donors are shown in Scheme 1. From these data, it is confirmed that two nitrogens N(2), N(4) are slightly raised with respect to the other two nitrogens N(1), N(3) atoms. Also, dihedral angles between relevant planes from the least-squares plane are as follows: plane(1)-(2); 5.95°, plane(1)-(3); 9.94°, plane(2)-(3); 6.65°. The plane (1), (2) and (3) indicate the planes which are composed of N(1)-C(4)-C(5)-N(4), N(2)-C(2)-C(1)-N(3) and N(4)-C(6)-C(7)-N(3), respectively. Thus, we identified the fact that the four nitrogen atoms of the ligand are mostly coordinated coplanarly, and the Cu(II) ion is raised slightly (0.0931 Å) out of the plane of the four nitrogen atoms towards O(1) coordinated in the apical position. The methyl group and amide oxygen are oriented slightly down from the least-squares plane.

Furthermore, the five membered chelate rings conformation are shown in Scheme 2. From the least-squares plane data, carbons were distant C(1); 0.1628 Å, C(2); 0.0281 Å, C(4); 0.2332 Å, C(5); −0.3752 Å, C(6); −0.4034 Å and C(7); 0.1282 Å, respectively. The distances of C(1), C(2) within peptide portion are all positive values; therefore, the conformation is envelope (ε). But, two chelate ring conformations of the dien backbone are considerably deviated from the envelope. They have a δ and λ conformation, respectively. The ring conformation of N(1)-C(4)-C(5)-N(4) [δ] is more puckered than N(4)-C(6)-C(7)-N(3) [λ]. From this result, we suggest that the fixed orientation of chiral carbon in the ligand and the planar preference of amide portion affect the pucker of neighboring dien moiety.

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Oxidative Decomposition of Di-tert-butyl azodicarboxylate and *Ab Initio* Studies on Fragmentation Mechanism

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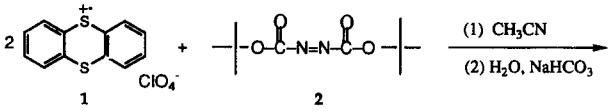
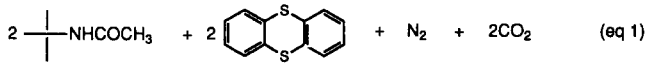
Oxidative decomposition of 1,1'-azoadamatane[1,2] and *t*-butyl phenyl carbonate[3] upon one-electron oxidation has sparked special interest to us in the nature of azocarboxylate cation radicals, and their fragmentation mechanism. Some azoalkanes, especially tertiary azoalkanes, reacted with cation radical at room temperature lead to rapid evolution of nitrogen *via* C-N bond cleavages.[4-6] Also, fast decarboxylations of t-butyl phenyl carbonate and di-*t*-butyl dicarbonate[7] *via* C-O bond cleavages were observed at the same reaction conditions. Here, we describe a reaction of thianthrene cation radical ($Th^{+\cdot}ClO_4^-$, **1**) with di-*tert*-butyl azodicarboxylate (**2**) and plausible mechanistic postulates and

also predict the most viable fragmentation mechanism of di-*t*-butyl azodicarboxylate cation radical ($2^{+\cdot}$) by *ab initio* Hartree-Fock calculations.

We selected **2** as a model compound to examine the mechanistic pathway because it has both azo and carboxyl linkages in a molecule. Chemical oxidation of **2** with 2 mol equiv of **1** in acetonitrile at room temperature results, after basic hydrolytic workup, in a 87% yield of *N*-*tert*-butylacetamide (**3**) along with rapid evolution of N_2 and CO_2, and 90% of reduced oxidant (Th) as determined by quantitative GC and GC/MS analyses (eq. 1). In addition to reduced oxidant Th, a small amount (0.4%) of thianthrene 5-oxide (ThO) was also obtained.[8]





