Surface-Doped Graphitic Carbon Nitride Catalyzed Photooxidation of Olefins and Dienes: Chemical Evidence for Electron Transfer and Singlet Oxygen Mechanisms

Apostolos Chatzoudis \(^1\), Vasileios Giannopoulos \(^1\), Frank Hollmann \(^2\) and Ioulia Smonou \(^1,\)*

\(^1\) Department of Chemistry, University of Crete, University Campus-Voutes, 71003 Heraklion, Crete, Greece  
\(^2\) Department of Biotechnology, Biocatalysis Group, Delft University of Technology, Van der Maasweg 9, 2629HZ Delft, The Netherlands  
* Correspondence: smonou@chemistry.uoc.gr; Tel.: +30-2810545010

Received: 2 July 2019; Accepted: 25 July 2019; Published: 27 July 2019

Abstract: A new photocatalytic reactivity of carbon-nanodot-doped graphitic carbon nitride (CD-C\(_3\)N\(_4\)) with alkenes and dienes, has been disclosed. We have shown that CD-C\(_3\)N\(_4\) photosensitizes the oxidation of unsaturated substrates in a variety of solvents according to two competing mechanisms: the energy transfer via singlet oxygen (\(1^\text{O}_2\)) and/or the electron transfer via superoxide (O\(_2^\cdot\)). The singlet oxygen, derived by the CD-C\(_3\)N\(_4\) photosensitized process, reacts with alkenes to form allylic hydroperoxides (ene products) whereas with dienes, endoperoxides. When the electron transfer mechanism operates, cleavage products are formed, derived from the corresponding dioxetanes. Which of the two mechanisms will prevail depends on solvent polarity and the particular substrate. The photocatalyst remains stable under the photooxidation conditions, unlike the most conventional photosensitizers, while the heterogeneous nature of CD-C\(_3\)N\(_4\) overcomes usual solubility problems.

Keywords: photocatalyst; photosensitizer; graphitic carbon nitride; singlet oxygen; photooxidation mechanism; ene products

1. Introduction

Graphitic carbon nitride (g-C\(_3\)N\(_4\)) is recently one of the most studied heterogeneous, metal-free photocatalysts. g-C\(_3\)N\(_4\) is a polymeric material, composed of highly abundant elements such as carbon and nitrogen, thermally stable and nontoxic. Ever since the synthesis of this material in bulk quantities \([1–3]\), a large number of reports concerning the photochemical properties and photocatalytic activity were published. Next, the demand to optimize the photocatalytic properties of g-C\(_3\)N\(_4\) was inevitable. The relatively low band gap energy \(E_g\) of 2.7 eV and high conduction and valence bond positions of the photocatalyst \([4]\) prompted many research groups to improve the photocatalytic activity of g-C\(_3\)N\(_4\). This was achieved by doping the surface of the catalyst with a variety of metallic elements \([3,5–11]\), oxides \([12,13]\), sulfides \([14]\) even graphene \([15]\) and carbon nanotubes \([16]\).

It is important to note here that structure-controlled g-C\(_3\)N\(_4\) is a highly efficient photocatalyst for water splitting to produce hydrogen, in an internal quantum yield of 26.5% under visible light \([17]\). In a more recent article \([18]\), the metal-free carbon-nanodot-doped graphitic carbon nitride (CD-C\(_3\)N\(_4\)) impressively photocatalyzed the water splitting via a two-electron mechanism. Although many studies concern the photochemical activity and spectroscopic data analysis of g-C\(_3\)N\(_4\) as well as modification of its surface \([19]\), applications to organic transformations are limited. For example, graphitic C\(_3\)N\(_4\) as well as its surface-doped-materials, catalyze a few reactions; a) photoacetalization of aldehydes/ketones \([20]\)  
b) the Friedel-Crafts reaction of benzene \([21]\) c) oxidation of alcohols using transition metal doped...
1,4-diazabicyclo[2.2.2]octane (DABCO), a well-known 1O2 quencher [51,52], into the reaction mixture, Scheme 1, retarded completely the production of allylic hydroperoxides. The so produced nanodots were deposited by heating on the g-C3N4 photocatalyst. While bubbling oxygen at 20 °C, the solution was irradiated for a period of 30 min. A 300 W xenon lamp was utilized as the visible light source. The photooxidation reaction was followed by GC and/or 1H NMR analysis of product 1b, as can be seen in S2, showed identical results with those when typical singlet oxygen photosensitizers, such as rose Bengal (RB) or tetraphenyl-porphyrine (TPP), were utilized. The production of allylic hydroperoxides by the sensitized photooxygenation of alkenes, the so called “ene or Schenck” reaction, was studied several years ago, for its synthetic [43,44], mechanistic [47,48] and theoretical [49,50] point of view. Furthermore, addition of a small amount of 1,4-diazabicyclo[2.2.2]octane (DABCO), a well-known 1O2 quencher [51,52], into the reaction mixture, Scheme 1, retarded completely the production of allylic hydroperoxides. This is an additional indication of the 1O2 involvement as the reactive intermediate in the above-mentioned reaction.

**2. Results and Discussion**

In the present work, the photocatalyst g-C3N4 was prepared according to the procedure described by Tang and coworkers [45], while the carbon nanodots via thermal decomposition of sucrose [46]. The so produced nanodots were deposited by heating on the g-C3N4 surface to provide the metal-free carbon-nanodot-doped g-C3N4 (CD-C3N4). Details on the experimental conditions as well as the spectroscopic characterization are described in our previous work [30].

Photosensitized oxidations were performed in a 4 mL pyrex cell containing 0.09 M solution of 2,3-dimethylbut-2-ene (1) in a variety of solvents with 4 mg/mL of the insoluble CD-C3N4 photocatalyst. While bubbling oxygen at 20 °C, the solution was irradiated for a period of 30 min. A 300 W xenon lamp was utilized as the visible light source. The photooxidation reaction was followed by GC and/or 1H NMR analysis after filtration from celite followed by reduction of the allylic hydroperoxides with triphenylphosphine to the corresponding allylic alcohols.

We report here the unprecedented photooxygenation of alkenes utilizing CD-C3N4 as the photosensitizer. The electron rich tetramethylethylene (1) was chosen as the singlet oxygen acceptor, Scheme 1. Within a few minutes of irradiation, the allylic hydroperoxide 1a (see GC chromatograms S16, S17 and S18) was formed followed by reduction with Ph3P to the corresponding allylic alcohol 1b (GC chromatogram S19).

