

Oxygenation of the phenylhalocarbenes. Are they spin-allowed or spin-forbidden reactions?

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Abstract Oxygenation mechanisms of phenylhalocarbenes in vacuum are investigated through the use of density functional theory and CASSCF-PT2 approaches. Reactions with both substituted and unsubstituted phenylhalocarbenes are strongly exothermic. The reactions with nitrosubstituted halocarbenes are predicted to be spin allowed due to the practical degeneracy of the singlet and triplet carbene states. Conversely, for the unsubstituted compounds, the equilibrium between the triplet carbene and $^3\text{O}_2$ requires a previous singlet–triplet state crossing. The large spin-orbit coupling at this crossing suggests a rather efficient tunneling rate. This would help to explain why the rate constant in solution in these cases is only one order of magnitude smaller than those involving a spin-allowed process. Moreover, the action of the solvent as a third body appears to play a fundamental role in prompting relatively smooth rates.

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Introduction

Spin selectivity experiments in solution for the oxygenation of spin-singlet phenylhalocarbenes (PHCs) with spin-triplet state dioxygen have been reported by Makihara et al. and interpreted by performing in vacuo DFT calculations [1]. In solution, these reactions are kinetically slow but exothermic. This raised the question as to whether or not these processes are spin forbidden. To shed some light on the issue, an ab initio study using two methodologies, DFT and CASSCF-PT2, was carried out, and the results of that study are reported here.

Reaction mechanism discussions are usually based on an in vacuo analysis of a single potential energy surface with total spin conservation. For exothermic reactions in vacuum, as mentioned above, energy conservation requires a third body to absorb the energy, or the emission of a photon. In our theoretical survey of the mechanisms behind the oxygenation of some PHCs, we assume that solvent effects only manifest themselves in the energy exchange process.

In the simplest picture that is useful for discussing reactivity issues, the concerted oxygenation process would evolve from the potential energy minimum of reactants to the potential energy minimum associated with products through a single transition state. This reaction could also proceed through a more complex pathway, incorporating multiple transition state structures and intermediates. Although this concept represents only one aspect of chemical reactivity, it has been very useful in rationalizing a great number of chemical reactions. However, there are a

wide variety of reactions in organic [2–6], organometallic [7–13], and inorganic [14–20] chemistry that involve spin changes when reactants transform into products. In these cases, more than one state with different spin multiplicities must be incorporated to determine the minimum-energy reaction path.

Recently, a two-state reactivity model was proposed to rationalize this kind of reactions [21]. In this model, a thermal reaction involving spin crossover along a reaction coordinate connecting reactants and products must be described in terms of (at least) two potential energy surfaces, hence the term “two-state reactivity” (TSR) [21]. This is correct if product formation arises from the interplay of spin inversion with the respective barrier heights on both spin surfaces. In this case, the system surfaces are strictly diabatic. The TSR model provides low-energy paths, which may help to identify the dominant steps in the kinetics and the selectivity of the reaction [21–25]. Several authors have contributed to the rationalization of numerous processes involving multiple state reactivity (MSR) in metallic complexes [22, 23, 25]. Recently, Harvey discussed the kinetics of spin-forbidden chemical reactions [26] through the use of transition state theory. Two factors were found to determine the observed reactivity: (1) the critical energy required for the reaction to occur, and (2) the probability of hopping from one surface to the other in the vicinity of the crossing region [26, 27].

For the Born–Oppenheimer adiabatic TSR description [28–30], these reactions would follow a spin-forbidden mechanism where the spin-orbit (SO) operator couples potential energy surfaces of different multiplicities, usually triplet and singlet; this procedure leads to a smooth change in spin state from reactants (triplet) to products (singlet) in the neighborhood of a crossing point as the result of the SO interaction. It is commonly accepted that the SO effect must be large enough to produce significant separation of the adiabatic potential energy surfaces, so that nonadiabatic effects become negligible.

In view of the limited computational scope reported in [1], it is apparent that there is room for a more detailed theoretical study of possible reaction mechanisms in vacuum; this includes calculations of potential energy profiles, as well as reactivity descriptors that suggest local properties which global energy descriptors normally miss. This work is a step toward the combination of global and local quantities related to reactivity issues.