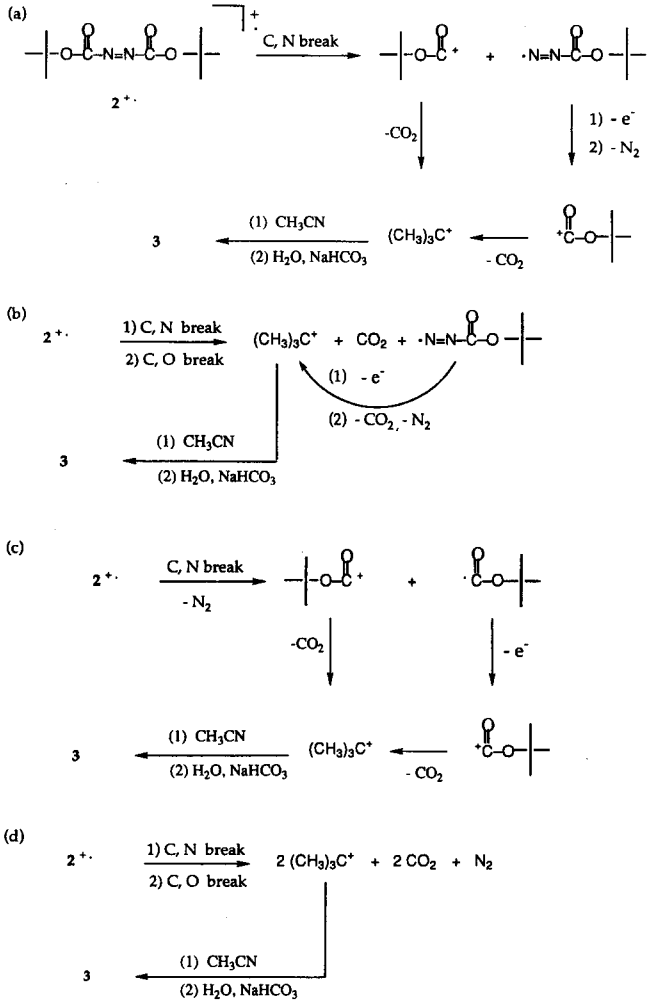
We suspect that trace acid generated from electron transfer (ET) reaction may catalyze the decomposition of **2**. To exclude all doubts of acid-derived chemistry, we have conducted a control reaction of perchloric acid and **2** in acetonitrile. A large amount (99.5%) of starting azodicarboxylate, **2** was recovered, which indicates that only **2** reacts exclusively by an ET mechanism.

The net reaction upon removing electrons from **2** is deazetation and decarboxylation *via* heterolytic cleavages of both C-N and C-O bonds. We want to know whether the rupture of the C-N and C-O bonds in $2^{+\cdot}$ proceeds concertedly or stepwise as that of C-N bonds in azoalkanes, which is still being debated.[9] The decomposition of $2^{+\cdot}$ provides four comparisions of interest as shown in Scheme 1: (a) stepwise cleavage of one C-N bond *via* diazenyl radical, (b) cleavage of both C-N and C-O bonds at one side of $2^{+\cdot}$ *via* diazenyl radical, (c) simultaneous cleavage of two C-N bonds with deazetation, and (d) cleavage of both C-N and C-O bonds with loss of CO_2 and N_2 at once.

Theoretical study on the most viable fragmentation mechanism of $2^{+\cdot}$ was carried out based on *ab initio* MO calculations.[10] All structures including cation radical, radical and neutral species were fully optimized by UHF/3-21G*[11] and RHF/3-21G*[12] basis set[13] respectively. All stationary structures were confirmed by vibrational frequency analyses.[14]

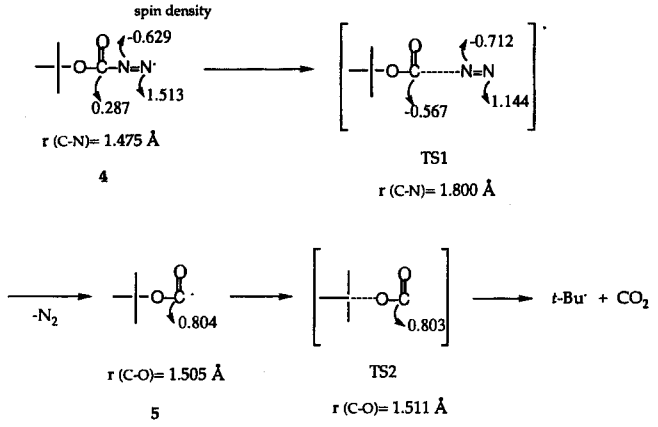
According to the full optimization for the geometry of $2^{+\cdot}$, which was not in the stationary point, facile C-N and C-O breaking occurred at some stage under the oxidative conditions to give *t*-butyl cation, carbon dioxide, and *t*-butoxycarbonyl diazenyl radical (**4**) as in depicted (b) in Scheme 1. From the MO calculations, it is clear that (a) and (c) in Scheme 1 can be ruled out from possible mechanistic postulates.

