

Oxidation of phenyl trifluoromethyl sulphide: A pulse radiolysis and theoretical study

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Abstract

Pulse radiolysis technique and quantum chemical calculations have been employed to study the pH dependent reaction of the $\bullet\text{OH}$ radical with phenyl trifluoro methyl sulphide (PTFMS). The transient absorption spectrum in neutral conditions with maximum at 330–340 nm ($\epsilon_{340} = 2750 \text{ dm}^3(\text{mol cm})^{-1}$) consisted of the $\bullet\text{OH}$ addition product and its yield decreased at pH 1 with 15% $\bullet\text{OH}$ contributing to the formation of the monomeric sulphur radical cation. The yield and the lifetime of the radical cation were observed to increase with acid concentration reaching 100% at $6.8 \text{ mol dm}^{-3} \text{ HClO}_4$ with molar absorptivity values of 11,500 and $6150 \text{ dm}^3(\text{mol cm})^{-1}$ at 320 and 560 nm respectively. Quantum chemical studies at MP2 level with PTFMS and phenyl methyl sulphide (PMS) revealed that the $\bullet\text{OH}$ radical adds to the aromatic ring and not to S atom. The *para* OH adduct of PTFMS is the most stable (binding energy = $22.41 \text{ kcal mol}^{-1}$) whereas the *ipso* addition product is less stable ($5.10 \text{ kcal mol}^{-1}$). The optimized geometries of PMS and PTFMS monomeric sulphur radical cations have shown the charge distribution mostly on the S atom in the former but was extended to the aromatic ring in the latter. Neither the oxidation of PTFMS by pulse radiolysis ($\text{Cl}_2^{\bullet-}$, $\text{Br}_2^{\bullet-}$ or $\text{SO}_4^{\bullet-}$) nor by cyclic voltammetry was observed.

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1. Introduction

The free radical chemistry of organic sulphur compounds is important because the radicals and ions derived from these compounds play an important role in understanding many chemical and biological processes [1–6]. Such studies are of current interest as these species are considered to be possible intermediates in redox reactions of sulphur containing biomolecules. The chemistry of sulphur centred species has gained importance as they also act as intermediates in some organic synthesis and environmental studies [7]. Hydroxyl radicals and specific one-electron oxidants are known to react with dialkyl sulphides (R_2S) and form sulphur centred dimer radical cations $(\text{R}_2\text{S})_2^{\bullet+}$ either directly or via a complex sequence of reactions involving OH-

adduct, α -thio radical and monomer radical cation [1,8–11]. A large number of investigations have been reported on aliphatic thioethers (R_2S) and their substituted derivatives [1–3,8–11]. However, studies on aromatic thioethers and their substituted derivatives are limited [12–15]. One-electron oxidation of aromatic thioethers has shown the formation of the sulphur centred monomer radical cation and no dimeric sulphur radical cations because of the spin delocalisation of the odd electron on the aromatic ring.

Hydroxyl radicals were observed [16] to react with thioanisole via two competitive addition pathways with almost equal probability, one with thioether functionality and the other with the aromatic ring. The addition to the sulphur atom leads to the prompt formation of monomer sulphur radical cation even at neutral pH. The reaction of $\bullet\text{OH}$ radicals with phenyl methyl sulphide (PMS) at high proton concentration ($\geq 0.1 \text{ M}$) has shown quantitative formation of sulphur centred monomer radical cation. It is interesting to study the reaction of $\bullet\text{OH}$ radicals with a related system but where the possibility of $\bullet\text{OH}$ radical addition to the sulphur atom is minimised. In the present

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study, phenyl trifluoromethyl sulphide (PTFMS) has been chosen because the electron-withdrawing power of fluorine is higher (+3.08) than the hydrogen atom (+0.49) [17].

