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Kinetics of Oxidation of Ethyldigol by Vanadium(V) in Aqueous Acidic Medium

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The kinetics of oxidation of ethyldigol by vanadium(V) in aqueous acidic medium has been carried out. The reaction is first order with respect to vanadium(V) and the substrate and is acid catalysed. *Hammett* acidity function (H_0) and *Bunnett* hypothesis have been applied. The formation of free radicals during the course of the reaction has been indicated. A probable reaction mechanism is proposed.

[Keywords: Bunnett hypothesis; Hammet acidity function; Kinetics; Vanadium(V)]

Die Kinetik der Oxidation von Ethyldigol mit Vanadium(V) in wäßrigem saurem Medium

Es wurde die Kinetik der Oxidation von Ethyldigol mittels Vanadium(V) in wäßriger saurer Lösung untersucht. Die Reaktion ist erster Ordnung bezüglich Vanadium(V) und Substrat und ist säurekatalysiert. Es wurden die *Hammett*-Aciditätsfunktion (H_0) und die *Bunnett*-Hypothese angewandt. Die Bildung von freien Radikalen während der Reaktion konnte bestätigt werden. Es wird ein Reaktionsmechanismus vorgeschlagen.

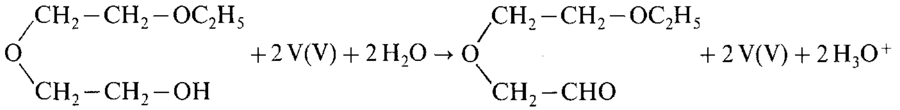
Introduction

In continuation to our study [1–3] on the kinetics of oxidation of substituted dihydric alcohols by vanadium(V) in aqueous acidic medium we report now the kinetics of oxidation of ethyldigol by vanadium(V) in aqueous acidic medium (sulphuric, perchloric and hydrochloric acids).

Experimental

All the chemicals used were of AR grade. The stock solution of ammonium metavanadate was prepared by dissolving the sample in sulphuric, perchloric or hydrochloric acid of known concentrations. Ethyldigol solution was prepared by weight. Calculated amounts of ammonium metavanadate solution and the acid (sulphuric, perchloric or hydrochloric) were mixed together. Freshly prepared ethyldigol solution and the mixed vanadate-acid solutions were thermostated separately for half an hour. After the solutions had attained the temperature of the bath, the reaction was initiated by the addition of a calculated amount of ethyldigol to the vanadate—acid solution. An aliquot (5 ml) was withdrawn at a suitable interval of time and was quenched by pouring into known excess of ferrous ammonium sulphate solution. The unreacted solution was titrated against standard solution of ceric ammonium sulphate using N-phenylanthranilic acid as indicator.

Stoichiometry: One mole of ethyldigol consumes two moles of the oxidant. The oxidation reaction may thus be represented as shown below:



Results and Discussion

Order with Respect to Vanadium(V)

Kinetic runs were carried out at different concentrations of vanadium (0.02 to 0.01 *M*) under the condition $[S] \gg [\text{oxidant}]$ keeping the concentration of the substrate and the acid constant. Plots of $\log V_\infty - V_0/V_\infty - V_t$ vs. time were found to be straight lines passing through the origin, indicating the order with respect to vanadium (V) to be unity.

Order with Respect to Substrate

The plot of k vs. [ethyldigol] was found to be a straight line passing through the origin (Fig. 1), showing first order dependence of rate on [ethyldigol].

Effect of Hydrogen Ion Concentration

The reaction was studied in H_2SO_4, $HClO_4$ and HCl. The rate of reaction at the same molar concentration of the acid was found to follow the order $H_2SO_4 > HClO_4 > HCl$. In each of the three acids, there is very little change in the rate up to a certain $[H^+]$ and after that the rate increases abruptly (Fig. 2). At high acid concentration the specific rate has been found to increase much faster than expected. Under this condition

