

Vanadium(V). Part VII.* Kinetics of the Oxidation of Triethanolammonium Ion with Vanadium(V)

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The kinetics of the oxidation of triethanolammonium ions with vanadium(V) have been studied in sulfuric and perchloric acidic solutions. The reaction is of first order with respect to the triethanolammonium ion and vanadium(V) concentrations, but of second order with respect to the hydrogen ion concentration. The reaction is faster in sulfuric acid than in a corresponding perchloric acid solution. Both added sodium hydrogen sulfate and perchlorate accelerate the reaction, the effect of the former salt being greater. At a constant hydrogen ion concentration and at constant ionic strength the reaction is of first order with respect to the bisulfate ion concentration. The activation parameters have been determined. The substituent effect of the positively charged ammonium group is very small. A reaction mechanism involving $V(OH)_2^{3+}$ in perchloric acid as well as VO_2HSO_4 and $V(OH)_3HSO_4^+$ in sulfuric acid is suggested.

The kinetics of the oxidation of several aliphatic^{2–8} and alicyclic^{9,10} as well as benzyl alcohols^{1,11} with vanadium(V) have been studied in detail but different oxidizing species and different mechanisms have been suggested for the reactions. Continuing our investigations, we have now studied kinetically the oxidation of triethanolammonium ion in order to obtain information on *e.g.* the positive charge on the rate constant.

EXPERIMENTAL

Ammonium metavanadate was a guaranteed reagent from E. Merck AG. Triethanolamine, diethanolamine and ethanolamine were commercial reagents distilled twice before use.

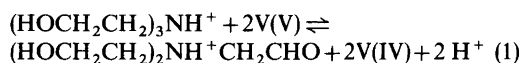
* Part VI, see Ref. 1.

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The method of analyzing the unreacted vanadium(V) was the same as that used earlier.^{1,2}

RESULTS

The rate constants were determined under pseudo first order conditions with ethanolammonium ion in excess. Vanadium is reduced to V(IV) which is seen from the increase of the absorption at 765 nm.¹³ All the rate constants reported in this work refer to the oxidation of the first alcohol group and the stoichiometric equation can therefore be expressed as:



A brief study reveals that the second alcohol group of triethanolamine oxidizes at a rate only slightly slower than that of the first alcohol group. This statistically less favoured side reaction thus cannot affect notably the numerical values of the rate constant observed and the correlation constant found was always close to 1. The oxidation of the aldehyde formed is much slower and does not interfere.^{1,11,14}

Table 1 shows that the rate of the oxidation is of first order with respect to both the vanadium(V) and the triethanolammonium ion concentrations.

As seen from Table 2, the addition of sodium perchlorate accelerates the rate. The increase of the rate constant follows the equation $\log \{(k_{obs}/[TEAH^+])/M^{-1} s^{-1}\} = (-3.93 \pm 0.01) + (0.208 \pm 0.003) \times [NaClO_4]/M$, $r = 0.9997$.

At a constant ionic strength maintained by variation of the concentrations of sodium perchlorate and bisulfate, the rate is the faster, the more the solution contains the latter salt.

Table 1. Variation of the rate constant with the concentration of vanadium(V) and triethanolammonium ion for the oxidation of triethanolammonium ion with vanadium(V) at 60 °C in water.

[V(V)]/M	[TEAH ⁺]/M	[H ₂ SO ₄]/M	$k_{\text{obs}}/\text{s}^{-1}$	r	$k_{\text{obs}}/[\text{TEAH}^+]/\text{M}^{-1}\text{s}^{-1}$
0.0059	0.394	2.29	1.42×10^{-4}	0.9996	3.60×10^{-4}
0.0118	0.394	2.29	1.55×10^{-4}	0.9996	3.93×10^{-4}
0.0177	0.394	2.29	1.56×10^{-4}	0.9997	3.96×10^{-4}
0.0236	0.394	2.29	1.60×10^{-4}	0.9999	4.06×10^{-4}
0.0296	0.394	2.29	1.61×10^{-4}	0.9998	4.09×10^{-4}
0.0177	0.197 ^a	1.74	6.34×10^{-5}	0.9994	3.22×10^{-4}
0.0177	0.394 ^a	1.74	1.28×10^{-4}	0.9998	3.25×10^{-4}
0.0177	0.591 ^a	1.74	1.99×10^{-4}	0.9991	3.37×10^{-4}
0.0177	0.788 ^a	1.74	2.64×10^{-4}	0.9999	3.35×10^{-4}
0.0177	0.985	1.74	3.29×10^{-4}	0.9999	3.34×10^{-4}

^aNaOH added, [TEAH⁺] + [Na⁺] = 0.985 M.

