

R E V I E W

## Non-sensitized photooxygenation of organic compounds

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### 1. INTRODUCTION

The light induced oxygenation of organic compounds is of great importance in many aspects. It includes the oxidative degradation of biologically significant compounds, the use of photooxidative reactions in synthesis, as well as attempts to discover the ways to suppress the reaction in order to improve the mechanical durability of synthetic polymers (in surface coatings, polypropylene products, etc.).

There are two mayor types of photooxygenation reactions — direct and photosensitized. In the former, the compound absorbing the light undergoes its own oxidative destruction. In the latter, certain compounds, *sensitizers*, capable of generating efficiently excited triplet state, transfer their electronic energy to oxygen, giving rise to a considerable concentration of excited singlet oxygen. This singlet oxygen is the efficient oxidizing agent.

The vast majority of publications in the field are concerned with the reactivity of singlet oxygen.<sup>1-9</sup> The mechanism of sensitized photooxygenation is known in detail.

The mechanism of direct photooxygenation was very puzzling for a rather long time, and in the early publications many reaction mechanisms (sometimes very strange) were invoked to explain particular cases.<sup>10</sup>

Our aim is to review the results concerning direct, nonsensitized photooxygenation.

There are two mayor ways for direct photooxygenation to take place:

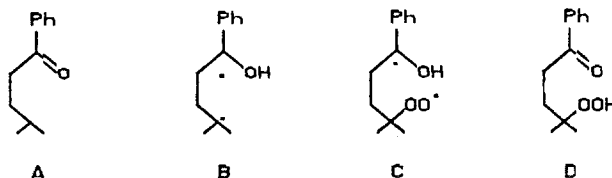
First: A substrate absorbs light. Then, from its excited singlet or triplet state it may directly react with oxygen. More frequently, a dissociation or atom transfer occurs, and free radicals or carbenes are formed, which then react with oxygen.

Second: A charge-transfer complex between the substrate and oxygen due to light absorption is formed. Thus formed exciplexes can relax in different ways. (A variant of this mechanism involves the formation of an exciplex between the oxygen and some catalyst, and intermediate products accomplish the oxygenation.)

## 2. NONSENSITIZED PHOTOOXYGENATION OF THE FIRST TYPE

### *Reaction of the excited substrate with oxygen*

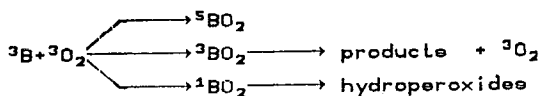
Small and Scaiano<sup>11</sup> demonstrated that triplet biradical (B in Scheme 1) formed in the Norrish type II reaction of alkyl-phenyl ketones (A, Scheme 1) can react with triplet oxygen.



Scheme 1

They found that the photolysis of these ketones (A) in the presence of oxygen gives hydroperoxides (D) and cyclization or fragmentation products in the ratio 1:3. These results are explained by assumption that the triplet biradical (type B in Scheme 1) reacts with triplet oxygen:

Due to the combination of two triplet-state moieties, an intermediate complex can have corresponding singlet, triplet, and quintet multiplicities:



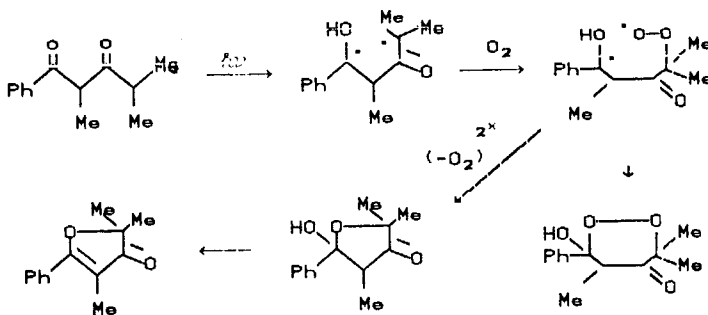
Scheme 2

The quintet state (with statistical probability 5/9) is strongly dissociative and cannot give any chemical product. The triplet state (probability 3/9) would account for the formation of fragmentation and cyclization products with regeneration of triplet-state oxygen, while the singlet state (probability 1/9) would yield hydroperoxides in the ground state.

