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Predicting Efficient C_{60} Epoxidation and Viable Multiple Oxide Formation by Theoretical Study

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The epoxidation of C_{60} by various oxidizing agents such as dimethyldioxirane (DMD), methyl(trifluoromethyl)dioxirane (MTMD), and bis(trifluoromethyl)dioxirane (BTMD) has been probed computationally by the AM1 method. The computations have revealed that for the reaction forming $C_{60}O$ through a concerted "spiro" transition state, the currently used DMD involves its HOMO lone-pair and the LUMO (π^*) of fullerene in an inverse electron demand fashion. This is distinct from the DMD reaction with ethylene. On the other hand, the addition of CF_3 groups lowers the LUMO (peroxide σ^*) of MTMD and BTMD by virtue of negative hyperconjugation; the oxidants can then attack the fullerene nucleophilically at an increased rate to the maximum extent. These estimations have thus established that the strong electrophilic oxidizing agents remarkably enhance the fullerene epoxidation. DMD further produces $C_{60}O_2$ and $C_{60}O_3$ via multiple epoxidations, as $C_{60}O$ might best be produced quantitatively by MTMD and BTMD. The regiochemistry of the multiple oxidation products in which the subsequent oxidations take place at the adjacent sites is consistent with the increased nucleophilicity of the nearest double bonds attached to the prevailing epoxide function.

Introduction

The fullerene epoxide, $C_{60}O$, is the simplest fullerene derivative and the key fullerene oxidation product[1−6] that plays an important role in the synthesis of various organic,[3−6] organometallic,[4−7] and polymeric[2b] fullerene derivatives. Numerous oxygenation[1−3] processes are frequently applied for the generation of $C_{60}O$, but the reports on the standard epoxidations via peracid,[4] dimethyldioxirane (DMD),[5] and metal peroxide[6] are scarce. Consequently, several attempts have been made to enhance the yield of $C_{60}O$. Murray and others[6] achieved some improvement in $C_{60}O$ yield by using methyltrioxorhenium−hydrogen peroxide agent. DMD[8] is one of the familiar oxidizing agents used for various olefin epoxidation; however, it provided a low yield of epoxide and a 1,3-dioxolane adduct with C_{60}.[5] Under several circumstances, C_{60} has been shown to give $C_{60}O$ in association with the higher oxides ($C_{60}O_n$, $n = 2−5$) in different oxidations.[1−4] Subsequently, it is also proposed[1b,4] that there are indeed eight possible regioisomers of $C_{60}O_2$ and 43 isomers of $C_{60}O_3$, and this is in light of the multiple reacting centers available on fullerene cluster. However, only a few of these isomers have been so far isolated,[3e,4] as both bis- and tris-oxides of C_{60} are shown to be highly unstable.[1a−c]

The epoxidation proceeds readily with electron-rich olefins in most cases. Owing to the electron-deficient[9] nature of C_{60}, epoxidations[1−6] often result in a poor $C_{60}O$ formation. Although the structure of $C_{60}O$ is well characterized,[1b,4,10] the mechanism of fullerene epoxida-

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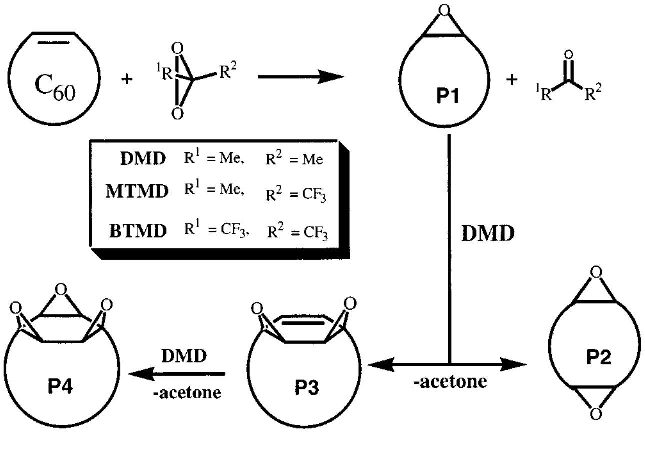
Scheme 1