Table 2. Variation of the rate constant with the concentration of sodium perchlorate and bisulfate for the oxidation of triethanolammonium ion with vanadium(V) at 60 °C in water. [V(V)] = 0.0177 M, [TEAH⁺] = 0.394 M, [HClO₄] = 3.09 M.

[NaClO ₄]/M	[NaHSO ₄]/M	$k_{\text{obs}}/\text{s}^{-1}$	r	$k_{\text{obs}}/[\text{TEAH}^+]/\text{m}^{-1}\text{s}^{-1}$
—	—	4.68×10^{-5}	0.9998	1.19×10^{-4}
0.99	—	7.49×10^{-5}	0.9999	1.90×10^{-4}
1.97	—	1.17×10^{-4}	0.9999	2.97×10^{-4}
2.96	—	1.88×10^{-4}	0.9999	4.77×10^{-4}
3.94	—	3.12×10^{-4}	0.9994	7.92×10^{-4}
—	3.94	8.36×10^{-4}	0.9994	2.12×10^{-3}
0.99	2.96	7.16×10^{-4}	0.9999	1.82×10^{-3}
1.97	1.97	6.10×10^{-4}	0.9990	1.55×10^{-3}
2.96	0.97	5.16×10^{-4}	0.9999	1.31×10^{-3}
3.94	—	3.12×10^{-4}	0.9994	7.92×10^{-3}

Table 3. Variation of the rate constant with the concentration of sulfuric and perchloric acid at constant ionic strength for the oxidation of triethanolammonium ion with vanadium(V) at 60 °C. [V(V)] = 0.0177 M, [TEAH⁺] = 0.394 M.

Acid	H_0^a	$k_{\text{obs}}/\text{s}^{-1}$	r	$k_{\text{obs}}/[\text{TEAH}^+]/\text{M}^{-1}\text{s}^{-1}$
0.83 M H ₂ SO ₄ ^b	-0.13	3.20×10^{-4}	0.9998	0.81×10^{-3}
1.70 M H ₂ O ₄ ^b	-0.68	4.41×10^{-4}	0.9999	1.12×10^{-3}
2.46 M H ₂ SO ₄ ^b	-1.09	5.52×10^{-4}	0.9997	1.40×10^{-3}
3.33 M H ₂ SO ₄ ^b	-1.54	7.29×10^{-4}	0.9999	1.85×10^{-3}
4.08 M H ₂ SO ₄ ^b	-1.89	8.74×10^{-4}	0.9999	2.22×10^{-3}
4.97 M H ₂ SO ₄	-2.27	1.13×10^{-3}	0.9999	2.87×10^{-3}
1.83 M HClO ₄ ^c	-1.78	6.01×10^{-5}	0.9998	1.53×10^{-4}
2.87 M HClO ₄ ^c	-2.10	1.04×10^{-4}	0.9995	2.64×10^{-4}
3.84 M HClO ₄ ^c	-2.40	1.68×10^{-4}	0.9999	4.26×10^{-4}
4.82 M HClO ₄	-2.72	2.44×10^{-4}	0.9999	6.19×10^{-4}

^aRef. 17. ^bNaHSO₄ added, $I = 4.97$ M. ^cNaClO₄ added, $I = 4.82$ M.

Table 4. Solvent effect of acetic acid for the oxidation of triethanolammonium ion with vanadium(V) at 60 °C. $[V(V)] = 0.0177$ M, $[TEAH^+] = 0.394$ M, $[H_2SO_4] = 2.29$ M.

AcOH/%(v/v)	k_{obs}/s^{-1}	r	$k_{obs}/[TEAH^+]/M^{-1}s^{-1}$
0	1.56×10^{-4}	0.9997	3.96×10^{-4}
10	2.20×10^{-4}	0.9999	5.58×10^{-4}
20	3.24×10^{-4}	0.9999	8.22×10^{-4}
30	5.01×10^{-4}	0.9999	1.27×10^{-3}
40	8.15×10^{-4}	0.9999	2.07×10^{-3}
50	1.33×10^{-3}	0.9999	3.38×10^{-3}

Table 5. Effect of temperature on the rate constant for the oxidation of triethanolammonium and diethanolammonium ions in water. $[V(V)] = 0.018$ M, $[amineH^+] = 0.40$ M, $[H_2SO_4] = 2.32$ M at 25 °C.

