# Chromium(III)-catalysed Cerium(IV) Oxidation of Arsenic(III) in Aqueous Sulphuric Acid

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The chromium(III)-catalysed cerium(IV) oxidation of arsenic(III) studied in aqueous sulphuric acid follows the rate law (i) where the right-hand side represents the catalysed path. In equation (i), the

$$-\frac{d[\mathrm{Ce^{IV}}]}{dt} - k_u[\mathrm{As^{III}}][\mathrm{Ce^{IV}}] = \frac{2k_a k_c \beta_4 K_{\mathrm{IP}}[\mathrm{Ce^{IV}}][\mathrm{Cr^{III}}][\mathrm{As^{III}}][\mathrm{SO_4}^{2-}]^3[\mathrm{HSO_4}^-]^2[\mathrm{H^+}]^2}{(1 + \beta_1[\mathrm{SO_4}^{2-}] + \beta_2[\mathrm{SO_4}^{2-}]^2 + \beta_3[\mathrm{SO_{42}})]^2[\mathrm{HSO_4}^-] + \beta_4[\mathrm{SO_4}^{2-}]^2[\mathrm{HSO_4}^-]^2[\mathrm{H^+}])(1 + K_{\mathrm{IP}}[\mathrm{SO_4}^{2-}])} \times \left\{\frac{k_b K_5[\mathrm{Ce^{III}}][\mathrm{SO_4}^{2-}]^3}{(1 + K_5[\mathrm{SO_4}^{2-}]^3)} + k_c[\mathrm{As^{III}}][\mathrm{H^+}]\right\}^{-1} \quad \text{(i)}$$

β's are the stability constants of the different cerium(IV) sulphate complexes and $K_{\mathrm{IP}}$ and $K_5$ are the equilibrium constants of the species $\mathrm{Cr^{3+}SO_4^{2-}}$ and $\mathrm{Ce(SO_4)_3^{3-}}$ respectively. A chromium(IV) species is involved in the catalysed path. Increasing sulphuric acid concentrations effect rate increases of both the uncatalysed and catalysed paths and the active oxidant is understood to be the species $\mathrm{H_3Ce(SO_4)_4^-}$.

The cerium(IV)–arsenic(III) reaction was first studied in aqueous sulphuric acid[1,2] but the results of different workers did not agree. The reaction was proposed to be both second order[1] and third order.[2] However, a more recent study of the reaction in perchloric acid medium found it to be second order and to proceed *via* detectable cerium(IV)–arsenic(III) complexes.[3] In sulphuric acid medium, several sulphate complexes of cerium(IV) form[4] but their role has not received attention so far. Thus, the reaction rate increases with sulphuric acid concentration and this effect has not been understood. During the course of this study of the chromium(III) catalysis of the cerium(IV)–arsenic(III) reaction, we have also made a study of the effect of increasing sulphuric acid concentration on the uncatalysed reaction and the results are discussed here.

A number of catalysts such as iodine,[5] osmium(VIII),[6] and ruthenium(IV)[7] have been used for the cerium(IV) oxidation of arsenic(III). Recently chromium(III) was used in a new analytical method for arsenic(III) with cerium(IV).[8] The details of the chromium(III) catalysis are of interest as catalysis may involve reactive chromium(IV) and chromium(V) species. Again, catalysed cerium(IV)–arsenic(III) reactions have involved the catalyst and only one of the reactants in the rate law and this aspect is also of interest.

## Experimental

*Materials.*—Reagent grade chemicals were used. A stock solution of arsenic(III) was prepared by dissolving arsenic(III) oxide (BDH, AR) in 1 mol dm$^{-3}$ sodium hydroxide and the solution standardised with potassium iodate.[9] The cerium(IV) stock solution was obtained by dissolving cerium ammonium sulphate (E. Merck) in 0.85 mol dm$^{-3}$ sulphuric acid and standardised with iron(II) ammonium sulphate solution. The stock solutions were diluted as required and standardised before use in a kinetic run. The chromium(III) catalyst was in the form of chromium(III) potassium sulphate (BDH, AR), $\mathrm{Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O}$. Doubly distilled water was used for the solutions.

*Kinetic Procedure.*—The reaction was initiated by mixing the pre-equilibrated reactant solutions which also contained known concentrations of sulphuric acid and sodium sulphate to give the required acidity and ionic strength. Runs were followed by withdrawing aliquots and estimating with iron(II) solutions. Some runs were also followed by back titration of excess iron(II) with standard cerium(IV). Kinetic runs were studied at 30 °C in most cases except for effect of acid, which was studied at 40 °C. Duplicate runs agreed within ±5%.

