

PHOTOCHEMICAL OXIDATION OF ETHYLBENZENE AND OTHER HYDROCARBONS IN THE PRESENCE OF COBALT(III) 2,4-PENTANEDIONATE

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The photochemical oxidation of ethylbenzene in the presence of cobalt(III) 2,4-pentanedionate has been investigated. On the basis of results for the kinetics of chemical transformation of catalyst in the course of this reaction, a hypothesis is advanced concerning photoinitiating effect of cobalt(III) 2,4-pentanedionate on ethylbenzene oxidation.

The way in which substrates are activated photochemically in oxidation reactions is not only of practical interest, but is also an important issue in the elucidation of mechanism of these processes. Some thermal and photochemical oxidations of aliphatic and aromatic hydrocarbons are accelerated by transition metal ions. For thermal reactions this effect has mostly been explained in terms of participation of metal ions in free radical chain mechanisms by which these processes have been assumed to occur. Acceleration of photochemical processes has usually been explained as being due to the ability of coloured metal complexes to act as photosensitizers¹ or photocatalysts². To date there are few instances in which the photocatalytic effect of metal ions has been demonstrated.³

The aim of this work was to study the effects of Co(III), Co(II), Fe(II) and Mn(III) 2,4-pentanedionates on photochemical oxidations of aromatic hydrocarbons, and to make an attempt, at least in one of the cases, to elucidate the mechanism of metal ion action.

EXPERIMENTAL

Chemical: Ethylbenzene was shaken with an aqueous solution of sodium sulphite, washed with water, dried with sodium, rectified on a 100 cm packed column in an atmosphere of nitrogen, and stored in sealed ampoules under nitrogen at -5°C . 2,4-pentanedionates of Co(III) (ref. 4), Co(II) (ref. 5) and Mn(III) (ref. 6) were prepared following published procedures. Iron(III) 2,4-pentanedionate was a commercial product (Merck).

Procedure: The photochemical oxidation was carried out in a thermostatted quartz vessel placed in a dark box and connected to a thermostatted gas burette. The vessel was provided with a closure which permitted sampling during experiment. The full output of a HBO 200 high-pressure mercury arc was used for irradiation. 10 ml of substrate was placed in vessel, and the apparatus was thermostatted at the required temperature. The vessel was shaken throughout the experiment. Oxygen consumption was measured as a function of time, and samples were taken for analysis.

Analytical: The rate of substrate oxidation was followed by measuring the volume of consumed oxygen. The hydroperoxide content was determined by iodometric titration.⁷ Other reaction products were analyzed using a Chrom IV gas chromatograph (1.2 m column, Inerton AW, 5% Carbowax 20M). Chemical changes of catalyst were followed as described by Vasvári and co-workers.⁸

RESULTS AND DISCUSSION

Trial experiments with benzene, toluene and ethylbenzene as substrates, and cobalt(III) 2,4-pentanedionate as model catalyst were carried out to choose a suitable hydrocarbon for the study of the effects of metal ions on photochemical oxidations. The criteria for the choice were sufficient differences in reaction rates of photo-initiated catalyzed and non-catalyzed reactions, and in rates of catalyzed thermal and photochemical reactions. Results of the trial experiments (Fig. 1) showed ethylbenzene⁹ to pass the test of both criteria. The data for the thermal oxidation of ethylbenzene were taken from the literature^{10,11}.

Testing various transition metal 2,4-pentanedionates in photochemical oxidation of ethylbenzene (Fig. 2) led to the choice of cobalt(III) 2,4-pentanedionate as catalyst for use in the present study. It is of interest to compare the rates of oxygen consumption for catalysts with cobalt in different oxidation states. As shown in Fig. 2, the reaction rate is the same for Co(III) and Co(II), but a marked induction period is observed with Co(II).

Reaction products of photochemical oxidation of ethylbenzene were determined by gas chromatography. 1-Phenyl-1-hydroperoxy ethane was analyzed by iodometric titration. It was found that the photochemical and thermal reactions yield the same products, namely 1-phenyl-1-hydroperoxy ethane, acetophenone, 1-phenyl ethanol, and traces of benzaldehyde and phenol. Kinetic data for the formation of the major products and for oxygen consumption are summarized in Table I.

