

PHOTO-OXIDATION OF CYCLOHEXANE BY ATMOSPHERIC OXYGEN IN ACETONITRILE, CATALYSED BY CHLORIDE COMPLEXES OF IRON, COPPER AND GOLD*†

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During the light irradiation in air of a solution of cyclohexane in CH_3CN in the presence of catalytic quantities of FeCl_3 , CuCl_2 or AuCl_4^- , the oxygenation of cyclohexane occurs. In the case of CuCl_2 , the intermediate hexylhydroperoxide decomposes rapidly, and the main products are cyclohexanol and cyclohexanone. In the case of catalysis by AuCl_4^- the main product is the peroxide, while in the case of FeCl_3 all three products are formed in roughly equal quantities. The photo-oxidation of cyclohexane catalysed by $\text{PW}_{12}\text{O}_{40}^{3-}$ chiefly yields cyclohexylhydroperoxide.

The particular attention of researchers has recently been directed towards the search for unconventional methods for processing oil and gas hydrocarbon feedstock [2–4]. One of these methods is the metal-complex catalysed oxidation of hydrocarbons with oxygen or hydrogen peroxide in solution during light irradiation [1, 5–27]. An advantage of this method is that the process is carried out at low temperature and consequently can yield only a small number of byproducts. In a number of reactions, solar radiation can be used.

In many studies of the oxidation of hydrocarbons by molecular oxygen it has been suggested that the primary products are alkylhydroperoxides, which later partially or completely decompose with the formation of the corresponding alcohols and ketones (aldehydes). The alcohols and ketones have been analysed by means of GLC using steel columns, and here, during elution, alkylhydroperoxide decomposes entirely, yielding roughly equal amounts of alcohol and ketone [28]. At the same time, knowledge of the current concentrations of peroxides in auto-oxidation reactions should promote a better understanding of the mechanism of the process. Furthermore, alkylperoxides are valuable products, and research into ways of producing these compounds in pure form is of great interest (see, for example, [29–32]). In the present work an attempt was made to investigate the formation of cyclohexylhydroperoxide during the photochemical auto-oxidation of cyclohexane, catalysed by certain metal complexes. For comparison, the corresponding reaction sensitized by anthraquinone was also studied.

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EXPERIMENTAL

Cyclohexane was purified by shaking it with sulphuric acid and distillation. Acetonitrile was distilled over P_2O_5 .

Reactions were carried out in air in cylindrical glass vessels of 20 mm diameter, equipped with jackets cooled by running water ($\sim 10^\circ C$). The reaction solution was stirred by means of a magnetic stirrer. The volume of the solution was 10 ml. Irradiation was carried out with the full light of a DRL-250 luminescent lamp (250 W) or a DRSh-1000 high-pressure mercury lamp (1000 W). The progress of the process was followed by taking samples after certain time intervals, and these were analysed by means of GLC (each specimen was analysed twice — before and after the addition of a portion of triphenylphosphine, which reduced the cyclohexylhydroperoxide to cyclohexanol). Use was made of an LKhM-80/6 chromatograph (column length 2 m, diameter 4 mm, sorbent INERTON AW-HMDS 315–320 μm , impregnated with 5% Carbowax 1500; carrier gas argon).

RESULTS AND DISCUSSION

Earlier we showed that, during the light irradiation in air of solutions of alkanes and alkylaromatic compounds in CH_3CN in the presence of $FeCl_3$ [22], $CuCl_2$ [23] or $AuCl^{4-}$ [1], the oxygenation of the hydrocarbon occurs. According to GLC, the reaction products were the corresponding alcohol and ketone (aldehyde), although the formation of alkylhydroperoxides was also assumed. The aim of the present work was to follow, with time, the process of the formation and decomposition of cyclohexylhydroperoxide during cyclohexane oxidation catalysed by chlorides of Fe(III), Cu(II) and Au(III).

