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Final Report

Title: The Oxidation of Arsenic (III) and Antimony (III)

Principal Investigator: John G. Mason
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, Virginia 24061

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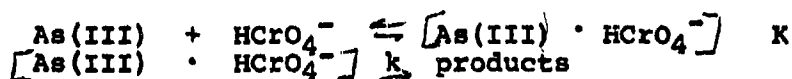
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Abstract

The oxidation of As(III) by Cr(VI) has been studied in detail for a variety of systems. In acetic acid-acetate buffers and aqueous acetic acid the rate law obtained is of the general form:

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(k_0 + k_1[\text{HOAc}])K[\text{As(III)}][\text{Cr(VI)}]}{1 + K[\text{As(III)}]}$$

Numerical values of K and k_0 are the same for both systems, but the coefficient for the acetic acid catalyzed system is different. The mechanism suggested by the rate law is



The decomposition of the mixed anhydride is acid-catalyzed.

In dilute perchloric acid solution, the rate law found was

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(k_0 + k_1[\text{H}^+] + k_2[\text{H}^+]^2)K[\text{As(III)}][\text{Cr(VI)}]}{1 + K[\text{As(III)}]}$$

The interpretation here is essentially the same since k_0 and K have approximately the same values as before. The two term hydrogen ion dependence is taken to be the protonation of the mixed anhydride.

In hydrogen phosphate (HPO_4^{2-}) - dihydrogen phosphate (H_2PO_4^-) buffers, a different mechanism is operative. The reaction appears to be simple first order in As(III) and first order in Cr(VI). The Cr(VI) complexes with the buffer components and analysis of the data shows the most significant activated complex to have the composition $(\text{HCrO}_4^- \cdot \text{HPO}_4^{2-})$ or $(\text{CrO}_4^{2-} \cdot \text{H}_2\text{PO}_4^-)$. The

most significant solution complex was found to be $\text{HCrO}_4^- + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HCrPO}_7^{3-} + \text{H}_2\text{O}$. No evidence for As(III)-Cr(VI) association was found in NH_4NO_3 - KNO_3 media.

The primary reaction between As(III) and Cr(VI) was found to induce the oxidation of tartaric acid producing a catalytic rate enhancement. Detailed kinetic studies showed that the catalysis was pH dependent in acetic acid-acetate buffers in contrast to the primary reaction and that the most reasonable reactant was the monoanion of tartaric acid. Tartaric acid was found incorporated in the reduction product of Cr(VI). Essentially the same spectrum was produced by heating Cr(III) with tartaric acid as by reduction of Cr(VI) in tartrate medium. The kinetics thus far have been too complex for simple interpretation. Oxalate ion also exhibited a "catalytic" effect on the disappearance of Cr(VI), presumably by induced oxidation.

The reaction of Cr(VI) with antimony tartrate was much too rapid to measure. However, essentially the same observations with respect to both the stoichiometry and to the nature of the Cr(III) product were made.

FINAL REPORT

Personnel:

For the period covered, the research personnel consisted of John G. Mason, Principal Investigator, A. D. Kowalak, and P. T. Chang, Research Assistants, and R. M. Tuggle, part-time technician summer 1965 and academic year 1966. Dr. Kowalak terminated in June 1965 having completed the doctorate. Mr. Chang was terminated without degree, December, 1967.

Scope and Objectives:

The original objective was to investigate the kinetics and mechanisms of the oxidation of arsenic(III) and antimony(III) by chromium(VI) and cerium(IV). Further, it was hoped to investigate the catalysis of these reactions with a view to (1) clarification of the mechanisms and (2) possible analytical applications. Work was initiated with the detailed study of the Cr(VI)-As(III) in acetic acid-acetate buffer solutions. Detailed studies were made in acetic acid-acetate buffer solutions, acetic acid solutions, dilute acid solutions, and dihydrogen phosphate-mono-hydrogen phosphate buffer systems. This work has been prepared for submission and copies of the two manuscripts so prepared are appended to this report as attachments. The studies of utilizing cerium(IV) were incorporated into the Ph.D. program of Mr. Ping-Tzu Chang. Unfortunately, only a few measurements were performed due to the early termination of Mr. Chang.

Accomplishments:

The work accomplished will be summarized according to the reactions studied.

The Chromium(VI)-Arsenic(III) Reaction.

This reaction was studied in considerable detail under a variety of conditions. Since the initial work has been published (J. G. Mason and A. D. Kowalak, Inorg. Chem. 1964) and the rest is incorporated in the attached manuscripts, only a brief summary will be made here.

The primary reaction of Cr(VI) with As(III) was found to have the expected stoichiometry in outgassed solutions



In acetic acid-acetate buffers, the rate of the disappearance of Cr(VI) was found to be essentially pH independent and to obey the following rate law

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(k_o + k_{\text{HOAc}} [\text{HOAc}]) K [\text{As(III)}] [\text{Cr(VI)}]}{1 + K [\text{As(III)}]}.$$

In solutions of high Cr(VI), where the reactions were studied titrimetrically by following the As(III) the following rate law was obtained.

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(k_o + k_{\text{HOAc}} [\text{HOAc}]) K [\text{As(III)}] [\text{Cr(VI)}]}{1 + K [\text{As(III)}]} + (k_o' + k_{\text{HOAc}}' [\text{HOAc}]) [\text{As(III)}] [\text{Cr}_2\text{O}_7^{2-}]$$

