Kinetics of the Chromic Acid Oxidation of Arsenic(III)

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The kinetics of oxidation of arsenic(III) by chromium(VI) has been studied in the temperature range 30—45 °C. The energy and entropy of activation, where a high concentration of arsenic(III) reacts with a low concentration of chromium(VI) to give a 1 : 1 complex, have been evaluated to be 9·1 ± 0·6 kcal mol^{-1} and −43·5 ± 0·1 cal K^{-1} mol^{-1} respectively. Corresponding values for reaction of low arsenic(III) with high chromium(VI) concentrations are not widely different from those above and have been found to be 9·4 ± 0·1 kcal mol^{-1} and −39·95 ± 0·15 cal K^{-1} mol^{-1}. The formation of an unstable 1 : 1 complex in the latter case is also suggested.

THE oxidation of arsenic(III) by several oxidants has been studied previously.[1-4] A considerable amount of work has also been done on the pH effect [5-7] on the chromic acid oxidation of arsenic(III). The preliminary work of Mason and Kowalak [8] indicated that arsenic(III) is oxidised by $HCrO_4^-$ at low, and by $Cr_2O_7^{2-}$ at high, chromium(VI) concentrations. The stoicheiometry of reaction with respect to arsenic(III) and chromium(VI) has been reported [8] as that in equation (1). The present work on the reaction between arsenic(III) and chromium(VI) was, therefore, initiated over a wide range of temperature and experimental conditions in an attempt to elucidate the mechanism of the reaction.

$$3As^{III} + 2Cr^{VI} \longrightarrow 3As^{V} + 2Cr^{III} \qquad (1)$$

EXPERIMENTAL

Sodium arsenite solution was prepared by a standard method using As_2O_3 (E. Merck) and NaOH (E. Merck). Inorganic materials were of E. Merck's grade. Dioxan and pyridine were purified by distillation.[9]

The reaction between arsenic(III) and chromium(VI) at low chromium(VI) concentrations was followed spectrophotometrically at 350 nm using a 0·5 cm cell in a Beckman DU model spectrophotometer; the details have been described elsewhere.[10] The reaction at high chromium(VI) concentrations was investigated titrimetrically following the procedure of Mason and Kowalak.[8] All the runs were carried out using an acetic acid–acetate ion buffer at constant pH 4·6. The ionic strength of the reaction mixture was adjusted by addition of sodium perchlorate where necessary. Experiments were carried out at 35 °C unless otherwise mentioned.

RESULTS

Pseudo-first-order rate constants (k_1) at low chromium(VI) concentrations were calculated from plots of log [Cr^{VI}] against time, t. Each reaction was carried out at an ionic strength of I = 1·0M. The concentrations of $HCrO_4^-$ were calculated from relation (2), assuming the concentration of the dimeric species $Cr_2O_7^{2-}$ as the total chromium(VI) concentration, where Cr^{VI} and $HCrO_4^-$ denote total and reacting species of chromium(VI) respectively. The value of the equilibrium constant K_d for the reaction $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ at 35 °C has been reported [11] to be 76 l mol^{-1} at I = 1·0M and was used for the calculation of $HCrO_4^-$ concentrations. The dissociation $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$ was, however, neglected for the equilibrium constant K_d' is 1·75 × 10^{-6} mol l^{-1} in comparison with the hydrogen-ion concentration of the medium which is 2·5 × 10^{-5} mol l^{-1}. Values of $k_1[Cr^{VI}]/[HCrO_4^-]$ at total chromium(VI) concentrations of 2·02 × 10^{-4}, 4·04 × 10^{-4}, 8·10 × 10^{-4}, and 16·20 × 10^{-4}M have been computed to be 0·95 × 10^{-2}, 0·92 × 10^{-2}, 0·99 × 10^{-2}, and 1·10 × 10^{-2} min^{-1} respectively. The results indicate that $HCrO_4^-$ is the reacting species at low chromium(VI) concentrations.

$$K_d = ([Cr^{VI}] - \tfrac{1}{2}[HCrO_4^-])/[HCrO_4^-]^2 \qquad (2)$$

The rate of oxidation increased with increase in the substrate concentration. The order with respect to arsenic(III) at low chromium(VI) concentrations can be expressed as in (3), where k and K denote the specific reaction rate and

$$\frac{-d[Cr^{IV}]}{dt} = \frac{kK[Cr^{VI}][As^{III}]}{1 + K[As^{III}]} \qquad (3)$$

