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Oxidation of phenyl vinyl sulphide and phenyl vinyl sulphoxide in aqueous solution: A pulse radiolysis and theoretical study

M. Shirdhonkar^a, H. Mohan^b, D.K. Maity^c, B.S.M. Rao^{a,*}

^a National Centre for Free Radical Research, Department of Chemistry, University of Pune, Pune 411007, India

^b Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India
^c Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre, Mumbai 400085, India

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Dedicated to the memory of Dr. Hari Mohan, a co-author of this Letter and a source of inspiration to all of us, who suddenly died during the course of this work.

1. Introduction

Radiation chemical oxidation studies on aliphatic sulphides and sulphoxides have been well studied [1-4] but the corresponding work on aromatic compounds is limited. Only a few reports exist in the literature on the generation of radical cations of aromatic thioethers by photochemical [5,6] or radiolytical [7–11] methods. Highly acidic aqueous medium has been shown to be effective in generating and stabilising radical cations of aromatic systems [12–17]. The 'OH radicals react with aromatic sulphides by the adduct formation and the subsequent water/OH⁻ elimination process leads to the formation of the radical cation. One of the widely studied systems is phenyl methyl sulphide (thioanisole) where it was shown that the radiation induced oxidation finally leads to the formation of the sulphur centred radical cation. Our recent experimental results and theoretical calculations on its derivative - phenyl trifluromethyl sulphide revealed very high acid concentration is required to stabilise the radical cation and the charge is distributed over sulphur and the aromatic ring [18].

Other interesting models in this class of systems are phenyl vinyl sulphide and the corresponding sulphoxide. The 'OH radical addition to the vinyl carbon is an important reaction channel in the former as such an attack in the case of cinnamate derivatives was shown [19,20] by us to be significant. Sulphoxide functional group is important in organic synthesis [21,22] as well as due to its involvement in the biological activity of sulphides [23–25]. Because of its high oxidation potential, its electron transfer reactions have not been studied extensively [26,27]. The present work is,

* Corresponding author. Fax: +91 20 25691728.

E-mail address: bsmr@chem.unipune.ernet.in (B.S.M. Rao).

ABSTRACT

Pulse radiolysis and quantum chemical methods were employed to study the oxidation of phenyl vinyl sulphide (PVS) and phenyl vinyl sulphoxide (PVSO) by 'OH and SO₄⁻⁻ radicals. The 'OH radical reacts by addition ($k \sim (1-2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and the PVS–OH (λ_{max} = 310 nm) adduct was entirely converted into PVS'⁺ (λ_{max} = 310 and 550 nm) at pH 1. DFT calculations revealed that the vinylic OH adducts are in general more stable than the ring addition products and the odd electron spin in both radical cations is located over S and C atoms.

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therefore, undertaken to examine the possible reaction pathways of the 'OH radical induced oxidation of phenyl vinyl sulphide and its sulphoxide in aqueous solution using pulse radiolysis and quantum chemical methods. The structures of the compounds used in this study are shown in Schemes 1 and 2.

2. Experimental

PVS and PVSO obtained from Aldrich Chemicals were of high purity and used without any further purification. Solutions were prepared in water (conductivity = $18.2 \text{ M}\Omega \text{ cm}$), obtained from a Millipore water purification system and freshly prepared solutions were used for each experiment. The pH of the solution was adjusted using HClO₄, phosphate buffer or NaOH. High purity N₂O or N₂ gas was used for purging the solutions. All other chemicals used were also of high purity. The absorption spectra of PVS and PVSO were recorded on Shimadzu spectrophotometer model 1601.

2.1. Pulse radiolysis experiments

Pulse radiolysis experiments were carried out with high energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator at National Centre for Free Radical Research of University of Pune which was supplied by AS&E USA. All other details of the machine are described elsewhere [28]. The pulse radiolysis experiments were carried out in suprasil cuvettes with a cross-sectional area of 1 cm² at 25 °C. The 'OH reaction was studied in N₂O saturated solutions of PVS and PVSO and due to their limited solubility in water (<10⁻³ mol dm⁻³), solutions were stirred for about 30 min at 35 °C.

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Scheme 1. Oxidation reaction mechanism of phenyl vinyl sulphide.



Scheme 2. Oxidation of reaction pathways of PVSO.

