

KINETICS AND MECHANISM OF OXIDATION OF SELENIUM(IV) BY PERMANGANATE ION IN AQUEOUS PERCHLORATE SOLUTIONS

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Received January 7, 1992

Accepted May 27, 1992

The kinetics of permanganate oxidation of selenium dioxide in perchloric acid solutions at a constant ionic strength of 2.0 mol dm^{-3} has been investigated spectrophotometrically. A first-order reaction in $[\text{MnO}_4^-]$ and fractional order with respect to selenium(IV) were observed. The reaction rate was found to be pH-independent at lower acid concentrations ($[\text{H}^+] < 0.5 \text{ mol dm}^{-3}$) and was acid-catalyzed beyond this range. Addition of Mn^{2+} and F^- ions leads to the prediction that MnO_4^- is the sole reactive species in the oxidation process. A tentative reaction mechanism consistent with the reaction kinetics has been proposed.

Although the oxidation of selenious acid by potassium permanganate at lower concentrations of sulfuric acid ($\leq 0.6 \text{ mol dm}^{-3}$) was reported by Keshava and Haldar¹, a detailed reaction mechanism has not yet been established. This redox reaction, merits further investigation using moderate concentrations of perchloric acid as a non-complexing agent in order to shed more light on the reaction mechanism. Also, it would be of interest to extend investigations on redox systems including selenium(IV) (ref.²) or permanganate ions³⁻⁷.

EXPERIMENTAL

Materials and Methods

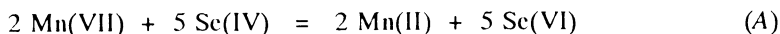
All materials were of analytical grade. Doubly distilled water was used in all preparations. Temperature was controlled within $\pm 0.1^\circ\text{C}$. The preparation and standardization of the stock solutions of selenium dioxide (BDH) and potassium permanganate (BDH) were made as described earlier^{2,3}. Absorbance vs concentration plots for acidified permanganate ion showed that Beer's law is obeyed at wavelengths 526 and 566 nm, where the molar absorption coefficients were 2.245 ± 18 and $1.265 \pm 10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively, in good agreement with previous results⁸. Sodium perchlorate was prepared by neutralization of a slurry of sodium carbonate (Analar) with 60% perchloric acid (BDH). Solid sodium perchlorate was obtained by partial crystallization followed by three recrystallization as described elsewhere⁶.

All kinetic measurements were carried out under pseudo first-order conditions where the $[\text{Se(IV)}]$ is present in a large excess over permanganate ion concentration. Kinetic measurements were carried out in the same way as described previously^{7,8}. The course of the reaction was followed spectrophotometrically by recording a decrease in the absorbance of permanganate ion at 526 nm (absorption maximum) as a

function of time. It was proved that there is no interference from other reagents at this wavelength. The values of the observed first-order rate constants, k_{obs} , and the second order rate constants, k_2 , were calculated using the least squares method.

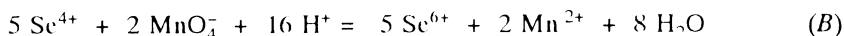
RESULTS

The estimated reduction potential for Mn(VII)/Mn(II) (+1.51 V) and Se(VI)/Se(IV) (+0.47 V) pairs⁹ provide evidence that the reaction (A) is favoured thermodynamically and should go to completion.

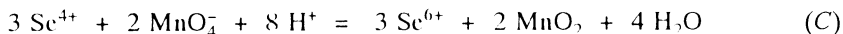


Stoichiometry

The spectrophotometric measurements with solutions of Se(IV) and MnO_4^- ions of different initial proportions ($10^{-3} \sim 10^{-4} \text{ mol dm}^{-3}$) revealed the complete reduction of the permanganate to the manganous ion when the molar ratio of Se(IV)/ MnO_4^- was ≥ 2.5 . The reaction takes place in few minutes, as indicated by the complete disappearance of the pink color of the manganate ion and by the formation of colorless solutions of the product. The stoichiometric equation of the overall reaction can be expressed as follows (Eq. (B)).



On the other hand, when the ratio of $[\text{Se(IV)}]_0/[\text{MnO}_4^-]_0$ is ≤ 1.5 , the reduction of the permanganate takes place with the formation of MnO_2 as a precipitate. The net reaction can be expressed stoichiometrically by Eq. (C).