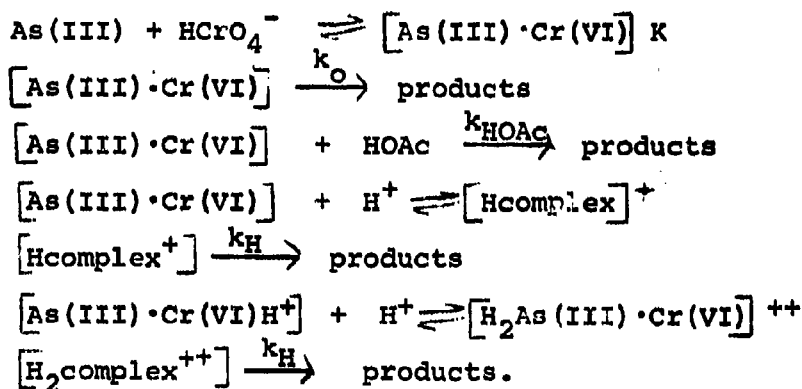
For solutions of dilute acetic acid

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(k_o + k_{\text{HOAc}} [\text{HOAc}]) K [\text{As(III)}] [\text{Cr(VI)}]}{1 + K [\text{As(III)}]}$$

For solutions containing low concentrations of perchloric acid

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{(k_o + k_H [\text{H}^+] + k [\text{H}^+]^2) K [\text{As(III)}] [\text{Cr(VI)}]}{1 + K [\text{As(III)}]}$$

The mechanism proposed to rationalize these results is in essence the following:



Values of K found in all acid media were essentially the same, approximately 17. The only significant anomaly lies in the fact that k (which is also constant in acid solution) is not numerically equal to the value of k_o in NH₄NO₃ solutions. However, no retardation by As(III) was observed so that the same mechanism is not operative. It appears that if a sufficiently strong acid is present, the equilibrium reaction is not rate determining. In the absence of an acid of sufficient strength, the rate determining step is the formation of the

activated complex without the pre-equilibrium step. The catalytic coefficient for acetic acid catalysis likewise is numerically different and a function of the acetic acid concentration and/or hydrogen ion. Contrary to published reports we observed spectral changes in the acetic acid solutions which suggest that Cr(VI) and acetic acid complexation occurs which could account for the more profound effect of acetic acid in the absence of acetate. There is also the possibility that in the acetate-acetic acid solutions homoconjugation occurs to produce the species $\text{H}(\text{OAc})_2^-$ and alter the catalytic properties of the solutions.

The Cr(VI)-As(III) Reaction in H_2PO_4^- - $\text{HPO}_4^{=}$ Buffers.

The reaction was found to proceed via a very complex path. The principal results found are these:

(1) Acid chromate (HCrO_4^-) forms a complex with H_2PO_4^- which is kinetically active. Spectral evidence was in accord with the kinetics.

(2) The most kinetically active form however, has the composition $\text{HCrO}_4^- \cdot \text{HPO}_4^{=}$ or $\text{CrO}_4^{=} \cdot \text{H}_2\text{PO}_4^-$. No physical evidence was found for its existence in finite quantities.

(3) Serious salt effects were observed and detailed corrections were attempted.

(4) No retardation at high As(III) was observed; the reaction remaining second order without complications due to As(III).

(5) The final form of the rate law is

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{\{k_1[\text{HCrO}_4^-][\text{H}_2\text{PO}_4^-] + k_2[\text{CrO}_4^{=2}][\text{H}_2\text{PO}_4^{=2}]\}[\text{As(III)}]}{1 + K[\text{H}_2\text{PO}_4^-][\text{HCrO}_4^-]}$$

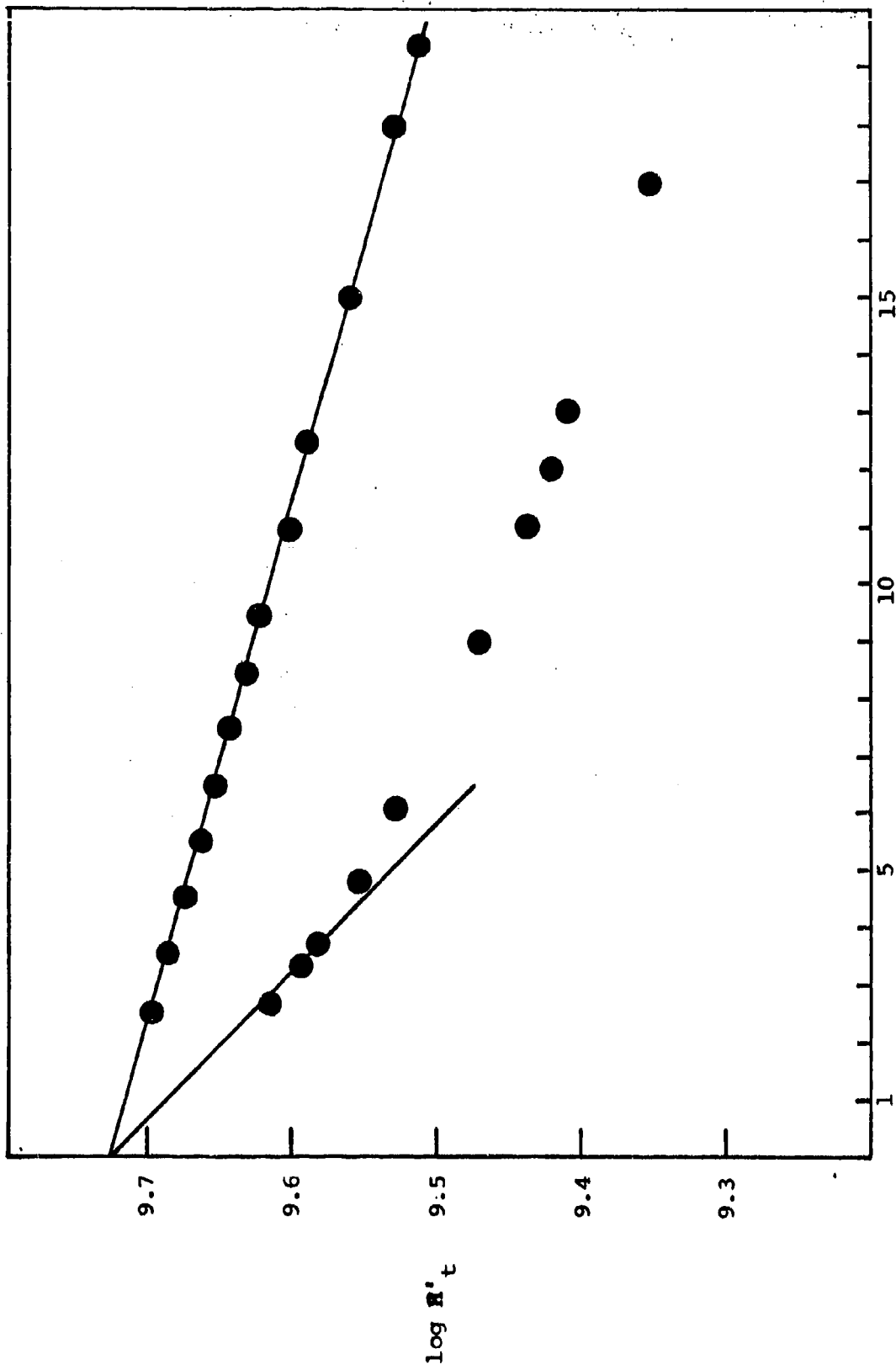
In no case was evidence found for the presence of As(IV).