Because di-*tert*-butyl oxalate ($Me_3CO_2CCO_2CMe_3$) has no azo linkage compared to the structure of **2**, we have conducted a comparative study of oxalate reactivity under oxidative conditions. Product analysis of the reaction of di-*tert*-butyl oxalate with **1** in MeCN shows only 23% of C-O bond cleavage products, **3**. From this experimental data, we



Scheme 1

find that the oxalate is considerably more reluctant toward oxidative decomposition than **2**. This result supports that the oxidative decomposition of **2** would be accelerated by the presence of two nitrogens in a double bond and that C-O bond cleavage may not compete with C-N bond cleavage during the decomposition of azodicarboxylate **2**. Therefore, we could rule out (d) from our considerations for the mechanistic possibilities in Scheme 1.



Scheme 2

Table 1. Hartree-Fock energies at the 3-21G* level for the various species involved in cation radical induced oxidation of di-*t*-butyl azodicarboxylate (**2**)

Species	Energy (a.u.)
di-*t*-butyl azodicarboxylate	−793.03278
t-butoxycarbonyl diazenyl radical (**4**)	−450.62987
transition state 1 (TS1)	−450.61995
t-butoxycarbonyl radical (**5**)	−342.35975
transition state 2 (TS2)	−342.35374
t-butyl cation	−156.71780
CO_2	−186.56126
N_2	−108.30095

We also examined the subsequent fates of diazenyl radical, **4**. MO results show that the radical **4**, if no more react with cation radical, is prone to fast deazetation *via* TS1 to *t*-butoxycarbonyl radical (**5**), followed by faster decarboxylation *via* TS2 as in Scheme 2. Hartree-Fock energies for all stationary structures are summerized in Table 1. The calculated activation energy for decarboxylation, 15.76 kJ/mole, is less than that for deazetation, 26.00 kJ/mole.

In addition, the C-N bond of **4** has lengthened from 1.475 Å to 1.800 Å in TS1 and the C-O bond length of **5** has been changed only a little from 1.505 Å to 1.511 Å. Furthermore, while the large spin density of terminal N atom (1.513) in **4** has moved onto both C and N to be cleaved in TS1, the spin density changes for decarboxylation in TS2 were negligibly small. This results reveal that **5**, if formed, decomposes much more rapidly than **4** to afford t-butyl radical with decarboxylation and the decomposition is expected to proceed through earlier transition state, TS2, according to the Hammond postulate.

In closing, a thermally stable azoalkane with carboxyl linkages has been shown to undergo facile deazetation and decarboxylation under mild conditions. Products balances are high, and the reaction stoichiometry requires 2 equiv. of cation radical salt to one of **2**. Although the details of the fragmentation mechanism are not yet certain, theoretical study on $\mathbf{2}^{+\cdot}$ shows that (b) type fragmentation in Scheme 1 is the most viable mechanistic postulate for the transformation.

Experimental Section

Reaction of di-*tert*-butyl azodicarboxylate with $Th^{+\cdot}ClO_4^-$. Di-*tert*-butyl azodicarboxylate (115.1 mg, 0.50 mmol) and 322 mg (1.02 mmol) of $Th^{+\cdot}ClO_4^-$ were placed in a 100-mL, round-bottomed flask. The flask was capped with a septum, evacuated, and filled with argon into which 30 mL of CH_3CN was injected by syringe. The dark purple color of $Th^{+\cdot}$ was discharged within 5 minutes, but stirring was continued overnight. Thereafter, the solution was diluted with 10 mL of water, neutralized with $NaHCO_3$ solution, and extracted with 3×30 mL portions of CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$, and evaporated. The residue was dissolved in 10 mL of CH_2Cl_2. 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 m×1/8 in. stainless steel column packed with 10% OV-101 on Chrom W, with naphthalene as an internal standards.

Recation of di-*tert*-butyl oxalate with $Th^{+\cdot}ClO_4^-$. The reaction was carried out using, 101.5 mg (0.502 mmol) of di-*tert*-butyl oxalate and 318 mg (1.00 mmol) of $Th^{+\cdot}ClO_4^-$ in 20 mL of CH_3CN as described for di-*tert*-butyl azodicarboxylate.

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