Oxidative Decarboxylation of Di-*tert*-butyl Dicarbonate and Theoretical Studies on the Mechanism

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Whereas the oxidative decarboxylation initiated by oxidizing agents is richly documented,[1] the decarboxylation with sulfur cation radical has only marginally been investigated.[2-5] For example, treatment of di-*t*-butylazodicarboxylate (Me$_3$-CO$_2$C-N=N-CO$_2$CMe$_3$) with two equivalents of thianthrene cation radical perchlorate (Th$^+ \cdot$ClO$_4^-$, **1**)[6] in acetonitrile solution produced primarily carbon dioxide, nitrogen, and cation-derived products.[5] This led to the interesting investigation that the azo linkage accelerates decarboxylation with clean loss of N$_2$ without more cation radical. However, we have found that C-C bond cleavage of di-*tert*-butyl oxalate (Me$_3$CO$_2$C-CO$_2$CMe$_3$) which has no extrusive linkage such as azo group of azodicarboxylate is very difficult.[7] These results sparked special interest to us in the possibility of oxidative decomposition of a model compound, di-*tert*-butyl dicarbonate (**2**) with C-O-C instead of C-N=N-C bond. Along with experimental work, we have undertaken theoretical studies for the geometries and energetics of **2** to predict its fragmentation pattern.

Di-*tert*-butyl dicarbonate (**2**) reacts with 2 mol equiv of cation radical, **1** in acetonitrile solvent at room temperature and undergoes oxidative decarboxylation with C-O bond cleavage, giving a 76% (0.76 mmol) of *N-tert*-butylacetamide (**3**) along with rapid evolution of CO$_2$, 16% (0.16 mmol) of thianthrene-5-oxide (ThO), and 73% (0.73 mmol) of reduced oxidant, thianthrene (Th) as determined by quantitative GC and GC/MS analyses (Scheme 1). Without doubt, amide, **3** arose from hydration, during workup, of a Ritter-type intermediate (Me$_3$CN=$^+$CMe) from reaction of Me$_3$C$^+$ with solvent acetonitrile. ThO is often obtained very small amounts (>0.5%) as a side product in reactions of **1**, arising from hydrolysis of **1** by water[8] either present adventitiously or added during workup. In the present reaction, however, the ThO (16% based on **1**) was a primary rather than a side product of reaction. This result suggests that the oxygen atom in ThO comes entirely from **2**. The more detailed mechanism is explained later. Analogous results for the formation of ThO from reactions of *t*-butyl peroxide,[9] oximes,[10] cyclic alcohol,[11] and 2,3-dimethyl-2,3-butanediol[12] with **1** have been reported.

In order to exclude all doubts of autocatalytic effects by the trace acid liberated from the electron transfer (ET) reaction, we have studied the control reaction of HClO$_4$ and **2** in MeCN. A large amounts (99.8%) of starting dicarbonate, **2** were recoverd. These observations indicate that the oxida-
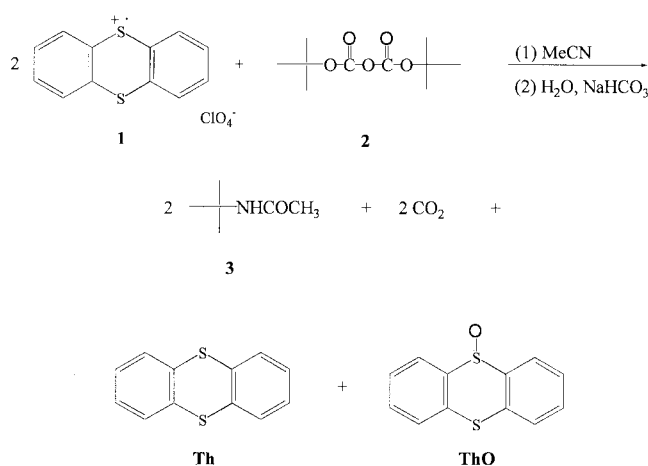
Scheme 1

tive decarboxylation of **2** is not catalyzed by the acid but is proceeded by ET mechanism exclusively.

A theoretical study of the fate of newly-formed dicarbonate cation radical (**2$^+$**), an electrophilic reactive intermediate, will be promising for understanding experimental results. In a comparative study of different theoretical methods for the calculation of the geometries and energetics of the stationary states Hartree-Fock (HF)[13] and density functional theory (DFT) methods were examined. It was found that the calculated geometries and energetics do not differ dramatically between two methods, but the best agreement with the experimental results is found with unrestricted Becke's three-parameter hybrid functional (B3LYP). The B3LYP methods using the UB3LYP/6-31G*//UB3LYP/6-31G* basis level[14] was found to be the best DFT technique for calculating the activation energy barriers for decomposition of **2$^+$**. All structures including the cation radical, radicals, and neutral species were fully optimized and all stationary structures were confirmed by vibrational frequency analyses.[15]