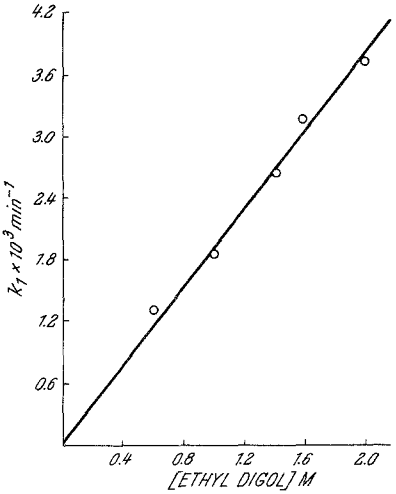


Fig. 1. Plot of [ethyldigol] vs. k_1 $[NH_4VO_3] = 0.04M$; $[H_2SO_4] = 5.00M$; Temp. = 35 °C

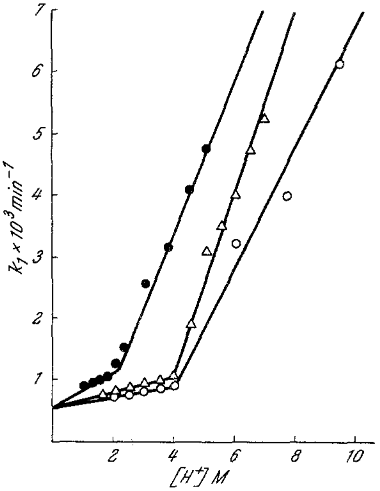


Fig. 2. Plot of $[H^+]$ vs. k_1 $[NH_4VO_3] = 0.04M$; [ethyldigol] = 1.00*M*; Temp. = 35 °C; ● H_2SO_4; ○ HCl; △ $HClO_4$

the *Hammett* acidity function [4] has been applied. A straight line with a slope less than the ideal value of unity has been found for each of the three acids (Fig. 3).

In an attempt to correlate the rate with acid concentration, *Bunnett*'s hypothesis in addition to the *Hammett* acidity function was tested.

Bunnett found that a plot of ($\log k + H_0$) versus $\log a_{H_2O}$ (where H_0 is the *Hammett* acidity function and a_{H_2O} is the activity of water in given solvent mixture) are generally linear. The slopes of the linear plots obtained are certainly useful in providing a method of empirical classification of acid-catalyzed reactions. *Bunnett*'s approach may also make it possible to obtain the relative number of molecules of water in the reactant and in the transition state, however, this point remains to be proved [5, 6]. According to *Bunnett* [7] the slopes of the linear plots of $\log(k + H_0)$ versus $\log a_{H_2O}$ defines a parameter ω. The ω values of -2.5 to zero indicate non-participation of water molecules in the transition state. Values between $+1.2$ to $+3.3$ indicate that water acts as a nucleophile and the values greater than 3.3 indicate that water acts as a proton abstracting agent.

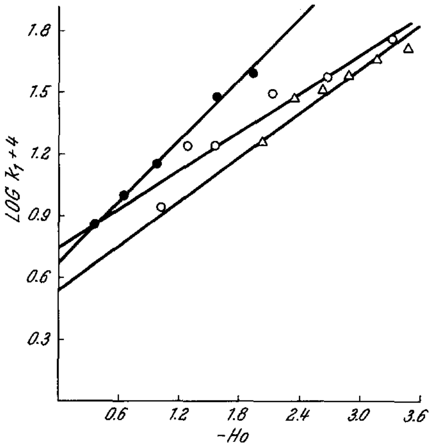


Fig. 3. Plot of $-H_0$ vs. $\log k_1$ [NH_4VO_3] = 0.04 *M*; [Ethyldigol] = 1.00 *M*; Temp. = 35 °C; ● H_2SO_4 (slope = 0.50); ○ HCl (slope = 0.31); △ $HClO_4$ (slope = 0.45)

In the present investigation, the *Bunnett* plots have been found to be linear (Fig. 4). The ω values (5.2 and 15.0 in sulphuric acid and hydrochloric acid respectively) indicate that during the course of reaction water acts as a proton abstracting agent in both the acids used.

Effect of Addition of Na_2SO_4 *and* $NaHSO_4$

The rate of reaction was affected by the addition of both the salts at constant ionic strength. A decrease with Na_2SO_4 and an increase with

$NaHSO_4$ has been observed (Table 1). Since the second dissociation constant of H_2SO_4 is very small, $[HSO_4^-]$ increases with increasing concentration of $NaHSO_4$ which furnishes an extra amount of the active species. With Na_2SO_4, however, the formation of the active species is probably disfavoured.