tion still remains elusive. These issues thus prompted us to theoretically investigate improved methods to generate a basic fullerene oxide, $C_{60}O$, by various dioxiranes. Herein, we perform AM1 calculations to study the mechanism of epoxidation of C_{60} by DMD,[5] and through this, analyze the reactivity of fullerene in comparison to ethylene. Besides DMD,[8] methyl(trifluoromethyl)dioxirane (MTMD)[8b,c,11] and bis(trifluoromethyl)dioxirane (BTMD)[8b,c,] have also been chosen for epoxidation (Scheme 1) in order to understand their relative oxidative efficiency. The purpose of this investigation is to examine the epoxidation rate enhancement by MTMD and BTMD through the negative hyperconjugative CF_3 substituent.[11] The present work is then extended to probe the mechanism of certain sequential tandem epoxidations using DMD that lead to selected bis- and tris-epoxides ($C_{60}O_2$ and $C_{60}O_3$) as depicted in Scheme 1. These reactions are employed here mainly to explore the regiochemical strategies followed for the multiple oxide formations based on the nucleophilicity of the fullerene double bonds adjacent to the existing epoxides. Thus, the factors controlling the fullerene epoxidations are thoroughly analyzed through the transition structures (TSs), reaction energetics, and other relevant quantities. Preliminary results on this work have been reported[12] recently.

Computational Methods

Computations were performed at semiempirical AM1 level[13] using MOPAC 6.0 program[14] implemented on Pentium-based systems. In view of the large size of the systems under study, the present investigation prohibited the use of the state-of-the-art methods available in both ab initio and DFT techniques. Nevertheless, single point calculations were carried out using Gaussian 94[15] for the first set of epoxidations at the B3LYP/3-21G[16] level on the AM1-optimized geometry to show the relative energy trend. Baker's eigenvector following (EF) procedure[17] has been used to optimize the stationary point geometries. The harmonic vibration analysis has been done to ensure the characteristic zero and single imaginary frequency, respectively, of equilibrium (reactant and product) and saddle point (TS) geometries.

To follow the progress of a reaction, the extent of bond forming and cleaving of a 'i' or 'j' bond (BF_i and BC_j) at the TS has been calculated from the bond orders as indicated below. From this, the average percentage of bond formation (BF_{ave}), bond cleavage (BC_{ave}), and bond make-break (BFC_{ave}) at the TS has been obtained.

$$BF_i \text{ or } BC_j = \frac{BO_{i/j}{}^{TS} - BO_{i/j}{}^{R}}{BO_{i/j}{}^{P} - BO_{i/j}{}^{R}} \times 100$$

$$BF_{ave} = 1/n_i \sum BF_i \text{ and } BC_{ave} = 1/n_j \sum BC_j$$

$$BFC_{ave} = \frac{(BF_{ave} + BC_{ave})}{2}$$

The "early" and "late" nature of the TS can be identified from the average percentage of bond make-break (BFC_{ave}) at the TS.

Results and Discussion

Epoxidation of C_{60} by DMD, MTMD, and BTMD. The interaction of π-HOMO of alkene with the peroxide σ*-LUMO of DMD is dominant in the normal epoxidation,[18−20] because olefin behaves as a nucleophile while dioxirane acts as an electrophile. On the other hand, the isolated C_{60} is an electron-deficient cluster due to the effect of pyramidalization[9,21] as well as the aromaticity[9,22] on its surface. On account of this, the C_{60}-DMD reaction involves the π*-LUMO of fullerene and the HOMO lone-pair of dioxirane and thus determines an inverse electron demand epoxidation (**II** in Figure 1). This is contradictory to the normal reaction[18−20] as revealed by the FMO gaps presented in Table 1. The CF_3-substituted dioxiranes (MTMD and BTMD) seem to restrict the inverse electron demand process through negative hyperconjugative effect. Consequently, on moving from DMD to BTMD reaction, the dioxirane LUMO is decreased (1.92, 0.47, and −0.77 eV) and the C_{60} HOMO remains constant (−2.95 eV), and thereby the epoxidation becomes normal electron demand type (**I**); fullerene thus exhibits its

