Photooxidation of Cyclohexane by Visible and Near-UV Light Catalyzed by Tetraethylammonium Tetrachloroferrate

Kira M. Fahy, Adam C. Liu, Kelsie R. Barnard, Valerie R. Bright, Robert J. Enright and Patrick E. Hoggard *
Department of Chemistry and Biochemistry, Santa Clara University, Santa Clara, CA 95053, USA; kfahy@scu.edu (K.M.F.); acliu@scu.edu (A.C.L.); kbarnard@scu.edu (K.R.B.); vbright@scu.edu (V.R.B.); renright@scu.edu (R.J.E.)
* Correspondence: phoggard@scu.edu; Tel.: +1-408-554-7810
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Abstract: Tetraethylammonium tetrachloroferrate catalyzes the photooxidation of cyclohexane heterogeneously, exhibiting significant photocatalysis even in the visible portion of the spectrum. The photoproducts, cyclohexanol and cyclohexanone, initially develop at constant rates, implying that the ketone and the alcohol are both primary products. The yield is improved by the inclusion of 1% acetic acid in the cyclohexane. With small amounts of catalyst, the reaction rate increases with the amount of catalyst employed, but then passes through a maximum and decreases, due to increased reflection of the incident light. The reaction rate also passes through a maximum as the percentage of dioxygen above the sample is increased. This behavior is due to quenching by oxygen, which at the same time is a reactant. Under one set of reaction conditions, the photonic efficiency at 365 nm was 0.018 mol/Einstein. Compared to TiO$_2$ as a catalyst, Et$_4$N[FeCl$_4$] generates lower yields at wavelengths below about 380 nm, but higher yields at longer wavelengths. Selectivity for cyclohexanol is considerably greater with Et$_4$N[FeCl$_4$], and oxidation does not proceed past cyclohexanone.

Keywords: photocatalysis; cyclohexane; cyclohexanol; cyclohexanone; tetrachloroferrate; photooxidation

1. Introduction

The photochemical oxidation of hydrocarbons to alcohols, aldehydes, ketones, and carboxylic acids has been pursued as a particularly compelling goal of green chemistry. A successful process would use only molecular oxygen as the oxidizing agent, would run at room temperature and ambient pressure, and would have a high photonic efficiency at wavelengths well into the visible range so that sunlight could be a viable source of photons. The catalyst would be heterogeneous, thus easily recoverable, and would have a high turnover number. The environmental benefits of a successful approach to the photooxidation of hydrocarbons would extend much further, since the primary products are common starting materials for many other reagents.

Maldotti et al. published a very thorough review of the literature on hydrocarbon photooxidation processes in 2002 [1], drawing particular attention to TiO$_2$, zeolites, and polyoxometallate anions as catalysts, which together constitute by far the largest group of materials used for this purpose. All three types of materials can be very effective at catalyzing photooxidation. Titanium dioxide and polyoxometallate anions have in common the ability to create both oxidizing and reducing centers photochemically - holes and electrons on TiO$_2$ and oxidized and reduced forms of the polyoxometallate...
anions. This is crucial to the regeneration of the catalyst. Titanium dioxide, polyoxometallate anions, and zeolites share the ability to generate active sites or ions (such as \(-\cdot OH\)) that abstract hydrogen very efficiently, sometimes too efficiently for synthetic purposes, because oxidation often continues to complete mineralization, i.e., \(\text{CO}_2\), with extended irradiation [2].

Another disadvantage of these materials from the viewpoint of green chemistry is that all of them are white. They absorb little or nothing in the visible part of the spectrum, and are therefore restricted to the use of but a fraction of solar irradiance. Attempts have been made to dope these substances with compounds that absorb in the visible, generally with some improvement in the yield at higher wavelengths, but not always preserving efficiency in the UV.

Another approach to heterogeneously catalyzed photooxidation makes use of heterogenized tetrachloroferrate(III) ion, and was introduced by Maldotti et al. [3]. This approach is based on the ability of \(\text{FeCl}_3\) to catalyze photooxidation processes homogeneously [4–6]. Iron(III) chloride, which is actually \(\text{Fe}_2\text{Cl}_6\) in solvents of low polarity, undergoes photodissociation, and the ability of the dissociated chlorine atoms to abstract hydrogen from a carbon atom, while not as strong as that of hydroxyl radicals or holes on \(\text{TiO}_2\) or oxidized polyoxometallate anions, is still sufficient to initiate the oxidation of many substrates [7]. Oxygenation then follows through the creation of a peroxyl radical by reaction with \(\text{O}_2\).

\[
\begin{align*}
\text{Fe}^{II}\text{Cl}^3 \rightarrow \text{Fe}^{II} + \text{Cl}^- \quad (1) \\
\text{Cl}^- + \text{RH}_2 \rightarrow \text{HCl} + \text{HR}^- \quad (2) \\
\text{HR}^- + \text{O}_2 \rightarrow \text{HROO}^- \quad (3)
\end{align*}
\]

Regeneration of the catalyst can occur in several ways, but the most likely is by reaction of the reduced iron site with a hydroperoxide, the concentration of which generally increases with irradiation time.

\[
\begin{align*}
\text{HROOH} + \text{Fe}^{II} \rightarrow \text{Fe}^{III}\text{OH}^- + \text{HRO}^- \quad (4) \\
\text{Fe}^{III}\text{OH}^- + \text{HCl} \rightarrow \text{Fe}^{III}\text{Cl}^- + \text{H}_2\text{O} \quad (5)
\end{align*}
\]

We examined the potential of several materials to catalyze heterogeneously the photooxidation of cyclohexane by means of chlorine atom photodissociation: \(\text{FeCl}_4^-\) immobilized on an anion exchange resin, \(\text{FeCl}_3\) on silica gel, \(\text{Et}_4\text{N}[\text{FeCl}_4]\), and Dowex 1-X10 in the chloride form, which has been shown to be photocatalytically active in other systems [8]. Tetraethylammonium tetrachloroferrate, which is insoluble in hydrocarbons, was the best of these, and its properties as a photocatalyst were investigated in detail.

2. Results

2.1. Development of Products with Time

Figure 1 shows the production of cyclohexanol, cyclohexanone, and chlorocyclohexane during a typical irradiation in the presence of \(\text{Et}_4\text{N}[\text{FeCl}_4]\). Product development was, as in this graph, generally linear, indicating that at least during the time frame of a typical experiment, products were formed simultaneously and not sequentially.

