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Journal of Photochemistry and Photobiology A: Chemistry 157 (2003) 1–4

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Frontier orbitals control in the reactivity of singlet oxygen with lignin model compounds
An ab initio study

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Received 14 October 2002; received in revised form 2 December 2002; accepted 20 January 2003

Abstract

The photochemical oxidation of lignin models in the presence of singlet oxygen was studied by using ab initio calculations. The treatment of the non-phenolic β-*O*-4-aryl ether derivatives **1** [4-ethoxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone], **2** [1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanone], and **3** [1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanol] gave products deriving from a formal β-C–O cleavage formation. The reaction occurred in low yields when a 2,6-dimethoxyphenol derivative **2** is used. When the phenoxy part of the molecule showed a lower reactivity towards singlet oxygen [1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-propanol, **5**], the oxidation of the phenol moiety can occur. These results can be interpreted assuming a frontier orbitals control between the HOMO of the lignin model and the LUMO of singlet oxygen. In fact, in the case of the compounds **1**, **2**, and **3** the HOMOs show almost the same value and it is localized mainly on the phenoxy part of the molecule. In the case of compound **4** the HOMO shows higher energy than in the other model compounds. In compound **5** the HOMO is mainly localized on the phenolic part of the molecule.

Keywords: Lignin; Singlet oxygen; Frontier orbitals

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1. Introduction

Some years ago we reported that several β-*O*-4-aryl ether model compounds (Fig. 1) react with singlet oxygen to give interesting reaction products: in fact, we observed that the reactions occurred mainly on the phenoxy part of the molecule while the other part was not involved in the oxidation process [1,2]. Furthermore, when dimethoxy derivatives were used, only in this case the oxidation reactions occurred on the other part of the molecules.

This behavior could represent only an unusual chemical reactivity of the sample we used. However, more recently, we reported that the kinetics of singlet oxygen degradation of lignin depends on the presence of syringyl and guaiacyl units, being guaiacyl units more oxidizable than the other one [3].

Furthermore, we showed also that the treatment of lignin with singlet oxygen allowed to obtain variable amounts of some fine chemicals such as *trans*-sinapyl alcohol, 4-hydroxy-3, 5-dimethoxybenzaldehyde, 4-hydroxy-3, 5-dimethoxyphenylacetone, 4-hydroxy-3-methoxybenzalde-hyde, *cis*-sinapyl alcohol, and sinapyl aldehyde (Fig. 2) [4].

Most of these compounds derived from syringyl units in lignin, showing that guaiacyl units could be more easily oxidized than syringyl units. The only difference in the structure of these units is the presence of an additional methoxy group in the structure.

On the basis of these results we decide to study the reason of the different reactivity of these types of substrates towards singlet oxygen. We tested if the reactions of the above described model compounds could be explained assuming a frontier orbitals control. Frontier orbital control has been assumed in the ene reaction of singlet oxygen with alkenes, while it has not been considered in the reaction with phenolic compounds [5]. With this purpose we performed this ab initio study.

2. Results and discussion

The irradiation of **1** in the presence of Bengal Rose as sensitizer gave 2-methoxyphenol (**12**) as the main product

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doi:10.1016/S1010-6030(03)00068-6

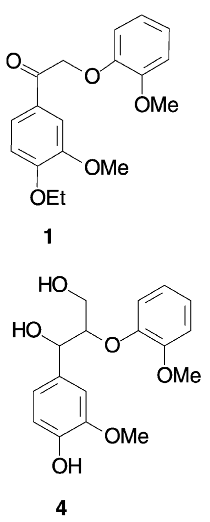
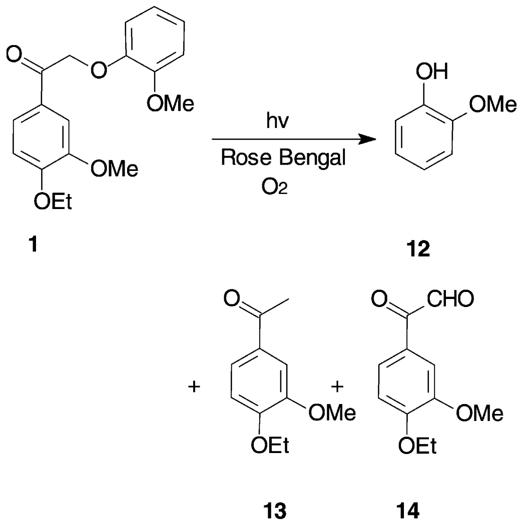


Fig. 1. Model compounds used in the reaction with singlet oxygen.



Scheme 1. Reaction with singlet oxygen of model compound **1**.