Obviously the probability of the formation of oxygenation products from the excited triplet state of the substrate is relatively low (1/9). Yet, compounds which efficiently generate excited triplet states may react with triplet oxygen at a reasonable rate. This can explain, at least partially, the observed photobleaching of dyes which do not react with singlet oxygen.

Many authors have paid no attention to this possibility, and there are examples of rather complicated mechanisms invoked to explain photooxygenation of dyes.<sup>12,13</sup>

Photolysis of 1,3-diones under nitrogen gave type II cyclization products from their triplet states. When the photolysis took place in the presence of oxygen,<sup>14</sup> no Norrish type II product were formed (Scheme 3).



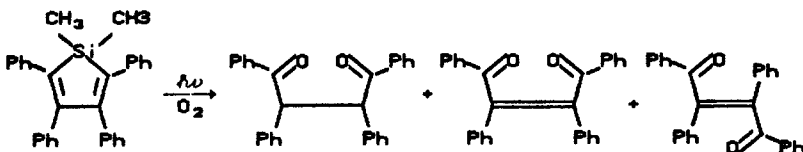
Scheme 3.

As can be seen, oxygen serves as a scavenger for the biradicals formed in the type II photolysis reaction.

This is in sharp contrast to the mechanism given in Scheme 2.

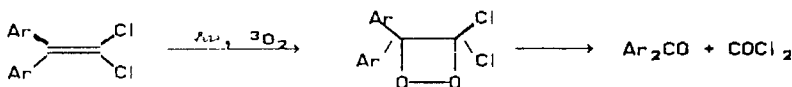
#### Reactions of the photolysis products with oxygen

The possibility of the direct formation of endoperoxide was proposed in the paper of Sato *et al.*<sup>15</sup> They found that the photooxygenation of silole derivatives yields, among the other oxidation products, a minor amounts of *E* and *Z* stilbene derivatives (Scheme 4).



Scheme 4

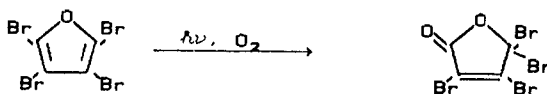
Few years later the photooxygenation of olefins with triplet oxygen, yielding dioxetane, was reported:<sup>16,17</sup>



Scheme 5

It was proved that this olefin does not react with singlet oxygen.

Examples are known when the substrate upon photolysis generates free-radicals that then readily react with triplet oxygen. For example, radicals, produced by the photolysis of tetrabromofuran, react with oxygen.<sup>18</sup> A mechanism involving the singlet oxygen was proposed, but with no reason given for singlet oxygen formation. An alternative mechanism was also proposed involving photo-cleavage of the C-Br bond, and radicals subsequently react with O<sub>2</sub> in ground state (Scheme 6).

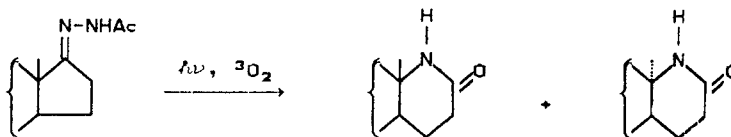


Scheme 6

In a subsequent paper on the same topic<sup>19</sup> Shoppee and Wu described strictly nonsensitized photooxygenation of tetrabromofuran, and the only product found was dibromomaleic anhydride. The possible mechanism involves the double elimination of bromine atoms and formation of a triplet biradical that is quenched with triplet oxygen.