Another product of cyclohexane photooxidation that has sometimes been reported is cyclohexyl hydroperoxide [6]. We were unable to observe this by GC-MS in these or any other experiments. In addition, we added \(\text{Bu}_4\text{NI}\) to photolysates produced under a variety of conditions to test for peroxides by oxidation of \(\text{I}^-\) to \(\text{I}_3^-\) [9], but amounts obtained were always insignificant relative to the other products, perhaps because the hydroperoxide is consumed as in Equation (4).
2.2. Polar Accelerants

The formation of peroxy radicals and subsequent oxidation processes involve polar molecules and molecular ions, the circulation of which might be improved in the presence of a small fraction of a polar additive, with an increase in yield. This in fact proved to be the case. Acetonitrile, acetone, and acetic acid in small amounts all increased the yield of oxygenated products. Results with acetic acid are shown in Table 1.

Table 1. Yield of photolysis products after 20-min irradiation (100 W Hg lamp, (λ > 360 nm) of 1.0 mL of cyclohexane with 20 mg of Et4N[FeCl4].

| Acetic Acid Content | Oxidized Products, μmol |
|---------------------|-------------------------|
| 0                   | 1.8                     |
| 0.2%                | 15.7                    |
| 0.5%                | 28.8                    |
| 2.0%                | 12.3                    |

It can be expected that the yield will eventually decrease at higher concentrations of acetic acid, due to dilution of the reactant and an increase in viscosity, but the large decrease at a concentration of just 2% implies a more specific mechanism. One possibility is that at this concentration acetic acid cages can form around polar species like cyclohexylperoxy radicals, reducing the rate at which they react. All subsequent experiments were done with cyclohexane containing 0.5% acetic acid.

2.3. Salt Addition

Halide anions have been found to increase the rate of photoprocesses initiated by the dissociation of a chlorine atom, through the formation of radical ions XCl\(^-\) that are better able than Cl\(^-\) to escape the solvent cage and avoid recombination [8,10,11]. Table 2 presents some representative data on the effect of added Bu₄NBr (abbreviations used in this paper: Chx, cyclohexane; Chx−OH, cyclohexanol; Chx=O, cyclohexanone; Chx−Cl, chlorocyclohexane).
Table 2. Yield (µmol) of photolysis products after 20-min irradiation (100 W Hg lamp, λ > 360 nm) of 1.0 mL of cyclohexane (0.5% acetic acid), with 20 mg of Et$_4$NFeCl$_4$ under an O$_2$ balloon, varying the amount of dissolved Bu$_4$NBr.

| Bu$_4$NBr | Chx−OH | Chx=O | Chx−Cl | Total |
|-----------|--------|-------|--------|-------|
| 0         | 6.1    | 1.7   | 1.4    | 9.2   |
| 10 mg     | 9.9    | 4.3   | 6.8    | 21.0  |
| 20 mg     | 7.5    | 4.0   | 9.1    | 20.5  |

The bromide salt did indeed enhanced the rate of formation of products. Considering data from other experiments as well, the yield was rather insensitive to the exact amount of Bu$_4$NBr used, presumably because even 1 mg of Bu$_4$NBr provides more than enough bromide ion to convert almost all free chlorine atoms to BrCl$^-$ radicals. It appeared from this experiment and others that the fraction of product represented by chlorocyclohexane increased with the amount of salt added, probably due to longer radical lifetimes due to stabilization by bromide and consequently higher rates of termination with cyclohexyl radicals. Since all the chlorine in chlorocyclohexane must come from the FeCl$_4^-$ ion, and thus represents a loss of catalyst, we sought to minimize the amount of chlorocyclohexane whenever possible. Therefore, when Bu$_4$NBr was used, it was at a concentration of 1 mg per mL.

2.4. Optimum Amount of Catalyst

The total yield of oxidized cyclohexane, cyclohexanol plus cyclohexanone plus chlorocyclohexane, increased with the amount of Et$_4$N[FeCl$_4$] to a maximum near 20 mg of catalyst in 1.0 mL of cyclohexane (see Figure 2).

![Figure 2](image-url) 

**Figure 2.** Total yield of oxidized products from the irradiation (100 W Hg lamp, λ > 360 nm) of stirred suspensions of Et$_4$N[FeCl$_4$] in 1.0 mL of cyclohexane (with 0.5% acetic acid and 1 mg Bu$_4$NBr) as a function of the amount of catalyst employed. Solid line is a fit to Equation (6) with $\beta = 0.20$, $\gamma = 0.99$, and $\delta = 0.0035$.

A decline in yield with higher catalyst amounts is expected for heterogeneous photocatalysts and is due to increased reflectance from the front face, and decreased penetration, as the amount of catalyst increases [12]. An equation that has been used to represent this behavior is shown below and was used to fit the experimental data in Figure 1 [11]. The equation is for the fraction of light absorbed by the catalyst, upon which the total yield depends directly. The constants $\beta$, $\gamma$, and $\delta$ are related to the
absorptivity and reflectivity of the material, but may here be taken as empirical, with the constraint that \( \gamma \leq 1 \).

\[
f = 1 - e^{-\beta m} - \gamma(1 - e^{-\delta m})
\]  

(6)

The fit to the data in Figure 2 was to this equation. What one may infer from the data is that although a gradual decrease in rate is apparent between 10 and 100 mg/mL of Et4N[FeCl4], the dependence of the reaction rate on the amount of catalyst employed is not great within that range.

2.5. Variation of Yield with Fraction of Oxygen above the Reaction Mixture

Balloons containing mixtures of air, nitrogen, or oxygen were used to vary the percentage of O2 over the reaction mixture. The variation in product yields from the set of experiments shown in Table 3 was typical of that obtained under other conditions (amount of catalyst, cutoff wavelength) as well. The total yield of oxidized cyclohexane appeared to pass through a maximum around 40% O2.

Table 3. Yields (\( \mu \)mol) of cyclohexanol, cyclohexanone, and chlorocyclohexane following a 20-min irradiation (100 W Hg lamp, \( \lambda > 360 \) nm) of 1.0 mL of cyclohexane (0.5% acetic acid + 1 mg Bu4NBr) with 25 mg of Et4N[FeCl4].

| O2 Fraction | Chx−OH | Chx=O | Chx−Cl |
|-------------|--------|-------|--------|
| 0.01        | 0.6    | 0.1   | 0.2    |
| 0.10        | 2.7    | 0.6   | 1.5    |
| 0.21        | 1.9    | 0.2   | 2.7    |
| 0.40        | 3.3    | 0.7   | 1.8    |
| 0.80        | 2.5    | 0.8   | 4.3    |

We have shown previously that a complex dependence of the reaction rate on the partial pressure of oxygen is expected from a simple model for a process in which dioxygen is both a reactant and a quencher of the excited state tetrachloroferrate, i.e.,

\[
\text{FeCl}_4^- + O_2 \rightarrow \text{FeCl}_4^- + O_2^*\]  

(7)

Chx− + O2 \rightarrow Chx-O-O→ oxygenated products

(8)

The equation has the general form:

\[
\frac{dP}{dt} = A \frac{1}{a[O_2]^2 + b[O_2] + c + \left( a^2[O_2]^4 + 2ab[O_2]^3 + (6ac + b^2)[O_2]^2 + 6bc[O_2] + c^2 \right)^{\frac{1}{2}}}  
\]  

(9)

In Equation (9), \( a, b, \) and \( c \) are derived from the rate constants in the mechanism [13], and \( P \) represents the combined yield of cyclohexanol and cyclohexanone. The data from Table 3 were fit to this equation, as shown in Figure 3. The third point (air; 21% O2) was an outlier, and was ignored in the fit. Similar overall results (albeit with more scatter) were obtained from several repetitions.
was 39 mW, which in one hour delivered 4.3 × 10^{-2} \text{mol/Einstein}.