By following oxygen consumption at various concentrations of cobalt(III) 2,4-pentanedionate, the reaction rate was found to increase most markedly at catalyst concentrations ranging between $1 \cdot 10^{-3} \text{ mol l}^{-1}$ and $1 \cdot 10^{-4} \text{ mol l}^{-1}$ (Fig. 3). Increasing the concentration above $1 \cdot 10^{-3} \text{ mol l}^{-1}$ no longer caused a change in the rate of oxygen consumption, but had a pronounced effect on the thermal reaction (the latter was followed in all cases 60 min before and after irradiation). It may be stated that within the catalyst concentration range $0 - 1 \cdot 10^{-2} \text{ mol l}^{-1}$ the thermal reaction prior to the photochemical process is negligible, the maximum

oxygen consumption being 1 ml/60 min. The rates of the thermal and photochemical reactions become comparable as the catalyst concentration approaches $1 \cdot 10^{-1}$

TABLE I

Build-up of products and consumption of oxygen in photochemical oxidation of ethylbenzene. $[\text{Co(III) 2,4-pentanedionate}] = 1 \cdot 10^{-3} \text{ mol l}^{-1}$; $T = 333 \text{ K}$; $[\text{O}_2]$ saturated

Time min	Acetophenone	1-Phenyl ethanol mol l ⁻¹	1-Phenyl-1-hydroperoxy ethane	O ₂ ml
0	0.008	0.004	0.001	—
60	0.032	0.026	0.005	5.3
120	0.060	0.047	—	12.1
180	0.094	0.081	—	21.0
240	0.135	0.112	—	30.4
300	0.174	1.141	—	47.1
360	0.194	0.161	0.016	58.4

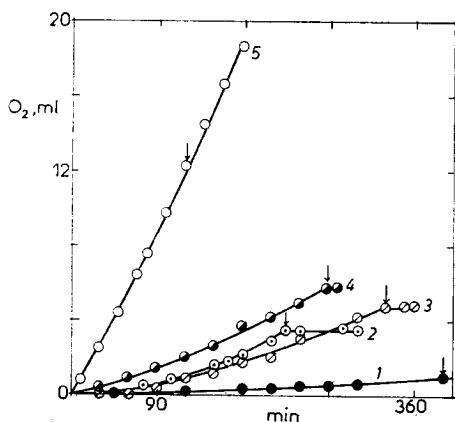


FIG. 1

Non-catalyzed and catalyzed photochemical oxidations of hydrocarbons. $[\text{Co(III) 2,4-pentanedionate}] = 1 \cdot 10^{-2} \text{ mol l}^{-1}$; $T = 333 \text{ K}$; $[\text{O}_2]$ saturated. The arrows indicate the end of irradiation. 1 toluene, no catalyst; 2 ethylbenzene, no catalyst; 3 benzene, with catalyst; 4 toluene, with catalyst; 5 ethylbenzene, with catalyst

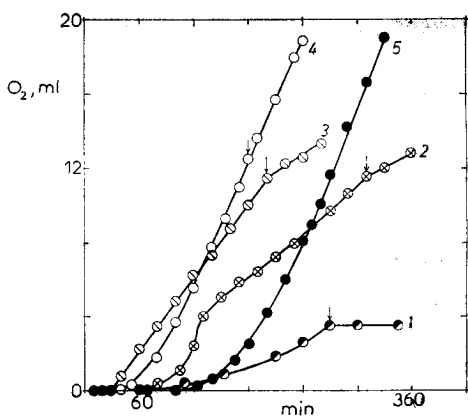


FIG. 2

Photochemical oxidation of ethylbenzene. $[\text{Catalyst}] = 1 \cdot 10^{-2} \text{ mol l}^{-1}$; $T = 333 \text{ K}$; $[\text{O}_2]$ saturated. Irradiation started at $t = 30 \text{ min}$ for 3, 4, and at $t = 60 \text{ min}$ for 1, 2, and 5. The arrows indicate the end of irradiation. 1 no catalyst; 2 Mn(acac)_3 ; 3 Fe(acac)_3 ; 4 Co(acac)_3 ; 5 Co(acac)_2

mol l^{-1} . The catalyst concentration has an even more pronounced effect on the rate of thermal reaction after irradiation. At low catalyst concentrations ($0-1 \cdot 10^{-3} \text{ mol l}^{-1}$), the thermal reaction is slowed down or stopped altogether on switching off the light, whilst no change in the rate is observed on terminating the irradiation if the catalyst concentration is $1 \cdot 10^{-2} \text{ mol l}^{-1}$ and higher.

