

due to greater ion association in the medium with lowered dielectric constant. We plan to try other mixed solvents.

The apparent similarity in activation energies for the nitrate and perchlorate systems may be only fortuitous. Eventually more extensive temperature coefficients should be obtained along with much more information concerning the equilibria and their temperature coefficients in these solutions.

The apparent photochemistry would be interesting to investigate further although it would be difficult to obtain quantitative data.

The absence of an effect due to low concentration of Cr(II) suggests that electron transfer may not be appreciably faster in liquid ammonia than in water. We hope to find a more useful salt than CrCl₂. Possibly CrI₂ could be used.

We plan to try to extend our studies to other metal ion-ammonia complexes. A wide range of rates has now been discovered (the Ni^{II}(NH₃)₆ exchange⁷ is very rapid) and some interesting comparisons can be expected.

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The Kinetics of the Chromium(VI)-Arsenic(III) Reaction in Acetic Acid-Acetate Buffer Solutions¹

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The kinetics of the oxidation of As(III) by Cr(VI) have been investigated over a wide range of As(III) and Cr(VI) concentrations in 0.2 *M* acetic acid-0.2 *M* potassium acetate buffers and a constant ionic medium of 1.5 *M* adjusted with potassium nitrate. In regions where the As(III) greatly exceeds the Cr(VI) the rate law is $-d[\text{Cr(VI)}]/dt = kK[\text{As(III)}][\text{Cr(VI)}]/(1 + K[\text{As(III)}])$ where *K* can be identified as the equilibrium constant for the reaction $\text{As(III)} + \text{HCrO}_4^- \rightleftharpoons \text{As(III)} \cdot \text{HCrO}_4^-$ and *k* is the specific rate constant for the decomposition of the complex. At high concentrations of Cr(VI), a second path involving Cr₂O₇²⁻ appears.

Introduction

The paths by which As(III) is oxidized by one- and two-equivalent reagents have been the subject of much discussion,³ most of which is concerned with the possibility of As(IV) as an intermediate. Recently, Woods, *et al.*,⁴ have studied the induced oxidation of As(III) by the Fe(II)-persulfate system in the absence and presence of oxygen. They conclude that As(IV) is produced as an intermediate in these reactions. Csanyi postulated As(IV) as an intermediate in the titration of a mixture of persulfate and hydrogen peroxide with one-equivalent oxidants⁵ and in the induced reduction of chlorate by arsenite.⁶ Mechanisms involving As(IV) as an intermediate have been postulated for the oxidation of As(III) initiated by X-rays⁷ and in the photosensitized reaction between arsenite and hydrogen peroxide.⁸

The oxidation of As(III) by Cr(VI) in acid solution was studied many years ago by DeLury,⁹ whose data

have been discussed and interpreted by Westheimer¹⁰ and Edwards.¹¹ The evaluation of Edwards leads to the rate law

$$R = k_a[\text{HCrO}_4^-][\text{H}_3\text{AsO}_3][\text{H}^+] + k_b[\text{HCrO}_4^-][\text{H}_3\text{AsO}_3][\text{H}^+]^2$$

which is analogous to the rate law for the oxidation of isopropyl alcohol by chromic acid.¹² Westheimer,¹⁰ from a detailed analysis of the induced oxidation of Mn(II), concludes that Cr(IV) is the unstable oxidation state of chromium produced in this reaction and that the formation of As(IV) is improbable.

Kolthoff and Fineman¹³ studied the reaction in alkaline buffers and reported the rate law $R = k[\text{As(III)}][\text{Cr(VI)}]$ with no dependence upon $[\text{H}^+]$ indicated above a pH of 9. They speculate that there should then be a series of terms varying with $[\text{H}^+]$ to describe the whole region from acid to alkaline solution.

This work was initiated to investigate the possibility of As(IV) as an intermediate in this reaction, determine the role of hydrogen ion more specifically, and test for general acid catalysis. Preliminary work indicated that the reaction appeared to be independent of hydrogen ion over the pH region 4.3 to 5.5 but dependent upon the concentration of acetic acid. Because of

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(2) Taken in part from the M.S. thesis of A. D. Kowalak, Virginia Polytechnic Institute, 1963.