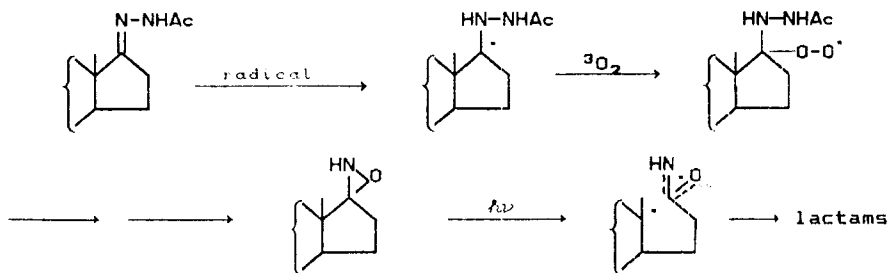
The photochemically produced radicals may abstract the hydrogen atom from substrate, yielding new radicals which then react with molecular oxygen. The photochemically produced  $\text{BzO}^\cdot$  radicals can induce the oxygenation of alkylaromates.<sup>20</sup> Similarly, the photochemically produced phenylthio radical induces  $^3\text{O}_2$  oxygenation of different phenylcyclopropanes.<sup>21</sup>

A study of the photolysis of some steroidal acetylhydrazones in the presence of oxygen<sup>22,23</sup> showed that this reaction yields a complex mixture of products. A number of products are identified and they are mostly lactams (Scheme 7).



Scheme 7

The mechanism was defined as follows<sup>23</sup>



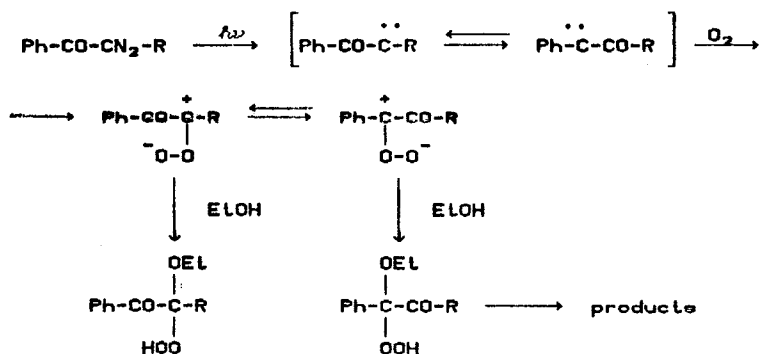
Scheme 8

The photoexcitation of some carbonyl compounds can initiate radicals formation.

Formation of epoxide (analogous to the intermediate oxaziridine) was detected after the prolonged irradiation of diosgenin in an acetone solution in the presence of  $\text{O}_2$ .<sup>24</sup>

Activation of the oxidation reaction by the photochemically generated radical was experimentally studied during the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  facilitated by the photolysis of  $\text{H}_2\text{CO}$ .<sup>25</sup>

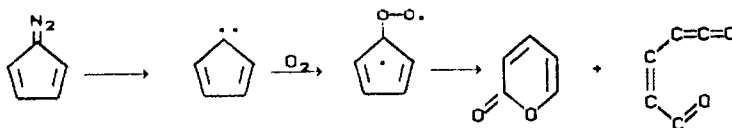
Diazoketones can be easily activated by photolysis (Scheme 9).<sup>26</sup>



Scheme 9

The intermediary formed carbene reacts with oxygen giving hydroperoxy derivatives that subsequently transform to final products.

Analogously photooxygenation of diazocyclopentadiene results in ring cleavage (Scheme 10).<sup>27</sup>



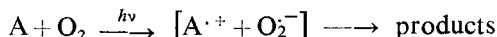
Scheme 10

Alkyl and alkenyl halogenides may give free radicals by photolysis. These radicals readily react with oxygen. Such a process is enhanced by the presence of  $\text{NO}$ , or ozone,<sup>28</sup> and it can serve as a path for the transformation of organic impurities in atmosphere.

### 3. NONSENSITIZED PHOTOOXYGENATION OF THE SECOND TYPE

#### *Formation of triplet exciplexes*

The other class of nonsensitized reactions involves the charge transition between the substrate and oxygen upon light absorption, as shown in the following equation:



The reliability of the CT mechanism can be justified by the following considerations.