The one-electron oxidants, $Cl_2^ Br_2^-$ and SO_4^- were generated using appropriate solution conditions. Their reactions were carried out under conditions such that the one-electron oxidant and not 'OH radicals react with the solute. The dose delivered per pulse was determined using N₂O saturated aqueous solution of KSCN $(1 \times 10^{-2} \text{ mol dm}^{-3})$ by monitoring the transient (SCN)₂⁻ species [29] at 480 nm.

2.2. Computational methods

Full geometry optimisations on the ground state of PVS and PVSO, respective OH adducts, radical cations have been carried out following density functional theory (DFT) adopting a 6-31 + G(d,p) set of basis functions. Becke's half-and-half (BHH) nonlocal exchange and Lee-Yang-Parr (LYP) nonlocal correlation functionals (BHHLYP) have been reported [30,31] to perform well to describe a three electron bonded open shell doublet system. The gas phase optimised molecular geometries are reoptimised fully including solvent effect following the Onsager reaction field model with the cavity radius based on gas phase optimised geometry. Calculations have been performed to find out a few low lying electronic transitions at TDDFT (BHHLYP) level of theory, choosing the same set of basis functions both in the gas and solution phases, to determine λ_{max} values of the transient species. Polarizable Continuum Model (PCM) is also applied to include the solvent effect in the calculation of ground state geometry as well as excited state electronic transitions. All the geometry optimisations and TDDFT calculations were performed applying the GAUSSIAN 03 program [32]. Visualisations of the geometries were carried out adopting the MOLDEN [33] program system.

3. Results and discussion

The UV–VIS absorption spectra of PVS and PVSO were recorded in the region 200–800 nm at pH 7 in the aqueous medium and their spectra exhibited absorption maxima at 245 and 235 nm, respectively. The wavelength region 250–750 nm was monitored in pulse radiolysis studies to avoid any interference of the parent absorption <250 nm.

3.1. Reactions of 'OH radical with PVS

3.1.1. Acidic solutions

The reaction of the hydroxyl radical was studied out in N₂O saturated aqueous solutions of phenyl vinyl sulphide $(1 \times 10^{-3} \text{ mol dm}^{-3})$ at pH 1. The transient absorption spectrum of the species produced in this reaction exhibited two peaks at 310 and 550 nm (Fig. 1A) with a shoulder at 380 nm. The rate of the reaction of the 'OH radical with PVS at pH 1 was measured from the build up of the transient species at the absorption maximum in the concentration range $(0.2-1) \times 10^{-3} \text{ mol dm}^{-3}$ and the value of the rate constant for reaction 2, Scheme 1 was found to be $1.9 \pm 0.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the linear fit (inset Fig. 1A).

The transient bands at 310 and 550 nm decayed with nearly the same rate as can be seen from the time resolved spectra recorded at 5 and 40 μ s (Fig. 1A). This suggests that only a single transient species was formed and in order to identify its nature, measurements were carried out with SO₄⁻⁻ (E^0 = 2.45 V), a specific one-electron oxidant. Fig. 2 depicts the spectrum obtained in this reaction, which has peaks at 310 and 550 nm. The value of the second order rate constant obtained from the plot of k_{obs} versus [PVS] is



Fig. 1. The transient absorption spectra obtained in the reaction of 'OH radical with PVS $(1 \times 10^{-3} \text{ mol dm}^{-3})$ at (A) pH 1 and (B) pH 7 at (\blacksquare) 5 and (\bigcirc) 40 µs after the pulse. Insets: 1A: plot of k_{obs} versus [PVS] and 1B: decay traces at (a) 310 and (b) 550 nm. Dose/pulse: 12–14 Gy.



Fig. 2. The transient absorption spectra obtained in the reaction of SO_4^- with phenyl vinyl sulphide $(1 \times 10^{-3} \text{ mol dm}^{-3})$ at 10 µs after the pulse at pH 7. Inset: plot of k_{obs} as a function of [PVS]. Dose/pulse = 13.5 Gy.

 $k = 1.1 \pm 0.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (inset, Fig. 2). The ratio of the intensities of absorption at 310 and 550 nm is about 2.7, which is

in agreement with that obtained in the reaction of 'OH (Fig. 1A). Thus, these two bands are attributed to the solute radical cation. The shoulder at 380 nm (Fig. 1A) may arise from the reaction of 'H with PVS as an independent measurement of 'H atom reaction with PVS exhibited weak absorption in this wavelength region.