The Cr(VI)-As(III) Reaction--Kinetic Anomalies

In attempts to reproduce independently our previous results on the Cr(VI)-As(III) reaction anomalous results were obtained when low As(III) concentrations were tried. These anomalies were reflected in the $\log (A_t - A_\infty)$ vs. time plots which were composed of two linear segments. In most cases at long times the rate constant evaluated from the second segment was identical with the previously established value. However the initial portion was much faster than the normal or expected rate. A detailed investigation was instituted to discover the source of this anomaly. Ultimately it was discovered that the anomalous results were due to the stirring rate while the solutions were being mixed. Extremely efficient mixing produced normal behavior while a somewhat slower degree of mixing produced a perfectly homogeneous system but the kinetic behavior was different. These differences are illustrated in Fig. 1.

For the evaluation of the data several logical restrictions were placed upon the data selected as follows:

- (1) the zero time value of the absorbance should correspond to the initial absorbance calculated from the Beer's Law plot for the initial Cr(VI) concentration.



$t \times 10^{-2}$ sec

FIGURE 1

(2) the reaction should attain the appropriate steady state at long times.

These restrictions were placed upon the data to insure that the reaction mixture was truly homogeneous after mixing and only the method of initial addition produced the effect and that conditions were such that the true steady state region was achieved.

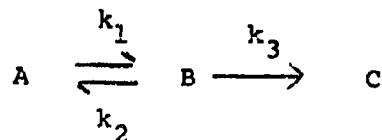
In order to analyze the selected data, the first step was to evaluate the initial rate constant for the disappearance of Cr(VI). These data are tabulated in Table 1. The initial rate of disappearance of Cr(VI) in the cases tried showed values for the initial rate of $7.9 \times 10^{-4} \text{ sec}^{-1}$ or lower. For comparison the steady state rate constants are $k = 7.5 \times 10^{-4}$ and $kK[\text{As(III)}] = 3.36 \times 10^{-4}$. If the interpretation is made that complex formation occurs without oxidation, i.e., complex formation is a non-productive path, then the product $kK[\text{As(III)}]$ is the pseudo first order rate constant for the formation of the activated complex. The initial rates are considerably higher than this value and remarkably close to the estimate of the decomposition of the complex. This suggests that the technique of mixing leads to an overproduction of the complex, that is, a concentration in excess of the steady state. Using this assumption it was possible to analyze the data according to the mathematical procedure of Alberty and Miller [J. Chem. Phys., 26, 1231 (1957)], who derived the detailed concentration

Table I
 Initial Rates
 $[\text{As(III)}] = 2 \times 10^{-2}$

$[\text{HCrO}_4^-] \times 10^4$	Initial $k \times 10^4$
1.04	7.4
1.04	8.3
1.55	6.2
2.33	8.3
3.1	5.2
3.1	7.6
6.2	4.49
6.2	5.52

Ionic strength 1.5M adjusted with KNO_3
 $T = 25^\circ\text{C}$. 0.2M KOAc - 0.2M HOAc Buffer.

time profile for the mechanism



In final form their results are

$$A = xe^{m_1 t} - ye^{m_2 t}$$

$$B = \frac{(m_1 + k_1)xe^{m_1 t}}{k_2} - \frac{(m_2 + k_1)ye^{m_2 t}}{k_2}$$

$$\text{where } x = \frac{k_2 B_0 - (m_1 + k_1)A_0}{m_1 - m_2}$$

$$y = \frac{k_2 B_0 - (m_1 + k_1)A_0}{m_1 - m_2}$$

$$m_1 = \frac{1}{2} \left[-(k_1 + k_2 + k_3) - \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right]$$

$$m_2 = \frac{1}{2} \left[-(k_1 + k_2 + k_3) + \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right]$$

It is necessary to know A_0 and B_0 in order to calculate the concentration-time curve. Further all previous work indicated that the complex and uncomplexed Cr(VI) had essentially the same absorption spectrum. Therefore to analyze the data required that $A + B$ at time t be known. To check on the assumption that what was being measured spectrophotometrically was in fact total Cr(VI), atypical runs for the same conditions which produced curvature were analyzed by a different method. Individual samples were taken during the run, quenched with

base, and quickly analyzed for $\text{CrO}_4^{=}$. The $[\text{Cr(VI)}]$ -time curve obtained in this way is different in no essential way from that obtained by the normal method.

Values of A_0 and B_0 were made on the assumption that only B_0 lead to product, hence the initial rate was a measure of B_0 ; A_0 was then calculated by material balance. On this basis the values of k_1 , k_2 , and k_3 were determined.

$$k_1 = 7.4 \times 10^{-4} \text{ sec}^{-1}$$

$$k_2 = 9.8 \times 10^{-4} \text{ sec}^{-1}$$

$$k_3 = 7.5 \times 10^{-4} \text{ sec}^{-1}$$

The agreement between calculated and measured absorbances was within 10%. The reaction is quite complex involving acid catalysis terms so that detailed analysis is not possible. However, these data support the argument that oxidation occurs via the complex rather than the direct oxidation.

