# Amine Oxidation. Part 16.[1] Kinetic Studies on the Oxidation of Some Aminoalcohols by Vanadium(v) Ions in Aqueous Perchloric Acid

**Richard J. Hutchinson and John R. Lindsay Smith** *
*Department of Chemistry, University of York, York YO1 5DD*
**Martyn V. Twigg**
*Imperial Chemical Industries plc, Agricultural Division, PO Box 6, Billingham, Teesside TS23 1LD*

The rate of oxidation of aminoalcohols by vanadium(v) ion in aqueous perchloric acid is first order with respect to vanadium(v) and the aminoalcohol. The dependence of the rate on the acidity of the reaction mixture is indicative of the active species being $V(OH)_3^{2+}$. The influence of substrate structure on the rate of oxidation has been studied with fifteen aminoalcohols, two deuteriated aminoalcohols, and two aminoethers. In the proposed mechanism for the oxidation, the rate-determining step is the homolytic decomposition of an aminoalcohol–vanadium(v) complex and involves hydrogen-atom abstraction from the C–H bond α to the hydroxy group.

In our previous paper[1] we showed, from a product and stoicheiometric study, that aminoalcohols are extensively oxidised by vanadium(v) ions in aqueous perchloric acid. The oxidations, which resemble those of simple alcohols, involve the initial removal of a hydrogen atom from the C–H bond α to the hydroxy group.

Although there have been numerous kinetic investigations on the oxidation of organic compounds by vanadium(v) ions,[2] including extensive studies of mono- and poly-hydric alcohols, there is only one very recent report on the kinetics of oxidation of aminoalcohols (TEA† and to a lesser extent DEA).[3] In this paper we describe some kinetic studies on the oxidation of a selection of aminoalcohols and related compounds in aqueous perchloric acid. These results, which are in agreement with the mechanism proposed in our previous paper, throw further light on these oxidations.

## Results

The main kinetic features of the oxidations have been identified with MEA, DMEA, and propan-1-ol as substrates by monitoring the formation of vanadium(IV) ions spectrophotometrically (670 nm).

*Dependence of Rate of Oxidation.*—(a) *Concentration of vanadium*(v) *ions.* Oxidations carried out in the presence of excess of MEA or DMEA with different initial concentrations of vanadium(v) species give good pseudo-first-order plots for at least 75% of the reaction (Table 1). The order of reaction with respect to vanadium(v), determined using the half-life method,[4] is 1.00 ± 0.05 for each substrate.

(b) *Concentration of aminoalcohol.* Oxidations were carried out with a constant initial concentration of vanadium(v) ion and with a 5—40-fold excess of substrate. For each substrate the pseudo-first-order rate constants ($k_{obs}$) were determined from the gradients of the first-order plots (Table 2). The order of the reaction for MEA (1.00 ± 0.05) and for the DMEA (1.03 ± 0.05) was determined from the gradient of the plot of log $k_{obs}$ against log [initial substrate].

**Table 1.** Dependence of the rate of oxidation of MEA and DMEA in aqueous perchloric acid on vanadium(v) ion concentration: [aminoalcohol] 0.1M, ionic strength 2.97M ($NaClO_4$), temp. 103 °C

| $10^3[V^V]$/M | 2 | 4 | 8 | 12 | 16 | 20 |
|---|---|---|---|---|---|---|
| MEA, [$HClO_4$] 2.0M | | | | | | |
| $10^5k_{obs}/s^{-1}$ [a] | 10.0 | 10.0 | 8.9 | 8.4 | 8.6 | 9.8 |
| DMEA, [$HClO_4$] 1.9M | | | | | | |
| $10^5k_{obs}/s^{-1}$ [a] | 10.0 | 9.3 | 8.9 | 9.0 | 8.6 | 9.5 |

[a] Error in $k_{obs}$ ±5%.