In PVS, the electron density is located on the benzene ring, -C=C- due to π electrons and on sulphur due to the lone pairs. Being an electrophile, the 'OH radical can add to all the above possible sites and the subsequent hydroxide ion elimination leads to the formation of the corresponding radical cation. In the earlier work [34] on phenyl methyl sulphide, it has been shown that though the addition of 'OH can occur initially at both the ring and sulphur; eventually it leads to the formation of the stable sulphur centred radical cation. Assuming complete formation of the sulphur radical cation in the OH radical reaction at pH 1 in conformity with the finding [34] in phenyl methyl sulphide and $G(\cdot OH) = 2.8$ in acidic solutions, the molar absorptivities for $(PhSCH=CH_2)^{+}$ were calculated to be $\varepsilon_{310} = 4900$ and $\varepsilon_{550} = 1900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. These values are lower than those found for phenyl methyl sulphide ($\varepsilon_{310} = 9200$ and $\varepsilon_{550} = 5400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Such lowering in ε was reported [7] for the radical cation having an unsaturated substituent e.g. $(PhSCH_2Ph)^+$ where $\varepsilon_{310} = 6300$ and $\varepsilon_{550} = 2100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ A comparison of the intensities observed in the spectra recorded in the SO_4 - and the OH radical reaction at pH 1 revealed that 75% of the latter reacted to produce the radical cation (reaction 3, Scheme 1) and the rest possibly reacted by abstraction/addition to the vinylic group.

3.1.2. Neutral solutions

At pH 7, the transient spectrum obtained in the reaction of the 'OH radical with phenyl vinyl sulphide has an absorption maximum at 310 and a weak peak around 550 nm (Fig. 1B), the ratio of their intensities being 4.8. Thus, the peak at 310 nm has the contribution from two absorbing transient species namely the OH adduct and the solute radical cation. From molar absorptivities of the radical cation determined in this work, its contribution was estimated to be only about 20% in neutral solutions. The value of the second order rate constant obtained for the reaction 'OH radical is $2.0 \pm 0.1 \times 10^9$ dm³ mol⁻¹ s⁻¹. The absorption traces depicting the decay at 310 (trace a) and 550 nm (trace b) are shown in Fig. 1B. The relevant reaction sequence for the reactions of 'OH radical with PVS at pH 7 (reaction 1) and 1 (reaction 2) and SO₄⁻⁻ (reaction 3) are shown in Scheme 1.

3.2. Reactions of OH radical with PVSO

The reaction of the 'OH radical with phenyl vinyl sulphoxide $(1 \times 10^{-3} \text{ mol dm}^{-3})$ was carried out in N₂O saturated aqueous solutions at pH 1, 7 and 9. The second order rate constants measured at pH 1 and 7 are $7.8 \pm 0.5 \times 10^9$ and $7.9 \pm 0.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively (reaction 1, Scheme 2). The time resolved transient absorption spectra recorded in this reaction at pH 7 exhibited a prominent peak at 330 nm (Fig. 3). However, the spectrum measured at pH 1 has low intensities due to poor signal to noise ratios and hence was not considered further.

In contrast, the transient absorption spectrum obtained in the reaction of SO_4 .⁻ with PVSO exhibited two bands at 330 and 650 nm (Fig. 4), which is attributed to the monomer radical cation (structure **4**, Scheme 2). This assignment is in accord with the earlier work of Baciocchi et al. [27] on aryl sulphoxide radical cations. The transient absorption was fully developed within 1 μ s (inset Fig. 4) and the rate constant value calculated from the growth of the transient band at 330 nm (reaction 2, Scheme 2) is about $2.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The 'OH radical reacts by addition and the molar absorptivity of the OH adduct taking $G_{OH} = 5.6$, was esti-



Fig. 3. The transient absorption spectra obtained in the reaction of \cdot OH with phenyl vinyl sulphoxide (1 × 10⁻³ mol dm⁻³) at pH 7: (\blacksquare) 0.5 and (\bullet) 40 µs after the pulse. Inset: Decay at 330 nm. Dose/ pulse = 12.8 Gy.



Fig. 4. Transient absorption spectra obtained in the reaction of SO_4^- with phenyl vinyl sulphoxide $(1 \times 10^{-3} \text{ mol dm}^{-3}, \text{ pH } 4)$ at 1 µs after the pulse. Inset: (a) Absorption build up at 330 nm. Dose/pulse = 12.2 Gy.

mated to be 1940 dm³ mol⁻¹ cm⁻¹. The OH adduct decays bimolecularly as can be seen from the trace shown in inset Fig. 1B. The SO₄⁻ radical reacts by electron transfer, but no reactivity with other one-electron oxidants (Cl_2^- or Br_2^-) with both PVS and PVSO was noticed.