*Stoicheiometry.*—Different reaction mixtures containing various concentrations of reactants in sulphuric acid–sulphate media were kept at 30 °C for 24 h and analysed for excess cerium(IV) with iron(II), cerium(III) by oxidation to cerium(IV) followed by estimation with iron(II), and arsenic(V) was found iodometrically. The results showed that cerium(IV) reacted with arsenic(III) in a 2:1 mol ratio. Similar experiments in the presence of chromium(III) also showed a 2:1 stoicheiometry. The catalyst, chromium(III), was found to be unchanged in concentration during the reaction by measuring the absorption at 583 nm with a Bausch and Lomb Spectronic 2000 instrument.

## Results

*Uncatalysed Reaction.*—The uncatalysed reaction was second order: first order in oxidant and arsenic(III). Second-order plots of $1/(a - x)$ *vs.* $t$ in the case of the runs where $a = [\mathrm{Ce^{IV}}]_0 = 2[\mathrm{As^{III}}]_0$ and $x$ is the amount reacted in time $t$ were found to be linear to about three half-lives. The rate constant of the uncatalysed reaction, $k_u$, was obtained from the slope. Added products had no effect on the reaction. The effect of sulphuric acid concentration is shown in Table 1. The rate increases by *ca.* 40 times as the acid concentration increases from 0.055 to 1.0 mol dm$^{-3}$. A plot of log $k_u$ *vs.* log $[\mathrm{H^+}]$ has a slope of 0.75. Also shown in Table 1 are the $\mathrm{H^+}$ concentrations calculated from the added sulphuric acid concentrations and the known equilibrium constant of the acid sulphate equilibrium.[10] From the concentrations of $\mathrm{H^+}$, cerium(IV),

**Table 1.** Effect of sulphuric acid concentration[a] on the uncatalysed reaction: $[Ce^{IV}] = 2[As^{III}] = 0.01$ mol dm$^{-3}$; $I = 3.5$ mol dm$^{-3}$, 40 °C

| | | | | | | | | | $10^2k_u$[b] | |
|---|---|---|---|---|---|---|---|---|---|---|
| $[H_2SO_4]$ | $[H^+]$ | $[HSO_4^-]$ | $[SO_4^{2-}]$ | $10^5[Ce^{4+}]$ | $10^3[CeSO_4^{2+}]$ | $10^3[Ce(SO_4)_2]$ | $10^4[HCe(SO_4)_3^-]$ | $10^5[H_3Ce(SO_4)_4^-]$ | Expt. | Calc. |
| 0.055 | 0.01 | 0.10 | 0.95 | 1.9 | 6.9 | 2.9 | 1.7 | 0.04 | 0.65 | 0.02 |
| 0.2 | 0.05 | 0.35 | 0.70 | 2.7 | 7.2 | 2.2 | 4.7 | 1.7 | 3.1 | 0.96 |
| 0.3 | 0.09 | 0.51 | 0.55 | 3.6 | 7.6 | 1.8 | 5.5 | 5.2 | 4.0 | 3.1 |
| 0.4 | 0.16 | 0.64 | 0.41 | 5.0 | 7.9 | 1.4 | 5.5 | 11 | 6.8 | 6.5 |
| 0.6 | 0.37 | 0.83 | 0.22 | 9.8 | 8.4 | 0.83 | 4.1 | 25 | 14 | 15 |
| 0.8 | 0.68 | 0.92 | 0.14 | 17 | 8.7 | 0.52 | 2.8 | 36 | 20 | 21 |
| 0.9 | 0.86 | 0.94 | 0.11 | 21 | 8.7 | 0.42 | 2.4 | 39 | 22 | 23 |
| 1.0 | 1.0 | 0.96 | 0.09 | 25 | 8.8 | 0.36 | 2.1 | 41 | 24 | 24 |

[a] All concentrations in mol dm$^{-3}$. [b] In dm$^3$ mol$^{-1}$ s$^{-1}$.