The $\bullet\text{OH}$ radicals however react with substituted benzenes containing electron-withdrawing group by addition [18]. The nature and redox properties of the transient species formed from substituted aromatic organic sulphur compounds under different pH conditions allow us to examine the redox behaviour. Highly acidic aqueous medium has been shown to be effective in generating and stabilising radical cations of aromatic systems [11,19–21]. Structure, nature of bonding and stability of intermediates formed on reaction of $\bullet\text{OH}$ radicals with PMS and PTFMS are studied by applying ab initio quantum chemical methods [22–24] coupled with pulse radiolysis.

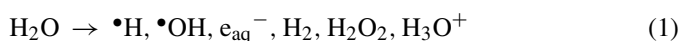
2. Experimental

Phenyl trifluoro methyl sulphide (Ph-S-CF_3) and phenyl methyl sulphide (Ph-S-CH_3) obtained from Aldrich Chemicals were of high purity and used without any further purification. The solutions were prepared in deionised ‘Nanopure’ water and freshly prepared solutions were used for each experiment. pH was adjusted with HClO_4 in phosphate buffer. Iolar grade high purity N_2O gas was used for purging the solutions. All other chemicals used were also of high purity. Detailed procedure of experiments is described elsewhere [11]. Cyclic voltammetric studies were carried out on a Autolab (100) System using a three-electrode system: platinum as working electrode, platinum rod as auxiliary electrode and Ag/AgCl as the reference electrode. The electrochemical cell containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ solution of the sample in 0.1 mol dm^{-3} KNO_3 was thermostated at 25°C .

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. The dose delivered per pulse was determined using N_2O saturated aqueous solution of KSCN ($1 \times 10^{-2} \text{ mol dm}^{-3}$) by monitoring the transient $(\text{SCN})_2\bullet^-$ species [25] at 480 nm. The pulse radiolysis experiments were carried out in suprasil cuvettes with a cross-sectional area of 1 cm^2 at 25°C .

Radiolysis of N_2 -saturated neutral aqueous solution leads to the formation of three highly reactive species (H , $\bullet\text{OH}$, e_{aq}^-) in addition to the formation of less reactive or inert molecular products e.g. H_2 , H_2O_2 , H_3O^+ [26].



The reaction of $\bullet\text{OH}$ radicals in neutral aqueous solution was carried out in N_2O -saturated solutions where e_{aq}^- is quantitatively converted to $\bullet\text{OH}$ radicals ($e_{\text{aq}}^- + \text{N}_2\text{O} \rightarrow \bullet\text{OH} + \text{OH}^- + \text{N}_2$). The reaction of $\bullet\text{OH}$ radicals in acidic solutions was carried out under aerated conditions to scavenge e_{aq}^- and $\bullet\text{H}$ atoms

($e_{\text{aq}}^- + \text{H}^+ \rightarrow \bullet\text{H}$; $\bullet\text{H} + \text{O}_2 \rightarrow \text{HO}_2\bullet$). The contribution of $\text{HO}_2\bullet$ radical was independently studied in presence of *t*-butyl alcohol, which acts as an $\bullet\text{OH}$ radical scavenger.

The transient species formed from pulse radiolysis were monitored using a 175 W Cermax parallel lamp, a monochromator (110 mm ruled grating with 1200 lines per nm) and Hamamatsu R-7400U-04 photomultiplier as the detector. The photomultiplier output was digitized with a 300 MHz TDS 3032B storage oscilloscope. The transient signals with very low absorbance values were always averaged for at least three signals. The output from storage oscilloscope was interfaced to a computer with LabView software. The complete detection system with software was supplied by Luzchem Canada. The data was analyzed for both first and second-order kinetics and those rate constant values were taken for which a very good correlation of fitting was observed. The rate constant values are an average of at least three independent experiments and the variation in the data is within $\pm 10\%$. All other details are described elsewhere [27].