The products of cyclohexane oxidation were analysed by means of GLC. Here, if a specimen of the reaction solution without any preliminary treatment was injected into the chromatograph, it proved possible to record the formation of cyclohexanol and cyclohexanone in roughly equal quantities. If, however, excess triphenylphosphine is added to the reaction solution specimen for 10–20 min before GLC analysis, the chromatogram obtained differs greatly in many cases from the chromatogram of a specimen not reduced by triphenylphosphine in that there is an appreciable increase in the cyclohexanol peak, whereas the intensity of the cyclohexanone peak is reduced. Here the total alcohol and ketone concentration in the reduced specimen is roughly equal to the total concentration of products in a solution not treated with triphenylphosphine. The results obtained indicate that a certain amount of cyclohexylhydroperoxide is formed during cyclohexane oxidation. As shown in [28], cyclohexylhydroperoxide decomposes entirely in the chromatograph to form cyclohexanol and cyclohexanone in a ratio of roughly 1:1. At the same time it is known that cyclohexylhydroperoxide is reduced readily and almost entirely by triphenylphosphine to cyclohexanol. In this way, by comparing the results of chromatographic analysis of the reaction solution before and after its reduction by triphenylphosphine, it is possible with a certain degree of accuracy to estimate the amounts of cyclohexylhydroperoxide and cyclohexanol and cyclohexanone formed by its decomposition that are present in the solution at a given moment in time. Some inaccuracy here is due to the fact that the ratio of the cyclohexanol and cyclohexanone formed by the decomposition of the hydroperoxide (both in the solution during the reaction and in the chromatograph during analysis) differs slightly from 1:1. Only the concentration of cyclohexanone can be determined at a given moment in time with absolute accuracy (from the area of the peak

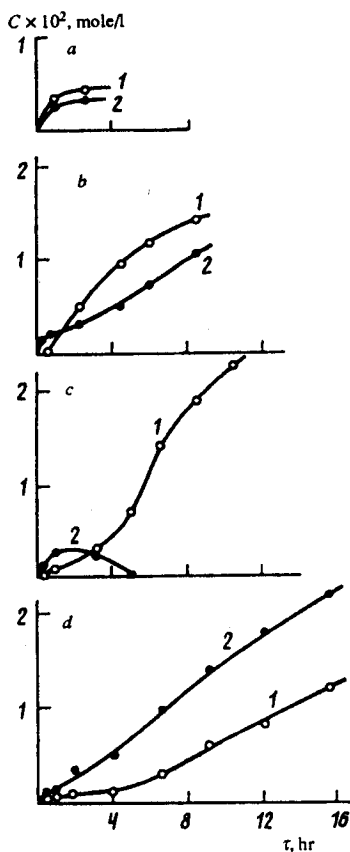


FIG. 1. Kinetic curves of accumulation of the total cyclohexanol and cyclohexanone (1) and cyclohexylhydroperoxide (2) during the oxidation of cyclohexane (0.46 mole/l) in air in a solution of CH_3CN (-10°C) during light irradiation by a luminescent lamp in the presence of 5×10^{-4} mole/l catalyst: anthraquinone (a), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (b), CuCl_2 (c) and HA and Cl_4 (d).

in the case of a reduced specimen). Note that simultaneous independent analysis of the hydroperoxide by titration provides even less accuracy, especially in those cases where the hydroperoxide concentrations and the alcohol and ketone concentrations differ sharply.

Figures 1 and 2 give the kinetic curves of accumulation of the intermediate cyclohexylhydroperoxide and of the final products (presented in the form of the total concentration of cyclohexanol and cyclohexanone) during the photo-oxidation of cyclohexane in the presence of catalytic amounts of iron (III), copper(II) and gold(III) chlorides. For comparison, corresponding curves of oxidation photocatalysed by anthraquinone and heteropolyanion $\text{PW}_{12}\text{O}_{40}^{3-}$ are also given.

From Fig. 1a it follows that the well-known photosensitizer anthraquinone is incapable of stimulating the formation of cyclohexylhydroperoxide over a long period of time. In this reaction, even in the initial period there is appreciable decomposition of the hydroperoxide with the formation of considerable quantities of alcohol and ketone. Metal complexes are much more stable photocatalysts and make it possible to carry out very extensive oxygenation of cyclohexane. The simplest form is possessed by the kinetic curves for oxidation catalysed

