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HYDROPEROXIDATION OF ALKANES BY ATMOSPHERIC OXYGEN IN THE
PRESENCE OF HYDROQUINONE OR QUINONE CATALYZED BY COPPER(II)
ACETATE UNDER VISIBLE LIGHT IRRADIATION

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When a solution of an alkane and hydroquinone (or quinone) in CH_3CN irradiated in air by visible light in the presence of catalytic amounts of $\text{Cu}(\text{OCOCH}_3)_2$, the alkyl hydroperoxide is formed.

При облучении видимым светом на воздухе раствора алкана и гидрохинона (или хинона) в CH_3CN в присутствии каталитического количества $\text{Cu}(\text{OCOCH}_3)_2$ образуется алкилпероксид.

Oxidation of alkanes by oxygen under mild conditions is an important aim of homogeneous catalysis and has been the subject of many studies in recent years [1]. In particular, alkanes can be oxidized by dioxygen in dark conditions by $\text{Fe}(\text{py})_4\text{Cl}_2$ - PhNHNHPH system [2] or under UV light irradiation in the presence of a sensitizer (anthraquinone) [3]. Complexes of catechol with Fe^{3+} or Cu^{2+} induce peroxidation of phospholipids in liposomes in vitro [4].

We have established that alkanes can be effectively oxidized by atmospheric oxygen when their solutions in CH_3CN are irradiated in the presence of hydroquinone or quinone and catalytic

amounts of $\text{Cu}(\text{OCOCH}_3)_2$. Reactions were carried out in a cylindrical glass vessel surrounded by a water-cooled (15°C) jacket with a total solution of volume 5 ml. Full light of two photolamps (150 W) was used. Cyclohexane, n-heptane and 3-methylhexane were used as substrates. The main products were alkyl hydroperoxides identified using GLC in the form of the corresponding alcohols after reduction of the reaction solution by triphenylphosphine [5]. Small amounts alcohols and carbonyl derivatives were also found.

Kinetic curves of cyclohexane oxidation are illustrated in Figs 1 and 2. As is seen, the yield of hydroperoxide after prolonged irradiation depends on the initial concentration of hydroquinone. The rate of cyclohexane oxidation grows with the concentration of $\text{Cu}(\text{OCOCH}_3)_2$.

It should be noted that in the presence of $\text{Cu}(\text{OCOCH}_3)_2$ and pyrocatechol or resorcinol the oxidation of cyclohexane does not occur. Only negligible amounts of hydroperoxide were detected when the solution was irradiated in the presence of only hydroquinone or $\text{Cu}(\text{OCOCH}_3)_2$.

Photooxidation of n-heptane (0.76 mol/L) in CH_3CN in the presence of hydroquinone (1.0 mmol/L) and $\text{Cu}(\text{OCOCH}_3)_2$ (0.2 mmol/L) for 5.5 h yields 6.8 mmol/L of isomeric hydroperoxides identified after reduction in the form of corresponding alcohols. Relative reactivities of the C-H bonds of n-heptane in positions 1, 2, 3 and 4 (normalized, taking into account the number of hydrogen atoms in these positions) are 1:15:15:5. Photooxidation of 3-methylhexane under the same conditions yields 6.5 mmol/L of isomeric hydroperoxides. In this case normalized relative reactivities of the C-H bond at primary, secondary and tertiary carbon atoms are $1^\circ:2^\circ:3^\circ=1:20:100$.

Cyclohexane is also hydroperoxidized when a solution of alkane in CH_3CN is irradiated in the presence of $\text{Cu}(\text{OCOCH}_3)_2$ and quinone instead of hydroquinone (Fig. 3).