2.2. Theoretical methods

Full geometry optimizations on the ground state of phenyl methyl sulphide and phenyl trifluoro methyl sulphide, respective OH-adducts and radical cations have been carried out. Post Hartree-Fock method, second-order Møller-Plesset (MP2) as well as density functional theory (DFT) adopting a correlated nonlocal density functional, BHHLYP have been applied for the calculations adopting split valence Gaussian atomic basis set, 6-31+G(d,p). BHHLYP functional has been reported to perform well to describe open shell doublet systems [22]. All the calculations have been performed by GAMESS suit of program on a pc-based cluster platform [28]. Visualization of the geometry and molecular orbitals has been carried out using Molden program system [29].

3. Results and discussion

3.1. $\bullet\text{OH}$ reaction: neutral conditions

Pulse radiolysis of an aerated neutral aqueous solution of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) exhibited a spectrum with a peak at 330–340 nm. This spectrum, shown in Fig. 1, is due to the reaction of the $\bullet\text{OH}$ radical with PTFMS because neither did it react with the hydrated electron nor with $\text{O}_2\bullet^-$ formed in reaction (2). The e_{aq}^- reaction was studied by pulsing



PTFMS solutions containing *t*-butyl alcohol to scavenge the $\bullet\text{OH}$ radical in the absence of oxygen and reaction (2) in its presence. Thus, the spectrum in Fig. 1 is attributed to the OH adduct of PTFMS. Under our experimental conditions, the entire yield of $\bullet\text{OH}$ radical is reacting with PTFMS to form OH adduct. Assuming $G(\bullet\text{OH}) = 2.8$ per 100 eV, the molar absorptivity at 340 nm was estimated to be $2750 \text{ dm}^3(\text{mol cm})^{-1}$.

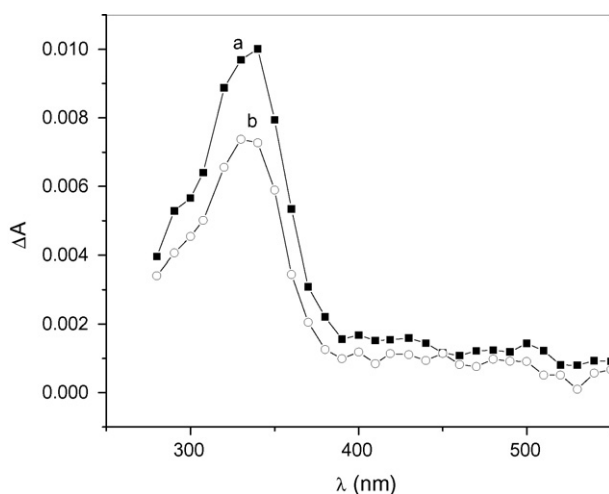


Fig. 1. Transient absorption spectra obtained on pulse radiolysis of aerated neutral aqueous solution of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) (a) $0.8 \mu\text{s}$ and (b) $15 \mu\text{s}$ after the pulse. Dose per pulse: 13 Gy.

3.2. $\bullet\text{OH}$ reaction: acidic conditions

Pulse radiolysis of aerated acidic aqueous solutions of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at pH 1 showed the formation of transient absorption bands at 320 and 560 nm (Fig. 2). The rate constant for the reaction of $\bullet\text{OH}$ with PTFMS at this pH was determined by competition kinetics using 2-propanol (IP) as a reference and ($k_{\text{IP}+\text{OH}} = 1.9 \times 10^9 \text{ dm}^3(\text{mol s})^{-1}$ [30]. The absorbance at 320 nm was observed to decrease linearly with increasing IP concentration and the second-order rate constant value was estimated as $3.6 \pm 0.5 \times 10^9 \text{ dm}^3(\text{mol s})^{-1}$.