The formation of radical-ion pairs is well known in the photochemistry of singlet exciplexes.<sup>29,30</sup> The wave function for the excited state is described as:

$$\Psi = c_1 (A^*D) + c_2 (AD^*) + c_3 (A^{\cdot+}D^{\cdot-})$$

Triplet exciplexes can be treated in a similar way, but  $c_1$  and  $c_2$  are always much smaller than  $c_3$ .

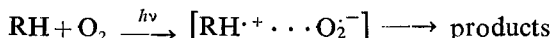
In a substrate-oxygen complex in the ground state the only attraction is due to the London forces. Namely, in the triplet state the exchange interactions are repulsive.<sup>31</sup> The result is that in the ground state only a loose complex can be formed between substrate and oxygen.

Repulsion potential is practically the same in the excited triplet state as in the ground state. MNDO calculations<sup>32,33</sup> show that the last energy transition in the  $X \cdots O_2$  complex is between HOMO, which is practically completely located on substrate moiety, and one of the SOMO orbitals on oxygen. In this way, the excitation is accompanied by the practically complete electron transfer from the substrate to oxygen. Excited states have a highly dipolar character and the two moieties, although not covalently bonded, are mutually attracted by a strong electrostatic force.

The potential energy curve for the excited triplet state can be evaluated by superposition of the ground state repulsive potential and electrostatic attraction of two moieties. The depth of the PE minimum for the excited state can be evaluated as more than 100 kJ/mol. This can account for the considerably high stability of oxygen-substrate exciplex. It provides a relatively long lifetime, enabling different relaxation paths, such as the spin flip, hydrogen ion migration, etc.

Oxygenations in the dark are also well known.<sup>35-41</sup> The mechanism outlined above can also be valid for these oxygenations if it could be proved that nonpolar and CT PE curves cross not far from the equilibrium distance for nonpolar structure.

Chien<sup>42</sup> reported a detailed study of the photooxidation of alkanes and aromatic compounds. A long wavelength tail absorption was detected. It was proportional to the oxygen concentration, and was explained as contact charge-transfer absorption.

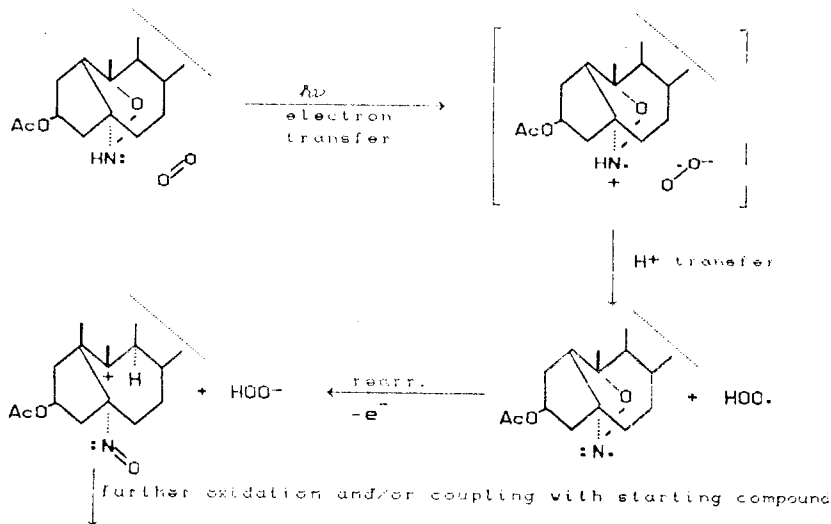


The fate of the intermediate pair of ion-radicals was not discussed in detail. It was found that hydroperoxides are formed as intermediates. The rate of photooxidation was found to be dependent on the energy of the weakest C-H bond in alkane (as calculated by the INDO method<sup>43</sup>).