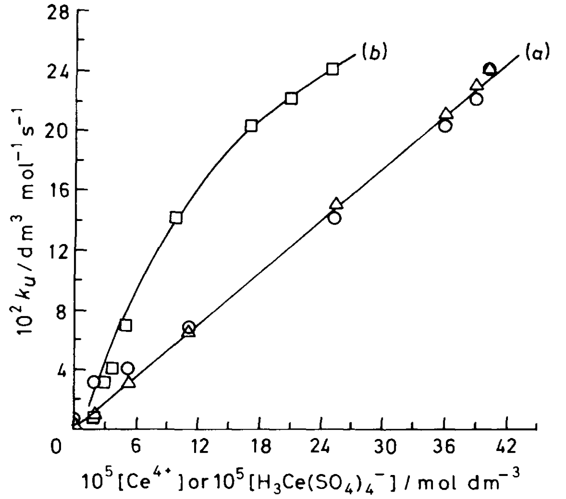

**Figure 1.** Uncatalysed reaction: plot of (*a*) $k_u$ *vs.* $[H_3Ce(SO_4)_4^-]$ (○); calculated rate constants (△); (*b*) $k_u$ *vs.* $[Ce^{4+}]$ (□)

sulphate, and bisulphate, approximate concentrations of free $Ce^{4+}$, $CeSO_4^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$, and $H_3Ce(SO_4)_4^-$,

$$Ce^{4+} + SO_4^{2-} \rightleftharpoons CeSO_4^{2+} \quad K_1 \qquad (1)$$

$$CeSO_4^{2+} + SO_4^{2-} \rightleftharpoons Ce(SO_4)_2 \quad K_2 \qquad (2)$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^- \quad K_3 \qquad (3)$$

$$HCe(SO_4)_3^- + HSO_4^- + H^+ \rightleftharpoons H_3Ce(SO_4)_4^- \quad K_4 \qquad (4)$$

forming as shown in equations (1)—(4) were calculated in the different cases from the respective equilibrium constants.[4,11] Figure 1, showing plots of $k_u$ *vs.* $[Ce^{4+}]$ and $k_u$ *vs.* $[H_3Ce(SO_4)_4^-]$, was obtained from the data of Table 1 and it is seen that the latter curve is linear.

*Catalysed Reaction.—Order of reaction.* The order of the catalysed reaction was found under conditions of low (0.2 mol dm$^{-3}$) and high (1.0 mol dm$^{-3}$) sulphuric acid concentration, keeping the ionic strength at 1.6 and 3.5 mol dm$^{-3}$ respectively. At a constant chromium(III) concentration of $1.0 \times 10^{-3}$ mol dm$^{-3}$, the order with respect to cerium(IV) in the concentration range $6.0 \times 10^{-3}$ to $1.4 \times 10^{-2}$ mol dm$^{-3}$ was found to be one in both cases of high and low acid concentrations; the order of arsenic(III), between $1.0 \times 10^{-3}$ and $8.0 \times 10^{-3}$ mol dm$^{-3}$, was fractional being 0.23 and 0.32 under the low- and high-acid conditions respectively as found from log(rate) *vs.* log (concentration) plots. Pseudo-first-order conditions were also employed for both cerium(IV) and arsenic(III) and led to first-order plots which were linear. In almost all catalysed runs, second-order plots were found to be linear to *ca.* 60% reaction and deviations from linearity occurred beyond this stage. The effect of chromium(III) catalyst was studied at low (0.2 mol dm$^{-3}$) and high (1.0 mol dm$^{-3}$) sulphuric acid concentrations, varying the chromium(III) concentrations from 0 to $1.0 \times 10^{-2}$ mol dm$^{-3}$ while keeping all other concentrations constant. The second-order rate, $k_{cat}$, obtained from the slopes of initial linear parts of plots of $1/(a - x)$ *vs.* $t$ of runs with equivalent reactant concentrations, increases with chromium(III) concentration (Table 2). The order both at low and high acid concentrations was found to be 0.8 from the plot of log $k_{cat}$ *vs.* log $[Cr^{III}]$.

**Table 2.** Effect of chromium(III) concentration* on the second-order rate, $k_{cat}$: $[Ce^{IV}] = 2[As^{III}] = 0.01$ mol dm$^{-3}$; 30 °C

| | $10^2k_{cat}$/dm$^3$ mol$^{-1}$ s$^{-1}$ | |
|---|---|---|
| $10^3[Cr^{III}]$ | $[H_2SO_4] = 0.2$ $I = 1.6$ | $[H_2SO_4] = 1.0$ $I = 3.5$ |
| 0 | 0.83 | 11 |
| 1.0 | 5.8 | 13 |
| 2.0 | 10 | 15 |
| 4.0 | 14 | 17 |
| 6.0 | 19 | |
| 8.0 | 26 | 28 |
| 10 | 29 | 33 |

* All concentrations and ionic strengths in mol dm$^{-3}$.

*Effect of added products.* The effect of added products, cerium(III) and arsenic(V), in the two cases of low and high acid concentrations is shown in Table 3. It is found that cerium(III) in the concentration range $2 \times 10^{-3}$ to $8 \times 10^{-3}$ mol dm$^{-3}$ causes a decrease of *ca.* 25% in the second-order rate, $k_{cat}$, whereas, for a similar range of added arsenic(V), the rate does not change appreciably.

