Monatshefte für Chemie 111, 927—933 (1980)

Monatshefte für Chemie

# Kinetics and Mechanism of Oxidation of *L*-Arabinose by Vanadium(V)

**R. P. Bhatnagar**[a,*] and **A. G. Fadnis**[b]

[a] School of Studies in Chemistry, Jiwaji University, Gwalior-474002, India

[b] Department of Chemistry, Govt. Science College, Gwalior-474002, India

*(Received 31 January 1978. Accepted 2 March 1978)*

Vanadium(V) oxidation of *L*-arabinose has been found to be first order with respect to oxidant and substrate concentrations. It has been found that the order with respect to $[H^+]$ changes from one in $2.5M$-$4.5M$ acid concentration range to two in $5.0M$-$6.5M$ acid concentration range. The oxidation rate has been found to increase with ionic strength and decrease with dielectric constant of the medium. Thermodynamic parameters $\Delta E$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ have been evaluated as $22.63 \pm 0.19$ kcal/mol, $-3.00 \pm 0.65$ e. u. and $23.59 \pm$ $\pm\ 0.05$ kcal/mol respectively. The reaction has been found to be initiated by the formation of free radical in a slow rate determining step.

*[Keywords: Kinetics of L-arabinose oxidation; Oxidation by vanadium(V)]*

*Kinetik und Mechanismus der Oxidation von L-Arabinose mit Vanadium(V)*

Die Vanadium(V)-Oxidation von *L*-Arabinose verläuft bezüglich des Oxidationsmittels und Substrats erster Ordnung. Bezüglich der Änderung von $[H^+]$ zeigte sich für den Bereich $2{,}5M$—$4{,}5M$ eine Abhängigkeit erster, im Bereich $5{,}0M$—$6{,}5M$ eine von zweiter Ordnung. Die Oxidationsgeschwindigkeit steigt mit der Ionenstärke und fällt mit der Dielektrizitätskonstanten des Mediums. Es wurden die thermodynamischen Parameter $\Delta E$, $\Delta S^{\ddagger}$ und $\Delta G^{\ddagger}$ bestimmt: $22{,}63 \pm 0{,}19$ kcal mol$^{-1}$, $-3{,}00 \pm 0{,}65$ e. u. und $23{,}59 \pm$ $\pm\ 0{,}05$ kcal mol$^{-1}$. Es wurde festgestellt, daß die Reaktion über die Bildung eines freien Radikals in einem langsamen, geschwindigkeitsbestimmenden Schritt initiiert wird.

## Introduction

Transition metal ion oxidants have been used for oxidations studies of several organic and inorganic substrates including carbohydrates, mainly hexoses[1–5]. Vanadium(V) is an important oxidant amongst this category of oxidants and has been also used for the oxidation studies of hexoses[6,7]. Earlier we have reported the oxidation of *D*-xylose by

0026-9247/80/0111/0927/$ 01.40

Mn(III) pyrophosphate[8]. In this communication we are reporting the results of the oxidation of *L*-arabinose, another pentose by vanadium(V).

## Experimental

All the chemicals used were of either E. Merck or Anala R (B. D. H.) grade. A standard solution of the oxidant was prepared by dissolving a ammonium meta vanadate (Reidel AR German) in appropriate concentration of sulphuric/perchloric acid. Solution of *L*-arabinose (E. Merck) was prepared fresh daily.

Oxidation reaction was followed by quenching aliquots withdrawn at definite intervals of time in an ice cold titration flask, and estimating unreacted vanadium with a standard solution of Fe(II) using *N*-phenyl-anthranilic acid as an indicator.