The same mechanism was proposed for the photooxidation of ethers with oxygen.<sup>44-47</sup> A long wavelength tail in the UV spectra of ethers was detected.<sup>45</sup> Maeda *et al.*<sup>47</sup> monitored the changes in the ESR spectrum of an ether-oxygen mixture. Formation of the alkylperoxy radical was detected. The yields of the reaction products of the prolonged irradiation of diethyl ether with oxygen were determined. Kulevsky *et al.*<sup>47</sup> found that the rates of oxygen uptake during the photochemical oxidation of acyclic and cyclic ethers correlates with their orders of basicity. Finally, Stenberg *et al.*<sup>44</sup> have synthesized the suspected intermediate peroxide in the photooxidation reaction of tetrahydrofuran, and found that its thermal decomposition gives rise to all the products found in the photochemical reaction.

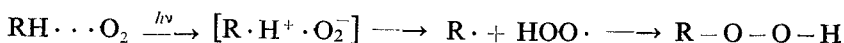


It was proven that Methylene blue and Crystal violet are inefficient in inducing oxygenation, indicating that the reaction does not proceed by the intermediacy of singlet oxygen. These results are consistent with the mechanism that involves, as the primary photoprocess, electron transfer from the substrate to molecular oxygen. The exciplex thus formed undergoes internal proton transfer to give the isoxazolidine radical and hydroperoxy radical (Scheme 12).



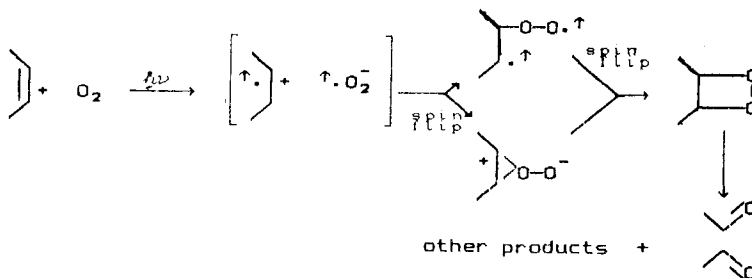
Scheme 12

This mechanism is also applied in the interpretation of the photooxidations of alkanes:<sup>59</sup>



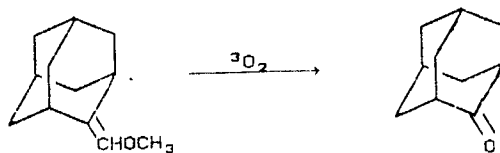
In experiments on the photooxygenation of nitrobenzyl ether derivatives, stable  $\alpha$ -hydroperoxy nitrobenzyl ethers were isolated.<sup>60</sup> It was shown that photooxygenation proceeds much faster and more efficiently at higher pH. Formation of benzylic anions can cause a rise in energy of the highest doubly occupied MO of the substrate resulting in a more efficient charge-transfer.

Along with the mechanism of photooxygenation of alkenes and alkynes proposed by Barton *et al.*<sup>10,77</sup> (to be presented in the last section), a number of articles<sup>37,61-64</sup> consider an alternative (and more reasonable) mechanism (Scheme 13).



Scheme 13

The reaction of olefins with triplet oxygen was studied on several systems. Meijer and Wynberg<sup>65</sup> reported the formation of chemiluminescent intermediate in the triplet oxygen oxygenation of methoxymethyleneadamantane. The only product in this reaction was the corresponding adamantanone (Scheme 14):



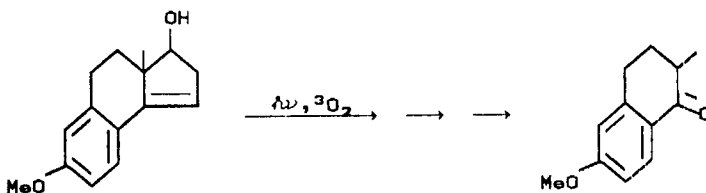
Scheme 14.

Analogous products were found in the photooxidation of dialkyl ethers,<sup>46</sup> but no chemiluminescence was reported.