*Effect of acid.* The effect of increasing sulphuric acid concentration on the catalysed reaction is shown in Table 4. The apparent second-order constant, $k_{cat}$, obtained from plots of $1/(a - x)$ *vs.* $t$ serves to illustrate the influence of sulphuric acid on the reaction. A plot of log $k_{cat}$ *vs.* log $[H^+]$ is linear with a slope of 0.83. As shown in the equilibria (1)—(4), cerium(IV) forms different sulphate complexes and the concentrations of the different cerium(IV) species for the different sulphuric acid concentrations are expressed as fractions ($\alpha$) of cerium (IV) dissolved and are shown in Table 4 where $\alpha_0$, $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$ represent the cerium(IV) species of increasing complexity. Over

**Table 3.** Effect of added products:* $[Ce^{IV}] = 2[As^{III}] = 0.01$, $[Cr^{III}] = 0.001$ mol dm$^{-3}$; 30 °C

| $[H_2SO_4] = 0.2, I = 1.6$ | | | | $[H_2SO_4] = 1.0, I = 3.5$ | | | |
|---|---|---|---|---|---|---|---|
| $10^3[Ce^{III}]$ | $10^2k_{cat}$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^3[As^V]$ | $10^2k_{cat}$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^3[Ce^{III}]$ | $10^2k_{cat}$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^3[As^V]$ | $10^2k_{cat}$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
| 0 | 5.8 | 0 | 5.8 | 0 | 13 | 0 | 13 |
| 2 | 5.0 | 2 | 5.2 | 2 | 12 | 2 | 12 |
| 4 | 4.7 | 4 | 5.4 | 4 | 9.8 | 4 | 12 |
| 8 | 4.4 | 8 | 5.7 | | | | |

* All concentrations and ionic strength in mol dm$^{-3}$.

**Table 4.** Variation of the different cerium(IV) species* with added sulphuric acid concentration: $[Ce^{IV}] = 2[As^{III}] = 0.01$, $[Cr^{III}] = 0.001$ mol dm$^{-3}$; $I = 3.5$ mol dm$^{-3}$, 40 °C

| $[H_2SO_4]$/mol dm$^{-3}$ | $10^3\alpha_0$ | $\alpha_1$ | $\alpha_2$ | $10^2\alpha_3$ | $10^3\alpha_4$ | $10^2k_{cat}$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| 0.055 | 1.9 | 0.69 | 0.29 | 1.7 | 0.036 | |
| 0.2 | 2.7 | 0.72 | 0.22 | 4.7 | 1.7 | 4.7 |
| 0.3 | 3.6 | 0.76 | 0.18 | 5.5 | 5.2 | 5.4 |
| 0.4 | 5.0 | 0.79 | 0.14 | 5.5 | 11 | 7.4 |
| 0.6 | 9.8 | 0.84 | 0.083 | 4.1 | 25 | 18 |
| 0.8 | 17 | 0.87 | 0.051 | 2.8 | 35 | 30 |
| 0.9 | 21 | 0.87 | 0.042 | 2.4 | 39 | 35 |
| 1.0 | 25 | 0.88 | 0.036 | 2.1 | 41 | 43 |

* $\alpha_0$, $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$ are the fractions of total cerium(IV) of the species $Ce^{4+}$, $CeSO_4^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$, and $H_3Ce(SO_4)_4^-$ respectively.

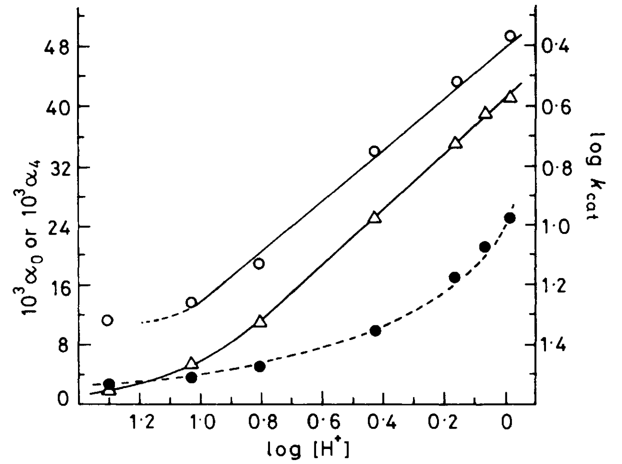

**Figure 2.** Catalysed reaction: variation of the concentrations [fractions of total cerium(IV)] of the different cerium(IV) species and $k_{cat}$ (○) with [H⁺]. $\alpha_0$ (●) and $\alpha_4$ (△) refer to the species $Ce^{4+}$ and $H_3Ce(SO_4)_4^-$. $\alpha_1$,$\alpha_2$, and $\alpha_3$, relating to $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $HCe(SO_4)_3^-$ respectively, do not change appreciably over the acid concentrations used and hence are not shown

the concentrations of sulphuric acid studied, the rate increases by about ten times, as shown by the data of Table 4 and Figure 2.