The mechanism of the reaction described is still open for discussion. Apparently, the crucial step of this reaction is

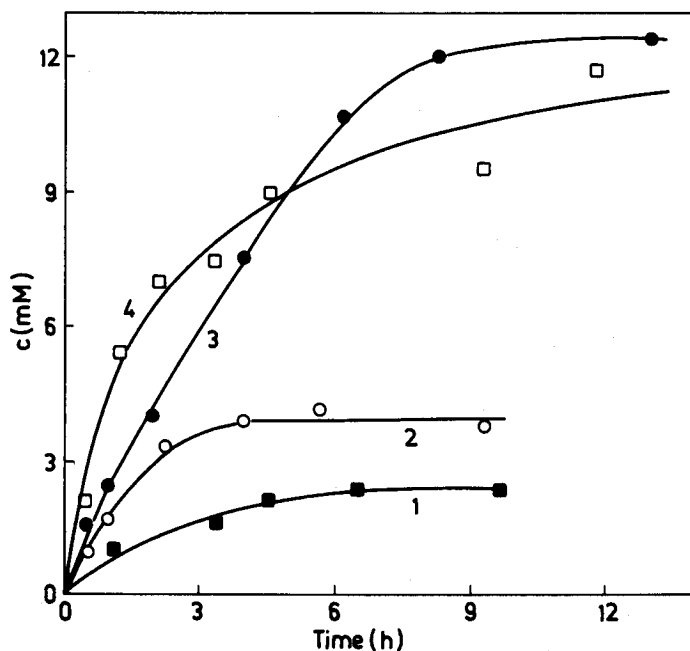


Fig. 1. Time dependence of concentration of cyclohexyl hydroperoxide in the reaction of cyclohexane (0.37 mol/L) and hydroquinone in CH_3CN in the presence of 0.2 mmol/L of $\text{Cu}(\text{OCOCH}_3)_2$ under light irradiation in air; concentrations of hydroquinone: 0.25 (1), 0.5 (2) and 2.0 (4) mmol/L

the abstraction of a hydrogen atom from alkane RH by a photo-excited species. The radical R^\cdot thus formed can react with molecular oxygen to produce ROO^\cdot radicals.

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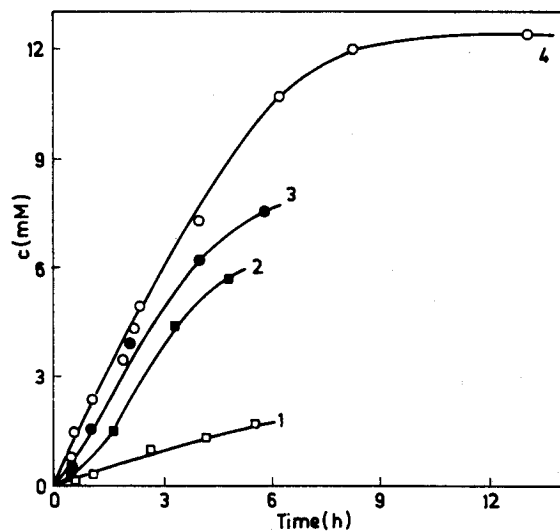


Fig. 2. Time dependence of the concentration of cyclohexyl hydroperoxide in the reaction of cyclohexane (0.37 mol/L) and hydroquinone (1.0 mmol/L) in CH_3CN under light irradiation in air in the presence of $\text{Cu}(\text{OCOCH}_3)_2$: 0.02 (1), 0.05 (2), 0.1 (3) 0.2 mmol/L (4)

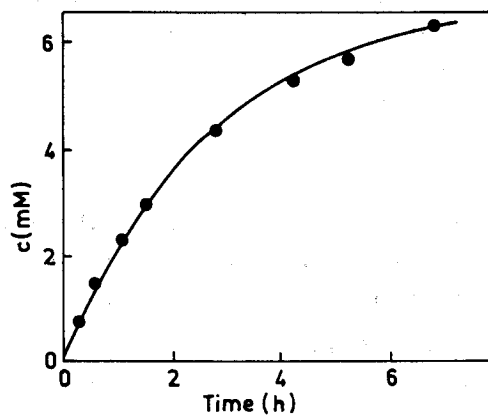


Fig. 3. Formation of cyclohexyl hydroperoxide in photooxidation of cyclohexane (0.37 mol/L) in CH_3CN in the presence of 1.0 mmol/L quinone and 0.2 mmol/L $\text{Cu}(\text{OCOCH}_3)_2$

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