Photoreactivity, experiments were carried out with different UV cutoff filters. A comparison under otherwise identical conditions is shown in Table 4.

Table 4. Product yields following a 30-min irradiation (100 W Hg lamp, \(\lambda > 360\) nm) of 1 mL of cyclohexane (with 0.5% acetic acid and 1 mg Bu\(_4\)NBr) with balloons containing different percentages of O\(_2\). Solid line is a fit to Equation (9) with \(b = 0, c = 1.38, d = 150\).

| Cutoff Filter | Chx=OH, \(\mu\text{mol}\) | Chx=O, \(\mu\text{mol}\) | Chx=Cl, \(\mu\text{mol}\) | Total Chx Reacted |
|---------------|-----------------|-----------------|-----------------|-----------------|
| None a        | 7.4             | 1.0             | 10.8            | 19.1            |
| 320 nm        | 4.6             | 1.5             | 3.3             | 9.4             |
| 360 nm        | 5.5             | 1.4             | 2.0             | 8.9             |
| 395 nm        | 2.0             | 0.4             | 0.7             | 3.1             |

a Glass cuvettes were approximately equivalent to a 300 nm cutoff filter.

Figure 3. Yield of cyclohexanol plus cyclohexanone following the 20-min. photolysis (100 W Hg lamp, \(\lambda > 360\) nm) of 1 mL of cyclohexane (with 0.5% acetic acid and 1 mg Bu\(_4\)NBr) with balloons containing 50% O\(_2\)/50% air. Portions of the UV cut off as noted.

One of the hypotheses underlying this work was that catalysis through the photodissociation of chlorine atoms would permit the selection of a catalyst with significant photoactive absorption in the visible, making better use of solar insolation. To illustrate the potential for visible light-induced photoreactivity, experiments were carried out with different UV cutoff filters. A comparison under otherwise identical conditions is shown in Table 4.

Et\(_4\)N[FeCl\(_4\)] retains photocatalytic activity at 395 nm, and of particular note is that the percentage of chlorocyclohexane decreases markedly as the cutoff wavelength moves toward the visible.

2.7. Photonic Efficiency

A 365 nm interference filter was used to irradiate cyclohexane (1 mL, 80 mg Et\(_4\)N[FeCl\(_4\)], 0.5% acetic acid, 1 mg Bu\(_4\)NBr) with nearly monochromatic light. The power incident on the sample was 39 mW, which in one hour delivered 4.3 × 10^{-4} \text{Einstein}. The yield was 7.7 \(\mu\text{mol}\) of oxidized cyclohexane, from which the photonic efficiency at 365 nm was 0.018 mol/Einstein under the specific conditions of this experiment. While photonic efficiencies in heterogeneous systems cannot be directly compared with quantum yields in homogeneous environments, it is instructive to note that very large quantum yields under visible irradiation have been achieved for the photoxidation of cyclohexane catalyzed homogeneously by p-benzoquinone derivatives, as high as 10 mol/Einstein [14,15].
2.8. Catalyst Reuse

A set of experiments was conducted in which the Et₄N[FeCl₄] remaining after each experiment was washed with hexanes, filtered, dried, and then reused under the same photolysis conditions. There was some loss of catalyst during each cycle, for the most part in the pores of the filter paper. Results are shown in Table 5.

**Table 5.** Photolysis of cyclohexane, reusing catalyst from previous run: 1 mL cyclohexane (0.5% acetic acid, 1 mg Bu₄NBr, 50% O₂/50% air balloon) with 60 mg Et₄N[FeCl₄] initially, irradiated (100 W Hg lamp, λ > 345 nm) for 20 min.

| Catalyst Mass | Chx−OH, µmol | Chx=O, µmol | Chx−Cl, µmol |
|---------------|---------------|-------------|--------------|
| 60 mg         | 5.0           | 3.9         | 6.3          |
| 50 mg         | 3.8           | 1.0         | 1.9          |
| 32 mg         | 2.8           | 0.7         | 1.6          |
| 11 mg         | 3.9           | 1.0         | 1.9          |

A significant decrease in yield occurred in the first repeat of the experiment with recycled catalyst, after which there was little change, despite the continued loss of catalyst in the filter paper. The relative independence of the yield on catalyst mass is consistent with our findings, reported above, when catalyst mass was the independent variable. All chlorocyclohexane formed represents, of course, a loss of catalyst. The amount of chlorocyclohexane produced during these four photolyses, 10.7 µmol, required approximately 1.5% of the chlorine in the original 60 mg of Et₄NFeCl₄.

2.9. Longer Irradiation Times

Several experiments were carried out with longer irradiation times and larger volumes. As can be seen in Table 6, a general result was that the fraction of chlorocyclohexane was significantly smaller than in shorter experiments, as long as the shorter wavelength UV was filtered out.

**Table 6.** Products (µmol) from the photolysis of cyclohexane (0.5% acetic acid, 1 mg Bu₄Br/mL) under 50% O₂/50% air, other conditions as noted.

| Experiment | Chx−OH, µmol | Chx=O, µmol | Chx−Cl, µmol | % Reaction |
|------------|---------------|-------------|--------------|------------|
| 1 mL Chx, 60 mg Et₄EtFeCl₄, 500 W lamp, water filter, 1 h | 121          | 28          | 50          | 2.1%       |
| 3 mL Chx, 50 mg Et₄NFeCl₄, 500 W lamp, λ > 395 nm, 2 h | 82           | 20          | 3           | 0.4%       |
| 3 mL Chx, 50 mg Et₄NFeCl₄, 500 W lamp, λ > 360 nm, 2 h | 559          | 173         | 17          | 2.6%       |
| 250 mL Chx, 500 mg Et₄NFeCl₄, 200 W immersion lamp, 3 h | 727          | 326         | 88          | 0.05%      |

2.10. Comparison of Et₄NFeCl₄ with Dissolved FeCl₃ and FeCl₃ on Silica Gel

Because iron(III) chloride has been used as a homogeneous catalyst for the photooxidation of hydrocarbons [5,6], we compared the performance of Et₄N[FeCl₄] with FeCl₃, both homogeneous and heterogenized on silica gel. Results are shown in Table 7.