Theoretical reactivity model

The spin-polarized density functional theory (SP-DFT) provides a suitable and general framework to discuss chemical reactivity to the extent that it provides an explicit

account of both electron and spin density. Galván and coworkers [31–34] were the first to present a general treatment of chemical reactivity that utilized global and local electronic chemical reactivity descriptors within SP-DFT. Recently, constrained philicities have been explored in the SP-DFT framework, extending the conceptual usefulness of the electrophilicity index ω first introduced by Parr et al. [35]. A constrained electrophilicity (i.e., constrained to a constant spin number N_S) has been defined as [36]

$$\omega_N \equiv \frac{(\mu_N)^2}{2\eta_{NN}}, \quad (1)$$

where μ_N and η_{NN} correspond to the constrained chemical potential and hardness [36]. ω_N measures the initial ability of a system to acquire electronic charge from the environment at constant spin number. Additionally, the meanings of the previously defined spin-philicity, ω_S^+ , and spin-donicity, ω_S^- , descriptors [37, 38] were further clarified: each is a philicity index that measures the ability of a given system to experience spin polarization [36],

$$\omega_S^\pm \equiv \frac{(\mu_S^\pm)^2}{2\eta_{SS}}. \quad (2)$$

The symbols μ_S and η_{SS} correspond to the spin potential and spin hardness, respectively [31–34]. In fact, the quantities in Eq. 2 have been found to be valuable when describing the global chemical reactivities of reactive species in the context of spin catalysis phenomena [38], as well as in the study of the spin-polarization reactivities of active species from groups IV [37] and V [39] and in substituted silylene families [40].

The SP-DFT operational formulae for obtaining numerical values for the spin potential μ_S^\pm , the spin hardness η_{SS} , and finally the philicity ω_S^\pm indices are given by

$$\begin{aligned} \mu_S^- &\approx \frac{1}{2} \left(\varepsilon_{\text{HOMO}}^\alpha - \varepsilon_{\text{LUMO}}^\beta \right), & \mu_S^+ &\approx \frac{1}{2} \left(\varepsilon_{\text{LUMO}}^\alpha - \varepsilon_{\text{HOMO}}^\beta \right), \\ \eta_{SS}^{M \rightarrow M'} &\approx \left(\mu_S^{(M')-} - \mu_S^{(M)+} \right) / \Delta N_S \end{aligned} \quad (3)$$

All indices are defined in terms of the one-electron energies, ε , of the frontier molecular orbitals HOMO and LUMO of a given α or β spin state for the system in the lower and upper spin multiplicities M and M' , respectively [36, 40]. Note that for a singlet ground state, these operational formulae for SP-DFT philicities are equivalent to those of the spin-restricted case [35]. Note also that spin hardness, $\eta_{SS}^{M \rightarrow M'}$, was calculated using the spin potentials $\mu_S^{(M')-}$ and $\mu_S^{(M)+}$, evaluated at the geometry of the ground state corresponding to multiplicity M . ΔN_S values correspond to the change in the spin number between the multiplicity states M and M' .

Oxygenation reaction: models

In a simplistic approach, considering their exothermicities, the oxygenation reactions of PHC should be near-explosive. However, the reactions of PHC with $O_2(^3\Sigma_g^-)$ to yield carbonyl oxides are smooth, while reactions with the singlet spin state of the oxygen are relatively slow [1]. These antecedents were used to suggest a mechanism that bypasses the spin-forbidden path, thereby introducing activation barriers that are dependent upon the nature of the halogen and the substitution of the phenyl ring. More specifically, the photolysis of a diazirine would produce a carbene as an intermediate, which could be converted to benzoyl halides in the presence of oxygen molecules (see Scheme 1). These are the reactions whose experimental velocities were measured and are reported in [1]. Whether or not the apparent spin-forbidden process for the reactive singlet carbenes found in vacuum does occur in solution is an open question.

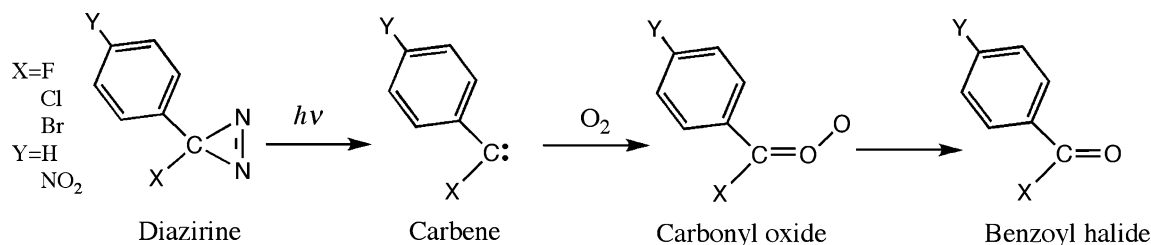
Our goal in the present paper is to get some insight into the gas phase mechanism involved in the interaction between oxygen and PHC (i.e., the mechanism governing the second step of the reaction in Scheme 1), and to establish its exothermicity. In [1], solution reactions involving six different compounds were investigated, where (X,Y)—as noted in Scheme 1—were (Cl,H), (Br,H), (F, NO_2), (Cl, NO_2) and (Br, NO_2) compounds. The initial set also included (Br,OMe) derivatives, but in this case no reaction with oxygen was observed. In our theoretical survey, we will include all of them as well as the (F,H) derivative for the sake of completeness. Note that neglecting solvent effects may lead to an error in the predicted nature of the ground state observed in solution. This is why an in vacuo study allows intrinsic relative stabilities and the electronic properties associated with different spin species to be established. Reactivity issues are examined within the spin-polarized density functional theory.