(51%), while the other products were 3-methoxy-4-ethoxyacetophenone (**13**) (8%) and (3-methoxy-4-ethoxy-2-phenyl)-2-oxoacetaldehyde (**14**) (15%) (Scheme 1) [1,2].

We performed some ab initio calculations using 6-31G** basis set on Gaussian 94, using UHF method. The calculations were usually done using Møller–Plesset perturbations (MP2). The Polak–Ribiere algorithm with gradient calculations was adopted for geometry optimizations. The open-shell states were treated at the same level of accuracy as the closed-shell states. We verified that the obtained structures were minima on the potential energy surfaces calculating the frequencies of the optimized structures.

Singlet oxygen showed the HOMO at −10.73 eV and the LUMO at −0.98 eV. Compound **1** had the HOMO at −8.83 eV and the LUMO at −0.66 eV. Therefore, the best interaction can be obtained between the HOMO of **1** and the LUMO of singlet oxygen. The atomic coefficients on the oxygen atoms of the singlet oxygen LUMO were 0.69 and −0.69 eV. The HOMO of **1** is represented in Fig. 3.

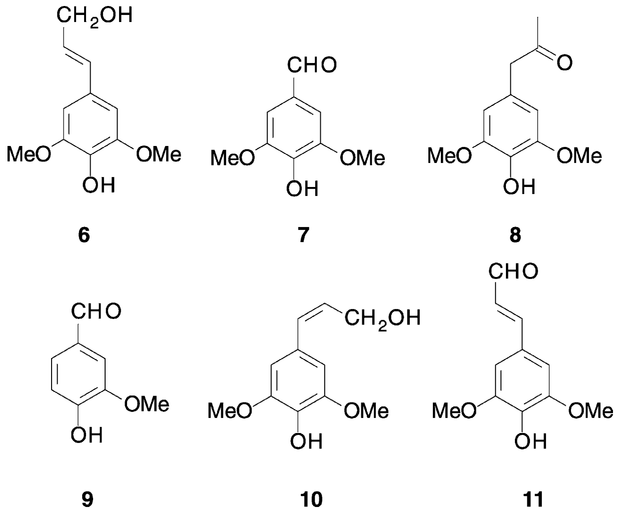


Fig. 2. Compound isolated in the residue of singlet oxygen degradation of a steam exploded lignin.

The analysis of Fig. 3 clearly showed that this orbital is restricted on the phenoxy part of the molecule. This result is in agreement with the experimental data showing that the reaction afforded a β-C–O cleavage involving the phenoxy part of the molecule. Interaction between the LUMO of singlet oxygen and this orbital could occur to give 1,2 addition to the O–C_{arom} bond or to give 1,4 addition to C_1 and C_4 atoms or to C_2 and C_5 atoms.

In our previous work we reported that the treatment of β-*O*-4-(2′,6′-dimethoxyphenyl ether) **2** in the presence of singlet oxygen gave degradation products in ca. 15% extent (Scheme 2) [2]. The main products (**15**, **13**, and **14**) were in a 2:1:3 ratio, respectively. In this case, the same β-C–O cleavage reaction occurred. However, the reactivity of the substrate was lower than in the previous case.

Ab initio calculations on compound **2** showed the HOMO orbital at −9.18 eV and the LUMO at −0.45 eV. The prevalent interaction will be between the HOMO of **2** and the LUMO of $^1O_2$. This result is in agreement with the observed low reactivity of **2** towards singlet oxygen. The HOMO of **2** is represented in Fig. 4.

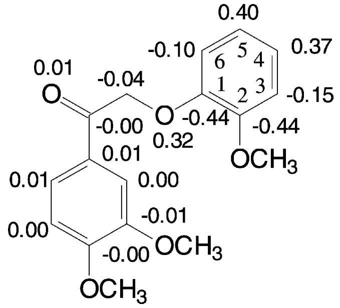
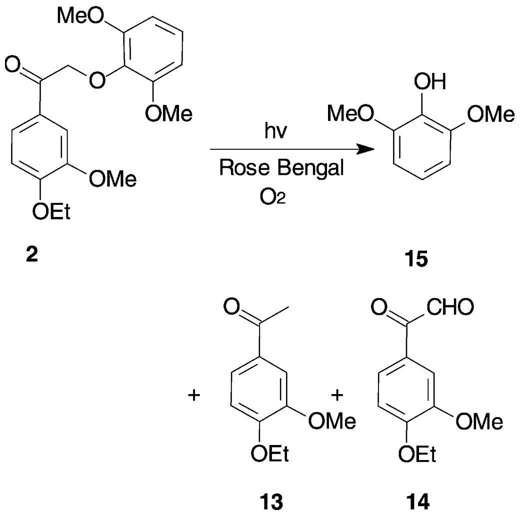


Fig. 3. Atomic coefficients in the HOMO of **1**.