Under the experimental conditions examined, the oxidation of Se(IV) by MnO_2 was found to be much slower than that by MnO_4^- ion and, hence, it could be neglected at least to two-half lives of the oxidation.

Selenium(IV) Species

The dissociation constant of H_2SeO_3 acid is (refs^{10,11}) $3 \cdot 10^{-3} \text{ mol dm}^{-3}$ at 25 °C. Again, Se(IV) is dimerizable in its concentrated solutions¹¹ with a dimerization constant of 5.6 ± 1.0 at ionic strength of unity (NaClO_4) and at 25 °C. In view of this dimerization, the present experiments were carried out with Se(IV) concentrations starting from $(1 - 5) \cdot 10^{-3} \text{ mol dm}^{-3}$, where the percentage of the monomer was as high

as 97 – 93%. Hence, SeO_2 may be presumed to exist as the monomer¹ under all the experimental conditions used.

Rate Dependence on $[\text{MnO}_4^-]$ and $[\text{Se(IV)}]$

The reaction order with respect to permanganate ion was determined by studying the oxidation reaction under pseudo-first order conditions where selenium(IV) was maintained in a large excess over permanganate ion concentrations. Plots of $\ln(\text{absorbance})$ vs time were linear to 90% completion of the reaction. This linearity shows that the reaction is first order in $[\text{MnO}_4^-]$. The pseudo first-order rate constants were determined from the gradients of such plots. The results are summarized in Table I. However, the first-order rate constant with respect to $[\text{Se(IV)}]$ was not obeyed as shown in Table I.

Some kinetic runs were performed under second-order conditions where the ratio of $[\text{Se(IV)}]_0/[\text{MnO}_4^-]_0$ was ≈ 2.5 . The second-order rate constants, k_2 , were calculated from the Eq. (1)

$$\frac{dx}{dt} = k_2 \left(a - \frac{5}{2}X \right) (b - X), \quad (1)$$

where a and b are the initial concentrations of Se(IV) and MnO_4^- , respectively, and X was the amount of the MnO_4^- which has disappeared at time t . Equation (1) was integrated and reformulated to Eq. (2), which was used to calculate the second-order rate constants (k_2), ϵ is the molar absorption coefficient

$$\begin{aligned} \ln \left(\frac{\epsilon [2 [\text{Se(IV)}]_0 - 5 [\text{MnO}_4^-]_0]}{2 \text{ Abs}} + 2.5 \right) &= \\ &= k_2 t (2 [\text{Se(IV)}]_0 - 5 [\text{MnO}_4^-]_0) + C \end{aligned} \quad (2)$$

TABLE I

Rate constants k_{obs} and k_2 for the oxidation of Se(IV) by MnO_4^- ion. $[\text{MnO}_4^-] = 2.21 \cdot 10^{-4}$, $[\text{H}^+] = 1.0$, $I = 2.0 \text{ mol dm}^{-3}$, 25°C

$[\text{Se(IV)}] \cdot 10^3$ mol dm^{-3}	$k_{\text{obs}} \cdot 10^2$ s^{-1}	k_2 $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
2.01	1.80	8.96
2.50	2.28	9.12
3.03	2.79	9.21
3.52	3.31	9.40
4.02	3.83	9.53

of MnO_4^- at 525 nm, Abs is the absorbance at time t and C is constant. Plots of the left-hand side of Eq. (2) against time were fairly linear for more than two half-lives of the reaction. The values of k_2 were found to be slightly dependent on $[\text{Se(IV)}]_0$. The consistency between the values of the second-order rate constants, k_2 , evaluated by the two methods (within experimental errors) confirms the reproducibility of the results obtained.

