The X-ray diffraction spectr awere obtained by the Debye–Scherrer method with a 143.2-mm diameter camera. Nickel-filtered copper radiation was used. The *d* values were calculated using the values $\lambda(K\alpha)$ 1.5418 Å and $\lambda(K\alpha_1)$ 1.54050 Å.

A preliminary indexing of the patterns was accomplished by comparison with previously published indexing of related systems. The lattice parameters were then calculated on an IBM 7040 computer using the least-squares program LSRSTR.[20]

The indexing of the rest of the observed reflections was accomplished by the use of the FORTRAN IV program POWDER.[21] This program calculates the expected powder pattern intensities for all *d* values of interest using atomic scattering factor tables, the general positions, the special extinctions, and the atomic positions of the atoms in the asymmetric unit. For this work the atomic positions determined by Wang for $ErSe_2$[14] were used. It was assumed that the positions could be used for the polyselenides of Tm, Yb, and Lu to calculate the approximate reference powder patterns. These calculated patterns were then used to assign indices to the observed diffraction lines on the basis of the calculated and observed intensities.

The lattice parameters obtained from the indexed patterns were used to generate reference patterns with which to index the full films. These indexings were then intercompared for consistency and the final lattice parameter refinements were made. The lattice parameters are given in Table I and compared with other work in Figure 4. X-Ray diffraction powder patterns are given in Table II.

Discussion

Tetragonal polyselenides of Tm, Yb, and Lu have been made for the first time. From the data collected in this work it is improbable that the change in valency accounts for Wang's inability to synthesize $YbSe_2$.[14] All of the new polyselenides were formed at pressures as low as 15 kbars. Ytterbium is known to undergo an electronic transition from the divalent to the trivalent state at 39.5 kbars and room temperature. At 400° this transition is lowered to about 30 kbars.[22] Thus, unless the polyselenide also tends to favor the trivalent state, this is not the limiting factor for the formation of $YbSe_2$. Decreasing size factors was the second restriction postulated by Wang. If a minimum pressure of formation does exist as has been recently found for the cubic RS_2 compounds,[8] it is below 15 kbars for lutetium, the smallest of the lanthanides studied, and apparently does not increase with increasing atomic number (or decreasing ionic radius) as rapidly as was found for the polysulfides.[8]

Acknowledgments.—We thank Norman L. Eatough, Jim Hoen, John F. Cannon, Karl Miller, M. D. Horton, Fred D. Childs, and Leo Merrill for their assistance in various phases of this work.

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The Kinetics of the Chromium(VI)–Arsenic(III) Reaction. II. Dihydrogen Phosphate–Hydrogen Phosphate Buffer Solutions[1,2]

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Received November 17, 1969

The kinetics of the Cr(VI)–As(III) reaction have been investigated in H_2PO_4–HPO_4^{2-} buffers. Complex kinetics have been obtained. The rate law found is first order in total Cr(VI) and As(III) with a complex dependence upon buffer composition. The data point to the reaction proceeding *via* two activated complexes $H_2PO_4^-\cdot HCrO_4^-\cdot$As(III) and $HPO_4^{2-}\cdot HCrO_4^-\cdot$As(III).

Introduction

In part I,[2] kinetic evidence for the formation of a complex between As(III) and Cr(VI) was presented. It was noted at that time that although the reaction appeared to be pH independent over the pH range 4.3–5.5, a path dependence upon the concentration of acetic acid was found to be present. This is in support of the analysis of Edwards,[4] who presented evidence for general-acid catalysis in Cr(VI) oxidations. Kolthoff and Fineman[5] suggested that the rate of the Cr(VI)–As(III) should increase with increasing acidity in solutions of pH less than 9. Preliminary

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[1] Research sponsored by AFOSR(SRC)-OAR, USAF, Grants AF-AFOSR-210-63 and AF-AFOSR-210-65.

[2] Part I: J. G. Mason and A. D. Kowalak, *Inorg. Chem.*, **3**, 1248 (1964).