**Table 2.** Dependence of the rate of oxidation of MEA and DMEA in aqueous perchloric acid on concentration of substrate: [$V^V$] 0.01M, [$HClO_4$] 2.0M, ionic strength 2.5M ($NaClO_4$), temp. 102 °C

| [aminoalcohol]/M | 0.05 | 0.1 | 0.2 | 0.3 | 0.4 |
|---|---|---|---|---|---|
| MEA | | | | | |
| $10^5k_{obs}/s^{-1}$ [a] | 3.3 | 6.3 | 13.3 | 19.1 | 25.7 |
| $10^4k_{obs}$[substrate]$^{-1}$/ $dm^3$ $mol^{-1}$ $s^{-1}$ | 6.5 | 6.3 | 6.7 | 6.4 | 6.4 |
| DMEA | | | | | |
| $10^5k_{obs}/s^{-1}$ [a] | 5.8 | 12.2 | 24.1 | 36.7 | |
| $10^4k_{obs}$[substrate]$^{-1}$/ $dm^3$ $mol^{-1}$ $s^{-1}$ | 11.5 | 12.2 | 12.0 | 12.2 | |

[a] Error in $k_{obs}$ ±5%.

**Table 3.** Dependence of the rate of oxidation of DMEA and propan-1-ol by vanadium(v) ion on perchloric acid concentration: [substrate] 0.1M, [$V^V$] 0.01M, ionic strength 6.0M ($NaClO_4$), temp., reflux

| [$HClO_4$]/M | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
|---|---|---|---|---|---|---|
| DMEA | | | | | | |
| $10^5k_{obs}/s^{-1}$ [a] | 0.2 | 0.42 | 0.73 | 1.04 | 1.37 | 2.1 |
| $10^5k_{obs}$[substrate]$^{-1}$ [$H_3O^+$]$^{-1}$/ $dm^6$ $mol^{-2}$ $s^{-1}$ | 2.0 | 2.1 | 2.4 | 2.6 | 2.7 | 3.1 |
| Propan-1-ol | | | | | | |
| $10^5k_{obs}/s^{-1}$ [a] | 0.91 | 2.07 | 2.8 | 3.7 | 4.4 | 6.0 |
| $10^5k_{obs}$[substrate]$^{-1}$ [$H_3O^+$]$^{-1}$/ $dm^6$ $mol^{-2}$ $s^{-1}$ | 9.1 | 9.85 | 9.2 | 9.2 | 8.8 | 10.6 |

[a] Error in $k_{obs}$ ±5%.

(c) *Perchloric acid concentration.* The rate of oxidation of DMEA by vanadium(v) ion, with added sodium perchlorate to maintain a constant ionic strength, increases with increasing perchloric acid concentration (Table 3). A plot of the pseudo-first-order rate constant ($k_{obs}$) against perchloric acid concentration passes through the origin and the log $k_{obs}$ *versus* log [$HClO_4$] plot is linear in the range 1.0—5.0M-perchloric acid with a slope 1.21 ± 0.20. For comparison propan-1-ol was

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† The following abbreviations are used in this paper: TEA, triethanolamine; DEA, diethanolamine; MEA, monoethanolamine; DMEA, *NN*-dimethylethanolamine; DMBA, *NN*-dimethyl-4-aminobutan-1-ol.

**Table 4.** Dependence of the rate of oxidation of DMEA by vanadium(v) ion in aqueous perchloric acid on ionic strength: [DMEA] 0.1M, [V$^V$] 0.01M, [HClO$_4$] 2.0M, temp. 102 °C

| [NaClO$_4$]/M | 0.0 | 1.0 | 2.0 |
|---|---|---|---|
| $10^5k_{obs}$/s$^{-1}$ [a] | 3.4 | 4.0 | 4.7 |
| $k_{obs}/k_0$ [b] | 1.0 | 1.20 | 1.4 |

[a] Error in $k_{obs}$ ±5%. [b] $k_0$ is $k_{obs}$ without added NaClO$_4$.

