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Linear free energy relationship analysis of solvent effect on singlet oxygen reactions with mono and disubstituted anthracene derivatives

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ABSTRACT

Detection of $O_2(^1\Delta_g)$ emission, λ_{max} = 1270 nm, following laser excitation and steady-state methods were employed to measure the total reaction rate constant, k_T, and the reactive reaction rate constant, k_R, for the reaction between singlet oxygen and seven mono and disubstituted anthracenes. In most solvents, the rate constants for the quenching of singlet oxygen by monosubstituted anthracenes are in the order of 10^6 M^{-1} s^{-1}, whereas for the disubstituted compounds the values are in the order of 10^7 M^{-1} s^{-1} indicating that both, mono and disubstituted anthracenes are good quenchers of singlet oxygen. The reactive rate constants were very close to the total rate constants, implying that quenching is essentially a chemical process. The analysis of solvent effect on k_T and k_R by using LSER equations indicates that singlet oxygen deactivation by the anthracene derivatives is accelerated by solvents with large values of both, dipolarity/polarizability and Hildebrand solvent parameters, being inhibited by hydrogen bond donor solvents in some cases. Solvent effect analysis support the formation of a loose, zwitterionic like exciplex for 9-methylanthracene and 9-methoxyanthracene, a loose exciplex with partial charge separation for di-substitutes anthracene and a compact exciplex with partial charge separation for anthracene and 9-phenylanthracene.

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1. Introduction

Oxygen acts as an universal quencher, capable of accepting the energy in excess from a electronically excited molecule transforming into a highly reactive species, singlet molecular oxygen, $O_2(^1\Delta_g)$, which can react physically and chemically with molecules of various classes. Among the substrates whose reactions with $O_2(^1\Delta_g)$ have been extensively studied anthracene derivatives are included [1]. Almost all these aromatic compound react with singlet molecular oxygen mainly through the chemical way to produce the corresponding endoperoxide. Thermal activation of the endoperoxide reverts the reaction to regenerate the parent anthracene and release oxygen in both, the ground and the excited state [2,3]. The reversibility of the anthracene derivatives oxidation by $O_2(^1\Delta_g)$ make possible the employ of these compounds as singlet oxygen carrier in synthesis [4], as photoresists [5–7] and in photochromic systems [8].

The mechanism of the addition of $O_2(^1\Delta_g)$ to aromatic compounds has been studied extensively employing theoretical and experimental methods [9]. From these studies, both a concerted pathway via the formation of an exciplex and a stepwise process have been proposed [10,11]. More recently, calculations based on the B3LYP method [12] suggest that biradical intermediates can be formed by the photooxygenation of anthracenes, but no experimental evidence supporting this proposition has been reported. On the contrary, Fudickar and Linker [13] in a recent study of remote substituent effects on the photooxygenation of 9,10-diarylanthracenes provide strong evidence for the formation of zwitterionic intermediates in a stepwise addition of singlet oxygen to the anthracene derivatives.

The reactivity of aromatic hydrocarbons towards $O_2(^1\Delta_g)$ depends on the aromatic ring (structural and steric effects) and on the media (solvent effect). Regarding the structural effects, has been shown that the reactivity of aromatic hydrocarbons toward $O_2(^1\Delta_g)$ increases with the electron density of the aromatic, due to the singlet molecular oxygen electrophilic character. Consequently, the reactivity increases with the number of fused aromatic rings in lineal systems and with π-relocalization energy in bent aromatic systems [14]. Also, the reactivity increases when electron-donor groups are present [13]. The reactivity of aromatic derivatives towards $O_2(^1\Delta_g)$ and the regioselectivity of the addition are also dependent on steric factors. Thus, the larger reactivity of 1,8-dimethylnaphthalene in comparison to the 1,4-isomer is explained in terms of the non-bonded *peri* interaction between the methyl substituents in the former molecule [15]. The steric tension resultant from this interaction is partially removed in the transition state generated by addition of singlet molecular oxygen to 1,8-disubstituted naphthalene. The same considerations were

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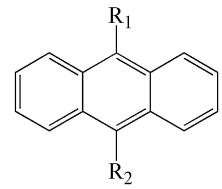
employed by Wasserman et al. [16] to explain the increased stability of 1,8-dimethylnaphthalene-1,4-endoperoxide when compared with the 1,4-disubstituted analogue. The bond rehybridization at C1 and C4 (sp^2 to sp^3) resulting from the formation of the endoperoxide should significantly reduce the *peri* methyl–methyl interaction in the endoperoxide compared to the parent naphthalene.