Scheme 2. Reaction with singlet oxygen of model compound **2**.

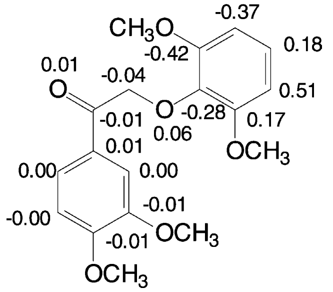
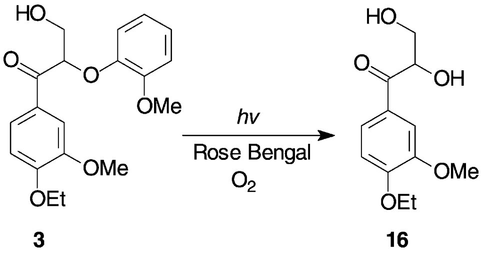


Fig. 4. Atomic coefficients in the HOMO of **2**.

Fig. 4 clearly showed that, also in this case, the orbital is restricted on the phenoxy part of the molecule. The superposition between the LUMO of singlet oxygen and this orbital could occur to give 1,2 addition to the O–C_{arom} bond (with lower efficiency than in the previous case) or to give 1,4 addition to C_2 and C_5 atoms. The interaction between the LUMO of singlet oxygen and the HOMO of **2** can occur also in order to give 1,4 addition of C_1 and C_4 atoms but, also in this case, with lower efficiency than in the previous case.

The irradiation of **3** under the same conditions described above gave the compound **16** in high yields (70–80%) (Scheme 3). In this case, no phenolic product was observed.

Calculations gave results in agreement with experimental results. The HOMO of **3** showed an energy level of −8.99 eV and this result is in agreement with the higher reactivity observed with **3** in comparison with **2**. The LUMO of **3** showed an energy of −0.70 eV. Furthermore the atomic coefficients of the HOMO (Fig. 5) allows both the interactions of the LUMO of singlet oxygen with both O–C_{arom} and C_1–C_4.



Scheme 3. Reaction with singlet oxygen of model compound **3**.

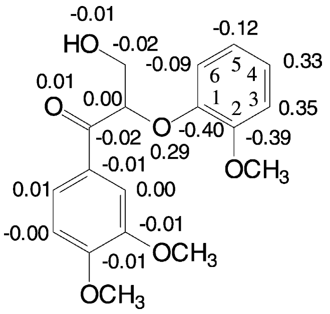


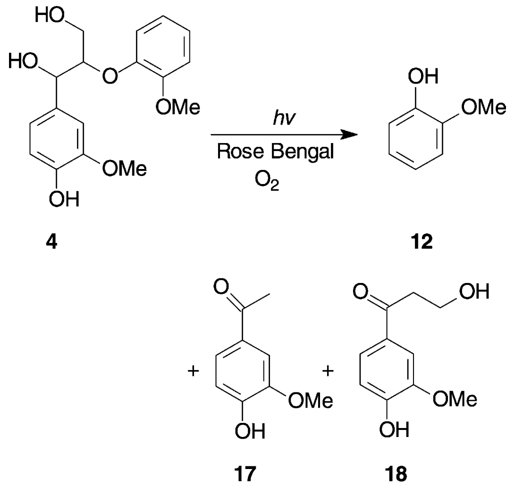
Fig. 5. Atomic coefficients in the HOMO of **3**.

The compounds **1–3** showed a carbonyl group: an alternative mechanism to the endoperoxide formation would be an ene reaction through the enol form of **1–3**. The enol formation in **1–3** can be promoted by the use of the anionic sensitizer which serves as a hydrogen bond acceptor [6,7]. In order to verify this hypothesis, we performed some calculations on **1** and **2**. The enol form of **1** showed the HOMO at −8.54 eV and the LUMO at −0.38 eV. The prevalent interaction will be that between the HOMO of **1** and the LUMO of singlet oxygen. The atomic coefficients on the HOMO were in agreement with a possible interaction: in fact, the atomic coefficient of β-carbon was 0.39, that of α-carbon 0.35, and that of enolic oxygen −0.23. The HOMO of **2** was obtained at −8.55 eV: the atomic coefficients of the HOMO showed the same trend observed in **1** (β-carbon −0.44, α-carbon −0.31, and enolic oxygen 0.22). However, this result is not in agreement with the observed lower reactivity of **2** towards singlet oxygen than **1**. On the basis of this result we can exclude a possible ene mechanism in the reaction of lignin model compounds with singlet oxygen.

