BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2413—2416 (1969)

The Autoxidation of Ethylbenzene in the Presence of the Aqueous Phase

Hiroshi HOTTA, Masayuki ITO and Hiroaki MURASHIMA

Japan Atomic Energy Research Institute, Takasaki, Gunma

(Received May 6, 1968)

Ethylbenzene was oxidized to acetophenone and a small amount of benzaldehyde in the presence of the aqueous phase under oxygen pressure at 190°C. The yield of acetophenone decreased in the presence of sulfuric acid, sodium sulfate, and iron and copper sulfates. The formation of benzaldehyde was promoted in the presence of iron and copper sulfates and sulfuric acid. These effects can be explained mainly by the decomposition of α-phenylethyl hydroperoxide by the solutes in the aqueous phase.

The autoxidation of benzene and toluene in the aqueous phase catalyzed by metal ions have been studied between 100°C and 200°C, and their reaction mechanisms have been confirmed by using stable isotopes.[1-4] In contrast, the autoxidation of ethylbenzene occurs without any metal ions in the aqueous phase. The yields of the products are affected by various solutes in the aqueous phase. In the present paper, these effects will be discussed in comparison with the results of previous studies.

Experimental

The oxidation procedure, using a 50 cc stainless-steel reactor, has been described in detail in a previous paper.[1] That is, 3 cc of ethylbenzene was placed in a hard-glass tube with 15 cc of an aqueous solution, containing various solutes, under an oxygen pressure of 30 atm, then the mixture was kept at 190°C for 30 min by a controlled heater.

The products were analyzed by gas chromatography using a column of PEG 6000 at 170°C; they were identified mainly by the retention time, but partly also by means of the mass spectrum and the NMR spectrum. An amount less than 10^{-4} mol is meaningless quantitatively in the present paper; it means just "less than 10^{-4} mol." The amount of iron species was analyzed by spectrophotometry by previously-reported methods.[5]

Results

The products were acetophenone, benzaldehyde, and a small amount of a product which has a longer retention time than that of acetophenone and which is produced upon the autoxidation of acetophenone. Although benzoic acid could not be detected by gas chromatography under the present conditions, the amount produced for each run may be the highest in the order of 10^{-5} mol, as estimated from the pH change in the aqueous phase after experimentation.

The autoxidation of ethylbenzene was carried out with the aqueous phase at various pH's, which were controlled by the addition of sulfuric acid or sodium hydroxide. After experimentation, the pH was nearly 3 for the runs; the pH was more than 3 initially. The yield of acetophenone decreased for an acidic medium of less than pH 3. Since the pH was measured at room temperature, the pH at 190°C is not known.

The effect of sodium sulfate is shown in Fig. 1 as a function of its concentration in the aqueous

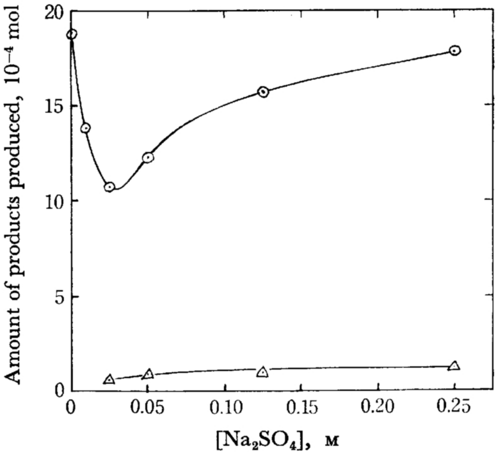

Fig. 1. The yields of acetophenone (⊙) and benzaldehyde (△) at 190°C in the sodium sulfate aqueous solution of various concentrations.

---

1) H. Hotta, A. Terakawa, K. Shimada and N. Suzuki, This Bulletin, **36**, 721 (1963).

2) H. Hotta, N. Suzuki and T. Abe, *ibid.*, **39**, 417 (1966).

