

Kinetics and mechanism of cooxidation of oxalic acid and arsenic(III) by chlorochromate in aqueous acetic acid

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The influence of oxalic acid on chromium(VI) oxidation of arsenic(III) is studied in the presence of chloride ion in 60% aqueous acetic acid and $I=0.80 \text{ mol dm}^{-3}$ (NaClO_4). It is found that both arsenic(III) and oxalic acid are oxidised concertedly in a three equivalent step. It has been found that one mole of Cr(VI) oxidises one equivalent of oxalic acid and two equivalents of arsenic(III). The details of such a process are discussed.

Chromium(VI) oxidation of a mixture of 2-propanol and oxalic acid in aqueous solution leads to the oxidation of both the substrates in a concerted step¹. A few other such cases of cooxidations by chromium(VI) have also been reported². Mechanistically, a concerted process whereby a single step three equivalent change from Cr(VI) to Cr(III) is expected to facilitate the reaction as the intervention of the energetically unfavourable Cr(IV) is avoided. Chlorochromate, ClCrO_3^- , is a less potent oxidant than acid chromate, HCrO_4^- , and the latter is almost fully converted into chlorochromate in 60% acetic acid in the presence of 0.60 mol dm^{-3} chloride^{3,4}. The chlorochromate oxidation of As(III) is slow enough to permit a study of the effect of oxalic acid on the reaction. The influence of oxalic acid on Cr(VI) oxidation of Ti(I) seems to be the only other known example besides the present study of cooxidation involving an inorganic reductant⁵.

Materials and Methods

Oxalic acid, arsenic(III) oxide, sodium chloride and potassium dichromate (all BDH, AR samples) were used as such. Other chemicals were of reagent grade. Doubly distilled water was used for preparing the solutions. Purified acetic acid was used. A stock solution of As(III) was made by dissolving arsenic(III) oxide in 1.0 mol dm^{-3} sodium hydroxide and the solution was standardised with potassium iodate^{6(a)}, while stock solutions of potassium dichromate and sodium chloride were prepared by dissolution of the required quantities in water.

Kinetic runs

Kinetics were followed in 60% acetic acid (v/v)

in the presence of 0.60 mol dm^{-3} chloride at 27°C unless otherwise stated. The ionic strength was maintained at 0.80 mol dm^{-3} with sodium perchlorate. The reaction rates were determined spectrophotometrically by following the decrease in absorbance of Cr(VI) at regular intervals at 360 nm ($\epsilon=1200 \pm 1\%$) using 1 cm cells in a Bausch and Lomb Spectronic 2000 spectrophotometer. Initial rates were obtained by plane mirror method⁷ and pseudo-first order rate constants (k) from the slopes of plots of $\log[\text{Cr(VI)}]$ versus time. The reaction obeyed good first order kinetics when $[\text{substrate}] \gg [\text{oxidant}]$. The rate constants were averages of multiple determinations and were reproducible within $\pm 5\%$.

Results

Stoichiometry

Reaction mixtures containing different amounts of reactants, As(III), Cr(VI) and oxalic acid, in the presence of 0.60 mol dm^{-3} chloride at $I=0.80 \text{ mol dm}^{-3}$ in 60% acetic acid were kept at 27°C for 24 hrs and analysed for As(III), oxalic acid and Cr(VI). The unreacted As(III) was analysed by (i) titration with standard iodate solution and (ii) titration with iodine solution^{6(b)}, while Cr(VI) was estimated spectrophotometrically at 360 nm . The total reductant of unreacted As(III) and oxalic acid (hot) was found by back titration of added excess Ce(IV) with Fe(II) solution^{6(c)}. This procedure for oxalic acid, obtained by difference of total reductant and unreacted As(III), was satisfactory as it was ensured that Cr(VI) had completely reacted under the reaction conditions and the Ce(IV)-Cr(III) reaction was too slow to interfere in the Fe(II) titration of excess Ce(IV). Runs were

also monitored to find the yield of carbon dioxide using a Warburg apparatus⁸. The results are indicative of a 2:3 reaction when As(III) or oxalic acid alone is present. However, Cr(VI) oxidation of a mixture of oxalic acid and As(III) consumes two equivalents of As(III) and one equivalent of oxalic acid. The marginal excess yield of As(V) is presumably due to the direct Cr(VI)-As(III) reaction which may also be occurring to a small extent.