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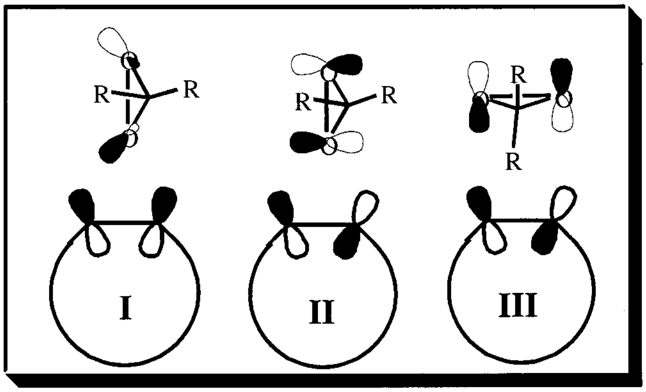

Figure 1. Schematic representation of the frontier orbital approach between dioxirane and fullerene that involves both epoxidation and cycloaddition.

Table 1. Calculated (AM1) Frontier Orbital Energy Gaps (eV), Quantum of Charge Transfer, Activation and Reactions Energies (kcal mol^{-1}) for the Epoxidation of Ethylene by DMD, and C_{60} by DMD, MTDM, and BTMD

reaction	TS	ΔE_a[a]	ΔE_b[a]	q_{CT}[b]	$\Delta E^{\ddagger}$	ΔE_r
DMD + ethylene	**1**	12.4	12.9	0.197	15.6(−11.8)	−85.3(−58.7)
DMD + C_{60}	**2**	11.6	8.6	0.160	28.1(−7.6)	−72.3(−48.7)
MTMD + C_{60}	**3**	10.1	9.6	0.238	23.5(−9.7)	−75.4(−49.1)
BTMD + C_{60}	**4**	8.9	10.5	0.294	18.7(−15.0)	−75.5(−49.5)

The relative energies calculated at B3LYP/3-21G//AM1 are given in parentheses. [a] $\Delta E_a = E_{HOMO}$(olefin) − E_{LUMO}(dioxirane); $\Delta E_b = E_{LUMO}$(olefin) − E_{HOMO}(dioxirane). [b] Quantum of charge transfer from epoxidant to epoxidate at the TS.

“pseudo” nucleophilic character. Calculated FMO gaps (Table 1) clearly indicate this effect. On the basis of these FMO strategies, the epoxidation of C_{60} by DMD, MTMD, and BTMD proceeds via “spiro” TSs, **2**, **3**, and **4** (Figure 2) concertedly[18,23] to yield $C_{60}O$ and ketone (Scheme 1). The differently substituted MTMD is sterically imbalanced by Me and CF_3 groups which exhibit opposite hyperconjugation, and hence this secures an asynchronous TS while the rest of the dioxiranes pass through the synchronous mechanism by their symmetry. The relative extent of the newly forming two C⋯O bonds (Figure 2) signifies the synchronous and asynchronous nature of the TSs. Moreover, the reaction of C_{60} with DMD[5] can form a 1,3-dioxolane derivative by cyloaddition (**III**). The involvement of diradicals[19d] in its formation prohibits the study of this type of reaction. The “earliness” and “lateness” of the TS is discussed based on both geometrical parameters (Figure 2) and bond order analysis (Table 2).