Rate Dependence on $[\text{H}^+]$

At lower acid concentrations ($[\text{H}^+] \leq 0.5 \text{ mol dm}^{-3}$), the observed first-order rate constants were found to be pH-independent, whereas they increased with increasing hydrogen ion concentrations beyond $[\text{H}^+] > 0.5 \text{ mol dm}^{-3}$. The results are summarized below $[\text{Se(IV)}] = 4.02 \cdot 10^{-3}$, $[\text{MnO}_4^-] = 2.21 \cdot 10^{-4}$, $I = 2.0 \text{ mol dm}^{-3}$, 25°C):

$[\text{H}^+]$, mol dm^{-3}	0.13	0.25	0.50	1.00	1.51	2.00
$k_{\text{obs}} \cdot 10^2$, s^{-1}	3.02	3.04	3.02	3.83	4.14	4.59

Rate Dependence on Added Salts

Since Mn^{2+} is one of the reaction products, its effect on the rate of the reaction had to be examined. It has been reported^{12,13} that the acidified permanganate ion is reduced by Mn^{2+} to Mn^{3+} and Mn^{4+} ions. It was found that the variation of $[\text{Mn}^{2+}]_0$ had an appreciable effect on the rate of the reaction. As the initial concentration of Mn^{2+} increased, the rate progressively decreased. The values of k_{obs} at $[\text{Mn}^{2+}] = 0, 2.5 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ and fixed $[\text{H}^+] = 1.0$, $[\text{MnO}_4^-] = 2.2 \cdot 10^{-4}$, $[\text{Se(IV)}] = 2 \cdot 10^{-3} \text{ mol dm}^{-3}$ and 25°C are $1.8 \cdot 10^{-2}$, $1.5 \cdot 10^{-2}$ and $1.4 \cdot 10^{-2} \text{ s}^{-1}$, respectively. This result indicates that neither Mn^{3+} nor Mn^{4+} is involved in the oxidation process. Again, the addition of sodium fluoride¹⁴ does not affect the reaction rate significantly. This also means that Mn^{3+} and Mn^{4+} are not the reactive species under experimental conditions, since if they were, the reaction would exhibit an induction period or a decrease in the rate after the addition of such a complexing agent.

DISCUSSION

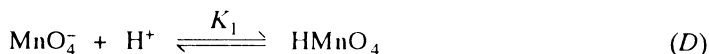
The first- and fractional-order dependences on the oxidant and reduction concentrations suggest the rate expression (3), where n is a fractional order.

$$\text{rate} = k_2[\text{oxidant}][\text{reductant}]^n \quad (3)$$

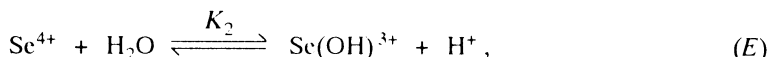
The slight deviation of the reaction order from unity with respect to the reductant may be explained by the formation of an intermediate complex between Se(IV) and

MnO_4^- or by the formation of a dimer species $[\text{Se(IV)}]_2$. Under experimental conditions, the main reaction species of selenium(IV) are the monomers, while the dimer is less reactive and, hence, may be neglected. Therefore, it may be suggested that more than one reductant complex can exist at slightly higher concentration of Se(IV) . At least one of these formed complexes appears to accelerate the oxidation process since increasing $[\text{Se(IV)}]_0$ tends to increase the reaction rate.

In acid solutions, permanganate ion tends to exist as the protonated species HMnO_4 (ref.¹⁵) (see Eq. (D)).

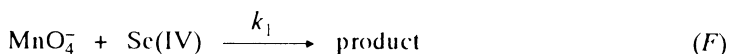


At low acid concentration ($[\text{H}^+] < 0.5 \text{ mol dm}^{-3}$), the pH-independence of the rate constant may suggest the hydrolysis of Se(IV) species^{10,11} as follows,



where K_1 and K_2 are the protonation and hydrolysis constants of MnO_4^- and Se(IV) ions, respectively.

The most likely reaction mechanism which can be suggested involves the following two competitive reactions.



Considering that reactions (F) and (G) are the rate-determining steps, the change in the rate constant with the change of the substrate and hydrogen ion concentrations can be expressed by the relationship (4)

$$\text{rate} = \frac{(k_1 + k_2 K_1 K_2) [\text{Se(IV)}][\text{MnO}_4^-]_{\text{T}}}{1 + K_1 [\text{H}^+]}, \quad (4)$$

where $[\text{MnO}_4^-]_{\text{T}}$ denotes the total analytical concentration of permanganate ion. Under the experimental conditions examined, $K_1 [\text{H}^+] \ll 1$, and, hence Eq. (4) takes the form (5).

$$\text{rate} = (k_1 + k_2 K_1 K_2) [\text{Se(IV)}][\text{MnO}_4^-]_{\text{T}} \quad (5)$$

In the presence of a large excess of Se(IV) over that of MnO_4^- ion concentration, the rate law is expressed by Eq. (6).