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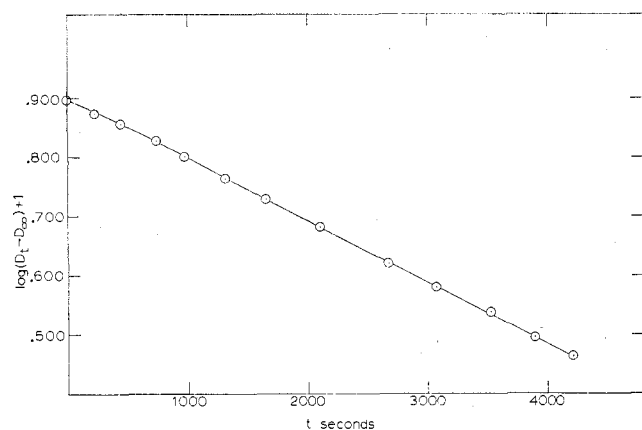


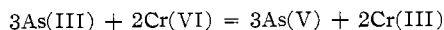
Fig. 1.—Typical first-order plot of the spectrophotometric data at 350 $m\mu$, $[\text{As(III)}] = 1.97 \times 10^{-2} M$.

the complexity of those data, the present report is confined to a discussion of the nature of the reaction between As(III) and Cr(VI) in buffers of 0.2 M acetic acid–0.2 M potassium acetate and a total ionic strength of 1.5 M .

Experimental

Materials.—Stock solutions of As(III) and Cr(VI) were prepared from primary standard As_2O_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ obtained from several commercial sources after appropriate drying. Rate data obtained were compared with As(III) solutions prepared from an N.B.S. sample of As_2O_3 . The data obtained were independent of the source of reagents. All other reagents were reagent grade. The acetic acid stock solutions were standardized using standard carbonate-free NaOH. The potassium acetate was checked for basic impurities.

Stoichiometry.—The stoichiometry of the reaction was investigated with respect to As(III) and Cr(VI) at pH 4.6 and 5.5. The expected stoichiometry



was confirmed to within 3 parts per thousand.

Kinetic Measurements.—Rate data were obtained by two methods: (a) spectrophotometric and (b) iodometric titration depending upon the region being investigated. Method (a) was used to follow the Cr(VI) as a function of time in solutions of low Cr(VI)–high As(III). Method (b) was used to follow As(III) as a function of time at high Cr(VI).

The spectrophotometric data were obtained at 350 $m\mu$ using a Beckman DU spectrophotometer thermostated to $25.0 \pm 0.1^\circ$. The validity of Beer's law with respect to Cr(VI) was checked using synthetic mixtures containing variable amounts of Cr(III) and As(V) generated *in situ* by the reduction of Cr(VI) with As(III). All solutions were purged with nitrogen which had been purified according to the method of Meites and Meites.¹⁴ The spectrophotometric cells were glass-stoppered and presumably air-tight.

For the runs high in Cr(VI), samples were removed periodically, quenched with a large volume of ice-cold saturated sodium borate solution, and titrated immediately with standard I_2 using starch as the indicator. The iodine solution was standardized prior to each kinetic run. All solutions were purged with purified nitrogen prior to mixing and maintained under nitrogen during the run.

The pseudo-first-order rate constants were obtained from plots of $\log(D_t - D_\infty)$ vs. t or $\log[\text{As(III)}]$ vs. t . The rate constants obtained spectrophotometrically were reproducible to better than 5%. The titrimetric results except at the highest Cr(VI) used were reproducible to better than 3%. The titrimetric data were also subjected to analytical evaluation by means of the equa-

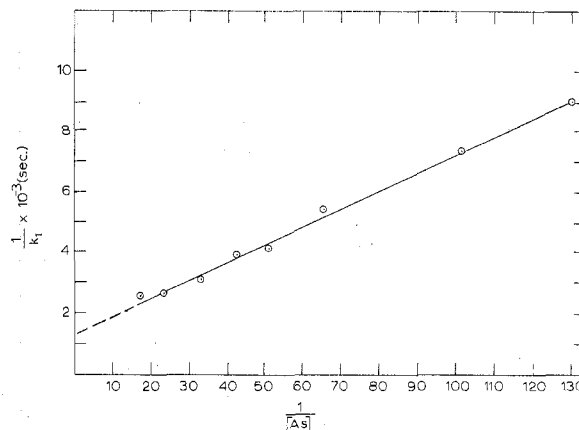


Fig. 2.—Plot of $1/k_1$ vs. $1/[\text{As(III)}]$.

tion for a reaction of the measured stoichiometry which is first order in each reactant

$$k_2 t = \frac{6.909}{3b - 2a} \log \frac{a}{3b} + \frac{6.909}{3b - 2a} \log \frac{(3b - 2x)}{(a - x)}$$

where x represents the amount of reaction at time t , b = initial concentration of Cr(VI) expressed as monomer, and a = initial concentration of As(III). The analytical rate constants so obtained showed excellent agreement with those obtained graphically.