While the band at 560 nm decayed completely within $10 \mu\text{s}$, only a slight decay at 320 nm on this time scale was seen (inset of Fig. 2). The difference in the nature of absorption–time profiles at 320 and 560 nm suggests the formation of two types of transient species. In acid solutions, $\bullet\text{OH}$ radicals are able to

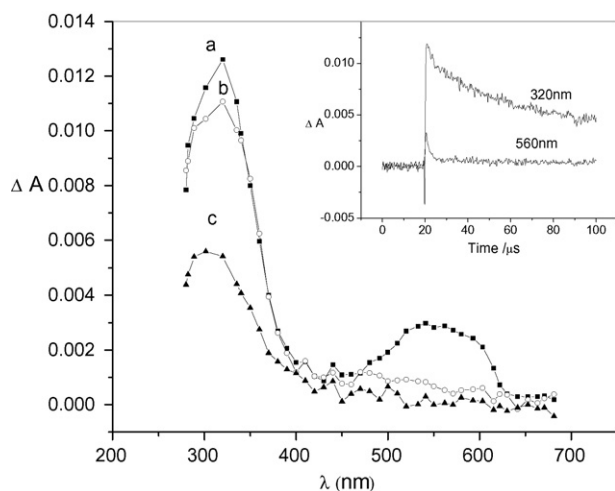


Fig. 2. Transient optical absorption spectra obtained on pulse radiolysis of aerated acidic aqueous solution of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at pH 1 (a) $0.4 \mu\text{s}$, (b) $8 \mu\text{s}$ and (c) $80 \mu\text{s}$ after the pulse. Inset shows absorption–time profiles at 320 and 560 nm.

abstract an electron easily since the removal of H_2O is more favoured than the removal of OH^- in neutral solutions [31]. At pH 1, only a part of the OH^- -adduct is converted to the solute radical cation. Therefore, the transient absorption spectrum (Fig. 2) consisted of the OH^- -adduct with a maximum around 320 nm and the solute radical cation with peaks at 320 and 560 nm.

Beyond pH 1, both the absorbance and lifetime of the transient absorption bands formed on pulse radiolysis of aerated acidic aqueous solutions of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) were observed to increase with HClO_4 concentration reaching nearly the saturation value at $\sim 7 \text{ mol dm}^{-3} \text{ HClO}_4$. The increase in the absorption and lifetime of the transient is shown in Fig. 3 for the two wavelengths at 320 and 560 nm. In highly acidic solutions, the entire radiation energy is not absorbed by water alone. The radiation energy absorbed by HClO_4 will not yield $\bullet\text{OH}$ radicals. Therefore, the $\bullet\text{OH}$ radical yield decreases with increasing concentration of HClO_4 . Based on their relative mole fractions, the $G(\bullet\text{OH})$ was calculated as 2.5 at $6.8 \text{ mol dm}^{-3} \text{ HClO}_4$ and was used in the determination of the values. The transient absorption spectra obtained on pulse radiolysis of an aerated acidic (6.8 mol dm^{-3}) solution of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) is shown in Fig. 4. The rates of decay at both the wavelengths are identical (inset of Fig. 4). Due to the similarity of the spectrum with that reported [16] for thioanisole, it is assigned to the monomeric sulphur radical cation.

The rate constant for the reaction of $\bullet\text{OH}$ radical with PTFMS was determined by the formation kinetics at 320 nm. The pseudo-first-order rate constant increased linearly with solute concentration and the second-order rate constant determined from the linear plot is $2.5 \pm 0.3 \times 10^9 \text{ dm}^3(\text{mol s})^{-1}$. The rate constant measured at 560 nm also produced similar results with $k = 3.1 \pm 0.4 \times 10^9 \text{ dm}^3(\text{mol s})^{-1}$.

