Diels–Alder reaction of acenes with singlet and triplet oxygen – theoretical study of two-state reactivity†

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An interesting change in mechanism (from concerted to biradical) is described for the reaction of acenes (benzene through pentacene) with molecular oxygen (either singlet oxygen, $^1\Delta_g$-O_2, or triplet oxygen, $^3\Sigma_g^-$-O_2).

Acenes (**1**) are polycyclic aromatic hydrocarbons (PAHs) consisting of linearly fused benzene rings and are currently the subject of great interest from fundamental and applied perspectives.[1,2] Benzene, naphthalene and anthracene are among the most studied organic molecules, while pentacene has received much attention as an active semiconducting material in field-effect transistors (FETs) due to its unusually high charge-carrier mobility.[2,3] The reactivity of acenes has been studied intensively.[1,2,4,5] It is well recognized that their reactivity increases with the number of rings in the acene molecule, and that the central ring is the most reactive.[1,2,5] The reactivity of longer acenes with oxygen is a subject of intense interest in biology[6] (all classes of PAHs are known to be carcinogenic), chemistry[4,7,8] and material science.[9] The instability of pentacene toward oxidation is one of the major limitations to its practical application as an active organic semiconductor in FETs.[9]

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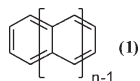
The reaction mechanism of singlet oxygen ($^1\Delta_g$-O_2) with benzene has been extensively studied theoretically.[10–13] Much less is known about the reaction of longer acenes with oxygen. A frontier molecular orbital (FMO) investigation of the reaction of acenes with $^1\Delta_g$-O_2 was published 26 years ago.[14] However, the mechanism for addition of molecular oxygen ($^1\Delta_g$-O_2 and $^3\Sigma_g^-$-O_2) to acenes was not studied until very recently. A recent report[13] on a theoretical study of the reaction of the acenes, benzene through pentacene, with $^1\Delta_g$-O_2 prompts us to communicate our results on the two-state reactivity[15] of acenes, in particular, the reactivity of anthracene and pentacene toward $^1\Delta_g$-O_2 and $^3\Sigma_g^-$-O_2. Only a concerted reaction pathway for the acenes, benzene through pentacene, was reported in the recent paper, which assumed higher activation barriers for the biradical mechanism.[13] As we will show below, this assumption does not apply to anthracene and longer acenes.

Gaussian 03[16] was used for all computations and analytical frequencies were calculated for all stationary points.[17] All energies include unscaled zero point vibrational energy corrections. Restricted B3LYP and unrestricted broken symmetry (U)B3LYP levels were used for all closed shell and open shell[18] species,

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respectively. Spin-projected energies were used throughout this paper.[19] The spin projected UB3LYP method nicely reproduces the singlet–triplet splitting for oxygen.[20] It has been shown that CASSCF and CASPT2 results are in good agreement with spin projected energies for reaction of $^1\Delta_g$-O_2.[21] All relative energies reported are *versus* ground state species of singlet acene and $^3\Sigma_g^-$-O_2 unless otherwise stated ($^1\Delta_g$-O_2 lies 20.8 kcal/mol above $^3\Sigma_g^-$-O_2 at B3LYP/6-31G*). Addition of oxygen to only the most reactive central ring of acenes is studied in this work. Density functional theory (using the B3LYP functional) has been shown to perform exceedingly well in studies of biradicals and, especially, in predicting the competition between the biradical and concerted pathways in Diels–Alder reactions.[18,19,22] B3LYP has also been successfully applied to study the reactions of $^1\Delta_g$-O_2.[23,24] In particular, the results obtained using B3LYP/6-31G* to calculate the potential energy surface (PES), geometries and energies for the reaction of molecular oxygen with conjugated systems are similar to those obtained using CASPT2.[21]

As with other Diels–Alder reactions,[19,22,25] the addition of $^1\Delta_g$-O_2 to acenes can proceed *via* one of two possible mechanisms, concerted or stepwise (Scheme 1). In this paper we report computational evidence showing that the reaction of $^3\Sigma_g^-$-O_2 with acenes leads to singlet products, and on the change in mechanism for the reaction of $^1\Delta_g$-O_2 from concerted (for benzene and naphthalene) to stepwise biradical (for pentacene). Competition between the two pathways is expected for anthracene.

