

## PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION-METAL COMPLEXES.

XII. OXIDATION OF TOLUENE TO BENZALDEHYDE BY OXYGEN  
IN THE PRESENCE OF THE Cr(VI)-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup> SYSTEM\*

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In previous articles we have described the photochemical oxidation of hydrocarbons by Cr(VI) oxo compounds both in homogeneous solution in CH<sub>3</sub>COOH and in a two-phase system in the presence of interphase carrier [1-3]. The reaction is stoichiometric with respect to Cr(VI) and the yields of oxidation products calculated with respect to Cr(VI) are not more than 50-80%.

Later we found that lowering the Cr(VI) concentration in the aqueous solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to approximately 10<sup>-4</sup> M and carrying out the toluene-oxidation reaction in a two-phase system in the presence of Bu<sub>4</sub>NBr increases the yield of benzaldehyde formed to considerably more than 100%. In the present communication we describe the first results obtained from an investigation of this process. When an aqueous solution containing 2.5·10<sup>-6</sup> mole K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with an excess of Bu<sub>4</sub>NBr and toluene is exposed for 60 min, 1.35·10<sup>-5</sup> mole benzaldehyde is formed. After this the accumulation of benzaldehyde ceases (Fig. 1). It is suggested that in this reaction the toluene is oxidized by oxygen dissolved in the water. In fact, when water is used which has been previously distilled in an argon atmosphere, only an insignificant amount of benzaldehyde is formed: 2.5·10<sup>-6</sup> mole K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> gives not more than 3·10<sup>-7</sup> mole benzaldehyde, i.e., a yield of not more than 10% calculated with respect to Cr. As a result of this reaction, the Cr(VI) for the most part remains unreduced (naturally, when the reaction time is increased, stoichiometric photooxidation of the toluene by the chromium oxo compounds occurs, as described previously [1-3]). When the concentration of Cr(VI) added to the reaction is increased, the absolute amount of benzaldehyde formed increases dramatically and then remains at approximately the same level over quite a large Cr(VI) concentration range (Fig. 2). The same type of dependence is shown by that of the amount of benzaldehyde formed on concentration of Bu<sub>4</sub>NBr added to the reaction (Fig. 3). We also found that addition of α,α'-dipyridyl or ammonium persulfate to the reaction mixture only lowers the amount of benzaldehyde formed. Moreover, additions of diphenylamine or α-picolinic acid scarcely affect the yield. It should be mentioned that photooxidation of toluene by oxygen in the presence of small amounts of Cr(VI) and Bu<sub>4</sub>N<sup>+</sup> takes place in a neutral medium, whereas the stoichiometric reaction with relatively large amounts of Cr(VI) needs addition of acid (H<sub>2</sub>SO<sub>4</sub>). It should also be emphasized that the reaction of toluene oxidation by oxygen becomes appreciable against a background of oxidation by the chromium oxo compound only when the Cr(VI) concentration is low and the process is carried out in a neutral medium, where the rate of toluene oxidation by the chromium oxo compound sharply falls. When the Cr(VI) concentration is increased by an order of magnitude and (or) the reaction is carried out in an acid medium, the amount of benzaldehyde produced by oxygen oxidation of toluene is very small compared with the amount formed in the stoichiometric reaction with the Cr(VI) oxo complex. The yields of benzaldehyde in the reaction in CH<sub>3</sub>COOH (i.e., in the absence of Bu<sub>4</sub>NBr) are not more than 100% with respect to Cr even at low concentrations of Cr(VI).

Thus, when Cr(VI) oxo compounds and Bu<sub>4</sub>NBr are present in the aqueous solution, atmospheric oxygen oxidizes toluene on exposure to light. Since it is known that the tetrabutylammonium ion is photochemically oxidized by the Cr(VI) oxo compound with formation of the Bu<sub>2</sub>NCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> radical according to the scheme shown below [4], it is suggested that this radical is an initiator of subsequent chain oxidation of toluene by oxygen [5].

\*For communication XI, see [1].