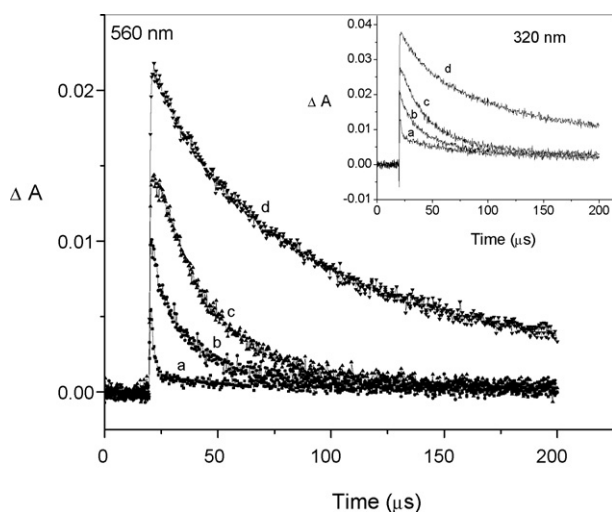


Fig. 3. Absorption–time profiles (560 nm) obtained on pulse radiolysis of aerated acidic aqueous solution of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) containing 0.58 mol dm^{-3} (a); 2.32 mol dm^{-3} (b); 7.0 mol dm^{-3} (c) and 9.28 mol dm^{-3} (d) concentrations of HClO_4 . Inset shows absorption–time profiles (320 nm) for 0.58 mol dm^{-3} (a), 2.32 mol dm^{-3} (b), 7.0 mol dm^{-3} (c) and 9.28 mol dm^{-3} (d) concentrations of HClO_4 .

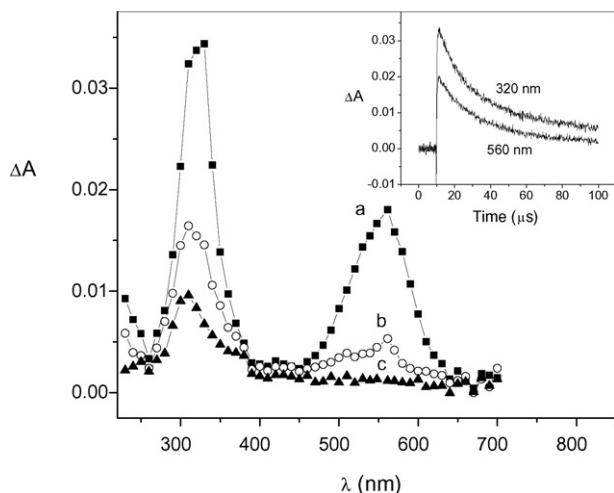


Fig. 4. Transient absorption spectra obtained on pulse radiolysis of aerated acidic ($\text{HClO}_4 = 6.8 \text{ mol dm}^{-3}$) aqueous solution of PTFMS ($1 \times 10^{-3} \text{ mol dm}^{-3}$) 2.2 μs (a), 25 μs (b), 85 μs (c) after the pulse. Inset shows absorption traces at 320 and 560 nm.

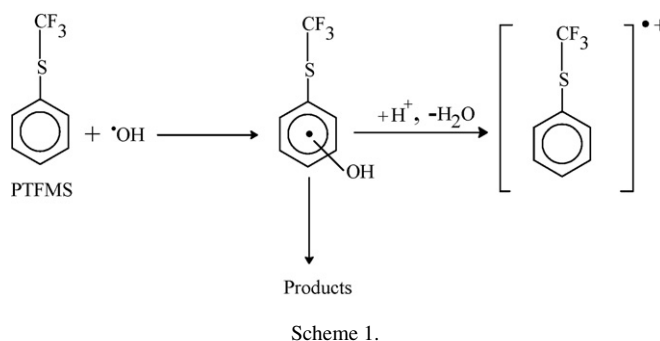
Considering the quantitative formation of the radical cation at 6.8 mol dm^{-3} HClO_4 with a G -value corresponding to 2.4 per 100 eV and the molar absorptivity values were evaluated as $\epsilon_{320} = 11,500$ and $\epsilon_{560} = 6150 \text{ dm}^3 (\text{mol cm})^{-1}$. Based on the ratio of absorbance at 320 and 560 nm in the spectrum shown in Fig. 4, ϵ_{560} and $G(\bullet\text{OH}) = 2.8$ per 100 eV, the yield of $\bullet\text{OH}$ radical contributing to the radical cation is calculated to be about 15% at pH 1 (Fig. 2). Thus, it is concluded that in neutral aqueous solution, the $\bullet\text{OH}$ radical reacts with PTFMS to form OH adduct and in highly acidic conditions, it leads to the formation of the sulphur centred radical cation. The latter assignment is based on similarity of the spectrum reported [13b,16] for the radical cation of thioanisole.

