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Kinetics of Oxidation of Methyl Orange & Methyl Red by V(V)*

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The kinetics of oxidation of methyl orange and methyl red by V(V) has been investigated in aqueous perchloric and sulphuric acid media. In perchloric acid medium, reaction obeys the rate law:

$$\frac{-d}{dt}[V(V)] = k'[VO_2^+]\ [Dye] + k''K_1[VO_2^+]\ [Dye]\ [H^+]^2$$

$H_2PO_4^-$, HSO_4^- and Cl ions are found to accelerate the reaction in the order, $H_2PO_4^- > HSO_4^- > Cl^-$. This has been ascribed to additional vanadium(V) species formed with these anions. The activation parameters have been determined and plausible mechanism proposed.

THOUGH kinetics of oxidation of a number of organic compounds by vanadium(V) have been reported, kinetic study of oxidation of aromatic azo compounds by V(V) has not been made so far. A detailed kinetic study of oxidation of methyl orange and methyl red in aqueous perchloric and sulphuric acid media has now been carried out. The influence of the added anions $H_2PO_4^-$, HSO_4 and Cl^- on the reaction has also been investigated. The results enable us to understand the nature of the species involved in the reaction and their relative reactivities.

Materials and Methods

All the chemicals used were of AR grade. Sodium vanadate solution was prepared and standardized according to the method of Gopala Rao and coworkers[1]. Methyl orange and methyl red solutions were standardized according to the method of Knecht and Hibbert[2].

Rate measurements — The course of the reaction was followed by measuring the optical density of the unreacted dye with a Klett-Summerson colorimeter using 540 nm filter. Under these conditions Beer's law was obeyed by both the dyes which have absorption maxima in this range.

Stoichiometry — The stoichiometry of the reaction was determined by mixing methyl orange or methyl red in $3M$ H_2SO_4 with a known excess of V(V) and the excess V(V) back-titrated with standard Mohr's salt, after the completion of the reaction which is indicated by the discharge of the pink colour of the dye in acid solution. One mole of either of the dyes was found to consume four moles of V(V). The authors also found that the products are the corresponding nitroso compounds which were detected using spot tests prescribed by Feigl[3]. The test for nitro compounds[3] gave a negative result. It was further found that under the experimental conditions employed in the kinetic study, there was no detectable interaction between V(V) and dimethylaniline during the time taken for following the kinetic run, showing that $-N(CH_3)_2$ group present in these dyes is not involved in the oxidation. It is believed that the site of attack by V(V) is the $-N{=}N-$ bond which by the uptake of two oxygen atoms yields nitroso compounds. This is in conformity with the stoichiometry of the reaction.

The authors employed the vinyl polymerization test described by Waters and Littler[4] for the detection of any free radical intermediate in the reaction. The test gave a negative result.

Results

The reaction is found to be first order in methyl orange or methyl red as evidenced by the plot of log (OD) versus time, which was linear under the conditions $[V(V)] \gg [Dye]$. The pseudo-first order constant (k_1) was calculated from the slope of the linear plot.

The values of k_1 were determined at varying $[V(V)]$ keeping the concentrations of either of the dyes and H^+ ion constant. Plot of k_1 versus $[V(V)]$ was linear passing through origin showing that the reaction is first order with respect to V(V) (Fig. 1).

The rate data in acid solutions of constant ionic strength yield a linear plot of k_1 against $[H^+]^2$ in both perchloric and sulphuric acid media (Fig. 2). However, a positive intercept was observed in both the acids indicating that the reaction involves two paths, one with a rate independent of H^+ ion and the other with a rate directly proportional to $[H^+]^2$. In the calculation of $[H^+]$ in H_2SO_4 medium which has a low second dissociation constant of 0·0097 any contribution by HSO_4^- has been neglected because it does not introduce appreciable error. Thus sulphuric acid was also regarded as a monobasic acid like perchloric acid and the ionic strength in the runs was maintained constant by adding $NaHSO_4$.