The photochemical oxidation of ethylbenzene in the presence of $1 \cdot 10^{-2} \text{ mol l}^{-1}$ cobalt(III) 2,4-pentanedionate is temperature dependent (Fig. 4). The reason for this observation may be that oxygen is consumed in a series of reactions where the rate-limiting step is not the primary photochemical process, but some of the subsequent thermal reaction.

The variation in oxygen consumption with time at 80°C is of autocatalytic character for both the photochemical and thermal reactions. At lower temperatures the rate of thermal reaction before irradiation is negligible. At a catalyst concentration of $1 \cdot 10^{-2} \text{ mol l}^{-1}$, a change of temperature has almost no effect on the rate of thermal reaction, and the thermal and photochemical reactions occur at the same rate.

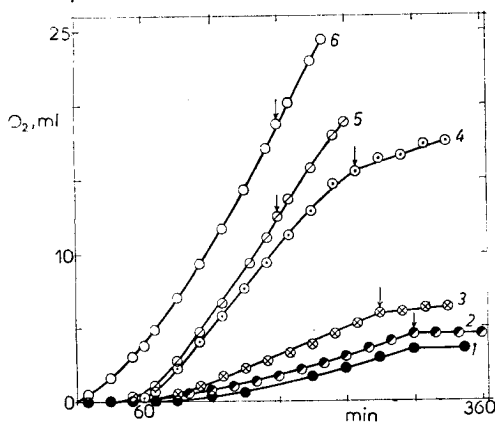


FIG. 3

Dependence of the rate of photochemical oxidation of ethylbenzene on the concentration of Co(III) 2,4-pentanedionate. $T = 333 \text{ K}$; $[\text{O}_2]$ saturated. Irradiation started at $t = 60 \text{ min}$. The arrows indicate the end of irradiation. 1 no catalyst; 2 $1 \cdot 10^{-5} \text{ mol l}^{-1}$; 3 $1 \cdot 10^{-4} \text{ mol l}^{-1}$; 4 $1 \cdot 10^{-3} \text{ mol l}^{-1}$; 5 $1 \cdot 10^{-2} \text{ mol l}^{-1}$; 6 $9.74 \cdot 10^{-2} \text{ mol l}^{-1}$

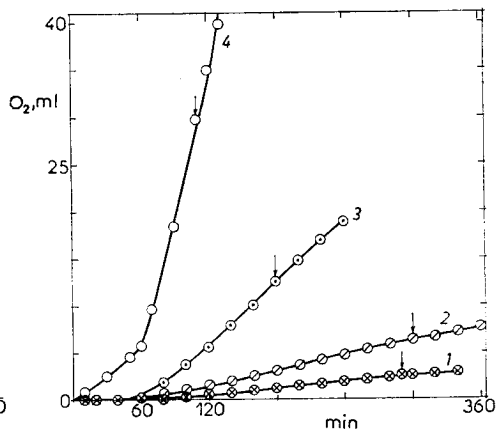


FIG. 4

Dependence of the rate of photochemical oxidation of ethylbenzene on temperature. $[\text{Co(III) 2,4-pentanedionate}] = 1 \cdot 10^{-2} \text{ mol l}^{-1}$; $[\text{O}_2]$ saturated. Irradiation started at $t = 60 \text{ min}$. The arrows indicate the end of irradiation. 1 293 K; 2 313 K; 3 333 K; 4 353 K