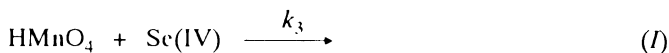
$$\text{rate} = k_{\text{obs}} [\text{MnO}_4^-]_{\text{T}} \quad (6)$$

From comparison of Eqs (5) and (6) it follows that

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_1} + \frac{1}{k_2 K_1 K_2} \right) \frac{1}{[\text{Se(IV)}]} \quad (7)$$

The absence of H^+ ion term in Eqs (6) and (7) confirms that the rate constant is independent of the hydrogen ion concentration as observed by Keshava and Haldar¹ earlier. Again, Eq. (7) requires the plots of $1/[\text{Se(IV)}]$ against $1/k_{\text{obs}}$ to be linear, as found experimentally.

On the other hand, at the higher acid concentrations $[\text{H}^+] > 0.5 \text{ mol dm}^{-3}$, the dependence of the rate constants on the hydrogen ion concentration suggests that the hydrolyzed species of selenium(IV), Se(OH)^{3+} , is small, and, hence the mechanism of the redox reaction is consistent with the competitive reactions (H) and (I) in the rate-determining steps.



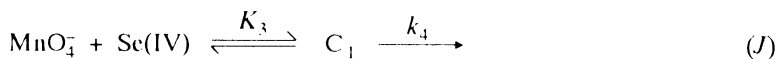
The change in the observed first-order rate constant with the change of the substrate and H^+ concentrations may be written as follows

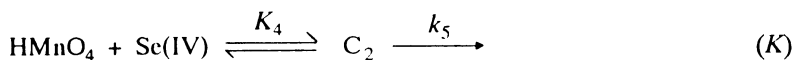
$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_1} + \frac{[\text{H}^+]^{-1}}{k_3'} \right) \frac{1}{[\text{Se(IV)}]} \quad (8)$$

where $k_3' = k_3 K_1$.

At constant $[\text{H}^+]$, a plot of $(k_{\text{obs}})^{-1}$ versus $[\text{Se(IV)}]^{-1}$ was found to be linear with a negligible intercept on $(k_{\text{obs}})^{-1}$ axis (Fig. 1). Again, $1/k_2$ against $1/[\text{H}^+]$ plots gave good straight lines from whose slopes and intercepts the values of k_1 and k_3' were calculated, respectively (Fig. 2). These values were calculated using the least-squares method and are summarized in Table II. Using K_1 value reported elsewhere, the k_3 value was found to be $1.23 \cdot 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C . The activation parameters of k_1 and k_3' were evaluated using Eyring's equation and are summarized in Table III.

An alternative reaction mechanism involving intermediate ion complexes C_1 and C_2 may be described as follows (Eqs (J) and (K)).





The complexes are formed and subsequently undergo further decomposition to give the reaction products. The variation of the rate constant with the change of the Se(IV) and hydrogen ion concentrations may be expressed by Eq. (9).

$$\text{rate} = \frac{(k_4 K_3 + k_5 K_1 K_4 [\text{H}^+]) [\text{Se(IV)}] [\text{MnO}_4^-]}{1 + K_1 [\text{H}^+] + K_3 [\text{Se(IV)}] + K_1 K_4 [\text{H}^+] [\text{Se(IV)}]} \quad (9)$$

Under our experimental conditions of low [Se(IV)], the terms in the numerator are negligibly small. Therefore, Eq. (9) can be rewritten similar to Eq. (8).

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_4 K_3} + \frac{1}{k_5 K_1 K_4 [\text{H}^+]} \right) \frac{1}{[\text{Se(IV)}]} \quad (10)$$

Unfortunately, the formation of such intermediates C_1 and/or C_2 could not be detected experimentally.

