



Kinetics of oxidation of hydroquinone by vanadium (V) under the conditions where decavanadates and VO_2^+ coexist-kinetic evidence for the reactivity of VO_2^+ and decavanadates

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ABSTRACT

Kinetics of oxidation of hydroquinone by vanadium (V) has been investigated in the pH range 3.1-4.3 where VO_2^+ and decavanadates, $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ exist in equilibria with each other. The kinetic patterns under these conditions are entirely different from that observed in strong acid media. The kinetic results show the simultaneous involvement of VO_2^+ , $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ in the electron-transfer. The reactivities are in the order of $\text{VO}_2^+ \gg \text{H}_2\text{V}_{10}\text{O}_{28}^{4-} > \text{HV}_{10}\text{O}_{28}^{5-}$.

Keywords: kinetics, decavanadate, oxidation, hydroquinone.

INTRODUCTION

In strongly acid solutions ($\text{pH} < 2$) vanadium(V) exists solely in monomeric form VO_2^+ whereas in the range of pH, 3.1-4.3, vanadium(V) exists in a number species; $\text{H}_4\text{V}_{10}\text{O}_{28}^{2-}$, $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$, $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$, $\text{HV}_{10}\text{O}_{28}^{5-}$, $\text{V}_{10}\text{O}_{28}^{6-}$ along with VO_2^+ [1-5]. The oxidation chemistry of vanadium (V) is highly attractive where all these species are present and in mutual equilibria. Wells and Kuritsyn [6] investigated the oxidation of hydroquinone (H_2Q) by vanadium (V) in aqueous perchloric acid medium using stopped-flow technique. These authors found that the reaction was found to obey first order kinetics with respect to vanadium (V). The reaction also obeys first order kinetics with respect to (H_2Q) at low acidities whereas it is less than first order at higher acidities.

Pelizzetti et al.[7] investigated the kinetics of oxidation of hydroquinone by vanadium (V) under the conditions ($[\text{V}(\text{V})]_t \gg [\text{H}_2\text{Q}]$). These authors also observed the dependence of rate on $[\text{V}(\text{V})]_t$. Kinetic study has been carried out under such conditions taking Fe(II), hydroxylamine and hydrazine as reductants [8,9]. The present authors extended this study to the pH conditions in which decavanadates are in equilibrium with VO_2^+ with a view to investigate whether there is a change in kinetic pattern under these conditions and also assess the reactivity of decavanadates. The study has established that there is a radical transform in kinetic pattern of vanadium(V) oxidations where decavanadates and VO_2^+ are present than in strong acid media where VO_2^+ is the only species.

MATERIALS AND METHODS

All the solutions were prepared using triple-distilled water. Sodium vanadate and hydroquinone were prepared and standardized using literature methods [10,11]. The pH of the solution was maintained constant using acetic acid and acetate buffer mixture. Ionic strength was maintained constant using standard sodium perchlorate.

Because of existence of VO_2^+ and decavanadates in the PH range, 3.1 - 4.3, Beer's Law is not obeyed with respect to vanadium(V). The reaction is monitored by measuring the increase in absorbance due to product, vanadium(IV) at 740nm using Shimadzu UV- visible recording spectrophotometer (UV-260) where all the other materials concerned have negligible absorbance. The method has been employed earlier with success [12-15]. Since molar absorbance of V (IV) at 750nm is small, long path cells (5cm) are used and Beer's Law is obeyed under experimental conditions employed. Kinetic runs were carried out in duplicate and the data agreed within $\pm 7\%$.

For the determination of stoichiometry of the reaction, a known concentration of hydroquinone is mixed with a known excess of vanadium(V). After the completion of the reaction (indicated by constancy of absorbance with time) unreacted vanadium(V) was determined by titration with standard iron(II) after acidifying the reaction mixture with 1:1 sulphuric acid to give an overall concentration of 1.0N and adding 5ml of syrupy phosphoric acid and two drops of 1% barium diphenyl sulphonate as indicator. In the oxidation of hydroquinone 2moles of vanadium(V) (stoichiometric vanadium(V)) are consumed by one mole of hydroquinone. The spectra of equivalent amounts of vanadium(V) and the substrate after the completion of reaction overlapped with that of an identical concentration of vanadium(IV) with the identical molar absorptivity ($18.0 \pm 2 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

RESULTS AND DISCUSSION

Kinetic investigation has been carried out in the pH range, 3.1 - 4.3, under conditions $[\text{V(V)}]_i \gg [\text{H}_2\text{Q}]$ (where $[\text{V(V)}]_i$ is stoichiometric concentration of vanadium(V)) thus isolating the latter with a view to assess the reactivity of VO_2^+ and decavanadates and their involvement in rate determining stages of reaction. The reaction has been found to obey first order kinetics with respect to H_2Q . The rate increases with increase in $[\text{V(V)}]_i$, the increase is less than corresponding to the first order kinetics in V(V) (Table 1). The rate decreases with increase in pH (Table 2).