The results indicate that the reaction is much slower in perchloric acid than in sulphuric acid medium. Kinetic runs were also made by adding sodium bisulphate or sodium chloride maintaining the ionic strength constant with sodium perchlorate. A linear increase of rate with $[HSO_4^-]$ or $[Cl^-]$ is observed in the case of oxidation of both the dyes leaving an intercept on k_1 axis (Fig. 3). In the case of dihydrogen phosphate ion plot of k_1 versus

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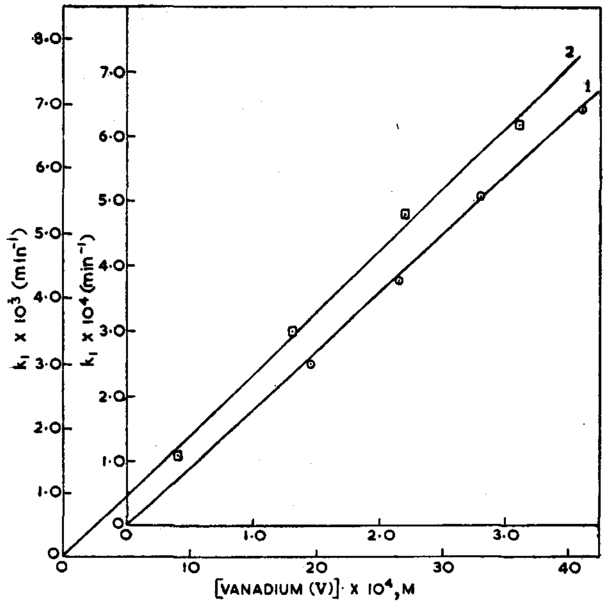


Fig. 1 — Plots of k_1 versus [V(V)] {For curve 1, [methyl orange] = 2·4 × $10^{-5}M$; [H_2SO_4] = 0·5*M*; [HSO_4^-] = 0·5*M*. For curve 2 [methyl red] = 2·4 × $10^{-5}M$; [H_2SO_4] = 0·5*M*; [HSO_4^-] = 0·5*M*; temp. = 30° ± 0·1°}

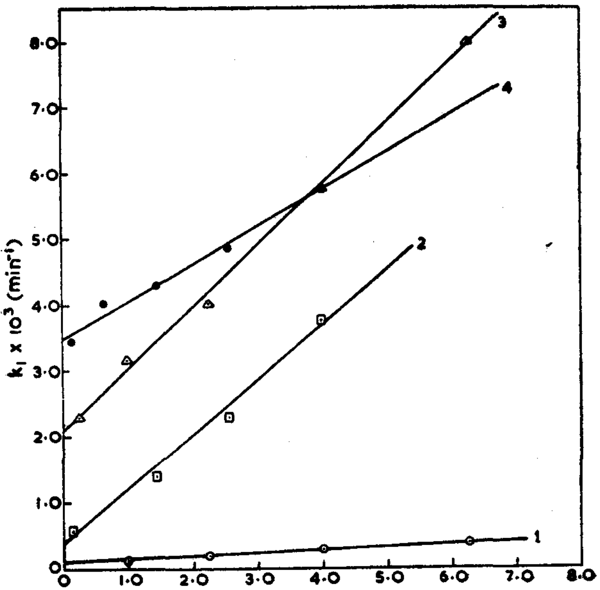


Fig. 2 — Plots of k_1 versus $[H^+]^2$ {[V(V)] = 1·0 × $10^{-3}M$; [methyl orange] = 2·4 × $10^{-5}M$; [ClO_4^-] = 3·0*M* (curve 1); and [HSO_4^-] = 3·0*M* (curve 3). [V(V)] = 1·0 × 10^{-3} *M*; [methyl red] = 1·4 × $10^{-5}M$; [ClO_4^-] = 2·0*M* (curve 2); [HSO_4^-] = 2·0*M* (curve 4); temp. = 30° ± 0·1°}

[$H_2PO_4^-$] was linear passing through origin showing direct dependence of rate on [$H_2PO_4^-$].

Reactive species of V(V)— In mineral acid solutions below *p*H 2·2 V(V) is known to be present as VO_2^+ and at higher acid concentrations $V(OH)_3^{2+}$ and VO^{3+} (ref. 6,7) were also supposed to be formed[5]. In aqueous perchloric acid medium complexation of these species with perchlorate ion may be neglected though in sulphuric acid medium[6,8], VO_2^+ is believed to exist as VO_2HSO_4. Therefore, in perchloric acid medium the active species of V(V) may be regarded as VO_2^+, $V(OH)_3^{2+}$ or VO^{3+} related by the equilibria (1 and 2).