On the other hand, media effect on singlet oxygen reaction with aromatic polycyclic derivatives has been previously revised. Early reports indicate only a small solvent dependence in the reaction rate for several aromatic compounds (anthracene, rubrene and 9,10-dimethylanthracene) [17,18]. However, in these studies, the lack of solvent effect comes from the fact that data were restricted to a narrow set of solvents, which did not include highly dipolar solvents. Data of Rubio et al. [19], on the bleaching of anthracene derivatives show that singlet oxygen quenching is extremely fast in formamide and other polar solvents, such as ethylene glycol. Later, a more comprehensive study of solvent effect on these reactions was performed by Aubry et al. [20], employing 1,4-dimethylnaphthalene as substrate. These data show the effect of the reaction media on the rate constant value, increasing by more than two orders of magnitude from cyclohexane to formamide. Results analyzed employing lineal solvation energy relationship of Abraham et al. [21–23], indicate that both the polarizability/dipolarity and the cohesive energy of the solvent play an important role in [2 + 4] singlet oxygen cycloadditions. The dependence on π^* is compatible with a partial charge transfer exciplex formation, which is also supported by a lower activation barrier. The dependence on the Hildebrand parameter suggests the formation of a compact exciplex, with the release of free solvent molecules, and a partially concerted character for this reaction. The synchronic or asynchronic collapse of the exciplex leads to the [2 + 4] cycloadduct. However, we also found that the reaction rate increases in HBD solvents and decreases in HBA solvents [24]. Dependence of k_T on the α parameter, can be interpreted in terms of stabilizing interactions between the HBD solvent and the negative charge density on the oxygen in the exciplex. No stabilizing interactions between the exciplex and HBA solvents could be expected, due to the presence of the π electronic system, able to delocalize the positive charge over the whole aromatic ring. Solvents with high β values could broke stabilizing interactions with the negative charge on the exciplex, leading to a decrease of the reaction rate constant. Furthermore, we found that theoretical linear solvation energy relationship analysis of data for the naphthalene–singlet oxygen reaction did not yield acceptable statigraphs. Within these limits, the process takes place with a negative activation volume, in accord with LSER results, and the stabilizing effect of HBD solvents on the exciplex involves mainly electrostatic interactions. On the other hand, data of Venedictov and Tulikova [25] suggest the presence of an exciplex with a high degree of charge transfer as a key intermediate in the [4 + 2]-cycloaddition of $^1O_2$ to tetracene. However, this result cannot be analyzed in terms of LSER equations due to the few solvents employed. Collected literature rate constants reported for other naphthalene and anthracene derivatives (mainly obtained from Wilkinson compilation [26]), analyzed by us in terms of LSER equations, did not give statistically acceptable correlations, probably due to the inhomogeneity of data measured in different laboratories. Extensive discussions in the literature demonstrate that solvent effect analyses performed in terms of linear solvation energy relationships are a powerful tool for interpreting singlet oxygen reaction mechanisms [24]. These treatments allow a quantitative evaluation of solvent effect in terms of different descriptors. The relative contribution of each descriptor included in the correlation equation depends on the type of substrate although common features are observed for compounds belonging to the same family reacting through the same mechanism. Then, the determination of the correlation equation for a model compound allows one to calibrate and validate the linear free energy relationship in a given solvent set, providing a sound basis for predictions regarding the behavior of the system in other solvents.



	A	MA	MTHA	PHA	DMA	DMTHA	DPHA
R_1	H	Me	MeO	Ph	Me	MeO	Ph
R_2	H	H	H	H	Me	MeO	Ph

Fig. 1. Structure of anthracene derivatives: A, anthracene; MA, 9-methylanthracene; MTHA, 9-methoxyanthracene; PHA, 9-phenylanthracene; DMA = 9,10-dimethylanthracene; DMTHA, 9,10-dimethoxyanthracene; DPHA, 9,10-diphenylanthracene.

In this work we report a deep study of the solvent effect on the reaction of singlet molecular oxygen with mono and disubstituted anthracene derivatives (Fig. 1). Our aim is to account for the change in the reactivity of mono and disubstituted anthracenes towards singlet molecular oxygen, to determine eventual differences in the substituent effect on the reaction rate when solvent is changed from non-polar to polar ones, and finally to predict the nature of the critical transients formed along the reaction coordinate.

2. Experimental

All solvents used in spectroscopic and kinetic measurements were spectroscopic or HPLC quality, and were purified by the usual procedures when necessary. Anthracene (A), 9-phenylanthracene (PHA), 9-methylanthracene (MA), 9-methoxyanthracene (MTHA), 9,10-diphenylanthracene (DPHA), 9,10-dimethylanthracene (DMA), 9,10-dimethoxyanthracene (DMTHA), 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP), and 1,3-diphenylisobenzofuran (DPBF) were used without further purification. Rose Bengal (RB) was recrystallized twice from ethanol and 2,5-dimethylfuran (DMF) was distilled under reduced pressure prior to use. UV–vis absorption spectra and steady-state kinetic experiments were performed in a Unicam UV-4 spectrophotometer. Chemical reaction rate constants were determined in different solvents by measuring the anthracene derivative consumption. Irradiation was performed in 1 cm path UV–vis cell, fitted in a cell holder equipped with a filter support that allows irradiation with light of a selected wavelength by using a Shott cut-off filter. The cell holder was thermostated by circulating water at 22 ± 0.5 °C. TPP or RB was employed as sensitizers. Illumination was performed with a visible, 200 W, or a halogen, 50 W, lamp. The distance between the light source and the cell was set for each experiment so that the initial substrate concentration diminish about 50% in 15 min. 1,3-Diphenylisobenzofuran was typically employed to evaluate the steady-state concentration of $O_2(^1\Delta_g)$. DPBF solutions were daily prepared in a dark room and an appropriate cut-off filter was used in these experiments, its auto-oxidation measured using UV–vis spectrophotometry, was lower than 1% under our experimental conditions. In some experiments, 9,10-dimethylanthracene or 2,5-dimethylfuran were employed to evaluate the $O_2(^1\Delta_g)$ steady-state concentration [27]. Consumption of DMF was followed by observing its decrease by gas chromatography employing a Hewlett Packard gas chromatograph equipped with a FID detector and a Hewlett Packard Ultra-2 capillary column. Time-resolved luminescence measurements were carried out in 1 cm path fluorescence cells. TPP or RB was excited by the second harmonic (532 nm, nominal power 9 mJ per pulse) of a 6-ns light pulse of a Q-Switched Nd:YAG laser. A liquid