Table 1. Effect of $[\text{V(V)}]$ on rate $[\text{H}_2\text{Q}]_i = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, pH = 3.42, $\mu = 0.20 \text{ mol dm}^{-3}$, Temp. = $25.0 \pm 0.1^\circ\text{C}$

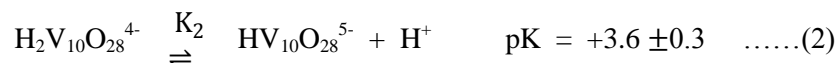
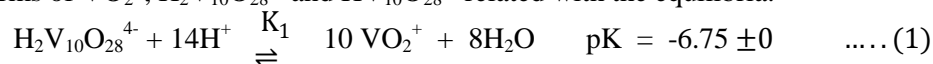
$10^2 [\text{V(V)}]_i \text{ mol dm}^{-3}$	$10^3 k' \text{ sec}^{-1}$
2.0	2.26 ± 0.16
4.0	3.80 ± 0.27
6.0	4.77 ± 0.33
8.0	6.02 ± 0.42
10.0	7.05 ± 0.50
12.0	8.39 ± 0.59

Table 2. Effect of varying pH on rate $[\text{V(V)}]_i = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2\text{Q}]_i = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.20 \text{ mol dm}^{-3}$, Temp. = $25.0 \pm 0.1^\circ\text{C}$

pH	$10^4 [\text{H}^+] \text{ mol dm}^{-3}$	$10^5 [\text{VO}_2^+] \text{ mol dm}^{-3}$	$10^3 k' \text{ sec}^{-1}$
3.10	7.940	4.1967	3.11 ± 0.22
3.42	3.802	1.4625	2.26 ± 0.16

3.79	1.622	0.4252	2.03 ± 0.14
3.94	1.148	0.2563	1.92 ± 0.13
4.24	0.575	0.0411	1.85 ± 0.13

Vanadium (V) is known to exist as decavanadate and VO_2^+ in this pH range. Thus the kinetic data has to be analysed in terms of VO_2^+ , $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ related with the equilibria:



From the equilibria (1) and (2), the concentration of the $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ are related to the total decavanadate concentration by the equation (4).

$$[\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}] = \frac{[\text{Decavanadate}]_t [\text{H}^+]}{(K_2 + [\text{H}^+])} = \frac{\left(\frac{[\text{V(V)}]_t - [\text{VO}_2^+]}{10}\right) [\text{H}^+]}{K_2 + [\text{H}^+]} \quad \dots (3)$$

$$[\text{HV}_{10}\text{O}_{28}^{5-}] = [\text{Decavanadate}]_t - [\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}] \quad \dots (4)$$

$$\text{and } [\text{VO}_2^+] \text{ is given by: } [\text{VO}_2^+] = (K_1 [\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}])^{0.1} [\text{H}^+]^{1.4} \quad \dots (5)$$

From equations (3) and (5)

$$[\text{VO}_2^+] = \left\{ \frac{K_1 \left(\frac{[\text{V(V)}]_t - [\text{VO}_2^+]}{10}\right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4} \quad \dots (6)$$

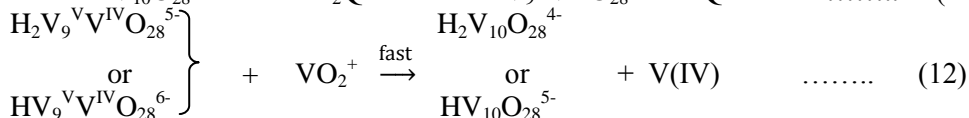
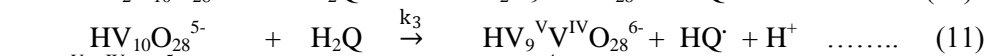
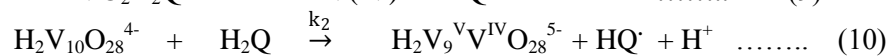
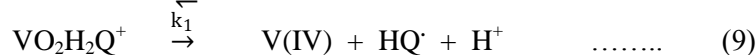
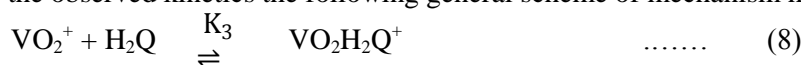
Applying the Newton-Raphson iteration method to eq. (6), we calculated the concentration of VO_2^+ in this pH range. Its concentration has found to be in the order of $10^{-5} \text{ mol dm}^{-3}$ which is far less than $[\text{V(V)}]_t$. Hence, $[\text{VO}_2^+]$, $[\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}]$ and $[\text{HV}_{10}\text{O}_{28}^{5-}]$ under these conditions are fairly accurately obtained from eq. (7a,b,c).