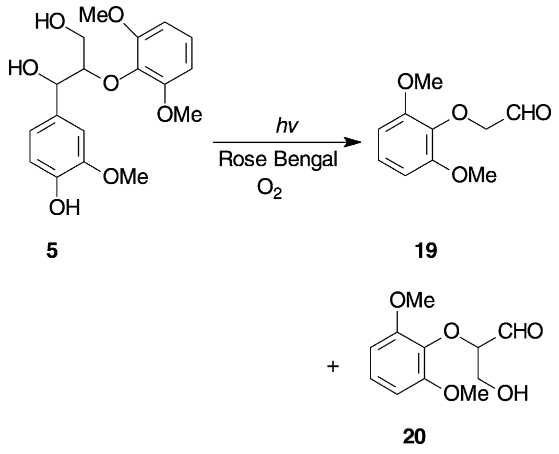
Our attention was then focused on the photochemical reactivity of the phenolic compounds **4** and **5**. Since these lignin models do not show the carbonyl group, we verified whether the same type of reactions could be observed also in this case. After the irradiation of the compound **4** in acetonitrile in the presence of both oxygen and Rose Bengal, we observed the formation of the phenol **12** (15%), acetovanillone (**17**) (30%) and 1-(3-methoxy-4-hydroxyphenyl)-3-hydroxy-1-propanone (**18**) (28%) (Scheme 4).

This result is in agreement with the above reported data, showing that the reactivity of singlet oxygen towards this type of molecules is due to an attack on the phenoxy moieties. In fact, in this case, the absence of the carbonyl group did not affect the reactivity of the substrate. It is noteworthy that the presence of an easily oxidizable phenolic function in **4** did not modify the reactivity pattern of the substrate.

The HOMO of compound **4** is represented in Fig. 6. This orbital showed the same energy of **3** (−8.89 eV). In this



Scheme 4. Reaction with singlet oxygen of model compound **4**.



Scheme 5. Reaction with singlet oxygen of compound **5**.

case the LUMO was at 0.04 eV. The prevalent interaction, as with the previous described compounds, is between the HOMO of **4** and the LUMO of singlet oxygen. Also in this case the orbital is mainly localized on the phenoxy part of the molecule. The atomic coefficients allow the interaction between the LUMO of singlet oxygen with O–C_{arom}, C_1–C_4, and C_2–C_5 in the HOMO.

Compound **5** showed a different behavior. In fact, the irradiation of **5** in the presence of oxygen and Rose Bengal gave (2,6-dimethoxypheno-xy)acetaldehyde (**19**) (53%) and 2-(2,6-dimethoxy-phenoxy)-3-hydroxy-propanal (**20**) (41%) (Scheme 5).

The reactivity of the phenoxy part, in agreement with the above reported results, was found depressed and the photochemical reaction occurred on the phenolic moiety. In this case, the known reactivity of phenols towards singlet oxygen to give quinones and further oxidation products can account for the observed reactivity.

Calculations in this case gave the following results: compound **5** showed the HOMO at −9.02 eV while the LUMO was at −0.09 eV. The interaction with singlet oxygen can occur between the HOMO of **5** and the LUMO of $^1O_2$. The HOMO of **5** is represented in Fig. 7.

The results reported in Fig. 7 clearly show that in this case the HOMO is mainly localized on the phenolic part of the molecule, in agreement with the experimental results. The interaction between the LUMO of singlet oxygen and the HOMO of **5** can occur with HO–C_{arom} or with HOC_{arom}–$C_{arom}OCH_3$.

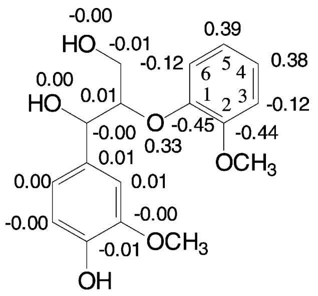


Fig. 6. Atomic coefficients in the HOMO of **4**.

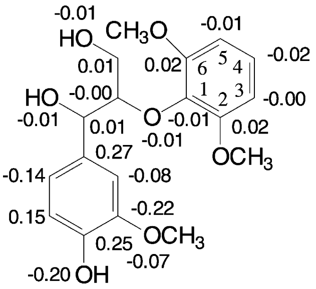


Fig. 7. Atomic coefficients in the HOMO of **5**.

In conclusion the results of this study are in agreement with a frontier orbitals control in the reaction of singlet oxygen with lignin model compounds. In fact, we observed a perfect superposition between theoretical and experimental results. Furthermore, these results confirm that 2,6-dimethoxyphenol moiety in lignin is not a suitable substrate for singlet oxygen and this is in agreement with both the kinetic results and the isolation of residual compounds after singlet oxygen treatment of steam exploded lignin [3,4].

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