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equilibrium constant for decomposition of the 1 : 1 complex. Plots of $1/k_1$ against $1/[\mathrm{As^{III}}]$ at different temperatures are shown in Figure 1. The equilibrium constants were calculated from the gradients and intercepts of this Figure. The enthalpy change associated with complex formation was calculated to be $-15{\cdot}2 \pm 2{\cdot}0$ kcal mol^{-1} from the gradient of a plot of log K against $1/T$ (Figure 2). Thermodynamic parameters (Table 4) associated with the equilibrium constant were then evaluated from the relations $\Delta G^0 = -RT \ln K$ and $\Delta H - T\Delta S^0$.

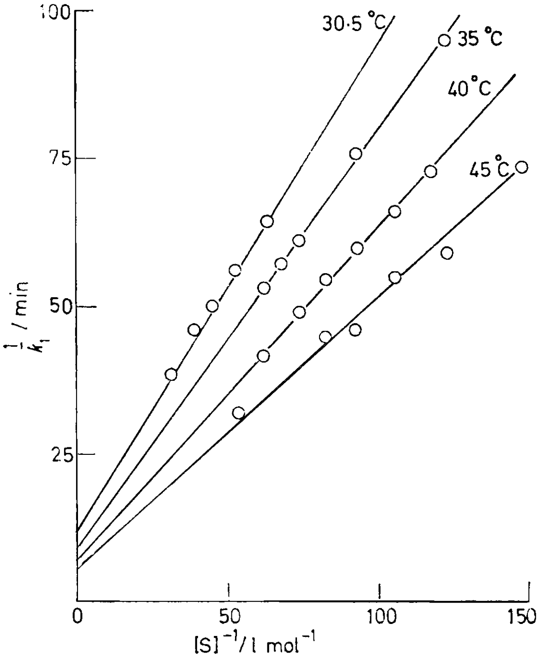

FIGURE 1 Plots of the reciprocal of the pseudo-first-order rate constant against the reciprocal of substrate concentration: $[\mathrm{Cr^{VI}}] = 4{\cdot}04 \times 10^{-4}$M; pH 4·6

Equation (4) was used to calculate second-order rate constants, k_2 at high chromium(VI) and low arsenic(III) concentrations. This equation is the integrated form of (5),

$$k_2 = \frac{6{\cdot}909}{t(3b - 2a)} \log \frac{a(3b - 2x)}{3b(a - x)} \tag{4}$$

$$\mathrm{d}x/dt = k_2(a - x)(b - \tfrac{2}{3}x) \tag{5}$$

where a = initial concentration of arsenic(III), b = initial concentration of chromium(VI) expressed as the monomer, and x = amount of reaction at time t. Rate constants obtained spectrophotometrically and titrimetrically were reproducible to within ±2 and ±3% respectively.

The increased rate of reaction on addition of sodium hydrogen phosphate has been studied (Table 1). A plot of log k_1 against ionic strength was linear, indicating reaction between an ion and uncharged molecule.[12] In the chromic acid oxidation of phenylphosphonous acid,[10] we have observed retardations in the presence of hydrogen phosphate anion. The contradiction obtained in the present study may be due to the fact that the hydrogen-ion concentration of the mixture is very small (*ca.* 10^{-4}M) in comparison with the previous study where the reaction was carried out in a great excess of $[\mathrm{H^+}]$ (> 1M), thereby minimising the formation of salts according to equation (6).[13,14]

TABLE 1

Effect of salt concentration on the pseudo-first-order rate constant k_1: $[\mathrm{Cr^{VI}}] = 4{\cdot}04 \times 10^{-4}$; $[\mathrm{As^{III}}] = 1{\cdot}45 \times 10^{-3}$M

10[Salt]/M	0	0·14	1·44	2·90
10^2k_1/min^{-1}	1·86	2·14	4·45	7·49

$$\mathrm{HCrO_4^-} + \mathrm{H^+} + \mathrm{A^-} \rightleftharpoons \mathrm{CrO_3A^-} + \mathrm{H_2O} \tag{6}$$