All data were obtained in solutions of 0.2 M HOAc–0.2 M KOAc with KNO_3 added for a final ionic strength of 1.5 M .

Determination of $2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ and $\text{HCrO}_4^- \rightleftharpoons \text{H}^+ + \text{CrO}_4^{2-}$ Equilibria.—The method used was essentially that of Neuss and Rieman.¹⁵ Multiple titrations were made of the following systems, each adjusted to 1.5 M with KNO_3 : 0.01 M K_2CrO_4 with 0.01 M K_2CrO_4 –0.02 M $\text{K}_2\text{Cr}_2\text{O}_7$, 0.01 M K_2CrO_4 with 0.01 M K_2CrO_4 –0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$, and 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ –0.02 M K_2CrO_4 with 0.001 M $\text{K}_2\text{Cr}_2\text{O}_7$ –0.02 M K_2CrO_4 . The pH was measured after each addition with a Radiometer pHM4 pH meter standardized using a Beckman pH 7 buffer. The ionic strength of these solutions was somewhat variable during the course of any single titration. However, only data obtained where the ionic strength was essentially constant were used to evaluate the equilibrium constants. The validity of this technique seems justified by the linearity of Neuss–Rieman plots and the precision of the data obtained from all titrations. A more serious question concerns the method of standardization of the pH meter. As a check, the meter was standardized using dilute HCl solutions in KNO_3 solutions of varying ionic strength and the pH of the buffer measured. In the more dilute solutions serious differences were observed. However, in the solutions of interest here a difference of approximately 0.01 of a pH unit was measured. Calibration of the pH meter as a pcH meter is not above criticism since it involves a rather serious assumption concerning the response of the glass electrode in solutions of hydrogen ion concentration much different from those used for the standardization. Fortunately, the interpretation of the kinetic data is not as sensitive to substantial variation in the equilibrium constants as might be supposed. The values obtained are: $K_D = [\text{Cr}_2\text{O}_7^{2-}]/[\text{HCrO}_4^-]^2 = 137 \pm 1$ and $K_a = [\text{H}^+][\text{CrO}_4^{2-}]/[\text{HCrO}_4^-] = 1.75 \times 10^{-6}$.

Results

Kinetics of the Reduction of Cr(VI) by As(III). Low Cr(VI)–High As(III).—Figure 1 shows a portion of a typical first-order plot of the spectrophotometric data. The spectrophotometric data yield accurate first-order plots up to 90% reaction. Data were usually obtained to between two and three half-lives.

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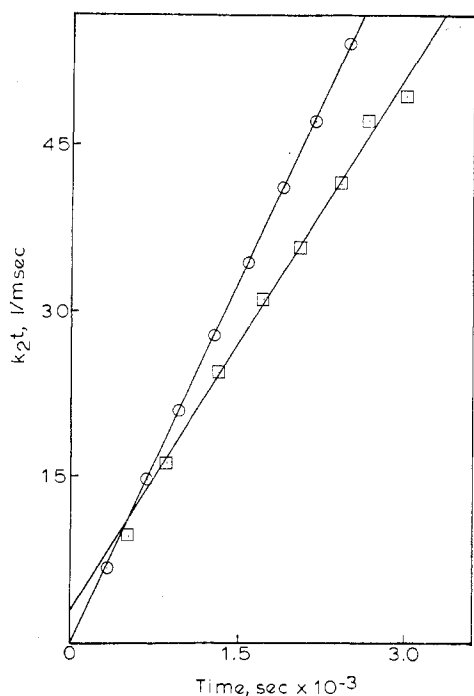


Fig. 3.—Kinetic data at high Cr(VI) plotted according to the integrated second-order rate expression (see Experimental section): O, $[\text{Cr(VI)}] = 3.632 \times 10^{-2} \text{ M}$; □, $[\text{Cr(VI)}] = 7.265 \times 10^{-2} \text{ M}$.