## Discussion

*Uncatalysed Reaction.*—As in the case of the study in perchloric acid medium,[3] the uncatalysed cerium(IV)–arsenic(III) reaction in acid sulphate media is catalysed by the acid concentration. The rate increases in the sulphuric acid medium are steeper than in perchloric acid where hydrolysed cerium(IV) species formed observable complexes with arsenic(III). We were unable to observe any such complexes in our media even when the reaction was initiated at a low temperature of 5 °C.

Cerium(IV) forms several complexes in acid sulphate media such as $CeSO_4^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$, and $H_3Ce(SO_4)_4^-$. The concentrations of these species were calculated by an approximate method[11] as indicated earlier and the results are shown in Table 1. It is found from the data of Table 1 that the substantial rate increases with increase of acid are paralleled only by the concentrations of the uncomplexed species, $Ce^{4+}$, and the complex, $H_3Ce(SO_4)_4^-$, while the other cerium(IV) species do not change in concentration substantially. When the rate, $k_u$, is plotted as a function of the concentrations of $Ce^{4+}$ and $H_3Ce(SO_4)_4^-$ as shown in Figure 1, it is found that the latter species can satisfactorily account for the experimental results.

In reactions involving cerium(IV), the role of hydrolysed cerium(IV) is important.[3] However, in view of the large concentrations of acid and sulphate in our media, the hydrolysed species could be expected to form to a lesser extent because of the smaller equilibrium constant as compared with the sulphate complexes. Furthermore, such species cannot account for the large rate increases with increase of acid concentration. We therefore conclude that $H_3Ce(SO_4)_4^-$ is the principal active oxidant in the uncatalysed reaction. Small contributions to rate can, however, arise from other cerium(IV) species present. The reductant, arsenic(III), is likely to be present almost entirely as $H_3AsO_3$ over the whole range of acid concentrations used in view of the fact that its first dissociation constant[12] is known to be extremely small, being (2—8) × $10^{-10}$.

The total cerium(IV) concentration, $[Ce^{IV}]_T$, is the sum of the different cerium(IV) species, $Ce^{4+}$, $CeSO_4^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$, and $H_3Ce(SO_4)_4^-$, the complexes having the cumulative equilibrium constants $\beta_1$, $\beta_2$, $\beta_3$, and $\beta_4$ respectively as shown in equation (5), where $\beta_1 = K_1$, $\beta_2 = K_1K_2$, $\beta_3 = K_1K_2K_3$, and $\beta_4 = K_1K_2K_3K_4$. If the rate constants

$$[Ce^{IV}]_T = [Ce^{4+}](1 + \beta_1[SO_4^{2-}] + \beta_2[SO_4^{2-}]^2 + \beta_3[SO_4^{2-}]^2[HSO_4^-] + \beta_4[SO_4^{2-}]^2[HSO_4^-]^2[H^+]) \quad (5)$$