The reaction rate decreased with increase in solvent concentration; the latter was varied by addition of dioxan (v/v) to the reaction mixture (Table 2). A plot of log k_1 against $1/D$ or log k_2 against $1/D$ gave a straight line up to a dielectric constant (D) of *ca.* 48·6, with a negative gradient in each case, beyond which the lines curved upwards. The

TABLE 2

Effect of dielectric constant on the reaction rate: (*a*) $[\mathrm{As^{III}}] = 1{\cdot}45 \times 10^{-3}$, $[\mathrm{Cr^{VI}}] = 4{\cdot}04 \times 10^{-4}$, $I = 0{\cdot}42$M; (*b*) $[\mathrm{As^{III}}] = 1{\cdot}225 \times 10^{-2}$, $[\mathrm{Cr^{VI}}] = 10 \times 10^{-2}$, $I = 1{\cdot}05$M

Expt. no.	% Dioxan	(*a*) 10^2k_1/min^{-1}	(*b*) $10k_2$/ l mol^{-1} min^{-1}
(1)	0	1·86	9·44
(2)	10	0·92	8·42
(3)	20	0·46	7·73
(4)	30	0·44	7·62

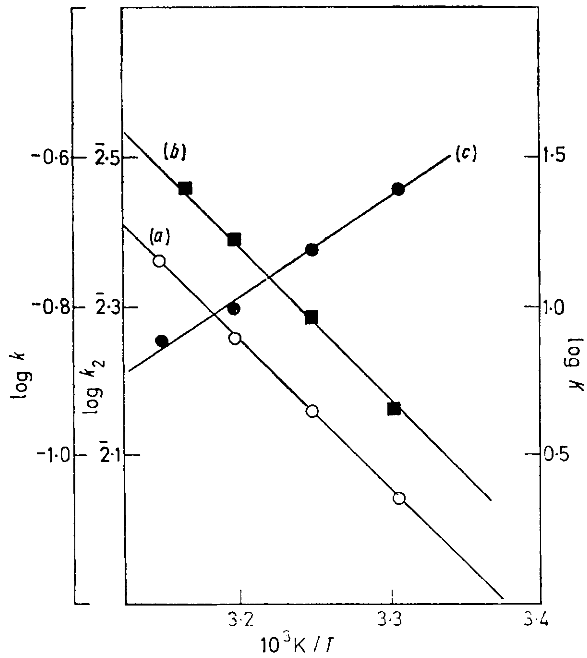

FIGURE 2 Variation of rate and equilibrium constants with temperature. Plots of (*a*) log k against $1/T$ for low chromium(VI) concentrations, (*b*) log k_2 against $1/T$ for high chromium(VI) concentrations, and (*c*) log K against $1/T$

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[12] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' John Wiley and Sons, New York, 1953, p. 140.

[13] D. G. Lee and R. Stewart, *J. Amer. Chem. Soc.*, 1964, **86**, 3051.

[14] K. B. Wiberg, 'Oxidation in Organic Chemistry,' Academic Press, New York, 1965, part A, p. 72.

addition of pyridine had no effect on the rate of reaction when [pyridine] $<$ [H$^+$], but at higher concentrations of the base, *e.g.* [pyridine] $> 2{\cdot}96 \times 10^{-3}$M, there was retardation. The retardation was appreciable (*ca.* 20%) when the pyridine concentration was 48×10^{-3}M. The results, however, indicate that pyridine does not catalyse the reaction (Table 3).

TABLE 3

Influence of pyridine on the reaction rate: [As^{III}] $= 1{\cdot}45 \times 10^{-3}$; [Cr^{VI}] $= 4{\cdot}04 \times 10^{-4}$; $I = 0{\cdot}42$M

10^3[Pyridine]/M	0	2·96	12·0	48·0
10^2k_1/min^{-1}	1·86	1·80	1·71	1·48

Values of k calculated from the intercepts of Figure 1 are recorded in Table 4. From the gradient of the plot of log k against $1/T$ (Figure 2) the energy of activation for the slow step (11) (see Discussion section) was calculated to be $9{\cdot}1 \pm 0{\cdot}6$ kcal mol^{-1}. Second-order rate constants at high chromium(VI) concentrations are recorded in Table 5.