As shown by the previous experiments, the rate of ethylbenzene oxidation is strongly dependent on the presence of cobalt ions in the reaction mixture. Since the irradiated solution changes its colour during the reaction, it may be expected that the catalyst undergoes a chemical change in the course of the oxidation process. Information on the mechanism of catalyst transformations, on products and intermediates of these processes may contribute significantly to the elucidation of the overall mechanism of photochemical oxidation of ethylbenzene. Drawing on previous work on thermal⁸ and photochemical¹² decompositions of cobalt 2,4-pentanedionates we investigated changes in oxidation state of the central atom and in the ligand field of Co(III) 2,4-pentanedionate. It was found that 2,4-pentanedionate is oxidized to acetate and Co(III) is reduced to Co(II) during photochemical oxidation of ethylbenzene (Fig. 5). The concentration of Co(III) 2,4-pentanedionate in the reaction mixture rapidly decreases and insoluble cobalt(II) acetate separates from the solution. The variation in the concentration of Co(II) 2,4-pentanedionate with time indicates that this compound is the intermediate of the overall process. For comparison, kinetics of Co(III) 2,4-pentanedionate photolysis in an inert solvent (benzene) under conditions comparable to those in photochemical oxidation of ethylbenzene are shown in Fig. 6.

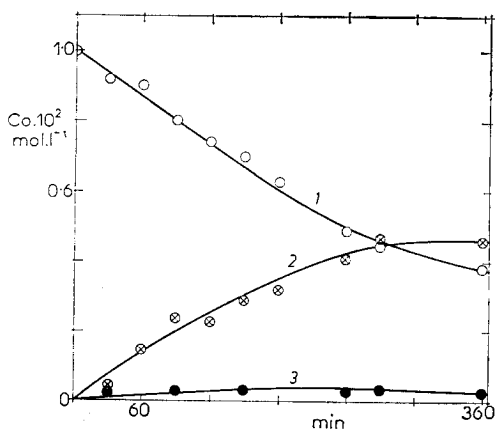


FIG. 5

Photochemical decomposition of Co(III) 2,4-pentanedionate. Oxygen consumption, 58.5 ml/360 min. [Co(III) 2,4-pentanedionate] = $1 \cdot 10^{-2}$ mol l⁻¹; $T = 333$ K; [O₂] saturated; solvent, ethylbenzene. 1 Co(acac)₃; 2 Co(OAc)₂; 3 Co(acac)₂

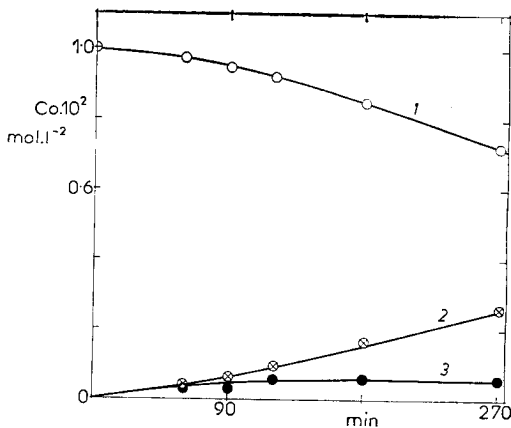


FIG. 6

Photochemical decomposition of Co(III) 2,4-pentanedionate. Oxygen consumption, 2.85 ml/270 min. [Co(III) 2,4-pentanedionate] = $1 \cdot 10^{-2}$ mol l⁻¹ in benzene; $T = 333$ K; [O₂] saturated. 1 Co(acac)₃; 2 Co(OAc)₂; 3 Co(acac)₂

It may be concluded that Co(III) 2,4-pentanedionate does not act as a genuine homogeneous catalyst in photochemical oxidation of ethylbenzene, since the concentration of the soluble form rapidly decreases. This decrease does not cause a slow-down of the rate of photochemical reaction, but at lower initial catalyst concentrations it has a marked effect on the subsequent thermal reaction. It is likely that Co(III) 2,4-pentanedionate plays an important role primarily in the initial stages of the photochemical reaction by acting as an initiator. Filipescu and Hla Way, who studied photolysis of Co(III) 2,4-pentanedionate in various organic solvents¹², have proposed a mechanism assuming the formation of several intermediates of peroxidic or free radical character which may, with great probability, initiate free radical processes. The products of the photolysis were almost the same as those identified in our system.

When the peroxide concentration has built up sufficiently, peroxide decomposition, which may occur by the combined effect of metal ions, light, and thermal energy, becomes the rate-limiting step. This is in line with the observation that at high catalyst concentrations, where the residual metal concentration is still relatively large, there is no marked change in the rate of thermal reaction on termination of irradiation. If the Co(III) concentration is low, all of the catalyst is rapidly converted into its insoluble form, and the rate-limiting step is hydroperoxide decomposition, which stops on terminating the irradiation. The thermal reaction does not occur in this case.

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