In agreement with previous studies[10,11,13] we find only the concerted mechanism for the reaction of $^1\Delta_g$-O_2 with benzene and naphthalene. The anti-biradical minimum ($^1M_{anti}$) collapses to the concerted path. The reaction barriers are 48.2 and 41.7 kcal/mol (*vs.* acene and $^3\Sigma_g^-$-O_2) for the reaction of $^1\Delta_g$-O_2 with benzene[26] and naphthalene, respectively.
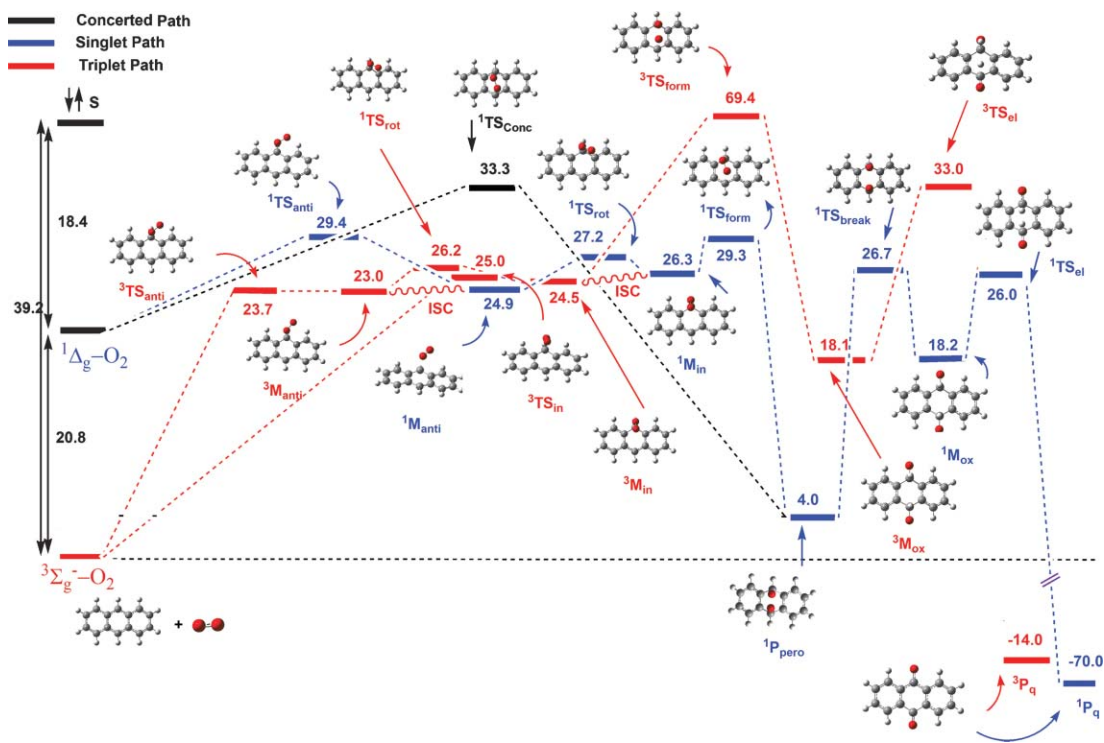
The concerted transition state ($^1TS_{conc}$) for the reaction of $^1\Delta_g$-O_2 with anthracene has been located using RB3LYP. However, in contrast to shorter acenes, the wave function for $^1TS_{conc}$ was unstable (Scheme 2). Reoptimization using UB3LYP
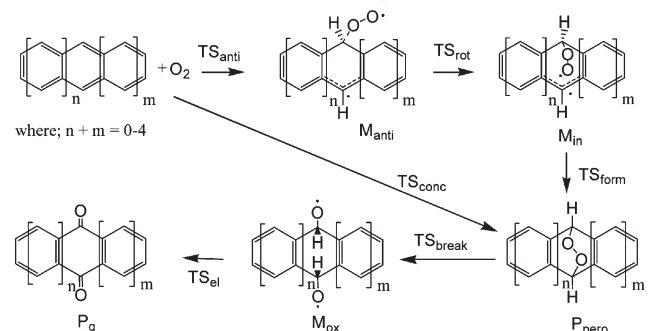
Scheme 1

Scheme 2 Calculated reaction energies (kcal/mol) for concerted and biradical pathways in the Diels–Alder reaction of anthracene with $^1\Delta_g$-O_2 and $^3\Sigma_g^-$-O_2.

