

## PHOTOCHEMICAL OXIDATION OF HYDROCARBONS BY ATMOSPHERIC OXYGEN IN SOLUTIONS, CATALYSED BY $\text{AuCl}_4^-$ COMPLEX\*†

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During light irradiation ( $\lambda > 310$  nm) in air (15°C), cyclohexane, *n*-hexane and ethyl benzene in a  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$  solution in the presence of catalytic amounts of ion  $\text{AuCl}_4^-$  are oxidized with the formation of the corresponding alcohols and carbonyl compounds. The reaction evidently proceeds by several routes with the participation of chloride ligands and the formation of catalytically active peroxide complexes of gold.

Great interest has recently been shown in finding ways of processing hydrocarbons, particularly alkylaromatic and saturated hydrocarbons, with the participation of complexes of transition metals in solutions [1-5]. A special field consists of recently found reactions of alkanes photocatalysed by metal complexes (see, for example, [1,6-11]), since they proceed under mild conditions at room and even lower temperatures at atmospheric pressure and in the long term may utilize solar energy. These reactions include processes of photo-oxygenation of alkanes and arylalkanes by atmospheric oxygen in organic solvents, catalysed by halide complexes of iron [6,12-17], copper [16-19], platinum [1,16,17] and rhodium and ruthenium [1,17]. Earlier we showed that, during the irradiation of a solution of  $\text{HAuCl}_4$  in  $\text{CH}_3\text{COOH}$  in the presence of saturated hydrocarbons, chlorination of the latter occurs [20]. With a decrease in the concentration of Au(III) and the reaction proceeding in air, the main product of toluene oxidation was benzaldehyde, its yield being several times greater than the stoichiometric [21]. The present paper presents the results of studying the photo-oxygenation of hydrocarbons catalysed by  $\text{AuCl}_4^-$  in aprotic organic solvents -  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  (see [22] for preliminary report).

### EXPERIMENTAL

All reactions were carried out in air in cylindrical glass vessels of 20 mm diameter, equipped with water-cooled sleeves, during vigorous stirring by magnetic stirrers. The volume of the reaction solutions was 10 ml. The oxidation product yields were determined by means of GLC: LKhM-80/6 chromatograph, 2 m × 4 mm column, sorbent INERTON AW-HMDS

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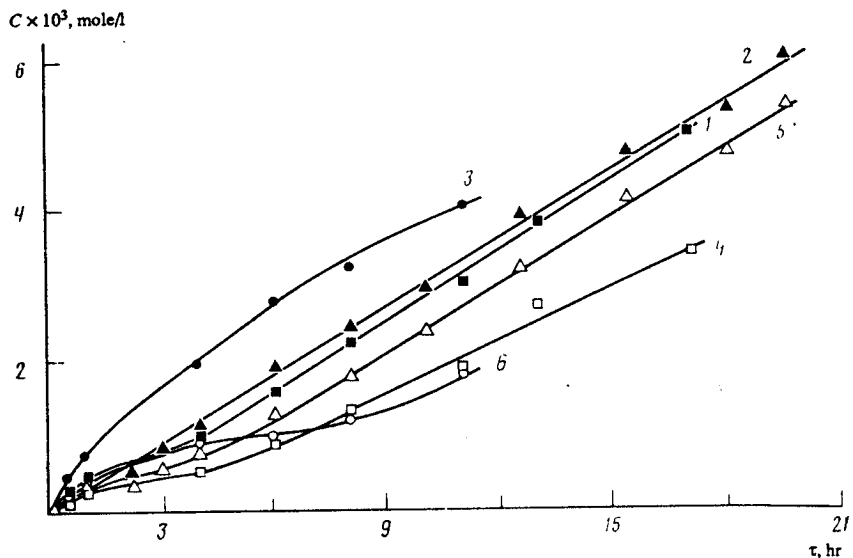


FIG. 1. Kinetic curves of accumulation of cyclohexanol (1-3) and cyclohexanone (4-6) during photo-oxidation of cyclohexane (0.46M) in presence of  $5 \times 10^{-4}$ M NaAuCl<sub>4</sub> in CH<sub>3</sub>CN without additions (1, 4) and with additions of  $2.0 \times 10^{-3}$ M 1,1-diphenylethylene (2, 5) and  $1.0 \times 10^{-3}$ M hydroquinone (3, 6).