The forming bonds (C1⋯O3, C2⋯O3, and C5−O4) are found to be stronger whereas the cleaving bonds (C1−C2, O3⋯O4, and C3−O5) are weaker in the TSs (**2**, **3**, and **4**) of fullerene epoxidations as compared to the TS (**1**) of the ethylene-DMD reaction (Figure 2). The bond criteria thus indicate the fact that the bonds are formed or cleaved at the TS to a lesser extent in **2**−**4** than in **1**. The bond order analysis (Table 2) reveals that the former TSs are formed relatively later than the prototypical TS, as the percentages of bond forming and cleaving at the TS (BF_{ave}, BC_{ave}, BFC_{ave}) are found to be reasonably higher in all TSs (**2**−**4**) in relation to **1**. The electrophilic nature of C_{60} upon epoxidation thus allows for such “late” matured TSs. Both analyses emphasize that the weakness of the formed bond and the tightness of the cleaved bond should have a lower percentage of bond make-break at the TS, implying an “early” type of TS. On moving from **2** to **4**, the strength of the forming bonds is decreased (Figure 2) with a gradual decrease in BF_i values (Table 2) while the strength of the cleaving bonds is increased with reduced values of BC_j except for peroxide bond. The decrease in O−O bond[24] strength with increasing BC_j from **2**−**4** is contrary to the expectation, and this can be attributed to the negative hyperconjugative effect of CF_3. However, the overall bond formation and cleavage (BF_{ave}, BC_{ave}, BFC_{ave}) thus predict that the “earliness” of the TS is found to increase in the order **2** < **3** < **4** as expected. The “early” TS would give a thermodynamically favored reaction according to the Hammond’s postulate.[25] The TSs further indicate that, due to the electronically different dioxiranes, the bond make-break process greatly alters the dioxirane geometry rather than the fullerene one in the TS series. This can be noticed from the appropriate bond angles and torsion angles presented in Figure 2.

The predictive accuracy of semiempirical MOs[12,20,26] for epoxidation indeed seems to be good in that the TS as well as the barrier are often comparable to the experimental observation,[23] and ab initio and DFT results.[18,19] Specifically, the calculated AM1 barrier[12,20] is found to be only 2.2 kcal mol^{-1} less than the B3LYP/6-31G* value[18b] which thus gives the impression of the applicability of AM1 model for these epoxidations. Calculated barriers listed in Table 1 show that C_{60} is less reactive than ethylene even with the efficient oxidizing agent, BTMD. This is due to the fact that the 6−6 junctions of C_{60} are highly electrophilic (LUMO: −2.95 eV) compared to ethylene (1.44 eV). Further, C_{60} epoxidations are less exothermic than the ethylene-DMD reaction as can be seen in the reaction energies (Table 1). In fullerene reactions, both strain release and aromaticity loss occur simultaneously during the product formation. Normally, the strain-relief should increase the exothermicity, but it is decreased compared to the ethylene reaction. Hence, the aromaticity offsets the strain factor to thereby dominate in the thermodynamic aspect of the reactions whereas the kinetic aspect is uniquely characterized by the electronic factor.[12]

Among C_{60} epoxidations, the BTMD-C_{60} reaction is faster than the MTMD-C_{60} process, and the DMD-C_{60} reaction is found to be the slowest. Evidently, the CF_3 group reduces the peroxide LUMO by the influence of negative hyperconjugation which thus decreases the barrier substantially (Table 1) from DMD to BTMD epoxidation. The charge transfer from C_{60} to dioxirane at the TS (q_{CT} values in Table 1) is increased with a decreasing barrier in the reaction series, and this is anticipated by the electrophilicity and nucleophilicity of

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(24) The weak peroxide bond is the most sensitive part on oxygen transfer reaction, and its cleavage during the TS formation would be greater than the other bond formations and cleavages. Accordingly, peroxide bond cleavage, BC_{O-O}, in the TSs **2**−**4** is in the range 42−46% (Table 2).

