J. Gen. Chem. USSR, vol. 60, No 9, part 2, pp. 1892-1894 (1990)

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION-METAL COMPLEXES.

XV.* PHOTOOXIDATION OF ALKYLAROMATIC AND SATURATED HYDROCARBONS BY AIR IN CH_3COOH IN THE PRESENCE OF $AuCl_4^-$ OR $PtCl_6^{2-}$

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UDC 547.127

Earlier we demonstrated that saturated and alkylaromatic hydrocarbons reduce $AuCl_4^-$ to metallic Au on irradiation by light with $\lambda > 250$ nm in CH_3COOH [2]. The hydrocarbons are oxidized to chlorinated alkyls and the relative content of products containing O is insignificant if the $AuCl_4^-$ concentrations are high enough (>0.1 M). In the present work, we found the products from air oxidation of organic substrates at low concentrations of $AuCl_4^-$ ($0.2 \cdot 10^{-3}$-$2 \cdot 10^{-3}$ M) are formed in amounts comparable to the amount of Au(III) complex.

Oxidation of toluene to benzaldehyde ws studied in most detail. The kinetic curves of benzaldehyde production for three initial concentration of $AuCl_4^-$ are plotted in Fig. 1. It can be seen that the concentration of $AuCl_4^-$ is 20% of the initial value ($1.7 \cdot 10^{-3}$ M) after only 1 h. However, the maximal rate of production is observed for the reaction period from 1 to 2 h. A distinct induction period is also evident at lower initial $AuCl_4^-$ concentrations. Production of benzaldehyde stops after a certain time. Regardless of the initial $AuCl_4^-$ concentration, the final benzaldehyde concentration is about $5 \cdot 10^{-3}$ M. Benzyl alcohol is not detected. The absolute yield of benzaldehyde begins to increase after 1 h if the $AuCl_4^-$ concentration is increased. It then remains constant.

Initial $AuCl_4^-$ concentration, $c \cdot 10^3$, M	0.85	1.7	2.5	3.9
C_6H_5CHO yield, $\times 10^3$, M	0.7	1.0	0.95	1.0

The dependence of benzaldehyde yield after 50 min irradiation as a function of initial toluene concentration has the same character.

Initial $C_6H_5CH_3$ concentration, c, M	0.35	0.87	1.7	3.5
C_6H_5CHO yield, $\times 10^3$, M	0.6	0.7	2.5	2.8

Carrying out the oxidation in an atmosphere of pure oxygen does not change the form of the kinetic curves of benzaldehyde production.

We propose that the induction period is due to the fact that Au(III) is reduced to a lower oxidation state, for example, Au(II) or Au(I), at the start of the reaction. The latter is active in production of benzaldehyde. In fact, such a proposal is supported by the fact that adding cyclohexene in the mole ratio Au(III):cyclohexene 1:1 to the reaction mixture completely eliminates the induction period (Fig. 1). It is interesting that the yield of benzaldehyde falls practically to zero if the amount of added cyclohexene is slightly increased further (Fig. 2). The presence of a small amount of hydrazine also eliminates the induction period. The yield of benzaldehyde (concentration, M) after 50 min irradiation in the presence of $AuCl_4^-$ ($1.7 \cdot 10^{-3}$ M) as a function of added hydrazine hydrate concentration is given below.

NH_2NH_2 concentration, $c \cdot 10^3$, M	0	0.02	0.03	0.17	0.34
C_6H_5CHO yield, $\times 10^3$, M	0.7	1.4	1.4	2.0	0.5

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*For communication XIV, see [1].

N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Zhurnal Obshchei Khimii, Vol. 60, No. 9, pp. 2121-2124, September, 1990. Original article submitted January 25, 1989.

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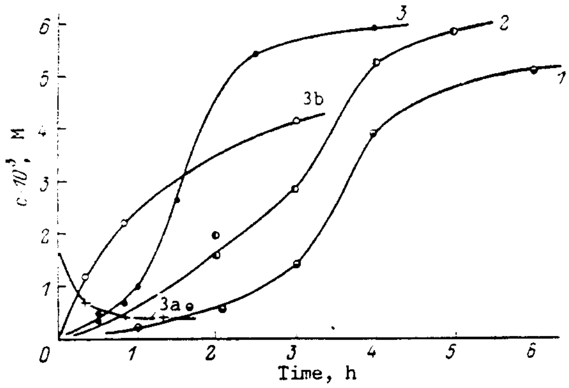

Fig. 1. Kinetic curves of benzaldehyde production from a solution of toluene (0.87 M) in CH_3COOH on irradiation by an unfiltered high-pressure mercury lamp in the presence of $AuCl_4^-$ at various initial concentrations, M: 1) $0.17 \cdot 10^{-3}$, 2) 0.85, 3) $1.7 \cdot 10^{-3}$. Consumption of $AuCl_4^-$ in the same reaction (3a). Production of benzaldehyde in the same reaction in the presence of $1.7 \cdot 10^{-3}$ M cyclohexene (3b).

