

Formation and Disproportionation of Arene Sulfenic Acids

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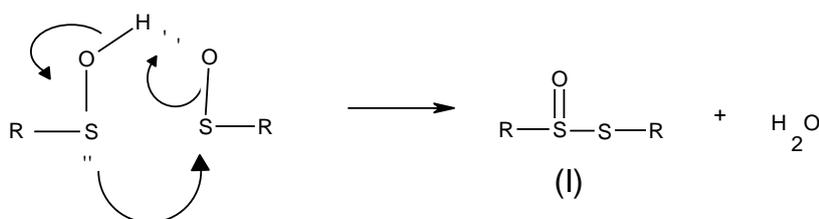
I. Introduction

Sulfenic acids, R-SOH, may be regarded as derivative of unknown inorganic acid, H₂SO₂ that may be derived from highly unstable oxide of sulfur, sulfur monoxide, SO. RSOH may be obtained by hydrolytic cleavage of S-X bond in sulfenyl halides, RSX. Sulfenic acids exist as RS-OH rather than



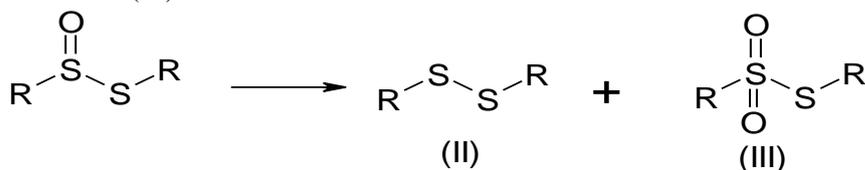
due to the fact that a formal S=O bond energy (373 KJ/mol) is not much higher than the S-O bond energy (340 KJ/mol) so that the loss of the strong O-H bond energy would not be compensated for in the S=O bond.

In many respects these oxyacids of sulfur are rather esoteric compounds. Their instability arises from their ability of forming intermolecular hydrogen bonding which results in self-condensation to thiolsulfinate esters (I)

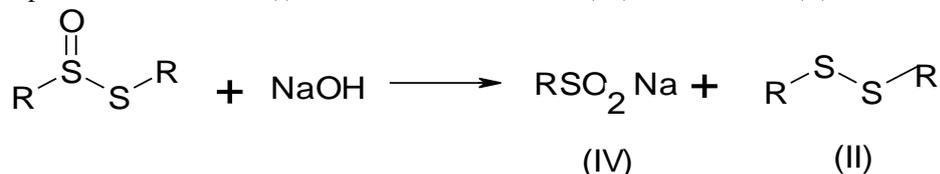


The fate of thiolsulfinate esters (I) depends on the pH of the medium.

At pH ≤ 7 the thiolsulfinate esters undergo disproportionation reaction to form corresponding disulfides (II) and thiolsulfonates (III)



At pH > 8 thiolsulfonates (I) form salts of sulfinicacids (IV) and disulfides (II)



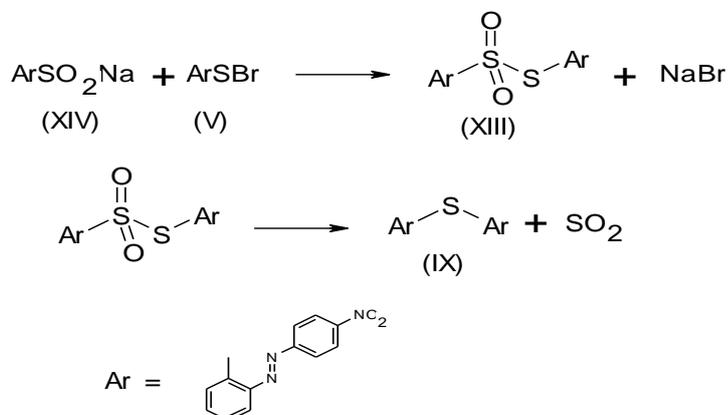
For these reasons only a very few stabilized sulfenic acids could be prepared till today. The aim of the present work is to prepare a stabilized aromatic sulfenic acid.

II. Results & Discussion

4'-Nitroazobenzene-2-sulfenyl bromide (v) has been synthesized as a stabilized sulfenium carrier for the purpose. Since the inherent instability of sulfenic acids lies primarily in the ability of the S-OH group to undergo intermolecular hydrogen bonding and also on the nucleophilicity of the sulfur atom increase in the bulk of the Ar group in Ar-SOH & in the presence of an electron withdrawing group in the Ar moiety should prevent the self condensation of SOH group to thiolsulfinate esters (I). In the compound (V) the 2-(4'-Nitro) phenylazophenyl unit is a bulky group & the azo group is electron withdrawing. Moreover the azo group acts as