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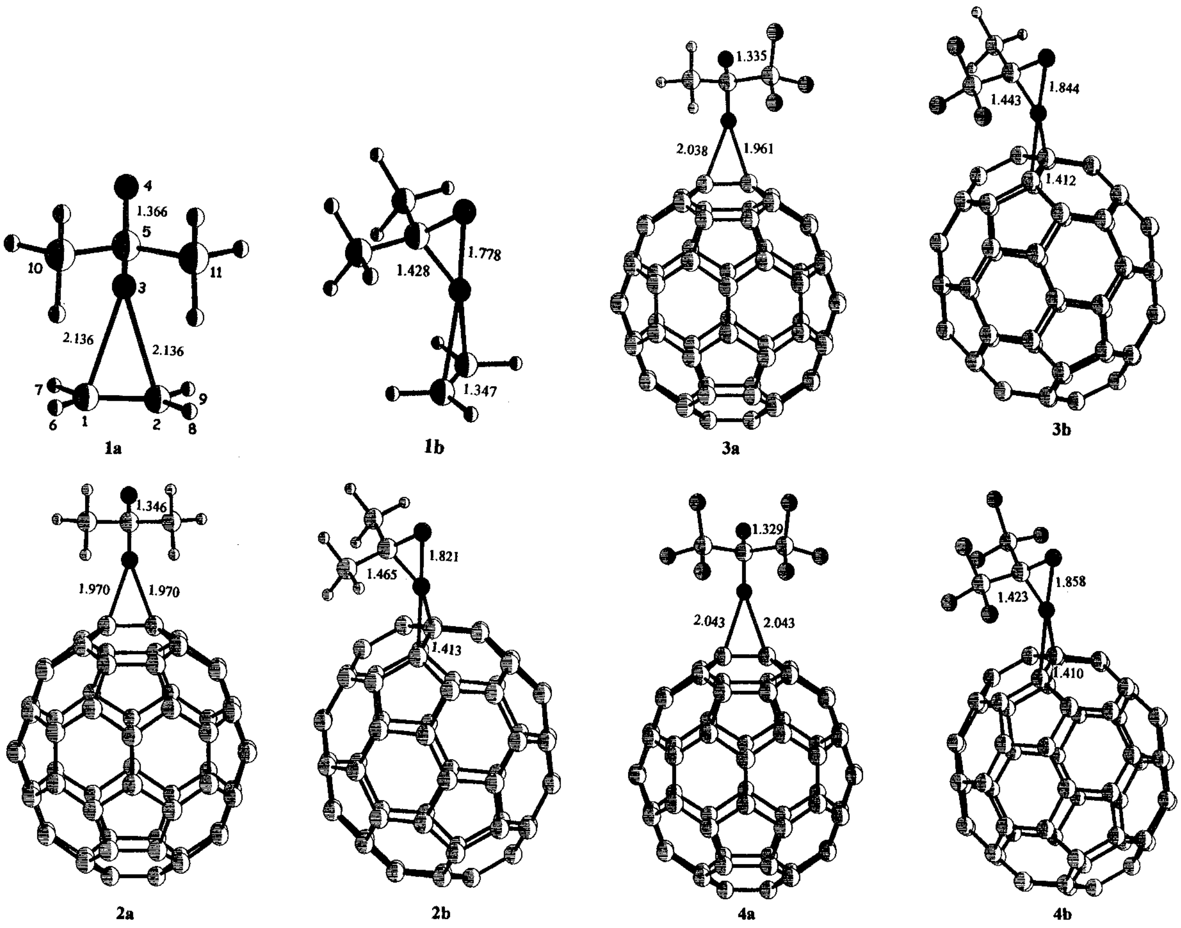

Figure 2. Computed TSs (**1**−**4**) for the epoxidations of ethylene and C_{60} by DMD, and C_{60} by MTMD as well as BTMD, with selected geometric parameters. ϕ indicates the angle around dioxirane carbon (C5). The structure types **a** and **b** indicate the "front" and "side" view of the "spiro" TS with the forming and cleaving bond lengths, respectively.