315–320  $\mu$ m impregnated with 5% Carbowax 1500, carrier gas argon, working regime 50–170° at 4 deg/min.

To determine the quantum yield, the oxidation of cyclohexane was carried out in a heated (25°C) cylindrical quartz vessel connected to a gas burette filled with oxygen. The vessel was irradiated with monochromatic light ( $\lambda = 365$  and 436 nm) of an NVO mercury lamp (200 W). The intensity of the incident light  $I_{365} = 1.10 \times 10^{17}$  and  $I_{436} = 1.58 \times 10^{17}$  quant/sec. Absorption spectra were taken on a Philips PU 8700 spectrophotometer. Chemically pure reagents were used.

## RESULTS AND DISCUSSION

During the oxidation of cyclohexane by an NaAuCl<sub>4</sub> complex in a CH<sub>3</sub>CN solution in a relatively large concentration ( $1.5 \times 10^{-2}$ M), the main reaction products are chlorocyclohexane and also cyclohexene (which was identified after the addition of bromine in the form of 1,2-dibromocyclohexane).

Decrease in the concentration of AuCl<sub>4</sub><sup>-</sup> in CH<sub>3</sub>CN during irradiation of a cyclohexane solution in air results in cyclohexanol and cyclohexanone becoming the main reaction products, their quantity exceeding considerably the amount of complex used. With an AuCl<sub>4</sub><sup>-</sup> concentration of  $5 \times 10^{-4}$ M, chlorocyclohexane was not found in the mixture of reaction products. The kinetics of accumulation of the alkane oxygenation products in this case is shown in Fig. 1a. As can be seen, the accumulation of both oxygenation products begins at a relatively high rate, after which, after roughly 1 hr, the rate (especially in the case of cyclohexanol) falls, and only 3 hr after the start of irradiation there is an increase in the accumulation rate of oxygenation products, then continuing at a constant rate. The curves of accumula-

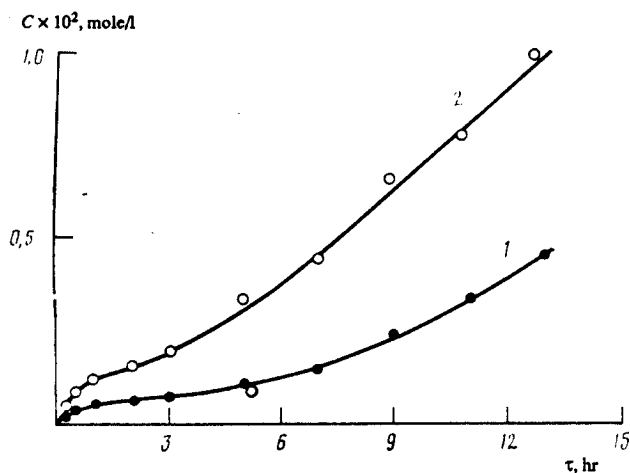


Fig. 2. Kinetic curves of accumulation of 1-phenylethanol (1) and acetophenone (2) during photo-oxidation of ethyl benzene (0.46M) in air in  $\text{CH}_3\text{CN}$  in presence of  $5 \times 10^{-4}\text{M}$   $\text{HAuCl}_4$ .

tion of products of ethyl benzene oxygenation have a similar form (it is significant that, in contrast to the oxidation of cyclohexane, ketone predominates in the products in this case) (Fig. 2). The photo-oxidation of cyclohexane in  $\text{CH}_2\text{Cl}_2$  proceeds in an even more complex manner, leading to the formation of cyclohexanol, cyclohexanone and chlorocyclohexane; in the developed period, the reaction proceeds autocatalytically (Fig. 3).