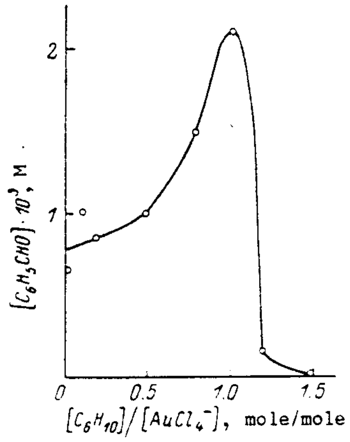

Fig. 2. Amount of benzaldehyde formed during 50 min irradiation of a solution of toluene (0.87 M) in CH_3COOH in the presence of $1.7 \cdot 10^{-3}$ $AuCl_4^-$ as a function of the amount of cyclohexene added.

We note that metallic Au is formed on the walls of the cylinder during the reaction. This might be responsible for the oxidation of toluene. However, we found that the yield of benzaldehyde does not decrease if the metallic Au is separated by filtration of the reaction mixture into a new cylinder at the time when the production of benzaldehyde is rapid. Moreover, irradiation in the presence of a suspension of metallic Au prepared by reducing a solution of $HAuCl_4$ with excess hydrazine does not produce benzaldehyde. These data suggest that a soluble unstable Au(I) or Au(II) compound that arises on reduction of $AuCl_4^-$ catalyzes oxidation of toluene by air. A special experiment showed that oxidation in the presence of these compounds occurs only under the influence of light. The nature of the Au compounds catalyzing the oxidation is unknown. It can only be stated that adducts of molecular oxygen with complexes of monovalent copper, an analog of Au, are known to be involved in oxidation processes [3, 4].

We also found that cyclohexanol ($1.6 \cdot 10^{-3}$ M) and cyclohexanone ($1.2 \cdot 10^{-3}$ M) are formed on irradiation for 3.5 h of a solution of $HAuCl_4$ ($0.17 \cdot 10^{-3}$ M) and cyclohexane (0.53 M). Moreover, irradiation of a solution of $HAuCl_4$ ($1.7 \cdot 10^{-3}$ M) in CH_3COOH (4 h, 15°C) saturated under an atmosphere of methane produces a small amount of formaldehyde ($7 \cdot 10^{-5}$ M).

Production of benzaldehyde by photochemical reaction of toluene with $PtCl_6^{2-}$ was also studied. The principal products of this reaction with alkanes are chlorinated alkyls and π-olefin complexes of Pt(II) [5]. Benzaldehyde is produced in small quantities at low $PtCl_6^{2-}$ concentrations. Thus, irradiation of a solution of H_2PtCl_6 and toluene (0.87 M) in CH_3COOH for 1 h produces benzaldehyde in the concentrations given below.

Initial H_2PtCl_6 concentration, $c \cdot 10^3$, M	1.7	3.2	5.8
C_6H_5CHO yield, $\times 10^3$, M	0.5	0.95	0.67

The maximal yield of benzaldehyde is seen to be 30% per mole of H_2PtCl_6.

EXPERIMENTAL

The concentration of oxidation products was determined by GLC on LhM-80-6 chromatograph (0.25-0.315 mm Inerton AW-HMDS support coated with 5% Carbowax 1500, column length 2 m, argon carrier gas). Spectrophotometric measurements were made on a Specord spectrophotometer. Silufol-254 plates and hexane—$CHCl_3$ (5:2) eluent were used for TLC. All reactions were carried out in air with vigorous stirring using a magnetic stirrer in a 2-cm diameter glass cylinder cooled by a water jacket (15°C) with illumination by an unfiltered DRSh-1000 (1000 W) mercury lamp. The oxidation products of toluene were determined by TLC; of cyclohexane, by GLC. The formaldehyde concentration was measured spectrophotometrically by adsorption at λ 570 nm after reaction with chromotropic acid.

CONCLUSIONS

Irradiation of a solution of toluene and $AuCl_4^-$ in CH_3COOH in air produces benzaldehyde, the yield of which can reach 30 moles per mole of $AuCl_4^-$. The reaction is autocatalytic in nature.

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