**Table 7.** Products formed (µmol) during the photolysis (100 W Hg lamp, λ > 360 nm, 50% O₂/50% air balloon, 20 min irradiation) of 1.0 mL of cyclohexane (1% acetic acid) with FeCl₃ and Et₄N[FeCl₄] as catalysts.

| Catalyst                  | mg | Chx−OH, µmol | Chx=O, µmol | Chx−Cl, µmol | Oxy Products |
|---------------------------|----|--------------|-------------|--------------|--------------|
| Et₄N[FeCl₄]               | 20 | 6.1          | 1.7         | 1.3          | 7.8          |
| FeCl₃ 5% on SiO₂          | 20 | 1.0          | 0.3         | 1.0          | 1.3          |
| FeCl₃ (dissolved)         | 5  | 2.7          | 2.9         | 13.7         | 5.6          |

The results with homogeneous FeCl₃ are roughly comparable to those reported by Shulpin and Katz in acetonitrile solution. They found 85 µmol of oxygenated products after a two-hour irradiation.
of a 5 mL solution (~0.5M C₆H₁₂) with a 125-W “street lamp” in an immersion well. It was expected that Et₄NFeCl₄ would yield better results than FeCl₃ on silica gel when wavelengths below 360 nm were eliminated, because the ion has an absorption maximum at 360 nm, while that of FeCl₃ on silica gel is at 340 nm [16]. It was somewhat surprising to find that Et₄N[FeCl₄] also produced more oxygenated products than homogeneous FeCl₃, though dissolved FeCl₃ caused more net reaction, due to the formation of a large amount of chlorocyclohexane.

2.11. Homogeneous Catalysis with Et₄N[FeCl₄] and Other Compounds

The homogeneous catalysis of cyclohexane photooxidation by Bu₄N[FeCl₄] has been reported by Maldotti et al. [3], carried out in a solution of cyclohexane mixed with dichloromethane and acetonitrile, in which Bu₄N[FeCl₄] is soluble. These experiments may be compared with those of Shulpin and Katz, in which FeCl₃ was used to catalyze the photooxidation of cyclohexane dissolved in acetonitrile [5].

We carried out several experiments with Et₄N[FeCl₄] as a catalyst in which cyclohexane was mixed with a solvent in which the tetrachloroferrate salt was soluble, one of which used acetone and is shown in Table 8. This table also shows some literature results with FeCl₃ as a homogeneous catalyst. It is difficult to compare yields from vastly different experimental conditions, but in general FeCl₃ and appear to behave in a way that is similar to homogeneous photocatalysts.

Table 8. Comparison of yield of oxygenated products from the homogeneously catalyzed photooxidation of cyclohexane diluted in another solvent.

| Catalyst | Chx Environment | Catalyst Conc. | Light Source | Irrad Time, min | Chx−OH+Chx=O μmol | Reference |
|----------|----------------|----------------|--------------|-----------------|--------------------|-----------|
| FeCl₃    | 0.5 M in CH₃CN | 5 × 10⁻⁴ M     | 150 W b      | 120             | 6                  | [5]       |
| FeCl₃    | 0.5 M in acetone| 5 × 10⁻⁴ M     | 150 W b      | 300             | 225                | [5]       |
| Bu₄N[FeCl₄]| 40% CH₂Cl₂ 10% CH₃CN | 3 × 10⁻⁴ M | 400 W Hg | 240 | 67 | [3] |
| Et₄N[FeCl₄]| 50% acetone a | 0.06 M         | 100 W Hg     | >360 nm         | 20                 | 48 c      |

a 0.5% acetic acid, balloon with 60% O₂. b immersion lamp. c this work. Conc.: Concentration.

Diluting the cyclohexane in polar solvents appears to favor the formation of oxygenated over chlorinated photoproduc ts. The literature experiments in Table 8 that used FeCl₃ and Bu₄N[FeCl₄] as catalysts reported negligible amounts of chlorocyclohexane. This was also true in experiments we performed with Et₄N[FeCl₄] in cyclohexane/acetone and cyclohexane/acetonitrile mixtures.

Derivatives of p-benzoquinone have been recently reported to catalyze the photooxidation of alkanes with high quantum yields, as noted above [14,15]. Those experiments were undertaken in neat solvents, in which reaction rates tend to be considerably slower than in the mixed systems reported in Table 8. To facilitate comparison, cyclohexane was photolyzed in the presence of heterogeneous Et₄N[FeCl₄] under conditions similar to those published with homogeneous p-xyloquinone, except for the irradiation time. The results are shown in Table 9.

Table 9. Comparison of homogeneously and heterogeneously catalyzed photooxidation of cyclohexane.

| Catalyst | Catalyst Amount | Sample Volume | Light Source | λ | Irrad Time | Chx−OH+Chx=O μmol | Reference |
|----------|----------------|---------------|--------------|---|------------|--------------------|-----------|
| PSQ a    | 2 × 10⁻³ M     | 3 mL          | 500 W Xe     | >390 nm | 26 h | 225 d | [14] |
| Et₄N[FeCl₄] b | 50 mg | 3 mL          | 500 W Hg     | >395 nm | 2 h | 102 c   | |

a 2% acetonitrile; b 0.5% acetic acid, balloon with 60% O₂; c this work; d includes Chx−OOH.

Despite the very high quantum yield found for the p-xyloquinone-catalyzed homogeneous photooxidation of cyclohexane by visible light [14], heterogeneous Et₄N[FeCl₄] appears to perform as well or better.

Not shown in the table is that with Et₄N[FeCl₄] as the catalyst the ratio of cyclohexanol to cyclohexanone was 4:1, while the p-xyloquinone-catalyzed experiments yielded a ratio of about 3:2, with, however, a still larger product fraction being cyclohexyl hydroperoxide, the concentration of which was negligible in our experiments catalyzed heterogeneously by Et₄N[FeCl₄].
2.12. Sunlight

Part of the impetus for undertaking this study was the hypothesis that cyclohexanone and cyclohexanol could potentially be synthesized using the sun as the only energy source, with the reactants at ambient temperature and pressure. With that in mind, several experiments were undertaken in sunlight. No lenses were used to direct more photons into the reaction mixture, and the mixtures were not stirred. Some representative results are shown in Table 10. Yields were modest, but probably in line with those achieved in the laboratory, considering the difference in incident light intensity.

| Experiment | Chx−OH | Chx=O | Chx−Cl | % Oxidation |
|------------|--------|-------|--------|-------------|
| 6 mL, Erlenmeyer, 150 mg Et₄NFeCl₄, no balloon, 3 h | 103 | 53 | 7 | 0.3% |
| 6 mL, Erlenmeyer, 200 mg FeCl₃/SiO₂, no balloon, 3 h | 18 | 0 | 76 | 0.2% |
| 1.5 mL, 1-cm rect. cuvette, 300 mg Et₄NFeCl₄, 60% O₂, 6 h | 27 | 7 | 14 | 0.3% |
| 1 mL, 1-cm triangular cuvette, 80 mg Et₄NFeCl₄, 60% O₂, 6 h | 27 | 11 | 6 | 0.5% |
| 3 mL, 4-cm rectangular cuvette, 200 mg Et₄NFeCl₄, 60% O₂, 4 h | 60 | 10 | 17 | 0.3% |

* Latitude 37.3 °N, experiments performed between 1 August and 15 August.