Three possible fragmentation patterns for **2$^+$** were examined: (a) *t*-butyl cation and the remaining radical ($^\cdot$OCOOCO$_2$-*t*-bu), (b) *t*-butoxy radical and the remaining cation ($^+$COO-CO$_2$-*t*-bu), and (c) (*t*-buOCOO$^\cdot$) and (*t*-buOCO$^+$). From the calculations, there are no transition states (TS) in (a) and (b) fragmentation patterns at the B3LYP level respectively, *i.e.*, TS are not located on the potential surface at all. Also, the radical ($^\cdot$OCOOCO$_2$-*t*-bu) in (a) and the cation ($^+$COOCO$_2$-*t*-bu) in (b) were not in the stationary point. Furthermore the radical ($^\cdot$OCOOCO$_2$-*t*-bu) is too unstable to retain its structure and decomposes into CO$_2$ and *t*-butoxy radical. However, only in the (c) pattern there have been TS at the B3LYP

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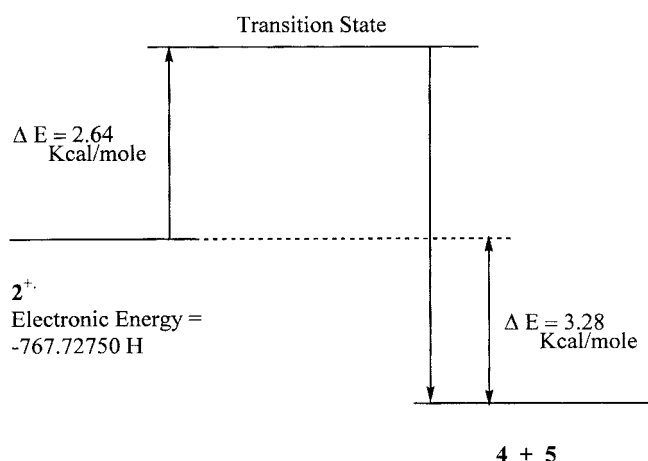
$\Delta E = 2.64$
Kcal/mole

2$^{+\cdot}$
Electronic Energy =
-767.72750 H

$\Delta E = 3.28$
Kcal/mole

Transition State

4 + 5

Figure 1. B3LYP energy profile for the decomposition of **2**$^{+\cdot}$.

level as shown in Figure 1. The calculated TS energy is -767.72750 H which was confirmed by one imaginary vibrational frequency at -166.4 cm^{-1} and the activation energy is 2.64 Kcal/mole.

Furthermore, B3LYP-DFT calculations were performed on radical **4** and **5**. The B3LYP calculations indicate that **4** and **5** decompose very rapidly to afford *t*-butoxy radical (**6**) and *t*-butyl cation with loss of CO_2 respectively. The fully optimized structures for the cation radical and the transition state with B3LYP bond distances (Å) and bond angles (deg) are depicted in Figure 2. Thus it appears that the *t*-butyl carbon-oxygen and the carbonyl carbon-center oxygen bonds breakage occurred by lengthening of the C-O bonds from 1.562 to 1.766, and from 1.542 to 1.932 respectively. While
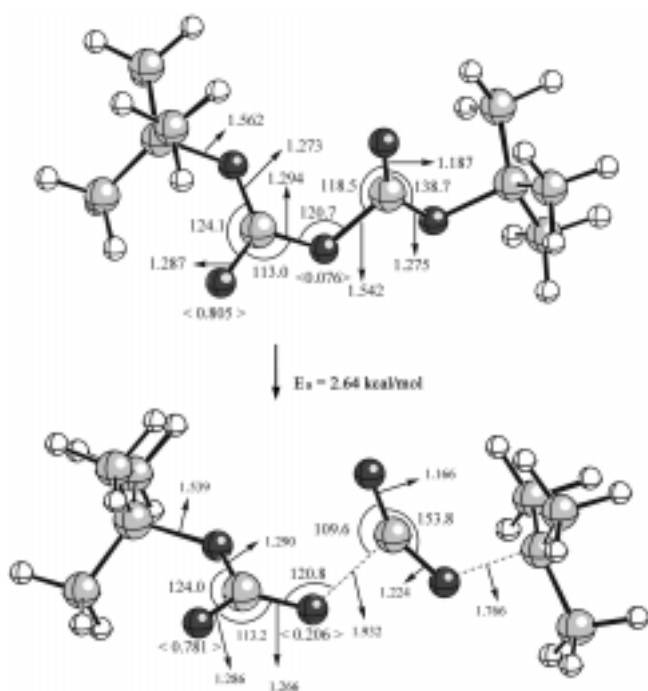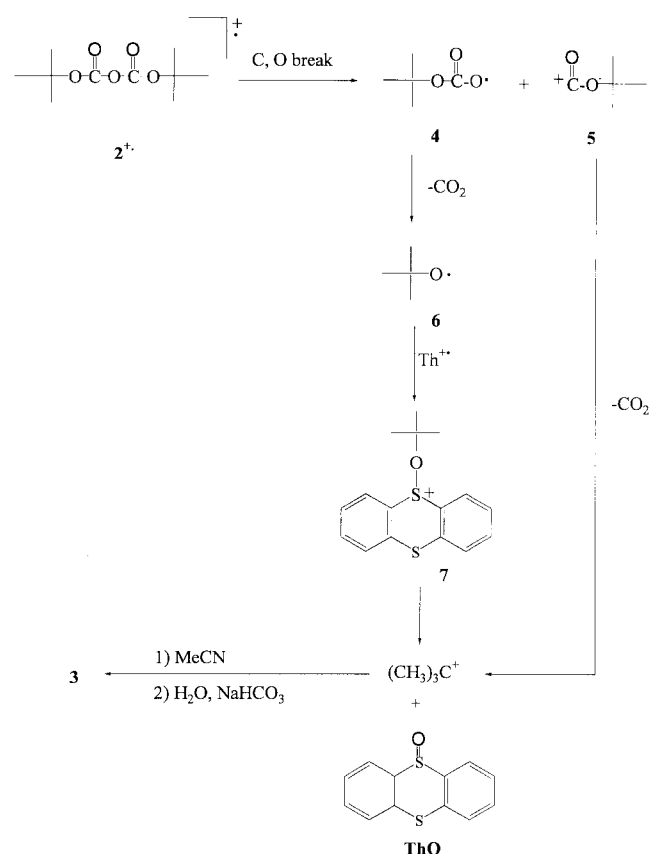
the spin density of C=O bond has little changed from 0.805 in cation radical **2**$^{+\cdot}$ to 0.781 in the TS the spin density of central oxygen has greatly changed from 0.076 to 0.206. This result reveals that the majority of the unpaired spin in the radical, **4** is centered on the terminal oxygen unlike totally delocalized structure of *t*-butoxycarbonyl diazenyl radical. Consequently, the cation radical of **2**$^{+\cdot}$ underwent decomposition, giving *t*-butyl cation, carbon dioxide, and the radical **6**. Based on the results calculated here, the most viable, stepwise fragmentation mechanism can be proposed as in Scheme 2.