## Results and Discussion

One mole of *L*-arabinose has been found to consume ten moles of vanadium(V) for the complete oxidation. The over all oxidation reaction may be represented stoichiometrically as:

$$C_5H_{10}O_5 + 10\,V(V) + 5\,H_2O \longrightarrow 5\,HCOOH + 10\,V(IV) + 10\,H^+$$

The formation of formaldehyde during the course of reaction was confirmed by chromotrophic acid spot test[9], whereas HCOOH as end product by $HgCl_2$ test. The formation of free radicals during the course of reaction was also confirmed by the induced polymerisation reaction with acryl nitrile.

The kinetic studies were performed under pseudo first order conditions with the *L*-arbinose and sulphuric acid concentrations taken

Table 1. *Effect of Vanadium(V) and L-arabinose concentrations*
($3.5M$—$H_2SO_4$; $[\mu] = 3.51M$; 40 °C)

| [Vanadium(V)] × $10^2 M$ sec$^{-1}$ | [*L*-arabinose] × $10^2 M$ | $10^4 k_1$ / sec$^{-1}$ | $10^4 k_1$ / [*L*-arabinose] |
|---|---|---|---|
| 0.5 | 10.0 | 0.70 | — |
| 0.6 | 10.0 | 0.74 | — |
| 0.7 | 10.0 | 0.71 | — |
| 0.8 | 10.0 | 0.73 | — |
| 0.9 | 10.0 | 0.72 | — |
| 1.0 | 10.0 | 0.69 | 6.90 |
| 1.0 | 12.0 | 0.77 | 6.42 |
| 1.0 | 14.0 | 0.89 | 6.36 |
| 1.0 | 16.0 | 1.04 | 6.50 |
| 1.0 | 18.0 | 1.22 | 6.77 |
| 1.0 | 20.0 | 1.37 | 6.85 |

Average $10^4\, k_1/[L\text{-arabinose}] = 6.63 \pm 20$ mol$^{-1}$ sec$^{-1}$.

in large excess over that of oxidant concentration. It was found that the rate at which vanadium(V) disappeared followed a first order rate law uniformly for each individual run. The pseudo first order rate constant $k_1$ at different initial [vanadium(V)] has been found to be almost constant, where as it increases with[*L*-arabinose] (Tab. 1). The order with respect to [*L*-arabinose] has been found to be one. Further, a linear graph passing the origin can be obtained if drawn between $1/k_1$ and 1/[*L*-arabinose] showing no kinetic evidence of an intermediate complex formation between *L*-arabinose and vanadium(V).

Table 2. *Effect of* $H^+$ *concentration.* [Vanadium(V)] = $1.0 \times 10^{-2}\,M$; [*L*-arabinose] = $1.0 \times 10^{-1}\,M$

(A) *Lower Range* (2.5*M* to 4.5*M*); [$ClO_4^-$] = 4.5*M*; 40 °C

| $[H^+]M$ | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
|---|---|---|---|---|---|
| $-H_0$ | 1.01 | 1.23 | 1.47 | 1.72 | 1.97 |
| $10^4\,k_1/\text{sec}^{-1}$ | 0.96 | 1.27 | 1.46 | 1.70 | 2.20 |
| $10^4\,k_1/[H^+]$ | 0.38 | 0.43 | 0.42 | 0.42 | 0.49 |

Average $10^4\,k_1/[H^+] = 0.43 \pm 0.03\,\text{mol}^{-1}\,\text{sec}^{-1}$

(B) *Higher range* (5.0*M* to 6.5*M*); [$ClO_4^-$] = 6.5*M*; 30 °C

| $[H^+]\,M$ | 5.0 | 5.5 | 6.0 | 6.5 |
|---|---|---|---|---|
| $-H_0$ | 2.23 | 2.52 | 2.84 | 3.22 |
| $10^4\,k_1/\text{sec}^{-1}$ | 2.79 | 3.92 | 5.11 | 5.84 |
| $10^4\,k_1/[H^+]^2$ | 0.11 | 0.13 | 0.14 | 0.14 |

Average $10^4\,k_1/[H^+]^2 = 0.13 \pm 0.01\,\text{mol}^{-2}\,\text{sec}^{-1}$

The effect of $H^+$ concentration was studied in perchloric acid medium because of its expected non-complexing behaviour. The order with respect to $[H^+]$ was found to be one in the acid concentration range 2.5*M*-4.5*M* at constant [$ClO_4^-$] (4.5*M*); whereas a second order dependence was found in the acid concentration range 5.0*M*-6.5*M* at constant [$ClO_4^-$] (6.5*M*) (Tab. 2A and B).