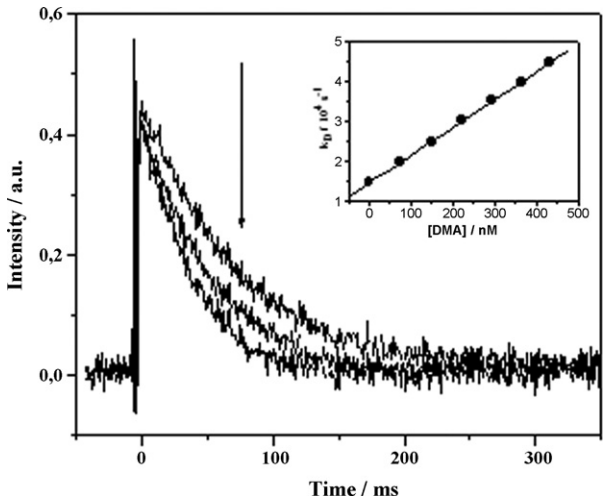


Fig. 2. Singlet oxygen phosphorescence decay at 1270 nm, following Nd:YAG laser excitation at 532 nm. Arrow indicates increasing DMA concentration. Inset: Stern–Volmer plot for deactivation of singlet oxygen by DMA in acetonitrile.

nitrogen cooled germanium photodiode detector with a built-in preamplifier was used to detect infrared radiation from the cell. The detector was set at a right-angle to the cell. An interference filter (1270 nm) and a cut-off filter (995 nm) were the only elements between the cell face and the diode cover plate. The preamplifier output was fed into the 1 MΩ input of a digitizing oscilloscope. Computerized experiment control, data acquisition, and analysis were performed with a LabView-based software developed in our laboratory. Geometry optimizations, energy evaluations, and Fukui function calculations were carried out with Gaussian 03W, Revision B.03 package using the DTF formalism with the basis set B3LYP-6311g [28].

3. Results and discussion

3.1. Total quenching rate constant

The values of total (physical and chemical) quenching rate constant, k_T, for the reaction of $O_2(^1\Delta_g)$ with the anthracene derivatives in several solvents were obtained from the experimentally measured first-order decay of $O_2(^1\Delta_g)$ in absence (τ_o^{-1}) and in presence of the anthracene (τ^{-1}) according to

$$\tau^{-1} = \tau_o^{-1} + k_T\,[\text{anthracene}] \quad (1)$$

Fig. 2 shows a typical Stern–Volmer plot obtained for DMA in acetonitrile. The triplet decay of the sensitizer (TPP or Rose Bengal) was not affected by the presence of the anthracene derivatives even at concentrations higher than those used to quench the excited oxygen. Linear plots of τ^{-1} versus anthracene concentration were obtained in all the solvents employed. The intercept of these plots corresponds to the singlet oxygen lifetime in the employed solvent. In all experiments, these values match very nearly with singlet oxygen lifetimes determined independently in a large set of experiments performed in our laboratory during past few years. The k_T values calculated from the slope of these plots are given in Tables 1 and 2. Possible rapid chemical changes of samples during illumination, or interference of the $O_2(^1\Delta_g)$ luminescence with the scattered laser light and the tail end of the sensitizer fluorescence [29] can be disregarded since the rate constants measured in some solvents by using competitive steady-state methods (data

Table 2
Values of total rate constant, k_T, for reactions of disubstituted anthracene derivatives with $O_2(^1\Delta_g)$ in different solvents obtained from time-resolved methods.

Solvent	k_T ($\times 10^6$ M^{-1} s^{-1})		
	DPHA	DMA	DMTHA
Ethyl acetate	1.48 ± 0.04	26.52 ± 0.31	17.39 ± 0.51
Acetone	2.36 ± 0.05	35.17 ± 0.79	18.28 ± 0.66
Acetonitrile	4.06 ± 0.13	68.63 ± 1.03	30.37 ± 0.24
Benzyl alcohol	4.38 ± 0.11	64.35 ± 0.99	31.84 ± 0.29
Benzene	1.11 ± 0.02	30.98 ± 0.20	15.71 ± 0.26
1-Butanol	2.64 ± 0.24	19.65 ± 0.35	10.84 ± 0.13
Butyl ether	0.75 ± 0.01	13.01 ± 0.22	9.00 ± 0.10
Chloroform	1.41 ± 0.05	27.01 ± 0.64	11.30 ± 0.39
Methylene chloride	2.80 ± 0.05	41.71 ± 0.40	28.37 ± 0.78
Dimethylacetamide	4.80 ± 0.09	71.31 ± 1.39	41.41 ± 1.01
N,N-Dimethylformamide	5.83 ± 0.10	85.25 ± 1.52	45.72 ± 0.50
Dioxane	1.87 ± 0.10	47.30 ± 0.97	25.54 ± 0.50
Ethanol	–	27.42 ± 0.39	12.72 ± 0.17
n-Heptane	–	7.55 ± 0.12	5.10 ± 0.05
n-Hexane	–	7.65 ± 0.09	5.32 ± 0.09
Methanol	–	43.03 ± 0.70	17.02 ± 0.25
1-Pentanol	1.85 ± 0.07	16.43 ± 0.33	8.32 ± 0.20
Propylencarbonate	6.06 ± 0.31	127.05 ± 1.32	51.57 ± 0.79
Tetrahydrofuran	1.28 ± 0.03	24.33 ± 0.37	18.55 ± 0.40
Trifluoroethanol	–	20.53 ± 0.93	7.80 ± 0.17

Table 1
Values of total rate constant, k_T, for reactions of monosubstituted anthracene derivatives with $O_2(^1\Delta_g)$ in different solvents obtained from time-resolved methods.