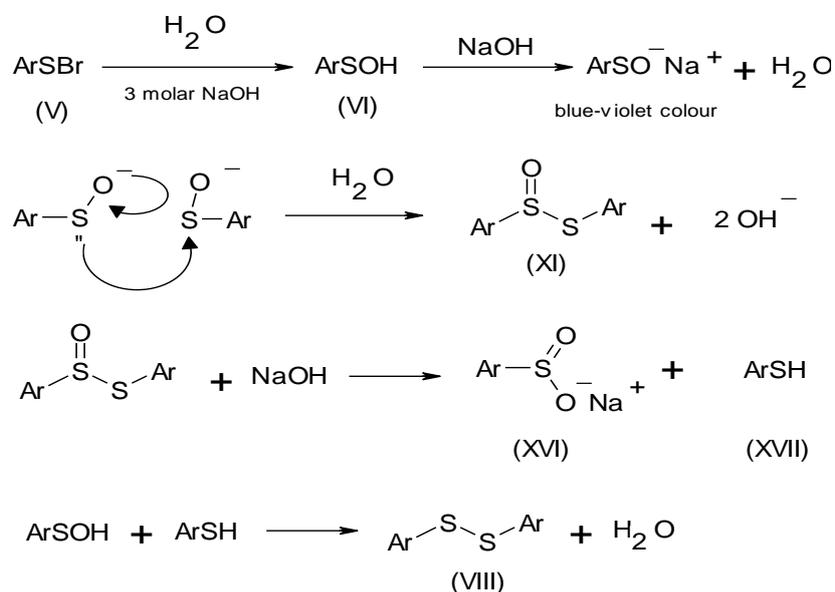
of the thiosulfonate (XIII) has also been established by a direct synthesis of the compound from the corresponding sodium sulfinate (XIV) & sulfenyl bromide (V) when a yellow flocculant ppt is obtained from the from the aq. solution.

This yellow ppt slowly turns red during filtration & crystallization to give the diarylthioether (IX) & SO₂ gas which turns yellow dichromate paper green.

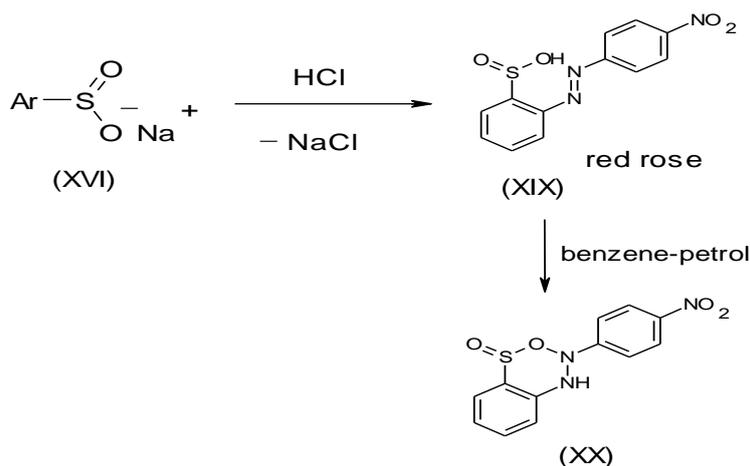


When the hydrolysis has been performed three molar proportion of alkali, the reaction takes place much faster due to the formation of sulfenate salt (XV) which imparts a transient blue violet colour to the solution due to charge transfer phenomenon in the sulfenate anion. The sulfenic anion being more nucleophilic than the sulfenic acid undergoes self-condensation to thiosulfinate (XI) much faster. The electrophilic sulfenyl sulfur of (XI) is readily attacked by excess alkali to form the corresponding soluble sodium sulfinate (XVI) and the mercaptan (XVII). The latter undergoes a rapid condensation with any unreacted sulfenic acid to form the corresponding insoluble disulfide (VIII). The formation of the products can be explained as per the scheme II.

Scheme- II



The free sulfinic acid (XIX) can be liberated as a rose red ppt by acidification of the aq. filtrate containing the sodium sulfinate. On crystallization from benzene-light petrol mixture this rose red sulfinic acid (XIX) gives colourless plates of the tautomeric form (XX) of the sulfenic acid.



Our endeavor to prepare a stabilized sulfenic acid has failed perhaps, due to the fact that the conjugate acid of OH being a very weak acid H₂O, the sulfenyl sulfur atom of the sulfenic acid group S-OH remains strongly nucleophilic. This keeps the -SOH group away from the ortho arylazo group thereby precluding any proton transfer from -SOH to the azo group -N=N-, to attain tautomeric stability. Though the bulky ortho arylazo naphthyl moiety attached with the sulfur atom raises the activation energy of the self condensation reaction to the thiosulfinate, as is reflected in the relatively long time (2 hour) taken for the completion of the reaction with equimolar amount of NaOH, it can not prevent the reaction but only can slow it down.