Effect of chloride and acetic acid—It was found that in the media of 60% acetic acid and 0.60 mol dm⁻³ chloride, virtually all the Cr(VI) employed (~98.5% or higher) was in the form of chlorochromate^{3,4}.

Order of reaction—Under the conditions 60% acetic acid, 0.60 mol dm⁻³ chloride, $I=0.80$ mol dm⁻³, in the range of [As(III)] of 8.0×10^{-5} to 2.0×10^{-3} mol dm⁻³ and fixed [oxalic acid] of 5.0×10^{-4} mol dm⁻³, the order in As(III) was approximately unity. At a constant [As(III)] of 4.0×10^{-4} mol dm⁻³, in the range of [oxalic acid] 5.0×10^{-4} to 3.0×10^{-3} , the order in oxalic acid was 0.95. Between 2.0×10^{-5} and 4.0×10^{-4} mol dm⁻³ [Cr(VI)], the order in Cr(VI) was 0.96 at fixed [oxalic acid] (2.0×10^{-3} mol dm⁻³) and [As(III)] (4.0×10^{-4} mol dm⁻³).

Effect of acidity—Measurement of pH (employing a digital pH-meter, Elico model LI-120) and acidity function (H_0) by spectrophotometry⁹ showed that no significant variation in acidity occurred in the reaction mixture containing varying amounts of oxalic acid. However, in the presence of small quantities of perchloric acid, the acidity function (H_0) falls and the increase in the first order rate constant corresponds to an order of approximately 0.4 in acidity.

Free radical intervention—In the presence of added acrylamide, the reaction mixture containing 1.6×10^{-2} , 3.0×10^{-2} and 8.0×10^{-3} mol dm⁻³ of As(III), oxalic acid and Cr(VI), respectively, shows polymer formation on dilution with methanol. This indicates the free radical intervention in the reaction. Furthermore, in the presence of acrylamide, the yield of carbon dioxide is marginally decreased whereas that of As(V) increased.

Effect of added products—Initially added products, As(V) and Cr(III) did not change the pseudo-first order rate constants to any appreciable extent; the pseudo-first order rate constants of the Cr(VI)-As(III) reaction were measured in presence of oxalic acid and As(V)/Cr(III).

Effect of aluminium chloride—When aluminium chloride was present in the reaction medium, the pseudo-first order rate constant decreased substantially. For example at [As(III)] = 4.0×10^{-4} ,

[oxalic acid] = 2.0×10^{-3} , [Cl⁻] = 0.60, $I=0.80$ mol dm⁻³, temp. = 300 K, $10^3 k$ decreased from 0.72 to 0.58 s⁻¹ when added [AlCl₃] $\times 10^2$ was changed from 1.0 to 5.0 mol dm⁻³.

Discussion

The chlorochromate oxidation of arsenic(III) and oxalic acid is approximately third order, first order in oxidant, arsenic(III) and oxalic acid. The effect of arsenic(III) on the chromium(VI) oxidation of oxalic acid is shown in Fig. 1 while the influence of oxalic acid on the chromium(VI)-arsenic(III) reaction is shown in Fig. 2. The latter reaction is rather fast as compared to the chromium(VI)-oxalic acid case but the data are clearly indicative of the combined effect of both oxalic acid and arsenic(III) in the reaction. When the two reductants are present together, the reaction is faster as compared to the case when only one of them is present. Thus, for example, the plots of log k versus log [As(III)] in respect of first order rate constants of the chromium(VI)-oxalic acid reaction, at several [oxalic acid], are linear and lie well above zero [oxalic acid] (Fig. 1). Likewise, the rate constants of the Cr(VI)-As(III) reaction at constant acidity and [As(III)] are influenced positively by the presence of even small amounts of oxalic acid of around 1% of As(III). These results together with the stoichiometry of two and one equivalents of As(III) and oxalic acid respectively being oxidised by a mole of oxidant indicate the likelihood of cooxidation.

