Photocatalysed oxidation of cyclohexane by $W_{10}O_{32}^{4−}$ irradiation with natural sunlight

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ABSTRACT. Using global sun UV-emission, dioxygen, $W_{10}O_{32}^{4−}$ as a photocatalyst in acetonitrile solution we have performed cyclohexane oxidation. Such photooxidation was very effective and could be applied in a large scale. The best result was obtained using 20% acetonitrile/cyclohexane emulsion and $W_{10}O_{32}Na_4$ as a catalyst.

1. INTRODUCTION

The oxidation of hexane in mild conditions still have a great interest and an important industrial significance. Large amounts of prepared of cyclohexanol and cyclohexanone are made for nylon production [1]. Enzymes are able to oxidize cyclohexane to cyclohexanone at room temperature with high selectivity [2], but it is difficult to use them in a very large scale.

Many studies using cytochrome P-450, metalloporphyrins and metallophthalocyanines [3–5] and Gif reagents types [6] have been reported, but in these systems secondary reactions stop the catalysis.

About 50% of the solar irradiation reaching the surface of the earth fall in the range of 300–700 nm and can be used to drive a wide variety of photochemical reactions [7,8] and in the near future, industrial realizations in production of fine chemicals using solar energy will be considered as a field with relatively good prospects.

Photochemical synthesis usually proceeds efficiently and selectively. Some specific compounds of interest can only be produced in a reasonable way photochemically by direct irradiation or by activation with a photocatalyst.

Several groups have used artificial UV light and $W_{10}O_{32}^{4−}$ anion as a photocatalyst to undertake the alkane photooxidation [9] our contribution has been to suggest that peroxides are formed quantitatively by direct irradiation or by activation with a photocatalyst.

If we compare the optical spectrum of the catalyst $W_{10}O_{32}^{4−}$ and the solar emission in the useful region (300–400 nm) we can notice that about 42% of the sun UV-emission is absorbed by the catalyst [7].

2. MATERIALS AND METHODS

Acetonitrile (AN) SDS analytical or technical grade (for large scale experiments), tetramethyl phosphate (TMP) from Aldrich were used as purchased, adamantane (Ad) (Aldrich, reagent grade) was purified by recrystallization from heptane, cyclohexane (Fluka reagent grade) was either purified with $H_2SO_4$ then washed with water till neutrality then dried over Na$_2$SO$_4$ or used as purchased (large scale experiments). The decatungstate $W_{10}O_{32}Na_4$ and [(C$_4$H$_9$)$_4$N]$_4$$W_{10}O_{32}$ noted ($W_{10}O_{32}$TBA) were prepared according to literature methods [1]. The decatungstates were crystallised three times from acetonitrile and checked for purity by UV-visible spectroscopy $\lambda_{\text{max}}$ (CH$_3$CN) 323 nm $\epsilon = 13.800 \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ and by microanalysis: $W_{10}O_{32}Na_4$ found: Na 3.36, W 63.95 required: Na 3.20, W 63.97; C$_{60}$H$_{154}$N$_4$, $W_{10}O_{32}$, 2$H_2$O tetrabutylammonium decatunstate ($W_{10}O_{32}$TBA) $\lambda_{\text{max}}$ (CH$_3$CN) 323 nm $\epsilon = 14500 \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ found C 22.98, H 4.13, N 1.68, W 55.40 required: C 23.1, H 4.33, N 1.68, W 55.40.

Irradiation samples were prepared by dissolving the alkane (Ad) $1.8 \times 10^{-4}$ mol and the decatungstate catalyst ($5.5 \times 10^{-7}$ mol) in the acetonitrile/$H_2O$ 98:2 which was saturated with dioxygen during 15 min and then quickly transfered into the photochemical reactor for irradiation. Cyclohexane was added as mentioned in the text. Sun irradiations have been done at Plataforma Solar de Almeria (CIEMAT).

The reactor geometry and the catalyst's concentration ensure the absorption of at least 99.9% of the incident light. Aliquots of the photolyte (1 ml) were removed for analysis at appropriate time intervals. The iodometric determination of hydroperoxides was performed by using a standard method, modified for organic media [12,13].