The Cr(VI)-Sb(III) Reaction.

Under all conditions tried comparable to those which were used for the analogous reaction with arsenic(III), the reaction rate was found to be too rapid for convenient study. However, the solubility of Sb_2O_3 was so low that attempts were made to improve the solubility by complexation. The complexing agent selected was tartaric acid. Initial investigations of the stoichiometry of the Sb(III)-Cr(VI) reaction in tartrate containing solutions indicated a dependence upon tartrate suggesting the induced oxidation of tartaric acid had occurred. This was later confirmed and will be discussed in the following section.

Since the reaction of Cr(VI) with As(III) had been thoroughly studied it was decided to study the effect of tartrate on the Cr(VI)-As(III) reaction.

The Cr(VI)-As(III) Reaction in the Presence of Tartaric Acid.

A. Stoichiometry. The stoichiometry was studied under essentially the same conditions as the kinetic measurements. An excess of As(III) was used and the stoichiometry studied as a function of the tartaric acid. The reaction was allowed to reach completion by standing for three days. The buffers used were 0.2M KOAc-0.2M HOAc adjusted to 1.5M ionic strength with KNO_3 . The excess of As(III) was determined by titration with standard I_2 . The initial attempts produced rather curious results: (1) the initial color of the solution was red-purple, adjustment

of the pH to 10 followed by titration with I_2 showed a progressive change in color as the titration proceeded the expected green of the Cr(III) product in this solution being formed.

(2) End point location was found to be impossible because a slow reaction consuming I_2 was found to be proceeding in the vicinity of a rational end point. Titration at ice-temperatures did not eliminate the progressive fading of the end point. (3) The addition of excess I_2 followed by back titration with standard As(III), produced as a total slightly more equivalents of As(III) than were originally present.

These results suggested that an oxidation product of tartaric acid was either coordinated with Cr(III) and slowly released via alkaline hydrolysis where it was further oxidized by I_2 or was present and slowly oxidized by I_2 . Pozhidaev and Gorbachev [Russ. J. Phys. Chem. 1597 (1964)] studied the oxidation products of tartaric acid by Fenton's reagent. One of the products identified was dihydroxy-maleic acid. Lundblad (Arhiv. Kemi. Mineral. Geol. 25A, 1947; C. A. 42; 7249.) has reported upon the chemistry of dihydroxy-maleic acid and I_2 . Iodine oxidizes dihydroxymaleic acid to dihydroxytartaric acid among other things. Further, dihydroxymaleic acid is rather unstable and rapidly loses one carboxyl group.

A modified version of the original procedure was then adopted. After the completion of the Cr(VI)-As(III) reaction in tartaric acid, a sample was treated with sodium borate and heated to boiling. The solution was cooled immediately to about

5 C⁰ and titrated with I₂. End points were sharp and stoichiometries were reproducible. It is these results which are tabulated in Tables II and III.

These results clearly indicate the presence of an induced oxidation of tartaric acid. The fact that as the tartaric acid is increased at fixed As(III), the $\frac{\text{As(III)}}{\text{Cr(VI)}}$ ratio becomes constant suggests that the reaction is not a typical chain reaction. The decrease is in the direction expected. The $\frac{\text{As(III)}}{\text{Cr(VI)}}$ ratio at high tartaric acid and low As(III) leads to different results which may be due to experimental difficulties in accurately determining the unreacted As(III) or perhaps incomplete reaction.

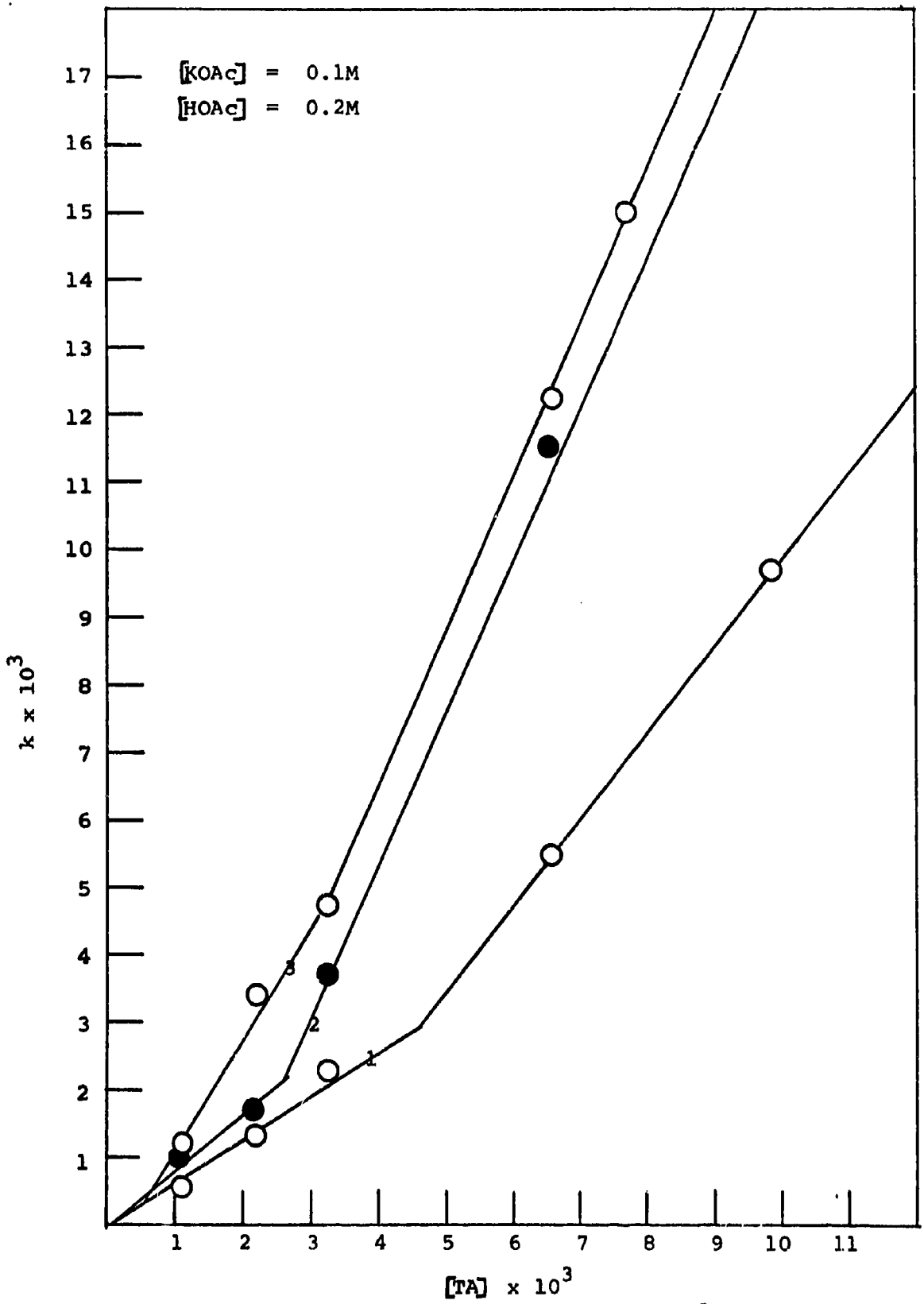
The significance of the stoichiometric analysis is simply that while the reaction is quite complex and accelerated by tartrate it does not appear to be a chain reaction.

