# New Mechanism for the Reaction of Thianthrene Cation Radical Perchlorate with *tert*-Butyl Peroxide

**Bo Kyung Park, Chang Kook Sohn, and Wang Keun Lee**[*]

*Department of Chemistry Education, Chonnam National University, Kwang-Ju 500-757, Korea*

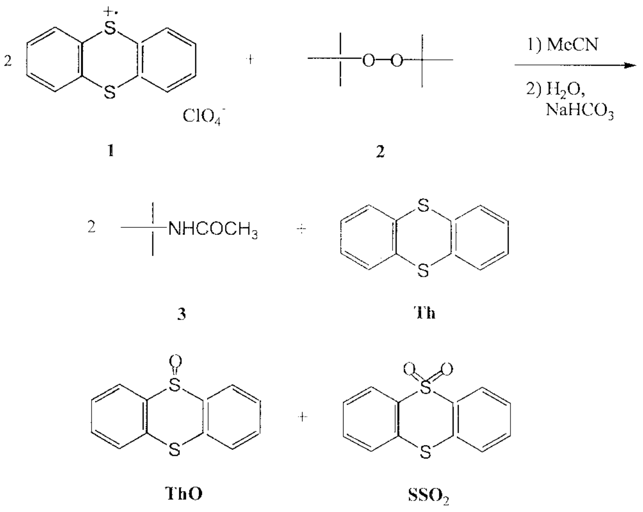
*Received October 24, 2001*

A new reaction mechanism is proposed for the reaction of thianthrene cation radical perchlorate ($Th^{+\bullet}ClO_4^-$) and *tert*-butyl peroxide in acetonitrile at room temperature on the basis of experimental and theoretical results. Rapid C-O bond rupture instead of O-O bond cleavage was observed by a good peroxy radical trapping agent, thianthrene cation radical. Products were N-*tert*-butyl acetamide, thianthrene 5-oxide (ThO), thianthrene 5,5-dioxide ($SSO_2$), and thianthrene (Th). Thianthrene 5,10-dioxide (SOSO) was not obtained. A comparative computational study of the cation radical of *tert*-butyl peroxide is made by using B3LYP and CBS-4. The computational results are helpful to explain the reaction mechanism.

**Keywords :** Thianthrene cation radical, *t*-Butyl peroxide, B3LYP and CBS-4 methods.

In the course of studies in the C-O bond cleavages by one-electron oxidant, thianthrene cation radical perchlorate ($Th^{+\bullet}ClO_4^-$, **1**), we have discovered that thianthrene cation radical is a good peroxy radical trapping agent. In this study, a new reaction mechanism is proposed on the basis of our experimental and theoretical results for the particular case of **1** and *tert*-butyl peroxide (**2**). Dialkyl peroxides usually give in the initial stage two alkoxy radicals via O-O homolysis on photochemical and thermal decomposition, which are apt to react further with other substrates or decompose to more stable compounds.[1] Likewise, **2** undergoes conventional thermolysis into *tert*-butoxy radicals in solution at reasonable rates only if heated at above 100 °C.[2] In contrast, reaction of this very stable **2** with **1** at room temperature leads to rapid C-O bond rupture instead of O-O cleavage. The subjects of this report are the issue of electron transfer versus nucleophilic addition, and of C-O cleavage versus O-O cleavage.

In the present study, we have carried out the reaction of 2 : 1 $Th^{+\bullet}$/**2** stoichiometry in MeCN at room temperature and products were *N*-*tert*-butyl acetamide (**3,** 80%, 0.80 mmol), thianthrene 5-oxide (ThO, 96%, 0.48 mmol), thianthrene 5,5-dioxide ($SSO_2$, 52%, 0.13 mmol) and thianthrene (Th, 104%, 0.26 mmol) as determined by quantitative GC and GC/MS analyses (Scheme 1). Work somewhat analogous to ours has been reported by Kim and Shin[9], which describes the nucleophilic addition of **2** to **1** in a molar ratio of 1.23:1.00 and the characteristics of oxidation of thianthrene, reduced oxidant. Kim had shown that the major products were not characteristic of *tert*-butyl cations but acetone was obtained from *tert*-butyl peroxy radical. For example, products of the reaction in MeCN at room temperature were Th (66%), ThO (27%), thianthrene 5,10-dioxide (SOSO, 7.7%), 5-acetonylthianthrenium perchlorate (1.1%), and **3** (12%). Unusual is that, in the report of Kim nor $SSO_2$ was formed at room temperature but more SOSO was obtained than $SSO_2$ at reflux temperature.



