steps would require an improbably low value of the acidity constant for the protonated intermediate.

As another possible reaction path the catalytic base (B) could attack an OH group on phosphorus and transfer its proton to the OH on chromium, giving rise to an activated complex differing from that given above by one hydrogen atom.



Since the chemical action evidently takes place on chromium(VI) in this reaction, the mechanistic picture is likely to resemble that of the dimerization of hydrogen chromate and the reverse reaction.

Recent studies by Perlmutter-Hayman[26] and Wilkins[27] and their collaborators show that the basic catalyst is involved in the rate law of the base hydrolysis of dichromate ion. The mechanism generally accepted

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[24] B. Perlmutter-Hayman, *J. Phys. Chem.*, **69**, 1736 (1965).

[25] M. Eigen, *Discussions Faraday Soc.*, **39**, 7 (1965).

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

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

involves a nucleophilic attack on chromium by the base as the slow step. General acid catalysis has never been proven for the hydrolysis of dichromate ion, although that reaction is catalyzed by hydrogen ion.

In these investigations on dichromate hydrolysis the reverse reaction was not considered, but in our study both the forward and the reverse reaction are important. The mechanism proposed above offers a reasonable alternative for the base hydrolysis of dichromate, involving an attack by water in the presence of a base which transfers a proton from the water to the other chromium center, before the five-coordinated intermediate is split. The path catalyzed by hydrogen ion might occur *via* a protonated dichromate ion, with water acting as the base.

One cannot by kinetic means distinguish between the two possibilities of a direct nucleophilic attack and a purely protolytic effect. It is not improbable that in our case not only acid–base catalysis but also nucleophilic catalysis are involved.

Our future plans include further investigation of the kinetics of the condensation of hydrogen chromate with other monoacids.

**Acknowledgment.** We wish to thank Dr. Bassam Z. Shakhashiri for his help with the oxygen-exchange experiment.

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# The Interaction of Thorium(IV) with Hydroxyethylethylenediaminetriacetic Acid and Other Ligands in Aqueous Solution[1]

**R. F. Bogucki and A. E. Martell**[2b]

*Contribution from the Departments of Chemistry, Clark University, Worcester, Massachusetts, Purdue University, Lafayette, Indiana, and Texas A&M University, College Station, Texas.*

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**Abstract:** Potentiometric equilibrium measurements of hydrogen ion concentration were employed to investigate the interaction of the Th(IV) ion with N-hydroxyethylethylenediaminetriacetic acid (HEDTA) and with the related ligands nitrilotriacetic acid (NTA), N-hydroxyethyliminodiacetic acid (HIMDA), N-methyliminodiacetic acid (MIMDA), oxybis(ethylenenitrilo)tetraacetic acid (OETA), and ethylenebis(oxyethylenenitrilo)tetraacetic acid (EOTA). Evidence is presented for hydrolysis reactions of the Th(IV) chelates of all these ligands as the pH is increased. Mononuclear monohydroxo species are formed from 1:1 chelates of OETA and EOTA and with the 2:1 chelate of NTA. Fractional neutralization values in the potentiometric titration curves of the 1:1 HEDTA chelate and the 2:1 HIMDA chelate indicate the formation of hydrolyzed polynuclear chelates containing three or some multiple of three Th(IV) ions. The formation constant of the 1:1 Th(IV)–HEDTA chelate was determined to be $10^{18.5}$ from spectrometric measurement of equilibrium competition between Cu(II) and Th(IV) for the ligand. Equilibrium constants are also reported for the formation of the hydroxo mononuclear Th(IV)–HEDTA chelate, the binuclear $\mu$-dihydroxo Th(IV)–HEDTA chelate, the mononuclear hydroxo 1:1 chelates of OETA and EOTA, and the mononuclear hydroxy 1:2 Th(IV)–NTA chelate. Possible arrangements of ligand donor groups and metal ions in the ternuclear and hexanuclear Th(IV)–HEDTA chelate species are inferred, and the possible involvement of the hydroxyethyl group as a bridging ligand is suggested.

In view of the successful analyses of the Th(IV)–ethylenediaminetetraacetic acid (EDTA), Th(IV)–1,2-diaminocyclohexanetetraacetic acid (CDTA), and Th(IV)–diethylenetriaminepentaacetic acid (DTPA) systems described previously,[3] it was decided to investigate the Th(IV)–HEDTA and Th(IV)–HIMDA systems. This study should extend the information on the role of hydroxyethyl groups of organic ligands in hydrolysis and olation of Th(IV) chelates.

The role of ether oxygen as a donor group in the Th(IV) chelates was also investigated by potentiometric titration of solutions of the Th(IV) chelates of a monoether compound, [oxybis(ethylenenitrilo)]tetraacetic acid (OETA), and of a diether compound, [ethylenebis(oxyethylenenitrilo)]tetraacetic acid (EOTA).

Potentiometric equilibrium studies have also been carried out on solutions containing 1:2 molar ratios of Th(IV) ion to nitrilotriacetic acid (NTA) and to methyliminodiacetic acid (MIMDA). These chelates are analogous, with respect to the possible number of donor atoms, to the 1:1 Th(IV) chelates of DTPA and EDTA, respectively. These systems afford an interesting comparison, since in each case the 1:2 chelates have one less chelate ring than the analogous 1:1 chelate.

The structures of the ligands used in this investigation are indicated by formulas I–VI.

## Experimental Section

**Spectrophotometric Measurements.** Spectrophotometric measurements were made with a Cary Model 14 PM recording spectrophotometer. Spectra of all solutions were measured in the same silica cell of 1.000-cm path length. All solutions were 0.10 *M* with respect to $KNO_3$.

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[2] Author to whom correspondence should be addressed at Department of Chemistry, Texas A&M University, College Station, Texas 77843.

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