Solvent	k_T ($\times 10^6$ M^{-1} s^{-1})			
	A	PHA	MA	MTHA
Ethyl acetate	0.21 ± 0.01	0.39 ± 0.01	3.40 ± 0.06	3.17 ± 0.44
Acetone	0.38 ± 0.01	0.82 ± 0.01	5.50 ± 0.09	4.19 ± 0.10
Acetonitrile	0.94 ± 0.02	2.26 ± 0.03	12.40 ± 0.08	7.81 ± 0.11
Benzyl alcohol	1.22 ± 0.05	3.16 ± 0.11	12.40 ± 0.18	11.51 ± 0.24
Benzene	0.23 ± 0.01	0.40 ± 0.01	3.05 ± 0.04	3.51 ± 0.03
1-Butanol	–	0.95 ± 0.01	2.12 ± 0.03	1.81 ± 0.05
Butyl ether	–	0.20 ± 0.01	1.40 ± 0.02	1.15 ± 0.02
Chloroform	0.24 ± 0.01	0.76 ± 0.02	3.01 ± 0.11	3.01 ± 0.11
Methylene chloride	0.44 ± 0.01	1.26 ± 0.03	6.96 ± 0.12	5.73 ± 0.12
Dimethylacetamide	0.87 ± 0.01	2.31 ± 0.02	13.21 ± 0.12	13.06 ± 0.21
N,N-Dimethylformamide	0.95 ± 0.01	2.69 ± 0.03	17.61 ± 0.33	10.55 ± 0.19
Dioxane	0.27 ± 0.01	0.86 ± 0.02	6.31 ± 0.09	5.08 ± 0.05
Ethanol	–	1.93 ± 0.05	2.64 ± 0.06	1.95 ± 0.03
n-Heptane	–	0.10 ± 0.01	0.45 ± 0.01	0.41 ± 0.02
n-Hexane	–	0.11 ± 0.01	0.37 ± 0.01	0.50 ± 0.01
Methanol	–	7.03 ± 0.15	6.73 ± 0.14	3.35 ± 0.07
1-Pentanol	–	1.00 ± 0.04	1.80 ± 0.04	1.16 ± 0.08
Propylencarbonate	1.77 ± 0.03	5.26 ± 0.06	21.79 ± 0.68	13.87 ± 0.20
Tetrahydrofuran	0.26 ± 0.01	0.47 ± 0.02	3.01 ± 0.03	2.78 ± 0.04
Trifluoroethanol	–	–	2.54 ± 0.09	1.65 ± 0.06

Table 3
LSER correlation equations for the reaction of singlet oxygen with monosubstituted anthracene derivatives.

$\log k_T^O = \log k_0 + s\pi^* + d\delta + a\alpha + b\beta + h\rho_H^2$

	$\log k_0$	s	d	a	b	h
A						
Coeff.	4.315	0.832	–	–	–	0.007
±	0.077	0.156	–	–	–	0.001
t-stat.	55.724	5.329	–	–	–	9.244
P(2-tail)	<0.0001	0.0005	–	–	–	<0.0001
VIF	–	2.22	–	–	–	2.22
	N = 12, R = 0.989, SD = 0.053, F = 207.712					
PHA						
Coeff.	4.596	0.748	–	–	–	0.008
±	0.058	0.087	–	–	–	0.001
t-stat.	79.184	8.601	–	–	–	14.458
P(2-tail)	<0.0001	<0.0001	–	–	–	<0.0001
VIF	–	1.51	–	–	–	1.51
	N = 19, R = 0.988, SD = 0.086, F = 324.210					
MA						
Coeff.	5.433	1.210	–	−0.429	–	0.005
±	0.056	0.085	–	0.051	–	0.001
t-stat.	96.242	14.163	–	−8.356	–	7.595
P(2-tail)	<0.0001	<0.0001	–	<0.0001	–	<0.0001
VIF	–	1.70	–	1.60	–	2.42
	N = 20, R = 0.988, SD = 0.080, F = 221.705					
MTHA						
Coeff.	5.551	1.247	–	−0.435	–	0.003
±	0.051	0.077	–	0.046	–	0.001
t-stat.	109.549	16.252	–	−9.449	–	5.190
P(2-tail)	<0.0001	<0.0001	–	<0.0001	–	<0.0001
VIF	–	1.70	–	1.60	–	2.42
	N = 20, R = 0.989 SD = 0.072 F = 230.681					

not included) afforded the same values than those obtained by time-resolved methods. As linear plots were obtained over a wide range of the anthracene derivatives concentrations in competitive steady-state experiments, the possible excited sensitizer quenching by anthracenes can be ignored.

Table 1 shows that the rate constants for the quenching of singlet oxygen by monosubstituted anthracenes are in the order of $10^6\,M^{-1}\,s^{-1}$ in most solvents, whereas for the disubstituted compounds (Table 2) the values are in the order of $10^7\,M^{-1}\,s^{-1}$ indicating that both, mono and disubstituted anthracenes are good quenchers of singlet oxygen. The lower k_T values, as expected, were observed for anthracene. Also, for this compound we were able to measure k_T in only 12 solvents, due to the low solubility of anthracene. In addition, the k_T values for all compounds were solvent-dependent, increasing when the solvent is changed from non-polar to polar ones. The largest change was observed for the methyl and dimethyl derivatives.