**Scheme 1**

In our reaction, SOSO and 5-acetonylthianthrenium perchlorate were not observed but $SSO_2$[10] was obtained as the only product of a second oxidation of Th. The major products are characteristic of *tert*-butyl cations, which says predominantly carbocationic chemistry is observed from an alkyl peroxide, a traditional source of free radical.[1] While **1** was reduced quantitatively to Th, the major product from **2** was **3**. Without doubt, this product arose from hydration, during work-up, of a Ritter-type intermediate ($Me_3CN{=}^{+}CMe$) from reaction of $Me_3C^+$ with solvent MeCN. Carbocationic chemistry was observed predominantly in the reaction of azo compounds,[5-7] carbonates,[8,9] carbamates,[10] with **1** in these laboratories recently. Accordingly, all reactions were carried out with 2 : 1 stoichiometry of **1** and oxidized compounds. Generally, in reactions of **1**, ThO is obtained as a side product from hydrolysis of **1** by water either adventitiously in the solvent or added during workup.[11] However, in these

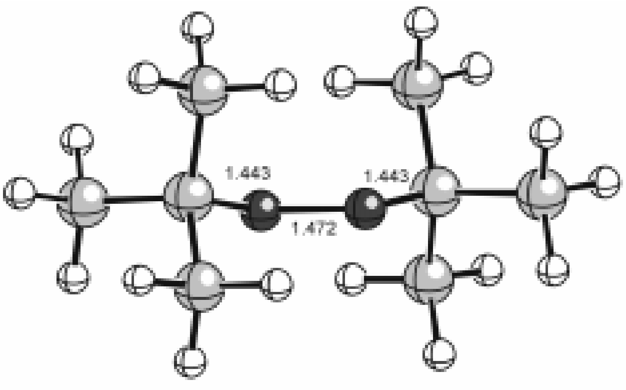
---

[*] Corresponding Author. Tel: +82-62-530-2493; Fax: +82-62-530-2499; e-mail: wklee@chonnam.ac.kr

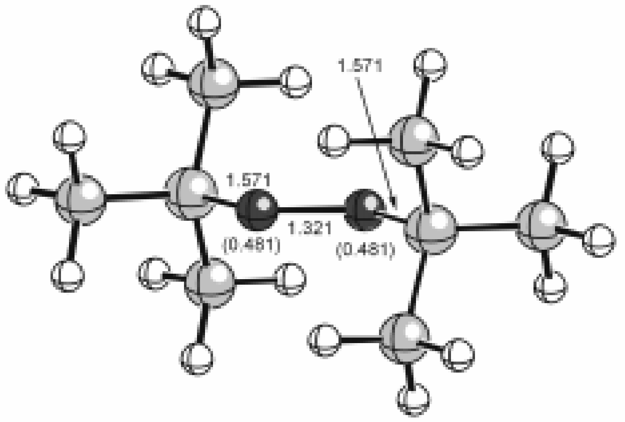
reactions the ThO was a primary rather than a side product of all reactions. This result suggests that the oxygen atom in ThO comes entirely from **2**. The formation of ThO as a primary product has been previously reported from the reactions of oximes,[12] cyclic alcohol,[13] and 2,3-dimethyl-2,3-butanediol[14] with **1**.

In order to exclude all doubts of autocatalytic effects by the trace acid generated from the electron transfer (ET) reaction, we have conducted a control reaction of perchloric acid and **2** in acetonitrile. Quantitative amounts of starting peroxide, **2** were recovered. These observations indicate that the oxidative C-O cleavage of **2** is not catalyzed by the acid but is proceeded by ET mechanism exclusively.