Amine	$t/^\circ C$	k_{obs}/s^{-1}	r	$k_{obs}/[amineH^+]/M^{-1}s^{-1}$
TEA	40	2.36×10^{-5}	0.9999	5.94×10^{-5}
TEA	50	6.31×10^{-5}	0.9998	1.59×10^{-4}
TEA	60	1.56×10^{-4}	0.9997	3.96×10^{-4}
TEA	70	3.91×10^{-4}	0.9999	9.98×10^{-4}
DEA	40	8.86×10^{-6}	0.9998	2.23×10^{-5}
DEA	50	2.26×10^{-5}	0.9995	5.71×10^{-5}
DEA	60	5.37×10^{-5}	0.9997	1.36×10^{-4}
DEA	70	1.16×10^{-4}	0.9998	2.96×10^{-4}

The effect of the acid concentration was studied by diluting 4.97 M sulfuric acid and 4.82 M perchloric acid with sodium hydroxide. The results in Table 3 indicate that for the same concentration of the acid, the rate is faster in sulfuric than in perchloric acid. The rate constant increases with an increasing acetic acid concentration (Table 4).

The effect of temperature on the rate of the oxidation of triethanolammonium and diethanolammonium ions is seen in Table 5. The values of 81.1 ± 0.9 kJ mol⁻¹ and 74.4 ± 0.8 kJ mol⁻¹ for the enthalpy of activation and the values of -67.4 ± 2.8 J mol⁻¹ K⁻¹ and -96.6 ± 2.5 J mol⁻¹ K⁻¹ for the entropy of activation at 50 °C have been evaluated from $k_{obs}/[amineH^+]$ for the oxidation of triethanolammonium and diethanolammonium ions, respectively.

The triethanolammonium ion reacts about three times faster than the diethanolammonium ion. This is about the same as the value obtained for the oxidations with Cr(VI), where $k_{obs}(TEAH^+) \approx 2k_{obs}(DEAH^+) \approx 4k_{obs}(EAH^+)$.¹⁵ The values for ethanolammonium ion are now not reported in the table, because we did not find good first order kinetics for this ion.

DISCUSSION

The addition of triethanolamine to acidic solutions of vanadium(V) deepens the colour of the solutions. This can be taken to indicate a formation of a vanadium(V) – substrate complex, it was as earlier often suggested for the similar oxidations of different alcohols.^{2,6,8-10}

The rate constant of the oxidation of ethanol with vanadium(V) in 4 M sulfuric acid at 50 °C is $8.67 \times 10^{-5} M^{-1} s^{-1}$.² The rate constant of triethanolammonium ion in similar conditions can be approximated to be $2.6 \times 10^{-4} M^{-1} s^{-1}$ (Tables 5 and 3), which is the statistical value, three times the rate constant of ethanol. Thus the substituent effect of the positively charged ammonium group is very small, which fact clearly excludes the possibility of hydride ion transfer^{11,16} or electron transfer from oxygen atom³ as the rate-determining stage. As the rate increases with the increasing ionic strength (Table 2), ionic species are involved in the rate-determining step. The results are best accordant with a mechanism where a radical is formed in the rate-determining decomposition of a charged complex and either more charges are formed or the

spreading of the charges decreases at the same time.

The decomposing complex may be cyclic or acyclic. A comparison of the values of the rate constants and activation entropies for triethanolammonium and diethanolammonium ions (Table 5) suggests the former alternative, but the available information is far from sufficient.

