

Oxidation of polyalkylated aromates. I. The influence of 3,5-dimethylbenzaldehyde on oxidation of mesitylene

M. HRONEC and V. VESELÝ

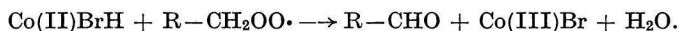
*Department of Chemistry and Technology of Petroleum, Slovak Technical University,
880 37 Bratislava*

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It has been shown that the oxidation of mesitylene to aromatic acids with oxygen in acetic acid at 90°C catalyzed by Co(II) and bromine salts is manifested on the absorption curves of oxygen by an inflection due to a rapid oxidation of 3,5-dimethylbenzaldehyde, the content of which in the mixture is approximately 26 mole %. Under these reaction conditions the oxidation of 3,5-dimethylbenzaldehyde is influenced mainly by the presence of mesitylene and organic bromides formed during the oxidation. In the initial stage of oxidation, 3,5-dimethylbenzaldehyde added to mesitylene does not markedly accelerate the reaction rate; when added after the rapid oxidation period associated with the inflection on the absorption curve, 3,5-dimethylbenzaldehyde accelerates the reaction several times.

Oxidation of alkylaromatic hydrocarbons to yield polycarboxylic acids proceeds well in solutions of aliphatic acids and under catalysis of cobalt and bromine salts, or compounds of the latter. The influence of these salts on single elementary reactions has been studied by several authors [1–4]. A complex formed from bromide anions and salts of cobalt takes part in the propagation as shown by the reaction scheme



This reaction suggested by *Kamiya* [5] has been studied by *Zakharov* [6] with toluene and *p*-xylene by means of chemiluminescence.

Since oxidation of methylbenzenes affords peroxides, aldehydes, acids, and other substances as transitive products, which can form complexes with metallic ions [7], or oxidate with the starting hydrocarbon, the problem of kinetic analysis becomes quite complicated. *Morimoto* and *Oga'a* [8] who investigated the influence of benzaldehyde on the cobalt acetate catalyzed oxidation of toluene ascertained that benzaldehyde accelerated oxidation, whereas benzylalcohol retarded it. The above-mentioned authors observed, when examining the influence of organic bromides, that the increasing concentration of bromobenzene resulted in an enhanced rate of oxygen consumption, but the absorption curves exhibited inflections [9]. The number of these inflections increases with the concentration of toluene; the rate does not, however, depend on the concentration of toluene. The rationalization was sought in the influence of bromides: it was assumed that they are responsible for another rapid type of oxidation associated with

consumption of benzaldehyde and toluene. This reaction is branched *i.e.* the concentration of radicals increases and requires the presence of bromides.

This paper refers to the influence of 3,5-dimethylbenzaldehyde on the inorganic bromine and cobalt salts catalyzed autoxidation of mesitylene in acetic acid. The influence of further intermediates formed by oxidation of mesitylene is also studied.

Experimental

Reagents

Mesitylene (99.3%) was washed with sulfuric acid, dried with anhydrous calcium chloride and sodium metal and distilled.

3,5-Dimethylbenzaldehyde was prepared by oxidation of mesitylene with manganese(IV) oxide, dried and distilled under reduced pressure [10].

3,5-Dimethylbenzoic acid was synthesized by oxidation of 3,5-dimethylbenzaldehyde with silver oxide and crystallized twice from acetic acid.

Acetic acid, cobalt acetate and sodium bromide were anal. grade and used without further purification.

Apparatus

Oxidations were carried out in a 50-ml well-shaked glass vessel the temperature of which was kept constant in an oil bath. The pressure in the whole system was maintained at 760 torr and the oxygen consumption was recorded automatically.

Absorption spectra were measured with a SPECORD (Zeiss, Jena) spectrometer.

Analysis

3,5-Dimethylbenzaldehyde was determined using polarographic method on an LP-60 apparatus (Laboratorní přístroje, Praha) immediately after the withdrawal of sample from the reaction medium. The amount of the mesitylene consumed and acids formed was estimated by gas chromatography using a Hewlett—Packard 5750 gas chromatograph. The column (1.8 m by 2 mm) was packed with 10% UCCW 982 (methylvinylsilicone elastomer) on Chromosorb W HMDS (80—100 mesh). The temperature was programmed from 100 to 200°C at a 10°C/min rate and above this temperature isothermically. Acids were analyzed as methyl esters. Hemimellitene, 3,4-dimethylbenzoic and 2-methylterephthalic acids were the internal standards. The concentration of bromide ions was determined by potentiometric titration on silver electrode.