3.1.1. Solvent effect analysis for monosubstituted anthracenes

The increase in the k_T values in polar solvents can be related to the formation of a charge transfer exciplex, consequence of the presence of specific solute–solvent interactions. In this case, in order to understand the effect of solvent on the singlet oxygen–anthracene interaction is convenient to perform multilinear correlations of the logarithm of total rate constant with solvent microscopic parameters, by using linear solvent free energy relationships (LSER). Then, we analyzed the quenching rate constant dependence on the microscopic solvent properties employing the equation of Abraham et al. [21–23] (Eq. (2)):

$$\log k = \log k_0 + s\pi^* + d\delta + a\alpha + b\beta + h\rho_H^2 \quad (2)$$

where π^* accounts for dipolarities and polarizabilities of solvents [23,30], δ parameter is a correction term for polarizability, α is related to the hydrogen bond donor solvent ability, β indicates the solvent capacity as hydrogen bond acceptor, and ρ_H^2, the square of Hildebrand parameter, that accounts for the solvent cohesive energy density, and models the cavity effects [30]. Table 3 gives the coefficients of Eq. (2) obtained by multilinear correlation.

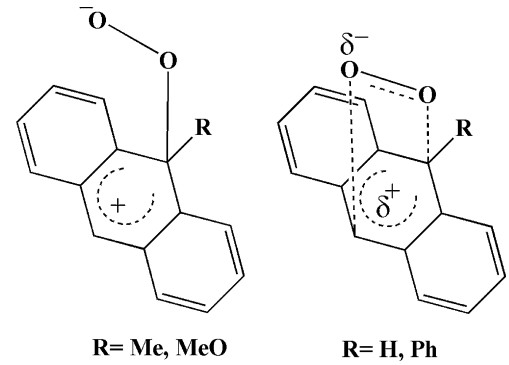


Fig. 3. Exciplex structure for reaction of singlet molecular oxygen with monosubstituted anthracenes.

Reported correlation equations result from purely statistical criteria. The overall correlation equation quality is indicated by the sample size, N, the product correlation coefficient, R, the standard deviation, SD, and the Fisher index of equation reliability, F. The consistency of each term is indicated by the standard error, ±, the 2-tail probability, P(2-tail), and the t-statistic. Good quality is indicated by higher F and t-stat values and smaller SD ones.

Results show that not all the descriptors are significant, they were accepted in the correlation equation when having a significance level ≥0.95. For these reasons, parameters δ and β were excluded from LSER equations. According to the coefficients included in Table 3, not all the compounds studied have the same solvent dependence. The values of k_T depend largely on the parameters π^* and ρ_H^2 increasing in solvents with larger capacities to stabilize charges and dipoles, and with high cohesive energy values. Also, for MA, and MTHA, k_T diminishes in solvents with larger α values.

Dependence of k_T on the microscopic solvent parameters is compatible with a concerted or partially concerted addition mechanism involving a charge transfer exciplex. Given that statistical weights corresponding to π^*, can be associated to the extent of charge separation, data of Table 3 indicate that for the monosubstituted anthracenes the exciplex polarity follows the sequence MA > MTHA > A > PHA. Previously, it has been established that singlet oxygen reactions involving an exciplex with partial charge separation are dependent on the solvent polarity, whereas concerted or partially concerted $O_2(^1\Delta_g)$ reactions are insensitive. Accordingly, k_T dependence on the solvent microscopic parameters can be interpreted as follows: the larger coefficient in the solvatochromic equation corresponding to π^* parameter for MA and MTHA, implies the formation of an exciplex with a larger charge separation than A and PHA and consequently, we propose a "more open" exciplex structure for MA and MTHA than corresponding to A and PHMA, as shown in Fig. 3.

This proposal allows us to explain the differences in the coefficient associated to the Hildebrand parameter. The larger values observed for A and PHA are compatible with the formation of a compact exciplex, a partially concerted singlet oxygen addition to the anthracene derivative and the release of a significant number of solvent molecules from the solvation sphere (when compared with free solvated reactants previous to the interaction). In addition, the proposed exciplex structure allows us to understand the small k_T values observed in polar protic solvents, such as ethanol and methanol, observed for MA and MTHA in comparison to the obtained in polar non-protic solvents, such as dimethylacetamide,

Table 4
LSER correlation equations for the reaction of singlet oxygen with disubstituted anthracene derivatives.

$\log k_T^Q = \log k_0 + s\pi^* + d\delta + a\alpha + b\beta + h\rho_H^2$						
	$\log k_0$	s	d	a	b	h
DPHA						
Coeff.	5.406	0.834	−0.191	–	–	0.004
±	0.050	0.086	0.038	–	–	0.001
t-stat.	108.879	9.650	−5.070	–	–	7.768
P(2-tail)	<0.0001	<0.0001	0.0005	–	–	<0.0001
VIF	–	2.00	1.27	–	–	1.87
	N = 14, R = 0.990, SD = 0.046, F = 159.744					
DMA						
Coeff.	6.683	0.728	–	−0.362	–	0.004
±	0.039	0.059	–	0.036	–	4.73×10^{-4}
t-stat.	170.577	12.270	–	−10.163	–	9.276
P(2-tail)	<0.0001	<0.0001	–	<0.0001	–	<0.0001
VIF	–	1.70	–	1.60	–	2.42
	N = 20, R = 0.988, SD = 0.056, F = 215.806					
DMTHA						
Coeff.	6.580	0.695	–	−0.416	–	0.003
±	0.042	0.063	–	0.038	–	0.001
t-stat.	156.897	10.954	–	−10.902	–	6.354
P(2-tail)	<0.0001	<0.0001	–	<0.0001	–	<0.0001
VIF	–	1.70	–	1.60	–	2.42
	N = 20, R = 0.983, SD = 0.059, F = 153.576					

Table 5
Substituent parameters for monosubstituted anthracenes.

