

OXIDATION OF ETHYLBENZENE BY ATMOSPHERIC OXYGEN AND IODOSOBENZENE CATALYZED BY  $\text{CrO}_3$ 

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Iron or manganese porphyrin complexes [2-4] are usually employed as models of enzyme systems [1], which oxidize saturated and alkylaromatic hydrocarbons [2, 3]. Molecular oxygen is used as the oxidizing agent [5, 6]. Iodosobenzene,  $\text{C}_6\text{H}_5\text{IO}$ , may serve as a donor of an oxygen atom transferred by a metal complex catalyst to the substrate [7, 8]. Transition metal complexes with chelating nitrogen-containing ligands have been used as oxygen transfer catalysts [9-11]. The first step in the catalyzed oxidation is presumably the transfer of an oxygen atom [12] to the metal ion with formation of an oxo derivative of the metal in a high oxidation state. Cr(VI) oxo compounds may serve as models for such species. We note that the oxygen atom transfer to chromium porphyrin complexes [13, 14] and to Cr(III) complexes with chelating ligands [11].

In the present work, we report the first results of an investigation of the catalytic properties of  $\text{CrO}_3$ . Ethylbenzene was used as the substrate and the reactions were carried out in acetonitrile. In the presence of  $\text{CrO}_3$ , ethylbenzene is slowly oxidized to acetophenone by atmospheric oxygen (Fig. 1, curve 1). After about 50 h, 1 mole  $\text{C}_6\text{H}_5\text{COCH}_3$  is formed per mole  $\text{CrO}_3$ . In the case of higher initial concentrations of ethylbenzene and  $\text{CrO}_3$ , the reaction proceeds more rapidly and about 2 moles acetophenone are accumulated per mole  $\text{CrO}_3$  after 50 h (Fig. 1, curve 5). The addition of a solution of  $\alpha$ -picolinic acid somewhat accelerates the oxidation (Fig. 1, curve 2), but the reaction proceeds more slowly in the presence of trifluoroacetic acid (Fig. 1, curve 3). Irradiation above 310 nm markedly accelerates the reaction (Fig. 1, curve 4). Carrying out the reaction in acetonitrile, which was previously distilled in an argon atmosphere and containing traces of oxygen, leads to a decrease in the rate of the thermal reaction by a factor of about 1.5. We note that the electronic spectrum of the solution in the visible region hardly changes over 180 h (the intensity of the absorption at 380 nm drops by only 17%). This invariance apparently indicates that chromium in the oxo derivative catalyzing the reaction does not alter its valence state.

Ethylbenzene in the presence of  $\text{CrO}_3$  is much more rapidly oxidized by iodosobenzene. In this case, 0.2 mole acetophenone per mole iodosobenzene is formed over about 80 h, after which there is no further accumulation of the oxidation product (Fig. 2a, curve 1). The addition of  $\alpha$ -picolinic acid, which is capable of stabilizing Cr(V) and Cr(IV) oxo compounds [15], characteristically leads to a sharp increase in the rate of accumulation and yield of acetophenone (Fig. 2a, curve 2). The species formed from  $\text{CrO}_3$  and  $\alpha$ -picolinic acid does not lose its catalytic activity over a long period and is capable of catalyzing the oxidation of ethylbenzene upon the addition of a new portion of iodosobenzene (Fig. 2b). The orange color of the solution disappears only several hours after mixing of the reagents and the maximum at 380 nm is no longer observed. A Cr(III) derivative may be formed (see the work of Kochi et al. [11]). When the reaction is carried out in acetonitrile subjected to prior distillation in an argon atmosphere, the acetophenone yield after 180 h is reduced by 40%, indicating that oxygen takes part in the oxidation.

Thus,  $\text{CrO}_3$  in the presence of  $\alpha$ -picolinic acid is a catalyst for the oxidation of ethylbenzene by iodosobenzene in acetonitrile. Further investigation is required to elucidate the mechanism for this reaction.

