

Kinetics of V(V) Oxidation of Esters of Mandelic Acid

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The kinetics of V(V) oxidation of esters of mandelic acid ($\text{PhCHOHCO}_2\text{R}$, $\text{R} = \text{Me, Et, Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^s, \text{Bu}^i$ and $-\text{CH}_2\text{Ph}$) is first order in $[\text{V(V)}]$ and $[\text{substrate}]$ and second order in $[\text{H}^+]$. A kinetic isotope effect ($k_H/k_D = 2.6$) in the oxidation of ethyl mandelate ($\alpha\text{-H}$) and ($\alpha\text{-D}$) is observed. Oxidation products rule out the possibilities of rate limiting or concomitant hydrolysis. On the basis of product analyses and the absence of vinyl polymerization V(V) seems to behave as a two electron oxidant. No definite order in the reactivity is observed when the rates of oxidation of the esters at different temperatures are compared and the order does not conform to the isokinetic model.

IN its reactions V(V), like Cr(VI), can act both as one and two electron oxidant¹. While Jones *et al.*² maintain that oxidation of α -hydroxy acids by (V) proceeds through one electron oxidant involving C-C bond cleavage in the rate determining step. Bakore and Shanker³, in the reaction of glycollic acid with V(V) suggest that V(V) acts as a two electron oxidant involving C-H bond rupture in the slow step, similar to the oxidation of α -hydroxy acids by Cr(VI)⁴. Since no information is available on the reaction of esters of α -hydroxy acids with V(V), oxidation of esters of mandelic acid was undertaken. While this work in progress, a kinetic study of the oxidation of ethyl mandelate by chromic acid⁵ has been published and it is of interest to compare the reactivities of these oxidants.

Materials and Methods

V(V) solution in perchloric acid was prepared from ammonium metavanadate (Riedel). Acetic acid (E. Merck) was purified by refluxing over CrO_3 and subsequent fractional distillation. Esters of mandelic acid [$\text{PhCHOHCO}_2\text{R}$, $\text{R} = \text{Me, Et, Pr}^n, \text{Bu}^n, \text{Bu}^s, \text{Bu}^i$ and CH_2Ph] were prepared by Fischer's method⁶ and their purity checked. Mandelic acid ($-\alpha_d$) was prepared by the method of Kemp and Waters⁷ (98% deuterated; PMR analysis).

Reactions were carried out in acetic acid-water mixture at $30 \pm 0.02^\circ$ unless otherwise specified and followed colorimetrically using Hilger pattern Biochem absorptiometer by measuring the absorbance of V(V) at 680 nm. The cell was kept in a metal block through which water from the thermostat was circulated. Perchloric acid (60%, AR, Baker) was used as a source of hydrogen ions. Ionic strength was kept constant or varied by adding NaClO_4 (AR, Baker).

Product Analysis

Product study was made under kinetic conditions. Oxidized mixture was completely neutralized by

sodium bicarbonate and then extracted with ether (3 to 4 times). Aqueous layer gave no precipitate with 2,4-DNP indicating the absence of benzoylformic acid(s). Ethereal layer when treated with 2,4-DNP gave hydrazones which were identified by m.p. and mixed m.p. determination. Keto esters formed were also identified by elemental analysis and IR spectroscopy.

For quantitative analyses, control and blank experiments were run along with the test experiments. The results showed that $90 \pm 5.0\%$ of the mandelate esters were converted to the corresponding keto esters (cf. Table 1).

No induced polymerization of vinyl cyanide was observed in all the cases indicating the absence of free radicals.

Results and Discussion

All the esters of mandelic acid, $\text{PhCHOHCO}_2\text{R}$ (where $\text{R} = \text{Me, Et, Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^s, \text{Bu}^i$ and $-\text{CH}_2\text{Ph}$) behave alike. The data presented in this paper is, therefore, typical of all and represents the reaction of ethyl mandelate with V(V). Pseudo-first order rate constants do not change with varying initial $[\text{V(V)}]$. The order of reaction with respect to substrate is one and with respect to hydrogen ions comes out to be two (Table 2). The extent of variation of these parameters are limited by the solubilities of the esters in acetic acid-water and their rates.