It was reported that the nonsensitized photooxygenation of  $\beta$ -ionone<sup>66</sup> and diosgenin<sup>24</sup> gives high yield of the corresponding epoxides.

Very similar results were obtained with several other electron-rich olefins. An interesting is the mechanism outlined in the paper of Turro *et al.*<sup>64</sup> on the reaction of strained acetylene oxygenation. It was found that strained acetylenes readily undergo photooxygenation with triplet oxygen. The proposed mechanism involves the formation of a loose triplet complex that can give singlet intermediates by a spin flip. This spin flip is associated with the electron transition between two  $p$ -orbitals in oxygen, thus giving a complex between the singlet oxygen and the substrate. This singlet complex can give several products similar to those presented in Scheme 13. The authors found that the only difference between oxygenation by singlet and by triplet oxygen was in several order of magnitude higher rate of reaction with the former one.

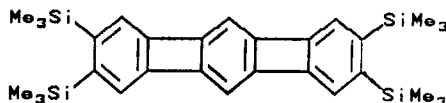
Nonsensitized photooxidation of styrene derivatives gives analogous products (Scheme 15)<sup>67</sup>



Scheme 15

According to the authors, the reaction appears to be autosensitized.

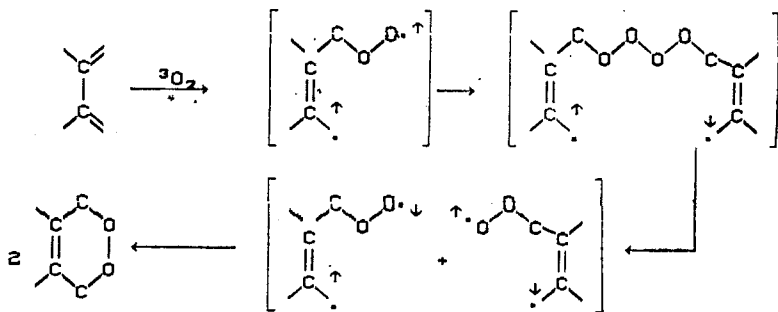
Another nonsensitized oxygenation of electron-rich olefins is reported by Mestdagh and Vollhardt:<sup>68</sup>



Scheme 16

It was pointed out that 2,3,7,8-tetrakis(trimethylsilyl)benzo[3,4]cyclobuta [1,2-b]-biphenylene (Scheme 16) can react both with singlet and with triplet oxygen. During oxidation the central ring is opened, and corresponding aromatic ketones and non-benzenoid quinones are formed. A very similar reaction was found with tetraphenylbenzo[1,2:4,5]dicyclobutadiene where one cyclobutadiene ring opens giving *o*-quinomethide,<sup>37</sup> and with *trans*-1,2,3,4-tetramethyl-3,3-bis(phenylethynyl)cyclobutene that adds oxygen and rearranges upon heating giving aromatic diketones and keto-esters.<sup>38</sup>

There is a limited number of *cis,cis* dienes which can form endoperoxides spontaneously by reaction with triplet oxygen. For these reactions a rather peculiar mechanism, shown in Scheme 17, is proposed.<sup>10</sup>



Scheme 17.

The study of the photooxidation of polymer materials is very important. These investigations usually are concerned with the rate and extent of the oxygen uptake upon irradiation in an oxygen atmosphere.<sup>69-76</sup> No doubt, there is a non-sensitized photooxygenation in effect, and it can be explained by the CT mechanism.

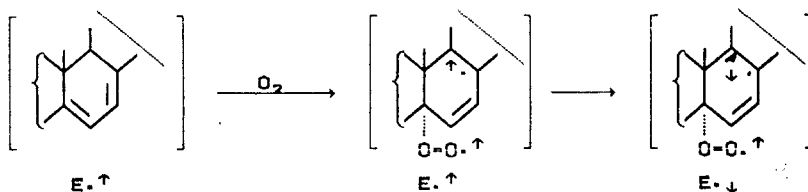
An analytical study of photodegraded Kevlar (an aromatic polyamide) in  $^{18}O_2$  atmosphere was reported.<sup>76</sup> Photooxidation rates were determined under experimental conditions of accelerated oxidation under daylight exposure. The authors presume that oxygen insertion in an amide bond and endoperoxide formation can occur.