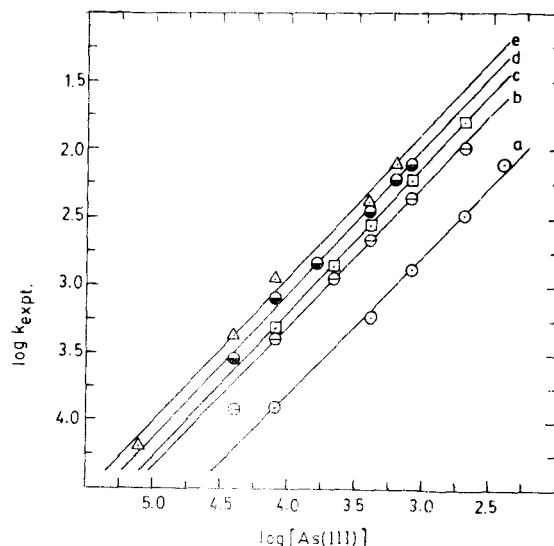


Fig. 1—Effect of arsenic(III) on the experimental rate constants at several constant oxalic acid concentrations (a) Zero, (b) 5.0×10^{-4} , (c) 10.0×10^{-4} , (d) 15.0×10^{-4} and (e) 30.0×10^{-4} mol dm⁻³ respectively and constant acidity. ([Cr(VI)] = 4.0×10^{-5} mol dm⁻³, [Cl⁻] = 0.60 mol dm⁻³, $I=0.80$ mol dm⁻³, 60% HOAc (v/v) and temp. = 300 K).

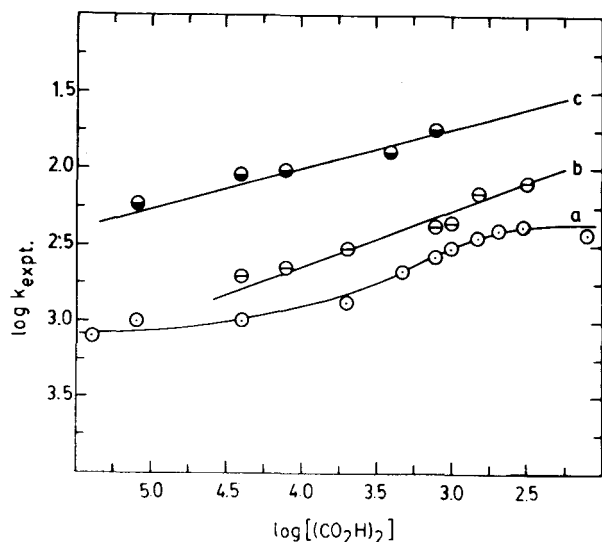
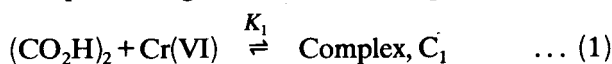


Fig. 2—Effect of oxalic acid on the experimental rate constants at several constant arsenic(III) concentrations (a) 4.0×10^{-4} , (b) 8.0×10^{-4} and (c) 2.0×10^{-3} mol dm^{-3} respectively and constant acidity (other conditions as in Fig. 1).