Computational details

The two electrons of halocarbenes can occupy different orbitals, leading to singlet and triplet states. The interaction

of two triplet states can result in quintuplet, triplet, and singlet products; this also includes the triplet product provided by the singlet carbene and triplet oxygen. Hence, the resulting product in vacuum could be either a singlet or a triplet. The first question to address in our survey should therefore be: which of the two spin states of the species involved in the reaction is the most stable? For this purpose, the geometries of all stationary points on the potential energy surface associated with PHC oxygenation were optimized using the B3LYP functional, which combines Becke's three-parameter nonlocal hybrid exchange potential [41] with the nonlocal correlation functional of Lee, Yang and Parr [42]. For the geometry optimizations, a 6-31G* basis set expansion was used for both singlet and triplet states using the spin-unrestricted formalism. No significant spin contamination was detected for any of the triplet stationary points calculated. The final energies were obtained through single point calculations carried out at the B3LYP/6-311++G(3df,2p) level of theory. All of these calculations were performed with the Gaussian03 suite of programs [43]. The harmonic vibrational frequencies of the different stationary points of the potential energy surface were calculated at the same level of theory used for their geometry optimization, in order to identify local minima and transition states as well as to estimate the corresponding zero-point energy (ZPE) corrections.

The large changes in electronic structure involved in the systems under study imply that more advanced quantum chemical computational methods are required. For this reason, the B3LYP minima were reoptimized using the multiconfigurational complete active space self-consistent field (CASSCF) method [44]. This method, combined with the extended relativistic ANO-RCC basis set [45] contracted to $H[2s1p]/C,N,O[3s2p1d]/Br[4s4p2d]/Cl[4s3p1d]$, permits a fairly reliable representation of the electronic structures involved in these mechanistic issues. To account for not only static but also dynamic electron correlation effects, singlet and triplet CASSCF wavefunctions were subsequently used as a reference in second-order perturbation theory multistate (MS-CASPT2) calculations to re-evaluate singlet/triplet energy gaps. An active space comprising ten electrons distributed in nine orbitals, which



Scheme 1 Photochemical transformation for diazirine in benzoyl halide through a carbene intermediate

includes 3π and $3\pi^*$ aromatic molecular orbitals, the in-plane sp and perpendicular p orbitals sitting in the carbene atom, and a lone pair from the halogen atom, was used in the CASSCF characterization of the unsubstituted halocarbenes. For the nitrosubstituted halocarbenes, the size of the active space was extended to 12 active electrons and 11 orbitals. Here, the lone pair on the halogen atom was replaced with three molecular orbitals localized on the NO_2 moiety (i.e., the bonding, nonbonding, and antibonding π orbitals π_{NO_2} , p_{NO_2} and $\pi_{\text{NO}_2}^*$). Figure 1 shows the

