

OXIDATION OF ALKANES AND ARYLALKANES IN SOLUTIONS BY ATMOSPHERIC OXYGEN DURING LIGHT IRRADIATION, CATALYZED BY COPPER HALIDES*†

G. B. SHUL'PIN, G. V. NIZOVA and M. M. KATS

N. N. Semenov Institute of Chemical Physics, U. S. S. R. Academy of Sciences, Moscow

(Received 29 October 1990)

Earlier we showed that iron(III) chloride is an effective photocatalyst for the oxidation of saturated and alkylaromatic hydrocarbons by atmospheric air during the light irradiation of solutions in acetonitrile, methylene chloride or acetone [1,2]. It was of interest to extend this reaction to halide complexes of other transition metals. The present paper gives the results of investigating the photocatalytic properties of anhydrous copper halides in the oxygenation of alkanes and arylalkanes. A preliminary report has been published [3]. It should be noted that the photocatalytic properties of copper complexes are well-known [4]. For example, in stoichiometric and catalytic reactions these complexes dehydrate alcohols [5,6], induce the photoaddition of acetonitrile and methanol to olefins [7], dimethoxylate olefins [8], isolate hydrogen from water under light irradiation [9] and photooxidize alkylbenzenes [10]. The photolysis of chloride complexes in organic solvents has been studied in detail in [11,12]. The stoichiometric photooxidation (chlorination) of organic derivatives by copper(II) chloride was described as far back as 1962 [13].

EXPERIMENTAL

Anhydrous CuCl_2 and CuBr_2 were produced by vacuum drying during heating of the corresponding crystal hydrates. Experiments on the photooxidation of alkanes and arylalkanes and an analysis of the products were carried out as described in a previous report [1]. The full light of a luminescent lamp (125 W) was used for irradiation. The triphenylphosphin oxide formed by the oxidation of triphenylphosphine was isolated on Silufol plates (eluent acetone/hexane 3:5), a strip of the product was cut out and eluted with chloroform and the amount of triphenylphosphin oxide was determined from absorption in the UV region of the spectrum (Specord UV-VIS).

RESULTS AND DISCUSSION

Irradiation in air of a cyclohexane solution in the presence of anhydrous copper(II) chloride

* *Neftekhimiya* 31, No. 5, 658-665, 1991.

† Report XXI from series "Photoinitiated reactions of organic compounds with metal complexes"; see [1] for report XX.