B. Kinetics of the Cr(VI)-As(III) Reaction in the Presence of Tartrate.

Some features of the kinetics are demonstrated in Figs. 2, 3, 4, and 5 and Tables (IV), (V) and (VI). The general characteristics of these data in summary are (1) the catalysis is markedly pH dependent paralleling the concentration of mono acid tartrate in a general way;

(2) Plots of rates of the reaction as a function of tartaric acid at fixed As(III) all show two slopes, indicating quite complex behavior.

3) At fixed tartaric acid with variable As(III), all



Curve 1; $[As] = 3.3 \times 10^{-3}$; 2; $[As] = 6 \times 10^{-3}$ 3; $[As] = 9.9 \times 10^{-3}$

FIGURE 2

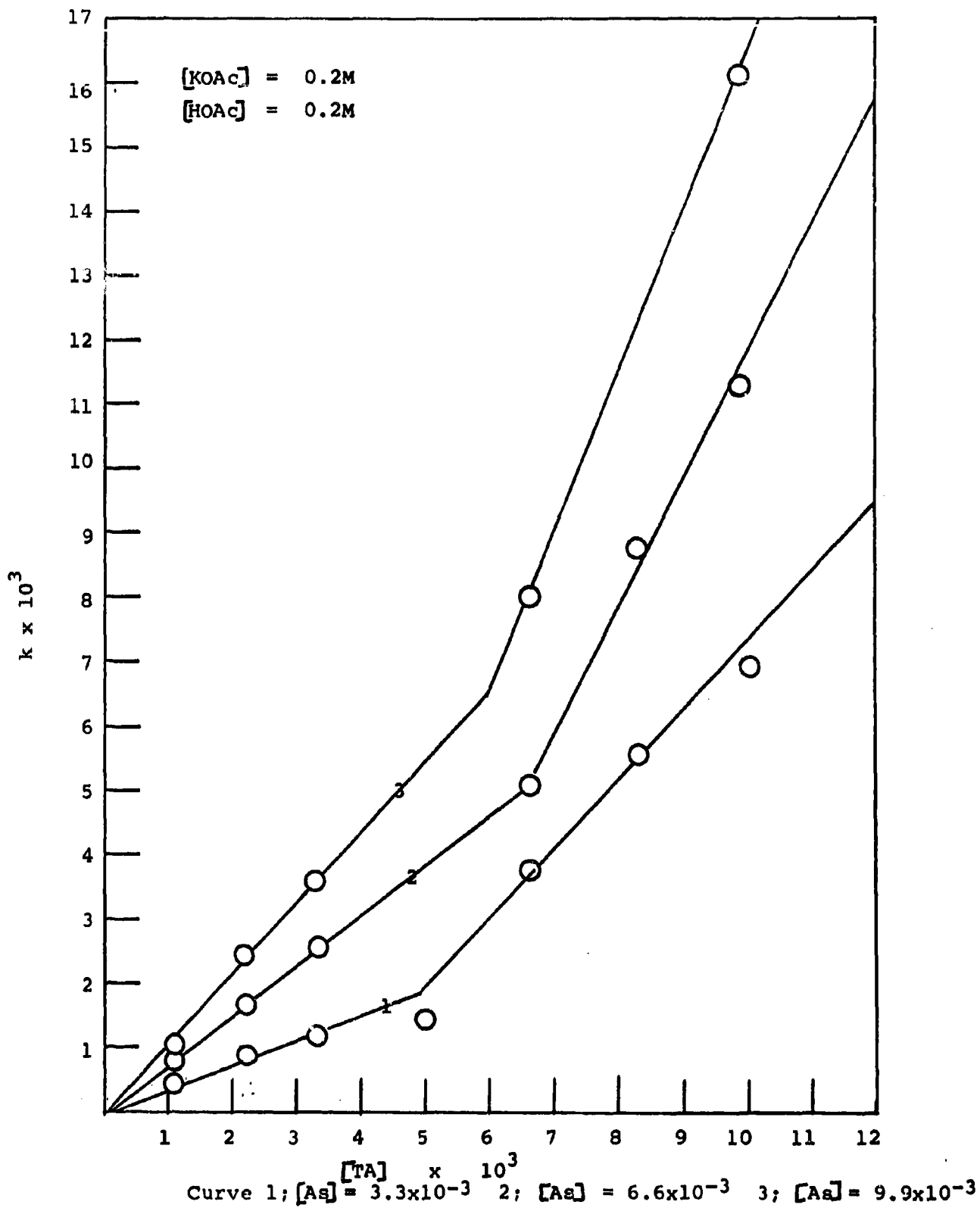
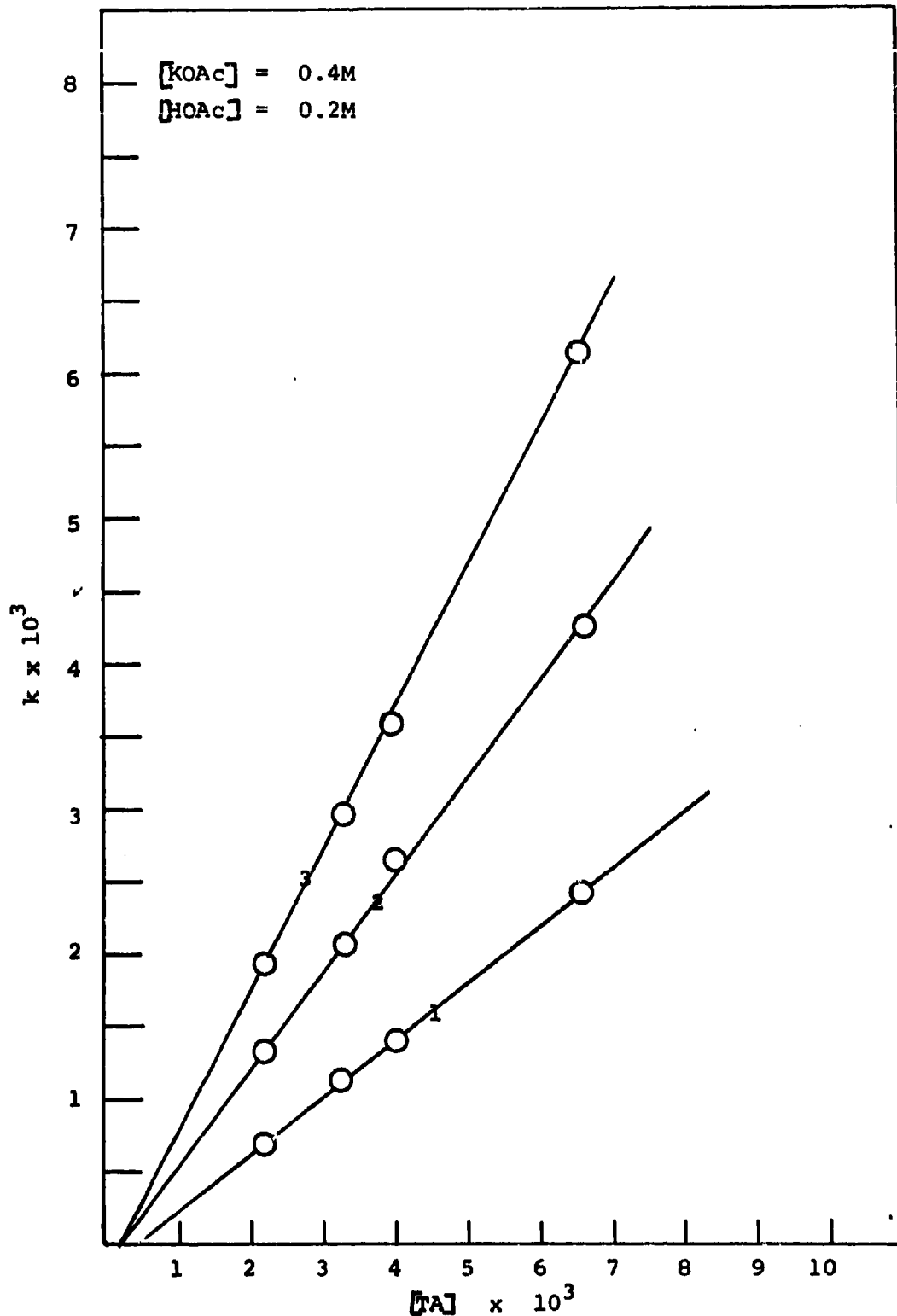


FIGURE 3



Curve 1; $[As] = 3.3 \times 10^{-3}$ 2; $[As] = 6.6 \times 10^{-3}$ 3; $[As] = 9.9 \times 10^{-3}$