![Scheme 1. CD-C3N4 photosensitized oxidation of tetramethylethylene (1).](image)

The GC and/or 1H NMR analysis of product 1b, as can be seen in S2, showed identical results with those when typical singlet oxygen photosensitizers, such as rose Bengal (RB) or tetraphenyl-porphyrine (TPP), were utilized. The production of allylic hydroperoxides by the sensitized photooxygenation of alkenes, the so called “ene or Schenck” reaction, was studied several years ago, for its synthetic [43,44], mechanistic [47,48] and theoretical [49,50] point of view. Furthermore, addition of a small amount of 1,4-diazabicyclo[2.2.2]octane (DABCO), a well-known 1O2 quencher [51,52], into the reaction mixture, Scheme 1, retarded completely the production of allylic hydroperoxides. This is an additional indication of the 1O2 involvement as the reactive intermediate in the above-mentioned reaction.

**Catalysts 2019, 9, x FOR PEER REVIEW**

2 of 12

g-C3N4 [22–25] d) oxidation of sulfides to sulfoxides using oxidized g-C3N4 (CNO). In addition, selective oxidations of benzylic C-H bonds utilizing mesoporous g-C3N4 with N-OH co catalysts have been reported [26–29].

Herein, following our recent work in this field [30], we report a new approach that utilizes carbon-nanodot-doped g-C3N4 (CD-C3N4) as a visible light photocatalyst for the direct photooxidation of alkenes via the intermediacy of singlet oxygen to allylic hydroperoxides as well as the [4 + 2] cycloaddition of singlet oxygen to hexacyclodiene. We also demonstrate chemically that in CD-C3N4 photosensitized reactions, electron transfer and singlet oxygen mechanisms are in competition, depending mostly on the nature of the substrate and the polarity of the solvent. In addition, the CD-C3N4 mediated photooxygenation results were compared with those derived using conventional singlet oxygen photosensitizers.

Singlet molecular oxygen (1O2, 1∆g) plays an important role in chemical [31], biological [32,33] and therapeutic processes [34,35], as well as in the degradation of food and materials [36–38]. Historically, although 1O2 was discovered more than 80 years ago [39,40], and until the early 1960s was considered to be a molecular species of passing astrophysical interest and rather limited as a research subject. The pioneering work by Foote and Wexler [41,42], provided strong evidence for the formation of 1O2 as the reactive intermediate in photosensitized processes in solution. Today, the use of 1O2 as a reagent in organic synthesis has received remarkable attention [43,44].

---

**Catalysts 2019, 9, x FOR PEER REVIEW**

2 of 12

g-C3N4 [22–25] d) oxidation of sulfides to sulfoxides using oxidized g-C3N4 (CNO). In addition, selective oxidations of benzylic C-H bonds utilizing mesoporous g-C3N4 with N-OH co catalysts have been reported [26–29].

Herein, following our recent work in this field [30], we report a new approach that utilizes carbon-nanodot-doped g-C3N4 (CD-C3N4) as a visible light photocatalyst for the direct photooxidation of alkenes via the intermediacy of singlet oxygen to allylic hydroperoxides as well as the [4 + 2] cycloaddition of singlet oxygen to hexacyclodiene. We also demonstrate chemically that in CD-C3N4 photosensitized reactions, electron transfer and singlet oxygen mechanisms are in competition, depending mostly on the nature of the substrate and the polarity of the solvent. In addition, the CD-C3N4 mediated photooxygenation results were compared with those derived using conventional singlet oxygen photosensitizers.

Singlet molecular oxygen (1O2, 1∆g) plays an important role in chemical [31], biological [32,33] and therapeutic processes [34,35], as well as in the degradation of food and materials [36–38]. Historically, although 1O2 was discovered more than 80 years ago [39,40], and until the early 1960s was considered to be a molecular species of passing astrophysical interest and rather limited as a research subject. The pioneering work by Foote and Wexler [41,42], provided strong evidence for the formation of 1O2 as the reactive intermediate in photosensitized processes in solution. Today, the use of 1O2 as a reagent in organic synthesis has received remarkable attention [43,44].

---

**2. Results and Discussion**

In the present work, the photocatalyst g-C3N4 was prepared according to the procedure described by Tang and coworkers [45], while the carbon nanodots via thermal decomposition of sucrose [46]. The so produced nanodots were deposited by heating on the g-C3N4 surface to provide the metal-free carbon-nanodot-doped g-C3N4 (CD-C3N4). Details on the experimental conditions as well as the spectroscopic characterization are described in our previous work [30].

Photosensitized oxidations were performed in a 4 mL pyrex cell containing 0.09 M solution of 2,3-dimethylbut-2-ene (1) in a variety of solvents with 4 mg/mL of the insoluble CD-C3N4 photocatalyst. While bubbling oxygen at 20 °C, the solution was irradiated for a period of 30 min. A 300 W xenon lamp was utilized as the visible light source. The photooxidation reaction was followed by GC and/or 1H NMR analysis after filtration from celite followed by reduction of the allylic hydroperoxides with triphenylphosphine to the corresponding allylic alcohols.

We report here the unprecedented photooxygenation of alkenes utilizing CD-C3N4 as the photosensitizer. The electron rich tetramethylethylene (1) was chosen as the singlet oxygen acceptor, Scheme 1. Within a few minutes of irradiation, the allylic hydroperoxide 1a (see GC chromatograms S16, S17 and S18) was formed followed by reduction with Ph3P to the corresponding allylic alcohol 1b (GC chromatogram S19).

![Scheme 1. CD-C3N4 photosensitized oxidation of tetramethylethylene (1).](image)

The GC and/or 1H NMR analysis of product 1b, as can be seen in S2, showed identical results with those when typical singlet oxygen photosensitizers, such as rose Bengal (RB) or tetraphenyl-porphyrine (TPP), were utilized. The production of allylic hydroperoxides by the sensitized photooxygenation of alkenes, the so called “ene or Schenck” reaction, was studied several years ago, for its synthetic [43,44], mechanistic [47,48] and theoretical [49,50] point of view. Furthermore, addition of a small amount of 1,4-diazabicyclo[2.2.2]octane (DABCO), a well-known 1O2 quencher [51,52], into the reaction mixture, Scheme 1, retarded completely the production of allylic hydroperoxides. This is an additional indication of the 1O2 involvement as the reactive intermediate in the above-mentioned reaction.
The kinetics of the CD-C₃N₄ photosensitized oxygenation of 1, Scheme 1, was examined in a variety of solvents. Reaction progress at several conversions was easily monitored by GC analysis. Diglyme was used as the internal standard. First, assuming that during the photooxygenation, the oxygen concentration remains constant while there is a first-order dependence of the reaction rate on the tetramethylethylene (1) concentration, the following equation can be applied: \( kt = \ln (1 - x) \) where \( k \), \( t \), and \( x \) define the rate constant, the irradiation time, and the conversion of tetramethylethylene, respectively. However, an adequate linear correlation was not found. Therefore, we simply plot the conversion of tetramethylethylene (1) vs the illumination time, as shown in Figure 1. The plot (Figure 1) shows that the rate of product formation depends on solvent polarity, e.g., in EtOAc, is favored compared to CCl₄ by roughly a factor of two.