3) N. Suzuki and H. Hotta, *ibid.*, **40**, 1361 (1967).

4) H. Hotta and N. Suzuki, *ibid.*, **41**, 1537 (1968).

5) H. Hotta and N. Suzuki, *ibid.*, **36**, 717 (1963).

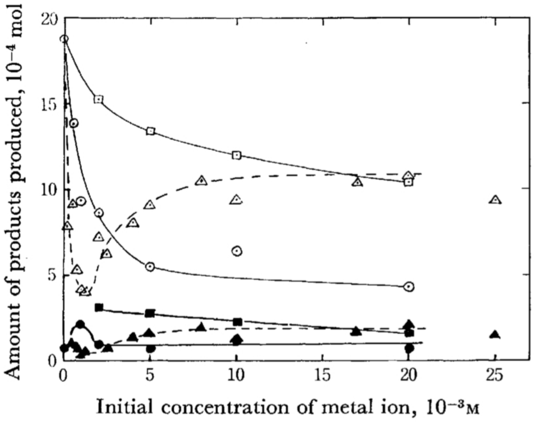

Fig. 2. The yields of acetophenone (open marks) and benzaldehyde (solid marks) at 190°C in the aqueous solution of ferrous (⊙ and ●), ferric (△ and ▲) and cupric (⊡ and ■) sulfates.

phase. The yield of acetophenone decreases at first and then increases upon further addition.

The effects of iron and copper sulfates were also examined. The amounts of acetophenone (open marks) and benzaldehyde (solid marks) produced are shown in Fig. 2 as a function of the initial concentrations of ferrous (⊙ and ●), ferric (■ and ▲), and cupric (⊡ and ■) sulfates. The yield of acetophenone decreases in the presence of these sulfates; especially, it gives a minimum at 0.001M in the case of ferric sulfates. On the other hand, the amounts of the total iron species and ferrous species, dissolved in the aqueous phase after experimentation, are shown in Fig. 3 as a function of the initial concentration of iron sulfates. The initial concentration in Figs. 2 and 3 is represented not by that of sulfate, but by that of iron.[1]

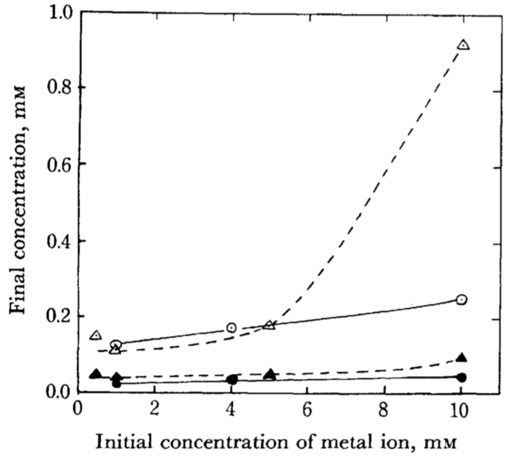

Fig. 3. The concentration of total iron species (open marks) and ferrous species in it (solid marks), dissolved in the aqueous phase after experimentation at 190°C in the aqueous solution of ferrous (⊙ and ●) and ferric (△ and ▲) sulfates.

When the autoxidation of ethylbenzene was initiated at 70°C by Fenton's reagent, as has been described in a previous paper,[4] the yield of methyl phenyl carbinol was more than twice that of acetophenone.

Discussion

So far, commercially-available ethylbenzene of a special grade was used without further purification. When this reagent was shaken several times with an aqueous solution of 0.1M ferrous sulfate, washed with water, and then distilled carefully, the amount of the products, oxidized with water at 190°C, decreased gradually with further purification, as is shown in Table 1. The amount of benzaldehyde produced was less than 10^{-5} mol in all the cases. The gas chromatogram of the reagent did not change with the purification.