TABLE 4

Equilibrium constants and thermodynamic constants for the 1 : 1 complex at different temperatures, together with activation parameters for the reaction at high arsenic(III) and low chromium(VI) concentrations

t/°C	10^2k/min^{-1} (K/l mol^{-1})	$-\Delta S^‡ \pm 0{\cdot}1$/ cal K^{-1} mol^{-1} ($\Delta S^0 \pm 0{\cdot}6$/ cal K^{-1} mol^{-1})	$-\Delta G^‡ \pm 0{\cdot}12$/ kcal mol^{-1} ($\Delta G^0 \pm 0{\cdot}03$/ kcal mol^{-1})
30·5	8·62 (25·1)	43·7 (43·9)	10·8 (1·92)
35·0	11·43 (15·4)	43·5 (44·3)	10·4 (1·67)
40·0	14·29 (9·8)	43·6 (44·2)	10·5 (1·42)
45·0	18·18 (6·2)	43·1 (44·3)	10·5 (1·16)

* Figures in parentheses represent values for the complex.

TABLE 5

Activation parameters for the reaction at low arsenic(III) and high chromium(VI) concentrations of $10{\cdot}0 \times 10^{-2}$M

t/°C	10^3[As^{III}]/ M	$10k_2$/s^{-1}	$-\Delta S^‡ \pm 0{\cdot}15$/ cal K^{-1} mol^{-1}	$\Delta G^‡ \pm 0{\cdot}1$/ kcal mol^{-1}
30·0	3·24	1·46	39·8	21·5
	2·66	1·41		
	3·98	1·45		
35·0	8·88	1·96	40·3	21·3
	7·56	1·89		
	6·30	1·88		
	5·45	1·97		
40·0	8·88	2·39	39·8	21·5
	7·56	2·47		
	6·30	2·44		
	5·04	2·50		
44·7	8·88	2·85	39·9	21·5
	7·56	2·87		
	6·30	2·92		
	5·04	2·92		

Averages of these rate constants were utilised in calculating the energy of activation for the slow step (14) from a plot of log k_2 against $1/T$ (Figure 2); the value has been found to be $9{\cdot}4 \pm 0{\cdot}1$ kcal mol^{-1}. The two values are almost of the same order indicating that the same type of mechanism may be operative in both cases. Values of pZ, where p is the probability or steric factor and Z the collision number, at different temperatures were then calculated by equating experimentally obtained rate constants with $pZ\mathrm{e}^{-E/RT}$ and have been computed to be $(5{\cdot}1 \pm 0{\cdot}4) \times 10^3$ and $(8{\cdot}94 \pm 1{\cdot}6) \times 10^4$ s^{-1} for steps (11) and (14). Entropies and free energies of activation were then calculated from the relations $pZ = \mathrm{e}^n(RT/N\boldsymbol{h}) \exp (\Delta S^‡/R)$ [where $n = 1$ for step (11) and $n = 2$ for the bimolecular process (14)] and $\Delta G^‡ = \Delta H^‡ - T\Delta S^‡$. The results are summarised in Tables 4 and 5.

It has been pointed out by Nikolov [15] that there exists a relation between activation energies and oxidation potentials for two redox reactions using the same substrate. The energy of activation for vanadium(V) oxidation of arsenic(III),[3] which is a bimolecular reaction, has been found to be 7·1 kcal mol^{-1}, whereas the activation energy in the present study is 9·44 kcal mol^{-1}, for the strictly bimolecular reaction. Considering the oxidation potentials of the chromium(VI)–chromium(III) and vanadium(V)–vanadium(IV) couples as 1·36 and 1·0 V respectively, the ratios of the two parameters are found to be 1·34 and 1·36 : 1 respectively, thus supporting the proposition made by Nikolov.[15]