From the data obtained in Tab. 2 linear graphs can be obtained if drawn between $\log k_1$ and $H_0$ (values taken from *Paul* and *Long*'s Table[10]) with slope values —0.40 and —0.43 in the lower and higher acid concentration ranges. From the linear plots obtained between $\log k_1 + H_0$ and $\log a_{H_2O}$[11] "ω" values have been computed as 6.0 and 3.0 in the two ranges respectively.

Further, it has been observed that the pseudo first order rate constant $k_1$ increases with ionic strength varied by adding sodium perchlorate (Tab. 3) and decreases with the dielectric constant of the medium, varied by changing the composition of binary mixture of acetic acid-water (Tab. 4).

Table 3. *Effect of ionic strength variation.* [Vanadium(V)] = $1.0 \times 10^{-2}$ *M*; [*L*-arabinose] = $1.0 \times 10^{-1}$ *M*; [H$^+$] = 3.5 *M*; 40 °C

| [$NaClO_4$]/*M* | [$\mu$]/*M* | $10^4 k_1$/sec$^{-1}$ |
|---|---|---|
| 0.0 | 3.51 | 1.15 |
| 1.0 | 4.51 | 1.46 |
| 2.0 | 5.51 | 1.63 |
| 2.5 | 6.01 | 2.31 |
| 3.0 | 6.51 | 2.71 |

Table 4. *Effect of dielectric constant variation.*
[Vanadium(V)] = $1.0 \times 10^{-2}$ *M*; [*L*-arabinose] = $1.0 \times 10^{-1}$ *M*; [$H_2SO_4$] = 1.35 *M*; 40 °C

| % acetic acid *v*/*v* | "*D*" | $10^3/D$ | $10^4 k_1$/sec$^{-1}$ | $4 + \log k_1$ |
|---|---|---|---|---|
| 70 | 25.29 | 38.04 | 19.88 | 1.2984 |
| 60 | 33.01 | 30.36 | 7.31 | 0.8639 |
| 50 | 39.73 | 25.17 | 3.84 | 0.5843 |
| 40 | 46.44 | 21.53 | 2.34 | 0.3692 |
| 30 | 53.15 | 18.81 | 1.26 | 0.1004 |

Table 5. *Thermodynamic parameters.*
[Vanadium(V)] = $1.0 \times 10^{-2}$ *M*; [*L*-arabinose] = $1.0 \times 10^{-1}$ *M*; [$H_2SO_4$] = 3.5 *M*

| Temp. °C | $10^4 k_1$ sec$^{-1}$ | $\Delta E$ kcal/mol | $\Delta S^{\ddagger}$ e. u. | $\Delta G^{\ddagger}$ kcal/mol |
|---|---|---|---|---|
| 35 | 0.44 | 22.73 | —2.42 | 23.47 |
| 40 | 0.69 | 22.82 | —2.48 | 23.60 |
| 45 | 1.24 | 22.81 | —2.47 | 23.60 |
| 50 | 2.23 | 22.38 | —3.79 | 23.60 |
| 55 | 3.72 | 22.40 | —3.83 | 23.66 |
|  | Average | 22.63 ± 0.19 | —3.00 ± 0.65 | 23.59 ± 0.05 |

A linear plot can be obtained between $\log k_1$ and $1/D$ with a positive slope showing that the oxidation reaction under study is of an ion-dipole type. It can be assumed that the *L*-arabinose molecule behaves as a dipole in aqueous medium and a positive ionic species of vanadium(V) is involved in the reaction.

