

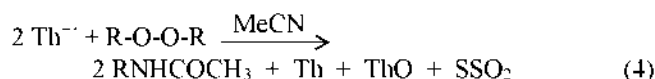
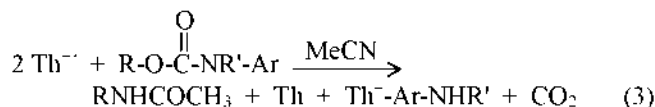
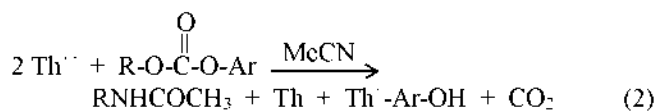
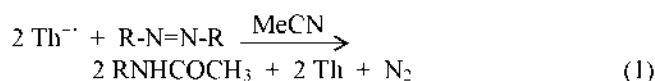
The First Example of Cation Radical Induced Desulfurization from Disulfides

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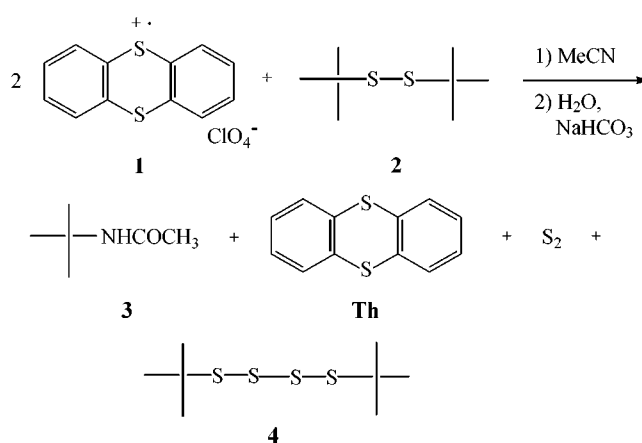
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Over the last several years we have discovered cation radical induced oxidative decomposition of azo compounds (eq 1),¹⁻³ carbonates (eq 2),^{4,5} carbamates (eq 3),⁶ and peroxides (eq 4).⁷ It was recognized in those discoveries that carbocationic chemistry with C-N or C-O bond cleavages was predominant with the 2 : 1 stoichiometry, two moles of aromatic cation radical and one mole of oxidized molecules in acetonitrile at room temperature.

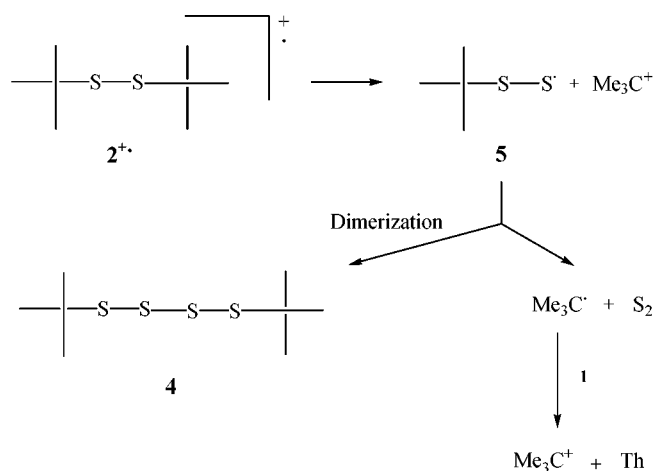


In continuing our work with these oxidative decomposition of disulfide, we have found that thermally stable *tert*-butyl disulfide is readily oxidized by thianthrene cation radical perchlorate ($\text{Th}^{\cdot+}\text{ClO}_4^-$, **1**) with evolution of S_2 in acetonitrile at room temperature. This is a novel reaction of disulfides and offers the first example of cation radical induced desulfurization. Work for desulfurization of disulfides with C-S bond rupture has been reported.⁸ For example, a number of natural products contain a cyclic disulfide unit involve the Diels-Alder addition of *in situ* generated singlet S_2 to dienes. In the present study, as the other oxidative decomposition,¹⁻⁷ the major products from the reaction of the disulfide, **2**, with **1** are characteristic of *tert*-butyl cations while the minor ones imply a free sulfur radical component of the reaction. In other words, carbocationic chemistry is observed predominantly from a alkyl disulfide, a source of free radicals.⁹ The major products were *N-tert*-butylacetamide (**3**) from *tert*-butyl cation, which was isolated in 80% yield, and thianthrene (Th, 95%) by reducing of $\text{Th}^{\cdot+}$. Without doubt, *tert*-butyl cations reacted with the solvent acetonitrile to give a Ritter-type intermediate ($\text{Me}_3\text{CN}=\text{CMe}$), which hydrated during workup, to give **3**. The unexpected dimeriz-

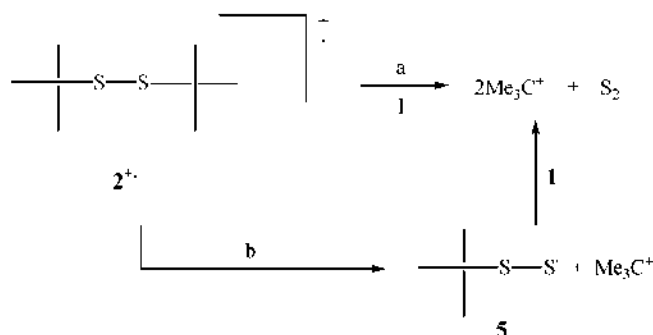


ed product, di-*tert*-butyl tetrasulfide, **4** (10%), must have been formed from dimerization of *tert*-butylperthiyl radical (**5**, $\text{Me}_3\text{C-S}^{\cdot}$). Product balances account for 90% of the *tert*-butyl groups which appears as cations, and 95% of the cation radicals.