$k_0$, $k_1$, $k_2$, $k_3$, and $k_4$, in order, characterise the different

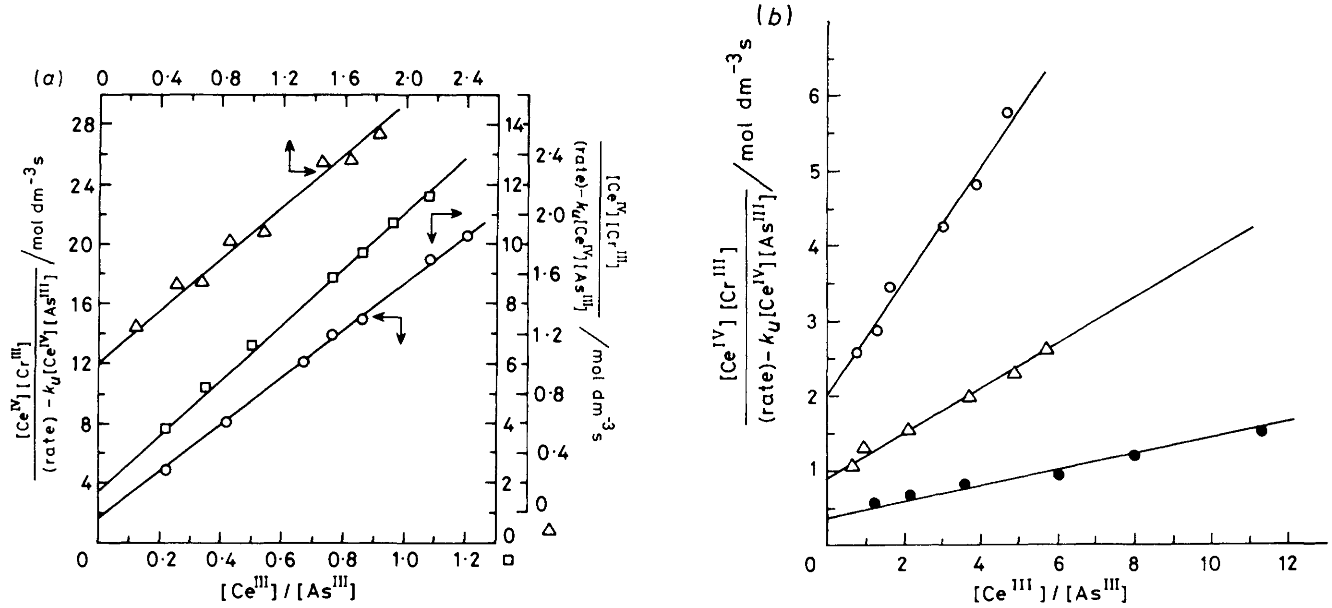

Figure 3. Verification of rate law (8). (*a*) Effect of acid concentrations: 0.2 (○), 0.4 (□), and 0.8 mol dm$^{-3}$ (△) (conditions as in Table 4). (*b*) Effect of temperature: 30 (○), 40 (△), and 50 °C (●) (conditions as in Table 5)

$$k_u = \frac{(k_0 + k_1\beta_1[SO_4^{2-}] + k_2\beta_2[SO_4^{2-}]^2 + k_3\beta_3[SO_4^{2-}]^2[HSO_4^-] + k_4\beta_4[SO_4^{2-}]^2[HSO_4^-]^2[H^+])}{(1 + \beta_1[SO_4^{2-}] + \beta_2[SO_4^{2-}]^2 + \beta_3[SO_4^{2-}]^2[HSO_4^-] + \beta_4[SO_4^{2-}]^2[HSO_4^-]^2[H^+])} \quad (6)$$

cerium(IV) species of increasing complexity, it can be seen that the experimental second-order rate constant, $k_u$, is given by equation (6). The main contribution to $k_u$ comes from $k_4$ for the complex $H_3Ce(SO_4)_4^-$ and with a value of 5.85 dm$^3$ mol$^{-1}$ s$^{-1}$ for $k_4$, all the $k_u$ values for the different sulphuric acid concentrations above 0.3 mol dm$^{-3}$ can be seen to arise from this single source. The values of $k_u$ calculated in this way are given in Table 1 and indicated in Figure 1 alongside the experimental values. For concentrations lower than 0.3 mol dm$^{-3}$, the calculated values are lower than the experimental rates probably because the method of calculation of the active species at the low [H$^+$] is no longer satisfactory. This also indicates that the other species which may also be responsible for the reaction have very much smaller rate constants.

*Catalysed Reaction.*—The cerium(IV) oxidation of arsenic(III) in acid sulphate medium proceeds with measurable speeds in the absence of the chromium(III) catalyst. Hence, in the presence of the catalyst, the reaction is understood to occur in parallel paths with contributions from the uncatalysed and catalysed paths.

In view of the rate increases caused by increasing acidity, the rate law has been studied under both low (0.2 mol dm$^{-3}$) and high (1.0 mol dm$^{-3}$) sulphuric acid conditions and is found to be the same under both conditions. The rate law (7) accommodates all the experimental results including the effect of acidity, the first and second terms on the right-hand side representing the uncatalysed and catalysed paths respectively. From rate law (7) the catalysed path is in agreement with Schemes 1 and 2. The

$$-\frac{d[Ce^{IV}]}{dt} = k_u[Ce^{IV}][As^{III}] + \frac{2k_ak_c[Ce^{IV}][Cr^{III}][As^{III}][H^+]}{k_b[Ce^{III}] + k_c[As^{III}][H^+]} \quad (7)$$

$$\begin{aligned} &Ce^{IV} + Cr^{III} \rightleftharpoons Ce^{III} + Cr^{IV} && k_a,k_b \\ &Cr^{IV} + As^{III} + H^+ \longrightarrow Cr^{III} + As^{IV} && k_c \\ &Ce^{IV} + As^{IV} \longrightarrow Ce^{III} + As^{V} && \text{fast} \end{aligned}$$