Thermodynamic parameters have been computed from the data obtained from the temperature effect on the reaction rate (Tab. 5).

The earlier oxidation studies[12–16] have indicated that the active form of vanadium(V) species depends on the acid type and its concentration range. In aqueous acid medium vanadium(V) exists either as $VO_2^{+}$[17] or $V(OH)_4^{+}$[18], but this form can change depending on the concentration and type of the acid.

In the present case it seems that only protonated species of vanadium(V) are active in both ranges. Thus, in lower acid concentration range (2.5*M* to 4.5*M*) where $[H^+]$ dependence is one and the "ω" value is > 3.3 suggesting the involvement of a water molecule as proton transferring agent[11], the formation of active oxidant species may be explained considering the following equilibria[13, 19, 20].

$$VO_2^{+} + H_3O^{+} \overset{K_1}{\rightleftharpoons} V(OH)_3^{+2} \tag{1}$$

In higher acid concentration range (5.0*M* to 6.5*M*), where the rate depends on $[H^+]^2$ the following equilibria can be assumed to be operative[21, 22].

$$VO_2^{+} + 2H^{+} \overset{K_2}{\rightleftharpoons} V(OH)_2^{+3} \tag{2}$$

Now it can be assumed that the oxidation reaction is initiated by the formation of a free radical as an intermediate by the interaction of *L*-arabinose with the above species of vanadium(V) in the slow rate determining step as

$$L\text{-arabinose} + V(OH)_3^{+2} \xrightarrow[\text{slow}]{k'} R^{\cdot} + HCHO + V(IV) + H^{+} \tag{3 a}$$

in the lower acid concentration rage (2.5*M* to 4.5*M*) or

$$L\text{-arabinose} + V(OH)_2^{+3} \xrightarrow[\text{slow}]{k''} R^{\cdot} + HCHO + V(IV) + H^{+} \tag{3 b}$$

in the higher acid concentration rage (5.0*M* to 6.5*M*); or in general

$$L\text{-arabinose} + V(V) \xrightarrow[\text{slow}]{k} R^{\cdot} + HCHO + V(IV) + H^{+} \tag{3}$$

where $R^{\cdot}$ is $CHOCHOHCHOH\dot{C}HOH$.

The free radical $R^{\cdot}$ in a further fast step breaks into HCHO and HCOOH:

$$CHOCHOHCHOH\dot{C}HOH + V(V) + H_2O \xrightarrow[\text{fast}]{k'''} HCOOH + 3HCHO + V(IV) + H^{+} \tag{4}$$

where $k''' \gg k$ or $k'$ or $k''$.

The HCHO formed in steps (3) and (4) can further be oxidised to HCOOH in a fast step:

$$4\,\mathrm{HCHO} + 8\,\mathrm{V(V)} + 4\,\mathrm{H_2O} \xrightarrow[\text{fast}]{} 4\,\mathrm{HCOOH} + 8\,\mathrm{V(IV)} + 8\,\mathrm{H^+} \tag{5}$$

On the basis of above proposed mechanism steps, the general rate expression can be derived at constant $[\mathrm{H^+}]$ as:

$$-\frac{\mathrm{d}[\mathrm{V(V)}]}{\mathrm{d}t} = k[\mathrm{V(V)}][L\text{-arabinose}] + k'''[\mathrm{R}^{\cdot}][\mathrm{V(V)}][\mathrm{H_2O}] \tag{6}$$

Applying a steady state treatment to free radical $R\cdot$ it can be shown that

$$\frac{\mathrm{d}[R^{\cdot}]}{\mathrm{d}t} = k[\mathrm{V(V)}][L\text{-arabinose}] - k'''[\mathrm{R}^{\cdot}][\mathrm{V(V)}][\mathrm{H_2O}] = 0 \tag{7}$$

substituting (7) in (6) we obtain

$$-\frac{\mathrm{d}[\mathrm{V(V)}]}{\mathrm{d}t} = 2k[\mathrm{V(V)}][L\text{-arabinose}]. \tag{8}$$