\[ \text{Figure 1. Conversion % vs irradiation time of CD-C}_3\text{N}_4 \text{ sensitized photooxidation of tetramethylethylene.} \]

Next, we examined the regioselectivity of the present oxidation system with an alkyl trisubstituted alkene, Scheme 2. For this purpose, the regiospecifically deuterium labeled alkene 2 was synthesized (see S3, S4, S5 and S6) and was used as an appropriate substrate for sensitized photooxygenation using two different catalysts, one conventional photosensitizer (TPP) and the photocatalyst CD-C₃N₄. It is well established that double bond formation via singlet oxygen ene reaction will occur preferentially in the most substituted side of the alkyl substituted double bond [53]. Indeed, as seen in Table 1 (entries 1 and 2), both conventional (TPP) and CD-C₃N₄ photocatalysts upon visible light irradiation show, within experimental error, identical regioselectivity. For example, 2a and 2b which can be seen in S7 and S8, are the main products (cis effect) [53], while the E-methyl group is highly unreactive. This result is again a strong evidence of \(^1\text{O}_2\) involvement, excluding the involvement of other reactive oxygen species (ROS).

\[ \text{Scheme 2. Sensitized Photooxidation of 2-(1,1,1-trideuteromethyl)-5-methylhex-2-ene (2).} \]
The second mode of $^1\text{O}_2$ reactivity is the $[4 + 2]$ cycloaddition to conjugated dienes to yield endoperoxides. We demonstrate here, Scheme 3, that CD-C$_3$N$_4$ photosensitizes the addition of singlet oxygen to 1,3-cyclohexadiene (3) to produce efficiently endoperoxide 3a (Figure 2, S9) in ambient conditions.

\begin{align*}
\text{3} & \xrightarrow{\text{hv}} \text{CD-C}_3\text{N}_4 / \text{O}_2 \\
& \text{CDCl}_3 \\
& 30 \text{ min} \ 0 \degree \text{C} \\
& \text{3a}
\end{align*}

**Scheme 3.** Photooxidation of 1,3-cyclohexadiene in CDCl$_3$ with CD-C$_3$N$_4$ as photocatalyst.

![Figure 2. $^1$H-NMR spectrum of 3a.](image)

Furthermore, apart from oxygen photoactivation, the CD-C$_3$N$_4$ catalyst was tested for promoting an electron transfer process. The proposed two mechanisms for the sensitized photooxygenation of organic substrates were initially classified by Gollnick [54] as Type I and Type II as shown below in Scheme 4.

\begin{align*}
\text{Sens} & \xrightarrow{\text{hv}} ^1\text{Sens} \\
& \xrightarrow{\text{ISC}} ^3\text{Sens} \\
& \xrightarrow{\text{Substrate}} \text{Radicals} \\
& \text{O}_2 \\
& \text{products}
\end{align*}

\begin{align*}
\text{Type I} & \rightarrow ^3\text{O}_2 \\
\text{Type II} & \bigg\{ \\
& \text{O}_2^\cdot \text{by electron transfer} \\
& ^1\text{O}_2 \text{by energy transfer} \\
\bigg\}
\end{align*}

**Scheme 4.** Type I and Type II photosensitized mechanisms.

### Table 1. Photooxidation of alkyl trisubstituted alkene 2 with TPP and CD-C$_3$N$_4$.

| Entry | Photocatalyst | Conversion (%) $^a$ | Irradiation Time (min) | Regioselectivities (%) $^b$ |
|-------|---------------|---------------------|------------------------|---------------------------|
| 1     | TPP           | 100                 | 5                      | 56 31 13                  |
| 2     | CD-C$_3$N$_4$ | 34                  | 30                     | 58 29 13                  |

$^a, b$ Determined by $^1$H NMR analysis.

Catalysts 2019, 9, x FOR PEER REVIEW 4 of 12

Conversion (%) $^a$

| Irradiation time (min) | 2a | 2b | 2c |
|------------------------|----|----|----|
| 1 TPP                  | 100| 5  | 56 |
| 2 CD-C$_3$N$_4$        | 34 | 30 | 58 |

Photooxidation of alkyl trisubstituted alkene 2 with TPP and CD-C$_3$N$_4$. 

The two mechanisms, Type I and Type II as well as singlet oxygen ($^1\text{O}_2$) and superoxide ($\text{O}_2^\cdot$) formation, are always in competition. Which of them will prevail depends on the nature of the irradiation conditions.

Furthermore, apart from oxygen photoactivation, the CD-C$_3$N$_4$ catalyst was tested for promoting an electron transfer process. The proposed two mechanisms for the sensitized photooxygenation of organic substrates were initially classified by Gollnick [54] as Type I and Type II as shown below in Scheme 4.
The two mechanisms, Type I and Type II as well as singlet oxygen (1^1O_2) and superoxide (O_2^-) formation, are always in competition. Which of them will prevail depends on the nature of the photocatalyst, the solvent, the substrate’s nature and the concentration. In Type II mechanism singlet oxygen is produced by energy transfer whereas superoxide anion (O_2^-) by electron transfer mechanism. To check the electron transfer ability of CD-C_3N_4 catalyst, the electron rich 2-(4-methoxyphenyl)-3-methylbut-2-ene (4) was prepared (see S11). This substrate apart from 1^1O_2 acceptor is also a good electron donor. The results from the irradiation of aryl alkene 4 in a variety of solvents and sensitizers, Scheme 5, are shown in Table 2.

![Scheme 5](image)

**Scheme 5.** Sensitized photooxygenation of aryl alkene 4.

**Table 2.** Regioselectivities and activities of various sensitizers in the photooxygenation of 4.

| Entry | Photocatalyst | Solvents | 4a % | 4b % | 4c % | Conversion % |
|-------|--------------|----------|------|------|------|--------------|
| 1     | TPP          | CCl_4    | 76   | 24   | -    | 100^d        |
| 2     | RB           | CDCl_3   | 70   | 30   | -    | 100^d        |
| 3     | MB           | CH_3CN   | 66   | 34   | -    | 100^d        |
| 4     | DCA          | CD_2CN   | 61   | 27   | 12   | 87^d         |
| 5     | CD-C_3N_4    | CDCl_3   | 53   | 31   | 16   | 80           |
| 6     | CD-C_3N_4    | CD_2CN   | 58   | 27   | 15   | 70           |
| 7     | CD-C_3N_4    | Benzene  | 53   | 31   | 16   | 67           |
| 8     | CD-C_3N_4    | EtOAc    | 53   | 29   | 18   | 65           |
| 9     | CD-C_3N_4    | EtOH     | -    | -    | 100  | 100          |
| 10    | CD-C_3N_4    | CDCl_3   | -    | -    | -    | -^e          |
| 11    | no catalyst  | CDCl_3   | traces | traces | traces | <1^f       |

^a,b ene reaction products; ^c electron transfer products determined by ^1H-NMR analysis; ^d 5 min irradiation at 0 °C; ^e in the dark for 3 h, determined by ^1H NMR and GC analysis; ^f irradiated without any photocatalyst. Samples after 0.5 h, 1.0 h and 2 h were analyzed by ^1H NMR and GC analysis.