DISCUSSION

The paths by which arsenic(III) is oxidised by one- and two-equivalent reagents have been the subject of much discussion,[16] mainly concerned with the possibility of arsenic(IV) as an intermediate.[17-19] Watanabe and Westheimer [20] from a detailed analysis of the induced oxidation of manganese(II) and iodide ions in the chromate–arsenate reaction in an acidic medium concluded that chromium(IV) is the unstable oxidation state and formation of arsenic(IV) is improbable. Moreover, it has been argued by Waters *et al.*[16] that arsenic(III) is not oxidised by one-electron oxidants without the addition of a catalyst, but is readily oxidised by two-electron oxidants. The reaction at low chromium(VI) concentrations may therefore be explained according to steps (10)—(13), where a 1 : 1 complex is formed initially by condensation of arsenic(III) with chromium(VI). The complex then decomposes slowly to give an arsonium ion of the type $>\overset{+}{\text{As}}{=}\text{O}$ and chromium(IV). The arsonium ion finally, by reacting with water, produces the stable product arsonic acid. Chromium(IV), on the other hand, is a highly reactive species and besides steps (7) and (8), which have been considered in many reactions,[5] its reaction with substrate to give chromium(III) according to step (9) is also known.[21]

$$2\,\mathrm{Cr^{IV}} \longrightarrow \mathrm{Cr^{III}} + \mathrm{Cr^{V}} \qquad (7)$$

$$\mathrm{Cr^{IV}} + \mathrm{Cr^{VI}} \longrightarrow 2\mathrm{Cr^{V}} \qquad (8)$$

$$\mathrm{Cr^{IV}} + \mathrm{e^-} \longrightarrow \mathrm{Cr^{III}} \qquad (9)$$

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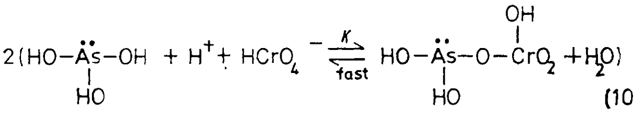
[21] G. P. Haight, J. Tracy, J. Huang, and B. Z. Shakhashiri, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2169.

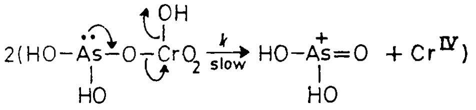
Oxidation-potential data of several species of chromium[5] as well as of arsenic[3] which are mentioned below provide information regarding the reactivity of chromium(IV) in the present reaction.

Redox couple	E^0/V
$\mathrm{Cr^{V}{-}Cr^{III}}$	$\geqslant 1{\cdot}75$
$\mathrm{Cr^{IV}{-}Cr^{III}}$	$> 1{\cdot}75$
$\mathrm{Cr^{VI}{-}Cr^{III}}$	$1{\cdot}36$
$\mathrm{As^{V}{-}As^{III}}$	$0{\cdot}56$

The above data indicate that chromium(IV) should react more readily with arsenic(III) than chromium(VI) and formation of chromium(V) by step (8) is improbable, since E^0 for the $\mathrm{Cr^{VI}{-}Cr^{III}}$ couple is greater than that for $\mathrm{As^{V}{-}As^{III}}$. Moreover, a free radical would be generated in solution if chromium(IV) reacted with the substrate according to step (9). The addition of acrylamide to the reaction mixture failed to induce polymerisation indicating the absence of free radicals in solution. Consequently, chromium(IV), which is generated in step (11), should undergo disproportionation to give chromium(III) and chromium(V), the latter reacting with arsenic(III) to give the arsonium ion according to step (12). Thus two thirds of the total oxidation is affected by chromium(VI) and one third by chromium(V) according to the following mechanism.

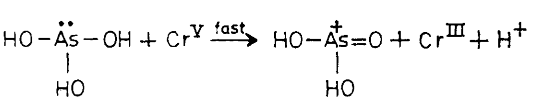


$$2\left(\mathrm{HO{-}\underset{HO}{\ddot{A}s}{-}OH} + \mathrm{H^+} + \mathrm{HCrO_4^-} \underset{fast}{\overset{K}{\rightleftharpoons}} \mathrm{HO{-}\underset{HO}{\ddot{A}s}{-}O{-}\overset{OH}{Cr}O_2} + \mathrm{H_2O}\right) \qquad (10)$$

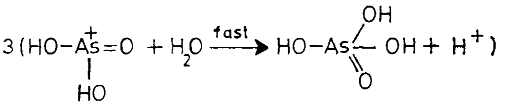


$$2\left(\mathrm{HO{-}\underset{HO}{\ddot{A}s}{-}O{-}\overset{OH}{Cr}O_2} \xrightarrow[slow]{k} \mathrm{HO{-}\underset{HO}{\overset{+}{A}s}{=}O} + \mathrm{Cr^{IV}}\right) \qquad (11)$$

$$2\mathrm{Cr^{IV}} \xrightarrow{fast} \mathrm{Cr^{III}} + \mathrm{Cr^{V}} \qquad (7)$$