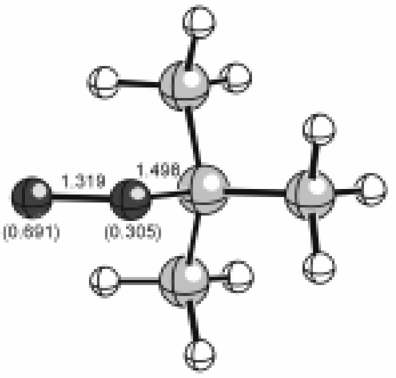
A comparative computational study as well as experimental studies on the fate of newly-formed *tert*-butyl peroxide cation radical, **2**$^{+\cdot}$ will give a clue to explain the fragmentation patterns of the alkyl peroxide cation radical. In practice, cation radicals pose a challenge to computational chemistry. However, standard *ab intio* computational methods such as unrestricted Hartree-Fock (UHF), even with corrections, have been found to yield erroneous results in certain cases. This makes it necessary to go to much higher computational levels that are intrinsically more accurate to investigate the reaction pathways of cation radicals. The another goal of this paper is benchmarking the newly developed high-level *ab initio* method CBS-4 using the CBS-4//B3LYP/6-31G* basis level[15] for the calculation of the peroxide cation radical. The CBS results are compared with the B3LYP density functional theory (DFT) approach using the B3LYP/6-31G*//B3LYP/6-31G* basis level.[16] In comparision, B3LYP is more computationally efficient than CBS-4,[17] but both calculations make similar predictions regarding the experimental results. Inspection of Table 1 shows that B3LYP and CBS-4 do not differ dramatically, but the *ab initio* method gives higher energy value except entropy in comparision with the B3LYP. However, it presents challenges to computational chemistry to assess which method is more reliable and available for cation radical model chemistry. All structures including the cation radical, radicals, and neutral species were fully optimized and all stationary structures were confirmed by vibrational frequency analyses.[18]



< *tert*-Butyl peroxide, **2**>



< *tert*-Butyl peroxide cation radical, **2**$^{+\cdot}$ >



< *tert*-Butyl peroxide radical, **4** >

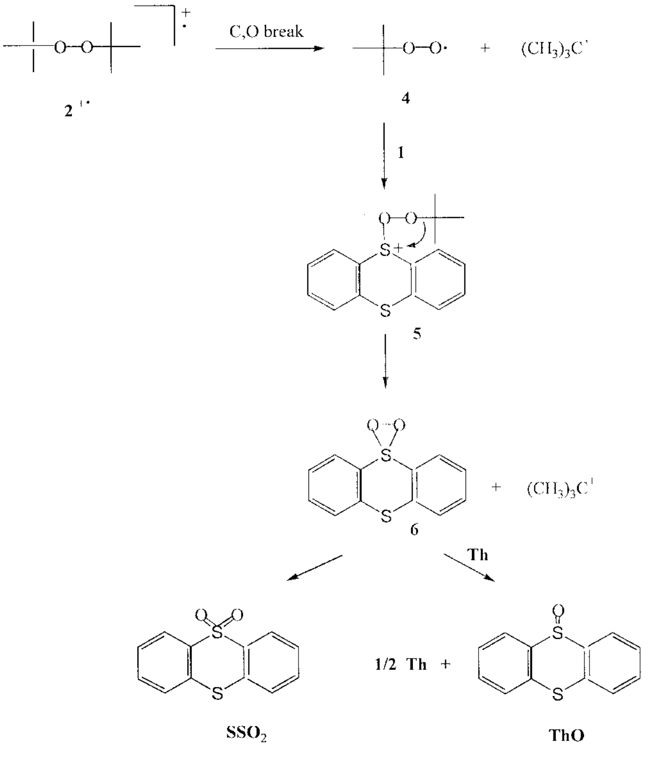
**Figure 1**. Optimized structures at UB3LYP/6-31G* level. Bond lengths are in **A** and values in parentheses are spin densities in au.

For the decomposition of **2**$^{+\cdot}$ four possible fragmentation patterns can be considered: (a) concerted pathway, (b) *tert*-butylperoxy radical and *tert*-butyl cation, (c) *tert*-butylperoxy cation and *tert*-butyl radical, and (d) *tert*-butoxy cation and *tert*-butoxy radical. However, in the calculations at B3LYP/6-31G* level, the *tert*-butylperoxy cation and *tert*-butoxy cation, which will be produced by paths (c) and (d) respectively, were not existed as stable species on the potential energy surface (PES). Thus, the pathways (c) and (d) can be excluded. This indicates that the fragmentation proceeds *via* the concerted pathway (a) or stepwise pathway (b), which the *tert*-butyl cation, *tert*-butyl radical and oxygen molecules would be formed in the absence of second molecule of Th$^{+\cdot}$ and solvent. This results is well agreed with the experimental findings. However, unfortunately, we can not determine which pathway, (a) or (b), is more favorable, since the transition state (TS) structures on the PES of paths (a) and (b) are not able to locate in the theoretical calculations. We can not acquire any information for the multiplicities in the expecting TS structures because the complicate multiplicity changes are accompanied in the both decomposition processes through reaction paths (a) and (b). Nevertheless, it can be predicted that the stepwise path (b) is more plausible, since the *t*-butylperoxy radical (**4**) is existed, and relatively stable that it could not decompose or oxidize, although the TS structure are not located in this path. The