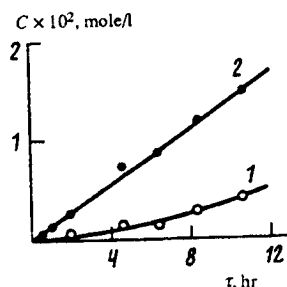
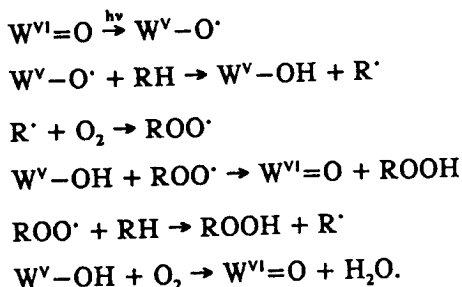
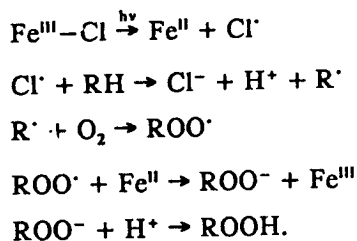


FIG. 2. Kinetic curves of accumulation of the total cyclohexanol and cyclohexanone (1) and cyclohexylhydroperoxide (2) during the oxidation of cyclohexane (0.46 mole/l) in air in a CH_3CN solution (-10°C) in the presence of $(\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (5×10^{-4} mole/l) during irradiation by the full light of a high-pressure mercury lamp.

by cyclohexyltungstate (Fig. 2). In this case, cyclohexylhydroperoxide accumulates (by a linear law) and, after the induction period, begins slowly to decompose with the formation of alcohol and ketone. This behaviour is consistent with the scheme by which, at the first stage of photoexcitation, a particle of the oxo complex detaches a hydrogen atom from the alkane. The radical produced reacts rapidly with molecular oxygen in the solution. The peroxide radical then oxidizes the W^{V} derivative, as a result of which alkylhydroperoxide and the initial photocatalyst particle are formed. The W^{V} compound can also be re-oxidized by molecular oxygen. In this case the ROO^{\cdot} radical should detach the hydrogen atom from other particles in the solution, for example from the alkane (then the reaction acquires a chain nature, and the oxo complex acts as its initiator).



In a reaction photocatalysed by iron chloride, cyclohexylhydroperoxide is formed in the initial period (Fig. 1b). The following simplified order of stages can be assumed:



After a short induction period there is a sharp increase in the concentration of alcohol and ketone. Evidently, in contrast to the reaction in the presence of polytungstate, in this case the decomposition of cyclohexylhydroperoxide is catalysed by an iron complex (for example, by an Fe^{II} derivative, which accumulates during the induction period). The decomposition of the intermediate hydroperoxide is even more rapid in a photoreaction catalysed by copper(II) chloride (Fig. 2c). As shown in [33], in this reaction, in the first hours there is a change in the absorption spectrum characteristic of CuCl_2 . It can be assumed that here a Cu^{I} derivative is formed. It is known that transition metal complexes effectively catalyse the low-temperature decomposition of cyclohexylhydroperoxide with the formation of alcohol and ketone [34]. It is interesting that the photo-oxygenation of cyclohexane catalysed by a gold chloride complex (Fig. 1d), as in the case of polytungstate, chiefly yields cyclohexylhydroperoxide, while appreciable amounts of alcohol and ketone appear only in the developed period of the reaction. A characteristic feature of the process is acceleration of accumulation both of the peroxide and of stable products after about 4 hr irradiation. In the initial period of the reaction there is a change in the absorption spectrum of the solution [33] and even partial precipitation of metallic gold on the walls of the vessel. It can therefore be assumed that, in this process also, in its developed period, the catalytically active particle is a gold complex in a low degree of oxidation.

However, in contrast to the particle formed from CuCl_2 that is catalytically active in oxidation, the gold complex is incapable of effectively breaking down the cyclohexylhydroperoxide arising during oxidation.

Thus, although all three $\text{Fe}(\text{III})$, $\text{Cu}(\text{II})$ and $\text{Au}(\text{III})$ chlorides effectively catalyse the photo-oxygenation of cyclohexane by atmospheric oxygen, the distribution of the oxidation products in these cases is different. In the developed period of the reaction with catalysis by CuCl_2 , only alcohol and ketone are present in the reaction solution, whereas with catalysis by AuCl_4^- it is mainly alkylhydroperoxide that is formed. In the case of FeCl_3 , the peroxide, alcohol and ketone are formed in roughly identical concentrations.

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