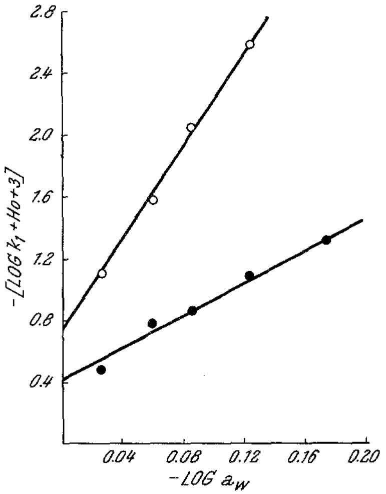


Fig. 4. Plot of $-\log a_W$ vs. $-\log k_1 + H_0 + 3$) $[NH_4VO_3] = 0.04\,M$; [Ethyldigol] $= 1.00\,M$; Temp. = 35 °C; ● H_2SO_4 (slope = 5.2); ○ HCl (slope = 15.0)

Table 1. $[NH_4VO_3] = 0.04\,M$; $[H_2SO_4] = 5.0\,M$; *Ionic strength* $= 2.0\,M$; *Temp.* = 35 °C

$[Na_2SO_4]\,M$	$k \cdot 10^3\,\text{min}^{-1}$	$[NaHSO_4]\,M$	$k \cdot 10^3\,\text{min}^{-1}$
0.2	4.55	0.2	4.95
0.3	4.35	0.4	5.20
0.4	4.16	0.8	5.61
0.5	3.90	1.2	5.98
0.6	3.54	1.6	6.37
2.0	2.81	2.0	6.80

Activation Parameters

The temperature dependence of the reaction was studied at four different temperatures (25°, 30°, 35° and 40 °C). The plots of $\log k$ vs $1/T$ were found to be straight lines showing that the reaction obeys *Arrhenius* temperature dependence. From this plot E_a and $\Delta S^{\neq}$ have been calculated:

$$(E_a = 67.2\,\mathrm{kJ\,mol^{-1}};\ \Delta S^{\neq} = -79.8\,\mathrm{J\,K^{-1}\,mol^{-1}}).$$

Presence of Free Radical

That a free radical is formed during the course of the reaction was established by the fact that polymerization of acrylonitrile within a short interval of time took place when it was added to the reaction mixture. Acrylonitrile, however, failed to undergo polymerization when it was added to the reactants separately. It may, therefore, be concluded that this reaction involves a one electron transfer process.

Evidence for the Complex Formation

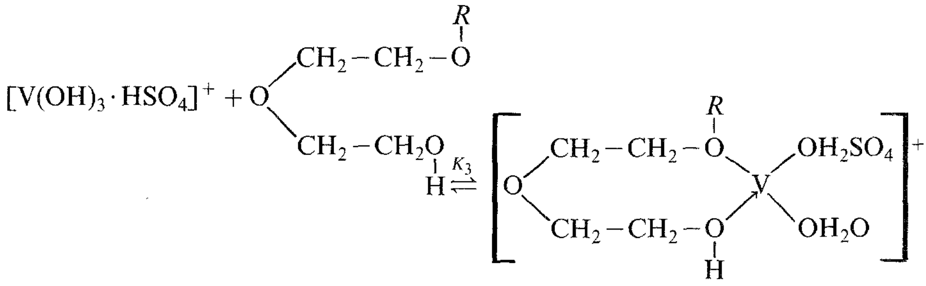
Optical density measurements were made for two solutions, one containing vanadium(V) and sulphuric acid and the other containing vanadium(V), sulphuric acid and ethyl digol. An appreciable exaltation in absorbance of the reaction mixture around 400 nm provides positive evidence for the formation of some type of intermediate complex during the course of the reaction.