Cyclohexane is known to photooxidize much more rapidly in mixtures with dichloromethane [3,17,18]. To test this under sunlight we exposed a solution of Et₄N[FeCl₄] in C₆H₁₂/CH₂Cl₂ for six hours in direct sunlight, with no stirring. The results are shown in Table 11.

| Product | Yield, µmol |
|---------|-------------|
| Chx−OH  | 993         |
| Chx=O   | 902         |
| Chx−Cl  | 22          |

The total yield of oxygenated products was 14%, dramatically higher than what can be achieved without the admixture of dichloromethane. It should be noted that Et₄N[FeCl₄] dissolves in this solvent mixture, hence the process involves homogeneous rather than heterogeneous catalysis.

2.13. Comparison with Other Studies

In Table 12, we have compiled data from published results on the photooxidation of neat (or almost neat) cyclohexane, using titanium dioxide or FeCl₄⁻ supported on an Amberlite anion exchange resin as catalyst, which allows some basis for comparison of these catalysts with Et₄N[FeCl₄].
Table 12. Product yield after extended radiation of cyclohexane (containing 0.5% acetic acid and 1 mg Bu$_4$NBBr per mL) in the presence of Et$_4$N[FeCl$_4$], with literature data for other catalysts in neat cyclohexane.

| Catalyst  | Ref | Sample Volume mL | Catalyst Mass mg | Gas Above cn | Radiation Source | Irrad Time, min | Yield Chx OH µmol | Yield Chx=O µmol | % Chx = Cl | % Chx Reacted |
|-----------|-----|------------------|------------------|--------------|-----------------|----------------|-------------------|-----------------|------------|-------------|
| TiO$_2$   | [17] | 2.5 *            | 10 air           | 150 W Hg λ = 360 nm | <1              | 18             | n/a               | 0.08%           |            |             |
| TiO$_2$   | [19] | 20 air           | 450 W he no filter | 150          | 45              | 105 | n/a               | 0.08%           |            |             |
| TiO$_2$   | [18] | 1.0              | 2 air            | not statedλ = 303 nm | 45              | 0.7             | 2 | n/a               | 0.03%           |            |             |
| W$_4$O$_7$ | **b** | 3.0              | 45 O$_2$         | 150 W Hg λ > 380 nm | 90              | 11              | 11 | n/a               | 0.1%           |            |             |
| FeCl$_4$ on Amberlite | [8] | 2.5 | 625 air | 400 W Hg λ > 300 nm | 240              | 0.7             | 0.1 | 1.8          | 9 µmol 100% | 0.04% |            |
| Et$_4$NFeCl$_4$ | **c** | 1.0 | 50 | 60%O$_2$ | 50 W Hg glass filter | 120              | 121             | 28 | 100%         | 2%           | 2.7% |            |
| Et$_4$NFeCl$_4$ | **d** | 3.0 | 50 air | 500 W Hg λ > 360 nm | 120              | 599             | 173 | 2%           | 2%           | 2.7% |            |
| Et$_4$NFeCl$_4$ | **e** | 3.0 | 50 air | 500 W Hg λ > 395 nm | 120              | 82              | 20 | 3%           | 0.4%          |            |             |

* Not reported; 2.5 mL assumed from other publications from this laboratory.
** (n-Bu$_4$N)$_4$W$_10$O$_{32}$ on silica

This work

Direct comparison of Et$_4$N[FeCl$_4$] with TiO$_2$ (anatase), under identical conditions. Results are shown in Table 13.

Table 13 reveals that the comparison with literature data in Table 12 is deceptive, appearing, as it does, to show a decided advantage for Et$_4$N[FeCl$_4$] over TiO$_2$ under almost any circumstances. In a direct comparison, Et$_4$N[FeCl$_4$] was superior only at wavelengths above approximately 380 nm, where the absorptivity of undoped TiO$_2$ becomes negligible. The ketone to alcohol ratios were in the range expected for TiO$_2$-catalyzed photooxidation (see Table 12), but were unexpectedly in the same range with Et$_4$N[FeCl$_4$].

2.15. Selectivity

A mixture of cyclohexanol and cyclohexanone in variable ratios, referred to as KA oil, is used for the industrial synthesis of adipic acid, an intermediate in the production of Nylon 6,6. Thus the oxidation of cyclohexane may be profitably carried out without the need to separate the (oxygenated)
products. Despite this, experimental studies on the photooxidation of cyclohexane frequently focus on selectivity for cyclohexanol [17–19], a desirable synthetic goal.

Brusa and Grela found, using TiO$_2$ as the photocatalyst in neat cyclohexane, that lower irradiation wavelengths and higher intensity each increase the cyclohexanol/cyclohexanone (A/K) ratio, the intensity dependence being linear at all wavelengths tested [18]. They found no change in the A/K ratio with irradiation time [18], indicating that the further oxidation of cyclohexanol plays no role in the early stages of photooxidation. Boarini et al., also with TiO$_2$ as the photocatalyst, likewise found the A/K ratio unchanged during the irradiation of neat cyclohexane, but reported a fivefold increase in the A/K ratio during the first two hours of irradiation in a mixture of cyclohexane and dichloromethane, the ratio thereafter remaining approximately constant [17]. Boarini et al. also found no dependence of the A/K ratio on the partial pressure of O$_2$, except at very low oxygen fractions, which favored the alcohol over the ketone [17]. Almquist and Biswas repeated this experiment with similar results [19].

It appears that the catalyst used has a much greater influence on the A/K ratio. With TiO$_2$ as the catalyst the A/K ratio is typically much less than one, usually around 0.1 in fact [17–19]. Li et al. have reported that reducing the size of the TiO$_2$ particles to 30 nm or less is accompanied by A/K ratios above 1.0, and as high as 9 [2]. Unfortunately, these experiments were done in 1:1 cyclohexane/acetonitrile mixtures, and the findings cannot be compared directly with the results in neat cyclohexane. Also in mixed solvents, an A/K ratio around 1.0 was achieved with a variety of polyoxotungstates and with an iron(III)-porphyrin complex [21].