TABLE 1 — ESTIMATION OF KETO ESTERS

| Ester $\text{PhCHOHCO}_2\text{R}$ | Wt (g) of 2,4-DNP of keto esters | | Reaction (%) |
|--------------------------------------|-------------------------------------|--------|-----------------|
| | Expected | Found* | |
| 1. $\text{R} = \text{Et}$ | 0.25 | 0.2310 | 92.4 |
| 2. $= \text{Pr}^i$ | 0.30 | 0.2702 | 90.0 |
| 3. $= \text{Bu}^n$ | 0.25 | 0.2260 | 90.4 |

* Average of three determinations after correcting for the control experiments.

TABLE 2 — EFFECT OF VARYING [SUBSTRATE] AND [H⁺] ON THE REACTION RATE

{[V(V)] = 0.042M; solvent: 60% AcOH (v/v); $\mu = 4M$; temp. = 30°C}

| [Ester] $\times M$ | $k_1 \times 10^4$ sec ⁻¹ [H ⁺] = 0.27M | $k_1/[\text{Ester}] \times 10^4$ litre mole ⁻¹ sec ⁻¹ | [H ⁺] $\times M$ | $k_2 \times 10^2$ litre mole ⁻¹ sec ⁻¹ [Ester] = 0.021M | $k_2/[\text{H}^+] \times 10^2$ litre ³ mole ⁻³ sec ⁻¹ |
|------------------------|---|--|------------------------------|---|---|
| 0.21 | 25.3 | 120 | 1.16 | 5.50 | 4.08 |
| 0.24 | 29.0 | 121 | 1.60 | 9.10 | 3.50 |
| 0.27 | 33.3 | 123 | 2.06 | 16.8 | 3.96 |
| 0.32 | 38.9 | 121 | 2.50 | 23.0 | 3.68 |
| 0.35 | 42.7 | 122 | 2.95 | 30.9 | 3.56 |
| 0.40 | 48.3 | 121 | 3.20 | 38.0 | 3.71 |
| Average: (121 \pm 2) | | | Average: (3.71 \pm 0.3) | | |

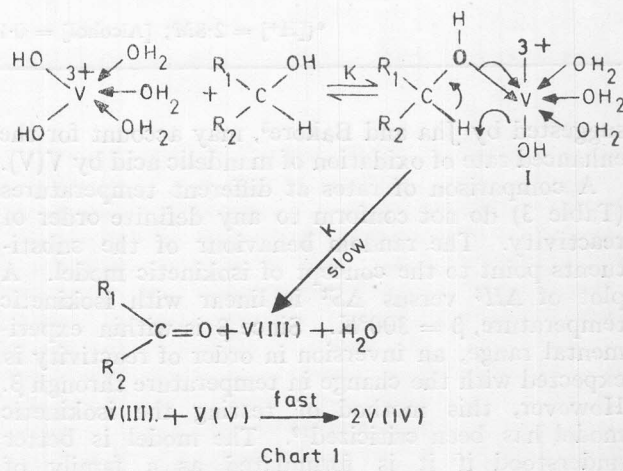
Effect of added NaClO₄— Addition of NaClO₄ increases the rate constants considerably. The values of rate constant (k_2) are 4.6, 9.4, 11.6 and 21.5 $\times 10^2$ litre mole⁻¹ sec⁻¹ at [NaClO₄] = 2.05, 2.85, 3.25 and 4.05M respectively. The increase in rate may be attributed to the decrease in activity of water molecules thereby decreasing the microscopic dielectric constant. However, dependence of rate on NaClO₄ is almost second order. This unusually strong effect cannot be solely attributed to the medium effect alone and may be due to specific effect of one of the ions, viz. Na⁺.