Results and discussion

Mesitylene was catalytically oxidized with oxygen in acetic acid at 90°C and 760 torr in the presence of cobalt acetate and sodium bromide. The curve showing the consumption of oxygen differed from that of common oxidations. The short-lived slowing down period of oxidation was followed by a rapid absorption of oxygen.

It has been observed that the absorption curves exhibit an identical course at various concentrations of mesitylene and lower conversions; the enhanced concentration of mesitylene extends the range of temporal retardation of oxidation (Fig. 1). The measured zero order of relation between the oxidation rate and concentration of mesitylene indicates the cleavage of hydrogen from the methyl group not to be the rate determining stage.

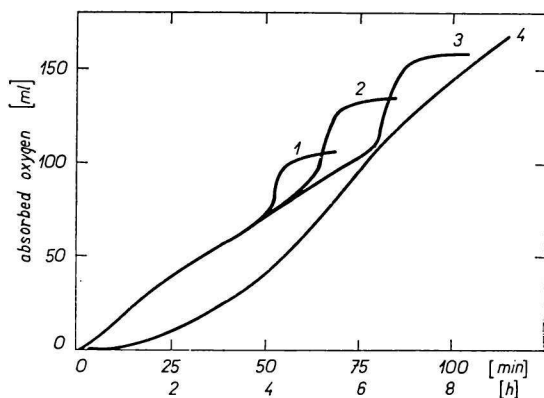


Fig. 1. Oxygen consumption curve; the dependence on concentration of mesitylene and bromide ions.

Conditions: 90°C , $[\text{NaBr}] = [\text{Co}] = 4.35 \times 10^{-2} \text{ M}$.

1. 0.445 M; 2. 0.594 M; 3. 0.743 M; 4. 100°C .

$[\text{Co}] = 8.7 \times 10^{-2} \text{ M}$; $[\text{mesitylene}] = 0.445 \text{ M}$; $[\text{NaBr}] = 0$; reaction time on the lower scale is given in hours.

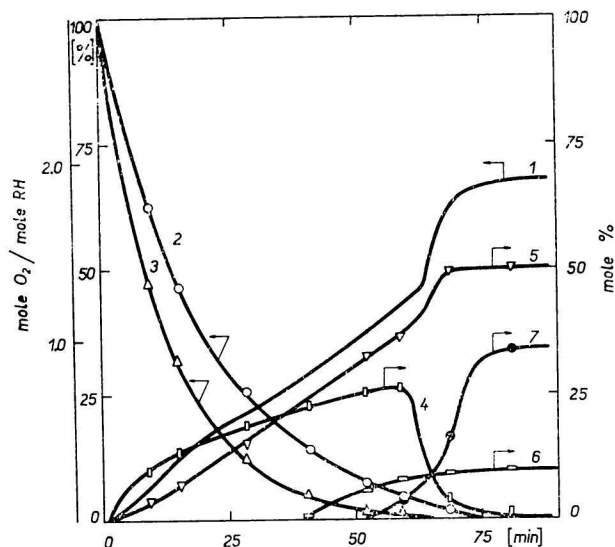


Fig. 2. The dependence of reaction medium composition on the reaction time.

90°C ; $[\text{Co}] = 4.35 \times 10^{-2} \text{ M}$; $[\text{NaBr}] = 4.35 \times 10^{-2} \text{ M}$; $[\text{mesitylene}] = 0.594 \text{ M}$.

1. absorption of oxygen; 2. % of unreacted mesitylene; 3. % Br^- ; 4. 3,5-dimethylbenzaldehyde; 5. 3,5-dimethylbenzoic acid; 6. 3-formyl-*m*-toluic acid; 7. 5-methylisophthalic acid.

The reason for such a behaviour was sought in the influence of the temporarily formed products on the oxidation of mesitylene. During the oxidation of mesitylene the samples were withdrawn from the reaction medium in various time periods and analyzed on the aldehydes and acids content, consumption of hydrocarbon and bromine ions and change in the concentration of cobalt(III) (Fig. 2). The concentration of bromine anions decreases proportionally to the consumption of mesitylene in such a manner as reported by *Sakota et al.* [2]. The content of 3,5-dimethylbenzaldehyde gradually increases and after a fast initiation of the reaction its amount rapidly decreases. During this period of reaction the content of 3,5-dimethylbenzoic acid and cobalt(III) increases. The formation of 5-methylisophthalic acid is particularly fast. In this time the concentration of bromine anions is very low (approximately 2% of the original concentration) and practically does not undergo changes.