By contrast, with Et$_4$N[FeCl$_4$] as the catalyst, the photooxidation of cyclohexane typically yielded an A/K ratio around 4 (Table 13 data representing a significant exception), and, as can be seen in Figure 1, the ratio did not change during irradiation. In most of the experiments reported here the cyclohexane contained 0.5% acetic acid, but acetic acid additions between 0 and 2% had no appreciable effect on the A/K ratio. We did not see a wavelength effect (Table 4) or an oxygen effect (Table 3). The addition of small quantities of Bu$_4$NBr, while increasing the overall yield, reduced the A/K ratio.

One factor that appeared to offer a means to increase selectivity in favor of the alcohol was the mass of catalyst employed. Though there was considerable scatter in the results, higher A/K ratios were obtained with smaller quantities of Et$_4$N[FeCl$_4$]. Brusa and Grela concluded from their work that selectivity is controlled not by the incident light intensity but by the intensity per particle, and this is consistent with our observation that fewer particles yielded a higher A/K ratio, other conditions being equal.

2.16. Mechanistic Considerations

When chlorine atoms initiate the oxidation process, cyclohexylperoxy radicals are formed as in Equation (3). A great deal of experimental work has been done on alkylperoxy radicals, most of it in the gas phase. There are several channels through which they are known or suspected to react, often spawning radicals that themselves react through several channels. The various pathways lead to a variety of outcomes with respect to the A/K ratio.

1. Peroxyl Radical Channel A

An important reaction channel is the Russell mechanism [22], whereby the bimolecular termination of peroxyl radicals generates cyclohexanol and cyclohexanone in equal amounts.

$$2\text{Chx}−\text{O}−\text{O}−\rightarrow \text{Chx}=\text{O} + \text{Chx OH} + \text{O}_2$$  \hspace{1cm} (10)

2. Peroxyl Radical Channel B
Another common pathway in the autoxidation of hydrocarbons is the self-reaction of peroxyl radicals to yield molecular oxygen and alkoxyl radicals [23].

\[ 2 \text{Chx} - \text{O} - \text{O}^\cdot \rightarrow 2 \text{Chx} - \text{O}^\cdot + \text{O}_2 \] (11)

Additional reaction channels have been proposed for the cyclohexylperoxyl radical during the thermal autoxidation (T = 145 °C) of cyclohexane, involving, for example the abstraction of hydrogen from cyclohexylhydroperoxide [24–26]. None of these pathways can explain an A/K ratio greater than one, because they either produce the ketone alone or the ketone and the alcohol in equal amounts.

3. Peroxy Radical Channel C

Hermans et al. propose that the cyclohexylperoxyl radical can, at least at elevated temperature, abstract hydrogen from cyclohexane, with rupture of the O–O bond, and they have shown by theoretical calculations that the reaction is favorable [25].

\[ \text{Chx} - \text{O} - \text{O}^\cdot + \text{Chx} \rightarrow \text{Chx} - \text{O}^\cdot + \text{Chx} - \text{OH} \] (12)

4. Alkoxyl Radical Channel a

Channels B and C both produce cyclohexoxyl radicals, and these can react in several ways, among them the abstraction of hydrogen from cyclohexane.

\[ \text{Chx} - \text{O}^\cdot + \text{Chx} \rightarrow \text{Chx} - \text{OH} + \text{Chx}^\cdot \] (13)

The cyclohexyl radical can then react with oxygen to form another cyclohexylperoxyl radical, extending the chain. Hermans et al. maintain that, at least in thermal autoxidation, this channel is not as important as others in producing cyclohexanol [25].

5. Alkoxy Radical Channel b

Another pathway for alkoxy radicals consists in the reaction with molecular oxygen to produce an aldehyde or, in this case, a ketone plus a hydroperoxyl radical.

\[ \text{Chx} - \text{O}^\cdot + \text{O}_2 \rightarrow \text{Chx} = \text{O} + \text{HOO}^\cdot \] (14)

In the presence of other peroxy radicals the hydroperoxyl radical generally loses its weakly bound hydrogen and forms a hydroperoxide [26].

\[ \text{HOO}^\cdot + \text{Chx} - \text{O} - \text{O}^\cdot \rightarrow \text{Chx} - \text{OOH} + \text{O}_2 \] (15)

The cyclohexyl hydroperoxide formed may accumulate in solution, but in the reactions studied here it should be reduced by Fe(II) species, as in Equation (4). Together with Equation (5) this serves to regenerate the catalyst.

The bifurcating radical pathways allow the possibility of a high degree of variability in the A/K product ratio. To summarize the photochemical experiments reported above,

- In neat C₆H₁₂ catalysis by Et₄N[FeCl₄] usually yielded an A/K ratio of about 4.
- In mixed acetone/cyclohexane solutions catalyzed homogeneously by Et₄N[FeCl₄] the A/K ratio was about 10.
- In mixed dichloromethane/cyclohexane solutions catalyzed homogeneously by Et₄N[FeCl₄] the A/K ratio was approximately 1.

A tentative inference is that in solution an A/K ratio of about 10 may be considered normal for catalysis through the photodissociation of FeCl₄⁻ ions, implying that peroxy radical channels B and C
are more rapid than channel A and that alkoxy radical channel a is more rapid than b. In the presence of dichloromethane, additional pathways are likely to be important, including, for example, hydrogen abstraction from CH$_2$Cl$_2$ and the formation of CHCl$_3$OO radicals, leading to greatly accelerated rates and accompanied by high amounts of the side product chlorocyclohexane. The smaller A/K ratio in the presence of solid E$_4$N$\left[\text{FeCl}_4\right]$, relative to that in solution, implies changes in the relative channel reaction rates when the cyclohexylperoxyl radical is adsorbed on the solid surface, having presumably been formed there, as in Equation (3), in the first place.

A fundamental question remaining is why the A/K ratio is so much lower when TiO$_2$ is the catalyst, often being in the 0.1 to 0.2 range. The answer appears to be that with TiO$_2$ most of the oxidation chemistry takes place while substrates are adsorbed on the surface. Almquist and Biswas explored in detail the photooxidation of cyclohexane catalyzed by TiO$_2$ in the presence of other solvents that competed for adsorption sites [19]. They concluded that polar solvents competed effectively against cyclohexane and cyclohexanol for sites, reducing the overall yield but increasing the A/K ratio [19]. In other words, adsorbed cyclohexane is oxidized preferentially to cyclohexanone, while cyclohexane in free solution is more likely to produce cyclohexanol. It has been proposed that adsorbed cyclohexane is initially oxidized on TiO$_2$ to even more strongly adsorbed cyclohexanol, which remains adsorbed long enough to be oxidized again, forming the ketone [17]. This contrasts to the process in solution, in which in the early stages of the reaction a cyclohexanol has little chance of encountering a hydrogen-abstracting radical such as ·OH, simply because such radicals will react with cyclohexane before they have the chance to encounter a cyclohexanol.