**Table 5.** Pseudo-first-order rate constants for the oxidation of a selection of aminoalcohols and related compounds by vanadium(v) ion in aqueous perchloric acid; [substrate] 0.1M, [V$^V$] 0.01M, [HClO$_4$] 2.0M, temp. 102 °C

| Substrate | $10^5k_{obs}$/s$^{-1}$ [a] |
|---|---|
| H$_2$N(CH$_2$)$_n$OH $n = 2$ | 3.9 |
| $n = 3$ | 4.4 |
| $n = 6$ | 19.1 |
| MeNHCH$_2$CH$_2$OH | 5.8 |
| Me$_2$N(CH$_2$)$_n$OH $n = 2$ | 7.3 |
| $n = 3$ | 5.6 |
| $n = 4$ | 10.1 |
| $n = 5$ | 13.7 |
| Me$_2$NCH$_2$CH$_2$OMe | 0.4 |
| NH$_2$CH$_2$CHMeOH | 3.2 |
| NH$_2$CH$_2$CMe$_2$OH | 0.8 |
| NH$_2$CH$_2$CMeOH<br>CH$_2$CH$_2$Me | 0.69 |
| NH$_2$CH$_2$CHPhOH | 8.5 |
| Me$_2$NCH$_2$CHPhOH | 1.09 [b] |
| Me$_2$NCH$_2$CDPhOH | 1.18 [b] |
| Me$_2$NCD$_2$CHPhOH | 1.90 [b] |
| NH$_2$CHCH$_2$OH<br>CH$_2$Me | 3.5 |
| NH$_2$CMe$_2$CH$_2$OH | 1.8 |
| Morpholine | 0.18 |
| *N*-(2-Hydroxyethyl)morpholine | 7.9 |
| MeCH$_2$CH$_2$OH | 9.6 |
| HN(CH$_2$CH$_2$Me)$_2$ | 0.16 |
| HN(CH$_2$CH$_2$CH$_2$Me)$_2$ | 0.39 |

[a] Error in $k_{obs}$ ±5%. [b] Temperature 60 °C.

oxidised under identical conditions and the data give very similar graphs. The gradient of the log $k_{obs}$ *versus* log [HClO$_4$] plot is 0.95 ± 0.10. Neither substrate gives linear graphs when log $k_{obs}$ is plotted against either $H_0$ or $H_0$ values obtained from perchloric acid–sodium perchlorate solutions of constant ionic strength (μ 6.0M).[5,6]

(d) *Ionic strength.* The addition of sodium perchlorate at constant concentration of reactants and perchloric acid gives a linear increase in the pseudo-first-order rate constant for oxidation of DMEA (Table 4). This small positive salt effect is very comparable to those found for the vanadium(v) ion oxidation of other substrates, for example cyclohexanone,[7] 2-hydroxy-2-methylpropionic acid,[8] pyruvic acid,[9] and phosphorous acid.[10]

*Influence of Structure on the Rate of Oxidation of Some Aminoalcohols and Related Compounds.*—The pseudo-first-order rate constants ($k_{obs}$) for the oxidation of a selection of aminoalcohols and related compounds are recorded in Table 5. All the reactions with rate constants >2.0 × 10$^{-5}$ s$^{-1}$ give good first-order plots for at least 50% reaction. The slower oxidations give linear plots but were only monitored for 33—44% reaction.

The pseudo-first-order rate constant for the oxidation of *NN*-dimethyl-1-phenylethanolamine, [1-$^2$H]-*NN*-dimethyl-1-phenylethanolamine, and [2-$^2$H$_2$]-*NN*-dimethyl-1-phenylethanolamine (Table 5) have been used to calculate kinetic isotope effects. Deuteriation of the 1-position gives a primary isotope effect, $k_H/k_D = 1.74 \pm 0.04$ and deuteriation of the 2-position a secondary isotope effect, $k_H/k_D = 1.08 \pm 0.02$.

*Oxidation of Diethanolamine.*—The oxidation of DEA by vanadium(v) ion under the conditions used for the other aminoalcohols does not follow pseudo-first-order kinetics for the formation of vanadium(iv) ions. The absorbance *versus* time plots are S-shaped. Carrying out the reaction under nitrogen or in the presence of trace amounts of iron(ii) perchlorate or copper(ii) chloride had no effect on these plots. Similarly adding small quantities of vanadyl sulphate or of a reaction mixture which had undergone partial reaction did not change the appearance of the plots.