The distribution of products at various time shows the fast period of oxidation of mesitylene to be associated with a rapid oxidation of 3,5-dimethylbenzaldehyde the content of which reaches about 26 mole % in the mixture. The influence of 3,5-dimethylbenzaldehyde on the oxidation of mesitylene is given in Fig. 3. As seen, the addition of 3,5-dimethylbenzaldehyde to mesitylene at the beginning of oxidation increases the reaction rate, but regarding high concentrations used, this increase is rather low. 3,5-Dimethylbenzaldehyde itself undergoes oxidation under similar reaction conditions substantially faster (Fig. 4, curve 4).

Also the influence of 3,5-dimethylbenzoic acid, which is formed from the very beginning of the reaction has been studied. The oxidation rate is not markedly influenced by its presence, nevertheless the range of slow oxidation extends and one can observe an inflection on the oxygen absorption curve.

When 3,5-dimethylbenzaldehyde was injected into the reaction medium through a fused inlet at various stages of oxidation, different influence on the oxidation course has been found (Fig. 4). Arrows show the time at which 3,5-dimethylbenzaldehyde was added in such an amount as to give 0.31 M solution. Thus, in the 12th minute of reaction, the oxidation rate slightly increased and then gradually decreased to the value at which

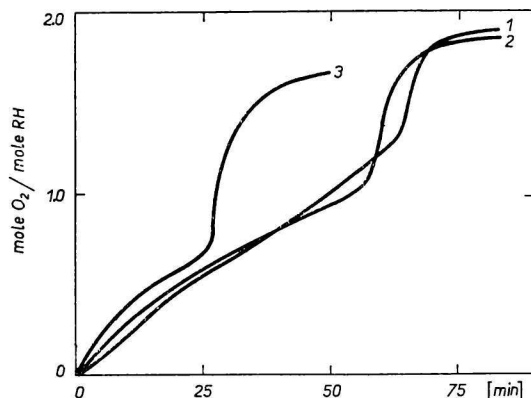


Fig. 3. The effect of 3,5-dimethylbenzaldehyde on the oxidation of mesitylene at 90°C. $[\text{NaBr}] = 4.35 \times 10^{-2} \text{ M}$; $[\text{Co}] = 4.35 \times 10^{-2} \text{ M}$; $[\text{mesitylene}] = 0.594 \text{ M}$; [3,5-dimethylbenzaldehyde].

1. 0; 2. 0.375 M; 3. 0.585 M.

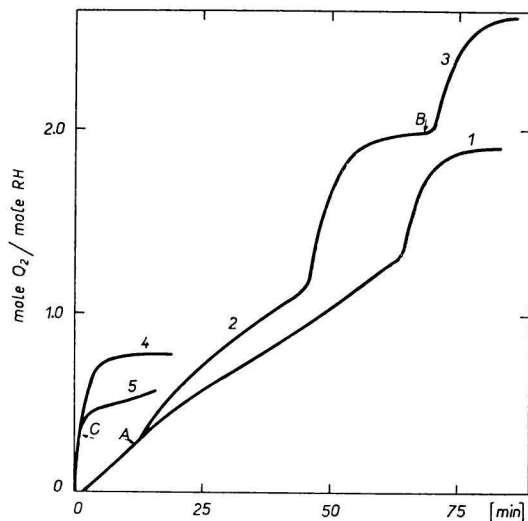


Fig. 4. The effect of addition of 3,5-dimethylbenzaldehyde (A, B) during the oxidation of mesitylene and the effect of addition of mesitylene (C) during the oxidation of 3,5-dimethylbenzaldehyde.

90°C; $[\text{Co}] = 4.35 \times 10^{-2} \text{ M}$; $[\text{NaBr}] = 4.35 \times 10^{-2} \text{ M}$.

1. $[\text{mesitylene}] = 0.594 \text{ M}$; 2. 0.310 M of 3,5-dimethylbenzaldehyde added; 3. as in 2. with 0.310 M more 3,5-dimethylbenzaldehyde; 4. $[\text{3,5-dimethylbenzaldehyde}] = 0.594 \text{ M}$; 5. $[\text{mesitylene}] = 0.300 \text{ M}$.

mesitylene itself was oxidized. When the same amount of aldehyde was added in the 59th minute after the rapid oxidation period, the oxidation rate increased many times almost immediately. Such a different behaviour, however, must be caused by some component of the oxidation system, which is present in the mixture until the rapid oxidation process takes place in such an amount as to be capable to retard the oxidation of 3,5-dimethylbenzaldehyde. The decrease of its concentration to a value at which it does not influence the oxidation of the aldehyde in such an extent results in propagation of the oxidation process; now, the amount of aldehyde accumulated in the reaction mixture undergoes rapid oxidation. This phenomenon is reflected in a sharp inflection on the absorption curve of oxygen. When single 3,5-dimethylbenzaldehyde is oxidized under the same reaction conditions as mesitylene and after one minute of reaction mesitylene is injected into the flask to a 0.3 M concentration, the rapid oxidation is retarded (Fig. 4, curve 5). A similar case is encountered also when mesitylene is added to the reaction mixture before the rapid stage of oxidation: the range of the temporal retardation of oxidation is extended, none the less after some time an inflection on the curve becomes evident. The latter finding reveals the gradual enlargement of the retardation region to be dependent on the increasing initial concentration of mesitylene (Fig. 1).