3.3. DFT calculations

3.3.1. Radical cations of PVS and PVSO

DFT calculations were performed with GAUSSIAN 03 program to optimise the geometry of phenyl vinyl sulphide, phenyl vinyl sulphoxide, their radical cations and different OH addition products using BHHLYP/6-31 + G(d,p) level of theory. The gas phase optimised geometry of PVS has shown that the benzene ring and the vinyl group are in two different planes. The angle between the ipso carbon–sulphur–vinyl carbon is (\angle CSC = 103.0°). The optimised geometry revealed that the molecule is symmetric about the plane passing through S atom-*ipso* and *para* carbons. On the other hand, the gas phase optimised geometry of PVSO indicated that the molecule is not symmetric. The calculated angle between *ipso* carbon–sulphur–vinyl carbon is \angle CSC = 97°. No significant changes

were observed in PVS and PVSO geometries when the gas phase geometry was reoptimised by including the solvent effect applying both the Onsager's reaction field and PCM models. The atomic charge (Mulliken) distributions have shown a significant difference at the two different levels of theory. The fully optimised structures of PVS and PVSO calculated using the dipole and PCM models are shown in Fig. 5A and B along with Mulliken charges. The analysis shows that the hydroxyl radical may add to both ring and vinyl carbons as well as sulphur atoms, though with different probabilities.

Both the gas and solution phase calculations were also carried out on the radical cations of PVS and PVSO. The gas phase optimised geometry of PVS cation has shown that the molecule loses its symmetry when one electron is removed from the system. The angle between *ipso* carbon–sulphur–vinyl carbons was increased by 6.1°. In the PVSO radical cation, the ∠CSC increase is 13°. The fully optimised geometries of PVS and PVSO radical cations in the solvent phase are shown in Fig. 5C and D along with the Mulliken spin densities applying dipole and polarizable continuum models for the solvent effect.

Our calculations revealed that in both PVS (Fig. 5C) and PVSO (Fig. 5D) radical cations the odd electron spin is over S and C atoms. This is in contrast to the earlier finding on the phenyl methyl sulphide radical cation [34] where the entire charge has been shown to be located on S atom, but is in good agreement with the work of Baciocchi et al. [27] on the corresponding phenyl methyl sulphoxide radical cation which was attributed to the conjugative interaction between MeSO and the ring. Such delocalisation of charge/ spin is also possible in the PVS system due to the vinylic group. A comparison of spin densities in PVS system shows that it is



Fig. 5. Optimised structures of (A) PVS and (B) PVSO showing Mulliken charges on C, S and O atoms, (C) PVS and (D) PVSO radical cations showing Mulliken spin population on non-hydrogen atoms. Values were obtained applying dipole (upper lines) and polarizable continuum (lower lines) models for the solvent effect. Yellow ball refers S, red ball to O atom and dark and light grey balls to C and H atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

located not only on S and ring carbons (\sim 35% each) but also on one of the vinylic carbon (25%). On going to PVSO, the distribution is changed with S and O atoms carrying about 35% each and the rest equally located on ring and vinylic carbons.

3.3.2. OH adducts of PVS and PVSO

The hydroxyl radical can add to eight carbon atoms (six of the ring i.e. two each of *ortho* and *meta*, one each of *para* and *ipso* (C1 to C6) and two vinyl carbon atoms (C7 and C8) and also to sulphur atom (S1) to form the corresponding OH adducts of PVS and PVSO. We have calculated the spin densities and binding energies of the products obtained by adding the OH to all the above positions and the optimised geometries in both gas and solution phases, but the values in the two cases remained nearly the same.

The different (PVS–OH) adducts numbered C1 to C8 and S1 are depicted in Fig. 6. In the case of PVSO, no stable structure was obtained by addition of OH to S and the optimised geometries of (PVSO–OH) adducts at C1, C7 and C8 are shown in Fig. 7 while the spin densities and binding energies for the rest are tabulated in Table 1.