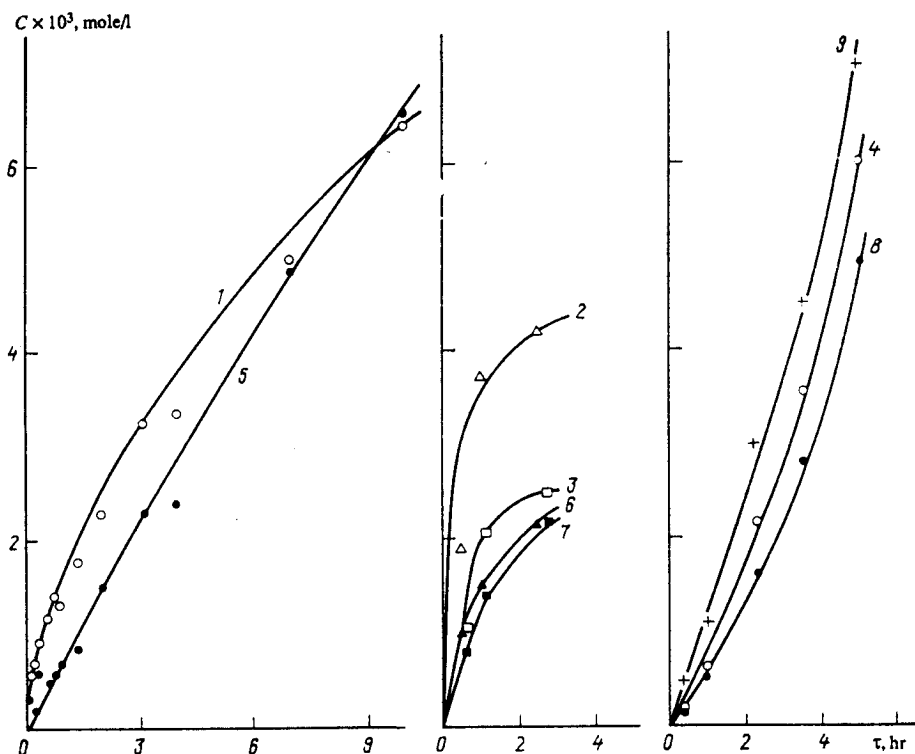


FIG. 1. Accumulation of cyclohexanol (1-4), cyclohexanone (5-8) and cyclohexyl chloride (9) during irradiation in air of solution of cyclohexane (0.46 mole/l) and CuCl_2 (5×10^{-4} mole/l) in acetonitrile (1, 5) (data from three experiments are given) and also with addition of 2×10^{-3} mole/l ionol (2, 6) or methyl methacrylate (3, 7), and in methylene chloride with addition of 5×10^{-4} mole/l $\text{C}_6\text{H}_5\text{CH}_2(\text{C}_2\text{H}_5)_3\text{NCl}$ (reaction was carried out in Ar atmosphere containing traces of O_2) (4, 8, 9).

(here and below, if not otherwise stipulated, the concentration was 5×10^{-4} mole/l, and the temperature 10–15°C) in acetonitrile (Fig. 1) or methylene chloride (in this case, $\text{C}_6\text{H}_5\text{CH}_2(\text{C}_2\text{H}_5)_3\text{NCl}$ was added for dissolution of the copper salt) leads to the formation of cyclohexanol and cyclohexanone in roughly equal quantities, and here, if the reaction takes place in CH_2Cl_2 with a shortage of oxygen, cyclohexyl chloride is formed as the main product. As in the case of the photooxidation of cyclohexane in the presence of other metal chlorides, with catalysis by CuCl_2 , cyclohexyl hydroperoxide is formed in considerable quantity, decomposing during elution to form the corresponding ketone and alcohol.

As follows from Fig. 1, the addition of small amounts of ionol or methyl methacrylate to the solution has no appreciable effect on the rate or nature of accumulation of oxygenation products. In the presence of 2,2'-dipyridyl, the product formation rate decreases roughly by 30%. The shape of the kinetic curves of cyclohexanol and cyclohexanone accumulation in acetonitrile is noteworthy: initially the reaction proceeds at high speed, but in the course of the first hour the rate gradually decreases, and, after this, accumulation continues linearly.

The quantum yields [14] of products of oxygenation of cyclohexane in acetonitrile in an atmosphere of pure oxygen do not change with increase in irradiation time during the first three hours:

Irradiation time, hr	1	2	3
Quantum yield of cyclohexanol			
300 nm	0.022	0.013	0.022
365 nm	0.023	0.021	0.023
435 nm	0.009	0.007	0.006
Quantum yield of cyclohexanone			
300 nm	0.012	0.018	0.016
365 nm	0.021	0.019	0.023
435 nm	0.008	0.006	0.006

It must be noted that, in the first hour of irradiation, initial decolorization of the yellow solution occurs, which is reflected in the absorption spectra of the reaction solution [14].