**Scheme 1.**

intervention of arsenic(IV) in oxidation reactions of arsenic(III) has been suggested in several cases.[13] However, in the present case, experiments with added acrylamide did not result in polymerisation. It may be that the reduction of arsenic(IV) is faster than the initiation of polymerisation of acrylamide. In Scheme 2 the chromium(IV) formed in the first step is reduced by arsenic(III) to chromium(II) in the second step. Again, there is no evidence of chromium(II) in the catalysed reaction but any such chromium(II) formed is likely to undergo instantaneous oxidation by cerium(IV) to chromium(III).

$$\begin{aligned} &Ce^{IV} + Cr^{III} \rightleftharpoons Ce^{III} + Cr^{IV} && k_a,k_b \\ &Cr^{IV} + As^{III} + H^+ \longrightarrow Cr^{II} + As^{V} && k_c \\ &Ce^{IV} + Cr^{II} \longrightarrow Ce^{III} + Cr^{III} && \text{fast} \end{aligned}$$

**Scheme 2.**

As in the case of the uncatalysed reaction, in view of the very low dissociation constant of $H_3AsO_3$, the predominant form of arsenic(III) is $H_3AsO_3$ itself. The chromium(III) catalyst has an order of 0.8 in the reaction probably because of its active species being the labile ion-pair complex, $Cr^{3+}SO_4^{2-}$, with a low equilibrium constant.[14] Inner-sphere complexes of chromium(III) are unlikely to be of much importance in the reaction. The data of Table 2 also indicate that a sulphate complex is the likely active form of the catalyst. In the two cases of low and high acid concentrations studied (Table 2), the free sulphate concentrations can be calculated as 0.28 and 0.093 mol dm$^{-3}$ respectively. Over a similar range of a ten-fold increase in

$$-\frac{d[\mathrm{Ce^{IV}}]}{dt} - k_u[\mathrm{As^{III}}][\mathrm{Ce^{IV}}] = \frac{2k_ak_c\beta_4K_{IP}[\mathrm{Ce^{IV}}][\mathrm{Cr^{III}}][\mathrm{As^{III}}][\mathrm{SO_4}^{2-}]^3[\mathrm{HSO_4}^-]^2[\mathrm{H}^+]^2}{(1+\beta_1[\mathrm{SO_4}^{2-}]+\beta_2[\mathrm{SO_4}^{2-}]^2+\beta_3[\mathrm{SO_4}^{2-}]^2[\mathrm{HSO_4}^-]+\beta_4[\mathrm{SO_4}^{2-}]^2[\mathrm{HSO_4}^-]^2[\mathrm{H}^+])(1+K_{IP}[\mathrm{SO_4}^{2-}])} \times \mathrm{04n}\left\{\frac{k_bK_5[\mathrm{Ce^{III}}][\mathrm{SO_4}^{2-}]^3}{(1+K_5[\mathrm{SO_4}^{2-}]^3)} + k_c[\mathrm{As^{III}}][\mathrm{H}^+]\right\}^{-1} \quad (8)$$

**Table 5.** Application of equation (8) to the rate data and effect of temperature on the catalysed reaction:* $[\mathrm{Ce^{IV}}] = 2[\mathrm{As^{III}}] = 0.01$, $[\mathrm{Cr^{III}}] = 0.001$, $[\mathrm{H_2SO_4}] = 0.2$ mol dm$^{-3}$; $I = 1.6$ mol dm$^{-3}$

| Temp. (°C) | 30 | 40 | 50 |
|---|---|---|---|
| $k_a$/dm$^3$ mol$^{-1}$ s$^{-1}$ | 0.25 | 0.59 | 1.4 |
| $k_b/k_c$ | 0.4 | 0.4 | 0.3 |

$\Delta H^\ddagger = 67.0$ kJ mol$^{-1}$
$\Delta S^\ddagger = -38$ J K$^{-1}$ mol$^{-1}$

* $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for uncatalysed reaction under similar conditions are 72.9 kJ mol$^{-1}$ and $-55$ J K$^{-1}$ mol$^{-1}$ respectively.

catalyst concentration employed in the two cases, the rate increase is nearly ten times in the former low-acid case as compared to the latter higher acid conditions.

