

Remote substituent effects on the photooxygenation of 9,10-diarylanthracenes: strong evidence for polar intermediates†

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Two different reaction pathways in the photooxygenation of 9,10-diarylanthracenes are identified, with strong evidence for polar (forward, singlet oxygen addition) and radical (backward, thermolysis) intermediates.

Anthracenes are important aromatic compounds,¹ which react with singlet oxygen (¹O₂) to form the corresponding endoperoxides.² For 9,10-diphenylanthracene (**1a**), the addition is fully reversible and the parent anthracene is regenerated by the release of oxygen, to a certain extent in the excited state.^{2,3} The reversibility of the reaction enabled applications of anthracenes as part of photochromic systems,⁴ as photoresists⁵ and carriers of singlet oxygen.⁶

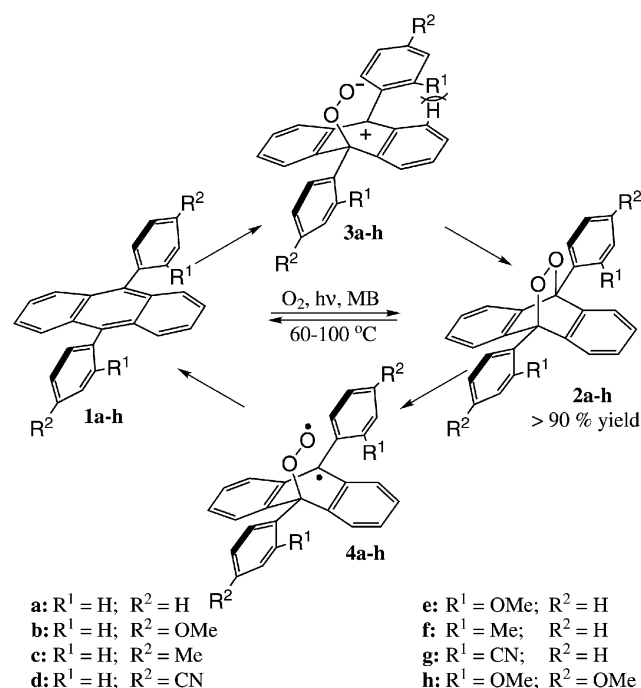
The mechanism of the addition of ¹O₂ to polyacenes is still a subject of intensive theoretical and experimental research.⁷ In principle both a concerted pathway *via* the formation of exciplexes and a stepwise process are evident.⁸ Recent calculations based on the UB3LYP method indicated that biradical intermediates were formed by the photooxygenation of anthracenes.⁹ However, a stepwise mechanism characterized by polar or zwitterionic intermediates has not been considered for the reaction of polyacenes. We observed rotations around the aryl–aryl bond during the photooxygenation of *ortho* substituted 9,10-diarylanthracenes for the first time, which resulted in an efficient molecular switch between *cis* and *trans* isomers.¹⁰ This process required a planarization of the biaryl moiety in the transition state or intermediates, but no mechanistic rationale could be provided. To elucidate the reaction mechanism, we synthesized eight different 9,10-diarylanthracenes, **1**, by Suzuki coupling from commercially available starting materials in only one step.¹¹ Thus, the electronic nature of the two appending benzene rings could be altered by the substitution pattern. The photooxygenation afforded the corresponding endoperoxides, **2**, in high yields. Remote substituent effects on the reactivity give strong evidence for zwitterionic intermediates, **3**, during the reaction with singlet oxygen (Scheme 1).

First, the ground state geometries of the anthracenes **1a–h** were compared by UV-vis spectroscopy (Table 1). Assuming a coplanar alignment of the arene rings, the acceptor and donor

groups should shift the absorption bands. However, for all systems almost same UV-vis spectra were obtained, which indicates the orthogonal orientation of the benzene rings in the ground state. These observations are also in accordance with X-ray analyses.^{†11,12} In contrast, remote effects should be operative for the photoionized radical cations, supported by strong spectral shifts in the transient absorption spectra and their trapping with nucleophilic solvents.¹³

To prove the coplanar alignment of the anthracenes **1a–h** in the radical cations, we determined the redox potentials by cyclic voltammetry (Table 1). Indeed, the oxidation potentials vary strongly with the electronic nature of the substituents and the electron-withdrawing cyano group (**1d,g**) shifts the potential by about 200 mV compared to the methoxy group (**1b,e**). The different propensities to form the radical cations should also be reflected in the reactivity of the anthracenes with ¹O₂, but only if a zwitterionic intermediate, **3**, and not a radical, **4**, would be formed.

Therefore, anthracenes **1a–h** were photooxygenated to the corresponding endoperoxides **2a–h** by irradiation in the presence



Scheme 1 Reaction of the diarylanthracenes, **1**, with singlet oxygen to form the endoperoxides, **2**, *via* zwitterions, **3**, and reversible thermolysis *via* biradicals, **4**.