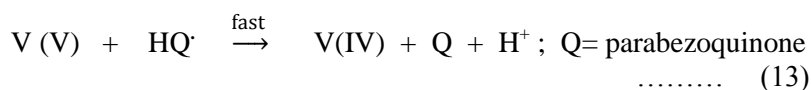
$$[\text{VO}_2^+] = \left\{ \frac{K_1 \left(\frac{[\text{V(V)}]_t}{10}\right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4} \quad \dots (7a)$$

$$[\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}] = \frac{\left\{ \frac{([\text{V(V)}]_t [\text{H}^+])}{10} \right\}}{K_2 + [\text{H}^+]} \quad \dots (7b)$$

$$[\text{HV}_{10}\text{O}_{28}^{5-}] = \frac{\left\{ \frac{K_2 [\text{V(V)}]_t}{10} \right\}}{K_2 + [\text{H}^+]} \quad \dots (7c)$$

Mc Auley et al.[16] observed that these inter conversions are fast and taking place within the time of mixing. To explain the observed kinetics the following general scheme of mechanism has been suggested.





Giving the rate law:

$$\text{rate} = k_1[\text{VO}_2\text{H}_2\text{Q}^+] + k_2[\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}][\text{H}_2\text{Q}] + k_3[\text{HV}_{10}\text{O}_{28}^{5-}][\text{H}_2\text{Q}] \quad \dots\dots\dots (14)$$

In this mechanism, the reaction involving $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ or $\text{HV}_{10}\text{O}_{28}^{5-}$ is believed to proceed with the transfer of electron from H_2Q to terminal V(V) atom in decavanadate forming reduced decavanadate $\text{H}_2\text{V}_9\text{V}^{\text{IV}}\text{O}_{28}^{5-}$ or $\text{HV}_9\text{V}^{\text{IV}}\text{O}_{28}^{6-}$ respectively. According to Watts et al [4] the conversion of unstable reduced decavanadates into decavanadates and V(IV) takes place even in the absence of added acid. The observed kinetics shows that this is relatively fast and not rate determining.

Had this been rate determining, plots of $\log(D_a - D_t)$ versus time or Guggenheim's plots would have been biphasic appearance because now the reaction conforms to the consecutive scheme $\text{A} \rightarrow \text{B} \rightarrow \text{C}$. But these plots were always very good straight lines ruling out any possibility of consecutive mechanism and that the conversion of reduced decavanadates, $\text{H}_2\text{V}_9\text{V}^{\text{IV}}\text{O}_{28}^{5-}$ or $\text{HV}_9\text{V}^{\text{IV}}\text{O}_{28}^{6-}$ to decavanadate is not rate determining step.

Applying the mass balance with respect to $[\text{H}_2\text{Q}]$ one gets

$$[\text{H}_2\text{Q}]_t = [\text{H}_2\text{Q}] + [\text{VO}_2\text{H}_2\text{Q}^+] \quad \dots\dots\dots (15)$$

$$[\text{H}_2\text{Q}] = \frac{[\text{VO}_2\text{H}_2\text{Q}^+]}{K_3[\text{VO}_2^+]} \quad \dots\dots\dots (16)$$

$$\therefore [\text{VO}_2\text{H}_2\text{Q}^+] = \frac{K_3[\text{VO}_2^+][\text{H}_2\text{Q}]_t}{1 + K_3[\text{VO}_2^+]} \quad \dots\dots\dots (17)$$

Combining the eq. 7(a,b,c) 14, 17 the rate law modifies into

$$\begin{aligned} -\frac{d[\text{H}_2\text{Q}]}{dt} = & \frac{k_1 K_3 \left\{ \frac{K_1 \left(\frac{[\text{V(V)}]_t}{10} \right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4} [\text{H}_2\text{Q}]_t}{1 + K_3 \left\{ \frac{K_1 \left(\frac{[\text{V(V)}]_t}{10} \right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4}} \\ & + \frac{k_2 [\text{H}^+] \left(\frac{[\text{V(V)}]_t}{10} \right) [\text{H}_2\text{Q}]_t}{K_2 + [\text{H}^+]} + \frac{k_3 K_2 \left(\frac{[\text{V(V)}]_t}{10} \right) [\text{H}_2\text{Q}]_t}{K_2 + [\text{H}^+]} \quad \dots\dots\dots (18) \end{aligned}$$