As the concentration of copper(II) chloride in the acetonitrile solution increases, initially (Fig. 2) there is an increase in the yield of oxygenation products (particularly acute in the case of cyclohexanol), reaching a peak at a CuCl_2 concentration of $\sim 6 \times 10^{-3}$ mole/l. At the same time there is a steady increase in the cyclohexyl chloride yield. With a cyclohexane concentration of >0.18 mole/l with a fixed CuCl_2 concentration (5×10^{-4} mole/l), the rate of the reaction depends little on the initial substrate concentration (irradiation for 1 hr):

Cyclohexane concentration, mole/l	0.18	0.46	0.74	0.92	1.16
Cyclohexanol yield $\times 10^3$, mole/l	2.0	2.5	3.0	2.1	3.0
Cyclohexanone yield $\times 10^3$, mole/l	1.2	1.1	1.3	1.1	1.6

The rate of the reaction is directly proportional to the intensity I of incident light (irradiation for 1 hr):

Intensity I , %	100	50	45	35	22
Cyclohexanol yield $\times 10^3$, mole/l	2.3	1.4	1.0	0.8	0.7
Cyclohexanone yield $\times 10^3$, mole/l	1.3	0.6	0.5	0.4	0.3

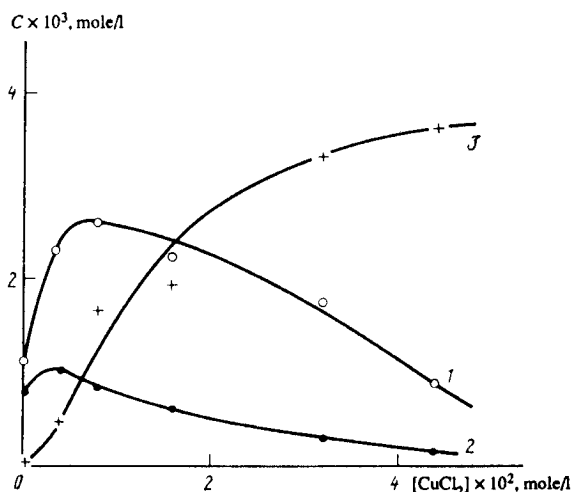


FIG. 2. Dependence of yield of cyclohexanol (1), cyclohexanone (2) and cyclohexyl chloride (3) within 0.5 hr irradiation in air of solution of cyclohexane (0.46 mole/l) in acetonitrile on concentration of CuCl_2 .

Replacement of cyclohexane with C_6D_{12} hardly leads to any decrease in the oxidation rate, and the kinetic isotopic effect is very low: 1.2 ± 0.2 . Measurement of reaction rates at different temperatures in the 4–59°C range made it possible to determine the apparent activation energy (~5 kJ/mole).

During photooxidation in an acetonitrile solution in the presence of anhydrous $CuCl_2$, *n*-hexane (0.46 mole/l) gives a whole series of products (concentration $\times 10^2$, mole/l):

Irradiation time, hr	4.5	7.5
Hexanol-1	0.07	0.15
Hexanol-2	0.18	0.28
Hexanol-3	0.18	0.26
Hexanal	0.42	0.39
Hexanone-2	0.49	0.64
Hexanone-3	0.49	0.66

Ethyl benzene (0.46 mole/l) is converted under these conditions (6 hr irradiation) into 1-phenylethanol (0.34×10^{-2} mole/l) and acetophenone (1.1×10^{-2} mole/l). The combined