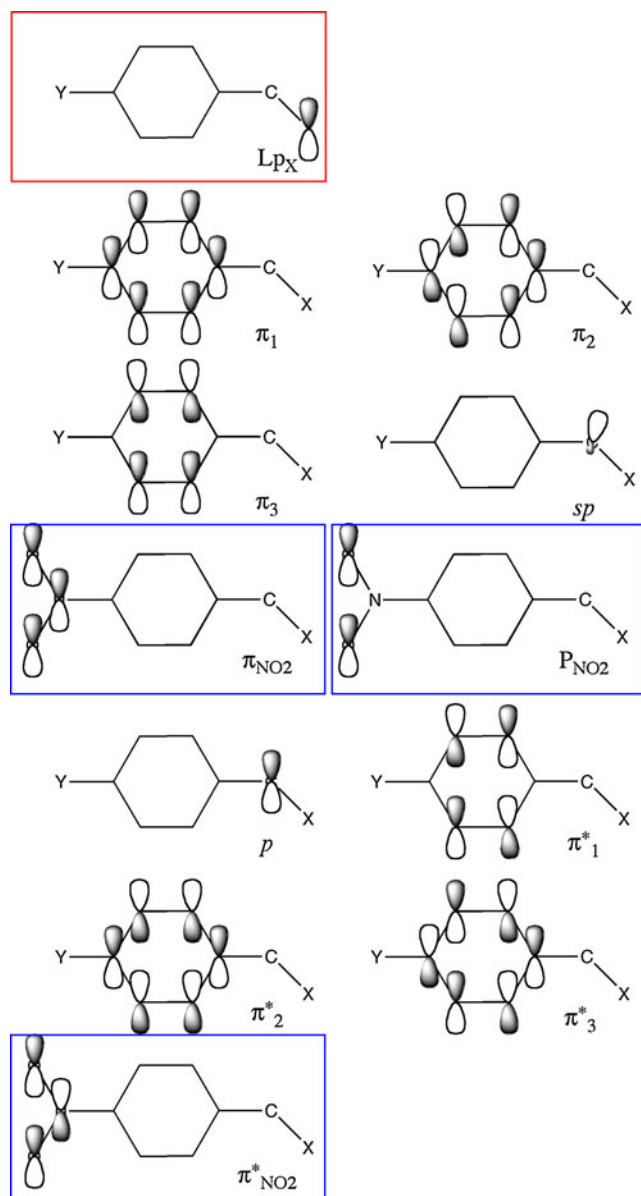


Fig. 1 Molecular orbitals included in the (10,9) and (12,11) active spaces used to characterize the S_0 and T_1 states of the unsubstituted and nitrosubstituted phenylhalocarbenes. Red and blue frames indicate orbitals that belong exclusively to the (10,9) and (12,11) active spaces, respectively

molecular orbitals present in the active spaces described above. CASSCF and CASPT2 calculations were carried out with the MOLCAS suite of programs [46].

To locate the corresponding minimum-energy singlet/triplet crossing points (MECP) that are relevant to the reactions in vacuum, we used the state-averaged crossing point multiconfigurational self-consistent field (SA-CPMSCF) procedure implemented in the MOLPRO package [47]. The active space that was chosen for the corresponding (CASSCF) calculations consisted of 12 electrons and 11 orbitals, and the basis set expansion was 6-31 G(d). Once the MECPs had been located, the spin-orbit coupling between the corresponding singlet and triplet states was estimated using the method of Palmieri and coworkers [48] at the same level of theory.

Results and discussion

The total in vacuum energies, ZPE corrections, and the S^2 expectation values of the located minima for phenylfluorocarbene (F,H), phenylchlorocarbene (Cl,H), phenylbromocarbene (Br,H), and the corresponding p -nitrophenylhalocarbene (X,NO_2) species are given in Table S1 of the “Electronic supplementary material” (ESM). The B3LYP relative energies of the different entrance channels with respect to the most stable product of the reaction are summarized in Table 1.

It is apparent from Table 1 that, as far as the products are concerned, spin-singlet species are the most stable states in all cases. As expected, solvent effects do not change this order of stability, as confirmed by the results of the solution experiments performed by Makihara et al. [1]. Furthermore, the supermolecule singlet–triplet energy gap is so large that there is no doubt that the singlet carboxylic oxide is the most abundant product after oxygen interacts with halocarbenes, regardless of the spin state of the latter at the beginning of the reaction.

The largest energy difference is observed for $\text{X} = \text{F}$, but this energy gap decreases systematically when the aromatic ring is substituted at the *para* position with a NO_2 group. Noting that p -substitution with a methoxy group of the bromine derivative leads to the opposite effect, we could conclude that electron-withdrawing substituents at the *para* position decrease the singlet–triplet energy gap in vacuum, while electron-donating groups increase it. However, the most dramatic effects are observed when we consider the reactants, as the relative stabilities of the singlet and triplet states change noticeably with the nature of the substituent at the *para* position of the aromatic ring (see Table 1). For unsubstituted compounds, the singlet–triplet energy gap is significantly large (between 21 and 59 kJ mol^{-1}), with the singlet state being systematically the more stable. Moreover, this gap decreases dramatically for Cl and Br

Table 1 B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) energies relative to the most stable product of each stationary point along the potential energy profile leading to singlet and triplet products. R is the reactantphenylhalocarbene, P is the reaction product, and TS is the transition state in the triplet PES (all values are in kJ mol⁻¹)

