

Reaction of Azodioxide with Thianthrene Cation Radical

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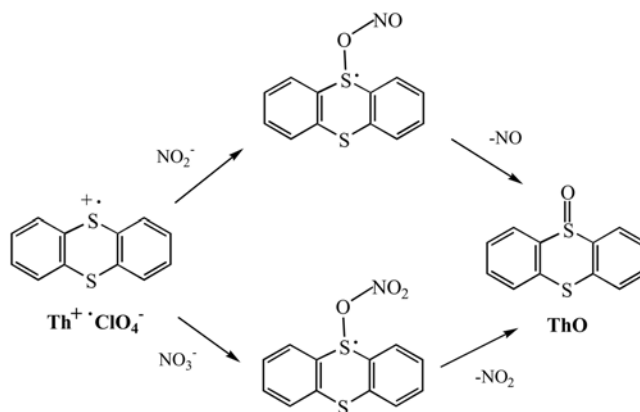
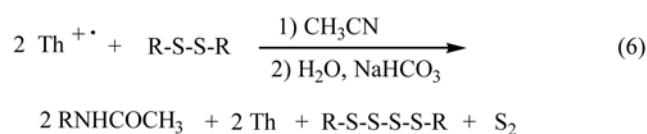
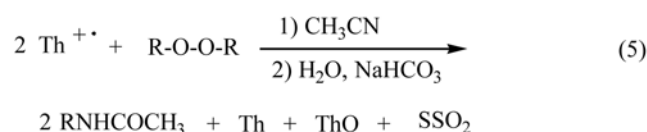
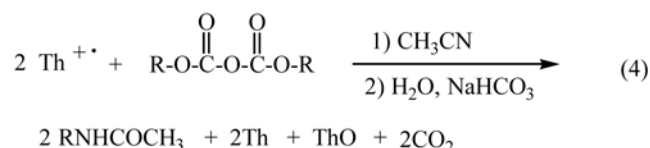
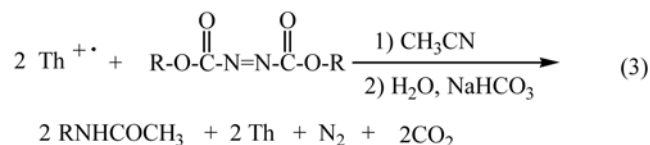
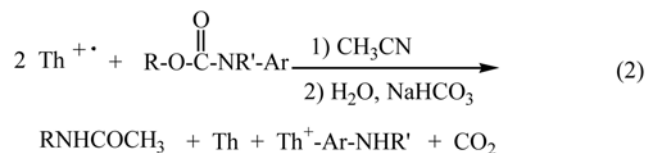
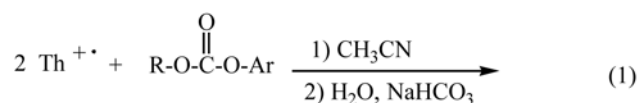
We recently reported on the thianthrene cation radical perchlorate ($\text{Th}^{+\cdot}\text{ClO}_4^-$) induced oxidative decomposition of carbonates (eq 1),¹ carbamates (eq 2),² azodicarboxylate (eq 3),³ dicarbonate (eq 4),⁴ peroxides (eq 5),⁵ and disulfide (eq 6)⁶ where R in equations is *tert*-butyl. In each of these reactions, electron-transfer-mediated C,N, C,O or C,S bond cleavage was found. Substantial bond weakening was shown to accompany the *tert*-butyl cation due to the electron loss from these substrates.

In a continuation of our work on *N,N'*-dioxoazobis(2-methyl-2-propane) (**1**) in acetonitrile solution at room temperature, C,N and N,O cleavages, followed by addition

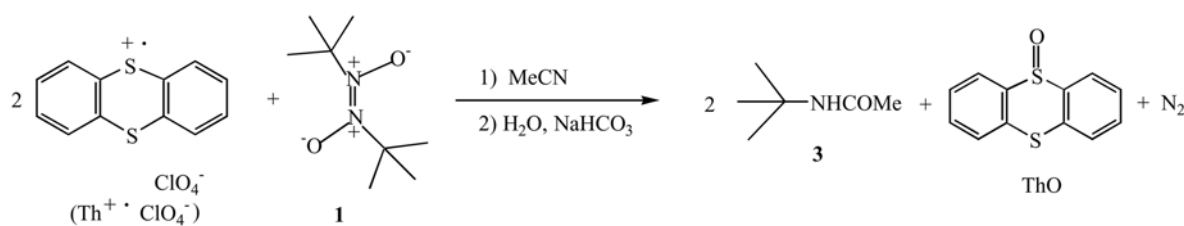
of $\text{Th}^{+\cdot}\text{ClO}_4^-$ to azodioxide, **1**, was found to give thianthrene oxide (ThO) and *N-t*-butylacetamide (**3**), with evolution of nitrogen gas. Reactions of $\text{Th}^{+\cdot}\text{ClO}_4^-$ with anions, such as nitrite and nitrate ions, have been reported,⁷ but its reactions with molecules with an abnormal number of bonds have not been documented. This work affords the first example of the addition of a cation radical to formal negatively charged oxygen within a neutral molecule.

