

Substituent Effects & Mechanism of Oxidation of some Aryl Methyl Sulphides with Vanadium(V)

P V V SATYANARAYANA*, Y NAGESWARA RAO† & N NAGESWARA RAO†

Department of Chemistry, Nagarjuna University, Nagarjunanagar 522 510

Received 5 July 1984; revised and accepted 24 September 1984

Oxidation of aryl methyl sulphides by vanadium(V) in aqueous acetic acid follows overall second order kinetics, first order each in [sulphide] and [V(V)]. Electron-donating substituents in the benzene ring accelerate the rate while electron-withdrawing ones retard the rate. Good Hammett plot is obtained for *meta*-substituted phenyl methyl sulphides with high negative value of the reaction constant. The correlation of the *para*-substituted phenyl methyl sulphides with σ^+ values is good. A possible mechanism for the oxidation is suggested.

We report in this paper our kinetic results on the oxidation of some *meta*- and *para*-substituted phenyl methyl sulphides by V(V) in aqueous acetic acid in the presence of sulphuric acid. Though Srinivasan *et al.*¹ have reported the oxidation of aryl alkyl sulphides by Cr(VI) in aqueous acetic acid and proposed a mechanism for this reaction, no attempts have so far been made to study the kinetics of oxidation of these substrates by other metal oxidants.

Materials and Methods

All the sulphides viz. *m/p*-methoxy-, *m/p*-methyl-, *m/p*-chloro-, *m/p*-bromo-, *m/p*-nitro- and *p*-iodo-phenyl methyl sulphides were prepared by known methods² and purified by distillation under reduced pressure or recrystallization from suitable solvent (TLC pure). Acetic acid was purified over chromium trioxide. All other chemicals used were of AR grade. Doubly distilled water was used throughout.

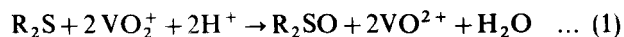
Kinetic measurements

Vanadium(V) solution was prepared and standardized according to the method of Gopal Rao and coworkers³. The reactant solutions were equilibrated at the desired temperature (maintained with an accuracy of $\pm 0.1^\circ\text{C}$) and mixed. The reaction was followed by quenching aliquots of the reaction mixture at definite intervals of time in sulphuric acid solution containing known excess of Fe(II) solution and the unreacted Fe(II) titrated against V(V) solution using *N*-phenylanthranilic acid as an indicator.

Unless otherwise stated the solvent used was aq acetic acid (50%, v/v). Measurements were made at 30°, 40° and 50° $\pm 0.1^\circ$ and are reproducible within $\pm 3\%$.

In a typical experiment with methyl phenyl sulphide, the product isolated after carrying out the reaction for 48 hr at room temperature was identified (co-TLC) as methyl phenyl sulphoxide.

Stoichiometric runs indicated that two mol of V(V) were consumed for the oxidation of one mol of sulphide in accordance with Eq. (1)



Results and Discussion

The kinetics of oxidation of methyl phenyl sulphide was studied in detail under second order conditions because of the difficulty involved in the solubility of sulphide. Varying either [V(V)] or [sulphide] has no appreciable effect on the second order rate constants. For example, at fixed $[\text{H}_2\text{SO}_4] = 1 \text{ mol dm}^{-3}$ and temp. = 30°C, (i) [V(V)] was varied from 2.35×10^{-3} to $5.88 \times 10^{-3} \text{ mol dm}^{-3}$ at constant $[\text{C}_6\text{H}_5\text{SCH}_3] = 6.54 \times 10^{-3} \text{ mol dm}^{-3}$ and (ii) $[\text{C}_6\text{H}_5\text{SCH}_3]$ was varied from 2.62×10^{-3} to $6.54 \times 10^{-3} \text{ mol dm}^{-3}$ at constant $[\text{V(V)}] = 2.35 \times 10^{-3} \text{ mol dm}^{-3}$. In all these cases $10^3 k_2$ remained constant at $17.3 \pm 0.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ indicating that the reaction followed second order kinetics—first order each in sulphide and V(V).