Investigations on poly(ether-*block*-amide)s<sup>75</sup> and poly(*n*-butyl-acrylate)<sup>74</sup> have confirmed the formation of hydroperoxides and hydroperoxy radicals.

#### *Direct photooxygenation in the presence of Lewis acids or cation-radicals*

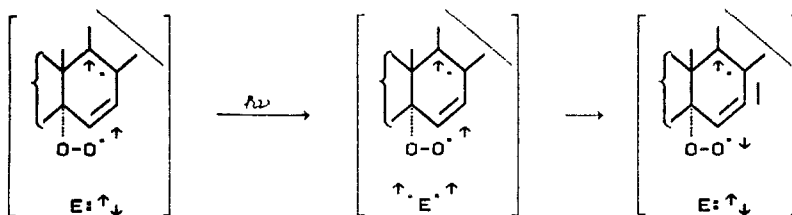
Barton and coworkers<sup>10,77</sup> have made a detailed examination of the photo- and thermal oxygenation of ergosteryl acetate. They found that Lewis acids catalyze the formation of endoperoxides in photochemical as well as thermal reactions. It was proposed that an adduct is formed between diene and triplet oxygen. The spin inversion can be promoted by interaction with the catalyst.

When a stronger electrophile is used it can be reduced by a certain Lewis base, and give the corresponding radical anion. This species with unpaired spin can also promote spin flip and catalyze the formation of hydroperoxides (Scheme 18).



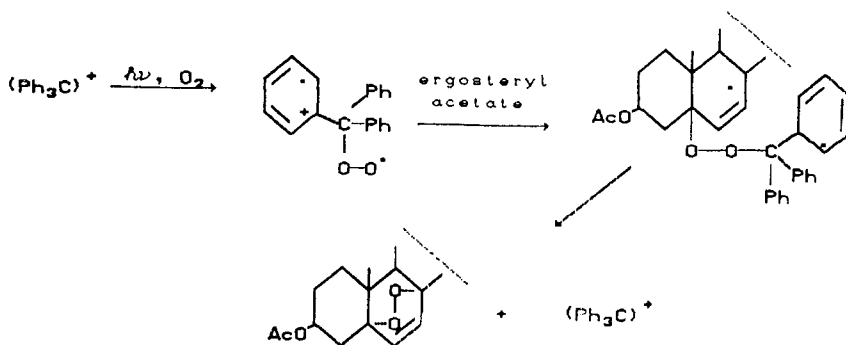
Scheme 18

Weaker electrophiles need photochemical excitation to their triplet state and then it can be annihilated with the triplet state of diene-oxygen adduct (Scheme 19).



Scheme 19

Ergosteryl acetate endoperoxide was obtained by photooxygenation in the presence of tris(*p*-bromophenyl)ammoniumyl tetrafluoroborate,<sup>78</sup> and of triphenylmethyl cation.<sup>77</sup> In the first case, charge-transfer complex between ammonium salt and diene is formed upon photooxidation. Diene radical-cation moiety, then reacts with oxygen. In the second case the intermediate formation of a triphenylmethylperoxide cation was proposed (Scheme 20):