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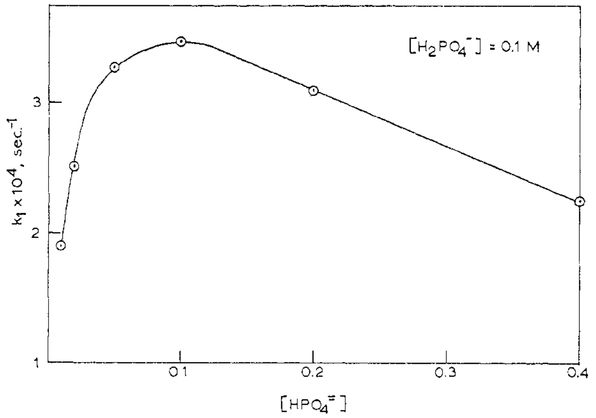

Figure 1.—The effect of $[HPO_4^{2-}]$ on the rate of reaction at fixed $[H_2PO_4^-]$. $[As(III)] = 8.00 \times 10^{-3}$ *M*; $[Cr(VI)] = 1.2 \times 10^{-4}$ *M*.

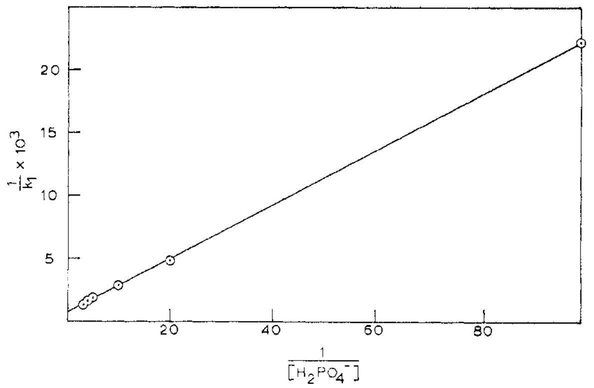

Figure 2.—Evaluation of the effect of $[H_2PO_4^-]$ in 1:1 $H_2PO_4^-$–HPO_4^{2-} buffers. $[As(III)] = 8.00 \times 10^{-3}$ *M*; $[Cr(VI)] = 1.2 \times 10^{-4}$ *M*.

experiments were performed in $H_2PO_4^-$–HPO_4^{2-} buffers with the surprising result that the rates were considerably more rapid than those obtained in acetic acid–acetate buffers even though the buffer system was much less acidic and appreciable quantities of chromate ion were present. A more detailed investigation of the kinetics of the Cr(VI)–As(III) reaction in phosphate buffers was then initiated to determine at what pH the reaction would show a pH dependence and whether such a pH dependence was due solely to the conversion of $HCrO_4^-$ to CrO_4^{2-}. While this work was being started, Ware and Traylor[6] showed that for the oxidation of boronic acids, $RB(OH)_2$, the pH–rate profile coincided with $HCrO_4^-$ being the oxidizing agent in solutions of pH between 4 and 9. The kinetics reported here reveal more complexity than those of Ware and Traylor for the $H_2PO_4^-$–HPO_4^{2-} system.

Experimental Section

Stock solutions of Cr(VI) were prepared from primary standard $K_2Cr_2O_7$ and redistilled water. Stock solutions of As(III) were prepared by boiling primary standard As_2O_3. The concentration of the As(III) was checked by titration with standard iodine. All other chemicals were reagent grade and used without further purification. All kinetic measurements were made spectrophotometrically using a Beckman DU spectrophotometer thermostated at 25.0 ± 0.1°. The wavelength used was 370 mμ, the wavelength of maximum absorption of Cr(VI) in these buffers. Conformance to Beer's law was established at 310, 350, and 370 mμ. Rate constants were determined graphically from −2.303 times the slope of log $(A_t - A_\infty)$ *vs.* *t* plots where A_t represents the absorbance of the solution at time *t*, and A_∞, the absorbance at infinite time. Rate constants obtained in this manner were in general reproducible to 5% although, in some cases, the agreement was slightly less than 10%. Some dependence of the rate constants on the initial concentration of Cr(VI) was apparent and at the higher concentrations of Cr(VI), definite curvature of the log $(A_t - A_\infty)$ *vs.* *t* plots developed after the first half-life. In these cases the initial linear portion was used for the determination of the rate constants and data so obtained were compared for the same concentration of Cr(VI). When these data were compared with those obtained at lower Cr(VI) concentrations, the results were essentially the same (±10%). All solutions were purged with nitrogen prior to kinetic analysis. The ionic strength was maintained at 1.5 with KNO_3. All pH measurements were made with a Radiometer pHM4 pH meter.