In the case of As(III), increase in [oxalic acid] increases the rate constant initially and then reaches a plateau at higher [oxalic acid] and the order in [oxalic acid] tends to become zero. This behaviour is similar to that of Cr(VI) oxidation of 2-propanol in the presence of oxalic acid and is characteristic of the formation of an intermediate complex¹. The formation of a 1:1 Cr(VI)-oxalic acid complex may be shown as in steps (1) and (2) in Scheme 1 and the concentration of the complex, C_1 , is given by Eq. (3) where the total [Cr(VI)] is the sum of the free and complexed [oxidant]. The rate of reaction is given by Eqs (5) and (6). Since the reaction in the absence of oxalic acid may not be neglected, the total rate at constant acidity may be taken to be the sum of the rates of the two reactions, one due to the direct Cr(VI)-As(III) reaction and the other due to the faster Cr(VI) oxidation of As(III) and oxalic acid present together as shown in Eq. (6).



Scheme 1

$$[C_1] = \frac{K_1[(\text{CO}_2\text{H})_2][\text{Cr(VI)}]_{\text{total}}}{(1 + K_1[(\text{CO}_2\text{H})_2])} \quad \dots (3)$$

$$\text{Rate} = k_2[C_1][\text{As(III)}] \quad \dots (4)$$

$$= \frac{k_2 K_1[(\text{CO}_2\text{H})_2][\text{Cr(VI)}]_{\text{total}}[\text{As(III)}]}{(1 + K_1[(\text{CO}_2\text{H})_2])} \quad \dots (5)$$

$$\text{Rate}_{\text{total}} = k_1[\text{Cr(VI)}]_{\text{total}}[\text{As(III)}] + \frac{k_2 K_1[(\text{CO}_2\text{H})_2][\text{Cr(VI)}]_{\text{total}}[\text{As(III)}]}{(1 + K_1[(\text{CO}_2\text{H})_2])} \quad \dots (6)$$

From Eq. (6), a plot of

$$\frac{[\text{Cr(VI)}]_{\text{total}}[\text{As(III)}]}{(\text{Rate}_{\text{total}} - k_1[\text{Cr(VI)}]_{\text{total}}[\text{As(III)}])} \text{ versus } \frac{1}{[(\text{CO}_2\text{H})_2]}$$

should be linear (k_1 , $1.41 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, being taken from runs in the absence of oxalic acid, (Fig. 3). Values of K_1 and k_2 result from Fig. 3 as $42.9 \pm 2.0 \text{ dm}^6 \text{ mol}^{-2}$ and $100 \pm 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. Rates obtained from the calculated values of K_1 and k_2 show satisfactory agreement with the experimentally measured initial rates under different conditions.

The data of stoichiometry, that is, the products (As(V) and carbon dioxide) formed in approximately 1:1 ratio support a concerted three-electron reaction. In the Cr(VI) oxidation of As(III) and oxalic acid, the product ratio was around one mole of As(V) to 1.1-1.2 mole carbon dioxide which becomes almost a 1:1 ratio in the presence of free radical scavengers. In the presence of free radical scavengers, as argued by Rocek and Hasan¹, the free radicals are removed by nonoxidative bimolecular destruction so that the 1:1 reaction only is facilitated. As a matter of fact, there is

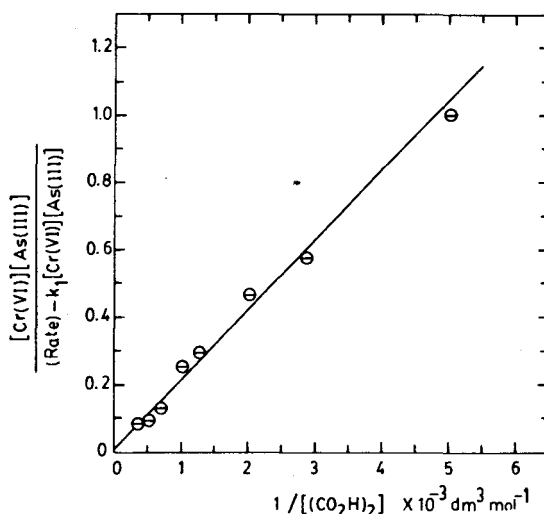
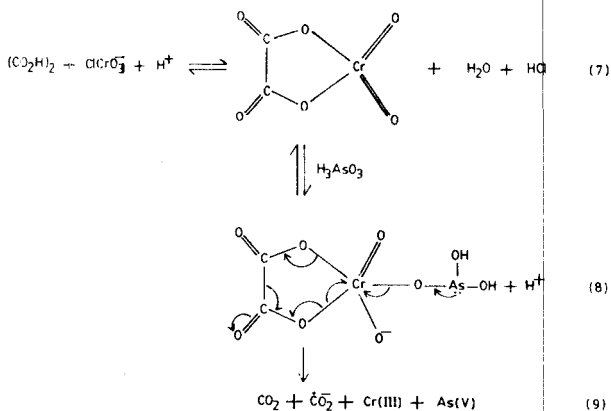


