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 prepared of cyclohexanol and cyclohexanone are made for nylon production [1]. Enzymes are able to oxidize cyclohexane to cyclohexanol 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 through the formation of an intermediate X which gives rise to a caged radical pair reacting with dioxygen and building up selectively the corresponding hydroperoxide [7].

We are interested in using sun energy because we believe that the cheapest way to photooxidize hydrocarbons is to use natural sunlight and dioxygen [7, 10, 11].

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 phosphite (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_2SO_4 or used as purchased (large scale experiments). The decatungstate $W_{10}O_{32}Na_4$ and $[(C_4H_9)_4N]_4W_{10}O_{32}$ 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 λ_{max} (CH_3CN) 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; $C_{64}H_{154}N_4$, $W_{10}O_{32}$, $24H_2O$ tetrabutylammonium decatungstate ($W_{10}O_{32}TBA$) λ_{max} (CH_3CN) 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) $1.8 \times 10^{-3} \text{ mol}$ and the decatungstate catalyst ($5.5 \times 10^{-5} \text{ mol}$) in the acetonitrile/ H_2O 98:2 which was saturated with dioxygen during 15 min and then quickly transferred 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 mirror 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-

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lated the solution was about 7 mm. Small magnetically coupled centrifugal pump (polypropylene) was circulating the reaction mixture through the outer compartment 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 bottle with bottom outlet and inlet for sampling and introduction 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/m^2) which take into account direct and scattered radiation, was recorded every day. Integration of the UV-power gives the incident energy Wh/m^2 received by the sample during the irradiation.

For larger size experiments (4 to 5 l) same type equipment 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 cyclohexane was vacuum evaporated and the residue was distilled under reduced pressure (0.1 mmHg). The different fractions were GC analysed and the yield of cyclohexanol, 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 $25\text{ m} \times 0.25\text{ mm}$ (i.d.) flame ionisation detector and a Varian 4400 electronic integrator. Nitrogen was the carrier gas. The 1.0 ml aliquots of the photolytes were treated with 0.1 ml of TMP [14]. The samples were analysed at a temperature of 50°C (2 min) which was then increased to 200°C at a rate of $10^\circ\text{C min}^{-1}$. Control experiments showed that TMP did not reduce adamantanone or cyclohexanone to the corresponding alcohols. The GC-MS analysis were performed on a Finnigan 4000 instrument. The UV spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer and the CI-MSS spectra were recorded on AEI MS9 instrument with methane, isobutane or NH_3 as the reactant gases. Microanalyses were performed by the Laboratory of Microanalysis (ICSN-CNRS).

Experiment with 4 l solution 5% cyclohexane/AN. 2.4 mM of $\text{W}_{10}\text{O}_{32}\text{TBA}$ were dissolved under magnetic stirring in mixture of 3.717 l of technical AN, 70 ml of water, the solution was dioxygen saturated and 213 ml (5% in volume) of cyclohexane was then added. The solution was transferred in irradiation apparatus and continuously saturated with dioxygen. After three days of sun irradiation (850 Wh/m^2) 150 ml of cyclohexane were added and again exposed to the sun irradiation during two more days. The solution received 1857 Wh/m^2 during all the week irradiation. The solution was then reduced by an excess of TMP during 12 hours then AN and residual cyclohexane were removed under reduced pressure and the residue was vacuum distilled (0.1 mmHg) and the fractions were GC

analysed for products quantification and identification. We got 7.98 g of mixture cyclohexanol, cyclohexanone and 6.31 g of polyoxidation products.

We have determined coefficient $k = [\text{distillable oxidation products}]/\text{Wh} \cdot \text{m}^{-2} \times [\text{catalyst}]$ [] molar concentration, for this experiment k was found to be 3.5×10^{-2} .

Experiment with 1.3 l solution 10% cyclohexane/AN. 0.85 mM of $\text{W}_{10}\text{O}_{32}\text{TBA}$ were dissolved under magnetic stirring of 1.144 l of technical AN and 26 ml of water, the solution mixture was saturated with dioxygen and 130 ml of cyclohexane were added before pouring the solution in the irradiation apparatus. During the sun irradiation, the solution was saturated with dioxygen. After the first and second day irradiation 20 ml of cyclohexane were added. After three days irradiation (it was sometimes very cloudy) the solution received 386 Wh/m^2 . After working up we have obtained 1.42 g of cyclohexanol 2.56 g of cyclohexanone and 0.8 g distillable of polyoxygenated compounds, $k = 3.54 \times 10^{-2}$.

Experiment with 1.3 l solution 20% cyclohexane/AN. 0.85 mM of $\text{W}_{10}\text{O}_{32}\text{TBA}$ were dissolved under magnetic stirring in a mixture of 1.014 l of technical AN, 26 ml of water and was saturated with dioxygen then 260 ml of cyclohexane were added. After the working up we got 3.64 g of cyclohexanone, 1.41 g of cyclohexanol and 6.11 g of polyoxidation products, the overall received UV sun energy was 354 Wh/m^2 and coefficient k was 41×10^{-2} .