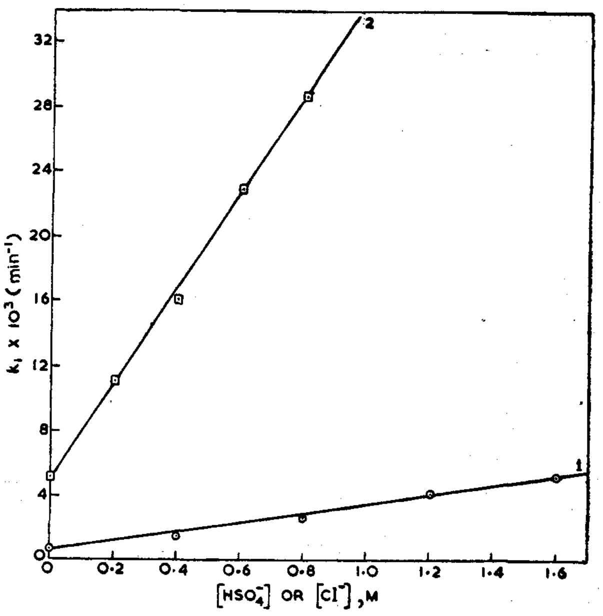
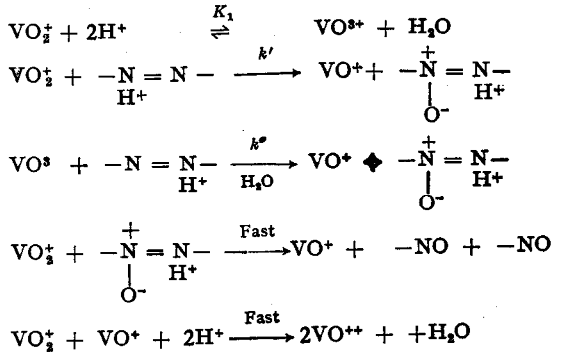


Fig. 3 — Plots of k_1 versus [HSO_4^-] (⊙) and [Cl^-] (⊡) {[V(V)] = 1·0 × $10^{-3}M$; [methyl orange] = 2·4 × $10^{-5}M$; [$HClO_4$] = 2·0*M*) and [ClO_4^-] = 4·0*M* (curve 1); and [$HClO_4$] = 3·5*M* and [ClO_4^-] = 4·5*M* (curve 2); temp. = 30° ± 0·1°}

$$VO_2^+ + H^+ + H_2O \rightleftharpoons V(OH)_3^{2+} \quad \ldots(1)$$

$$VO_2^+ + 2H^+ \rightleftharpoons VO^{3+} + H_2O \quad \ldots(2)$$

The hydrogen ion-independent path presumably involves VO_2^+, and the linear dependence of rate on $[H^+]^2$ rules out equilibrium (1). Thus the hydrogen ion-dependent path involves VO^{3+}. Methyl orange and methyl red having *pK* values of 3·46 and 5·0 can be considered to exist in protonated forms under the acid conditions employed. On the basis of results gathered a mechanism shown in Scheme 1 may be proposed.



$$VO_2^+ + 2H^+ \overset{K_1}{\rightleftharpoons} VO^{3+} + H_2O$$

$$VO_2^+ + \underset{H^+}{-N}=N- \xrightarrow{k'} VO^+ + -\overset{+}{\underset{O^-}{N}}=\underset{H^+}{N}-$$

$$VO^3 + -N=\underset{H^+}{N}- \xrightarrow[H_2O]{k''} VO^+ + -\overset{+}{\underset{O^-}{N}}=\underset{H^+}{N}-$$

$$VO_2^+ + -\overset{+}{\underset{O^-}{N}}=\underset{H^+}{N}- \xrightarrow{\text{Fast}} VO^+ + -NO + -NO$$

$$VO_2^+ + VO^+ + 2H^+ \xrightarrow{\text{Fast}} 2VO^{++} + +H_2O$$

Scheme 1 — Mechanism of V(V) oxidation of dyes

This mechanism involves two-electron transfer (O-transfer), V(III) formed being rapidly oxidized by V(V) to V(IV). The suggested mechanism appears more probable because a mechanism involving one-electron transfer must lead to free radical intermediates for which, however, the test gave a negative result. The mechanism leads to the rate-law.