	Phenylhalocarbene			<i>p</i> -Nitrophenylhalocarbene			<i>p</i> -Methoxyphenylhalocarbene
	F	Cl	Br	F	Cl	Br	Br
R(S)+O ₂ (T)	221.7	222.9	222.0	224.4	226.3	138.8	199.3
R(T)+O ₂ (T)	280.8	243.7	250.1	283.1	226.5	134.1	234.3
TS(T)	232.6	227.1	228.0	230.8	226.4	137.5	200.6
P(S)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
P(T)	109.4	99.3	99.8	95.7	89.1	89.9	106.5

derivatives when a nitro group is introduced at the *para* position on the aromatic ring. As a matter of fact, for the Cl derivative, the singlet and triplet states become practically degenerate, whereas for the Br derivative, the triplet becomes slightly more stable than the singlet. In order to check that this progressive degeneracy of the two multiplicities observed upon descending the halogen group is not an artifact of the DFT approach used, the energies of the singlet and triplet states were recalculated using the MS-CASPT2/CASSCF formalism and the optimized CASSCF geometries. The results obtained clearly confirm that, for the two heaviest *p*-NO₂-haloderivatives considered, the singlet and the triplet states are almost degenerate: the triplet is only 2.13 kJ mol⁻¹ above the singlet in the case of the (Br,NO₂) derivative (see Table 2). The energy gap between the singlet and the triplet increases upon *p*-substitution with electron-donating groups. Hence, the

singlet state for the (Br,MeO) compound is about 35 kJ mol⁻¹ below the triplet (see Table 1). It is worth mentioning that a similar behavior has been reported in the case of aryl carbenes, where the triplet state is stabilized by a *p*-nitro group and destabilized by a *p*-methoxy one [24].

These changes in the relative stabilities of the two spin states translate into significant differences in the reaction mechanisms of these species. There are three different situations. For the unsubstituted parent compounds, the singlet carbene is lower in energy than the triplet (see Fig. 2a). For the *p*-NO₂ derivatives, there are two cases: when X = Cl, the singlet and the triplet are practically degenerate; when X = Br, the triplet is slightly more stable than the singlet if DFT calculations are considered. Hence, as illustrated in Fig. 2a, the reaction between the unsubstituted (Cl,H) and (Br,H) derivatives and triplet molecular oxygen, namely R(S) + O₂(T), must occur through a crossing point between the singlet and triplet potential energy surfaces. This means that a spin-forbidden mechanism is involved, since the most stable products are always singlet states, as mentioned above (Fig. 2a). Conversely, for the (Cl,NO₂) and (Br,NO₂) compounds, the reaction is spin allowed, since the practical degeneracy between the singlet and triplet states will populate the latter (see Fig. 2b).

Comparisons with experimental data in solution are delicate and certainly not conclusive. If solvent effects were not influential, the present results would ratify the interpretation offered in [1]. In this reference, it was assumed that all processes are essentially spin allowed through an equilibration between the triplet and the singlet carbene. Our results clearly indicate that although this equilibration between the triplet and the singlet carbene is a fundamental mechanism, for this equilibration to occur, a crossover from the singlet to the triplet manifold should take place through spin-orbit coupling for the unsubstituted compounds. Since this is an important step in the mechanism, we have located the MECPs between the singlet and triplet potential energy surfaces for the (Cl,H), (Br,H) and (F,NO₂) derivatives. In all cases, the spin-orbit

Table 2 Spin potential (μ_S^\pm), spin hardness (η_{SS}), philicity for spin polarization (ω_S^\pm), vertical excitation energy (ΔE^{ST}), obtained using the model of Vargas et al. [34]), and adiabatic excitation energy (ΔE^{ad})

	μ_S^-	μ_S^+	η_{SS}	ω_S^+	ΔE^{ST}	ΔE^{ad} *
<i>F</i>						
H	-4.76	1.70	-3.23	-0.45	62.0	59.1 (57.7)
<i>p</i> -NO ₂	-5.57	1.42	-3.49	-0.29	59.5	58.7 (46.0)
<i>Cl</i>						
H	-4.84	1.43	-3.13	-0.33	26.5	20.8 (20.8)
<i>p</i> -NO ₂	-5.54	1.23	-3.38	-0.22	2.6	0.2 (7.5)
<i>Br</i>						
H	-4.87	1.37	-3.12	-0.30	35.3	28.1 (16.5)
<i>p</i> -NO ₂	-5.59	1.15	-3.37	-0.20	-3.6	-4.7 (2.1)
<i>p</i> -OMe	-4.53	1.44	-2.99	-0.35	43.2	35.0