TABLE 1. PURIFICATION OF ETHYLBENZENE

Shaking times	Acetophenone, 10^{-4} mol
0	17.7
4	12.1
10	9.7

When the autoxidation of ethylbenzene was carried out by adding it up to 7 cc to 15 cc of water, the yield of acetophenone increased linearly with the amount of ethylbenzene added. On the other hand, when 0.5 cc of ethylbenzene was oxidized without water, the yield of the products decreased with further purification. The pattern of the products was almost the same as in the presence of water.

These facts indicate that the autoxidation is not initiated by the thermal decomposition of ethylbenzene itself, but by that of a trace amount of some hydroperoxide in ethylbenzene; this substance is probably α-phenylethyl hydroperoxide to be stable at room temperature:

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \cdot\mathrm{OH} \qquad (1)$$

where R represents α-phenylethyl radical (ϕ–$\dot{\mathrm{C}}$H–CH_3). The bond dissociation energy of this reaction is much less than that required for either hydrogen abstraction or C–C bond scission.[6–8]

The autoxidation is propagated in both the ethylbenzene and aqueous phases. On the other hand, the present findings indicate that the yield of the products is remarkably affected by solutes in the aqueous phase. This means that at least the main part of the propagation processes in a

---

[6] L. A. Muzychenko, *Chem. Abstr.*, **59**, 5782d (1963).

[7] J. A. Kerr, *Chem. Revs.*, **66**, 465 (1966).

[8] S. W. Benson and J. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

system containing the aqueous phase occur in the aqueous phase or in the participation of the hydrated solutes dispersed in the ethylbenzene phase. Since the oxygenated species are hydrophilic, they prefer either to be extracted in the aqueous phase or to be oriented to the hydrated solutes in the ethylbenzene phase. In the present paper, the effects of the solutes will be illustrated below by reactions in the above aqueous environment. Although some reactions independent of the solutes might occur in the non-aqueous phase, reactions with the solutes occur in the aqueous envivonment in the above meaning.

After reaction (1), the autoxidation is propagated as follows:

$$\mathrm{RH} + \cdot\mathrm{OH} \rightarrow \mathrm{R}\cdot + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{ROO}\cdot \qquad (3)$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot \qquad (4)$$

with reaction (1). Furthermore, the following reactions may be expected in the aqueous phase, containing metal ions, M^+ (ferrous or cuprous ions) and M^{2+} (ferric or cupric ions):

$$\mathrm{H_2O} \xrightarrow{M^+,O_2} \cdot\mathrm{OH} \qquad (5)$$

$$\mathrm{ROOH} + M^+ \rightarrow \mathrm{RO}\cdot + \mathrm{OH^-} + M^{2+} \qquad (6)$$

$$\mathrm{ROOH} + M^{2+} \rightarrow \mathrm{ROO}\cdot + \mathrm{H^+} + M^+ \qquad (7)$$

The chain process is terminated by:

$$\mathrm{RO}\cdot \rightarrow \text{Acetophenone} \qquad (8)$$

$$2\mathrm{ROO}\cdot \rightarrow \mathrm{RO}\cdot \ etc. \qquad (9)$$

The yield of acetophenone decreases upon the addition of a small amount of sodium sulfate, as may be seen in Fig. 1. Since the sulfate group becomes sulfur trioxide as a transient state at higher temperatures due to equilibrium thermal decomposition, according to studies as using oxygen-18:[9,10]

$$\mathrm{Na_2SO_4} \rightleftarrows \cdot\mathrm{SO_3} + \mathrm{NaO} \qquad (10)$$

This intermediate might scavenge the hydroxyl radical from reaction (1) as an initiator of the propagation process (reaction (2)) in this manner:

$$\mathrm{OH} + \cdot\mathrm{SO_3} \rightarrow \cdot\mathrm{HSO_4} \qquad (11)$$

The curve between 0 and 0.02M in Fig. 1 is almost identical with the curve of cupric sulfate in Fig. 2, as suggesting that these curves correspond to this effect of the sulfate group.