As seen from all these experiments, an inflection appears on the absorption curve of oxygen at certain concentration of mesitylene, or more exactly, at certain concentration ratio of mesitylene to 3,5-dimethylbenzaldehyde in the oxidation mixture. When the ratio between mesitylene and 3,5-dimethylbenzaldehyde concentration drops under a

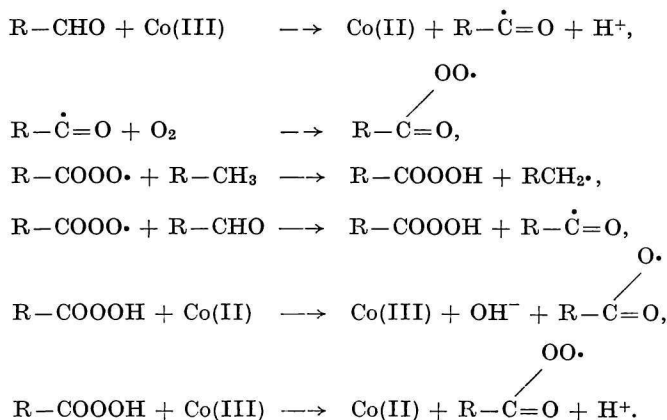
certain value, which is dependent on temperature, concentration, composition of the catalyst and other parameters, an acute consumption of oxygen associated with rapid oxidation of the accumulated 3,5-dimethylbenzaldehyde takes place. Whether or not an inflection appears on the absorption curve of oxygen will depend on affecting the single elemental reactions mainly by temperature, composition, and concentration of the catalyst.

To preclude the influence of bromides, mesitylene was oxidized in acetic acid with cobalt acetate as catalyst in the absence of bromine-containing compounds. The oxidation proceeds very slowly at 100°C and at a double concentration of the catalyst and exhibits an autocatalytical course (Fig. 1, curve 4). A rapid increase in the rate under discussion has not been observed. 3,5-Dimethylbenzaldehyde, which was added to mesitylene at the beginning of oxidation accelerated (after a short induction period) the oxidation many times; the oxidation rate had a gradually decreasing tendency.

Experiments to oxidize 3,5-dimethylbenzaldehyde together with mesitylene in acetic acid in the absence of cobalt and bromine showed that the increased concentration of mesitylene resulted in a substantially dropped rate. The co-oxidation of benzaldehyde with tetraline or cumene in chlorobenzene are in accordance with experiments so far published [11].

Although salts of cobalt influence the reaction, they are obviously not responsible for the inflection on the oxygen absorption curve under the given reaction conditions. The inflection is due to the oxidation of 3,5-dimethylbenzaldehyde influenced by the presence of mesitylene and bromides. Since the concentration of bromine anions is approximately only 2% of the original concentration at this reaction time, this phenomenon is caused by some organic bromine-containing compounds formed during oxidation proportionally to the decrease of Br⁻ concentration. Thus an inflection on the absorption curve of oxygen can be observed when oxidizing mesitylene with cobalt acetate in the presence of *p*-bromobenzyl bromide and benzyl bromide, although their course differs from that of NaBr. The effect of some organic forms of bromides on single elemental oxidation reactions of mesitylene and 3,5-dimethylbenzaldehyde lasts until the point of the rapid oxidation period.

When the above-mentioned organic forms of bromides ceased to influence markedly the oxidation of 3,5-dimethylbenzaldehyde, the oxidation of 3,5-dimethylbenzaldehyde *via* benzoyl radicals takes place to furnish the proper peroxy acid as is the case with benzaldehyde upon oxidation with cobalt(II) catalyst in acetic acid [12]:



Peroxo acid is in turn decomposed in the presence of cobalt salts to give radicals, which accelerate the rate of initiation process. Since the concentration of mesitylene is rather low in this stage of oxidation, the increase of initiation provokes the oxidation of 3,5-dimethylbenzoic acid, thereby enhancing the amount of 5-methyl-isophthalic acid in the reaction mixture several times in a short period. The reaction of cobalt(III) with peroxo acids proceeds slowly, this being reflected in the increase of cobalt(III) concentration in the range of rapid oxidation period; this phenomenon is visualized by a green colour of the reaction solution.

Other effects, particularly the action of various kinds of bromides are subjected to our further investigation.

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