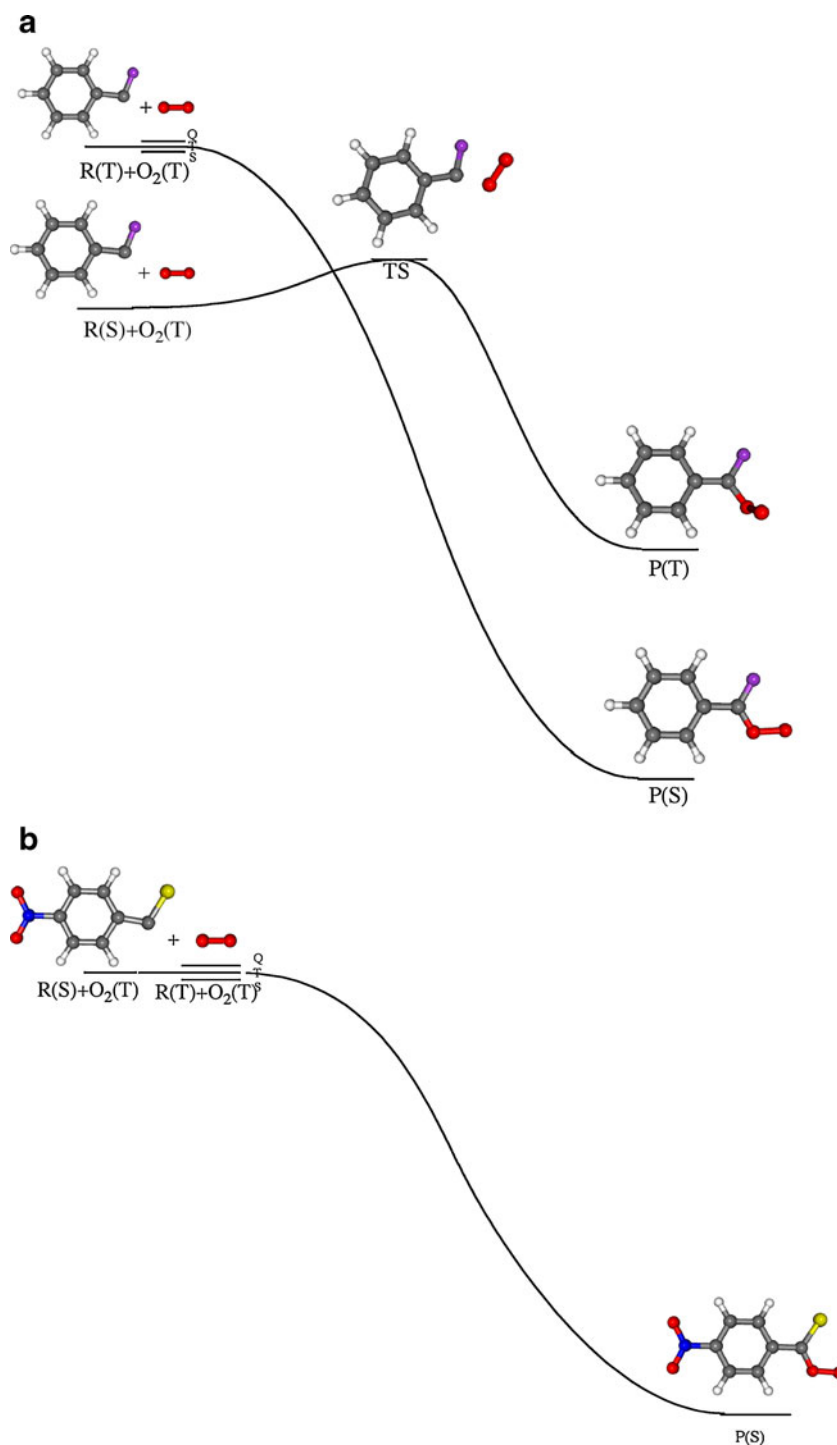
Values of ΔE (in kJ mol⁻¹), μ_S^\pm , η_{SS} , and ω_S^\pm are in eV

Values of ΔE^{ST} were obtained from Eq. 4. See the text for details

$\Delta E^{ad} = E^T(\text{B3LYP}/6-311+G(3df,2p)//\text{B3LYP}/6-31G(d)) - E^S(\text{B3LYP}/6-311+G(3df,2p)//\text{B3LYP}/6-31G(d))$ (scaled ZPE is included)

* Singlet–triplet energy gaps calculated at the MS-CASPT2//CASSCF/ANO-RCC level of theory are given in parentheses