Compound	k_T ($\times 10^6$ M^{-1} s^{-1})	s	f^-	σ_p
A	0.23	0.83	0.1755	0
PHA	0.40	0.75	0.1678	−0.01
MA	3.05	1.21	0.1716	−0.17
MTHA	3.51	1.25	0.1941	−0.27

N,N-dimethylformamide or propylencarbonate. The minor k_T value in polar protic solvents and the negative coefficient associated to the α parameter in solvatochromic equations for MA and MTHA would be due to the steric blocking of the nucleophilic reactive center by hydrogen bonding between the HBD solvent and the aromatic ring. An eventual HBD solvent effect involving hydrogen bonding with the negative "free oxygen" after the interaction $O_2(^1\Delta_g)$-monosubstituted anthracene, assisting an eventual back-reaction of the exciplex to the parent compounds can be disregarded because the same dependence on the α parameter was found for DMA, and DMTHA, and both react through a closely concerted exciplex (see the following section).

3.1.2. Solvent effect analysis for disubstituted anthracenes

For these compounds LSER correlation equations, summarized in Table 4, were obtained using the same statistical criteria discussed in the previous section.

The data of Table 4 show that reaction of disubstituted anthracenes with singlet molecular oxygen depends on the solvent parameters in a different way than that found for A, PHA, MA and MTHA. Also, in this series, k_T values depend mainly on the microscopic solvent parameters π^* and ρ_H^2, increasing in solvents with larger capacities to stabilize charges and dipoles and with higher cohesive energy values. Also, for DMA and DMTHA, k_T diminishes in solvents with larger α values. This dependence of k_T on the microscopic solvent parameters can be interpreted in terms of a partially concerted mechanism involving a charge transfer exciplex such as in monosubstituted anthracenes.

However, comparable values of the coefficient corresponding to the π^* parameter in the solvatochromic equation for DPHA (s = 0.83), DMA (s = 0.73) and DMTHA (s = 0.70) and low and very similar values for the Hildebrand parameter (0.003–0.004) coefficient, imply the formation of a loose exciplex with partial charge separation and a non-symmetric partially concerted singlet oxygen addition to the disubstituted anthracene derivative as shown in Fig. 4. This proposition also allows us to explain the decrease of k_T observed for DMA and DMTHA in HBD solvents. The lack of dependence on the α parameter for DPHA, probably is due to the more important steric effect of the bulky phenyl substituents, mainly located perpendicular to the aromatic system plane as predicted by theoretical calculations.

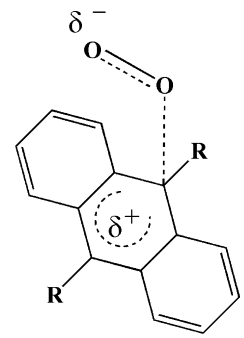


Fig. 4. Exciplex structure for reaction of singlet molecular oxygen with disubstituted anthracenes.

3.1.3. Substituent effect

Solvent effect analysis for the reaction between singlet molecular oxygen and anthracene derivatives shows that both the mechanism and reactivity are determined by the electronic characteristics of the subtituents. We perform several efforts to explain quantitatively the substituent effect on the reactivity, but not consistent correlations were obtained. In Table 5, the values of k_T in benzene, the coefficient associated to the π^* parameter, the local Fukui function for the electrophillic attack (f^-), calculated by using the DFT formalism and the σ_p Hammett parameters for A, PHA, MA, and MTHA are included.

The table data can only be interpreted in qualitative terms. Both, the total rate constant in benzene and the s value, the coefficient associated to the π^* parameter in the corresponding LSER equation, increases with the increase on the σ_p and f^- values. This result can be explained in terms of the electronic requirements for the reaction. In the monosubstituted family, the increase of the electronic density on the reactive center is supplied by the substituent. Then, the larger electron-donating capacity of the substituent, reflected by the σ_p and f^- values, promotes larger values of k_T and s. On the opposite, for the disubstituted compounds, π^* do not depend in an important way on the substituent. For these compounds the electronic requirement for the formation of a loose exciplex with partial

Table 6
Values of chemical rate constant, k_R, for reactions of monosubstituted anthracene derivatives with $O_2(^1\Delta_g)$ in different solvents obtained from steady-state methods.