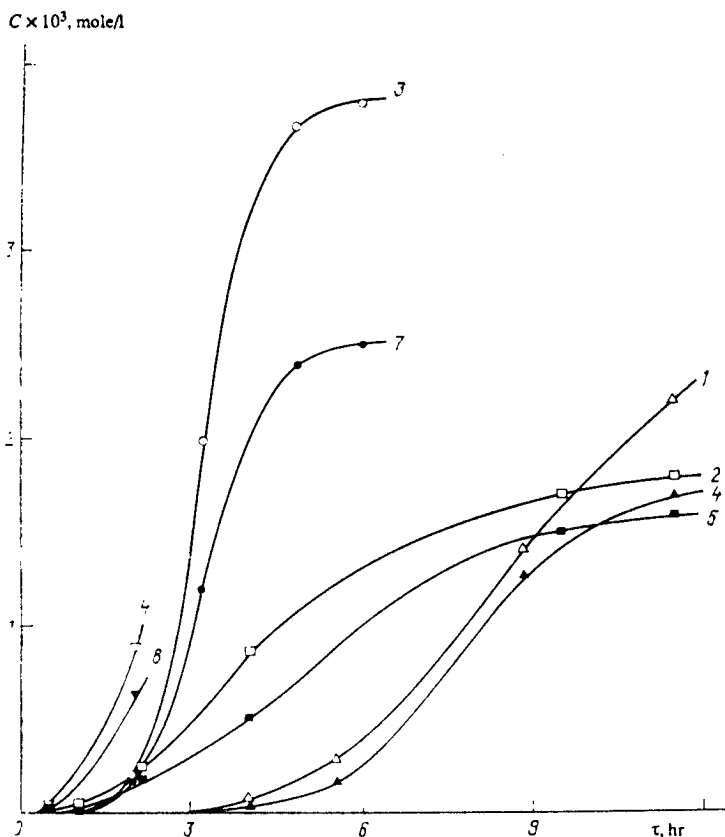


FIG. 3. Accumulation of cyclohexanol (1–4) and cyclohexanone (5–8) during irradiation in air of cyclohexane (0.46 mole/l) and $CuBr_2$ (5×10^{-4} mole/l) in acetonitrile with hydroquinone additions of 2.5×10^{-4} (2, 6) and 5×10^{-4} mole/l (3, 7), and also with preliminary irradiation of solution of $CuBr_2$ and 5×10^{-4} mole/l hydroquinone for 2.25 hr, after which cyclohexane was added (4, 8).

competing oxygenation of ethyl benzene and cyclohexane made it possible to determine the ratio of reactivities Ψ of the CH_2 groups (in terms of a single C-H bond) in these hydrocarbons: 2.6. This value is similar to that obtained for photooxidation in the presence of FeCl_3 (1.55) [1]. Competing reactions of $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3\text{-C}_6\text{H}_4\text{CH}_3$ and $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-C}_6\text{H}_5\text{CH}_3$ pairs (the methyl group is oxidized to hydroxymethyl and aldehyde groups) showed that the value of the Hammett-Brown parameter is $\rho^+ = -1.5$ (for FeCl_3 this quantity amounts to -1.1). Styrene (0.46 mole/l) in the presence of CuCl_2 in acetonitrile is oxidized with the formation of benzaldehyde (1.05×10^{-2} mole/l within 6 hr irradiation).

When CuCl_2 is replaced with CuBr_2 as the photocatalyst, it turns out that cyclohexane in an acetonitrile solution is oxidized fairly slowly after a long induction period (Fig. 3). When a small quantity of hydroquinone is added, this induction period is appreciably shorter. The fact that a catalytically active complex is formed during irradiation of a CuBr_2 and hydroquinone solution without cyclohexane is indicated by the curves in Fig. 3.

In contrast to cyclohexane, ethyl benzene is oxygenated in the presence of CuBr_2 without an induction period (Fig. 4). Ionol and methyl methacrylate additions reduce the reaction rate. The apparent activation energy of ethyl benzene oxygenation amounts to 11.3 kJ/mole (the initial rates were measured in the 8–60°C temperature range). Competing photooxidation of ethyl benzene and cyclohexane in acetonitrile in the presence of CuBr_2 showed that, in the initial period of the reaction, relative reactivity Ψ in terms of a single C-H bond exceeds 1000. During combined oxygenation of toluene and p -xylene it was found that, in the initial period