leads to a concerted TS exhibiting some degree of biradical character ($E_a = 33.3$ kcal/mol, $S^2 = 0.16$). In contrast to benzene and naphthalene, the anti biradical minimum ($^1M_{anti}$) for anthracene is a minimum on the PES. The biradical mechanism for the reaction of $^1\Delta_g$-O_2 with anthracene to produce the corresponding quinone is very complex and includes four intermediates and five TSs (Scheme 2). The reaction starts from an anti-attack ($^1TS_{anti}$, $E_a = 29.4$ kcal/mol) leading to an anti-biradical minimum ($^1M_{anti}$, $\Delta E = 24.9$ kcal/mol). $^1M_{anti}$ undergoes rotation around the C–O bond (via $^1TS_{rot}$, $E_a = 27.2$ kcal/mol) which, in contrast to many [4 + 2] reactions,[19,22,25] does not collapse to the product $^1P_{pero}$, but leads to another biradical minimum ($^1M_{in}$, $\Delta E = 26.3$ kcal/mol) with $\angle$C–C–O–O of 0.04°. $^1M_{in}$ then cyclizes to give endoperoxide ($^1P_{pero}$, $\Delta E = 4.0$ kcal/mol) through a rate determining TS ($^1TS_{form}$, $E_a = 29.3$ kcal/mol) with $\angle$C–C–O–O of 19.2°. $^1TS_{form}$ is not common for symmetry-allowed Diels–Alder reactions[19,22,25] however, it resembles the TS for symmetry-forbidden [2 + 2] reactions.[27] $^1P_{pero}$ undergoes O–O bond cleavage through a TS ($^1TS_{break}$, $E_a = 26.7$ kcal/mol, O–O bond length of 1.401 Å) to a biradical intermediate ($^1M_{ox}$, $\Delta E = 18.2$ kcal/mol) that can eliminate hydrogen through a TS ($^1T_{el}$, $E_a = 26.0$ kcal/mol), resulting in formation of the quinone (^1P_q, $\Delta E = -70.0$ kcal/mol).[28] The energy difference between the concerted (33.3 kcal/mol) and the stepwise biradical (29.3 kcal/mol) pathways is relatively small, however, the stepwise biradical pathway nevertheless lies below the concerted pathway.[29] The preference of longer acenes for the biradical reaction is in line with early predictions[30] that the longer acenes will have a significant biradical contribution to their ground state and is the reason for the change in mechanism with increasing acene length.

Similarly to $^1\Delta_g$-O_2, triplet oxygen, $^3\Sigma_g^-$-O_2, can add to anthracene through an anti-attack ($^3TS_{anti}$, $E_a = 23.7$ kcal/mol)

leading to a minimum ($^3M_{anti}$, $\Delta E = 23.0$ kcal/mol). $^3M_{anti}$ then undergoes rotation via $^3TS_{rot}$ ($E_a = 26.2$ kcal/mol) to form a new minimum $^3M_{in}$ ($\Delta E = 24.5$ kcal/mol, $\angle$C–C–O–O = 0.0°). $^3\Sigma_g^-$-O_2 can also react with anthracene via $^3TS_{in}$ ($E_a = 25.0$ kcal/mol) which leads directly to $^3M_{in}$. The overall barrier for the singlet pathway to reach $^1M_{in}$ is 29.4 kcal/mol while for the triplet pathway, the barrier to reach $^3M_{in}$ is only 25.0 kcal/mol (Scheme 2). In contrast to the reaction of anthracene with $^1\Delta_g$-O_2, in the case of $^3\Sigma_g^-$-O_2 the barrier for ring closure ($^3TS_{form}$) is very high ($E_a = 69.4$ kcal/mol). Thus, to overcome such a high barrier, inter-system-crossing (ISC) should be favorable from the triplet to the singlet state in either $^3M_{anti}$ or $^3M_{in}$, which opens up the possibility that the reaction of acenes with $^3\Sigma_g^-$-O_2 may result in singlet products.[31]

We have explored two-state reactivity in the reaction of oxygen with anthracene (Scheme 2) and an overall predicted reaction mechanism proceeds either via biradical addition of $^1\Delta_g$-O_2 (which can be generated from triplet oxygen and anthracene, with the latter acting as a sensitizer) or by addition of $^3\Sigma_g^-$-O_2 followed by ISC from the triplet to the singlet state, followed by ring closure. The PESs for both singlet and triplet addition appear very similar, except for the ring closure TS ($^3TS_{form}$).