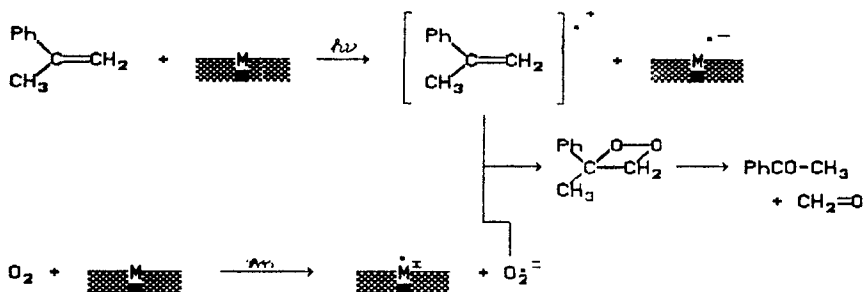
Scheme 20

The same mechanism is used in the work of Nelsen *at al.*,<sup>79</sup> to explain the oxygenation of biadamantylidene catalyzed by tris[2,4-dibromophenyl]ammoniumyl hexachloroantimonate.

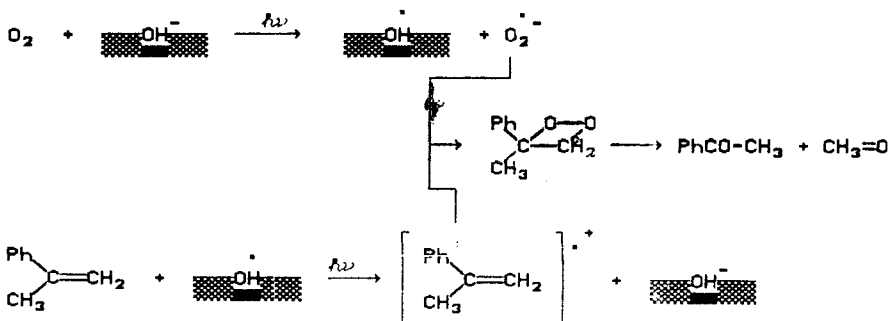
This specific type of cation radical catalyzed chain oxygenations of alkylated olefins and dienes is reviewed in the work of Nelsen.<sup>80</sup>

A specific case of Lewis acid catalyzed photooxygenation was found when the photolysis of olefins adsorbed on silica or alumina was studied.<sup>63,81</sup> Here, the surface of the adsorbent serves as the charge-transfer mediator for the catalysis of oxygenation. Two mechanisms are outlined:

For acidic solids:



For basic solids:



When 1,1-diphenylethylene, and its derivatives were used as substrate,  $\text{Ph}_2\text{CO}$  and corresponding epoxides were obtained.<sup>82</sup>

A study on the photooxidation of organic impurities in water using thin film of titanium dioxide was reported<sup>83</sup> as a possible efficient method for the purification of water.

Almost the same mechanism was proposed for the photoactivated reaction of CO with  $\text{O}_2$  on a silica gel surface.<sup>84</sup>

#### 4. CONCLUSION

Nonsensitized photooxygenation is a frequently encountered reaction. There is no doubt that it plays an important role in a number of processes such as the aging of materials, autooxidation of organic substances, oxidative degradation of organic impurities in water, *etc.* Although this type of reaction has

not been completely investigated, a mechanism that can be outlined that includes the formation of a C-T complex between oxygen and the substrate. Such a mechanism is compatible with all experimental data, and can be easily adapted for cases when pH or additives affect the reaction rate or reaction path.

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#### SUMMARY

The nonsensitized reactions of organic compounds with triplet oxygen are reviewed. Several mechanisms are outlined. The formation of triplet exciplexes between organic substrate and molecular oxygen is discussed in detail. This appears to be the most general and simplest mechanism of the photooxygenation without sensitizer.

#### ИЗВОД

#### НЕСЕНЗИБИЛИЗОВАНЕ ФОТООКСИГЕНАЦИЈЕ ОРГАНСКИХ ЈЕДИЊЕЊА

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Дат је преглед несензибилизованих реакција органских једињења са триплетним кисеоником. Скицирано је неколико механизма. Детаљно је дискутовано формирање триплетних ексциплекса између органских супстрата и молекулског кисеоника. То је, по свему, најопштији и најједноставнији механизам фотооксигенације без присуства сензибилизатора.

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