Products obtained from reaction of **1** with very stable **2** are shown in Scheme 1 and an explanation of the formation of products is shown in Scheme 2. The cation radical ($2^{\cdot+}$) of *tert*-butyl disulfide leads to rapid C-S bond cleavage instead of S-S bond rupture at room temperature to give *tert*-butylperthiyl radical (**5**) and *tert*-butyl cation in Scheme 2. The perthiyl radical, **5**, exhibited two subsequent transformations. Major pathway is oxidation of **5** by **1** with great facility to carbocation and evolution of S_2 . Minor one is



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dimerization of free **5** to **4**. The question of whether the rupture of the C-S bonds in **2**^{•+} proceeds concertedly (a) or stepwise (b) can be debated (Scheme 3). A stepwise mechanism implies a radical intermediate **5**, whereas a concerted reaction requires that *tert*-butyl cations and S₂ be formed directly and at the same rate. Di-*tert*-butyl tetrasulphide (**4**) has shown promise as a probe for differentiating stepwise (b) from concerted (a) mechanism in this reaction. In the oxidation of **5**, it has been found that **5** was not oxidized to *tert*-butylperthiyl cation directly but oxidized to *tert*-butyl cation via *tert*-butyl radical with evolution of S₂ by C-S bond cleavage. In support of the reluctant oxidation of **5**, it should be noted that the ionization potential (IP) of Th is near 7.90 eV,^{11,12} while the IP of **5** is 8.25 eV.⁹ Since Th has not enough oxidation potential (1.3 V) to oxidize **5** rapidly the small amounts of **5** can reasonably be expected to survive long enough to yield **4**.

If the Scheme 2 were the right reaction pathways, the reaction stoichiometry would not be 2.00 : 1.00 1/2. Careful, repeated five measurements of the ratio of reactants, made by adding **2** until the color of the **1** disappeared, showed that 1.78 mole of **1** was used per mole of **2**. As expected, we obtained a molar ratio of 2.00 : 1.12 1/2. This ratio can be well adjusted by sulfur radicals escaping from oxidation and undergoing dimerization. In that case, more **2** would be needed for the reaction with unused **1** than required by oxidation with the ratio 2.00 : 1.00. The stoichiometric ratio found, 2.00 : 1.12, says that 89.3% of *tert*-butyl groups were oxidized to carbocation, which corresponds well with the 90% yield of *tert*-butyl cation-derived products. Control reaction of perchloric acid, 70% and **2** in MeCN was carried out to exclude all doubts of autocatalytic effects by trace acid generated from the electron transfer (ET) reaction. Quantitative amounts of starting disulfide, **2** were recovered. These observations indicate that the oxidative C-S cleavage of **2** is not catalyzed by the acid but is proceeded by ET mechanism exclusively.

In conclusion, a thermally stable disulfide has been shown

to undergo facile oxidative C-S bond cleavage instead of S-S rupture by cation radical at room temperature. In the oxidative decomposition of disulfide we have found unexpected dimerization product from the stable *tert*-butylperthiyl radical. The new reaction described herein can be expands the scope of oxidation of disulfides.

Experimental Section

Reaction of disulfide (2) with Th⁺ClO₄⁻ (1). A general procedure was adopted. *tert*-Butyl disulfide (73.1 mg, 0.50 mmol) and Th⁺ClO₄⁻ (315 mg, 1.00 mmol) were placed in a 50 mL round-bottomed flask, containing a stirring magnet bar, and the flask was purged with dry argon after capping with a septum. Dry acetonitrile was introduced into the flask by syringe, and the dark purple color of **1** has disappeared, but the mixture was stirred overnight. Thereafter, 10 mL of water was added followed by aqueous NaHCO₃ to neutralize HClO₄ that had been formed in reaction. The solution was extracted with 3 × 30 mL portions of methylene chloride. The methylene chloride solution was dried over MgSO₄, and evaporated. The residue was dissolved in 10 mL of methylene chloride. Portions of this solution were used for identification of products by GC/MS and for quantitative analysis by GC. The column used was a 2 × 1/8 in. stainless steel column packed with 10% OV-101 on Chrom W, with naphthalene as an internal standard. Concentration factors for all products were determined with authentic materials.

tert-Butylacetamide (**3**)¹³ was prepared as described in the literature.

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