The addition product contains an unpaired electron and its localisation features can be understood in terms of the spin density (S_d) in the concerned system. Whenever the addition occurred at a ring carbon atom, high S_d values are located at the carbon atoms *ortho* and para with respect to the addition site. For example, in (PVS–C1OH) adduct, high S_d values are located on *ortho*: C2 (0.60) and C6 (0.60) and *para*: C4 (0.78) positions (Fig. 6). Similarly, in the (PVS–C5)OH adduct, high S_d values are seen on *ortho* C6



Fig. 6. Optimised geometries of (C1-C8)-OH) and (S1-OH) adducts of phenyl vinyl sulphide with binding energies and spin densities above 0.2.



Fig. 7. Optimised geometries of (PVSO-OH) adducts at C1, C7 and C8 with binding energies and spin densities above 0.2.

Table 1

Binding energies E_b (kcal/mol) in solution phase and atoms with spin density (S_d) values (above 0.2) of various OH addition products of PVSO.

System	E _b (kcal/mol)	S _d
C2	18.5	C3(0.779), C5(0.651), C1(0.573)
C3	11.4	C6(0.807), C4(0.684), C2(0.600)
C4	27.2	C1(0.725), C5(0.649), C3(0.647)
C5	12.6	C2(0.800), C4(0.681), C6(0.559)
C6	15.6	C3(0.791), C5(0.628), C1(0.514)
C7	29.2	C8(1.154)
C8	27.2	C7(1.1)

(0.60) and para C2 (0.80) and C4 (0.68) sites (Table 1). On the other hand, when the addition is to the vinyl carbon atoms (C7 or C8), the localisation of the unpaired electron is clearly seen on the other vinyl carbon atom. For instance, in the PVS system, when it adds to C7, S_d = 1.15 is observed on C8 and vice versa on addition with S_d (C7) = 0.97. Very similar features were also observed in the PVSO-OH addition products.

Our calculations in the solution phase on binding energies predict that the (C8-OH) and (C7-OH) adducts are relatively more stable than the ring carbon addition products. For example, the most stable product is the (C8-OH) adduct followed by the (C7-OH) adduct with binding energies of 29.7 and 26.6 kcal/mol whereas the (S1-OH) adduct is the least stable (2.1 kcal/mol) with the stabilities of the ring carbon addition products lying in between. This suggests that the OH radical preferentially adds to the vinylic carbons and its addition products to the ring carbons is much lower and is not selective with nearly equal binding energies of the (C1-C6)-OH adducts in the range 11.1-13.7 kcal/mol. Such preferential addition of hydroxyl radicals to the side chain carbon atoms over the ring carbon atoms was also reported [35] by us in our work on cinnamic acid derivatives.

An interesting finding is the dissociative reaction channel observed (reaction1, structure 3, Scheme 2) in the case of the ipso carbon OH adduct of PVSO. When the gas phase ipso OH adduct was reoptimised by including the solvent effect, the dissociation of the bond between sulphur and ipso carbon was observed. A product with hydrogen bond between the H atom from the hydroxyl group attached to the ring and the O atom of the sulphoxide group (Fig. 7C1) was seen.

Excited state calculations were carried out at TDDFT (BHHLYP) level of theory by both Onsager reaction field and PCM models. The optical absorption maxima for the PVS radical cation in solution using the former procedure are predicted at 295 and 450 nm which are blue shifted by 15 and 100 nm, respectively from the experimental values (310 and 550 nm). However, the excited states calculations with the PCM model have shown the maxima at 295 and 610 nm and the band at 610 nm is now 60 nm red shifted. Similar calculations for the PVSO radical cation predicted the maxima at 303 and 612 nm which are blue shifted from experimental values (330 and 650 nm). Furthermore, the bands at the longer wavelength were found to be mainly due to the HDOMO-2 (Highest doubly occupied molecular orbital) \rightarrow LSOMO (Lowest singly occupied molecular orbital) transition. It should be noted that in both systems several electronic transitions contribute to the predicted absorption band in the UV region (300 nm).

4. Conclusions

The 'OH radical reacts by addition to phenyl vinyl sulphide forming PVS-OH adduct and its dehydration was found to be pH dependent with complete conversion to the (PVS)⁺ at pH 1 $(\lambda_{\text{max}} = 310, 550 \text{ nm}, \text{ and } \varepsilon_{310} = 4900, \varepsilon_{550} = 1900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}).$ In contrast, no formation of the radical cation was seen in PVSO. Pulse radiolysis data complemented by theoretical calculations have proven useful in understanding the radiation induced oxidation mechanism of PVS and PVSO.

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