Kinetic Results

Reaction Order with Respect to Cr(IV) and As(III).—As mentioned in the Experimental Section, as long as the initial concentration of Cr(VI) was approximately 1.2×10^{-4} *M* or less, the disappearance of total Cr(VI) as measured spectrophotometrically followed pseudo-first-order kinetics. The order with respect to As(III) is shown by the data in Table I to be unity. These data were determined from initial slopes. The rate law is established to be of the form

$$\frac{-d[Cr(VI)]_T}{dt} = k_2[As(III)][Cr(VI)]_T$$

In 0.1 *M* $H_2PO_4^-$–0.1 *M* HPO_4^{2-} buffers k_2 has the value 4.7×10^{-2} M^{-1} sec^{-1}.

TABLE I

EFFECT OF As(III) ON THE DISAPPEARANCE OF Cr(IV) IN 0.1 *M* $H_2PO_4^-$–0.1 *M* HPO_4^{2-} BUFFER

[As(III)], *M*	10^4k_m,[a] sec^{-1}	10^2k_2, M^{-1} sec^{-1}
2.00	0.921	4.61
4.00	1.73	4.33
5.99	2.95	4.92
8.36	3.75	4.49
8.83	3.86	4.37
10.6	5.53	5.22
11.9	5.96	5.00
12.4	6.05	4.88
20.7	10.0	4.83
30.9	15.4	4.98
		Av 4.76 ± 0.24

[a] $[Cr(VI)]_T = 2.49 \times 10^{-4}$ *M*; temperature 25°.

Effect of Buffer Composition.—As the buffer composition is varied, (i) the concentrations of $H_2PO_4^-$ and HPO_4^{2-}, both potential complexing agents of Cr(VI), vary, (ii) the hydrogen ion concentration varies, and (iii) the distribution of Cr(VI) between $HCrO_4^-$ and CrO_4^{2-} changes. In addition all data may contain a residual kinetic component which is independent of buffer composition.

Figure 1 shows the effect of varying the concentration of HPO_4^{2-} at constant $[H_2PO_4^-]$. In this vari-

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[6] J. C. Ware and T. G. Traylor, *J. Amer. Chem. Soc.*, **85**, 3026 (1963).

ation both HPO_4^{2-} and the pH are changing. The rates pass through a maximum.

Figure 2 shows the effect of total buffer concentration at fixed buffer ratio. The data are presented in the form of a plot of $1/k_m$ *vs.* $1/H_2PO_4^-$ where k_m is the measured pseudo-first-order rate constant which effectively linearizes the data over a 30-fold variation in $H_2PO_4^-$.

Acid Chromate–Chromate Distribution.—The equilibrium constant for the reaction $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$, $K_A = [H^+][CrO_4^{2-}]/[HCrO_4^-]$, was determined previously[2] to be 1.75×10^{-6} in 1.5 M KNO_3. This value was confirmed by spectrophotometric measurement[7] of dilute Cr(VI) solutions in dilute acetic acid–acetate buffers with KNO_3 added. The concentration of $HCrO_4^-$ as a function of $[H^+]$ is given by $[HCrO_4^-] = [H^+][Cr(VI)]_T/(K_2 + [H^+])$; $[CrO_4^{2-}] = K_2[Cr(VI)]_T/(K_2 + [H^+])$.