No reaction occurs in the absence of sulphuric acid and the rate increases with increase in $[\text{H}_2\text{SO}_4]$ at constant ionic strength. For example under the conditions $[\text{V(V)}] = 2.34 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{C}_6\text{H}_5\text{SCH}_3] = 2.45 \times 10^{-3} \text{ mol dm}^{-3}$ and 30°, $10^3 k_2$ increased from 2.70 to 17.40 $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ when $[\text{H}_2\text{SO}_4]$ was varied from 0.5 to 1.0 mol dm^{-3} . The effect of the acid is not conforming to any order with respect to $[\text{H}^+]$. The reaction rate increases with increase in acetic acid content in the solvent mixture.

The rate increases only slightly with increase in ionic strength. For example at $\mu = 2.40, 2.55, 2.70$ and 2.85 the second order rate constants obtained are 9.49, 9.70,

†Present address: Department of Chemistry, P B Siddhartha College, Vijayawada 520010.

Table 1—Second Order Rate Constants, Enthalpies and Entropies of Activation for Oxidation of Substituted Phenyl Methyl Sulphides by V(V)

{[H₂SO₄] = 0.80 mol dm⁻³; solvent = aq. acetic acid (50%, v/v)}

Substituent	$k_2 \times 10^3$ (dm ³ mol ⁻¹ s ⁻¹)			ΔH^\ddagger kJ mol ⁻¹	$-\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹
	30°	40°	50°		
None	9.49	26.4	51.0	66.1	65.0
<i>p</i> -OCH ₃	647.5	—	—	—	—
<i>p</i> -CH ₃	75.80	156.9	269.5	49.2	103.7
<i>p</i> -Cl	6.56	16.5	32.3	62.6	79.9
<i>p</i> -Br	7.87	17.2	37.3	60.9	84.4
<i>p</i> -I	7.85	—	—	—	—
<i>p</i> -NO ₂	0.023	0.051	0.128	67.4	111.5
<i>m</i> -OCH ₃	16.7	33.6	66.4	53.5	102.0
<i>m</i> -CH ₃	23.4	41.2	85.7	50.3	110.5
<i>m</i> -Cl	1.03	2.62	6.08	69.9	71.3
<i>m</i> -Br	1.03	2.54	6.05	69.7	72.0
<i>m</i> -NO ₂	0.072	—	—	—	—

10.3 and 11.0 × 10⁻³ dm³ mol⁻¹ s⁻¹ respectively under similar reaction conditions.

The rates of oxidation of several *meta*- and *para*-substituted phenyl methyl sulphides indicate that electron-releasing substituents in the benzene ring accelerate the rate while electron-withdrawing substituents have opposite effect (Table 1). The ΔH^\ddagger and ΔS^\ddagger collected in Table 1 have been calculated using Eyring equation.

Linear free energy relationship could not be applied since in the present reaction neither the entropies are constant (Table 1) nor they vary linearly with ΔH^\ddagger . However, Exner plot gives very good correlation indicating that all the substrates undergo oxidation by a common mechanism.

The plot of log (rate constants) for *meta*-substituted phenyl methyl sulphides against Hammett constants is linear ($r = -0.977$, standard deviation = 0.094 at 30°) with high negative reaction constant, $\rho = -3.21$. Similar plot using *para*-substituted compounds is also good ($r = -0.974$, standard deviation = 0.128 at 30°) with still higher reaction constant, $\rho = -3.85$. However, the correlation is improved ($r = -0.982$, standard deviation = 0.101) when log k is plotted against σ^+ values of Brown and Okamoto⁴ giving $\rho^+ = -3.24$. Conformity to σ^+ values indicates that the transition state is stabilised by direct mesomeric interaction with electron-releasing *para*-substituents. The ρ^+ -values obtained in the present reaction are considerably higher as compared to the values reported for the oxidation of sulphides by earlier workers and are comparable to the values reported by Miotti *et al.*⁵ for the oxidation of aryl methyl sulphides with bromine.