**Table 1**. Comparative Computational Energies between Reactant ($2^{+\cdot}$) and Products (**4** and *tert*-Butyl Cation)

| Energy (unit) | DFT (B3LYP) | CBS (CBS-4) |
|---|---|---|
| E (hartree) | 33.72 | 43.05 |
| $E_{ZPE}$ (hartree) | 29.83 | 39.17 |
| H (hartree) | 30.42 | 39.76 |
| S (e.u) | 45.5 | 45.5 |
| G (hartree) | 16.84 | 26.17 |

fully optimized structures for the **2,** cation radical $\mathbf{2}^{+\cdot}$ and **4** with bond distances (Å) and bond angles (deg) along with spin density are depicted in Figure 1. The C-O-O valence angle of the cation radical is 100.1° and the two-dimensional angle of the peroxides is 112.3°. The cation radical $\mathbf{2}^{+\cdot}$ is not linear or positioned in same plane as expected. Thus it appears that the *t*-butyl carbon-oxygen bond breakage is occurred by shortening of C-O bond from 1.571 to 1.498. The spin density of oxygen atoms has changed from 0.481 in the cation radical to 0.691 and 0.305 in peroxy radical respectively. The result reveals that the majority of the unpaired spins in the radical **4** has been shifted to the terminal oxygen like in the case of the terminal oxygen of *tert*-butoxycarboxyl radical of di-*tert*-butyl dicarbonate.[6] The properties investigated include the structures and energetics of the cation radical as a reactant, *tert*-butyl cation and **4** as intermediates (Table 1). Consequently, the cation radical $\mathbf{2}^{+\cdot}$, which was not in the stationary point, facile C-O breaking occurred at some stage under the oxidative conditions to give *tert*-butyl cation and **4** as drawn schematically in Scheme 2.



**Scheme 2**

The intermediate **4** is trapped by a second molecule of $Th^{+\cdot}$, giving intermediate **5** ($ROOTh^+$). The amide **3**, was formed by $S_N1$ loss of **6** from the **5**. In other words, peroxide transfer occurs with the formation of the intermediate **6** and amide **3** of concordantly formed *tert*-butyl cations. Here, the supposition is that **4** can not be oxidized by **1** and instead, attacks as a nucleophile to the cation radical. If *tert*-butylperoxy cations are formed by the oxidation of **4** the perchloric acid salt, $Me_3COO^+ClO_4^-$ should be obtained. However, we could not find the salt from the product mixtures.

It is necessary to account for the formation of $SSO_2$ and ThO from the intermediate **6**. The sulfur containing dioxirane intermediate **6** exhibited two subsequent transformations: *homolysis* of the O-O bond which leads to $SSO_2$ *via* the O=S bond formation by radical coupling respectively. *Oxidation* of thianthrene by oxygen transfer from **6** with concomitant reduction of **6** to ThO as rationalized in Scheme 2. The stoichiometry for the formation of ThO we have described calls for one half unit of **6** for a half unit of Th. Our balance of products, Th and ThO is in accord with this requirement. The oxidation mechanism of ThO by dimethyldioxirane[19] or peracid[20] is analogous to the present results. They have shown that the nucleophilic oxidant such as peracid and dimethyldioxirane led exclusively to oxidation of the sulfoxide site than nucleophilic sulfide site to the $SSO_2$. In the present reactions, since the sulfur, postulated intermediary **5** is inherently electrophilic, only the sulfur containing dioxirane **6** should be obtained from sulfoxide oxidation of **5**. This observation strongly supports the possibility of Scheme 2. In principle, the sum of the yields of Th and $SSO_2$ should equal those of ThO. There are discrepancies in this run, for example, the yield of $SSO_2$ (52%) is less than expected, but the reason for which is not known. Unfortunately, we could not perform an $^{18}O$ labeling experiment as a diagnostic aid in tracing the source of the ThO and $SSO_2$ at this stage. In repeating our work with the electron transfer of peroxide to cation radical, we have found that both formation of $SSO_2$ and SOSO in this ET reaction is by no means the rule. The possibility of SOSO formation from **5** should be excluded because of electronic effects of the sulfur cation.