Addition of $^3\Sigma_g^-$-O_2 and $^1\Delta_g$-O_2 to pentacene proceeds similarly to the case of anthracene (Scheme 3), except that in the case of the addition of $^1\Delta_g$-O_2 to pentacene we could not locate a concerted TS ($^1TS_{conc}$), which should be a first order saddle point on the PES.[32] The overall barriers for all stationary points are roughly 10 kcal/mol lower in the case of pentacene than in the case of anthracene. The rate determining step for the addition of $^1\Delta_g$-O_2 to pentacene is $^1TS_{anti}$ with $E_a = 20.3$ kcal/mol, while for the pathway that includes ISC, the rate determining step is predicted to be $^1TS_{form}$ ($E_a = 18.0$ kcal/mol).
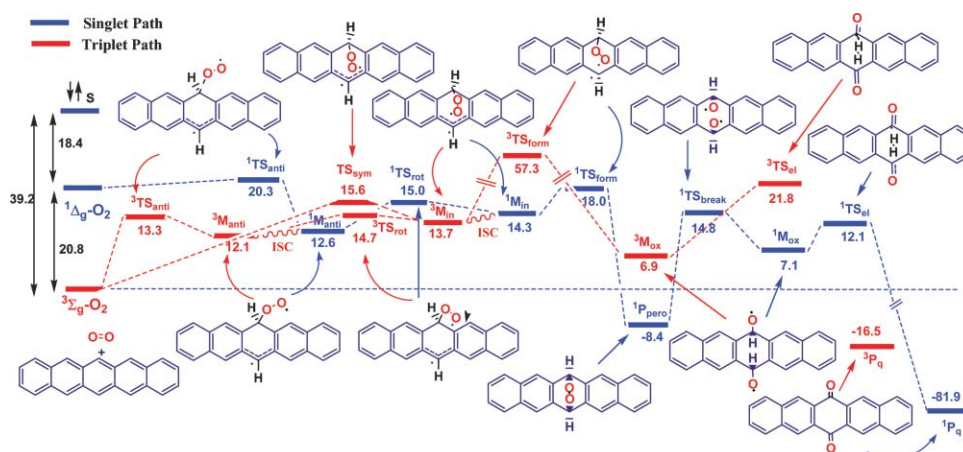
Scheme 3 Calculated reaction energies (kcal/mol) for concerted and biradical pathways in the Diels–Alder reaction of pentacene with $^1\Delta_g$-O_2 and $^3\Sigma_g^-$-O_2.

In conclusion, a detailed computational mechanistic study of two-state reactivity for the addition of oxygen to acenes has been performed. As expected, the energy barrier decreases with increasing number of linearly fused aromatic rings. Both $^3\Sigma_g^-$-O_2 and $^1\Delta_g$-O_2 can react with acenes resulting in singlet reaction products. We have found that, starting from anthracene, acenes react with oxygen *via* a biradical stepwise mechanism, in contrast to the recent report,[13] which suggests that only the concerted pathway is feasible.[33] The lowest energetic barriers predicted for the reaction of benzene, anthracene and pentacene with $^1\Delta_g$-O_2 are about 48, 29 and 20 kcal/mol, respectively (the barriers are *vs.* ground state species). The energy barrier for triplet peroxide formation ($^3TS_{form}$) is very high. Therefore, it is expected that ISC from triplet PES to singlet PES could occur.

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31 $^3TS_{anti}$ is lying 5.7 kcal/mol below its singlet analogue ($^1TS_{anti}$) while both minima ($^1M_{anti}$ and $^3M_{anti}$) possess similar energies and geometries (Scheme 2). Likewise, $^1M_{in}$ and $^3M_{in}$ are energetically and geometrically similar.
32 Chien *et al.*[13] have located such a TS only at the HF level, however failed to locate it at higher theoretical levels, which supports our conclusion that this TS is an artefact of the HF level.
33 In ref. 13, the concerted mechanism was checked using the MSSCF method only for naphthalene. Our DFT calculations also predict a concerted reaction mechanism for naphthalene with $^1\Delta_g$-O_2.