## EXPERIMENTAL

All the reactions were carried out in closed glass vessels with periodic agitation by a magnetic stirrer. The experimental conditions are given in the Fig. 1 legends. After

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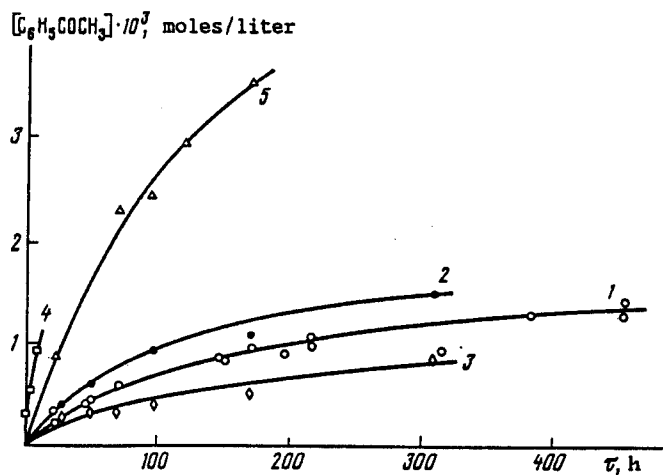


Fig. 1

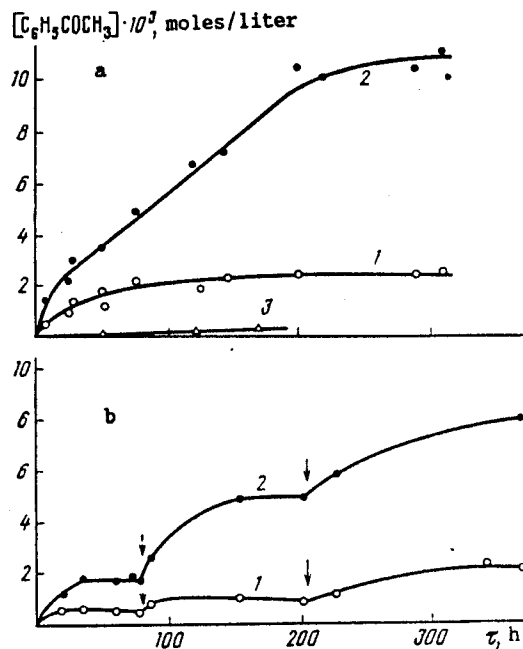


Fig. 2

Fig. 1. Kinetic curves for the accumulation of acetophenone upon the oxidation of 0.41 mole/liter ethylbenzene by atmospheric oxygen in acetonitrile at 25°C in the presence of catalyst (mole/liter): 1)  $\text{CrO}_3$  ( $0.5 \cdot 10^{-3}$ ); 2)  $\text{CrO}_3$  ( $0.5 \cdot 10^{-3}$ ) and  $\alpha$ -picolinic acid ( $10^{-3}$ ); 3)  $\text{CrO}_3$  ( $0.5 \cdot 10^{-3}$ ) and  $\text{CF}_3\text{CO}_2\text{H}$  ( $2.2 \cdot 10^{-2}$ ); 4)  $\text{CrO}_3$  ( $0.5 \cdot 10^{-3}$ ) upon irradiation with the full light of a high pressure mercury lamp; 5)  $\text{CrO}_3$  ( $0.77 \cdot 10^{-3}$ ) (1.23 mole/liter ethylbenzene).

Fig. 2. Kinetic curves for the accumulation of acetophenone upon the oxidation of 0.41 mole/liter ethylbenzene in  $\text{CH}_3\text{CN}$  at 25°C (the total volume of the solution was 10 ml) by iodosobenzene (a)  $10^{-4}$  mole iodosobenzene was added at the onset; b)  $0.25 \cdot 10^{-4}$  mole iodosobenzene was added at the onset and moments indicated by the arrows) in the air in the presence of catalyst (mole/liter): 1)  $\text{CrO}_3$  ( $0.5 \cdot 10^{-3}$ ); 2)  $\text{CrO}_3$  ( $0.5 \cdot 10^{-3}$ ) and  $\alpha$ -picolinic acid ( $10^{-3}$ ); 3) in the absence of catalyst.

given time intervals, 0.5 ml probes of the reaction mixture were taken. The solution was placed on a Silufol UV-254 plate and eluted with 2:1 hexane-chloroform. The acetophenone band was cut out and the product was eluted with 3 ml chloroform. The amount of acetophenone formed was found relative to its UV spectral intensity measured on a Specord UV-VIS spectrometer. Each curve in the figures is the superposition of the data of two or three independent experiments. The irradiation was carried out in a glass vessel cooled by a water flow by the full light of a DRS-1000 high-pressure mercury lamp.

#### CONCLUSIONS

1. Ethylbenzene in acetonitrile is slowly oxidized by atmospheric oxygen to acetophenone in the presence of a catalytic amount of  $\text{CrO}_3$ .
2. Ethylbenzene is oxidized to acetophenone by iodosobenzene in acetonitrile in the air in the presence of catalytic amounts of  $\text{CrO}_3$  and  $\alpha$ -picolinic acid.

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