In summary, application of B3LYP and high-level *ab intio* methods to investigate reliable structure of cation radical, its nature, and its energies reveals advantages to explain the fragmentation mechanism of **2** with the reaction of sulfur cation radical, **1**. In contrast with O-O homolysis of alkyl peroxide on photochemical and thermal decomposition, a stable **2** has been shown to undergo C-O bond cleavage by sulfur cation radical **1** under mild conditions.

## Experimental Section

**Reaction of *tert*-butyl peroxide (2) with $Th^{+\cdot}ClO_4^-$ (1).** A general procedure was adopted. *tert*-Butyl peroxide (73.12 mg, 0.5 mmol) and $Th^{+\cdot}ClO_4^-$ (315.6 mg, 1.0 mmol) were placed in a 50 mL rounded-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 $NaHCO_3$ to neutralize $HClO_4$ 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 $MgSO_4$, 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 quantitaitve 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.

**Thianthrene-5,10-dioxide (SOSO),**[20] and **thianthrene 5,5-dioxide ($SSO_2$),**[20] were prepared as described in the literature. The samples were submitted to GC and GC/MS analyses.

***t*-Butylacetamide** (**3**)[21] were prepared as described in the literature.

## References and Notes

1. Matsugo, S.; Saito, I. In *Organic peroxides*; Ando, W., Ed.; Wiley: New York, 1992; pp 157-194.
2. Huyser, E. S. In *Free-Radical Chain Reactions;* Wiley-interscience: New York, 1970; p 287.
3. Shin, J.; Kim, K. *Bull. Korean Chem. Soc.* **1984**, *5*, 211.
4. The retention time of thianthrene-5,10-dioxide (SOSO) and thianthrene 5,5-dioxide ($SSO_2$) were the same as 26.10 min. in 10% OV-101 on Chrom W packed column but mp and MS data were different form each other. mp: SOSO; 249 °C, $SSO_2$; 168-169 °C. MS data: m/e (relative intensity, %): SOSO; 248 (100), 232 (30), 216 (30), 200 (73), 184 (89), 171 (60), 139 (22), 108 (30), 96 (15), 74 (14). $SSO_2$; 248 (100), 216 (12), 200 (38), 184 (20), 171 (18), 139 (13), 108 (11), 100 (10).
5. Bae, D. H.; Engel, P. S.; Hoque, A. K. M. M.; Keys, D. E.; Lee, W. K.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* **1985.** *107, 2561.*
6. Lee, W. K.; Chung, C. T. *Bull. Korean Chem. Soc.* **1992**, *13*, 694.
7. Chung, J. H.; Lim, S.-H.; Sohn, C. K.; Lee, W. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 792.
8. Park, Y. S.; Lee, W. K. *Bull. Korean Chem. Soc.* **1997**, *18*, 360.
9. Choi, J. M.; Ma, E.-K.; Sohn, C. K.; Lee, W. K. *Bull. Korean Chem. Soc.* **2000**, *21*, 1254.
10. Park, Y. S.; Han, D. S.; Lee, W. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 615.
11. Shine, H. J.; Murata, Y. *J. Org. Chem.* **1969**, *34,* 3368.
12. Chiou, S.; Hoque, A. K. M. M.; Shine, H. J. *J. Org. Chem.* **1990**, *55*, 327.
13. Shine, H. J.; Yueh, W. *J. Org. Chem.* **1994**, *59*, 3553.
14. Han, D. S.; Shine, H. J. *J. Org. Chem.* **1996**, *61*, 3997.
15. (a) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900. (b) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. *J. Chem. Phys.* **1996**, *104*, 2598.
16. (a) Becke, A. D. *J. Chem. Phys. A* **1993**, 9*8*, 5648. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (c) Parr, R. G.; Yang, W. In *Density Functional Theory of Atoms and Molecules;* Oxford University Press: Oxford, 1989.
17. For example, geometry optimization and then frequency calculations for the cation radical took 14 h, respectively, on a compaq GS320 supercom. In comparision, corresponding B3LYP/6-311G computations took a total of 33.5 h.
18. (a) Wilson, E. B.; Cross, P. C. In *Molecular Vibrations;* McGraw-Hill: New York, 1955. (b) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. In *Ab initio Molecular Orbital Theory;* Wiley: New York, 1986.
19. Adam, W.; Hass, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020.
20. Adam, W.; Golsch, D. *J. Org. Chem.* **1997**, *62*, 115.
21. Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045.