The $HCrO_4^-$–$H_2PO_4^-$ Complex.—Holloway[8] has determined that $HCrO_4^-$ forms complexes with both $H_2PO_4^-$ and H_3PO_4. In preliminary data fitting a value of approximately 7 appeared as K for $HCrO_4^- + H_2PO_4^- \rightleftharpoons HCrPO_7^{2-} + H_2O$. In an attempt to evaluate K by independent means, a series of spectra were obtained for solutions of 1.2×10^{-4} M Cr(VI), 0.1 M $H_2PO_4^-$, variable $[HPO_4^{2-}]$, and total ionic strength of 1.5 maintained with KNO_3. The absorbance measured at 370 mμ (the absorbance maximum of CrO_4^{2-}), A_m, was plotted using

$$\frac{A_B - A_m}{A_m - A_0} = \frac{[H^+]}{K_A'}$$

where K_A' represents the apparent dissociation constant of $HCrO_4^-$ in the presence of phosphate; A_B, the absorbance in alkaline solution; A_0, the absorbance in acid solution. The value of A_B calculated from this relation was in good agreement with that calculated from published values for CrO_4^{2-}. The value of A_0 was significantly lower than that reported for $HCrO_4^-$ and that measured in our laboratory previously. The value of pK_A' found was 5.96 ± 0.05. Since $K_A' = K_A/(1 + K[H_2PO_4^-])$, if the assumption of only one complex is made, K for this system has the value of 6 M^{-1}. Since this work was completed, Frennesson, Beattie, and Haight[9] have published a detailed study of the $H_2PO_4^-$–$HCrO_4^-$ reaction. The value of K which they obtained is 6 ± 2 M^{-1} at 25° and ionic strength 3.0 M ($NaClO_4$). This value is in excellent agreement with the value reported here. The constancy of K_A' implies that only one solution complex is detectable at the wavelength used and under the experimental conditions used.

Formulation of the Rate Law.—Having established that the reaction is first order in both total Cr(VI) and total As(III) and that association occurs between Cr(VI) and $H_2PO_4^-$, the formulation of the dependence of the rate on buffer composition was accomplished in the following way. The total Cr(VI) may be expressed by $[Cr(VI)]_T = [HCrO_4^-] + [CrO_4^{2-}] + [HCrPO_7^{2-}]$ from which

$$[HCrO_4^-] = \frac{[Cr(VI)]_T[H^+]}{[H^+] + K_A + K[H^+][H_2PO_4^-]} = [Cr(VI)]_T\,\alpha'$$

At fixed As(III) concentration, values of k_m/α' were plotted *vs.* $[H_2PO_4^-]$ at each buffer ratio. From best fit analysis of the kinetic data a value of $K = 7$ was used in the computation of α'. These plots were linear and passed through the origin. The dependence of the slopes on the buffer ratio was graphically evaluated. In this way, the final form of the rate law was found to be

$$\frac{-d[Cr(VI)]_T}{dt} = \frac{[H^+][Cr(VI)]_T(k_1[H_2PO_4^-] + k_2[HPO_4^{2-}])}{[H^+] + K_A + K[H^+][H_2PO_4^-]} \times [As(III)]$$

Since unpublished data established a term independent of buffer composition in the acetic acid catalyzed reaction, another search was made by computer for a k_0 term.[10]

No statistically valid k_0 term was found and the final form of the rate law was confirmed. Table II contains the data and calculated values of the rate constant. At $[As(III)] = 8.00 \times 10^{-3}$ M, the pseudo-second-order rate constants k_1' and k_2' had the values $1.9 \pm 0.11 \times 10^{-3}$ and $2.05 \pm 0.04 \times 10^{-2}$ M^{-1} sec^{-1}. From these, values of $k_1 = 2.4 \pm 0.14 \times 10^{-1}$ M^{-2} sec^{-1} and $k_2 = 2.6 \pm 0.05$ M^{-2} sec^{-1} were computed.