Table I summarizes the data for the pseudo-first-order rate constant, k_1 , as a function of the concentration of As(III). The calculated second-order rate constant is given in the last column and shows significant variation.

TABLE I
EFFECT OF As(III) AND Cr(VI) ON THE DISAPPEARANCE OF HCrO_4^-

$[\text{Cr(VI)}] \times 10^4, \text{ M}$	$[\text{As(III)}] \times 10^3, \text{ M}$	$k_1 \times 10^4, \text{ sec.}^{-1}$	$k_2, \text{ l. mole}^{-1} \text{ sec.}^{-1}$
3.106	3.940	0.601	0.0230
3.106	9.850	1.42	0.0216
3.106	31.52	3.25	0.0155
6.213	7.700	1.11	0.0216
6.213	9.850	1.35	0.0206
6.213	15.41	1.91	0.0186
6.213	19.70	2.40	0.0183
6.213	23.64	2.51	0.0159 ^a
6.213	30.90	3.22	0.0156
6.213	43.34	3.82	0.0132
6.213	59.10	3.93	0.0102
12.42	30.90	3.30	0.0170

^a Average of two determinations.

Figure 2 shows a plot of $1/k_1$ vs. $1/[\text{As(III)}]$. The linearity of this plot indicates that the rate law has the form

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{A[\text{As(III)}][\text{Cr(VI)}]}{1 + B[\text{As(III)}]}$$

Analysis of the line by the method of least squares yields the values of $1.68 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ for A and $22.4 \text{ l. mole}^{-1}$ for B .

The Kinetics of Oxidation of As(III) by Cr(VI). High Cr(VI)—Low As(III).—Figure 3 shows typical plots of the data obtained using the integrated second-

TABLE II
EFFECT OF THE VARIATION OF Cr(VI) AND As(III) ON THE DISAPPEARANCE OF Cr(VI)^a; HIGH Cr(VI)—LOW As(III)

$[\text{Cr(VI)}]_{\text{T}} \times 10^3, \text{ M}^b$	$[\text{As(III)}] \times 10^3, \text{ M}$	$k_1' \times 10^4, \text{ sec.}^{-1}$
7.2648	3.234	8.40
7.2648	3.234	8.46
7.2648	7.974	8.56
4.8432	3.234	5.84
4.8432	7.974	6.06
3.6324	1.617	4.58
3.6324	3.234	4.62
3.6324	3.234	4.62
3.6324	4.043	5.00
3.6324	4.741	4.60
3.6324	6.468	4.80
3.6324	8.085	4.58
3.6324	8.085	4.26
2.4216	3.234	3.16
2.4216	4.851	3.20
2.4216	7.974	3.06

^a Computed from the rate of disappearance of As(III) as determined titrimetrically. ^b Total Cr(VI) expressed as monomer.

order equation (see Experimental section). For the evaluation of the data, first-order plots of the same data were used and found to be linear. The data obtained are summarized in Table II, where k_1' represents the pseudo-first-order rate constant obtained for the disappearance of Cr(VI) computed from the measured first-order rate constant and the stoichiometry of the reaction. The assumption that the rate law has the same form as that in the region of low Cr(VI) leads to the empirical rate law

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{1.38 \times 10^{-2}[\text{Cr(VI)}][\text{As(III)}]}{1 + 2.62[\text{Cr(VI)}]}$$

where $[\text{Cr(VI)}]$ = the total chromium expressed as monomer. These are significantly different from values found at low Cr(VI), where HCrO_4^- is the predominant species of Cr(VI), and indicate that more extended analysis is required. Neither $\text{Cr}_2\text{O}_7^{2-}$ nor HCrO_4^- individually can account for the measured rates at all concentrations measured.

To separate the HCrO_4^- contribution to the measured rate constant, the assumption was made that the HCrO_4^- path at high Cr(VI) could be computed from the empirical rate law at low Cr(VI) by simple substitution

$$k_{\text{HCrO}_4^-} = \frac{1.68 \times 10^{-2}[\text{HCrO}_4^-]}{1 + 22.4[\text{HCrO}_4^-]}$$

The test for a $\text{Cr}_2\text{O}_7^{2-}$ path was made by calculating values for $k_2 = (k_{\text{exptl}} - k_{\text{HCrO}_4^-})/[\text{Cr}_2\text{O}_7^{2-}]$. The results of such calculations are tabulated in Table III. The concentrations were calculated using the measured values of K_D , K_a , and the measured pH of the solutions (4.60). The relative constancy of the last column establishes that the rate law expressed in terms of Cr(VI) is