Similarly the rate expresion which can explain the results obtained in the lower acid concentration range can be derived by considering steps (1), (3 a) and (4):

$$-\frac{\mathrm{d}[\mathrm{VO_2^+}]}{\mathrm{d}t} = 2k'K_1\,[\mathrm{VO_2^+}][L\text{-}arabinose][\mathrm{H^+}] \tag{9}$$

and in the higher acid concentration range by considering steps (2), (3 b) and (4):

$$-\frac{\mathrm{d}[\mathrm{VO_2^+}]}{\mathrm{d}t} = 2\,K_2\,k''[\mathrm{VO_2^+}][L\text{-arabinose}][\mathrm{H^+}]^2 \tag{10}$$

The rate expressions and the proposed mechanism are consistant with the results obtained.

## References

[1] *R. N. Mehrotra*, Z. Physik. Chem. (Leipzig) **230**, 221 (1965).

[2] *C. R. Pottenger* and *D. O. Johnson*, J. Polym. Sci. Part-A-1 **8**, 301 (1970).

[3] *M. Santappa* and *A. Meenakshi*, Curr. Sci. (India) **37** (11), 313 (1968); ibid **38** (13), 311 (1969).

[4] *G. V. Bakore* and *M. S. Bararia*, Z. Physik. Chem. (Leipzig) **229**, 245 (1965).

[5] *G. V. Bakore* and *K. Tandon*, Z. Physik. Chem. (Leipzig) **222**, 320 (1963).

[6] *R. S. Tripathi*, Ph.D. Thesis, Jiwaji University, Gwalior (M.P.) India (1971).

[7] *P. N. Pathak*, *M. P. Singh*, and *B. B. L. Saxena*, Z. Physik. Chem. (Leipzig) **241**, 145 (1969).

[8] *R. P. Bhatnagar* and *A. G. Fadnis*, Mh. Chem. **109**, 319 (1978).

[9] *F. Feigl*, Spot test in organic chemistry, p. 349. Amsterdam: Elsevier. 1960.

[10] *M. A. Paul* and *F. A. Long*, Chem. Revs. **57**, 1 (1957).

[11] *J. F. Bunnett*, J. Amer. Chem. Soc. **83**, 4956 (1961).
[12] *G. S. S. Murthy*, *B. Sethuram*, and *T. Navaneeth Rao*, Indian J. Chem. **13**, 849 (1975).
[13] *W. A. Waters* and *J. S. Littler*, J. Chem. Soc. **1959**, 3014, 4046.
[14] *J. R. Jones* and *W. A. Waters*, J. Chem. Soc. **1963**, 352.
[15] *R. Sahankar* and *S. N. Joshi*, Indian J. Chem. **1**, 289 (1963).
[16] *N. C. Bhargava*, *R. Shankar*, and *G. V. Bakore*, Z. Physik. Chem. (Leipzig) **229**, 238 (1965).
[17] *H. C. Mishra* and *M. C. R. Symones*, J. Chem. Soc. **1962**, 4411.
[18] *C. D. Coryell* and *D. M. Yost*, J. Amer. Chem. Soc. **55**, 1909 (1933).
[19] *J. R. Jones*, *W. A. Waters*, and *J. S. Littler*, J. Chem. Soc. **1961**, 630.
[20] *G. V. Bakore* and *N. C. Bhargava*, Z. Physik. Chem. (Leipzig) **232**, 120 (1966).
[21] *R. N. Mehrotra*, J. Chem. Soc. (B) **1970**, 1722.
[22] *S. Saccubai* and *M. Santappa*, Indian J. Chem. **8**, 533 (1970).