$$\frac{-d[V(V)]}{dt} = k'[VO^+][Dye] + k''K_1[VO_2^+][H^+]^2[Dye]$$

TABLE 1 — RELATIVE ACCELERATING EFFECTS OF ANIONS

{[V(V)] = $1\cdot0 \times 10^{-3}M$; [$HClO_4$] = $4\cdot0M$; $\mu = 4\cdot0$; [Anion] = $0\cdot2M$; temp. = $30° \pm 0\cdot1°$}

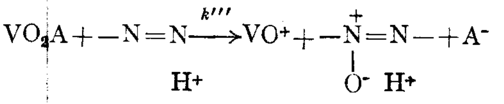
Anion	Cl^-	HSO_4^-	$H_2PO_4^-$	No added anion
$10^3\ k_1$ (min^{-1})	4·61	4·84	12·67	4·22

The rate-law explains the linear dependence of rate on $[H^+]^2$ with a positive intercept on rate axis. The values k' and $k''K_1$ for the oxidation of methyl orange and methyl red were found to be 0·05, 0·06 (μ, 3·0 and temp., 30°) and 0·5, 0·85 (μ, 2·0 and temp., 30°) respectively.

The linear decrease of rate on added HSO_4^-, $H_2PO_4^-$ and Cl^- suggests that the species VO_2HSO_4, $VO_2H_2PO_4$ and VO_2Cl are better oxidants than VO_2^+ or VO^{3+}. The results in Table 1 indicate the following order of accelerating effect: $H_2PO_4^- > HSO_4^- > Cl^-$ perhaps due to the increase in the stability of the complexes $VO_2H_2PO_4 > VO_2HSO_4 > VO_2Cl$. It is interesting to note that the stabilities of chloride, sulphate and phosphate complexes of iron(III) are also in the same order[9]. The complex formation between VO^{3+} and these anions was not considered because VO^{3+} is not supposed to be present in appreciable concentration in comparison with VO_2^+.

In sulphuric acid medium or in the presence of HSO_4^-, $H_2PO_4^-$ and Cl^- ions, therefore, the following steps must also be considered in addition to those postulated in perchloric acid medium (Scheme 1):

$$VO_2^+ + A^- \overset{K_2}{\rightleftharpoons} VO_2A \text{ where } A^- = HSO_4^-,\ H_2PO_4^- \text{ or } Cl^-$$



$$VO_2A + \underset{H^+}{-N=N-} \xrightarrow{k'''} VO^+ + -\overset{+}{\underset{O^-\ H^+}{N}}=N- + A^-$$

The rate will now be

$$\frac{-d[V(V)]}{dt} = k'[VO_2^+][Dye) + k''K_1[VO_2^+][H^+]^2[Dye] + K_2k''[VO_2^+][Dye][HSO_4^-]$$

Linear dependence of the rate on $[(H^+)]^2$ with an intercept shows that in addition to VO_2^+ and VO_2HSO_4, VO^{3+} also as the oxidizing species in sulphuric acid medium.

The values of $k''K_2$ in the presence of HSO_4^- for the oxidation of methyl orange and methyl red were found to be 3·0 (μ=4·0 and temp. 30°C) and 2·0 (μ=3·0 and temp. 30°C) respectively.

As has already been stated the plot of k_1 versus $[H_2PO_4]$ is linear without any intercept whereas the plots of k_1 versus $[HSO_4^-]$ or $[Cl^-]$ gave intercepts. This shows that in the rate-law $k''K_2$ in the case of $H_2PO_4^-$ may be so high that the other terms in rate-law can be neglected. This shows the high catalytic activity of $H_2PO_4^-$ in comparison with Cl^- or HSO_4^-.

The energy of activation and entropy of activation for the oxidation of methyl orange and methyl red calculated from Arrhenius plots are: 12·0 ± 1·0 kcal/mole, −39 ± 1 cal deg^{-1} mole^{-1} and 14·0 ± 1·0 kcal/mole, −32 ± 1 cal deg^{-1} mole^{-1} respectively.

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