In highly acidic solution, ClO_3 and ClO_4 radicals formed on pulse radiolysis of HClO_4 showed very weak absorption in 330–340 nm region [32]. $\text{HClO}_4^{\bullet+}$ is formed only when its concentration is $>10 \text{ mol dm}^{-3}$ and has absorption at 440 nm. In analogy with earlier studies, the transient absorption bands (Fig. 4) formed on pulse radiolysis of aerated acidic aqueous solution of PTFMS should be due to the reaction of $\bullet\text{OH}$ radicals and not due to radiolytic products of HClO_4 or their reaction with PTFMS [11,33].

The variation of transient absorption at 320 and 560 nm was studied as a function of solute concentration at two different concentrations of HClO_4 (0.05 and 4.5 mol dm^{-3}). At both these concentrations, the absorbance and lifetime remained independent of solute concentration ($0.6\text{--}1 \times 10^{-3} \text{ mol dm}^{-3}$). Due to solubility limitations, studies could not be carried out at higher solute concentrations. Our results suggest the formation of monomeric radical cation (Scheme 1) with no contribution from the dimer radical cation.

3.3. Reaction of one electron oxidants

The one electron oxidant $\text{Cl}_2^{\bullet-}$ ($\lambda = 345 \text{ nm}$) formed on pulse radiolysis of aerated acidic aqueous solution



($\text{Cl}^- = 5 \times 10^{-2} \text{ mol dm}^{-3}$, pH 1) did not show the formation of any new absorption band. On its reaction with PTFMS suggesting that the rate constant is low ($k \leq 1.5 \times 10^7 \text{ dm}^3 (\text{mol s})^{-1}$). Similarly, $\text{Br}_2^{\bullet-}$ ($\lambda = 360 \text{ nm}$) nor $\text{SO}_4^{\bullet-}$ failed to undergo electron transfer reaction suggesting that the oxidation potential of PTFMS is high.

3.4. Theoretical studies

The geometry of PMS and PTFMS optimized at MP2/6-31+G(d,p) level of theory are displayed in Fig. 5(i and ii). Geometries calculated at DFT level are very close with the MP2 geometries with a maximum error of $+0.02 \text{ \AA}$ in bond length. The calculated atomic charges over S atom in the two systems are $+0.291$ and $+0.443 \text{ a.u.}$ respectively for PMS and PTFMS systems at MP2 level. Highest occupied molecular orbital (HOMO) of the two systems are shown in Fig. 5(iii and iv). It is clearly observed that in the both systems S, *ipso*-, two *ortho*- and *para*-C atoms of the ring contribute to this particular MO. As the hydroxyl radical is an electrophilic agent, addition to any of these sites in PMS and PTFMS systems is likely. Geometry search of various possible $\bullet\text{OH}$ adducts with PMS and PTFMS is carried out and the optimized structures are displayed in Fig. 5(v–xiv).