As seen from Table 3, the reaction is acid-catalyzed. For a correlation of the rates of the oxidations of organic compounds with quinquevalent vanadium, the Hammett acidity function H_0 is generally used, although the protonating species here is *e.g.* VO^{2+} cation and organic indicators were used when determining the H_0 -scale. For the sake of comparison, we calculated for sulfuric acid solutions $\log \{(k_{\text{obs}}/[\text{TEAH}^+])/M^{-1} \text{ s}^{-1}\} = (-3.31 \pm 0.01) + (-0.25 \pm 0.01) \times H_0$, $r = 0.9996$, and for perchloric acid solutions $\log \{(k_{\text{obs}}/[\text{TEAH}^+])/M^{-1} \text{ s}^{-1}\} = (-4.96 \pm 0.09) + (-0.65 \pm 0.04) \times H_0$, $r = 0.9964$.¹⁷ Since the H_0 -scale is probably not correct for VO_2^+ solutions, no conclusions can be drawn from the numerical values of the slopes. However, the difference of the dependence of $\log \{(k_{\text{obs}}/[\text{TEAH}^+])/M^{-1}\}$ on H_0 of the two systems is so marked that factors other than acidity alone have to be considered.

The $\text{p}K_a$'s of different alcohols are around -3 .¹⁸ Therefore the alcohols studied in strongly acidic solutions are partly protonated. This phenomenon has been discussed in one case to decrease the reactivity,⁴ but it seems, on the basis of our results, that the possible protonation does not affect markedly the oxidation and that other effects are dominant. The protonation of alcohols follows fairly well the H_0 -scale, but, contrary to it, the Zucker-Hammett plots, $\log k$ vs. $-H_0$, found for the oxidation have slopes of less than unity.^{1,6,8,10}

The reaction is not of first order with respect to the hydrogen ion concentration. The dependence of the rate constant on the square of the acid concentration is seen in Fig. 1. The linear dependence in perchloric acid solutions is very good. In sulfuric acid solutions the dependence is linear in 2.5–5.0 M solutions but tends to curve down with a decreasing acid concentration. Both the reactivity and the slope are clearly higher in sulfuric acid than in perchloric acid solutions.

There is a linear correlation between the rate and bisulfate concentration at a constant hydrogen ion concentration and at constant ionic strength, $(k_{\text{obs}}/[\text{TEAH}^+])/M^{-1} \text{ s}^{-1} = (1.02 \pm 0.03) \times 10^{-3} + (2.74 \pm 0.10) \times 10^{-4} [\text{HSO}_4^-]/M$, $r = 0.9987$ (Table 2).

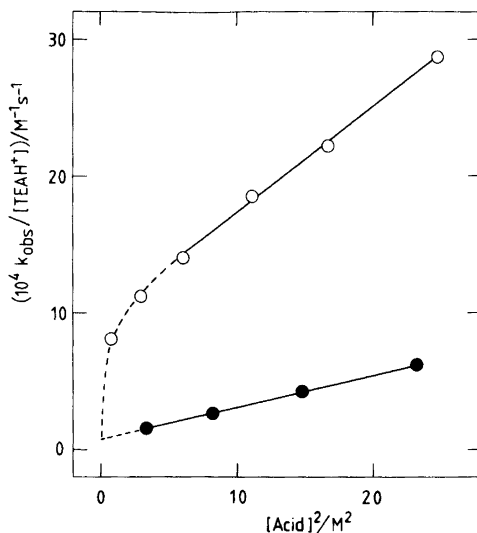
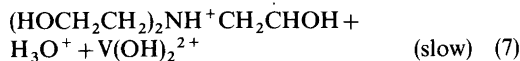
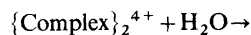
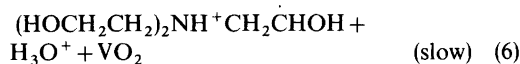
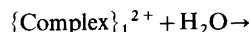
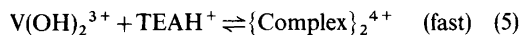
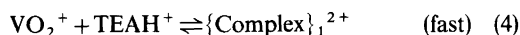
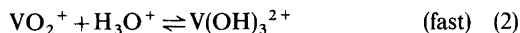
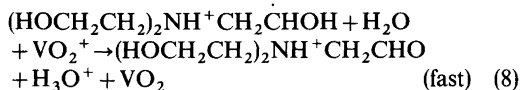


Fig. 1. Dependence of the rate constant $k_{\text{obs}}/[\text{TEAH}^+]$ on the square of the concentration of perchloric acid (black circles) and sulfuric acid (open circles) at constant ionic strength at 60°C.