It must be noted that, in the first hours of irradiation of a solution of cyclohexane in acetonitrile, in the absorption spectra of the reaction solution there is a decrease in the intensity of the absorption band with  $\lambda = 320$  nm (see [16]), which indicates reduction of the Au(III) derivative. The product of this reduction is evidently Au(I) and also partially metallic gold, which covers the walls of the vessel in a thin layer. The photoreduction of Au(III) is accelerated sharply in the presence of tin (1,1-diphenylethylene) or hydroquinone. The Au(I) formed in this case can be stabilized, in particular during formation of a  $\pi$ -olefin complex. Additions of Au(III)-reducing compounds lead to a change in the type of kinetic curves of accumulation of products of the oxygenation of cyclohexane (Fig. 1, curves *b* and *c*). In the presence of an olefin, the accumulation of products occurs linearly over the entire reaction. It is interesting that additions ( $5 \times 10^{-3}\text{M}$ ) of methyl methacrylate have no effect on the oxidation rate of cyclohexane in  $\text{CH}_3\text{CN}$  in the presence of  $\text{HAuCl}_4$ .

The quantum yields of cyclohexanol and cyclohexanone in acetonitrile, determined for light of two wavelengths, are given in Table 1 (irradiation was carried out in an atmosphere of pure oxygen). For  $\lambda = 365$  nm, the quantum yields in the first 3 hr decrease gradually, which corresponds to a decrease in the oxygenation rate (see Fig. 1a).

Experiments with cyclohexane- $d_{12}$  showed that the kinetic isotopic effect  $k_H/k_D$  of oxygenation at the early stage of the reaction (up to 1 hr) is close to unity. The activation energy of oxygenation of cyclohexane that is observed on the initial section amounts to 10 kJ/mole (the reaction rates were determined from the slopes of the curves of accumulation in the initial period of time with variation in the temperature of the reaction solution in the 2–60°C range).

Competing oxidation of ethyl benzene and cyclohexane was carried out. In the initial

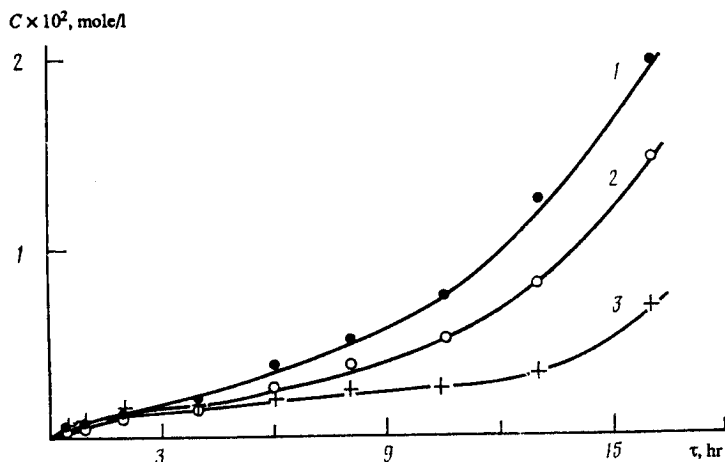


FIG. 3. Kinetic curves of accumulation of cyclohexanol (1), cyclohexanone (2) and chlorocyclohexane (3) in  $\text{CH}_2\text{Cl}_2$  in presence of  $5 \times 10^{-4}\text{M}$   $(\text{Bu}_4\text{N})\text{AuCl}_4$  in air.

period of the reaction, the reactivity of a single C-H bond in the  $\text{CH}_2$  group of ethyl benzene in relation to the same bond in cyclohexane amounts to 3-4. Similar values were obtained for the hydroxylation of a mixture of cyclohexane and ethyl benzene by  $\text{HO}^\cdot$  radicals from  $\text{H}_2\text{O}_2$  in  $\text{CH}_3\text{CN}$  during irradiation with UV light (2.9) and by a Fenton reagent  $\text{FeSO}_4\text{-H}_2\text{O}_2$  in  $\text{CH}_3\text{CN-H}_2\text{O}$  (3.6).

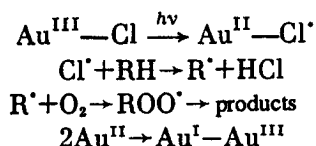
In the case of irradiation of a hexane solution (0.46M) in  $\text{CH}_2\text{Cl}_2$  in the presence of  $(\text{Bu}_4\text{N})\text{AuCl}_4$  ( $5 \times 10^{-4}\text{M}$ ),  $6.5 \times 10^{-4}\text{M}$  hexanol-1,  $1.33 \times 10^{-3}\text{M}$  hexanol-2,  $1.33 \times 10^{-3}\text{M}$  hexanol-3,  $7.7 \times 10^{-4}\text{M}$  hexanal,  $1.77 \times 10^{-3}\text{M}$  hexanone-2 and  $1.77 \times 10^{-3}\text{M}$  hexanone-3 are formed within 6 hr irradiation.