It is noticed that addition of the $\bullet\text{OH}$ radical to S atom and *ipso*- ring positions is largely different in PTFMS as compared to PMS. In fact, the $\bullet\text{OH}$ radical does not form an adduct with S atom in the case of PTFMS but the H atom of the $\bullet\text{OH}$ radical forms H-bond with one its F atoms as shown in Fig. 5(x). Such a difference in the addition of $\bullet\text{OH}$ radical is observed in the case of *ipso*- position of the ring. The $\bullet\text{OH}$ radical forms a weak complex from its H atom side to the *ipso*- position of the ring trifluoro system as shown in Fig. 5(xi). The calculated energy of stabilization for $\bullet\text{OH}$ -adducts is listed in Table 1. Structures of the respective radical cations are also calculated and the atomic charges over S atoms are $+0.538$ and $+0.668 \text{ a.u.}$ respectively for PMS and PTFMS. Based on the total energy of the systems calculated for PMS and PTFMS and their radical cations at MP2 level of theory, ionization potential (IP) are predicted to be 7.77 and 8.95 eV indicating the difficulty in one electron oxidation of PTFMS. Calculated atomic spins over S atoms in these open shell doublet systems are 0.289 and 0.349 a.u. respectively for PMS and PTFMS. To mark the specific position of the radical cation site, the distribution of odd electron spin population in PMS and PTFMS systems are viewed as contour plots with the maximum cut off value of 0.07 as shown in Fig. 5(xv and xvi).