For comparison reasons, apart from CD-C_3N_4, four sensitizers were utilized in the above reaction (entries 1–4). Rose Bengal (entry 2, RB), TPP (entry 1) and methylene blue (entry 3, MB) are well studied singlet oxygen photosensitizers. However, 9,10-dicyano-anthracene (entry 4, DCA), an electron poor compound, sensitizes the photooxygenation by both singlet oxygen and electron transfer mechanisms depending on the particular substrate and the polarity of the solvent [55].

Irradiation of 4 in the presence of TPP, RB or MB as photosensitizers afforded the allylic hydroperoxides 4a and 4b in a ratio of approximately 7:3. These hydroperoxides are typical singlet oxygen products whose ratio 7:3 is independent of solvent polarity [47,56] or the para-substitution of the phenyl ring. However, the DCA-photosensitized oxygenation of 4 in acetonitrile (entry 4), afforded apart from the ene products 4a and 4b considerable amount of p-methoxy-acetophenone (4c). In this case, the results are supported by both electron transfer and singlet oxygen mechanisms. Similarly, in the CD-C_3N_4 catalyzed photooxidation of 4 in non protic solvents, apart from the allylic hydroperoxides 4a and 4b, considerable amounts of 4c in the range of 15–18% were obtained. These results are also similar with those derived earlier from DCA photosensitized oxygenation of diphenyl-ethylene [55]. p-Methoxy-acetophenone 4c is most probably produced from the cleavage of dioxetane 4d via the intermediacy of superoxide anion (O_2^-) through an electron transfer mechanism, as shown in Scheme 6. The formation of superoxide anion O_2^- and not a hydroxyl radical has been also recently documented [20]. We must note here that control experiments either with the CD-C_3N_4 in dark (entry 10) or without the photocatalyst under irradiation conditions (entry 11) did not show any detectable oxidation products (entry 10) or small traces observed by ^1H NMR and GC analysis.
(entry 11). It is interesting to note here that when this reaction was run in EtOH as the solvent (entry 9, Table 2), the cleavage product 4c was exclusively obtained in 100% conversion. This result indicates that under these conditions, electron transfer is the only operating mechanism (Scheme 6). However, it is not clear at the present why the irradiation of CD-C3N4 surface in EtOH, promotes the electron transfer mechanism leading exclusively to cleavage products 4c, (entry 9, Table 2). Most probably, among some other unknown at the time reasons, the polar protic solvent ethanol stabilizes favorably the pair of radical ions (anion + cation) favoring dramatically the electron transfer path producing exclusively the superoxide anion (O·-) as the reactive intermediate.

![Scheme 6. CD-C3N4 photosensitized oxidation of alkene 4 by electron transfer mechanism.](image)

To assess further the extent of electron transfer efficiency of CD-C3N4 surface in a polar and non protic solvent, the photooxidation of 1,1-di(p-anisyl)ethylene (5) was performed (Scheme 7). An electron transfer test can be probed by utilizing substrate 5; an electron rich alkene, not reactive with singlet oxygen. Scheme 7 shows the CD-C3N4 sensitized photooxygenation of 5 in acetonitrile.

![Scheme 7. Photooxidation of 5 with CD-C3N4 as photocatalyst.](image)

This reaction afforded exclusively and quantitatively the cyclic peroxide 5a (Figure 3, S15), by cycloaddition of photochemically produced two radical cations of 5 and one super oxide anion. Similar results under the same conditions have been reported previously [57,58], when DCA was the photosensitizer. Furthermore, upon addition of a small quantity of 1,3,5-trimethoxybenzene, the above reaction, Scheme 7, was retarded. This result supports an electron transfer mechanism considering that the lower oxidation potential of a donor molecule (1,3,5-trimethoxybenzene) than the corresponding potential of the competing electron donor alkene, [55], quenches the electron transfer pathway from the alkene to the sensitizer. Similar mechanism was published earlier by Ericksen and Foote [55], when in their case, electron deficient DCA was used as the photocatalyst and 1,1-diphenylethylene or tetramethylethylene were used as the substrates.
3. Materials and Methods

3.1. General

All solvents and tetramethylethylene (1) (2,3-dimethylbut-2-ene), 4-bromoanisole, 3-methyl-2-butanone, 1,3-cyclohexadiene (3) were purchased from Sigma-Aldrich (Munich-Germany) in the highest purity and were used without any purification. In addition, the photosensizers 5, 10, 15, 20-tetraphenyl-21H,23H-porphyrine (TPP), 9,10-dicyano-anthracene (DCA), methylene blue (MB) and Rose Bengal (RB) were purchased from Sigma-Aldrich.

Column chromatographic separations were carried out by a flash chromatography system using silica gel and hexane/ethyl acetate or petroleum ether/ethyl acetate solvent mixtures. For thin layer chromatography (TLC), Merck silica gel (grade 60 F\textsubscript{254}, Merck & Co., Kenilworth, NJ, USA) was used.

The progress of the photooxidation reactions was monitored by gas chromatography using SHIMADZU GC-2014 gas chromatograph FID detector, (HP-5 capillary column 30 m × 0.32 mm × 0.25 μm, 5% diphenyl and 95% dimethylpolysiloxane) and by \textsuperscript{1}H-NMR. NMR spectra were recorded at room temperature on Bruker DPX-300 and Bruker Avance series 500. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak (CDCl\textsubscript{3}, δ: 7.26, \textsuperscript{13}CDCl\textsubscript{3}, δ: 77.0, CD\textsubscript{3}CN, δ: 1.94), and the multiplicity of each signal is designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants (J) are quoted in Hz.