Fig. 2 Schematic energy profiles for the oxygenation of **a** unsubstituted phenylhalocarbene, and **b** *p*-nitrochloro or -bromophenylcarbene



coupling must be reasonably large (see Table 3) for the crossover between both surfaces to be efficient; these theoretical results are in agreement with the relative high rate constants measured for these processes [1.2×10^6 and $1.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for (Cl,H) and (Br,H), respectively]. It is also worth noting that the spin-orbit coupling is slightly larger for (Br,H) than for (Cl,H), in agreement with the fact that the measured rate constant for the former is also

Table 3 Calculated spin-orbit coupling (LS, cm^{-1}) calculated for selected oxygenated phenylhalocarbene minimum energy crossing points (MECPs)

(X,Y)	LS
Cl,H	2.08
Br,H	5.93
F,NO ₂	21.03

Table 4 Thermochemical values associated with the reactions proposed in Scheme 2 (values shown are in kJ mol^{-1})

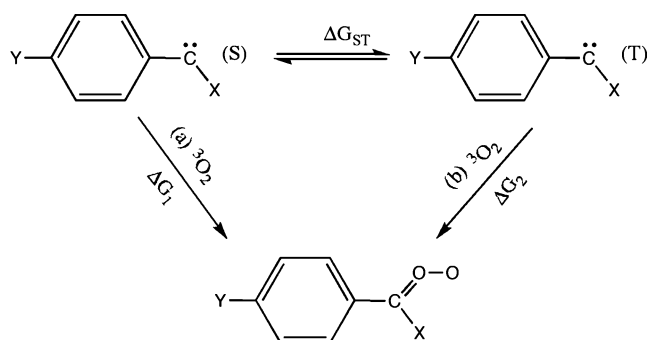
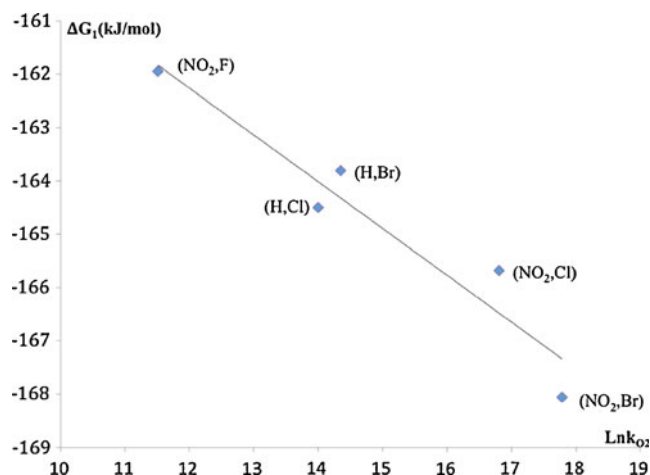
	ΔG^{ST}	ΔG_1	ΔG_2	$\ln k_{\text{O}_2}$	$\Delta G^{\text{ST}}_{\text{exp}}$ [1]
H,F	55.35	-163.71	-219.06	–	–
H,Cl	17.52	-164.50	-182.02	14.00	17
H,Br	24.92	-163.81	-188.72	14.35	16
NO_2,F	62.26	-161.95	-224.21	11.51	>23
NO_2,Cl	-0.03	-165.68	-165.64	16.81	10
NO_2,Br	-5.05	-168.06	-163.01	17.79	7.5
OMe,Br	32.16	-154.48	-186.63	11.51	>23

slightly larger. Our results also predict that the least efficient processes are those involving the fluorine derivatives.

Obviously, the rate constants for the (Cl, NO_2) and (Br, NO_2) compounds—where the oxidation is essentially a spin-allowed process—should be higher, as found experimentally in solution (2.0×10^7 and $5.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively).

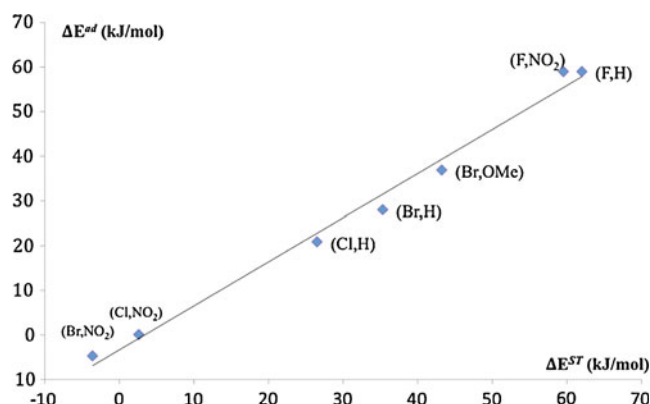
It is also apparent that our in vacuum estimates for the singlet–triplet free-energy gap, ΔG^{ST} (see Table 4), correlate well with the values estimated by Makihara et al. [1] using Scheme 2, with the only exceptions being those corresponding to the (Cl, NO_2) and the (Br, NO_2) derivatives. These discrepancies can be attributed to the fact that the experimental Gibbs energy [1] for the singlet–triplet equilibrium were deduced from the oxygenation rates obtained for mechanism (a) in Scheme 2, assuming (i) equilibrium between triplet and singlet halocarbenes and (ii) that mechanism (b) in Scheme 2 is a spin-allowed oxygenation process. However, this scheme cannot be applied to cases where singlet and triplet states are near-degenerate, or when the order of stability is reversed, which is the case for (Cl, NO_2) and (Br, NO_2), at least in vacuum.