For small size irradiation test, the photoreactor was 1 m long by 0.2 m wide, CPC miror with an optical concentration of 2. A 32 mm OD Liebig-type glass cooler (two coaxial tubes, forming an inner and outer compartment) was mounted in its line of focus. The thickness of the outer compartment inside where was circu-
lated the solution was about 7 mm. Small magnetically
coupled centrifugal pump (polypropylene) was circu-
lating the reaction mixture through the outer compart-
ment of the cooler where it was irradiated while cooling
water was circulated through the inner compartment.
The total circuit volume was 1 l including a 250 ml bot-
tle with bottom outlet and inlet for sampling and intro-
duction of dioxygen. The parabolic mirror was set with
an angle of 37° with respect to the horizontal since the
latitude of Almeria is around 37° and this inclination
allows the maximum yearly efficiency for this type of
solar collectors. The global UV power (Wh/m²) which
take into account direct and scattered radiation, was
solar collectors. The global UV power (Wh/m²) which
allows the maximum yearly efficiency for this type of

1857 Wh/m² during all the week irradiation. The so-
diation during two more days. The solution received
ane were added and again exposed to the sun irra-

For larger size experiments (4 to 5 l) same type equip-
ment with longer and wider irradiation tubes were used
[7].

After irradiation the solution mixture was reduced
by an excess of TMP, the solution was kept for 12 h at
room temperature in the dark, then AN and residual cy-
clohexane was vacuum evaporated and the residue was
distilled under reduced pressure (0.1 mmHg). The differ-
ent fractions were GC analysed and the yield of cyclo-
hexanone, cyclohexanone and polyoxygenated products
were determined. The quantitative GC analysis were
performed on a Varian 3400 instrument, equipped with
a DB-Wax fused silice capillary column 25 m ×0.25 mm
(i.d.) flame ionisation detector and a Varian 4400 elec-
tronic integrator. Nitrogen was the carrier gas. The
1.0 ml aliquots of the photolytes were treated with
1.0 ml of TMP and GC analysed.

We have noticed that the rate of hydroperoxide for-

3. RESULTS

As a first experiment (with 2 l solution Ad, AN,
W10O32TBA) we have undertaken the photooxidation
of adamantane (because Ad is less volatile and eas-
ier to analyse) and we have followed the sun photo-
chemical reaction by titration of the total amount of
in situ formed peroxide [1] (iodometric method on 1 ml
aliquots).

We have noticed that the rate of hydroperoxide for-

mation was decreasing when the sun intensity was de-
clining late in the afternoon and furthermore it is inter-
esting to note a very small decrease of hydroperoxide
formation when there was a shortage of the required
dioxygen, leading to a pale blue color of the solution.
The total amount of peroxide formation was following
first order kinetics. We have shown that it was possi-
ble to increase the volume and the size of the reactor and we have done one experiment with 5 l of solution mixture during two consecutive sunny days.

The concentration of adamantane was decreasing sharply according to the delivered solar energy whereas the concentration of 1-adamantanol and 2-adamantanol plus adamantanone, was first increasing and then decreasing slowly [7]. That was not due to the lack of efficiency of the catalyst (if the catalyst was filtered, washed with acetonitrile, it can be used again) but to the fact that the *in situ* formed compounds were also reacting with the excited $W_{10}O_{32}^-$ to produce several polyoxoygenated compounds. At the beginning of the reaction the total amount of polyoxoygenated products remains relatively small but sharply increases after several hours of irradiation, while at the same time the adamantanos and adamantanone concentrations were decreasing. The polyoxoygenated products have been studied by coupled GC-mass spectrometry analysis. For this study the reduction of the polyoxoygenated products by TMP has not been done before the GC mass spectrometry study to be aware of oxidation derivatives of TMP in the ionisation chamber. The hydroperoxides formed during the photolysis were decomposed in the chromatograph injector, then separated by the chromatographic column and analysed by mass spectrometry. By comparison of mass spectra of adamant-1 and adamant-2-ols, we have identified adamantan-1, 3-diol, adamantan-1, 2 and adamantan-2, 4-diol, in the reaction mixture. Similarly, comparing the fragmentation spectra of adamantanone, we have characterized adamantanol-2-one and adamantanondione. The structure of these products have been confirmed by IC mass spectrometry.

This experiment shows that there is no limit in volume and in duration, but while the reaction was proceeding, the amount of secondary products was increasing. In order not to have a very complicated mixture, it is better to irradiate only during one sunny day.

In the case of cyclohexane it is necessary, because of its volatility to use a completely closed apparatus under dioxygen atmosphere. After several small scale experiment (0.5-1 l) a large one (4 l solution mixture) was undertaken. In order to demonstrate the industrial feasibility in a large scale we have used commercially available cyclohexane and acetonitrile. We also added a large amount of cyclohexane during the running reaction (after 3 sunny days) to show the absence of the loss of the activity of the catalyst and to see whether the reaction stops or continues. The concentration of the cyclohexane was still decreasing with increasing amount of the sun energy received by the solution (Figure 1). It was noticeable that after addition of 150 ml of cyclohexane the behaviour of the reaction was following the same first order kinetics. That is very important because it shows that the catalyst is effectively regenerated and can be used for a long period of time.