Fig. 3—Verification of rate law (6) ($[\text{As(III)}] = 4.0 \times 10^{-4}$ mol dm^{-3} ; other conditions as in Fig. 1)

decrease in the yield of carbon dioxide with increase in [acrylamide] and increase in the yield of As(V). Only one mole of carbon dioxide would be expected from the cooxidation; however, the free radical resulting from the concerted process can also generate a mole of carbon dioxide and hence more than a mole of carbon dioxide may result in the absence of free radical scavengers.

Added support to the single step three-electron mechanism in this case, comes from the results of the use of aluminium chloride in the reaction¹⁰. Oxalic acid can preferentially complex with Al(III) and thus prevent Cr(VI)-oxalic acid complex intermediate formation in the reaction. Thus, the first order rate constant should decrease in presence of added aluminium chloride and this is borne out by experiment. The reaction mechanism is shown in Scheme 2.

A cyclic intermediate similar to that shown in Eq. (7) was postulated in the Cr(VI)-oxalic acid reaction mechanism¹¹ and other studies^{12,13}; it had an equilibrium constant of $9.5 \text{ dm}^6 \text{ mol}^{-2}$ in



Scheme 2

aqueous solution at 25°C and $I=0.63$ as against the value of $42.9 \text{ dm}^6 \text{ mol}^{-2}$ in the present case. A neutral complex is possible only if it is cyclic and such a neutral complex would be favoured in a less polar media to a greater extent as, in fact, indicated by the higher equilibrium constant of formation in the present case. The complex, C_1 , formed by the elimination of the elements of water and HCl, reacts with arsenic(III) in step (8) to undergo a rate-determining decomposition into products in step (9). The products, Cr(III), As(V) and carbon dioxide are all quantitatively fixed (results) and the free radical formation also verified by free radical trapping experiments.

References

- 1 Hasan F & Rocek J, *J Am chem Soc*, 94 (1972) 3181.
- 2 Granzow A, Wilson A & Ramirez F, *J Am chem Soc*, 96 (1974) 2454.
- 3 Cohen M & Westheimer F H, *J Am chem Soc*, 74 (1952) 4387.
- 4 Chimatadar S A, Nandibewoor S T & Raju J R, *J Indian chem Soc*, LXIV (1987) 187.
- 5 Gokavi G S, *Kinetics and mechanism of some oxidation reactions* Ph.D. Thesis, Karnatak University, Dharwad (1987) p. 101.
- 6 Vogel I, *Text book of quantitative inorganic analysis* (ELBS-Longman, New York) 1978 (a) p. 387, (b) p. 378, (c) p. 366.
- 7 Latshaw M, *J Am chem Soc*, 47 (1925) 793.
- 8 Umbreit W W, *Manometric techniques* (Burgess, Minneapolis, Minn) (1964).
- 9 Paul M A & Long F A, *Chem Rev*, 57 (1957) 1.
- 10 Chandra S, Shukla S N & Chatterji A C, *Z phys Chem (Leipzig)*, 237 (1968) 137.
- 11 Hasan F & Rocek J, *J Am chem Soc*, 94 (1972) 9073.
- 12 Vandegrift G F & Rocek J, *J Am chem Soc*, 98 (1976) 1371.
- 13 Hintze R E & Rocek J, *J Am chem Soc*, 99 (1977) 132.