It is well known that vanadium(V) exists in slightly acidic solutions as VO_2^+ , $\text{p}K_a = 3.70$ at 25°C.¹⁹ At higher acid concentrations $\text{V}(\text{OH})_3^{2+}$ species, and in sulfuric acid also $\text{V}(\text{OH})_3\text{HSO}_4^+$ are assumed to exist.⁹ In yet more acidic concentrations $\text{V}(\text{OH})_2^{3+}$ and $\text{V}(\text{OH})_2(\text{HSO}_4)^+$ species have been postulated to exist.⁸

Taking into consideration all the above-mentioned aspects, the following mechanism is assumed to explain well the data on perchloric acid solutions, where the order of the reaction with respect to the hydrogen ion concentration is two:



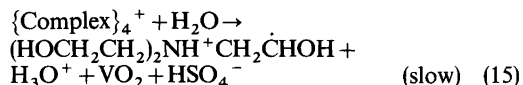
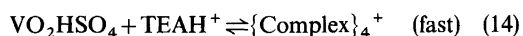
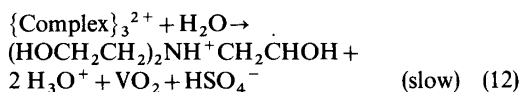
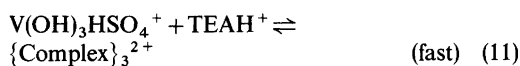
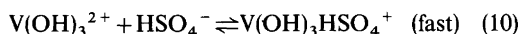


This mechanism leads to the rate law:

$$\text{Rate} = (k_6K_4 + k_7K_5K_3K_2[\text{H}_3\text{O}^+]^2)[\text{VO}_2^+][\text{TEAH}^+] \quad (9)$$

The lower line in Fig. 1 follows the equation ($k_{\text{obs}}/[\text{TEAH}^+]/\text{M}^{-1} \text{ s}^{-1} = (7.34 \pm 0.44) \times 10^{-5} + (2.36 \pm 0.03) \times 10^{-5} \times [\text{HClO}_4]^2/\text{M}^2$, $r = 0.9998$).

In sulfuric acidic solutions the rate law is complicated, as the species VO_2HSO_4 , $\text{V}(\text{OH})_3\text{HSO}_4^+$ and $\text{V}(\text{OH})_2(\text{HSO}_4)_2^+$ may contribute to the reaction. When considering the concentrations of hydrogen and bisulfate ions, we have assumed that sulfuric acid behaves like a strong monobasic acid. It follows that our results are in favour of a major contribution of $\text{V}(\text{OH})_3\text{HSO}_4^+$, because the reaction was found to be of first order with respect to the bisulfate ion concentration and because the rate increases linearly in Fig. 1 in the concentration range 2.46–4.97 M. If VO_2HSO_4 or $\text{V}(\text{OH})_2(\text{HSO}_4)_2^+$ were dominant, the line would curve downwards or upwards, respectively, with an increasing sulfuric acid concentration. This effect would be quite considerable, because the rate is so much higher in sulfuric acidic than in perchloric acidic solutions. If we write eqns. (10)–(12) for



the main reaction, and eqns. (13)–(15) for the probable minor reaction, the rate law is given by eqn. (16).

$$\begin{aligned} \text{Rate} = &(k_6K_4 + k_{15}K_{14}K_{13}[\text{HSO}_4^-] + \\ &+ k_{12}K_{11}K_{10}K_2[\text{H}_3\text{O}^+][\text{HSO}_4^-] \\ &+ k_7K_5K_3K_2[\text{H}_3\text{O}^+]^2)[\text{VO}_2^+][\text{TEAH}^+] \quad (16) \end{aligned}$$

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The solid line in Fig. 1 follows the equation ($k_{\text{obs}}/[\text{TEAH}^+]/\text{M}^{-1} \text{ s}^{-1} = (9.49 \pm 0.41) \times 10^{-4} + (7.77 \pm 0.25) \times 10^{-5} \times [\text{H}_2\text{SO}_4]^2/\text{M}^2$, $r = 0.9989$). Thus $k_{12}K_{11}K_{10}K_2 \approx (5.4 \pm 0.3) \times 10^{-5} \text{ M}^{-3} \text{ s}^{-1}$. Accordingly, the oxidizing ability of $\text{V}(\text{OH})_3\text{HSO}_4^+$ is about twice of that of $\text{V}(\text{OH})_2^{3+}$.

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