The strong adsorption of cyclohexanol and cyclohexanone on the TiO$_2$ surface, together with the high oxidation potential of the photogenerated surface holes, is also responsible for the mineralization to CO$_2$ that is commonly observed during the photooxidation of cyclohexane and other alkanes [17].

The adsorption of cyclohexane on the surface of E$_4$N$\left[\text{FeCl}_4\right]$ is evidently much weaker than adsorption on TiO$_2$, permitting a high fraction of the oxidation (Equations (1) through (3) and peroxyl radical channels A and B) to take place in solution. Polyoxometallates present an intermediate case. A variety of polyoxotungstate materials have yielded A/K ratios between those produced by TiO$_2$ and by E$_4$N$\left[\text{FeCl}_4\right]$ [27,28]. This may be because cyclohexane and cyclohexanol are adsorbed less strongly on polyoxotungstates than on TiO$_2$, but more strongly than on E$_4$N$\left[\text{FeCl}_4\right]$.

3. Materials and Methods

Tetraethylammonium tetrachloroferrate(III), titanium dioxide (anatase), iron(III) chloride on silica gel (5% by mass), cyclohexanol, cyclohexanone, and chlorocyclohexane were obtained from Sigma-Aldrich (St. Louis, MO, USA). Cyclohexane (GCMS grade) was obtained from VWR Scientific (Radnor, PA, USA). Dowex 1-X10 (200–400 mesh) was from J. T. Baker (Phillipsburg, NJ, USA). Tetrabutylammonium bromide was from Alfa Aesar (Tewksbury, MA, USA).

The photolysis of cyclohexane was carried out most frequently on 1.0 mL samples in glass spectrophotometer cells (Starna 1-SOG-10; Starna Cells, Atascadero, CA, USA; %T is attenuated to 50% at 315 nm). The irradiation source was a 100-W Osram HBO 100W/X3 (Osram GmbH, Munich, Germany) mercury lamp in an Oriel Q housing, passed through a lowpass filter to remove undesired portions of the UV, and focused on the sample. In most experiments a balloon containing air, O$_2$, N$_2$, or mixtures of these was affixed to the opening of the cuvette by means of a plastic pipette tip, which made a firm seal. A fan was used to maintain the temperature of the cuvette at 22 ± 2 °C. The light intensity incident on the sample was measured with a Thorlabs PM400 power meter (Newton, NJ, USA) with a Thorlabs S314C thermal sensor. Some irradiations were performed with a 500-W mercury lamp (Osram HBO 500 W/B; Osram GmbH, Munich Germany) in an Oriel housing with a glass focusing lens. Samples were placed in a glass cuvette with a stem (similar in design to a Starna 3-Q-10/SBT-Starna Cells, Atascadero, CA, USA), to which was attached a balloon with a desired gas mixture. When using either irradiation source the photolysate was stirred magnetically.
Additional experiments were performed in sunlight, in several different containers. Among these were a fused silica right triangular prism (Starna 24-SB-Q-10) and a fused silica rectangular prism (Starna 23-Q-40), both from (Starna Cells, Atascadero, CA, USA). A balloon was attached to the circular stopper hole in the prism by means of a plastic pipette tip bent to an angle of about 60°, and the prism, containing the cyclohexane and solid catalyst, was placed on its side in the sun. The mixture was not stirred and no focusing lens was used to increase the photon flux on the samples.

UV-visible spectra were recorded with a Cary 50 spectrophotometer (Varian Australia, Mulgrave, Australia). GC-MS measurements were carried out on a Shimadzu QP-2100 instrument (Shimadzu Scientific Instruments, Kyoto, Japan) with a Shimadzu 221-75954-30 column, containing a p-bis(dimethylsiloxy)phenylene/dimethylsiloxane crosspolymer as stationary phase. The oven start temperature was 40 °C, and this temperature was maintained for 12 mins, during which cyclohexanol, cyclohexanone, and chlorocyclohexane were eluted. Thereafter a 40 °C/min linear temperature gradient was applied to a final temperature of 280 °C. A 20:1 split ratio was applied to sample injections. Species were identified from their mass spectra and by comparison with authentic samples. Total ion count peak areas were measured for known concentrations of cyclohexanol, cyclohexanone, and chlorocyclohexane. There was some second order dependence of the peak areas on concentrations, yielding quadratic equations with an $R^2$ of 0.992 or better. The empirical equations were used to determine the concentrations reported herein.

4. Conclusions

Tetraethylammonium tetrachloroferrate has been shown to heterogeneously catalyze the photooxidation of neat cyclohexane to cyclohexanol and cyclohexanone, and to retain some photocatalytic activity into the blue region of the spectrum. In a direct comparison with TiO$_2$ under UV irradiation, Et$_4$N[FeCl$_4$] yielded only about 50% of what was achieved with TiO$_2$. Both the higher catalytic efficiency of TiO$_2$ (at irradiation wavelengths it absorbs) and the lower A/K ratio, in comparison to Et$_4$N[FeCl$_4$] can be attributed to stronger adsorption on TiO$_2$ of cyclohexane and its products. Since Et$_4$N[FeCl$_4$] absorbs light well into the visible, it has a strong advantage over TiO$_2$ when irradiation is mainly with visible light, and it has a distinct advantage when a high A/K ratio is required. Furthermore, long irradiation times can be employed with Et$_4$N[FeCl$_4$] without loss of product to mineralization.