Mechanism of oxidation

Under the conditions employed, it is assumed that the V(V) exists as [V(OH)₃HSO₄]⁺ (refs 6-9). The increase in oxidising power of V(V) with increase in [acid] is mainly due to the increase in the oxidation potential of V(V) species. The equilibrium (2) may be written for the formation of active oxidant species:

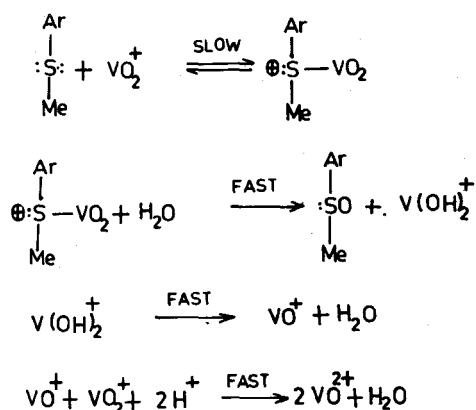


Increase in the percentage of water decreases the rate probably due to the solvation of sulphide, thereby decreasing its nucleophilicity. A similar decrease in rate with increase in water content of the solvent has been observed earlier in the oxidation of sulphides as well as sulphoxides¹⁰.

An increase in ionic strength shifts the equilibrium (2) to right giving rise to more of active species. Also the effect of ionic strength indicates that the reaction occurs between an ion and a neutral molecule.

Addition of manganous sulphate or mercuric chloride to the reaction mixture causes no appreciable change in the reaction rate. Also no polymerisation is observed when acrylonitrile is added to the reaction mixture. These tests exclude the possibility of the oxidation involving a radical mechanism.

On the basis of the foregoing kinetic data, a polar mechanism shown in Scheme 1 may be proposed for the oxidation of sulphides by V(V). The mechanism is consistent with negative value of ρ^+ obtained for the reaction. Electron depletion occurs at the reaction centre and is stabilised by electron-releasing *para*-substituents. Similar type of mechanism was proposed for the oxidation of aryl alkyl sulphides and phenylthioacetic acids by peroxydisulphate¹¹ where a low value of the reaction constant was reported.



Scheme 1

Exceptionally high negative ρ^+ values obtained in the present reaction may be due to the greater electrophilic nature of the oxidising agent. On the basis of Scheme 1

the rate law for the oxidation of methyl phenyl sulphide by V(V) can be written as

$$-d[V(V)]/dt = k_2 [\text{sulphide}][V(V)]$$

Acknowledgement

The authors thank Prof K V Jagannadha Rao for encouragement and the CSIR, New Delhi for the award of a JRF to one of them (YNR).

References

1 Srinivasan C, Kuthalingam P, Chellamani A, Rajagopal S & Arumugam N, *Proc Indian Acad Sci*, **93** (1984) 157.

2 Satyanarayana P V V, *Kinetics of oxidation and reduction of some aryl methyl sulphoxides*. Ph D Thesis, Annamalai University, Annamalaiagar, 1977.
 3 Gopal Rao G, Rao V P & Murthy B V S R. *Z analyt Chem*, **147** (1955) 161.
 4 Brown H C & Okamoto Y, *J Am chem Soc*, **79** (1957) 1913.
 5 Ruff F & Kuchman A, *J chem Soc Perkin II*, (1975) 509.
 6 Waters W A & Litle J S. *J chem Soc*, (1959) 3014, 4046.
 7 Jones J R & Waters W A. *J chem Soc*, (1962) 1629.
 8 Jones J R & Waters W A. *J chem Soc*, (1963) 352.
 9 Mehrotra R J, *J chem Soc (B)*, (1968) 642.
 10 Overberger C G & Cummins R W, *J Am chem Soc*, **75** (1953) 4783.
 11 Arumugam N, Srinivasan C & Kuthalingam P, *Indian J Chem*, **16A** (1978) 478.