3.2. General Photooxidation Method

In a suitable 4 mL pyrex cell were initially added 0.5–2.0 mL of the solvent and the CD-g-C\textsubscript{3}N\textsubscript{4} catalyst in concentration 4 mg mL\textsuperscript{-1}. Next, the compound, which will be oxidized was added, using a 25 μL syringe. The corresponding amounts were: 93 mM of tetramethylethylene (1), 12 × 10\textsuperscript{-3} mM of (E)-2-(1,1,1-trideuteromethyl)-5-methylhex-2-ene (alkene 2), 130 mM of 1,3-cyclohexadiene (3) and 110 mM of 1-methoxy-4-(3-methylbut-2-en-2-yl)benzene (aryl alkene 4). Also, the photosensitizers TPP, MB, DCA or RB were used for control experiments in catalytic amounts (0.5–1.0 mg). In the experiments which include the quenchers; 1,4-diazabicyclo[2.2.2]octane (DABCO) or 1,3,5-trimethoxybenzene, they were added in the amount of 1% mole in proportion to the oxidizing substance. The test tube was then placed into an ice bath in a pyrex receptacle, at a distance of approximately 10 cm from the visible light source (variable intensity Xenon bulb, Cermax 300 W). Oxygen was transferred inside the test tube by a syringe under gentle and continuous flow (gentle bubbling). The reaction was usually left for 30 min., or 60 min. At the end, the carbon nitride catalyst was removed by simple filtration through
cotton cloth and celite. In the cases where deuterated solvents were used, they were not evaporated, and the conversion was determined by $^1$H NMR analysis. In all the other cases with non-deuterated solvents, either they were evaporated under reduced pressure and the conversion was determined by $^1$H NMR analysis using CDCl$_3$ or with aprotic solvent the reaction progress was monitored by gas chromatography.

3.3. Synthesis of 2-(4-methoxyphenyl)-3-methylbut-2-ene (2)

- Synthesis of 2-(4-methoxyphenyl)-3-methylbutan-2-ol

Under dry nitrogen atmosphere, 220 mg of Mg turnings (9.00 mmol) were dissolved in dry diethyl ether (10 mL). Then, 0.8 mL (6.50 mmol) of 4-bromoanisole were initially dissolved in extra dry diethyl ether (4 mL) and the solution was added dropwise, while the mixture was stirred. In order to initiate the reaction, 1 granule of iodine was added to the mixture. The reaction was then heated at 35 °C (reflux) for about 45 min. The reaction was then cooled to room temperature and 3-methyl-2-butanone (0.7 mL, 6.50 mmol) was added dropwise. After the addition of the ketone, the reaction was heated again to reflux (35 °C) for 30 min. The reaction mixture was quenched with distilled water (20 mL) and after addition of saturated NH$_4$Cl (4 mL) the mixture was extracted with diethyl ether (2 × 15 mL). The combined organic layers were dried over MgSO$_4$ and evaporated to dryness. Pure 2-(4-methoxyphenyl)-3-methylbutan-2-ol was obtained after silica gel chromatography (petroleum ether/ EtOAc v/v, 10/1), 250 mg. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$: 7.33 (d, 2H, $J = 8.8$ Hz), 6.86 (d, 2H, $J = 8.8$ Hz), 3.80 (s, 3H), 1.99 (m, 1H), 0.86 (d, 3H, $J = 6.8$ Hz), 0.82 (d, 3H, $J = 6.8$ Hz).

- Synthesis of aryl alkene (4)

2-(4-methoxyphenyl)-3-methylbutan-2-ol (250 mg, 1.03 mmol) was heated neat with catalytic amount of I$_2$ (1/2 granule) at 120 °C for 1 minute. Then, the reaction was cooled to room temperature and then extracted with diethyl ether (3 × 10 mL), distilled water (10 mL) and saturated Na$_2$S$_2$O$_3$ (4 mL). The organic layers were dried over MgSO$_4$ and the solvents were evaporated to dryness. Pure 2-(4-methoxyphenyl)-3-methylbutan-2-ol was obtained after brief purification by a short pad of silica (cotton cloth and celite). In the cases where deuterated solvents were used, they were not evaporated, and the conversion was determined by $^1$H NMR analysis.

3.4. Synthesis of 2-(1,1,1-trideuteromethyl)-5-methylhex-2-ene (2)

Alkene 2 was prepared (synthesis of similar deuterated alkenes have been reported [59]) by the following method: Wittig coupling of the stabilized ylide methyl(triphenylphosphoranylidene)propionate (1.64 g, 4.7 mmol) with 2-methylbutanal (0.39 g, 4.5 mmol) in dry CH$_2$Cl$_2$ (10 mL) at RT overnight, gave the E configuration of the corresponding ester in 94–96% isomeric purity by $^1$H NMR analysis. The isolated yield was 80% (0.56 g). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.89 (d, $J = 7.0$ Hz), 1.72 (m, 1H), 1.75 (s, 3H), 2.02 (m, 2H), 3.69 (s, 3H), 6.76 (m, 1H).

Reduction of the above ester (0.7 g, 4.4 mmol) with LiAlD$_4$ (0.126 g, 3 mmol) in diethyl ether, at 0 °C, gave the corresponding dideuterio allylic alcohol, in 90% yield (0.52 g). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.89 (d, $J = 6.5$ Hz, 6H), 1.65 (m, 1H), 1.66 (s, 3H), 1.91 (t, $J = 7.0$ Hz, 2H), 5.43 (td, $J = 7.0$, 1.5 Hz, 1H).

Next, this allylic alcohol (0.5 g, 3.8 mmol) was brominated with Br$_2$ (0.76 g, 4.75 mmol) and Ph$_3$P (1.19 g, 4.55 mmol) in 10 mL of dry dichloromethane. The isolated yield of the allylic bromide was 50.6% (0.372 g, 1.92 mmol). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.89 (d, $J = 6.5$ Hz, 6H), 1.65 (m, 1H), 1.74 (s, 3H), 1.91 (t, $J = 7.5$ Hz, 2H), 5.62 (td, $J = 7.5$ Hz, 1.5 Hz, 1H).

Finally, reduction of the above allylic bromide (295 mg, 1.52 mmol) in dry diglyme (2 mL) with LiAlD$_4$ (23.8 mg, 0.57 mmol) in diglyme (2 mL) was left at RT overnight, followed by the usual quench with two drops of water. Finally, the reaction mixture was heated at 150 °C, for 1.5 h, and 75 mg of the alkene (E)-2 were distilled from diglyme.
Compound (E)-2: 1H NMR (500 MHz, CDCl₃) δ: 0.86 (d, J = 11.0 Hz, 6H), 1.55 (m, 1H), 1.56 (s, 3H), 1.85 (t, J = 7.0 Hz, 2H), 5.13 (t, J = 12.0 Hz, 1H).

3.5. Synthesis of 1,1-di(p-anisyl)ethylene (5)

Alkene 5 was prepared by the following method: in a solution of bis(4-methoxyphenyl)methanone (0.87 g, 3.6 mmol) in dry THF (40 mL), MeLi (2 mL) was added at 0 °C. After 24 h the reaction mixture was quenched with a few drops of H₂O. The reaction mixture was acidified with 3N HCl, and washed with NH₄Cl and H₂O solutions. After drying the organic layer, and evaporation of the solvent, 0.76 g (87 %) of alkene 5 was isolated as a solid. 1H NMR (500 MHz, CDCl₃) δ: 3.83 (s, 6H), 5.29 (s, 2H), 6.87 (d, J = 9 Hz, 4H), 7.28 (d, J = 9 Hz, 4H).