Again, in view of the behaviour of the added salts on the rate of the reaction, it may be suggested that MnO_4^- ion is the sole reactive species responsible for the oxidation process. In connection with this redox system of multi-equivalent changes, the most

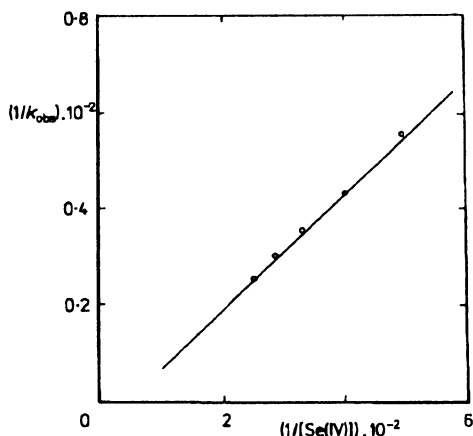


FIG. 1
Plot of $1/k_{\text{obs}}$ vs $1/[\text{Se(IV)}]$ ($\text{dm}^3 \text{ mol}^{-1}$) in the oxidation of Se(IV) by MnO_4^- ion. $[\text{MnO}_4^-] = 2.21 \cdot 10^{-1}$, $[\text{H}^+] = 1.0$, $I = 2.0 \text{ mol dm}^{-3}$, 25°C

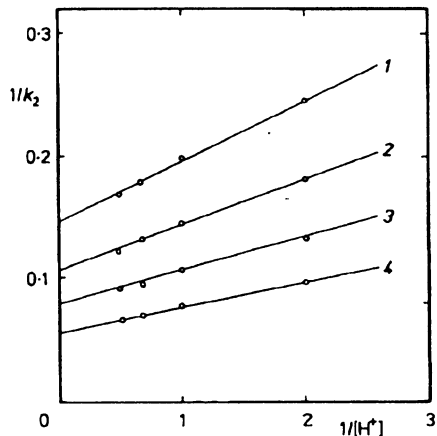
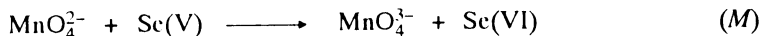
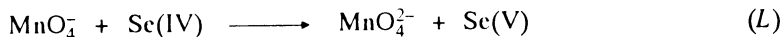
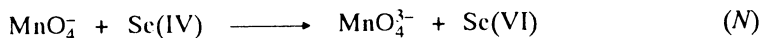


FIG. 2
Plots of $1/k_2$ vs $1/[\text{H}^+]$ ($\text{dm}^3 \text{ mol}^{-1}$) in the oxidation of Se(IV) by MnO_4^- ion. $[\text{MnO}_4^-] = 2.21 \cdot 10^{-1}$, $[\text{Se(IV)}] = 4.02 \cdot 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$. 1 15°C , 2 20°C , 3 25°C and 4 30°C

particular interest is whether electron transfer proceeds through successive one-electron changes (Eqs (L) and (M)):



or by two-electron transfer in a single step (Eq. (N)).



Assuming the steady state approximation of Se(V) in the former mechanism, a rate equation similar to that defined by expression (3) is obtained. It appears that while the one-equivalent pathway is more favourable on energetic grounds, the presence of two unstable transition for Se(V) and Mn(VI) is less probable and undesirable.

The thermodynamic parameters observed for a series of common reactions may be considered as a good evidence in support of the reaction mechanism¹⁶⁻¹⁸. The entropy of activation for the decomposition of the intermediate complexes in the rate-determining steps were found to be negative in accordance to the proposals made by Moore and Hicks^{16,17} for an intermediate complex formation. In view of these facts, we prefer an inner-sphere two-electron transfer mechanism proceeding via complex formation for the oxidation of Se(IV) by MnO_4^- ion. In this context it should be noted that there does

TABLE II

The values of k_1 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) and k_3' ($\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$). $[\text{Se(IV)}] = 4.02 \cdot 10^{-3}$, $[\text{MnO}_4^-] = 2.21 \cdot 10^{-4}$, $I = 2.0 \text{ mol dm}^{-3}$

Quantity	15 °C	20 °C	25 °C	30 °C
k_1	6.79	9.42	12.73	17.52
k_3'	20.66	27.02	36.87	52.49

TABLE III

Activation parameters for the oxidation of Se(IV) by MnO_4^- ion

Pathway	ΔS^* $\text{J K}^{-1} \text{mol}^{-1}$	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}
k_1	-78.75	43.12	66.59
k_3'	-71.75	42.53	63.91

not appear any confirmation of outer-sphere two electron transfer process^{5,19}, which in turn supports our suggestion.

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