The kinetic behaviour of DEA oxidation can be rationalised by treating the process as two consecutive first-order reactions[11] [reaction (1)]. From the product studies, described

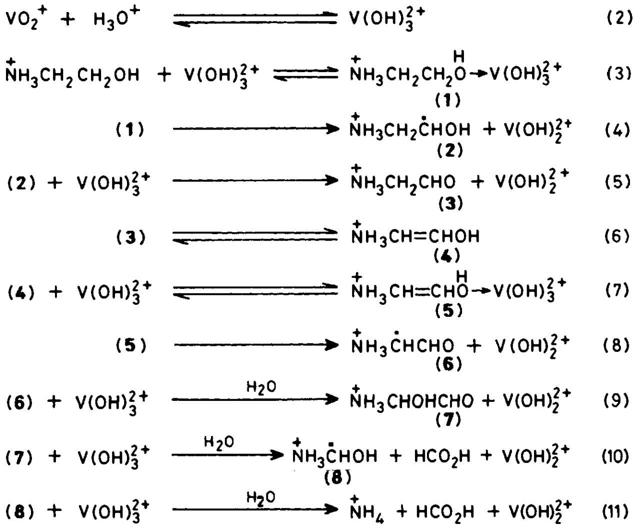
$$\text{DEA} \xrightarrow{k_1'} \text{Intermediate} \xrightarrow{k_2'} \text{products} \qquad (1)$$

previously,[1] the intermediate is MEA and $k_2'$ becomes its pseudo-first-order rate constant for oxidation (3.7 × 10$^{-5}$ s$^{-1}$). A series of absorbance–time curves were calculated for the overall reaction with equations for consecutive first-order reactions[11] using the experimentally determined $k_2'$ and a range of $k_1'$ values. Good agreement between calculated and observed curves resulted when $k_1' \approx 1.8 \times 10^{-4}$ s$^{-1}$, corresponding to $k_1'/k_2' \approx 5$. More detailed computer calculations, however, showed the number and precision of our data were not sufficient to place high reliability on the derived rate constant or the rate ratio (a common situation when trying to separate rate constants of similar magnitude[12]). Nevertheless, it is clear that DEA is more reactive than MEA.

## Discussion

The active form of vanadium(v) in aqueous perchloric acid is generally considered to be V(OH)$_3^{2+}$ arising from hydration of the vanadium dioxide cation[3,13] [reaction (2)]. Oxidation by such a species would account for the positive salt effect in the oxidation of DMEA and the dependence of the rate on the hydrogen ion concentration and not on $H_0$.

The suggested mechanism for the oxidation of a monoethanolamine by vanadium(v) ion in aqueous perchloric acid is shown in reactions (2)—(11). This is based on product and stoicheiometric studies in our previous paper[1] and on the



$$VO_2^+ + H_3O^+ \rightleftharpoons V(OH)_3^{2+} \qquad (2)$$

$$\overset{+}{N}H_3CH_2CH_2OH + V(OH)_3^{2+} \rightleftharpoons \underset{(1)}{\overset{+}{N}H_3CH_2CH_2\overset{H}{O}\rightarrow V(OH)_3^{2+}} \qquad (3)$$

$$(1) \longrightarrow \underset{(2)}{\overset{+}{N}H_3CH_2\dot{C}HOH} + V(OH)_2^{2+} \qquad (4)$$

$$(2) + V(OH)_3^{2+} \longrightarrow \underset{(3)}{\overset{+}{N}H_3CH_2CHO} + V(OH)_2^{2+} \qquad (5)$$

$$(3) \rightleftharpoons \underset{(4)}{\overset{+}{N}H_3CH{=}CHOH} \qquad (6)$$

$$(4) + V(OH)_3^{2+} \rightleftharpoons \underset{(5)}{\overset{+}{N}H_3CH{=}CH\overset{H}{O}\rightarrow V(OH)_3^{2+}} \qquad (7)$$

$$(5) \longrightarrow \underset{(6)}{\overset{+}{N}H_3\dot{C}HCHO} + V(OH)_2^{2+} \qquad (8)$$

$$(6) + V(OH)_3^{2+} \xrightarrow{H_2O} \underset{(7)}{\overset{+}{N}H_3CHOHCHO} + V(OH)_2^{2+} \qquad (9)$$

$$(7) + V(OH)_3^{2+} \xrightarrow{H_2O} \underset{(8)}{\overset{+}{N}H_3\dot{C}HOH} + HCO_2H + V(OH)_2^{2+} \qquad (10)$$

$$(8) + V(OH)_3^{2+} \xrightarrow{H_2O} \overset{+}{N}H_4 + HCO_2H + V(OH)_2^{2+} \qquad (11)$$

extensive research by Littler, Waters, and others on the vanadium(V) oxidation of alcohols, aldehydes, ketones, and sugars.[3,14] In this respect the reactions can be considered as oxidations of substituted alcohols since aminoalcohols are present as ammonium ions in strong acid solution and are not oxidised at nitrogen. In agreement with this conclusion the pseudo-first-order rate constant for oxidation of propan-1-ol is similar to that of the homomorphous aminoalcohol MEA, whereas amines are 10—20 times more inert to oxidation.