The effect of increasing sulphuric acid on the catalysed reaction is shown in Table 4 and it is seen that $k_{cat}$ increases with acidity. As understood earlier, the uncatalysed path involves the active oxidant species $\mathrm{H_3Ce(SO_4)_4}^-$. The catalysed path may involve any of the cerium(IV) species shown in equilibria (1)—(4). An examination of the data of Table 4 shows that, as the concentration of the acid increases, the corresponding increase in $k_{cat}$ is paralleled only by the concentrations of $\mathrm{Ce}^{4+}$ and $\mathrm{H_3Ce(SO_4)_4}^-$ while the concentrations of the other cerium(IV) species either do not change much or actually decrease. In Figure 2 the variation of the concentrations of $\mathrm{Ce}^{4+}$ and $\mathrm{H_3Ce(SO_4)_4}^-$ with acidity is compared with the variation of $k_{cat}$ with acidity and it is seen that the latter species shows better correlation with $k_{cat}$. In fact, as seen from the data of Table 4, there is a direct dependence of $k_{cat}$ on the concentration of $\mathrm{H_3Ce(SO_4)_4}^-$. Pseudo-first-order conditions, employed with different initial concentrations of cerium(IV) also support the conclusion that $\mathrm{H_3Ce(SO_4)_4}^-$ is the active species.

Cerium(III) forms two sulphate complexes, $\mathrm{Ce(SO_4)_3}^{3-}$, and $\mathrm{CeSO_4}^+$ with equilibrium constants of 1 950 dm$^9$ mol$^{-3}$ and 39 dm$^3$ mol$^{-1}$ respectively.[15] In solutions of sulphate concentration above *ca.* $10^{-2}$ mol dm$^{-3}$, as in the present case, only the trisulphate species is important.[15]

The mechanism of Scheme 1 or Scheme 2 will therefore involve the above species [see Scheme 3, where $K_{IP}$ is the ion-pair equilibrium constant of $\mathrm{Cr^{3+}SO_4}^{2-}$ and $K_5$ is the equilibrium constant of $\mathrm{Ce(SO_4)_3}^{3-}$]. This scheme, corresponding to Scheme 1, leads to the rate equation (8) which requires that plots of $[\mathrm{Ce^{IV}}][\mathrm{Cr^{III}}]/(\text{rate} - k_u[\mathrm{As^{III}}][\mathrm{Ce^{IV}}])$ *vs.* $[\mathrm{Ce^{III}}]/[\mathrm{As^{III}}]$ should be linear at the different acidities. This is verified in Figure 3(*a*) in the case of the catalysed reaction at 0.2, 0.4, and 0.8 mol dm$^{-3}$ sulphuric acid. From the slopes and intercepts of such plots the values of $k_b/k_c$ are obtained as 0.5, 0.9, 0.3, 0.6, and 0.5 and the values of $k_a$ as 3.5, 0.5, 0.3, 0.4, and 0.5 dm$^3$ mol$^{-1}$ s$^{-1}$ respectively at the sulphuric acid concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 mol dm$^{-3}$. There is reasonable agreement amongst the values of $k_b/k_c$ considering the substantially different acidities employed but the value of $k_a$ at the lowest acidity is large, presumably because of the uncertainty involved in the calculation of the concentration of the active species at a $\mathrm{H}^+$ concentration of *ca.* 0.5 mol dm$^{-3}$ (Table 1). The application of equation (8) to the reaction is also verified under conditions (under the conditions of lower ionic strength, Table 2) different from the above as shown in Figure 3(*b*) where the effect of temperature on the reaction is shown. The intercepts lead to the activation parameters (Table 5) under such conditions.

$$\mathrm{Ce^{4+} + 2SO_4{}^{2-} + 2HSO_4{}^- + H^+ \rightleftharpoons H_3Ce(SO_4)_4{}^-} \qquad \beta_4$$

$$\mathrm{Cr^{3+} + SO_4{}^{2-} \rightleftharpoons Cr^{3+}SO_4{}^{2-}} \qquad K_{IP}$$

$$\mathrm{H_3Ce(SO_4)_4{}^- + Cr^{3+}SO_4{}^{2-} \rightleftharpoons Ce(SO_4)_3{}^{3-} + 3H^+ + Cr^{IV}} \qquad k_a, k_b$$

$$\mathrm{Cr^{4+}(SO_4{}^{2-})_2 + 4H^+ + H_3AsO_3 \longrightarrow Cr^{3+}SO_4{}^{2-} + HSO_4{}^- + 3H_2O + As^{IV}} \qquad k_c$$

$$\mathrm{H_3Ce(SO_4)_4{}^- + As^{IV} + 4H_2O \longrightarrow Ce(SO_4)_3{}^{3-} + HSO_4{}^- + 7H^+ + H_3AsO_4} \qquad \text{fast}$$

**Scheme 3.** $\mathrm{Cr^{IV}}$ present as $\mathrm{Cr^{4+}(SO_4{}^{2-})_2}$

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