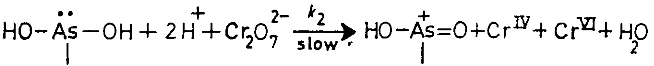


$$\mathrm{HO{-}\underset{HO}{\ddot{A}s}{-}OH} + \mathrm{Cr^{V}} \xrightarrow{fast} \mathrm{HO{-}\underset{HO}{\overset{+}{A}s}{=}O} + \mathrm{Cr^{III}} + \mathrm{H^+} \qquad (12)$$



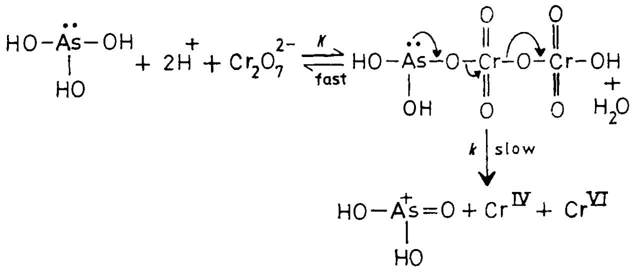
$$3\left(\mathrm{HO{-}\underset{HO}{\overset{+}{A}s}{=}O} + \mathrm{H_2O} \xrightarrow{fast} \mathrm{HO{-}\underset{\|\,O}{\overset{OH}{As}}{-}OH} + \mathrm{H^+}\right) \qquad (13)$$

The absence of complex formation at high chromium(VI) concentrations indicates that the arsonium ion is formed directly by the interaction of arsenic(III) with $\mathrm{Cr_2O_7^{2-}}$. It has been assumed that one $\mathrm{Cr_2O_7^{2-}}$ is equivalent to two $\mathrm{Cr^{VI}}$ species and the reaction is as in equation (14), followed by step (13). The activation parameters which have been calculated are not widely different and indicate further that the same type of mechanism may also be operative in the latter case.



$$\mathrm{HO{-}\underset{HO}{\ddot{A}s}{-}OH} + 2\mathrm{H^+} + \mathrm{Cr_2O_7^{2-}} \xrightarrow[slow]{k_2} \mathrm{HO{-}\underset{HO}{\overset{+}{A}s}{=}O} + \mathrm{Cr^{IV}} + \mathrm{Cr^{VI}} + \mathrm{H_2O} \qquad (14)$$

Although the reaction is strictly bimolecular at high chromium(VI) concentrations, the possibility of reaction *via* intermediate complex formation is, however, not improbable and the formation of a less stable complex between arsenic(III) and $\mathrm{Cr_2O_7^{2-}}$ is also possible prior to formation of the arsonium ion according to the following scheme, followed by step (13). However, if any such complex is formed in a large excess of chromium(VI), it would be very unstable because of the strong electron pull of $\mathrm{Cr_2O_7^{2-}}$. On the other hand, at low chromium(VI) concentrations, when $[\mathrm{As^{III}}] > [\mathrm{Cr^{VI}}]$, all the chromium(VI) remains in the form of a complex and this would be more stable. Thus the stability of the complex plays an important role in determining the order of the reaction and hence the order is strictly bimolecular at high chromium(VI) concentrations.



$$\mathrm{HO{-}\underset{HO}{\ddot{A}s}{-}OH} + 2\mathrm{H^+} + \mathrm{Cr_2O_7^{2-}} \underset{fast}{\overset{K}{\rightleftharpoons}} \mathrm{HO{-}\underset{OH}{\ddot{A}s}{-}O{-}\underset{O}{\overset{O}{Cr}}{-}O{-}\underset{O}{\overset{O}{Cr}}{-}OH} + \mathrm{H_2O}$$

$$\xrightarrow[slow]{k} \mathrm{HO{-}\underset{HO}{\overset{+}{A}s}{=}O} + \mathrm{Cr^{IV}} + \mathrm{Cr^{VI}}$$

We thank Professor M. N. Das for constant encouragement and the C.S.I.R. for award of a fellowship (to J. K. C.).

[3/095 *Received*, 15*th January*, 1973]