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Table 1 Spectroscopic and voltammetric data of anthracenes **1a–h** and their rate constants with singlet oxygen

Anthracene	$\lambda_{\text{max}}/\text{nm}$	E_{Ox}/V^a	$E_{\text{Red}}/\text{V}^a$	$k_d/10^6 \text{ M}^{-1} \text{ s}^{-1}$
1a	357, 376, 396	1.29	1.21	3.0 ± 0.15
1b	359, 377, 398	1.19 (1.4) ^b	1.11	5.44 ± 0.26
1c	357, 376, 397	1.26	1.15	4.1 ± 0.15
1d	356, 375, 395	1.45	1.36	0.74 ± 0.03
1e	357, 376, 396	1.25	1.18	2.09 ± 0.1
1f	357, 375, 396	1.32	1.24	0.46 ± 0.02
1g	355, 373, 394	1.55	1.45	0.11 ± 0.01
1h	357, 376, 396	1.10 (1.41) ^b	1.04	3.69 ± 0.16

^a In dichloromethane vs. standard calomel electrode at 100 mV s⁻¹, supporting electrolyte was Bu₄NClO₄ (0.1 M), measured vs. ferrocene oxidation ($E_a = 0.51 \text{ V}$ vs. SCE). ^b The value in parentheses gives the potential of the second oxidation peak.

of methylene blue (MB, Scheme 1) and their bimolecular rate constants (k_d) were determined spectroscopically (Table 1).^{11,14}

Indeed, the reactivity of the 9,10-diarylanthracenes **1a–d** with ¹O₂ strongly depends on the substituent in the *para* position. Thus, the rate constant increases, when switching from the electron-withdrawing cyano group to the electron-donating methoxy group, nicely correlating with the oxidation potentials (Table 1). A simple electron transfer mechanism in the first step, resulting in the formation of a superoxide radical anion as the sole reactive oxygen species, was disproved by quenching experiments using DABCO as singlet oxygen trap.¹⁵ Therefore, substituents affect exclusively the intermediate peroxy adduct electronically. Such a remote substituent effect was hitherto unknown and gives strong evidence for zwitterionic intermediates **3** with a coplanar alignment of the benzene moiety (Scheme 1). A radical intermediate **4**, which was previously postulated by theoretical studies,^{8,9} is therefore unlikely, since donor and acceptor groups stabilize radicals in a similar way.¹⁶

Interestingly, the *ortho* substituted 9,10-diarylanthracenes **1e–h** exhibit similar remote substituent effects as the *para* isomers **1b–d** (Table 1). Thus, the electron-withdrawing cyano group (**1g**) reduces the rate of the photooxygenation by a factor of 20 compared to the methoxy derivative **1e**. This remarkable result can again only be rationalized by polar intermediates **3** and a coplanar alignment of the aryl ring with the sp² hybridized carbenium ion, despite the unfavourable steric interaction with *peri* hydrogen atoms in the 1 position (Scheme 1). Indeed, the rotation barrier around the aryl–aryl bond of anthracene **1f** in the ground state was determined to

be 120 kJ mol⁻¹,¹⁷ but the high energy brought by oxygen in the excited state seems to overpower this barrier in a polar intermediate. Additionally, this result explains the function of the anthracenes **1e–h** as molecular switches.¹⁰ The lower reactivity of *ortho* (**1e–h**) compared to *para* (**1b–d**) substituents indicates that steric interactions are indeed operative, since the coplanar alignment is more difficult to achieve. Finally, the reactivities of the 9,10-diarylanthracenes **1e–h** with ¹O₂ again nicely correlate with their oxidation potentials (Table 1), which gives further evidence for zwitterions **3e–h**, even for *ortho* substituted systems.

To investigate the remote effects on the reverse reaction, we thermolyzed the endoperoxides **2a–h** at temperatures ranging from 60–110 °C, and obtained thermodynamic data from Arrhenius and Eyring plots.¹¹ The parent anthracenes **1a–h** were reisolated quantitatively and singlet oxygen yields were determined by trapping with tetracyclone (Table 2). The positive activation entropies and low yields of ¹O₂ affirm a strong participation of a stepwise pathway, which is in accordance to studies of Turro *et al.* for the cycloreversion of unsubstituted 9,10-diphenylanthracene (**1a**).³

Interestingly, *ortho* substituted systems react faster than the *para* derivatives (Fig. 1, Table 2). Steric and not electronic factors may play the dominant role, since the concave geometry of the endoperoxides **2** confines the space near the *ortho* substituents. On the other hand, the electronic nature of a substituent in the *para* position, in definite contrast to the addition of singlet oxygen, plays no role for the reactivity of endoperoxides **2a–d**, which is demonstrated by almost identical rates of thermolysis of the endoperoxides **2a–d** (Fig. 1, Table 2). Electronic effects are therefore not present in the family of *para* substituted endoperoxides. Consequently, cycloreversion proceeds *via* a different pathway as the cycloaddition and the principle of microreversibility is not fulfilled.³