parameter	1	2	3	4	parameter	1	2	3	4
1−3−2	36.7	42.0	41.3	40.4	1−3−2−4	180.0	167.2	157.3	156.9
3−5−4	79.0	80.6	83.1	84.9	1−3−2−5	−105.4	−111.6	−110.6	−114.6
6−1−2−9	180.0	135.5	135.6	136.0	ϕ	345.8	345.0	343.6	341.9
8−2−1−7	180.0	−135.5	−135.8	−136.0					

dioxirane and olefin, respectively. Despite the series of negative barriers in the B3LYP calculations, the trend in barriers parallels the AM1 values. This, thereby, gives an additional support to the usage of AM1 method. The decrease in the barrier height with a large difference along the reaction series accomplishes a greater enhancement in the oxidation efficiency. The reaction energy (Table 1) is calculated to be in the range −72.3 to −75.5 kcal mol^{-1}. This happens because the dioxirane is a strained cyclic peroxide which releases its strain in addition to the strain-release in C_{60} during the product formation. A small energy difference occurs in the series because the resulting major product, $C_{60}O$, is the same in all the reactions. This is also witnessed from the pyramidalization at the reacting bond which occurs between TS and product—when the reacting carbons are rehybridized roughly from $sp^{2.5}$ to sp^3—indicating its small strain-relief (7.6°, 7.7°, and 8.1°) in the epoxidation series. Moreover, the relative barrier movement exists along the reaction profile with respect to the "early"/"late" matured TS that can be realized from the plot sketched in Figure 3. Overall results indicate that the "earliness" of the TS is increased (BFC_{ave}, Table 2) with a decrease in the barrier while the reaction energy is increased (Table 1) from the DMD-C_{60} to the BTMD-C_{60} reaction. Therefore, the kinetic and thermodynamic control of the epoxidation are found to increase in the following order: DMD-C_{60} < MTMD-C_{60} < BTMD-C_{60}. Calculations thus establish that an efficient C_{60} epoxidation can be achieved by both MTMD and BTMD, and this can be of a great

Table 2. Percentages of Bond Forming and Cleaving at the TS for Ethylene and C_{60} Epoxidations by Dioxiranes

	BF_i[a]			BC_i[b]					
TS	C1−O3	C2−O3	C5−O4	C1−C2	O3−O4	C3−O4	BF_{ave}	BC_{ave}	BFC_{ave}
1	15.4	15.4	13.8	23.5	33.1	9.1	14.9	21.9	18.4
2	26.0	26.0	24.4	29.9	42.2	19.8	25.5	30.6	28.1
3	22.4	27.0	23.0	30.8	45.0	17.6	24.1	31.1	27.6
4	23.0	23.0	21.8	30.8	46.2	14.7	22.6	26.6	26.6

[a] Bond formation at the TS. [b] Bond cleavage at the TS.

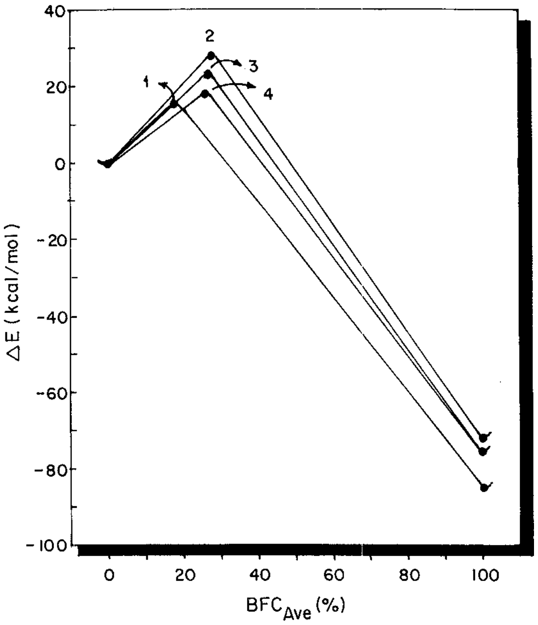

Figure 3. Plot of relative energy of TSs and products versus BFC_{ave}. 0% and 100% of BFC_{ave} values denote reactants and products, respectively. Reactant state is taken as reference. The representative plot is drawn for the title reactions.