On the basis of the data obtained it is possible to make the following assumptions concerning the mechanism of the reaction described. Under the action of light, excitation of gold(III) chloride occurs, leading to homolysis of the Au-Cl bond and to the formation, possibly in a cell of the solvent, of a  $\text{Cl}^\cdot$  radical. This radical attacks an alkane molecule and detaches a hydrogen atom. The alkyl radical produced reacts with an oxygen molecule in the solvent. As a result of a number of transformations requiring the participation of a metal complex and,

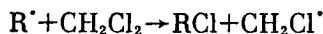
TABLE 1. YIELDS (CONCENTRATION  $c \times 10^3$ , M, AND QUANTUM YIELDS  $F$ ) OF PRODUCTS OF OXYGENATION OF CYCLOHEXANE IN PHOTOREACTION OF CYCLOHEXANE (0.46M) IN  $\text{CH}_3\text{CN}$  WITH CATALYSIS BY  $5 \times 10^{-4}\text{M}$   $\text{NaAuCl}_4$

Wavelength, nm	Oxygenation product	Irradiation time, hr					
		1		2		3	
		$c$	$F$	$c$	$F$	$c$	$F$
365	Cyclohexanol	3,9	0,024	6,9	0,020	8,8	0,018
	Cyclohexanone	4,6	0,028	8,2	0,024	11,5	0,024
436	Cyclohexanol	1,2	0,008	2,5	0,008	4,2	0,009
	Cyclohexanone	1,5	0,010	3,2	0,011	4,8	0,011

possibly, light, the peroxide radical passes into oxygenation products:



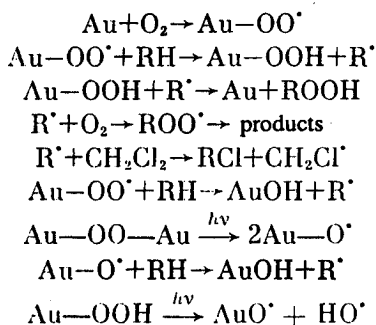
When the process is carried out in  $\text{CH}_2\text{Cl}_2$ , the alkyl radicals formed react with molecules of the solvent:



These reactions proceed fairly rapidly at the initial moment of the photoprocess and are accompanied by the accumulation not only of cyclohexane oxygenation products, but also of a gold derivative in a low state of oxidation. At this moment, decolorization of the solution occurs, and sometimes even the precipitation of metallic gold on the walls of the vessel is observed. As the low-valency gold complex accumulates, the formation rate of cyclohexanol and cyclohexanone falls.

Renewed acceleration of the oxygenation of cyclohexane, beginning after ~3 hr, can be attributed to the fact that the low-valency gold complex begins to coordinate molecular oxygen, as a result of which peroxide gold derivatives also capable of catalysing oxygenation of the hydrocarbon are formed. It is well known that complexes of metals in a low state of oxidation, in particular the gold analogue copper, readily coordinate molecular oxygen [23].

The photo-oxygenation of alkanes in the presence of peroxide complexes evidently proceeds in several directions. The following stages of the process can be put forward:



In these reactions, the state of oxidation of the metal can vary from 3+ to 1+ and vice versa. The possibility of the participation of ligands at this stage of the process must not be ruled out (although recently we showed that complexes of iron in a low state of oxidation, not containing  $\text{Cl}^-$  ligands, catalyse the oxygenation of alkanes effectively [24]). The final stages may be responsible for the autocatalytic nature of accumulation of products, which is clearly observed at least in  $\text{CH}_2\text{Cl}_2$  (Fig. 3). It is obvious that, to obtain evidence of the participation of peroxide derivatives in the process, additional investigations, in particular involving the peroxide metal complexes obtained, are required.

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