Solvent	k_R($\times 10^6$ M^{-1} s^{-1})			
	A	PHA	MA	MTHA
Ethyl acetate	0.10 ± 0.01	0.32 ± 0.01	2.55 ± 0.03	2.27 ± 0.04
Acetone	0.35 ± 0.01	0.71 ± 0.01	5.38 ± 0.06	3.59 ± 0.02
Acetonitrile	0.61 ± 0.01	1.72 ± 0.01	11.25 ± 0.02	6.16 ± 0.08
Benzene	0.10 ± 0.01	0.30 ± 0.01	2.73 ± 0.04	2.52 ± 0.04
Dimethylacetamide	0.63 ± 0.01	1.86 ± 0.02	11.86 ± 0.12	9.15 ± 0.10
Ethanol	–	1.25 ± 0.02	1.90 ± 0.02	1.63 ± 0.01
n-Heptane	–	0.09 ± 0.01	0.37 ± 0.01	0.42 ± 0.01
n-Hexane	–	0.09 ± 0.01	0.27 ± 0.01	0.57 ± 0.01
Propylencarbonate	1.78 ± 0.03	4.83 ± 0.10	26.64 ± 0.55	13.53 ± 0.25
Tetrahydrofuran	0.10 ± 0.01	0.29 ± 0.01	2.47 ± 0.03	2.12 ± 0.03

Table 7
Values of chemical rate constant, k_R, for reactions of disubstituted anthracene derivatives with $O_2(^1\Delta_g)$ in different solvents obtained from stationary methods.

Solvent	k_R ($\times 10^6$ M^{-1} s^{-1})		
	DPHA	DMA	DMTHA
Ethyl acetate	0.71 ± 0.01	25.36 ± 0.29	15.98 ± 0.24
Acetone	1.42 ± 0.01	34.75 ± 0.39	17.47 ± 0.33
Acetonitrile	3.03 ± 0.03	63.05 ± 1.04	28.41 ± 0.53
Benzene	0.85 ± 0.01	28.56 ± 0.37	15.39 ± 0.23
Dimethylacetamide	3.73 ± 0.04	67.44 ± 0.47	38.36 ± 0.44
Ethanol	–	19.37 ± 0.20	10.69 ± 0.13
n-Heptane	–	7.68 ± 0.06	5.41 ± 0.09
n-Hexane	–	7.47 ± 0.14	5.29 ± 0.11
Propylencarbonate	5.70 ± 0.12	116.98 ± 1.99	44.75 ± 0.88
Tetrahydrofuran	–	23.01 ± 0.46	13.95 ± 0.20

Table 8
Values of the ratio between the chemical rate constant, k_R, and total rate constant, k_T, for reactions of monosubstituted and disubstituted anthracene derivatives with $O_2(^1\Delta_g)$ in different solvents.

Solvent	k_Q/k_T						
	A	PHA	MA	MTHA	DPHA	DMA	DMTHA
Ethyl acetate	0.48	0.78	0.75	0.72	0.53	0.96	0.92
Acetone	0.95	0.87	0.98	0.86	0.60	0.99	0.96
Acetonitrile	0.65	0.78	0.91	0.79	0.76	0.92	0.93
Benzene	0.43	0.75	0.86	0.72	0.82	0.92	0.98
Dimethylacetamide	0.72	0.81	0.90	0.83	0.78	0.95	0.93
Ethanol	–	0.61	0.72	0.81	–	0.71	0.84
n-Heptane	–	0.90	0.82	0.88	–	1.02	1.00
n-Hexane	–	0.90	0.73	1.14	–	0.98	0.99
Propylencarbonate	1.01	0.92	0.93	0.98	0.94	0.92	0.87
Tetrahydrofuran	0.40	0.56	0.77	0.75	0.45	0.95	0.75

charge separation is provided by both substituents. Once the initial interaction $O_2(^1\Delta_g)$–anthracene derivative takes place, and the exciplex with a positive charge on the aromatic system is formed, the electron donor substituent on the opposite side operate stabilizing the exciplex. This proposition allows us to explain the smaller s values for this family (in comparison with the observed for MA and MTHA), the low h values compatibles with a non-compact exciplex and the larger reactivity of the disubstituted anthracenes than that observed for the monosubstituted derivatives. Furthermore, although the reactivity of the disubstituted compounds is larger than the monosubstituted, solvent effect is smaller for the disubsituted derivatives. The ratio between $k_T^{\text{propylencarbonate}}/k_T^{\text{hexane}}$ (approximately the extreme k_T values) is 59, 28, 17, and 10 for MA, MTHA, DMA and DMTHA, respectively. Clearly, the larger increase of k_T when solvent is changed from non-polar to non-protic polar is due to the large charge separation in the MA and MTHA, in spite of its reactivity.

3.2. Chemical reaction rate constants

The values of the chemical reaction rate constants, k_R, were determined in a more limited set of solvents by measuring the anthracene derivative consumption. The number of solvents in which we perform these experiments was only determined by the solubility of the anthracene derivatives. Under our experimental conditions, the consumption of the anthracene derivative fits a first-order kinetic according to Eq. (3):

$$\ln \frac{[A]_0}{[A]_t} = \frac{k_R[O_2(^1\Delta_g)]}{k_d} t = k_{Exp} t \quad (3)$$

where A represents the anthracene derivative, k_R the chemical reaction rate constant, k_d the $O_2(^1\Delta_g)$-lifetime in the solvent, $[O_2(^1\Delta_g)]$ is the steady-state singlet oxygen concentration, measured by using appropriate actinometers such as DPBF or DMF, and k_{Exp} is the rate constant calculated from the first-order fit. Tables 6 and 7 summarize the results obtained.

Tables 6 and 7 show that the chemical rate constants for the reaction of singlet oxygen with mono and disubstituted anthracenes are very close to the total rate constant in most solvents employed in these experiments. A better picture of the importance of the chemical way versus the physical quenching is obtained observing the data of Table 8, where the ratio between k_R and k_T in the solvent set is shown. The data show that the more prone anthracene derivatives for which the exciplex collapses to the parent compounds via physical quenching are A and DPHA, while for MA, MTHA, DMA and DMTHA the exciplex evolves mainly through the chemical way.