FIGURE 4

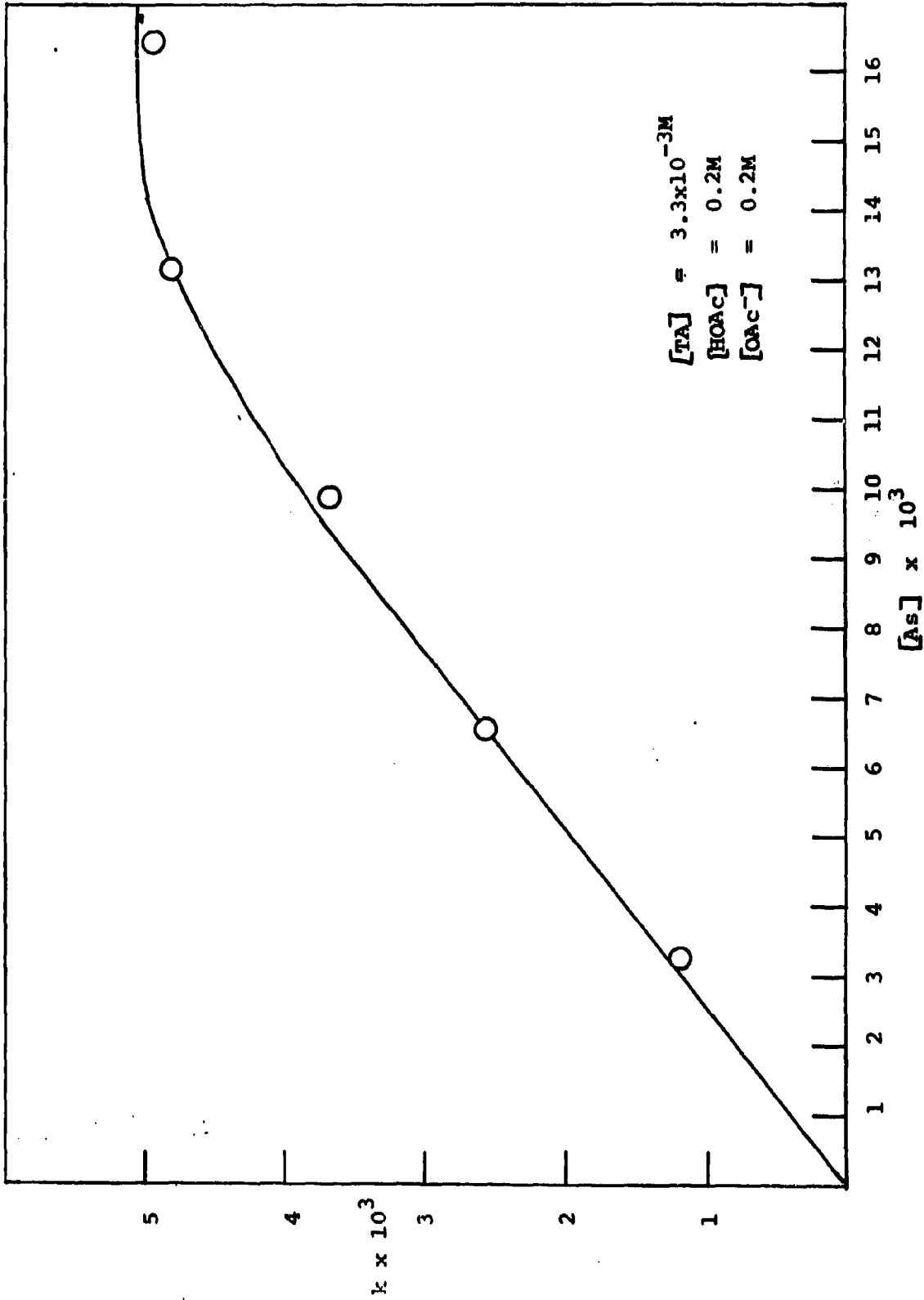


FIGURE 5

Table II

As/Cr Ratio as a Function of Tartaric Acid
(0.2M KOAc, 0.2M HOAc, 1.3M KNO₃)

Initial [As(III)] = $5 \times 10^{-3} \text{M}$
Initial [Cr(VI)] = $2 \times 10^{-3} \text{M}$

[Tartaric Acid]	$\frac{[\text{As(III)}]}{[\text{Cr(VI)}]}$
$1 \times 10^{-3} \text{M}$	0.71
$2 \times 10^{-3} \text{M}$	0.43
$5 \times 10^{-3} \text{M}$	0.41
$10 \times 10^{-3} \text{M}$	0.42
$20 \times 10^{-3} \text{M}$	0.43

Table III

As/Cr Ratio at Fixed Tartaric Acid
(0.2M KOAc, 0.2M HOAc, 1.3M KNO₃)

Initial [Cr(VI)] = $2 \times 10^{-3} \text{M}$
Initial [Tartaric Acid] = $10 \times 10^{-3} \text{M}$

[As(III)]	$\frac{[\text{As(III)}]}{[\text{Cr(VI)}]}$
$1 \times 10^{-3} \text{M}$	0.342
$2 \times 10^{-3} \text{M}$	0.39
$4 \times 10^{-3} \text{M}$	0.39
$5 \times 10^{-3} \text{M}$	0.42
$6 \times 10^{-3} \text{M}$	0.425
$7 \times 10^{-3} \text{M}$	0.475
$10 \times 10^{-3} \text{M}$	0.475

Table IV

Effect of Tartaric Acid on Cr(VI) Disappearance
in 0.1M KOAc - 0.2M HOAc Buffers.

$[\text{As(III)}] \times 10^3$	$[\text{TA}] \times 10^3$	$k \times 10^3$	pH
3.3	1.1	.594	4.315
3.3	2.2	1.32	4.305
3.3	3.3	2.29	4.300
3.3	6	4.35	4.297
	6.6	5.52	4.200
	9.9	9.71	4.155
	13.2	16.81	4.115
	16.5	23.8	4.11
6.6	1.1	1.02	4.315
6.6	2.2	2.67	4.255
6.6	3.3	3.74	4.260
6.6	6.6	11.6	4.215
6.6	9.9	19.2	4.125
9.9	1.1	1.18	4.310
9.9	2.2	3.45	4.276
9.9	3.3	4.71	4.225
9.9	6.6	12.25	4.207
9.9	7.7	15.0	4.262
9.9	9.9	25.1	4.150
9.9	9.9	23.6	4.150

$T = 25^\circ\text{C}$, $\mu = 1.5$ adjusted with KNO_3 .

Table V

Effect of Tartaric Acid on Cr(VI) Disappearance
in 0.2M KOAc-0.2M HOAc Buffers

$[\text{As(III)}] \times 10^3$	$[\text{TA}] \times 10^3$	$k \times 10^4$	pH
2.0	1	3.06	4.619
2.0	1	3.27	4.615
2.0	2	6.49	4.615
3.3	1.1	4.61	4.615
3.3	2.2	9.21	4.572
3.3	3.3	11.7	4.65
3.3	5.0	14.0	4.610
3.3	6.6	37.8	4.572
3.3	8.3	55.9	4.555
3.3	8.3	55.5	4.540
3.3	10.0	69.8	
3.3	12.0	95.2	4.552
3.3	13.2	105	4.473
3.3	13.2	103	4.60
3.3	16.5	149	4.440
3.3	16.5	149	4.668
6.6	1.1	7.69	4.620
6.6	2.2	16.8	4.625
6.6	3.3	25.6	4.630
6.6	6.6	50.7	4.579
6.6	8.3	87.5	4.532
6.6	9.9	113	4.658 (a)
	13.2	172	4.470
	13.2	165	4.645 (a)
9.9	1.1	10.5	4.538
9.9	2.2	24.3	4.525
9.9	3.3	36.6	4.618
9.9	3.3	35.6	4.522
9.9	6.6	80.7	4.495
9.9	9.9	162.0	4.435
13.2	3.3	48.4	4.612
16.5	3.3	49.4	4.610

a) pH adjusted prior to run.