TABLE II

RATE DATA FOR $H_2PO_4^-$–HPO_4^{2-} BUFFERS[a]

$[H_2PO_4^-]$, M	$[HPO_4^{2-}]$, M	pH	10^4k_m, sec^{-1}	10^4k_c,[b] sec^{-1}
0.10	0.01	5.36	1.92	1.85
0.20	0.02	5.33	2.79	2.84
0.30	0.03	5.31	3.48	3.42
0.10	0.02	5.65	2.60	2.42
0.20	0.04	5.63	4.04	3.82
0.30	0.06	5.62	5.02	4.70
0.10	0.05	6.14	3.27	2.96
0.20	0.10	6.08	5.53	5.39
0.01	0.01	6.43	0.45	0.39
0.05	0.05	6.44	2.07	1.81
0.10	0.10	6.44	3.47	3.43
0.20	0.20	6.49	5.30	5.73
0.25	0.25	6.52	6.10	6.45
0.30	0.30	6.54	7.0	7.32
0.10	0.20	6.81	3.09	3.29
0.15	0.45	7.25	3.05	2.86
0.05	0.20	7.14	1.53	1.60
0.10	0.40	7.30	2.25	2.28

[a] $[Cr(VI)] = 1.2 \times 10^{-4}$ M, $[As(III)] = 8.0 \times 10^{-3}$ M, temperature 25°, $\mu = 1.5$ M. [b] Calculated from the rate law. Average deviation 6% in the range 1.3–13%.

Discussion of Results

The final form of the rate law is

$$\frac{-d[Cr(VI)]}{dt} = \frac{[H^+][As(III)][Cr(VI)]_T}{[H^+] + K_A + K[H^+][H_2PO_4^-]} \times (k_1[H_2PO_4^-] + k_2[HPO_4^{2-}])$$

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(7) We are indebted to P. T. Chang for these measurements.

(8) F. Holloway, *J. Amer. Chem. Soc.*, **74**, 224 (1952).

(9) S. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *ibid.*, **90**, 6018 (1968).

(10) We are grateful to Mr. Gerald Dulaney for programming the data on the PDP8/I computer, Digital Equipment Corp.

It is evident that over the region studied no reaction due to the direct reduction of Cr(VI) by As(III) is detectable. It is also apparent that no denominator term in As(III) is found. The primary study of the effect of As(III) on the Cr(VI)–As(III)–$H_2PO_4^-$ system was carried out at pH 6.44 with some studies at pH 5.35. In neither case was the As(III) term in the denominator observed. It is possible that the As(III) complexation previously observed is pH dependent and is not important in this pH region. This matter is currently under investigation.

It appears reasonable to assign the first term to the direct oxidation of As(III) by the $HCrPO_7^{2-}$ complex. That the complex is an effective oxidizing agent does not seem unreasonable. In view of the absence of a k_0 term, acid catalysis for this system seems unlikely.

The second term is more difficult to interpret. The transition state consists of either $HCrO_4^- \cdot As(III) \cdot HPO_4^{2-}$, $CrO_4^{2-} \cdot As(III) \cdot H_2PO_4^-$, or $HCrO_4^- \cdot H_2PO_4^- \cdot As(OH)_2O^-$.

Either of the first two is equivalent to oxidation by means of $CrPO_7^{3-}$. The magnitude of the effect of HPO_4^{2-} seems contrary to the oxidizing ability expected for such a complex. No such complex was noted spectrophotometrically. The last formulation would have $HCrPO_7^{2-}$ oxidizing the arsenite anion $As(OH)_2O^-$. The highest pH value reported here (7.30) assures that only equilibrium amounts of $As(OH)_2O^-$ are present at any time.[11]

The oxidizability of As(III) in alkaline solution is well known and has been used by Willard and Manalo[12] for the estimation of As(III) with hexacyanoferrate(III) as the oxidant. However, in the pH region investigated by Kolthoff and Fineman[5] no effect was observed. Either chromate ion does not discriminate between the acid and anionic forms or other complications occur which mask the effect if it exists.[13] Schenk[14] has stated that the well-known I_2–As(III) reaction proceeds most probably through the anion.

