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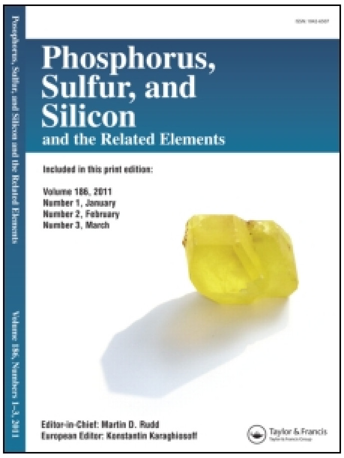

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Redox Activation of Molecular Oxygen by Arenesulfinic Acids

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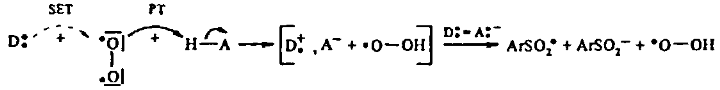
Principally, $^3O_2$ can be easily activated [1] via Single-Electron-Transfer (SET) from a suitable Donor D: and a concomitant proton transfer (PT) from a suitable proton donator H - A [2]:

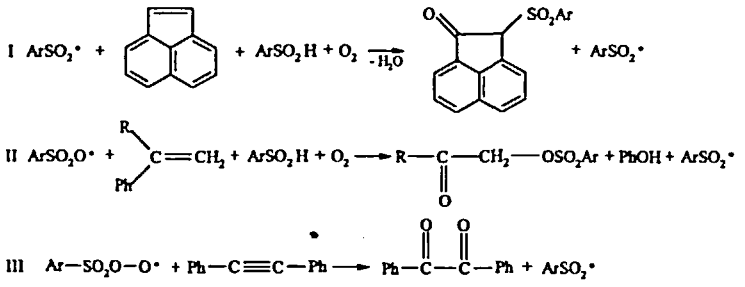


This scheme becomes particularly simple for D: = :A$^-$. The couple ascorbic acid /O_2 is known as *Udenfriend's reagent* [3], being able to oxygenate aromatics. The couple $NaHSO_3$ / O_2 [4], applied in daily life for risky [5] conservation purposes, is even able to oxidize Ag(I) to Ag(II) [6]. Sulfinic acids may be regarded in direct relation to the latter couple [7], autoxidation of benzenesulfinic acid has been studied kinetically in various solvents at 50 - 90°C [8] and subsequent mechanism has been deduced:

(1) $PhSO_2H + O_2 \rightarrow PhSO_2^{\bullet}$ (unknown way)
(2) $PhSO_2^{\bullet} + O_2 \rightarrow Ph\text{-}SO_2\text{-}O\text{-}O^{\bullet}$
(3) $PhSO_2\text{-}O\text{-}O^{\bullet} + PhSO_2H \rightarrow PhSO_2\text{-}O\text{-}OH + PhSO_2^{\bullet}$
(4) $PhSO_2\text{-}O\text{-}OH + PhSO_2H \rightarrow 2\ PhSO_3H$
(5) $2\ PhSO_2\text{-}O\text{-}OH \rightarrow Ph\text{-}SO_2O^{\bullet} + PhSO_2\text{-}O\text{-}O^{\bullet} + H_2O$ (7)

Being surprised by the accidental observation that a solution of 4-toluenesulfinic acid in $CHCl_3$ spontaneously evolved poisonous phosgene and HCl even at rt. under daylight, we decided to start more exhaustive investigations and were interested to compare the above autoxidation system with recent findings on arenesulfonylperoxy radicals [9] and on 4-toluenepersulfonic acid [10]. In detail, we investigated autoxidations of substituted (4-Me, 4-MeO, 4-Cl, 2-NO_2) benzenesulfinic acids at rt. in various solvents in the presence or absence of suitable oxygen acceptors and found that:

1) Solvents used, suitable: $CHCl_3$, CH_2Cl_2, $CO(OCH_3)_2$, Ac_2O; unsuitable: EtOH, MTBE, CH_3CN.
2) 2-Nitrobenzenesulfinic acid did not react with O_2 in $CHCl_3$.
3) 4-Chlorobenzenesulfinic acid / O_2 proved to be the most reactive oxygenating system, regardless whether under daylight or in the dark.
4) Thioanisole accelerated autoxidations considerably (opposite to earlier results [8]) forming corresponding sulfoxide; sulfoxides were oxidized to sulfones rather slowly.
5) In contrast to [9] and [10] epoxides could not be obtained from alkenes although a content of reactive oxygen up to 15% could be titrated in solutions of 4-toluenesulfinic acid in CH_2Cl_2 or $CHCl_3$ in the presence of air. However in the case of cyclohexene, addition products of 4-toluene sulfonic acid (main product) and sulfinic acid (by-product) from an assumed oxirane intermediate were the only cyclohexene based products whereas substituted styrenes even suffered C,C-cleavages.
6) Radical intermediates could be trapped by specific alkene and alkyne scavengers:



Three alternatives instead of equation (5) in which two oxidants are claimed to react with each other are favored as sources of $ArSO_2O^{\bullet}$ radicals:

(5a) $2\ ArSO_2^{\bullet} + O_2 \rightarrow [ArSO_2\text{-}O\text{-}O\text{-}SO_2Ar]^{\bullet} \rightarrow 2\ ArSO_2O^{\bullet}$ (cf. ref.[11])

(5b) $2\ ArSO_2^{\bullet} + 2\ O_2 \rightarrow 2\ ArSO_2\text{-}O\text{-}O^{\bullet} \rightarrow ArSO_2\text{ - O - O - O - O - }SO_2Ar \rightarrow 2\ ArSO_2O^{\bullet} + O_2$

or (5c) $ArSO_2^{-} + ArSO_2OOH + H^{+} \rightarrow ArSO_2^{\bullet} + Ar\text{-}SO_2O^{\bullet} + H_2O$ (cf. ref. [2b])

Finally, it can be concluded that this autoxidation system combines the results of sulfonylperoxy radical [9] and persulfonic acid [10] oxidations, except, that the acid medium prevents isolation of oxiranes. In order to offset this failure it is able to cleave certain C,C-bonds.

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