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{1.68 \times 10^{-2}[\text{HCrO}_4^-][\text{As(III)}]}{1 + 22.4[\text{HCrO}_4^-]} + \frac{2.47 \times 10^{-2}[\text{Cr}_2\text{O}_7^{2-}][\text{As(III)}]}{1 + 22.4[\text{HCrO}_4^-]}$$

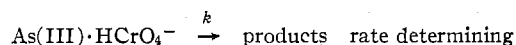
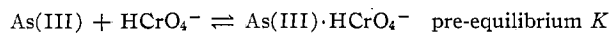
TABLE III
 DETERMINATION OF $\text{Cr}_2\text{O}_7^{2-}$ CONTRIBUTION

$[\text{Cr(VI)}]_{\text{T}} \times 10^2, M^a$	$[\text{HCrO}_4^-] \times 10^2, M^b$	$[\text{Cr}_2\text{O}_7^{2-}] \times 10^2, M^b$	$k_{\text{(calcd.)}}, \text{sec.}^{-1}$	$k_{\text{exptl.}}, \text{sec.}^{-1}$	$k_2, \text{l. mole}^{-1} \text{sec.}^{-1}$
2.422	7.64	8.01	1.10×10^{-4}	3.14×10^{-4}	2.54×10^{-2}
3.624	9.70	12.9	1.34×10^{-4}	4.64×10^{-4}	2.56×10^{-2}
4.843	11.5	18.0	1.52×10^{-4}	4.94×10^{-4}	2.44×10^{-2}
7.265	14.4	28.6	1.83×10^{-4}	8.48×10^{-4}	2.32×10^{-2}
					Av. 2.47×10^{-2}

^a Total Cr(VI) expressed as monomer. ^b Computed from $K_{\text{D}} = 137$, $K_{\text{a}} = 1.75 \times 10^{-4}$, and pH 4.60.

Discussion

The rate law found at low Cr(VI) has a form consistent with the following mechanism



For solutions where the As(III) is high relative to the HCrO_4^- and substantially constant throughout a given run, the rate law derived from the proposed mechanism is, after taking cognizance of the stoichiometry

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{2kK[\text{As(III)}][\text{HCrO}_4^-]}{1 + K[\text{As(III)}]}$$

The experimental parameters are $A = 2kK$ and $B = K$ with the values of k and K equal to $3.76 \times 10^{-4} \text{ sec.}^{-1}$ and $22.4 \text{ l. mole}^{-1}$, respectively.

Essentially the same mechanism is assumed to be operating for the $\text{Cr}_2\text{O}_7^{2-}$ path but the data do not seem to justify an attempt to evaluate the equilibrium constant for a complex of As(III) with $\text{Cr}_2\text{O}_7^{2-}$. This suggests that K for $\text{As(III)} \cdot \text{Cr}_2\text{O}_7^{2-}$ is significantly smaller than that for $\text{As(III)} \cdot \text{HCrO}_4^-$. The value of k_2 of $2.47 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ for the $\text{Cr}_2\text{O}_7^{2-}$ path compared with $2kK$ for HCrO_4^- of $1.68 \times 10^{-2} \text{ l.}$

$\text{mole}^{-1} \text{ sec.}^{-1}$ indicates that $\text{Cr}_2\text{O}_7^{2-}$ is more effective as an oxidant.

The data reported and the mechanism proposed permit no conclusions concerning the products formed in the rate-determining step. Westheimer¹⁰ has concluded that in acid solution, Cr(IV) and As(V) are the products. The stoichiometry of the reaction between As(III) and Cr(VI) in the presence of Fe(CN)_6^{4-} offers some support for this point of view for the system reported here.² Thus, the oxidation could occur by oxygen transfer and no production of As(IV) would be required. The oxidation of U(IV) to U(VI) with Cr(VI) has been shown to occur with significant oxygen transfer.¹⁶

The term designated here as $\text{Cr}_2\text{O}_7^{2-}$ might also be regarded as a path involving $[\text{HCrO}_4^-]^2$ where HCrO_4^- is serving as a catalyst as suggested by Edwards.¹¹ While the nature of the acid catalysis is not yet clear, such an interpretation would require that HCrO_4^- be a more effective catalyst than acetic acid, which seems unlikely.

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