4. Conclusions

In conclusion, we have shown that CD-C₃N₄ photocatalyst sensitizes the photooxidation of unsaturated compounds. With simple alkenes and dienes, the singlet oxygen mechanism operates efficiently producing the allylic hydroperoxides and endoperoxides respectively. In the case of aryl alkenes, efficient electron donor molecules, both O₂ and/or electron transfer mechanisms can be achieved. Which of these competing mechanisms will prevail depends on the nature of substrate and the protic-non protic solvents. Finally, the easy modification of graphitic carbon nitride to bulk amounts of CD-C₃N₄ shows the following advantages: a) photocatalyzes the oxidation of a variety of alkenes and dienes b) the reaction is heterogeneous, a simple celite filtration removes the catalyst which can be reused at least three times c) stability of the catalyst under the photooxidation conditions unlike most of the conventional photosensitizers and d) the heterogeneous nature of the present photocatalyst overcomes solubility problems.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/8/639/s1, 1H NMR spectra of compounds 1a and 1b: S2, 1H NMR spectrum of E-ester, precursor of alkene 2: S3, 1H NMR spectrum of allylic alcohol-d₂, precursor of alkene 2: S4, 1H NMR spectrum of allylic bromide-d₂ precursor of alkene 2: S5, 1H NMR spectrum of alkene 2: S6, 1H NMR spectrum of alkene 2: S7, 1H NMR spectrum of 2a, 2b, 2c (CD-C₃N₄ as the photocatalyst); S8, 1H and 13C NMR spectra of compound 3a: S9, 1H NMR spectrum of 2-(4-methoxyphenyl)-3-methylbutan-2-ol, precursor of alkene 4: S10, 1H and 13C NMR spectra of aryl alkene 4: S11, 1H NMR (CD₂CN) spectrum of 4a, 4b, 4c, products from the photooxidation of alkene 4: S12, 1H NMR (CDCl₃) spectrum of 4a, 4b, 4c, products from the photooxidation of alkene 4: S13, 1H NMR spectrum of alkene 5: S14, 1H and 13C NMR spectra of 5a after photooxidation of alkene 5: S15, GC Chromatogram of compound 1a in Acetonitrile: S16, GC Chromatogram of compound 1a in Ethyl acetate: S17, GC Chromatogram of compound 1a in Chloroform-d: S17, GC Chromatogram of compound 1a in Hexane: S18, GC Chromatogram of compound 1a in Carbon tetrachloride: S18, GC Chromatogram of compound 1b in Dimethyl sulfoxide: S19.

Author Contributions: Conceptualization, I.S.; methodology, I.S., A.C., V.G.; investigation, A.C., V.G.; resources, I.S., F.H.; data curation, I.S., F.H. A.C. V.G.; writing—original draft preparation, I.S., A.C.; writing—review and editing, I.S., F.H., A.C.; supervision, I.S.; project administration, I.S.; funding acquisition, I.S.

Funding: This work was supported by the Special Account for Research Funds of University of Crete (KA 39432, SARF UoC). V. Giannopoulos, acknowledges the support by a scholarship of “State Scholarships Foundation” of the Operational Program for the Human Resources Development, Education and Lifelong Learning 2014-2020.

Acknowledgments: We thank M. Orfanopoulos for his valuable comments and discussions. Wuyuan Zhang is acknowledged for providing useful information.

Conflicts of Interest: “The authors declare no conflict of interest.” “The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results”.

References
1. Kroke, E.; Schwarz, M. Novel group 14 nitrides. Coord. Chem. Rev. 2004, 248, 493–532. [CrossRef]
2. Liu, J.; Wang, H.; Antonietti, M. Graphitic carbon nitride “reloaded”: Emerging applications beyond (photo)catalysis. Chem. Soc. Rev. 2016, 45, 2308–2326. [CrossRef] [PubMed]
3. Liu, J.; Zhang, Y.; Lu, L.; Wu, G.; Chen, W. Self-regenerated solar-driven photocatalytic water-splitting by urea derived graphitic carbon nitride with platinum nanoparticles. *Chem. Commun.* 2012, 48, 8826–8828. [CrossRef] [PubMed]

4. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J.M.; Domen, K.; Antonietti, M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* 2009, 8, 76–80. [CrossRef] [PubMed]

5. Wang, Y.; Li, Y.; Bai, X.; Cai, Q.; Liu, C.; Zuo, Y.; Kang, S.; Cui, L. Facile synthesis of Y-doped graphitic carbon nitride with enhanced photocatalytic performance. *Catal. Commun.* 2016, 84, 179–182. [CrossRef]

6. Wang, Q.; Chen, A.; Wang, X.; Zhang, J.; Yang, J.; Li, X.A. Fe-species-loaded graphitic carbon nitride with enhanced photocatalytic performance under visible-light irradiation. *J. Mol. Cat. A Chem.* 2016, 420, 159–166. [CrossRef]

7. Li, X.; Bi, W.; Zhang, L.; Tao, S.; Chu, W.; Zhang, Q.; Luo, Y.; Wu, C.; Xie, Y. Single-Atom Pt as Co-Catalyst for Enhanced Photocatalytic H\(_2\) Evolution. *Adv. Mater.* 2016, 28, 2427–2431. [CrossRef]

8. Han, C.; Wu, L.; Ge, L.; Li, Y.; Zhao, Z. AuPd bimetallic nanoparticles decorated graphitic carbon nitride for highly efficient reduction of water to H\(_2\) under visible light irradiation. *Carbon* 2015, 92, 31–40. [CrossRef]

9. Xiong, T.; Cen, W.; Zhang, Y.; Dong, F. Bridging the g-C\(_3\)N\(_4\) Interlayers for Enhanced Photocatalysis. *ACS Catal.* 2016, 6, 2462–2472. [CrossRef]

10. Fu, Y.; Huang, T.; Zhang, L.; Zhu, J.; Wang, X. Ag/g-C\(_3\)N\(_4\) catalyst with superior catalytic performance for the degradation of dyes: A borohydride-generated superoxide radical approach. *Nanoscale* 2015, 7, 13723–13733. [CrossRef]

11. Kuriki, R.; Matsunaga, H.; Nakashima, T.; Wada, K.; Yamakata, A.; Ishitani, O.; Maeda, K. Nature-Inspired, Highly Durable CO\(_2\) Reduction System Consisting of a Binuclear Ruthenium(II) Complex and an Organic Semiconductor Using Visible Light. *J. Am. Chem. Soc.* 2016, 138, 5159–5170. [CrossRef] [PubMed]