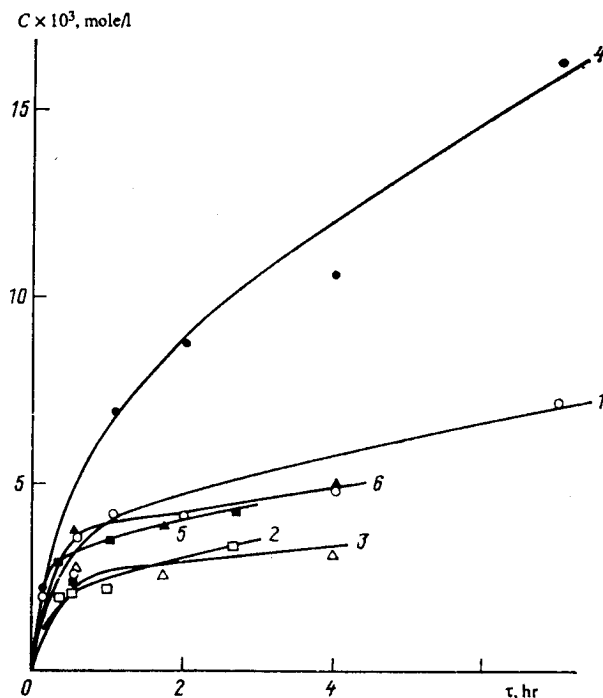
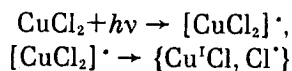


FIG. 4. Accumulation of 1-phenylethanol (1–3) and acetophenone (4–6) during irradiation in air of solution of ethyl benzene (0.46 mole/l) and CuBr_2 (5×10^{-4} mole/l) in acetonitrile with additions of 10^{-3} mole/l ionol (2, 5) and methyl methacrylate (3, 6).

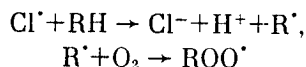
of the reaction, the Hammett–Brown parameter ρ^+ can be estimated at -2.4 . During photooxidation in the presence of CuBr_2 , styrene (0.46 mole/l) gives benzaldehyde and a small quantity of acetophenone. Both products accumulate by a linear law (concentration $\times 10^3$, mole/l):

Irradiation time, hr	1	2.5	5.5
Benzaldehyde concentration	0.7	1.8	3.8
Acetophenone concentration	0.04	0.1	0.2

When discussing the mechanism of photooxygenation of alkanes and arylalkanes in the presence of copper halides, it must be assumed that, at the first stage, photoexcitation of the complex occurs with the transfer of an electron from the ligand to the metal, as a result of which a halogen atom may be formed [11,12]. For example, for chloride



The chlorine (or bromine) radical reacts with the alkane to produce an alkyl radical, which rapidly adds to an oxygen molecule



At this stage of the reaction, the process is entirely identical to that assumed for the photooxygenation of alkanes in the presence of FeCl_3 . However, in contrast to FeCl_3 , the spectrum of the solution of which in a mixture with acetonitrile and cyclohexane does not change during irradiation in air, rapid decolorization of the solution occurs in the case of CuCl_2 [14]. Bearing this in mind, and also the fact that, during photooxygenation of cyclohexane in the presence of CuBr_2 , the long induction period is shortened in the presence of a reducing agent (hydroquinone), it can be assumed that, at the second stage of the reaction with CuCl_2 , besides the first reaction route, by which regeneration of a catalytically active particle occurs, for example by the scheme



a second route appears, employing a copper derivative in a low state of oxidation as the oxygenation catalyst. On the kinetic curve of cyclohexane oxidation, the second stage has a corresponding straight section at an irradiation time of >1 hr. The nature of the oxygenating particle remains unclear. However, it is well known that complexes of monovalent copper readily coordinate molecular oxygen [15] (see also [16]). The peroxide copper complex formed (such derivatives arise, for example, during the oxidation of a formate ion in the Fenton reaction [17], while a peroxide iron complex is formed during irradiation of an Fe(II) derivative in air [18]) can oxygenate alkane. A Cu(I) peroxide derivative is possibly capable of being converted into a Cu(III) oxo complex. Both these compounds can be donors of an oxygen atom [19] to an alkane molecule (see [20]). To confirm this hypothesis, we attempted to oxygenate triphenylphosphine (which is a good acceptor of an oxygen atom) under working

conditions of our systems. It turned out that, during irradiation in air of a solution of $(C_6H_5)_3P$ (2×10^{-2} mole/l) in acetonitrile in the presence of 4×10^{-4} mole/l $CuCl_2$ or $CuBr_2$, over a period of a few minutes triphenylphosphoxide is formed, and here, in the case of $CuBr_2$, the reaction is more rapid ($(C_6H_5)_3P=O$ concentration $\times 10^3$, mole/l)