If reaction (4) is slow relative to the other reactions and equilibria in the proposed mechanism, then reactions (2)—(11) lead to the rate law (12). Thus as observed, the rate law predicts

$$d[V^{IV}]/dt = \frac{6K_2k_3k_4}{(k_{-3}+k_4)}[\text{Substrate}][VO_2][H_3O^+] \quad (12)$$

that the rate of formation of vanadium(IV) is first-order in the concentrations of vanadium(V), substrate, and hydrogen ion. This dependence of the rate on the concentration of these three species is typical of many vanadium(V) oxidations.[3]

Further confirmation for the reaction scheme comes from the dependence of the observed pseudo-first-order rate constants on the structure of the substrate. Increasing the length of the carbon chain between the heteroatoms leads to an increase in the rate constant. The magnitude of this effect is very similar to that reported by Rao *et al.*[15] for the oxidation of homologous primary alcohols and emphasises the minor influence of the quaternary nitrogen on these oxidations.

Monoalkylation of the carbon chain has little effect on the rate of oxidation. However, with dialkylation there is a significant retardation and, as expected from the mechanism, the effect is more pronounced for alkylation $\alpha$ to the hydroxy group. Phenylation of the carbon $\alpha$ to the hydroxy group leads to a significant increase in reactivity, when account is taken of the statistical decrease in $\alpha$-hydrogen atoms. This is consistent with the homolytic cleavage of the $\alpha$-C–H bond and resonance stabilisation of the forming radical. Similarly, increased rates of reaction have also been observed in the vanadium(V) oxidation of the allylic alcohols prop-2-en-1-ol and but-2-en-1-ol.[16]

Alkylation of the heteroatoms reveals the involvement of the hydroxy group in the oxidation for whereas *N*-alkylation leads to a small rate enhancement *O*-alkylation produces a marked retardation.

The kinetic isotope effects from the oxidation of *NN*-dimethyl-1-phenylethanolamine and its [1-$^2$H]- and [2-$^2H_2$]-analogues ($k_H/k_D$ = 1.74 and 1.08, respectively) indicate that, in agreement with the proposed mechanism, cleavage of the C–H bond $\alpha$ to the hydroxy group but not the $\beta$-C–H bond is involved in the rate-determining step. Although the primary kinetic isotope effect is smaller than that from the vanadium(V) oxidation of cyclohexanol and [1-$^2$H]cyclohexanol ($k_H/k_D$ = 3.6),[17] it is similar to the value for the equivalent oxidation with cobalt(III) in perchloric acid ($k_H/k_D$ = 1.7)[18] and the vanadium(V) oxidation of $\alpha$-hydroxyphenylacetic acid and its [$\alpha$-$^2$H] analogue ($k_H/k_D$ = 2.0).[19] The small primary isotope effect may be ascribed to either an early or a late transition state in the rate-determining step.

We find that, as reported by Puutio and Virtanen,[3] the oxidation of DEA does not show pseudo-first-order kinetics. The deviation from simple first-order behaviour does not arise from autocatalysis, or interference from molecular oxygen, vanadium(IV), or traces of iron or copper compounds. However, we can account for the kinetics in terms of two consecutive first-order processes. The first initiates the oxidation sequence leading to MEA and the second the degradation of MEA. The best fit of the absorbance–time plot data is obtained with the first rate constant *ca.* 5 times greater than that for MEA. When one of the hydroxyethyl groups of DEA is incorporated into a ring, as in *N*-(2-hydroxyethyl)morpholine, good pseudo-first-order kinetics are obtained for 80% reaction. The hydroxyethylmorpholine is twice as reactive as MEA.