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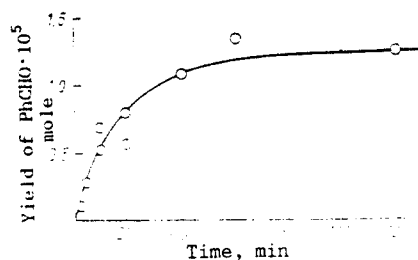


Fig. 1. Kinetic curve for accumulation of benzaldehyde during photochemical oxidation of toluene (0.5 ml in 1.5 ml  $\text{CH}_2\text{Cl}_2$ ) in an aqueous solution of  $\text{K}_2\text{-Cr}_2\text{O}_7$  ( $2.5 \cdot 10^{-6}$  mole in 5 ml water) in the presence of 5 mg  $\text{Bu}_4\text{NBr}$ .

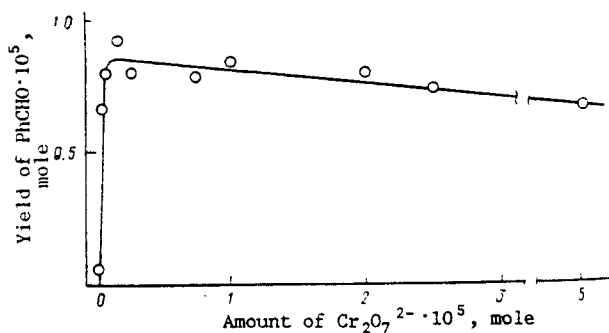


Fig. 2. Dependence of amount of benzaldehyde formed on amount of  $\text{Cr}_2\text{O}_7^{2-}$  in the oxidation reaction of toluene (for conditions see Fig. 1; reaction time 20 min).

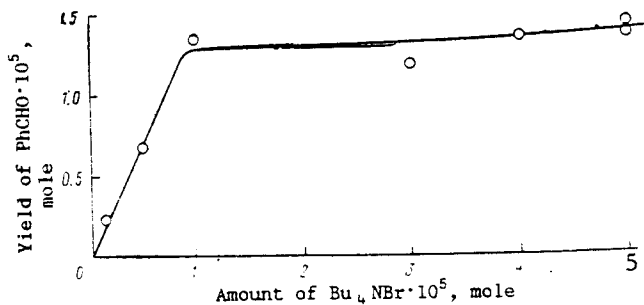
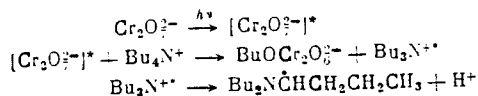


Fig. 3. Dependence of amount of benzaldehyde formed on amount of  $\text{Bu}_4\text{NBr}$  (for conditions see Fig. 1; reaction time 20 min).



We note that prior generation of radicals which are initiators of radical autooxidation of toluene has been achieved by photolysis of Co, Cr, and Fe acetylacetonates [6]. At the same time, it is known that alkylammonium salts inhibit autooxidation of cyclohexane [7].

#### EXPERIMENTAL

A solution of  $2.5 \cdot 10^{-6}$  mole  $\text{K}_2\text{Cr}_2\text{O}_7$  and 5 mg  $\text{Bu}_4\text{NBr}$  in 5 ml water was vigorously stirred in air with a mixture of 0.5 ml toluene and 1.5 ml dichloromethane in a cylindrical vessel with a cooling water jacket ( $17^\circ\text{C}$ ) during exposure to the total light from a DRSh-1000 (1000

W) high-pressure mercury lamp. After reaction had finished, the solution was extracted with chloroform (2 x 5 ml) and part of the solution was chromatographed on a Silufol UV-254 slide (eluent 1:2 chloroform:hexane). The benzaldehyde band was cut out, washed with chloroform, and the amount of benzaldehyde determined spectrophotometrically on a Specord UV-Vis apparatus by the absorption at 280 nm.

#### CONCLUSIONS

Exposure to light of a solution of  $K_2Cr_2O_7$  and  $Bu_4NBr$  in water in the presence of toluene leads to oxidation of the toluene to benzaldehyde by atmospheric oxygen, the benzaldehyde yield being much greater than 100% calculated with respect to Cr.

#### LITERATURE CITED

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