The *t*-butoxy radical, **6** was generated by the loss of CO_2 spontaneously from **4**, and was then trapped by **1**, giving intermediate **7**. The amide, **3** was formed by S_N1 loss of ThO from the **7** (ROTh$^+$).[11,12] In other words, oxygen-atom transfer occurs with the formation of ThO and **3** of concordantly formed alkyl cations. The function of the center oxygen atom of **2** is a good electron donor to **1** and is to promote oxidative decomposition. The supposition here is that **6** cannot be oxidized by **1** and behaves, instead, nucleophile. If *t*-butoxy cations are formed by the oxidation of **6** in this reaction *t*-butanol should be found by the hydrolysis of Me$_3$CO$^+$-ClO$_4^-$. However, we could not find *t*-butanol in the reaction and this observation supports Scheme 2. In principle, the yields of **3** should equal the sum of Th and ThO and the yield of Th and ThO should be the same. There are discrepancies in this run, for example, the yield of Th (73%) is much more than expected (50%), but the reason for which is

Figure 2. The fully optimized structures of the cation radical and the transition state showing bond longths (Å) and bond angles (deg.). Values in brackets indicate spin densities at oxygens.

Scheme 2

not known. Also, we have this time been unable to relate the formation of Th and ThO (89%) quantitatively to that of amide **3** (76%), nor have we used ^{18}O labeling as a diagnostic aid in tracing the source of the ThO.

In conclusion, these theoretical studies predict that the fragmentation mechanism of dicarbonate, **2** and are in agreement with experimental results. A thermally stable dicarbonate with only oxygen linkage loses two molecules of CO_2 when oxidized at room temperature by very effective sulfur cation radical. The central oxygen atom of **2** acts as a good electron donor to **1** and a promoter to the oxidative decomposition. Thus, we have found that **2** is much easier to be oxidized than di-*tert*-butyl oxalate.

Experimental Section

Recation of di-*tert*-butyl dicarbonate with $Th^+ClO_4^-$ (1). A general procedure was adopted. Solid $Th^+ClO_4^-$ (315.6 mg, 1.0 mmol) and the dicarbonate (109.1 mg, 0.5 mmol, **2**) in the mole ratio 2 : 1 were placed under argon in a septum-capped flask into which 20 mL of acetonitrile was injected by syringe. The dark purple color of **1** was discharged within 10 minutes, 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 4×20 mL of CH_2Cl_2, and the dried ($MgSO_4$) CH_2Cl_2 solution was evaporated. The tared residue thus obtained was taken up in a standard volume of CH_2Cl_2, and the solution was analyzed by GC and GC-MS. Concentration factors for all products were determined with authentic materials. The column used was a $2 \times 1/8$ in. stainless steel column packed with 10% OV-101 on Chrom W, with naphthalene as an internal standards.

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6. *Warning!* Thianthrene cation radical perchlorate ($Th^+ClO_4^-$) is a shock-sensitive explosive solid and should be handled with care.

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