Experiment with 1.3 l solution were $\text{W}_{10}\text{O}_{32}\text{TBA}$ was replaced by $\text{W}_{10}\text{O}_{32}\text{Na}_4$. After the working up we got 1.59 g of cyclohexanol and cyclohexanone and 4.773 g of polyoxidation products the total received UV sun energy was 196 Wh/m^2 (it was sometime cloudy) and the coefficient k was 50.98×10^{-2} .

The experiments using artificial UV irradiation (the UV source was a Hanovia 125 W medium-pressure Hg arc lamp) have been accomplished with classical UV irradiation apparatus on a 100 ml of continuously dioxygen saturated solution containing 0.1 mM of $\text{W}_{10}\text{O}_{32}\text{Na}_4$ as catalyst, 2 ml of water and 5%, 10% or 20% of cyclohexane respectively. 1 ml aliquots were reduced by TMP and GC analysed.

3. RESULTS

As a first experiment (with 2 l solution Ad, AN, $\text{W}_{10}\text{O}_{32}\text{TBA}$) we have undertaken the photooxidation of adamantane (because Ad is less volatile and easier to analyse) and we have followed the sun photochemical 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 formation was decreasing when the sun intensity was declining late in the afternoon and furthermore it is interesting 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 $W_{10}O_{32}^{4-}$ to produce several polyoxygenated compounds. At the beginning of the reaction the total amount of polyoxygenated products remains relatively small but sharply increases after several hours of irradiation, while at the same time the adamantanols and adamantanone concentrations were decreasing. The polyoxygenated products have been studied by coupled GC-mass spectrometry analysis. For this study the reduction of the polyoxygenated 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 adamantan-1 and adamantan-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 adamantandione. 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/m²) we have obtained 8 g of mixture of cyclohexanol, cyclohexanone

Figure 1. Evolution of the concentration of the cyclohexane (4 l experiments of 5% homogeneous cyclohexane/AN, $W_{10}O_{32}TBA 5.5 \cdot 10^{-5} M$ solution) during one week UV-sun irradiation and after addition of 150 ml of cyclohexane (after the third day) against received UV-sun energy.

and 6.3 g of distillable polyoxidation products. The overall oxidation product yield versus the total amount of cyclohexane 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/m² was 8.5×10^{-5} and the turn over of the catalyst was 66. The coefficient k (ratio of distilled oxidation product against delivered energy by m² and the number of mole of the catalyst) was 3.54×10^{-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 polyoxygenated 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 13×10^{-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 3.54×10^{-2} . It is noticeable that the efficiency of these reaction was

Figure 2. First order plot of the total peroxide formation against the global sun UV-emission during a 5% cyclohexane/AN, $W_{10}O_{32}TBA$ ($5.5 \cdot 10^{-5} M$), 41 experiment. The peroxide concentration has been calculated by iodometric dosage [12, 13] of the total peroxides formed during the course of the reaction.

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 ($196 Wh/m^2$) while the concentration of the cyclohexane in the acetonitrile was decreasing of about 50% with $W_{10}O_{32}TBA$ and 30% in the case of $W_{10}O_{32}Na_4$ (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, cyclohexadione and several dimeric products. The structure of these products have also been confirmed by IC mass spectrometry.

With $W_{10}O_{32}TBA$, 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 the mole of catalyst (k) was 58.333×10^{-2} . With $W_{10}O_{32}Na_4$ and after treatment 1.59 g of cyclohexanol and cyclohexanone while 4.73 g of polyoxygenated

Figure 3. Ratio of the cyclohexane, cyclohexanol, cyclohexanone and polyoxygenated products formed during UV-sun irradiation of one emulsion mixture (AN/cyclohexane 80:20, $W_{10}O_{32}TBA$). The reactant samples are analysed by GC analysis after TMP reduction.

Figure 4. Cyclohexane evolution and cyclohexanol, cyclohexanone and polyoxygenated products formed during sun irradiation of an emulsion mixture (AN/cyclohexane 80:20, $W_{10}O_{32}Na_4$). The reactant samples are analysed by GC analysis after TMP reduction.

compounds were found, the yield of the total oxidation products compared to cyclohexane transformed was 2.8% and the total turnover was 140 but as we have seen the UV-sun energy was much lower. The energetic ratio was found to be 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 $W_{10}O_{32}Na_4$ 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

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

Figure 6. cyclohexanol formation by UV-lamp irradiation in cyclohexane/AN mixture 5%, 10% and 20%, $W_{10}O_{32}Na_4$. The reactant samples are analysed by GC analysis after TMP reduction.

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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