12. Chai, B.; Peng, T.; Mao, J.; Li, K.; Zan, L. Graphitic carbon nitride (g-C\(_3\)N\(_4\))-Pt-TiO\(_2\) nanocomposite as an efficient photocatalyst for hydrogen production under visible light irradiation. *Phys. Chem. Chem. Phys.* 2012, 14, 16745–16752. [CrossRef] [PubMed]

13. Idrees, F.; Dillert, R.; Bahmann, D.; Butt, F.K.; Tahir, M. In-Situ Synthesis of Nb\(_2\)O\(_5\)/g-C\(_3\)N\(_4\) Heterostructures as Highly Efficient Photocatalysts for Molecular H\(_2\) Evolution under Solar Illumination. *Catalysts* 2019, 9, 169. [CrossRef]

14. Hong, J.; Wang, Y.; Wang, Y.; Zhang, W.; Xu, R. Noble-Metal-Free NiS/g-C\(_3\)N\(_4\) for Efficient Photocatalytic Hydrogen Evolution from Water. *ChemSusChem* 2013, 6, 2263–2268. [CrossRef] [PubMed]

15. Xiang, Q.; Yu, J.; Jaroniec, M. Preparation and Enhanced Visible-Light Photocatalytic H\(_2\)-Production Activity of Graphene/g-C\(_3\)N\(_4\) Composites. *J. Phys. Chem. C* 2011, 115, 7355–7363. [CrossRef]

16. Suryawanshi, A.; Dhanasekaran, P.; Mhamane, D.; Kelkar, S.; Patil, S.; Gupta, N.; Ogale, S. Doubling of photocatalytic H\(_2\) evolution from g-C\(_3\)N\(_4\) via its nanocomposite formation with multiwall carbon nanotubes: Electronic and morphological effects. *Int. J. Hydrogen Energy* 2012, 37, 9584–9589. [CrossRef]

17. Ong, W.-J.; Tan, L.-L.; Ng, Y.H.; Yong, S.-T.; Chai, S.-P. Graphitic Carbon Nitride (g-C\(_3\)N\(_4\))-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer To Achieving Sustainability? *Chem. Rev.* 2016, 116, 7159–7329. [CrossRef]

18. Liu, J.; Liu, Y.; Liu, N.; Han, Y.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S.-T.; Zhong, J.; Kang, Z. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* 2015, 347, 970–974. [CrossRef]

19. Wen, J.; Xie, J.; Chen, X.; Li, X. A review on g-C\(_3\)N\(_4\)-based photocatalysts. *Appl. Surf. Sci.* 2017, 391, 72–123. [CrossRef]

20. Khan, M.A.; Teixeira, I.F.; Li, M.M.J.; Koito, Y.; Tsang, S.C.E. Graphitic carbon nitride 10atalyzed photoacetalization of aldehydes/ketones under ambient conditions. *Chem. Commun.* 2016, 52, 2772–2775. [CrossRef]

21. Goettmann, F.; Fischer, A.; Antonietti, M.; Thomas, A. Chemical Synthesis of Mesoporous Carbon Nitrides Using Hard Templates and Their Use as a Metal-Free Catalyst for Friedel–Crafts Reaction of Benzene. *Angew. Chem. Int. ed.* 2006, 45, 4467–4471. [CrossRef] [PubMed]

22. Verma, S.; Nasir Baig, R.B.; Nadagouda, M.N.; Varma, R.S. Selective Oxidation of Alcohols using Photoactive VO@g-C\(_3\)N\(_4\). *ACS Sus. Chem. Eng.* 2016, 4, 1094–1098. [CrossRef]
Catalysts 2019, 9, 639

23. Han, H.; Ding, G.; Wu, T.; Yang, D.; Jiang, T.; Han, B. Cu and Boron Doped Carbon Nitride for Highly Selective Oxidation of Toluene to Benzaldehyde. *Molecules* 2015, 20, 12686–12697. [CrossRef] [PubMed]

24. Ding, Z.; Chen, X.; Antonietti, M.; Wang, X. Synthesis of Transition Metal-Modified Carbon Nitride Polymers for Selective Hydrocarbon Oxidation. *ChemSusChem* 2011, 4, 274–281. [CrossRef] [PubMed]

25. Verma, S.; Nasir Baig, R.B.; Nadagouda, M.N.; Varma, R.S.; Photocatalytic, C.-H. Activation of Hydrocarbons over VO@g-C₃N₄. *ACS Sus. Chem. Eng.* 2016, 4, 2333–2336. [CrossRef]

26. Zhang, P.; Deng, J.; Mao, J.; Li, H.; Wang, X.C. Selective aerobic oxidation of alcohols by a mesoporous graphitic carbon nitride/N-hydroxyphthalimide system under visible-light illumination at room temperature. *Chinese J. Catal.* 2015, 36, 1580–1586. [CrossRef]

27. Su, F.Z.; Mathew, S.C.; Lipner, G.; Fu, X.Z.; Antonietti, M.; Blechert, S.; Wang, X.C. mpg-C₃N₄-Catalyzed Selective Oxidation of Alcohols Using O₂ and Visible Light. *J. Am. Chem. Soc.* 2010, 132, 16299–16301. [CrossRef] [PubMed]

28. Long, B.; Ding, Z.; Wang, X. Carbon Nitride for the Selective Oxidation of Aromatic Alcohols in Water under Visible Light. *ChemSusChem* 2013, 6, 2074–2078. [CrossRef]

29. Zhang, P.; Yang, Y.; Wang, C.; Yan, C.; Antonietti, M.; Li, H. Visible-Light-Induced Metal-Free Allylic Oxidation Utilizing a Coupled Photocatalytic System of g-C₃N₄ and N-Hydroxy Compounds. *Adv. Synth. Catal.* 2011, 353, 1447–1451. [CrossRef]

30. Zhang, W.; Bariotaki, A.; Smonou, I.; Hollmann, F. Visible-light-driven photooxidation of alcohols using surface-doped graphitic carbon nitride. *Green Chem.* 2017, 19, 2096–2100. [CrossRef]

31. Wasserman, H.H.; Ives, J.L. Singlet Oxygen in Organic Synthesis. *Tetrahedron* 1980, 37, 1825–1832. [CrossRef]

32. Foote, C.S.; Clennan, E.L. Properties and Reactions of Singlet Dioxgen. In *Active Oxygen in Chemistry*; Foote, C.S., Valentine, J.S., Greenberg, A., Liebman, J.F., Eds.; Chapman and Hall: London, UK, 1995; pp. 105–140.