K_3 has been reported earlier[6] to be order of $5.5 \text{ mol}^{-1} \text{ dm}^3$, $\left[\frac{[\text{V(V)}]}{10} \right]_t^{0.1}$

is in the order of 0.54 and $\left\{ \frac{K_1 \left(\frac{[\text{V(V)}]_t}{10} \right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4}$ is in the order of 10^{-5} hence, the term $\left\{ \frac{K_1 \left(\frac{[\text{V(V)}]_t}{10} \right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4}$ can be

neglected in comparison with 1 in the first term and the rate law assumes the form:

$$-\frac{d[\text{H}_2\text{Q}]}{dt} = k_1 K_3 \left\{ \frac{K_1 \left(\frac{[\text{V}(\text{V})]_t}{10} \right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4} [\text{H}_2\text{Q}]_t$$

$$+ \frac{k_2 [\text{H}^+] \left(\frac{[\text{V}(\text{V})]_t}{10} \right) [\text{H}_2\text{Q}]_t}{K_2 + [\text{H}^+]} + \frac{k_3 K_2 \left(\frac{[\text{V}(\text{V})]_t}{10} \right) [\text{H}_2\text{Q}]_t}{K_2 + [\text{H}^+]} \quad \dots\dots\dots (19)$$

The pseudo- first order rate constant, k' is given by eq.

$$k' = k_1 K_3 \left\{ \frac{K_1 \left(\frac{[\text{V}(\text{V})]_t}{10} \right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4}$$

$$+ \frac{k_2 [\text{H}^+] \left(\frac{[\text{V}(\text{V})]_t}{10} \right)}{K_2 + [\text{H}^+]} + \frac{k_3 K_2 \left(\frac{[\text{V}(\text{V})]_t}{10} \right)}{K_2 + [\text{H}^+]} \quad \dots\dots\dots (20)$$

or

$$\frac{k'}{\left(\frac{[\text{V}(\text{V})]_t}{10} \right)^{0.1}} = k_1 K_3 \left(\frac{K_1 [\text{H}^+]}{K_2 + [\text{H}^+]} \right)^{0.1} [\text{H}^+]^{1.4} + \frac{k_2 [\text{H}^+] + k_3 K_2 \left(\frac{[\text{V}(\text{V})]_t}{10} \right)^{0.9}}{K_2 + [\text{H}^+]}$$

As per the eq.20 a plot of $\frac{k'}{\left(\frac{[\text{V}(\text{V})]_t}{10} \right)^{0.1}}$ Vs $\left(\frac{[\text{V}(\text{V})]_t}{10} \right)^{0.9}$ is a straight line (Fig.1) with positive slope and intercept from which $k_1 K_3$ has been calculated. A plot of

$$\left[k' - k_1 K_3 \left\{ \frac{K_1 \left(\frac{[\text{V}(\text{V})]_t}{10} \right) [\text{H}^+]}{K_2 + [\text{H}^+]} \right\}^{0.1} [\text{H}^+]^{1.4} \right] (K_2 + [\text{H}^+]) \text{ Vs } [\text{H}^+]$$

has been made using the literature values K_1 and K_2 . The plot is a straight line (Fig.2) with positive slope and intercept substantiating the rate law and hence mechanism.

CONCLUSIONS

From the values of slope and intercept (Fig.2), k_2 and k_3 have been calculated to be 0.14 and $0.048 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$ respectively at 25°C . The plot gives the kinetic evidence for simultaneous involvement of VO_2^+ , $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ in oxidation of hydroquinone and the values of $k_1 K_3$, k_2 and k_3 (33.8 , 0.14 and $0.048 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$) show that their reactivities are in the order of $\text{VO}_2^+ \gg \text{H}_2\text{V}_{10}\text{O}_{28}^{4-} > \text{HV}_{10}\text{O}_{28}^{5-}$.

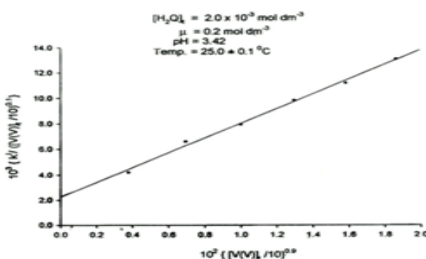
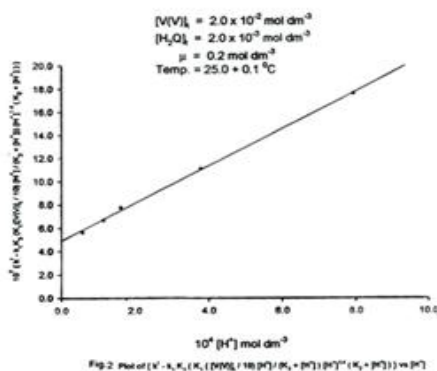


Fig. 1 Plot of $k' / \left(\frac{[\text{V}(\text{V})]_t}{10} \right)^{0.1}$ vs $\left(\frac{[\text{V}(\text{V})]_t}{10} \right)^{0.9}$



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