The fact that *para* substituents have no influence on the rate of the thermolysis of endoperoxides **2a–d** can be best rationalized by radical intermediates **4** (Scheme 1). Zwitterions **3** would be more stabilized by a methoxy group (**2b**), which is not the case. On the other hand, radicals are stabilized by electron donors as well as acceptors,¹⁶ and we found clear evidence for such intermediates during the thermolysis of endoperoxides.

In conclusion, the cycloreversion is strongly facilitated by introduction of substituents in *ortho* position and the kinetic data point at a rather non-concerted mechanism *via* radical intermediates. Although such intermediates were postulated

Table 2 Activation parameters and singlet oxygen yields from the thermolysis of the endoperoxides **2a–h**

Peroxide	$T_{1/2}^b/\text{min}$	$\Delta E_A/\text{kJ mol}^{-1}$	$\log A$	$\Delta H_A/\text{kJ mol}^{-1}$	$\Delta S_A/\text{J K}^{-1} \text{ mol}^{-1}$	Yield ¹ O ₂ (%)
2a ^a	121 ± 2	132 ± 2	14.4 ± 0.3	129 ± 2	$+21 \pm 4$	32
2b	88 ± 1	127 ± 3	13.9 ± 0.4	124 ± 3	$+12 \pm 8$	25
2c	119 ± 2	127 ± 6	13.8 ± 1.0	124 ± 4	$+9 \pm 8$	34
2d	78 ± 1	134 ± 6	15.0 ± 0.9	131 ± 2	$+33 \pm 4$	46
2e	21 ± 1	117 ± 1	13.2 ± 0.1	114 ± 2	-1 ± 5	23
2f	1 ± 0.5	108 ± 2	13.4 ± 0.4	105 ± 2	$+4 \pm 1$	28
2g	3 ± 1	115 ± 2	13.8 ± 0.4	113 ± 1	$+14 \pm 4$	35
2h	23 ± 1	117 ± 1	13.1 ± 0.1	114 ± 2	-2 ± 5	31

^a Literature data as reported in ref. 3. ^b At 373 K in xylene.

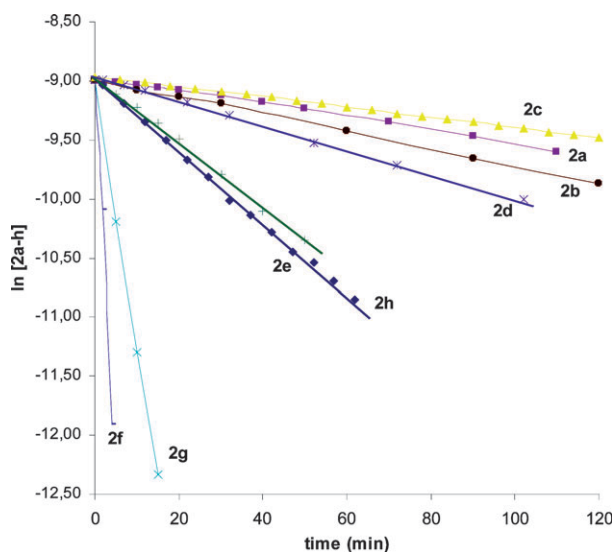


Fig. 1 Thermolyses of the endoperoxides **2a–h** at 100 °C.

for the thermolysis of endoperoxides previously,³ we found new sterical remote effects on the thermolysis of anthracene endoperoxides. Thus, the diarylanthracenes **1a–h** represent interesting mechanistic probes, which allow to distinguish between two different reaction pathways in the oxidation and cleavage step.

The reaction of $^1\text{O}_2$ with the methyl derivative **1f** merits special attention since, compared to the other anthracenes, subsequent singlet oxygen addition and thermolysis are fastest. It is therefore an interesting candidate for a photochromic system with tolerable fast write and excellent fast erasing characteristics.⁵

In summary, we have shown that the reactivity of 9,10-diarylanthracenes towards singlet oxygen and the rate of cycloreversion of the corresponding endoperoxides is strongly controlled by stereoelectronic remote substituent effects. The results support zwitterionic intermediates in a stepwise addition of singlet oxygen and biradical intermediates for the thermolysis. This change in the pathways of singlet oxygen reactions was hitherto unknown and should be of interest for future mechanistic discussions. Finally, the anthracenes are easily accessible and mark important examples of photochromic materials, whose performance can be tuned by a targeted choice of the substitution pattern.

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