T = 25°C, μ = 1.5 adjusted with KNO_3 .

Table VI

Effect of Tartaric Acid on Cr(VI) Disappearance
in 0.4M KOAc-0.2M HOAc Buffers

$[\text{As(III)}] \times 10^3$	$[\text{TA}] \times 10^3$	$k \times 10^4$	pH
2.0	2.2	4.51	5.069
2.0	3.3	7.55	5.057
2.0	4.0	9.21	5.039
2.0	6.0	16.4	5.040
3.3	2.2	7.02	5.060
	3.3	11.2	5.072
	4.0	14.0	5.081
	6.6	24.3	5.030
4.0	2.2	8.57	5.069
	3.3	14.0	
	4.0	16.9	5.048
	6.6	29.7	5.022
6.6	2.2	13.4	5.058
	3.3	20.5	5.055
	4.0	26.5	5.033
	6.6	42.6	5.022
9.9	2.2	19.4	5.082
	3.3	29.6	5.023
	4.0	35.9	5.078
	6.6	61.5	5.020

$T = 25^\circ\text{C}$, $\mu = 1.5$ adjusted with KNO_3 .

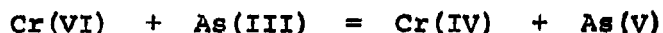
reactions studied show a "saturation effect" (rate becomes independent of As(III) at high As(III) concentrations). Plots of $\frac{1}{k}$ vs $\frac{1}{[\text{As(III)}]}$ are linear but the slopes and intercepts are complex functions of both the tartaric acid concentration and pH.

4) There is definitive evidence that some tartaric acid is consumed via coordination to the Cr(III) product. Due to the extreme inertness of Cr(III) with respect to substitution reactions it seems clear that the tartrate is incorporated in the Cr(V) or Cr(IV) stages. Similar incorporation reactions have been demonstrated by Beck and Bardi [Acta Chim. Hung., 29, 283 (1961)] and Rikens and Reilley [Anal. Chem., 34, 1707 (1962)].

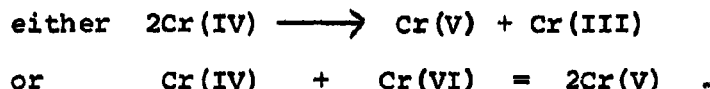
Many quantitative correlations have been attempted but without significant success. A major source of the difficulty is the appearance of two slopes. Such curves have been obtained in other systems containing complexing agents, notably the work of Margerum on EDTA complexes where some EDTA reacts with metal ions present in the system and produces a curve very similar to a titration curve. Our results however do not appear to be explicable on that basis. Efforts to establish association between As(III) and tartaric acid were not successful. In most instances, the best fit intercept at zero rate for the tartaric acid plots was not zero but corresponded to approximately $3 \times 10^{-4} \text{M}$ tartrate. This occurs in virtually all systems and seems definitely related to the Cr(III) expected at the end, namely $1.2 \times 10^{-4} \text{M}$.

The other inflection point is much harder to define but appears to be related to the As(III). A reasonable, but not quantitative, mechanism for the effect of tartaric acid can be written following Beck and Bardi.

The primary reaction produces Cr(IV) via the overall reaction



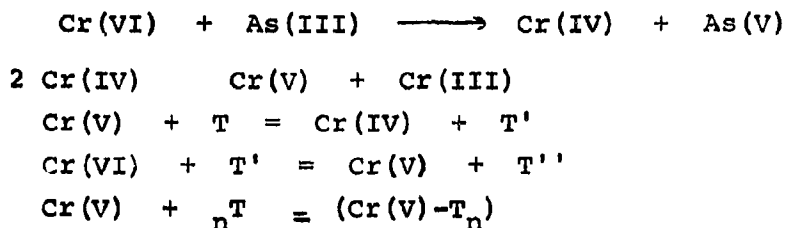
The fate of the Cr(IV) is not normally detectable but the following reactions may account for its disappearance:



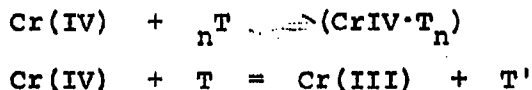
Of these the first with a calculated K of approximately 47 is the more likely according to Wetton and Higginson [J. Chem. Soc., 5890 (1965)]. In the presence of an oxidizable substrate Cr(V) may oxidize either As(III) or the substrate, or Cr(IV) may oxidize the substrate. The oxidation of tartaric acid by either Cr(IV) or Cr(VI) would produce organic products capable of further oxidation. At high tartrate Cr(IV) may be complexed by the tartrate leading to incorporation rather than destruction. It is possible that Cr(IV) might oxidize rather than coordinate and that this accounts for the rate enhancement at low tartrate. However it is clear that coordination of Cr(V) without any oxidation what so ever would not alter the stoichiometry if all Cr(V) was reduced by As(III) and indeed the rate of disappearance

of Cr(VI) would be unaffected.

These observations lead to a mechanism of this form:



At high tartrate



In either case Cr(VI) is reduced by oxidizable organic materials produced by the induced oxidation of tartaric acid.

Since no detailed study of Cr(III)-tartaric acid complexes seems to be available it was impossible to establish the nature of the complex formed or whether a variety of complexes was formed as the tartaric acid increased.

Experimentally, not enough tartrate is either incorporated or oxidized to alter the effective concentration of tartrate during one run. Further, product analysis of the actual organic species produced by the induced reaction could not be achieved successfully because of the very low concentrations.

Work is now in progress on the effect of oxalate with these initial results: oxalate incorporates and catalyzes the Cr(VI)-As(III) without alteration of the stoichiometry.

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13. ABSTRACT

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 $[HPO_4^{2-} \cdot HCrO_4^- \cdot As(III)]$.