In this respect, it is worth noting the rather good linear correlation between our values for ΔG_1 and $\ln k_{\text{O}_2}$ (see Fig. 3), which includes both the (Cl, NO_2) and the (Br,

**Scheme 2** Singlet-triplet equilibria used to deduce oxygenation rates in ref. [1]**Fig. 3** Correlation between ΔG_1 from Scheme 2 and $\ln k_{\text{O}_2}$

NO_2) derivatives. This good correlation appears to indicate that the singlet and triplet states for the aforementioned two derivatives are degenerate or near-degenerate in solution.

It is important to emphasize that philicity indices also predict different behaviors for the unsubstituted and the substituted compounds. In Table 2, we list the SP-DFT constrained spin potential μ_{S} , the spin hardness η_{SS} , and the constrained philicity $\omega_{\text{S}}^{\dagger}$ indices for the singlet ground states of all the compounds under investigation: (F,H), (Cl,H), (Br,H), (F, NO_2), (Cl, NO_2), (Br, NO_2), and (Br,OMe). It is clear that $\omega_{\text{S}}^{\dagger}$ increases in the order (F,H) < (Cl,H) < (Br,H) when the aromatic ring is unsubstituted. On the other hand, if the aromatic ring is substituted with an electron-withdrawing group like NO_2 , the order observed in $\omega_{\text{S}}^{\dagger}$ is (F, NO_2) < (Cl, NO_2) ~ (Br, NO_2). Hence, the highest philicity values are observed for (Cl, NO_2) and (Br, NO_2), indicating that they are able to undergo a spin polarization process. It is worth noting that this increase is slightly larger for (Br, NO_2) than for (Cl, NO_2), which is in agreement with the greater change in the singlet–triplet

**Fig. 4** Correlation between ΔE^{ad} and ΔE^{ST}

energy gap. The main conclusion is, however, that (Cl, NO₂) and (Br,NO₂) should react towards the oxygen molecule differently from the other compounds, in agreement with the experimental evidence. This is also corroborated by the quite good correlation between the calculated singlet–triplet energy gap (ΔE^{ad}) and the values (ΔE^{ST}) derived when using Eq. 4, based on the SP-DFT formalism [34] (see Fig. 4).

$$\Delta E^{\text{ST}} = \frac{1}{2} (\varepsilon_{\text{LUMO}}^{\text{S}} - \varepsilon_{\text{HOMO}}^{\text{S}} + \varepsilon_{\alpha\text{HOMO}}^{(\text{T})} - \varepsilon_{\beta\text{LUMO}}^{(\text{T})}) \quad (4)$$

The good correlation between ΔE^{ad} and ΔE^{ST} shows that the model of Vargas et al. [34] accurately describes the reactivities of the different spin states.

Conclusions

The oxygenation of phenylhalocarbenes in vacuum is predicted to be a spin-allowed process when the PHC is substituted with electron-withdrawing groups at the *para* position of the aromatic ring, because this kind of substitution leads to practical degeneracy of the singlet and triplet potential energy surfaces calculated here, equilibrium between the triplet carbene and ³O₂ requires a previous spin crossover between the singlet and the triplet states, calculated here as potential energy surfaces. According to our results, this process involves a reasonably large spin-orbit coupling, so the crossover should be rather efficient. If solvent effects do not significantly alter the quantum mechanism of the reaction, these results would explain why in these cases the rate constant is only one order of magnitude smaller than those involving spin-allowed processes. The hypothesis put forward by Makihari suggests that the change in spin state of carbenes from singlet to triplet would occur prior to reaction with oxygen. According to our survey, this is not possible for a reaction performed in vacuum, because, such a change would require a third body that is able to “pay” for the spin change energy. Hence, in the absence of solvent effects, the reactions for (F,H), (Cl,H), and (Br,H) should be spin-forbidden processes that proceed through the corresponding MECP.

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