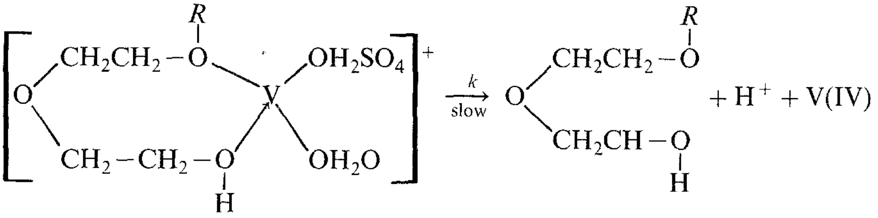
Mechanism

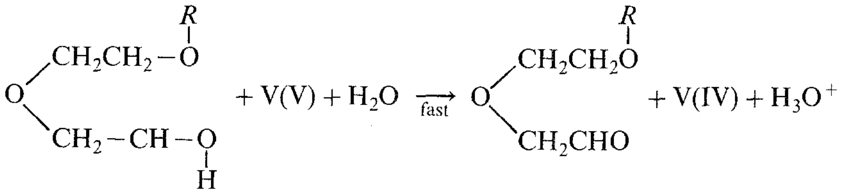
The oxidation of ethyldigol by vanadium(V) in aqueous acidic medium involves the formation of an intermediate complex and a free radical during the course of the reaction. The ω value suggests that water acts as proton abstracting agent. 100% sulphuric acid and other concentrated strong acids cleave ethers [8, 9]. Also cleavage of ether takes place by HBr and HI at high temperature [10]. Hence, under the present experimental conditions, the cleavage of the ether group in ethyldigol is most unlikely. Further, the distillate of the reaction mixture after completion of the reaction gave a positive test for aldehyde but a negative test for carboxylic acid, implying that the oxidation reaction terminates at the aldehyde stage. Several workers [11–13] have established the participation of $[V(OH)_3HSO_4]^+$ species in the reaction in presence of aqueous sulphuric acid. In the light of these evidences the following probable mechanism is being proposed ($R = C_2H_5$):

$$VO_2^+ + H_2O + H^+ \overset{K_1}{\rightleftharpoons} [V(OH)_3]^{+2} \tag{1}$$

$$[V(OH)_3]^{+2} + [HSO_4^-] \overset{K_2}{\rightleftharpoons} [V(OH)_3HSO_4]^+ \tag{2}$$


(3)


(4)


(5)

Based on steps (1)–(5) it follows:

$$\begin{aligned} \text{Rate} &= k\,[\text{Intermediate complex}] \\ &= kK_1'K_2K_3\,[\text{VO}_2^+]\,[\text{H}_2\text{SO}_4]\,[\text{Ethyldigol}] \\ &\qquad\qquad \text{where } K_1' = K_1\,[\text{H}_2\text{O}] \end{aligned} \tag{6}$$

Replacing $[\text{VO}_2^+]$ by $[\text{V(V)}]_T$, eq. (6) transforms to

$$-\frac{\mathrm{d}[\text{V(V)}]}{\mathrm{d}t} = \frac{k\,K_1'K_2K_3\,[\text{H}_2\text{SO}_4]\,[\text{Ethyldigol}]\,[\text{V(V)}]_T}{1 + K_1[\text{H}^+] + K_1'\,K_2[\text{H}_2\text{SO}_4]\,\{1 + K_3[\text{Ethyldigol}]\}} \tag{7}$$

Eq. (7) implies unit order of reaction with respect to V(V). Further, assuming K_1' to be very small, eq. (7) at constant vanadium (V) concentration changes to

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK_1'\,K_2K_3\,[\text{H}_2\text{SO}_4]\,[\text{Ethyldigol}]} + \frac{1}{kK_3\,[\text{Ethyldigol}]} + \frac{1}{k} \tag{8}$$

Under the condition $K_1' \ll kK_3$, $1/kK_3[\text{Ethyldigol}]$ may be neclected. Hence,

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK_1'K_2K_3[\text{H}_2\text{SO}_4][\text{Ethyldigol}]} + \frac{1}{k} \qquad (9)$$

The plots of $1/k_{\text{obs}}$ vs. $1/[\text{H}_2\text{SO}_4]$ and $1/k_{\text{obs}}$ vs. 1/[Ethyldigol] have been found to be straight lines with an intercept on the rate^{-1} axis which is in accordance with eq. (9), thus supporting the proposed mechanism.

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