On the other hand, the sulfate group can initiate the autoxidation of hydrocarbons at higher temperatures, as has been discussed in a previous paper,[9] because the sulfur trioxide of reaction (10) becomes a sulfur peroxide in the oxygenated aqueous phase. This peroxide can abstract the hydrogen atom of ethylbenzene, as in reaction (4). It has been reported that various aromatics are oxidized by sulfuric acid and aqueous sulfates.[11,12] The increase in the yield at the higher concentrations of sodium sulfate in Fig. 1 may be attributed to this action. Since the sulfur peroxide is not very reactive, and since the propagation step of reaction (7) is lacking in this system, as may be seen in Fig. 1, the yield decreases abruptly, and then gradually rises.

The decrease in the yield in the acidic medium, as has been mentioned already, can be interpreted by the following acid-catalyzed decomposition of the hydroperoxide for reaction (1);

$$\mathrm{ROOH} + \mathrm{H^+} \rightarrow \mathrm{RO^+} + \mathrm{H_2O} \qquad (12)$$

Then, spontaneously;

$$\mathrm{RO^+} \rightarrow \text{acetophenone} + \mathrm{H^+} \qquad (13)$$

These reactions give only stable species. In a previous paper,[4] reaction (8) in the presence of metal ions was illustrated as;

$$\mathrm{RO} + M^{2+} \rightarrow \text{acetophenone} + \mathrm{H^+} + M^+ \qquad (14)$$

Reaction (14) is analogous with reactions (12) and (13).

In Fig. 2 the yield of acetophenone in the iron sulfate solution is seen to decrease to a greater extent than in the cupric sulfate solution. Since iron sulfates are precipitated as ferric oxides at temperatures higher than 150°C, as is shown in Fig. 3,[1,5] an aqueous solution of iron sulfates becomes an aqueous solution of sulfuric acid containing a small amount of iron species. Therefore, the effect of iron sulfates in Fig. 2 can be attributed to the superposition of the actions of sulfate and acid (reactions (11) and (12)). On the other hand, since cupric sulfate is not decomposed even at 190°C, the aqueous solution is still neutral. Therefore, the curve of cupric sulfate in Fig. 2 is almost identical with that of neutral salt, namely, sodium sulfate, as has been mentioned already.

In Fig. 2, the yield of acetophenone in the ferric solution is smaller at first, and then it becomes larger in a more concentrated solution than in the ferrous solution. In the ferrous solution, the autoxidation is initiated by the production of the hydroxyl radical (reaction (5)), while it is terminated through reaction (6). On the other hand, in the ferric solution it is propagated by reaction (7). The phenomena in Fig. 2 result from these effects in addition to the above effects of sulfate and acid.

In Fig. 3, the fraction of ferrous species in the

---

[9] N. Suzuki, H. Hotta and H. Hashimoto, This Bulletin, **39**, 422 (1966).

[10] A. E. Brodsky and N. A. Vysotskaya, *Zh. Fis. Khim.*, **32**, 1521 (1958).

[11] M. Kilpatrick, M. W. Meyer and M. L. Kilpatrick, *J. Phys. Chem.*, **64**, 1433 (1960).

[12] W. G. Toland, *J. Am. Chem. Soc.*, **82**, 1911 (1960).

total iron sepcies is low in comparison with benzene[1] and toluene.[3] This suggests that most of the acetophenone is formed by some termination process independent of metal ions, for example, reaction (12) rather than reaction (14) and/or some reaction in the non-aqueous phase.

Some benzaldehyde is produced with acetophenone under all conditions. The ratio of benzaldehyde to acetophenone is comparatively large in the presence of iron and copper sulfates and sulfuric acid, and it increases with an increase in the temperature. Since benzaldehyde was not formed from acetophenone under the present conditions, it might be formed competitively from the same intermediate with that for acetophenone.

The authors wish to express their appreciation to Dr. Toshio Sugiura for his cooperation in the mass spectrometry and to Mr. Hironao Hayakawa for his measurement of the NMR spectrum.