Kinetic isotope effect— A kinetic isotope effect (k_H/k_D) = 2.6 is observed in the oxidation of ethyl mandelate (α -H) and (α -D) and the values of k_2 are 128 and 48.8 $\times 10^4$ litre mole⁻¹ sec⁻¹ respectively for ethyl mandelate and deuterated ethyl mandelate.

A second order dependence of rate on [H⁺] can be explained by postulating V(OH)₂(H₂O)₃³⁺ as the VO₂⁺ + 3H₂O + 2H⁺ \rightleftharpoons V(OH)₂(H₂O)₃³⁺ ... (1) active oxidant (Eq. 1). Existence of quinque-coordinated V(V) species has been demonstrated by Mishra and Symons⁸.

A primary kinetic isotope effect of 2.6 suggest that C-H bond is affected in the transition state. A comparison of the magnitude of isotope effects in the oxidation of cyclohexanol¹² (= 3.6) and mandelic acid⁷ (= 2.0) by V(V) points to some similarities in these reactions. However, on the basis of product analysis* and the absence of radical mechanism V(V), in its reaction with esters of mandelic acid seems to act as a two electron oxidant like Cr(VI) as suggested by Bakore and Shanker³ and Pickering and McAuley⁹. The mechanism of oxidation of these esters can be expressed as shown in Chart 1.

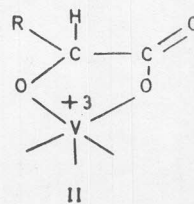
There is neither kinetic nor spectrophotometric evidence for the existence of intermediate (I) and an outer-sphere bimolecular interaction cannot be ruled out. However, in redox reactions involving sulphhydryl group (—SH) viz. 2-mercaptosuccinic acid⁹ and 2-mercaptoisobutyric acid (unpublished



work) and V(V), a transient intermediate complex formation has been characterized spectrophotometrically using stopped flow technique. The rate of ligand substitution is much faster than the rate of electron transfer. Paucity of relevant data does not permit one to conclude whether the reaction is inner sphere or outer sphere.

Absence of benzaldehyde(s) in the ethereal extract and benzoylformic acid(s) in the aqueous layer clearly rules out the possibility of a rate limiting or concomitant hydrolysis in the oxidation of these esters by V(V) (see also Jha and Bakore⁵).

For comparison the rates of oxidation of 1-phenylethanol and mandelic acid were determined. Under experimental conditions mandelic acid reacts too fast to be measured by conventional techniques. 1-Phenylethanol, however, reacts at a rate slower than those of the esters (Table 3). Although the order of reactivity COOH > COOR > CH₃ is in accord with the -I effect of the substituents, the rate of oxidation of mandelic acid is much faster than can be accounted for on the basis of -I effects alone. The formation of cyclic ester anhydride (II), as



*It is interesting to compare the products obtained in the oxidation of ethyl mandelate by V(V), Cr(VI) and Mn(III) under acid conditions. While 90% of the keto ester is obtained in case of Cr(VI) (cf. Jha and Bakore⁵) and V(V), benzaldehyde is the main product with Mn(III) — a typical one equivalent oxidant. [R. K. Malkani and K. S. Suresh (unpublished data)]. This, all the more supports the proposal that V(V) in the present study resembles Cr(VI) and behaves as a two electron oxidant.

TABLE 3 — EFFECT OF VARYING TEMPERATURE ON THE REACTION RATE

{[Ester] = 0.021M; [V(V)] = 0.042M; [H⁺] = 2.05M; solvent: 35% AcOH (v/v); μ = 2.2M}