After 5 day irradiation (1857 Wh/m$^2$) we have obtained 8 g of mixture of cyclohexanol, cyclohexanone and 6.3 g of distillable polyoxidation products. The overall oxidation product yield versus the total amount of cyclohexanol added was 5% this yield is not very significant since we have used a large excess of cyclohexane to increase the contact with the decatungstate excited state. The molecular ratio of the oxidation products versus the amount of received energy Wh/m$^2$ was $8.5 \times 10^{-5}$ and the turn over of the catalyst was 66. The coefficient $k$ (ratio of distilled oxidation product against delivered energy by m$^2$ and the number of mole of the catalyst) was $3.54 \times 10^{-2}$. That number is particularly interesting because it takes into account of the three important reaction parameters.

In the Figure 2 is reported the first order kinetics of the total amount of the peroxide formation (measured by iodometric method).

As in the case of adamantane, the total amount of peroxide formation follows first order kinetics (Figure 2). We also made one test experiment with 1.3 l of 10% cyclohexane/AN solution (20 ml of cyclohexane was added after the first and second day irradiation) to see if the evolution of the reaction was affected by such addition during the course of the reaction. We noticed that the decrease of the cyclohexane was remaining quite slow (20% after 3 days) and the formation of the cyclohexanol and that the cyclohexanone stayed below 10%.

After the working up 1.42 g of cyclohexanol, 2.56 g of cyclohexanone and 0.8 g of distillable polyoxoygenated products were obtained. The total oxidation products yield against the total amount of cyclohexane used was 3.6%, 5% without having added the two 20 ml fractions. The ratio of the oxidation products versus the received energy was $13 \times 10^{-5}$. In this experiment the catalyst turn over was found 63. The molar ratio of the distilled oxidation products versus the delivered energy and the number of the mole of catalyst ($k$) was $3.54 \times 10^{-2}$. It is noticeable that the efficiency of this reaction was
increased comparing to the 5% homogeneous solution one. It was interesting to note that in such a case there was more production of cyclohexanone than cyclohexanol and a small quantity of distillable polyoxidation products.

In order to increase the yield of the photooxidation reaction, we increase the ratio cyclohexane/AN till we get an emulsion and we have shown that the ratio of such reaction improved a lot much, reaching 20% of cyclohexanol formation, after two day irradiation (196 Wh/m²) while the concentration of the cyclohexane in the acetonitrile was decreasing of about 50% with W₁₀O₃₂TBA and 30% in the case of W₁₀O₃₂Na₄ (Figures 3 and 4). The formation of cyclohexanol and cyclohexanone is faster at the beginning of the irradiation, then the curves are flattening because, as we have already mentioned, the initially formed products are also oxidized giving polyoxygenated products. We remark that the yield of the polyoxygenated compounds starts increasing at the end of the first day (Figure 4). In the reaction mixture, after TMP reduction, by GC and mass spectrometry analysis we can identify the cyclohexane diol, cyclohexanol-one, cyclohexadiene and several dimeric products. The structure of these products have also been confirmed by IC mass spectrometry.

With W₁₀O₃₂TBA, after the working up we have obtained 11.16 g of oxidation products including 3.64 g of cyclohexanol and 1.41 g of cyclohexanone and also 6.11 g of distillable polyoxidation products the yield compared to cyclohexane transformed was 5%. The overall catalyst turn over was found to be 146 and the energetic ratio was 35 × 10⁻⁵. The ratio of the distilled oxidation products versus the delivered energy and the number of moles of catalyst was 71:760 × 10⁻².

The best result was obtained for 20% cyclohexane/AN using W₁₀O₃₂Na₄ as a catalyst (Figure 5) since k was the highest. In this case that was expected since we have previously shown that the tetrabutylammonium salt gives side reactions [1]. The sodium decatungstate is soluble in water and we tried to oxidize the cyclohexane in emulsion of water and cyclohexane at pH around
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Figure 5. Comparative cyclohexanol formation with $W_{10}O_{32}$ TBA, for various proportions of cyclohexane in cyclohexane/acetonitrile mixtures: a:5%, b:10%, and c:20%.

3 but it was impossible to detect the formation of any oxidation products.

Using UV-lamp (Figure 6) we have noticed that the best cyclohexanol yield was obtained for 10% of the mixture cyclohexane/AN. That could be explained by the difficulty to get good emulsion in the small volume of the lamp irradiation system. In such a case since the irradiation period was quite short (6 h) the yield of the oxidation product was very low.

4. CONCLUSION

We have shown that it is possible to oxidize efficiently adamantane and cyclohexane using oxygen and UV-sun irradiation. To be efficient the process should use short irradiation time (one day period) extract the oxidation products and recycle the acetonitrile and the catalyst.

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REFERENCES