Irradiation time, min	1	3	5	10	15	20	30
Catalyst $CuCl_2$	0.4	0.4	0.4	1.2	2.1	2.9	3.5
Catalyst $CuBr_2$	0.9	1.2	1.7	4.3	4.6	5.2	6.3

Note that peroxide complexes of transition metals readily oxygenate triphenylphosphine in a dark reaction [21].

A possible alternative mechanism is the formation from a O_2 molecule and $Cu(I)$ of $HO\cdot$ radicals, which hydroxylate alkane (see dark reactions of this kind [22]). In this case the hydroxyl radicals that could arise in our system should hydroxylate the aromatic nucleus. However, we found no cresols in the reaction solution after oxygenation of toluene in acetonitrile in the presence of $CuCl_2$ (the only products within 2 hr irradiation were benzaldehyde and benzyl alcohol), nor any phenol during the combined oxygenation in this system of cyclohexane and benzene (only cyclohexanol and cyclohexanone are formed). It is obvious that, to establish the mechanism of photooxygenation of alkanes in the presence of copper halides, additional investigations are necessary.

Finally, we found that, during irradiation in air of a solution of cyclohexane in acetonitrile in the presence of $Cu(NO_3)_2 \cdot 3H_2O$, cyclohexanol and cyclohexanone are slowly formed (Fig. 5). The mechanism of the reaction may be similar to the mechanism proposed for oxygenation in the presence of cerium ammonium nitrate [23].

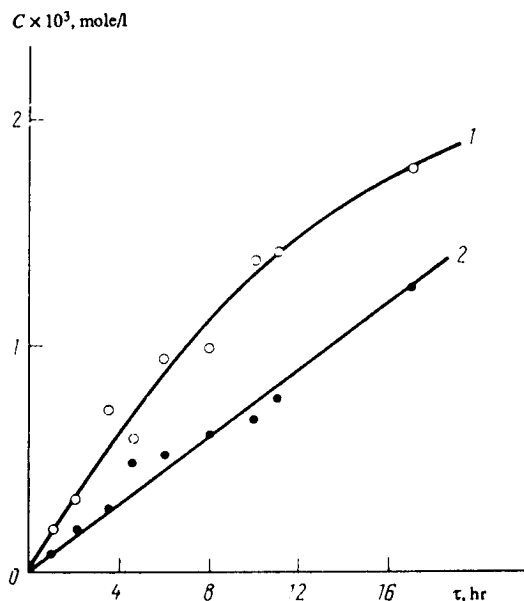


FIG. 5. Accumulation of cyclohexanol (1) and cyclohexanone (2) during irradiation in air of solution of cyclohexane (0.46 mole/l) and $Cu(NO_3)_2 \cdot 3H_2O$ (5×10^{-4} mole/l) in acetonitrile.

SUMMARY

Irradiation in air of a solution of a hydrocarbon (cyclohexane, *n*-hexane, ethyl benzene, toluene, styrene) and a catalytic quantity of anhydrous CuCl_2 in acetonitrile leads to the formation of oxygenation products – alcohols and carbonyl compounds. Irradiation of the solution in methylene chloride (in the presence of tetraalkylammonium chloride) in an argon atmosphere containing traces of oxygen yields alkylchloride as the main product. Oxidation of cyclohexane in acetonitrile in the presence of CuBr_2 proceeds with a long induction period, which is shortened appreciably when hydroquinone is added. It is assumed that oxygenation proceeds by two routes: the first by detachment of the hydrogen atom from the alkane by a halogen radical and rapid reaction of R^\cdot with O_2 ; the second by the oxygenation of alkane by the copper peroxide or oxo complex formed from Cu(I) and O_2 .

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