synthetic interest. It is worthwhile to highlight the recent experimental report on $C_{60}O$ formation by Curci and others[27] using MTMD. This section further suggests that a highly sensitive BTMD[8] can be controlled by fullerene alone on epoxidation in view of its high electrophilicity.

Sequential Epoxidation. Further oxidization of $C_{60}O$ was subsequently investigated with DMD to form two isomers of $C_{60}O_2$ (**P2** and **P3**) and the tris-epoxide, $C_{60}O_3$ (**P4**), as shown in Scheme 1. The regioselective isomers of $C_{60}O_2$ and $C_{60}O_3$ are difficult to envisage upon multiple oxidations[1a,c] due to the electron-poor nature of fullerene. This complication does not occur in the multiple Diels–Alder addition of diene to C_{60},[28] despite the fact that the fullerene is known to be electronically favorable for this reaction. Therefore, the sequential epoxidations studied here are all based on the relative nucleophilic junctions of C_{60} that brings a correct regiochemistry of the isomers. In view of the FMO vectors, DMD can oxidize $C_{60}O$ selectively at several sites to form various $C_{60}O_2$ isomers. One of the four *proximal* junctions attached to the epoxide framework and the *distal* junction opposite to that are candidates for oxidations to produce **P3** and **P2**, respectively. The former bond is found to be the most nucleophilic and thus most reactive site next to the adjacent electron-rich epoxide function, and hence the latter is the least reactive bond. This explains the selectivity of the oxidation and helps to categorize the $C_{60}O_2$ regioisomers. On the basis of this, viz., the reacting bonds adjacent to the existing epoxide unit hold more nucleophilic behavior; the alternate reacting bonds (AM1[expt]: 1.385[1.384] Å and 1.464[1.462] Å) of a six-membered ring are therefore fully oxidized to yield $C_{60}O_3$ (**P4**). This is also supported by the previously reported complete oxidation of a benzenoid[29] and a cyclooctatraene[30] ring by DMD.

All these reactions pass through concerted "spiro" TSs (**5**–**7**) in which one of the $C_{60}O_2$ isomers, **P3**, is formed due to asynchronous TS (**6**) while the rest of the products (**P2** and **P4**) are formed via synchronous TSs (**5** and **7**). The unsymmetrical nature of the proximal junction to epoxide produces **P3** form in an asynchronous manner. The TSs **6** and **7**, appear to be earlier than **5**, because the **b**, **c**, and **f** bonds of **6** and **7** (Figure 4) are formed fast due to their weakness while the remaining bonds (**a**, **d,** and **e**) are stronger and cleaved fast compared to **5**. As expected, the epoxidations involving the olefins *proximal* to epoxide group achieve "early" matured TSs (**6** and **7**) relative to **5**. The activation and reaction energies (Figure 4) predict that the product formation of **P2** is slower and less exothermic than the **P3** and **P4** forming processes. This is in tune with the "early"/"late" nature of the TS shown here. The relative energies (Figure 4) further reveal that **P3** formation is favorable both kinetically and thermodynamically over the C_{60}-DMD epoxidation whereas the **P2** process is slightly less favorable (Table 1). This is in good agreement with the experimental observations[3e,4] because **P3** is shown to be the most stable isomer among $C_{60}O_2$ isomers, but **P2** has never appeared in the mass fragmentation pattern.[3e] The tris-epoxide (**P4**) formation from **P3** is slightly favorable on account of its low barrier height (Figure 4), but it is less exothermic by 1.8 kcal mol^{-1}. The aromaticity loss occurs in the three 6–6 ring junctions during the formation of **P4** that reduces its exothermicity considerably as shown in the first section. The net results confirm the fact that the epoxidation would logically prefer the adjacent double bonds of the existing epoxide group rather than the farther ones for multiple oxygen transfer as shown by the sequential oxidation processes based on **P3** and **P4**. This is also reproduced by the recent experimental observations.[3e,4,27] However, the trioxide isomer (**P4**), where oxidation occurs on one benzenoid ring of C_{60}, is an extremely attractive synthetic target if one follows an efficient epoxidation as proposed above.