III. Experimental

REACTION WITH EQUIMOLAR SODIUM HYDROXIDE

To a solution of the sulfenyl bromide (1.068 gm, ~0.003M) in water (100 ml) was added a solution of sodium hydroxide (5.8 ml of 2% solution, ~0.003 M). The mixture was stirred well. The clear solution started becoming turbid in about 30 second & precipitation of a yellow substance was completed in about 2 hours. It was filtered off, washed & dried.

Yield: 0.72gm

This dried solid was now boiled with benzene (20 ml). The sulfite (X) remained insoluble & was filtered off and was washed with a little benzene and dried.

Yield: 90 mg

Crystallized from rectified spirit as orange yellow needles. Mp: 192-93

Analysis: C₂₄H₁₆N₆O₇S₃

Requires: C, 43.5; H, 2.4 & N, 12.6 pc

Found: C, 43.8; H, 2.1 & N, 12.9 pc

UV & visible spectra:

λ_{max} (nm, ethanol): 422 (ϵ_{max} 1500; $n \rightarrow \pi^*$), 352 (E_{max} 12000; $\pi \rightarrow \pi^*$)

IR spectra:

ν (/cm, KBr): 1585 (w, N=N),

1540 & 1400 (m, NO₂), 1140 (s, S=O)

From the filtrate the solvent was removed and the disulfide (VIII) present in the mixture was solubilized in water as the corresponding mercaptide (V, SBr= SNa) by boiling with ethanolic alkaline solution of sodium sulfide (300mg of NaOH in 50 ml of water + 50 ml of ethanol).

The diphenyl thioether (IX) remained insoluble and was filtered off, washed with water and dried.

Yield: 120mg

Crystallized from light petrol (bp 60-80) as red plates. Mp: 243-45

Analysis: C₂₄H₁₆N₆O₄S

Requires: C, 59.5; H, 3.3 and N, 17.4 pc

Found: C, 59.2; H, 3.6 and N, 17.2 pc

UV & visible spectra:

λ max (nm, benzene) 420 (ϵ_{max} 950, $n \rightarrow \pi^*$), 355 (ϵ_{max} 11000, $\pi \rightarrow \pi^*$)

IR spectra:

ν (/cm, KBr) 1585 (w, N=N), 1540 & 1400 (m, NO₂)

The filtrate containing sodium mercaptide (V, SBr= SNa) was acidified with moderately strong HCl and the resulting mixture was heated in a beaker for 5 minutes and then was allowed to stand at room temperature for 1 hour. The mercaptan (V, SBR=SH) formed on acidification underwent oxidation to the disulfide (VIII), which was then filtered off, washed and dried.

Yield: 150 mg

Crystallized from benzene-ethanol mixture (90:10 v/v) as red crystals. Mp: 197-98

Analysis: C₂₄H₁₆N₆O₄S₂

Requires: C, 55.8; H, 3.1 and N, 16.3 pc

Found: C, 55.5; H, 3.7 and N, 16.1 pc

UV and visible spectra:

λ_{maxi} (nm, benzene): 425 (ϵ_{max} 900, $n \rightarrow \pi^*$), 360 (ϵ_{max} 12000, $\pi \rightarrow \pi^*$)

IR spectra:

ν (/cm, KBr) 1590 (w, N=N), 1540 and 1395 (m, NO₂)

2. REACTION OF SULFENYL BROMIDE (v) WITH 3 MOLAR PROPORTION OF AQUEOUS SODIUM HYDROXIDE

To an aq solution of sulfenyl bromide (1.068 gm, ~ 0.003m) was added an aq solution of sodium hydroxide (6 ml of 6% solution, ~ 0.009m) when a red ppt was formed quickly from a transient blue-violet solution. The precipitated disulfide (VIII) was filtered off, washed and dried.

Yield: 400 mg (80% of the theory)

Crystallization from benzene-alcohol mixture (90:10, v/v) as red crystals. Mp & mixed mp 193-95.

The filtrate on acidification with moderately strong HCl gave a rose red ppt of the sulfinic acid (XIX), which was filtered off, washed with water and dried.

Yield: 180 mg (~ 60% of the theory)

Crystallized from benzene-light petrol mixture as nearly colourless plates due to the tautomeric form (XX) of the acid. Mp 144-45.

Analysis: C₁₂H₉N₃O₄S

Requires: C, 49.5; H, 3.1 and N, 14.4 pc

Found: C, 49.4; H, 3.0 and N, 14.0 pc.

UV and visible spectra:

λ_{max} (nm, benzene) 356 (ϵ_{max} , 12500 $\pi \rightarrow \pi^*$)

IR spectra:

ν (/cm, KBr) 3200(b, OH), 1540 and 1390 (m, NO₂), 1100 (s, S=O).

Reference:

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