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References

1. Maldotti, A.; Molinari, A.; Amadelli, R. Photocatalysis with organized systems for the oxofunctionalization of hydrocarbons by O$_2$. Chem. Rev. 2002, 102, 3811–3836. [CrossRef] [PubMed]
2. Li, X.; Chen, G.; Po-Lock, Y.; Kutal, C. Photocatalytic oxidation of cyclohexane over TiO$_2$ nanoparticles by molecular oxygen under mild conditions. J. Chem. Technol. Biotechnol. 2003, 78, 1246–1251. [CrossRef]
3. Maldotti, A.; Varani, G.; Molinari, A. Photo-assisted chlorination of cycloalkanes with iron chloride heterogenized with Amberlite. Photochem. Photobiol. Sci. 2006, 5, 993–995. [CrossRef] [PubMed]
4. Hoggard, P.E.; Gruber, M.; Vogler, A. The photolysis of iron(III) chloride in chloroform. Inorg. Chim. Acta 2003, 346, 137–142. [CrossRef]
5. Shulpin, G.B.; Kats, M.M. Ferric chloride catalyzed photooxidation of alkanes by air in organic solvents. React. Kinet. Catal. Lett. 1990, 41, 239–243. [CrossRef]
6. Shul’pin, G.B.; Nizova, G.V.; Kozlov, Y.N. Photochemical aerobic oxidation of alkanes promoted by iron complexes. New J. Chem. 1996, 20, 1243–1256.
7. The H–Cl Bond Energy Is 432 kJ/mol, While that of H–OH Is 497 kJ/mol. “Bond-Dissociation Energy”. Available online: https://en.wikipedia.org/wiki/Bond-dissociation_energy (accessed on 18 September 2018).
8. Hoggard, P.E.; Maldotti, A. Catalysis of the photodecomposition of carbon tetrachloride in ethanol by an Amberlite anion exchange resin. J. Catal. 2010, 275, 243–249. [CrossRef]
9. Solis Montiel, E.; Solano, J.A. Spectrophotometric analysis for chlorine by the extraction of triiodide formed in chloroform solution of tetrabutylammonium perchlorate. Ingeniería y Ciencia Química 1986, 10, 45–48.
10. Chan, A.M.; Harvey, B.M.; Hoggard, P.E. Photodecomposition of dichloromethane catalyzed by tetrachloroferrate(III) supported on a Dowex anion exchange resin. Photochem. Photobiol. Sci. 2013, 12, 1680–1687. [CrossRef] [PubMed]
11. Hoggard, P.E.; Cohen, L.R.; Peña, L.A.; Harvey, B.M.; Chan, A.M. The dependence of photocatalytic reaction yields on catalyst mass in solid-liquid suspensions. Curr. Catal. 2013, 2, 2–6. [CrossRef]
12. Loddo, V.; Addamo, M.; Augugliaro, V.; Palmisano, L.; Schiavello, M.; Garrone, E. Optical properties and quantum yield determination in photocatalytic suspensions. AIChE J. 2006, 52, 2565–2574. [CrossRef]
13. Barnard, K.R.; Bright, V.R.; Enright, R.J.; Fahy, K.M.; Liu, A.C.; Hoggard, P.E. Photooxidation of toluene by visible and near-UV light catalyzed by tetraethylammonium tetrachloroferrate. Catalysts 2018, 8, 79. [CrossRef]
14. Ohkubo, K.; Hirose, K.; Fukuzumi, S. Photooxygenation of alkanes by dioxygen with $p$-benzoquinone derivatives with high quantum yields. Photochem. Photobiol. Sci. 2016, 15, 731–734. [CrossRef] [PubMed]
15. Ohkubo, K.; Hirose, K.; Fukuzumi, S. Solvent-free photooxidation of alkanes by dioxygen with 2,3-dichloro-5,6-dicyano-$p$-benzoquinone via photoinduced electron transfer. Chem. Asian J. 2016, 11, 2255–2259. [CrossRef] [PubMed]
16. Peña, L.A.; Segura, R.E.; Chan, A.M.; Hoggard, P.E. Photodegradation of dichloromethane catalyzed by iron(III) chloride on silica gel. Curr. Catal. 2014, 3, 35–38. [CrossRef]
17. Boarini, P.; Carassiti, V.; Maldotti, A.; Amadelli, R. Photocatalytic oxygenation of cyclohexane on titanium dioxide suspensions: Effect of the solvent and of oxygen. Langmuir 1998, 14, 2080–2085. [CrossRef]
18. Brusa, M.A.; Di Iorio, Y.; Churio, M.S.; Grela, M.A. Photocatalytic air oxidation of cyclohexane in CH$_2$Cl$_2$-C$_6$H$_{12}$ mixtures over TiO$_2$ particles. An attempt to rationalize the positive effect of dichloromethane on the yields of valuable oxygenates. J. Mol. Catal. A Chem. 2007, 268, 29–35. [CrossRef]
19. Almqvist, C.B.; Biswas, P. The photo-oxidation of cyclohexane on titanium dioxide: An investigation of its competitive adsorption and its effects on product formation and selectivity. Appl. Catal. A 2001, 214, 259–271. [CrossRef]
20. Molinari, A.; Amadelli, R.; Andreotti, L.; Maldotti, A. Heterogeneous photocatalysis for synthetic purposes: Oxygenation of cyclohexane with H$_3$PW$_4$O$_{16}$ and (nBu$_4$N)$_4$W$_{10}$O$_{32}$ supported on silica. Dalton Trans. 1999, 1203–1204. [CrossRef]
21. Molinari, A.; Maldotti, A.; Amadelli, R.; Sgobino, A.; Carassiti, V. Integrated photocatalysts for hydrocarbon oxidation: Polyoxotungstates/iron porphyrins systems in the reductive activation of molecular oxygen. Inorg. Chim. Acta 1998, 272, 197–203. [CrossRef]
22. Simic, M.; Hayon, E. Spectroscopic investigation of cyclohexanol and cyclohexyl radicals and their corresponding peroxy radicals. J. Phys. Chem. 1971, 75, 1677–1680.
23. Howard, J.A.; Ingold, K.U. Absolute rate constants for hydrocarbon autoxidation. XV. The induced decomposition of some $t$-hydroperoxides. Can. J. Chem. 1969, 47, 3797–3801. [CrossRef]
24. Hermans, I.; Jacobs, P.A.; Peeters, J. Understanding the autoxidation of hydrocarbons at the molecular level and consequences for catalysis. J. Mol. Catal. A Chem. 2006, 251, 221–228. [CrossRef]
25. Hermans, I.; Nguyen, T.L.; Jacobs, P.A.; Peeters, J. Autoxidation of cyclohexene: Conventional views challenged by theory and experiment. ChemPhysChem 2005, 6, 637–645. [CrossRef] [PubMed]
26. Hermans, I.; Peeters, J.; Jacobs, P.A. Autoxidation of ethylbenzene: The mechanism elucidated. J. Org. Chem. 2007, 72, 3057–3064. [CrossRef] [PubMed]
27. Maldotti, A.; Molinari, A.; Varani, G.; Lenarda, M.; Storaro, L.; Bigi, F.; Mazzacani, A.; Sartori, G. Immobilization of (n-Bu$_4$N)$_4$W$_{10}$O$_{32}$ on mesoporous MCM-41 and amorphous silicas for photocatalytic oxidation of cycloalkanes with molecular oxygen. J. Catal. 2002, 209, 210–216. [CrossRef]
28. Maldotti, A.; Amadelli, R.; Carassiti, V.; Molinari, A. Catalytic oxygenation of cyclohexane by photoexcited (nBu$_4$N)$_4$W$_{10}$O$_{32}$: The role of radicals. Inorg. Chim. Acta 1997, 256, 309–312. [CrossRef]

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