Conclusions

AM1 computations were performed on a series of C_{60} epoxidations by DMD, MTMD, and BTMD to analyze the relative oxidative ability. Analysis shows that C_{60} is a LUMO (π*) epoxidant control when it reacts with DMD, and this is contradictory to the ethylene-DMD reaction. The CF_3 substitution in MTMD and BTMD drastically changes this reaction mode from inverse electron demand type to a normal through negative hyperconjugation. Therefore, their LUMO (peroxide σ* level) is considerably reduced and then can easily approach the fullerene π-HOMO to proceed to epoxidize via a "spiro" TS, as expected in the normal case. Calculated activation barriers establish the fact that BTMD is the most efficient epoxidizing agent toward C_{60}, and MTMD is relatively better than DMD. From the enthalpic considerations, the exothermicity of MTMD and BTMD reactions are almost similar, but it is higher than the DMD epoxidation. The kinetic and thermodynamic aspects of these epoxidations

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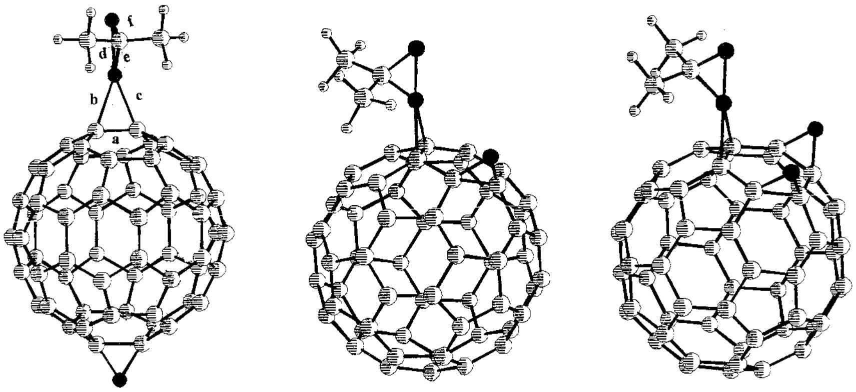

5 **6** **7**

Figure 4. The TSs (**5**−**7**) for the *sequential* tandem epoxidations and the activation and reaction energies (kcal mol^{-1}).

reaction	$\Delta E^{\ddagger}$	ΔE_r	TS	*a*	*b*	*c*	*d*	*e*	*f*
P1 + DMD	28.2	−72.2	**5**	1.413	1.969	1.969	1.821	1.466	1.346
P1 + DMD	27.3	−74.5	**6**	1.405	2.255	1.856	1.812	1.447	1.357
P3 + DMD	27.0	−72.7	**7**	1.403	1.980	1.980	1.814	1.465	1.347

are less favored than those of the prototype reaction. However, the resistance of fullerene to epoxidation is diminished by MTMD and BTMD, as the barriers are sufficiently reduced by them. Successive epoxidations predict that the adjacent bond to the existing epoxide group on C_{60} is nucleophilically more reactive than other bonds toward multiple oxide formation, and hence a progressive oxygen transfer performed on a six-membered ring of fullerene is very favorable. To conclude, an electrophilically strong oxidant can be the proper choice for the fullerene epoxidation and can also assist the multiple oxidative process.

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