3.2.1. Solvent effect analysis for the chemical reaction of mono and disubstituted anthracenes with singlet oxygen

Solvent dependence of k_R for chemical reaction of singlet molecular oxygen with the anthracene derivatives was also analyzed in terms of LSER correlation equations obtained using the same statistical criteria as discussed in the precedent sections, however the consistency of these data is smaller than that corresponding to the k_T analysis due to the more limited solvent set. Then, in spite of the larger errors in the coefficients, the data of Tables 9 and 10 show the k_R values for the different anthracene derivatives studied following the same dependence on the microscopic solvent parameters, than that observed for the k_T LSER equations. This result is easily understood, because the physical quenching and the chemical reaction take place through a common exciplex. A more relevant result is found when the coefficient values of the LSER correlation equations for the total and the chemical rate constants are compared. Within

Table 9
LSER correlation equations for the chemical reaction of singlet oxygen with monosubstituted anthracene derivatives.

$\log k_T^Q = \log k_0 + s\pi^* + d\delta + a\alpha + b\beta + h\rho_H^2$						
	$\log k_0$	s	d	a	b	h
A						
Coeff.	3.308	1.856	–	–	–	0.008
±	0.210	0.444	–	–	–	0.002
t-stat.	15.764	4.181	–	–	–	4.900
P(2-tail)	<0.0001	0.0139	–	–	–	0.0080
VIF	–	2.44	–	–	–	2.44
	N = 7, R = 0.989, SD = 0.090, F = 89.171					
PHA						
Coeff.	4.450	0.700	–	–	–	0.009
±	0.111	0.178	–	–	–	0.001
t-stat.	40.095	3.936	–	–	–	6.371
P(2-tail)	<0.0001	0.0056	–	–	–	0.0004
VIF	–	1.98	–	–	–	1.98
	N = 10, R = 0.981, SD = 0.126, F = 90.986					
MA						
Coeff.	5.143	1.168	–	−0.821	–	0.008
±	0.080	0.131	–	0.135	–	0.001
t-stat.	64.583	8.904	–	−6.086	–	6.426
P(2-tail)	<0.0001	0.0001	–	0.0009	–	0.0007
VIF	–	2.59	–	1.80	–	3.55
	N = 10, R = 0.995, SD = 0.081, F = 180.861					
MTHA						
Coeff.	–	0.901	–	−0.692	–	0.006
±	–	0.104	–	0.107	–	0.001
t-stat.	86.090	8.694	–	−6.497	–	5.979
P(2-tail)	<0.0001	0.0001	–	0.0006	–	0.0010
VIF	–	2.59	–	1.80	–	3.55
	N = 10, R = 0.994, SD = 0.064, F = 166.656					

Table 10
LSER correlation equations for the chemical reaction of singlet oxygen with disubstituted anthracene derivatives.

	$\log k_{\mathrm{T}}^{\mathrm{Q}} = \log k_0 + s\pi* + d\delta + a\alpha + b\beta + h\rho_{\mathrm{H}}^2$					
	$\log k_0$	s	d	a	b	h
DPHA						
Coeff.	4.532	1.660	–	–	–	0.005
±	0.064	0.125	–	–	–	4.40×10^{-4}
t-stat.	71.352	13.321	–	–	–	10.996
P(2-tail)	<0.0001	0.0009	–	–	–	0.0016
VIF	–	2.14	–	–	–	2.14
	$N = 6$, $R = 0.999$, SD = 0.025, $F = 549.844$					
DMA						
Coeff.	6.612	0.623	–	−0.620	–	0.005
±	0.042	0.068	–	0.070	–	0.001
t-stat.	159.103	9.106	–	−8.818	–	8.805
P(2-tail)	<0.0001	<0.0001	–	0.0001	–	0.0001
VIF	–	2.59	–	1.80	–	3.55
	$N = 10$, $R = 0.996$, SD = 0.042, $F = 247.184$					
DMTHA						
Coeff.	6.558	0.593	–	−0.494	–	0.004
±	0.052	0.086	–	0.088	–	0.001
t-stat.	125.889	6.913	–	−5.607	–	4.594
P(2-tail)	<0.0001	0.0005	–	0.0014	–	0.0037
VIF	–	2.59	–	1.80	–	3.55
	$N = 10$, $R = 0.990$, SD = 0.053, $F = 103.460$					

the statistical error, the values of *s*, *a* and *h* for both LSER equations are very similar, implying that the exciplex and the corresponding intermediate are structurally comparable and a lower energy barrier in the potential energy surface on which the system evolves to give the final endoperoxide product.

4. Concluding remarks

Solvent effect analysis of the singlet oxygen reaction with anthracene derivatives, performed in terms of the classical LSER equation allows us to account for the effect of substituents on the reaction rate and to depict the nature of the excited state encounter complex produced in the initial steps of the reaction. LSER analysis supports the formation of a loose, zwitterionic like exciplex for 9-methylanthracene and 9-methoxyanthracene, a loose exciplex with partial charge separation for di-substitutes anthracene and a compact exciplex with partial charge separation for anthracene and 9-phenylanthracene. A more deep understanding of the reaction can be achieved from theoretical calculations of the potential energy surface and modeling the critical complexes and intermediates that yield the final products. We look forward this open path will be closed in the near future.

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