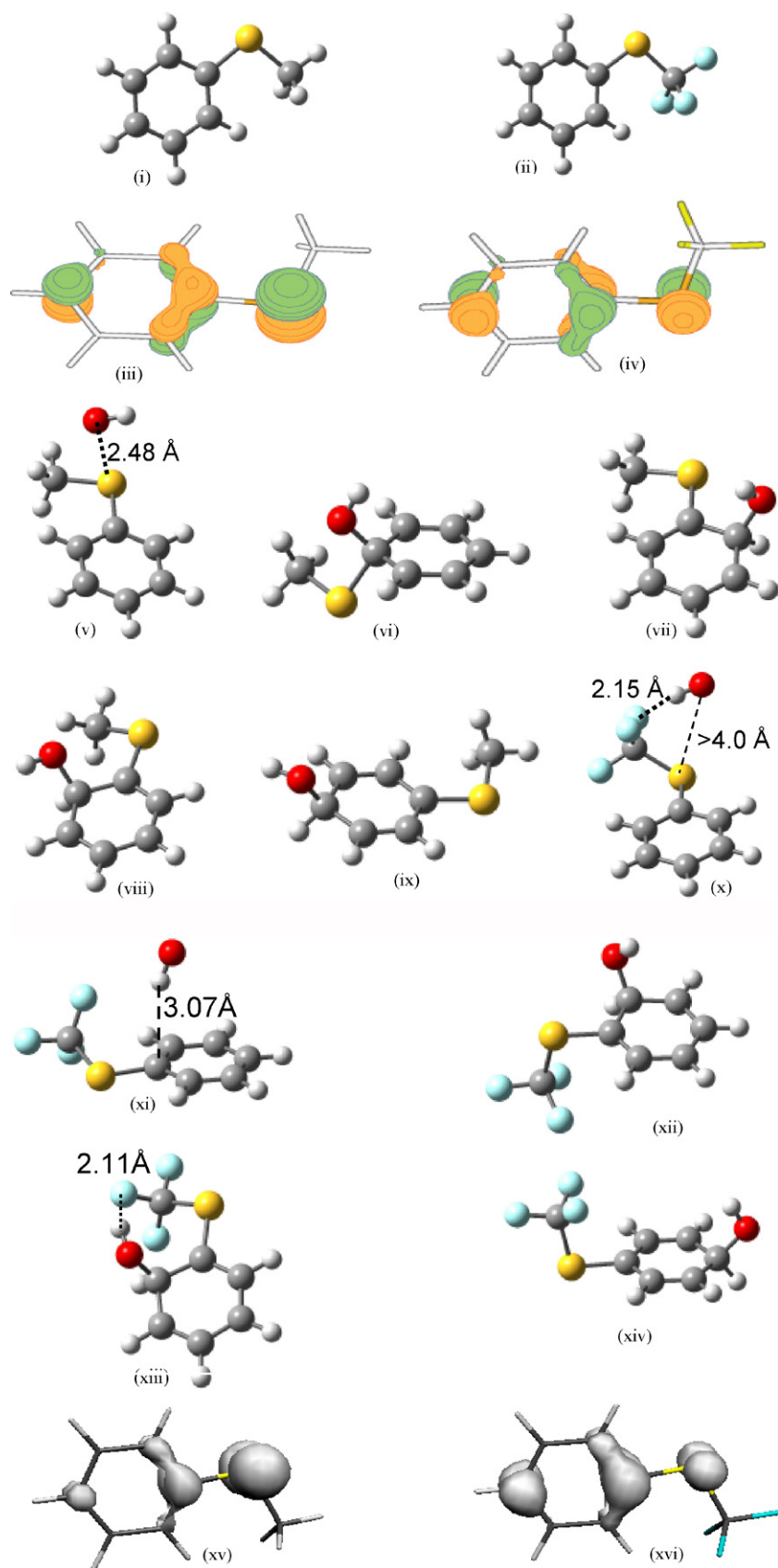


Fig. 5. Optimized structures of (i) phenyl methyl sulphide (PMS) and (ii) phenyl trifluoro methyl sulphide (PTFMS). The highest occupied MO of the two systems is shown in (iii) and (iv). Optimized structures of different intermediates formed on reaction of hydroxyl radicals with PMS are shown as (v)–(ix). Optimized structures of different intermediates formed on reaction of hydroxyl radicals with PTFMS are shown as (x)–(xiv). (xv–xvi) Contour plots on the spin density distribution of the odd electron in PMS and PTFMS radical cation systems are shown with the maximum cut-off value of 0.07.

Table 1

Stabilization energies for different intermediates formed on reaction of OH radicals with PMS and PTFMS systems at MP2/6-31+G(d,p) level of theory in kcal mol⁻¹

Structure corresponding to OH adduct of PMS and PTFMS	Stabilization energy for OH adducts of PMS and PTFMS systems (kcal/mol)	
	PMS	PTFMS
S atom (Fig. 5) (v and x)	8.64	6.32
<i>ipso</i> -position (Fig. 5) (vi–xi)	18.65	5.10
<i>ortho</i> -(Fig. 5) (vii–xii)	21.15	21.97
<i>ortho</i> -(Fig. 5) (viii–xiii)	17.97	18.67
<i>para</i> -(Fig. 5) (ix–xiv)	18.43	22.41

The respective structures are shown in Fig. 5.

It is observed that in PMS, hydroxyl radical adduct eventually leads to the formation of the sulphur centred radical cation. However, in the case of PTFMS, OH-adduct at phenyl ring leads to the formation of radical cation in which the charge is distributed over the S atom and was also extended to the ring.

3.5. Effect of CF₃ substitution

Cyclic voltammetric and quantum chemical calculations were performed on these systems to look for the possible reason behind the observed differences on the nature of the •OH radical reactions between PMS and PTFMS. Cyclic voltammetric studies showed the formation of a oxidation peak at a potential of 1.1 V for PMS whereas experiments under identical conditions did not show any oxidation peak for PTFMS up to a potential value of 1.8 V. Quantum chemical calculations revealed that the ionization potential of PTFMS is higher than that of PMS by ~1.2 eV. These studies suggest that oxidation of PTFMS is more difficult than PMS.

4. Conclusions

The reaction of the OH radical with PTFMS as a function of pH exhibited transient absorption spectra with maxima at 320 and 560 nm. The yield and the lifetime of these bands increased with acid concentration yielding fully the sulphur centred radical cation at 7 M HClO₄. The mechanism involves addition of the •OH radical to the aromatic ring and dehydration of the adduct is catalyzed by acid giving the monomeric sulphur radical cation. The charge on the monomeric sulphur radical cation of PTFMS is distributed not only on S atom but was extended to the aromatic ring. Fluorine substitution makes the one electron oxidation of PTFMS difficult.

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