| PhCHOHCO ₂ R R = | $k_2 \times 10^2$ litre mole ⁻¹ sec ⁻¹ | | | | | | ΔE^\ddagger (kcal mole ⁻¹) | ΔS^\ddagger (e.u.) |
|--------------------------------|--|------|------|------|------|------|---|-------------------------------|
| | 18° | 25° | 30° | 35° | 40° | 45° | | |
| Me | 6.8 | 10.8 | 15.7 | 20.0 | 27.6 | 36.9 | 11.5 | -25 |
| Et | 6.6 | 9.7 | 17.1 | 21.4 | 26.6 | 35.9 | 11.8 | -24 |
| Pr ⁿ | 4.7 | 7.5 | 11.0 | 14.6 | 19.0 | 25.7 | 11.4 | -26 |
| Pr ⁱ | 3.9 | 6.4 | 8.1 | 14.1 | 17.4 | 24.2 | 12.3 | -22 |
| Bu ⁿ | 2.1 | 3.8 | 4.5 | 7.4 | 11.9 | 12.6 | 14.1 | -17 |
| Bu ⁱ | 6.0 | 10.7 | 15.7 | 23.8 | 31.4 | 44.5 | 13.7 | -18 |
| Bu ^s | 6.1 | 8.5 | 10.9 | 14.3 | 16.2 | 22.3 | 8.0 | -37 |
| -CH ₂ Ph | — | 7.9 | 10.5 | 11.9 | 15.2 | — | 8.0 | -38 |
| 1-Phenyl ethanol* | — | — | 0.4 | 0.55 | 0.7 | 1.4 | 11.8 | -35 |

*{[H⁺] = 2.8M; [Alcohol] = 0.12M; [V(V)] = 0.021M; μ = 3.0M}

suggested by Jha and Bakore⁵, may account for the enhanced rate of oxidation of mandelic acid by V(V).

A comparison of rates at different temperatures (Table 3) do not conform to any definite order of reactivity. The random behaviour of the substituents point to the concept of isokinetic model. A plot of ΔH^\ddagger versus ΔS^\ddagger is linear with isokinetic temperature, $\beta = 300^\circ\text{K}$. Since β is within experimental range, an inversion in order of reactivity is expected with the change in temperature through β . However, this method of testing the isokinetic model has been criticized¹⁰. The model is better understood if it is formulated as a family of Arrhenius lines with a common point of intersection¹⁰. Thus a plot of $\log k$ at T_1 versus $\log k$ at T_2 should be linearly dependent according to the following Eq. (2).

$$\log k_{T_2} = a + b \log k_{T_1} \quad \dots(2)$$

The parameters a and b are dependent on the choice of T_1 and T_2 . When this criterion is applied to the present data (Table 3), no linearity is observed with the choice of T_1 and T_2 . It, therefore, appears that the variation of rates amongst the esters

themselves can be attributed to the operation of solvent and mild steric effects which have a mutually compensating effect on the changes in enthalpy and entropy, resulting in the linear plot of ΔH^\ddagger versus ΔS^\ddagger .

References

- HIGGINSON, W. C. E. & MARSHALL, J. W., *J. chem. Soc.*, (1957), 447.
- JONES, J. R., WATERS, W. A. & LITTLER, J. S., *J. chem. Soc.*, (1961), 630.
- BAKORE, G. V. & SHANKER, R., *Can. J. Chem.*, **44** (1966), 1717.
- BAKORE, G. V. & NARAIN, S., *J. chem. Soc.*, (1963), 3419.
- JHA, D. S. & BAKORE, G. V., *J. chem. Soc. (B)*, (1971), 1166.
- FISCHER, E. & SPENCER, A. S., *Ber. dt. chem. Ges.*, (1895), 3255.
- KEMP, T. J. & WATERS, W. A., *J. chem. Soc.*, (1964), 1192.
- MISHRA, H. C. & SYMONS, M. C. R., *J. chem. Soc.*, (1962), 4404.
- PICKERING, W. F. & MCAULEY, A., *J. chem. Soc., Dalton*, (1968), 1173.
- WOLD, S. & EXNER, O., *Chim. Scr.*, **3** (1973), 5.
- LITTLER, J. S. & WATERS, W. A., *J. chem. Soc.*, (1959), 4046.