33. Chin, K.K.; Trevithick-Sutton, C.C.; McCallum, J.; Jockusch, S.; Turro, N.J.; Scaiano, J.C.; Foote, C.S.; Garcia-Garibay, M.A. Quantitative Determination of Singlet Oxygen Generated by Excited State Aromatic Amino Acids, Proteins, and Immunoglobulins. *J. Am. Chem. Soc.* 2008, 130, 6912–6913. [CrossRef] [PubMed]

34. Kuimova, M.K.; Botchway, S.W.; Parker, A.W.; Balaz, M.; Collins, H.A.; Anderson, H.L.; Suhling, K.; Ogilby, P.R. Imaging intracellular viscosity of a single cell during photoinduced cell death. *Nat. Chem.* 2009, 1, 69–73. [CrossRef] [PubMed]

35. Dolmans, D.E.; Fukumura, D.; Jain, R.K. Photodynamic therapy for cancer. *Nat. Rev. Cancer* 2003, 3, 380–387. [CrossRef] [PubMed]

36. Ranby, B.; Rabek, J.F. Photodegradation, Photooxidation and Photostabilization of Polymers. In *Singlet Oxygen Reactions with Organic Compounds & Polymers*; Wiley: London, UK; John Wiley & Sons: New York, NY, USA, 1978. [CrossRef]

37. Abdou, M.S.A.; Holdcroft, S. Mechanisms of photodegradation of poly(3-alkylthiophenes) in solution. *Macromolecules* 1993, 26, 2954–2962. [CrossRef]

38. Scurlock, R.D.; Wang, B.; Ogilby, P.R.; Sheats, J.R.; Clough, R.L. Singlet Oxygen as a Reactive Intermediate in the Photodegradation of an Electroluminescent Polymer. *J. Am. Chem. Soc.* 1995, 117, 10194–10202. [CrossRef]

39. Herzberg, G. Photography of the Infra-Red Solar spectrum to Wave-length 12,900 A. *Nature* 1934, 133, 759. [CrossRef]

40. Kautsky, H. Quenching of luminescence by oxygen. *Trans. Faraday Soc.* 1939, 35, 216–219. [CrossRef]

41. Foote, C.S.; Wexler, S. Olefin Oxidations with Excited Singlet Molecular Oxygen. *J. Am. Chem. Soc.* 1964, 86, 3879–3880. [CrossRef]

42. Foote, C.S.; Wexler, S. Singlet Oxygen. A Probable Intermediate in Photosensitized Autoxidations. *J. Am. Chem. Soc.* 1964, 86, 3880–3881. [CrossRef]

43. Montagnon, T.; Tofi, M.; Vassilikogiannakis, G. Using Singlet Oxygen to Synthesize Polyoxxygenated Natural Products from Furans. *Acc. Chem. Res.* 2008, 41, 1001–1011. [CrossRef] [PubMed]

44. Hoffmann, N. Photochemical Reactions as Key Steps in Organic Synthesis. *Chem. Rev.* 2008, 108, 1052–1103. [CrossRef]

45. Martin, D.J.; Qiu, K.; Shevlin, S.A.; Handoko, A.D.; Chen, X.; Guo, Z.; Tang, J. Highly Efficient Photocatalytic H₂ Evolution from Water using Visible Light and Structure-Controlled Graphitic Carbon Nitride. *Angew. Chem. Int. Ed.* 2014, 53, 9240–9245. [CrossRef]
46. Pan, J.; Sheng, Y.; Zhang, J.; Wei, J.; Huang, P.; Zhang, X.; Feng, B. Preparation of carbon quantum dots/TiO₂ nanotubes composites and their visible light catalytic applications. J. Mater. Chem. A 2014, 2, 18082–18086. [CrossRef]
47. Alberti, M.N.; Orfanopoulos, M. Recent Mechanistic Insights in the Singlet Oxygen Ene Reaction. Synlett 2010, 999–1026. [CrossRef]
48. Stratakis, M.; Orfanopoulos, M. Regioselectivity in the Ene Reaction of Singlet Oxygen with Alkenes. Tetrahedron 2000, 56, 1595–1615. [CrossRef]
49. Singleton, D.A.; Hang, C.; Szymanski, M.J.; Meyer, M.P.; Leach, A.G.; Kuwata, K.T.; Chen, J.S.; Greer, A.; Foote, C.S.; Houk, K.N. Mechanism of Ene Reactions of Singlet Oxygen. A Two-Step No-Intermediate Mechanism. J. Am. Chem. Soc. 2003, 125, 1319–1328. [CrossRef] [PubMed]
50. Sheppard, A.N.; Acevedo, O. Multidimensional Exploration of Valley–Ridge Inflection Points on Potential-Energy Surfaces. J. Am. Chem. Soc. 2009, 131, 2530–2540. [CrossRef] [PubMed]
51. An, Y.-Z.; Chen, C.H.B.; Anderson, J.L.; Sigman, D.S.; Foote, C.S.; Rubin, Y. Sequence-specific modification of guanosine in DNA by a C₆₀-linked deoxyoligonucleotide: Evidence for a non-singlet oxygen mechanism. Tetrahedron 1996, 52, 5179–5189. [CrossRef]
52. Foote, C.S. Quenching of Singlet Oxygen. In Singlet Oxygen; Wasserman, H.H., Murray, R.W., Eds.; Academic Press: New York, NY, USA, 1979; pp. 139–171.
53. Orfanopoulos, M.; Grdina, M.B.; Stephenson, L.M. Site specificity in the singlet oxygen-trisubstituted olefin reaction. J. Am. Chem. Soc. 1979, 101, 275–276. [CrossRef]
54. Foote, C.S. Definition of Type I and Type II Photosensitized Oxidation. Photochem. Photobiol. 1991, 54, 659. [CrossRef] [PubMed]
55. Eriksen, J.; Foote, C.S. Electron-transfer photooxygenation. 5. Oxidation of phenyl-substituted alkenes sensitized by cyanoanthracenes. J. Am. Chem. Soc. 1980, 102, 6083–6088. [CrossRef]
56. Stephenson, L.M.; Grdina, M.J.; Orfanopoulos, M. Mechanism of the ene reaction between singlet oxygen and olefins. Acc. Chem. Res. 1980, 13, 419–425. [CrossRef]
57. Gollnick, K.; Schnatterer, A. Formation of 1,2-dioxane by electron transfer photooxygenation of 1,1-di(p-anisyl)ethylene. Tetrahedron Lett. 1984, 25, 185–188. [CrossRef]
58. Gollnick, K.; Schnatterer, A. Formation of 1,2-dioxanes by electron-transfer photooxygenation of 1,1-disubstituted ethylenes. Tetrahedron Lett. 1984, 25, 2735–2738. [CrossRef]
59. Orfanopoulos, M.; Stratakis, M.; Eleses, Y.; Jensen, F. Do rotational barriers dictate the regioselectivity in the ene reactions of singlet oxygen and triazolinedione with alkenes? J. Am. Chem. Soc. 1991, 113, 3180–3181. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).