Two mechanisms for the second step consistent with the data may be written

$$HCrO_4^- + H_2PO_4^- \rightleftharpoons HCrPO_7^{2-} \qquad (K = 7)$$

$$HCrPO_7^{2-} + As(III) \xrightarrow{k_1} product$$

$$HCrPO_7^{2-} + As(OH)_2O^- \xrightarrow{k_2} product \qquad (1)$$

$$HCrO_4^- + As(III) + HPO_4^{2-} \xrightarrow{k_2} product \qquad (2)$$

Application of steady-state kinetics and the known stoichiometry to the first scheme yields

$$\frac{-d[Cr(VII)]_T}{dt} = 2k_1[HCrPO_7^{2-}][As(III)] + 2k_2[HCrPO_7^{2-}][As(OH)_2O^-]$$

Since the following two relations hold

$$K = \frac{[HCrPO_7^{2-}]}{[HCrO_4^-][H_2PO_4^-]}$$

$$[Cr(VI)]_T = [HCrO_4^-] + [CrO_4^{2-}] + [HCrPO_7^{2-}]$$

then

$$[HCrPO_7^{2-}] = \frac{K[H^+][H_2PO_4^-][Cr(VI)]_T}{K_A + [H^+] + K[H^+][H_2PO_4^-]}$$

where $K_A = [H^+][CrO_4^{2-}]/[HCrO_4^-]$. If $K_{As} = [H^+][As(OH)_2O^-]/[As(III)]$, then

$$\frac{-d[Cr(VI)]_T}{dt} = \frac{[H^+][H_2PO_4^-][Cr(VI)]_T}{K_A + [H^+] + K[H^+][H_2PO_4^-]} \times \left(2k_1 + \frac{2k_2K_{As}}{[H^+]}\right)[As(III)]_T$$

Substitution of $K_2 = [H^+][HPO_4^{2-}]/[H_2PO_4^-]$ yields

$$\frac{-d[Cr(VI)]_T}{dt} = \frac{[H^+][H_2PO_4^-][Cr(VI)]_T}{K_A + [H^+] + K[H^+][H_2PO_4^-]} \times [As(III)]_T\left(2k_1 + \frac{2k_2K_{As}[HPO_4^{2-}]}{K_2[H_2PO_4^-]}\right)$$

Simplification produces

$$\frac{-d[Cr(VI)]_T}{dt} = \frac{[H^+][Cr(VI)]_T[As(III)]_T}{K_A + [H^+] + K[H^+][H_2PO_4^-]} \times \left(2k_1[H_2PO_4^-] + \frac{2k_2K_{As}[HPO_4^{2-}]}{K_2}\right)$$

This mechanism equates the experimentally observed k_2 with $2k_2K_{As}/K_2$. Using $pK_{As} = 9.13$ and $pK_2 = 6.45$, this interpretation yields a ratio of the reactivity of the arsenite anion to the acid of k_2/k_1 of approximately 5.1×10^3.

The second mechanism reproduces the experimental rate law with the identification of the measured k_2 with the second step, $2k_2$, which is not detailed except as to composition of the transition state. Certainly other mechanistic possibilities exist but they are indistinguishable from the two outlined here. More complex interpretation of the data is possible but does not seem warranted by the data. No evidence of As(III)–$H_2PO_4^-$ or As(III)–HPO_4^{2-} interaction was detected and, therefore, emphasis has been placed upon the Cr(VI)–$H_2PO_4^-$ association.

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[11] The pK_a of $As(OH)_3$ was measured by pH titration in 1.5 *M* KNO_3 and found to be 9.13. The structures $As(OH)_3$ and $As(OH)_2O^-$ have been established by T. M. Loehr and R. A. Plane, *Inorg. Chem.*, **7**, 1708 (1968).

[12] H. H. Willard and G. D. Manalo, *Ind. Eng. Chem., Anal. Ed.*, **19**, 167 (1947).

[13] Preliminary work on this reaction in our laboratory in THAM buffers shows a rate increase with pH increase in the region 8.6–9.

[14] G. H. Schenk, *J. Chem. Educ.*, **41**, 32 (1964).