## Experimental

*Materials.*—All the inorganic and organic materials were commercial reagent grade unless otherwise stated and were obtained from Aldrich Chemical Co. Ltd., Fisons Scientific Apparatus Ltd., or Koch-Light Ltd. The organic compounds were purified by distillation before use. AnalaR perchloric acid (12.4M) was from Fisons Scientific Apparatus Ltd. The nitrogen was British Oxygen white spot grade. *NN*-Dimethyl-4-aminobutan-1-ol, *NN*-dimethyl-5-aminopentan-1-ol, and *NN*-dimethyl-2-aminomethoxyethane were prepared as described previously.[20] *NN*-Dimethylaminoacetophenone was prepared from dimethylamine and phenacyl bromide following Chapman and Triggle[21] and was reduced with lithium aluminium hydride in diethyl ether. Work-up of the reaction mixture and distillation gave *NN*-dimethyl-1-phenylethanolamine (58%) with b.p. 118—126 °C at 10 mmHg (lit.,[21] 136—140 °C at 18 mmHg), $\delta_H(CDCl_3)$ 7.28 (5 H, m, ArH), 4.63 (1 H, dd, CH), 3.92 (1 H, s, OH), 2.45 (2 H, d, $CH_2$), and 2.30 (6 H, s, $CH_3$). Reduction of *NN*-dimethylaminoacetophenone with lithium aluminium deuteride gave [1-$^2$H]-*NN*-dimethyl-1-phenylethanolamine (65%) with b.p. 112—114 °C at 10 mmHg, $\delta_H$ 7.28 (5 H, m, ArH), 3.99 (1 H, s, OH), 2.36 (2 H, m, $CH_2$), and 2.29 (6 H, s, $CH_3$). $^1$H N.m.r. analysis showed that the 1-position of the latter compound was >99% deuteriated. [2-$^2H_2$]-*NN*-Dimethyl-1-phenylethanolamine (82.4% deuteriated) was prepared by reduction of [2-$^2H_2$]-*NN*-dimethylaminoacetophenone with lithium aluminium hydride. The deuteriated aminoketone was obtained by stirring *NN*-dimethylaminoacetophenone (6.0 g) with deuterium oxide (10 cm$^3$) for 18 h. The organic material was recovered by ether extraction and the deuteriation procedure repeated. Work-up by a second ether extraction gave [2-$^2H_2$]-*NN*-dimethylaminoacetophenone (5.5 g, 95%), 85% deuteriated ($^1$H n.m.r. analysis).

*Methods.*—The spectroscopic methods are described in the previous paper.[1] Reactions carried out at temperatures below reflux used a Grants LE20 low-temperature bath controlled to ± 0.2 °C.

*Kinetic Measurements.*—In the standard procedure a reaction mixture (80 cm$^3$) containing $10^{-2}$M-sodium metavanadate and $10^{-1}$M-aminoalcohol in 2.0M-perchloric acid was heated to reflux. Portions (5 cm$^3$) of the mixture were withdrawn, at suitable time intervals, and cooled to room temperature. The vanadium(IV) concentration was obtained spectrophotometrically by measuring the absorbance of the portion at 670 nm.

The influence of vanadium(V) ion concentration on the rates of oxidation of MEA and DMEA used the procedure described above. The sodium metavanadate concentration was varied between $2 \times 10^{-3}$ and $2 \times 10^{-2}$M and the ionic strength was maintained at 2.97M by the addition of sodium perchlorate. The dependence of the rate constants on substrate concentration (0.05—0.40M) used the above method with a 2.5M ionic strength.

The acid dependence of the rates of oxidation of $10^{-1}$M-DMEA and propan-1-ol by $10^{-2}$M-sodium metavanadate used the standard analytical procedure. The reactions were carried out at 60 °C with 1.0—6.0M-perchloric acid and 6.0M ionic strength.

The effect of ionic strength on the rate of oxidation of DMEA under the standard conditions was investigated by varying the ionic strength with sodium perchlorate.

In the oxidation of DEA under nitrogen the reaction mixture was deaerated by bubbling nitrogen through the solution for 1 h prior to reflux under nitrogen. The rate of formation of vanadium(IV) was measured as described above.

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