Reactions of nitrite and nitrate ions with $\text{Th}^{+\cdot}\text{ClO}_4^-$ were found to give thianthrene 5-oxide (ThO) quantitatively (Scheme 1). Reactions with ¹⁸O-labeled nitrite and nitrate ions showed that the oxygen in ThO came from the nitrite and nitrate ions respectively.

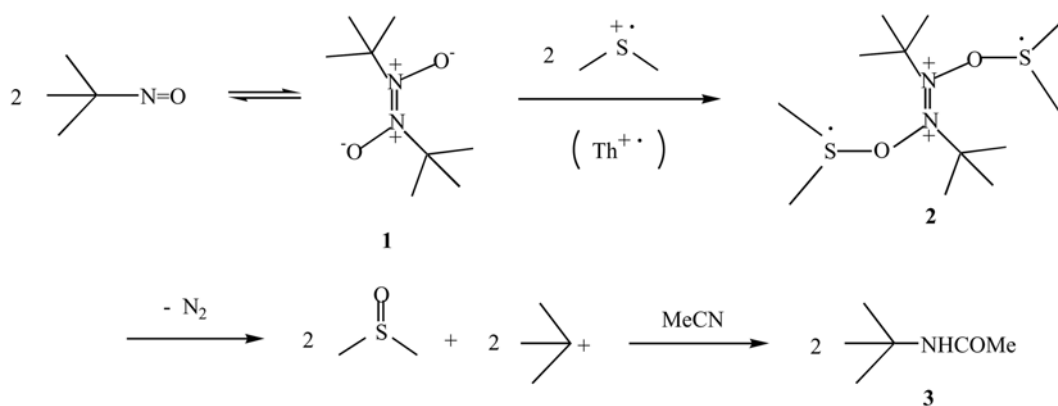
In the present study, as with the other oxidative decomposition,¹⁻⁶ the major products from the reaction of **1** with $\text{Th}^{+\cdot}\text{ClO}_4^-$ are also characteristic of *tert*-butyl cations, which imply carbocationic chemistry is predominantly observed from a nitrosoalkane dimer. The products obtained were *N-t*-butylacetamide (**3**), ThO and N₂ as determined by quantitative GC and GC/MS analyses. *N-t*-butylacetamide (**3**) from the *tert*-butyl cation, which was isolated in a yield of 91%, and ThO (76%) was obtained by oxygen transfer from **1**. Without doubt, **3** arose from hydration, during workup, of a Ritter-type intermediate ($\text{Me}_3\text{C}^+=\text{CMe}$) from the reaction of Me_3C^+ with the MeCN solvent. Accordingly, all reactions were carried out with a 2:1 stoichiometry of the cation radical and **1**. Generally, in the reaction of thianthrene cation radical perchlorate, ThO is obtained as a side product from the hydrolysis of $\text{Th}^{+\cdot}\text{ClO}_4^-$ by water, either adventitiously in the solvent or added during workup.⁸ However, in this



Scheme 1



Scheme 2



Scheme 3

reaction, the ThO was the primary product rather than a side product. This result suggests that the oxygen atom in ThO comes entirely from **1**. The formation of ThO, by oxygen transfer from the nucleophiles, as a primary product has been previously reported from the reactions of nitrite and nitrate ions,⁷ oximes,⁹ cyclic alcohol,¹⁰ and 2,3-dimethyl-2,3-butanediol¹¹ with Th⁺ClO₄⁻.

Products obtained from the reaction of Th⁺ClO₄⁻ with **1** are shown in Scheme 2, and an explanation for the formation of products is shown in Scheme 3. Azodioxide (**1**), as in Scheme 3, equilibrates with the 2-methyl-2-nitrosopropane monomer. Because the rate of approach to equilibrium in solution between dimer (**1**) and monomer is moderately slow (30-60 min) at room temperature and very slow at low temperature,¹² it is possible to prepare and maintain non-equilibrium solutions of the pure dimer (**1**). Scheme 3 shows that the nucleophile, the negatively charged oxygen of **1**, at a high negative charge density, attacks the thianthrene ring, at the sulfur (the 5 position). An intermediate cation radical (**2**) is formed, which can decompose into a stable product, ThO and **3**, with evolution of N₂. The order of initial bond cleavages either N,O or C,N in the cation radical intermediate, **2**, currently remains unknown. The reaction of **1** with Th⁺ClO₄⁻ is somewhat unlike the analogous reactions with *tert*-butyl containing compounds, such as carbonates, carbamates, azodicarboxylate, dicarbonate, peroxides and disulfide. These lead to electron-transfer-mediated oxidative

decomposition. In contrast, **1** is first added to Th⁺ClO₄⁻, which thereafter decomposes into stable products.

In conclusion, the first example of cation radical-induced thermal decay of stable azodioxide (**1**) is reported. In the reaction of **1** with a cation radical is quite unlike the analogous reactions described in eq. (1-6). From this reaction, thermal decay rather than electron-transfer-mediated bond cleavage, follows the addition of **1** to the cation radical.

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