BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1537—1539 (1968)

The Termination Processes of the Autoxidations of Benzene, Toluene and Ethylbenzene in the Aqueous Phase as Studied by Oxygen-18*1,*2

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(Received December 22, 1967)

The autoxidations of benzene, toluene and ethylbenzene were investigated at 70°C by using the oxygen-18 enriched Fenton's reagent. The oxygen-18 atom percentage in the products suggests that all the oxygen of benzaldehyde from toluene and of acetophenone from ethylbenzene is donated by molecular oxygen dissolved in the aqueous phase, while the oxygen of the hydroxylation products, namely, phenol from benzene, benzyl alcohol from toluene and methyl phenyl carbinol from ethylbenzene, is donated partly from water and partly from molecular oxygen. From the latter finding, the rate of the carbonium cation formation from the intermediate radicals without their oxidation to the peroxide is in the order of phenyl > α-methyl-benzyl > benzyl.

The autoxidations of benzene[1,2] and toluene[3], catalyzed by metal ions in the aqueous phase have been studied by using a stainless-steel reactor between 100°C and 200°C. Although this oxidation procedure is very suitable to obtain the main product due to the high selectivity, the oxygen-18 enriched Fenton's reagent was used at 70°C for the confirmation of the termination processes,

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*1 The Autoxidation of Aromatic Hydrocarbons in Aqueous Solutions. XI. This series succeeds "Thermal and Radiation Oxidations of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures."

*2 Partly presented at the 5th Symposium on Stable Isotopes, Leipzig (GDR), October, 1967.

1) N. Suzuki and H. Hotta, This Bulletin, **37**, 244 (1964).

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

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

because this method gives other products in addition to the main one. Since the accuracy in the previous study of toluene³⁾ was not so good due to the rather carelessness of the sampling method, the present study was carried out by the revised method for benzene, toluene and ethylbenzene.

Experimental

As in the previous study,³⁾ an oxygen-18 enriched aqueous solution of 1.5% hydrogen peroxide (10 cc) was added drop by drop, over a period of about 90 sec, in the oxygen-18 enriched 0.4 N sulfuric acid solution of 0.01 M ferrous sulfate (100 cc) at 70°C in a 300 cc flask opened to the air, in which 1 cc of aromatic hydrocarbons was suspended by a magnetic stirrer. Acetone (10 cc) was added except the case of benzene to increase the solubility of aromatic hydrocarbons. Such solutions seemed to be homogeneous at 70°C. The aqueous solutions were prepared by using the 1.64_5 ^{18}O-atom-% water.

For reference, the natural compounds (*ca.* 0.2 cc) corresponding to the products were treated for 10 min by the same conditions without hydrogen peroxide and aromatic hydrocarbons.

After the mixture had been stirred magnetically for 10 min from the beginning of dropping and then cooled, the products were extracted in ether and separated by gas chromatography at 165°C using a column of PEG 6000. The procedure after that was revised. That is, the fractions (*ca.* 100 mg) were converted to carbon dioxide by heating them for 12 hr at 500°C with mercuric chloride (100 mg) and mercuric cyanide (100 mg). The oxygen-18 atom percentage in the carbon dioxide was determined by mass spectrometry. Phenol was transformed to tribromophenol²⁾ in advance.

Results and Discussion

The observed values of the oxygen-18 atom percentage for the oxidation products (x) and the treated compounds for reference (x_0) are shown in Table 1 respectively. The values shown by an asterisk are for phenol produced from benzene at 150°C and 180°C in the ferrous sulfate solution by using a high-pressure reactor in the previous study.²⁾ As described in the experimental section, the values of x and x_0 for phenol were obtained without addition of acetone. The values of x_0 in the acetonic aqueous solution agreed within experimental error with those in the aqueous solution except benzaldehyde.

When it is assumed that the oxygen exchange reaction with water is of first order, this rate constant, k_e, can be estimated by equation

$$\frac{x_0-0.20_4}{1.64_5-0.20_4}=1-e^{-k_e t} \qquad \text{(i)}$$

where t is the exchange time, and 0.20_4 is the natural abundance of oxygen-18 in atom%. Since it takes some time for cooling, it is difficult to determine the effective exchange time. The k_e's in Table 1 are estimated on putting $t=10$ min. These values indicate that, as reviewed by Samuel and Silver,⁴⁾ aldehyde and ketone exchange oxygen rapidly with water, and methyl phenyl carbinol also does so considerably. On the other hand, phenol, benzyl alcohol and β-phenyl ethyl alcohol do not so practically.

For benzaldehyde and acetophenone, x is smaller than x_0. It is because, at the oxidation process, the product is accumulated gradually and may be partly lost by some secondary reaction during the oxidation time, while, at the reference treatment, all the reactant is present from the beginning and not lost by some secondary reaction. The smaller value of x suggests that oxygen-18 of these products is not enriched during their formation process, but done due to the oxygen exchange with water after their formation.

According to the previous studies,²·³⁾ the following reaction scheme can be assumed as the propagation processes of the present autoxidation after the formation of hydroxyl radicals:

$$\mathrm{RH} + \cdot\mathrm{OH} + \mathrm{O_2} \rightarrow \mathrm{R'OO}\cdot \qquad (1)$$

TABLE 1

Reactant	Product	^{18}O atom-%		k_e min^{-1}	F_w	Temp. °C
		x	x_0			
Benzene	Phenol	1.17_4	0.21_8	0.0010	0.67	70
		0.48*	—	—	0.18	150*
		0.90*	0.20_8	0.0003	0.47	180*
Toluene	Benzaldehyde	0.53_7	1.34_3	0.20	0	70
	Benzyl alcohol	0.37_7	0.21_1	0.0005	0.12	70
Ethylbenzene	Acetophenone	0.73_9	1.10_0	0.097	0	70
	Methyl phenyl carbinol	1.03_2	0.46_6	0.020	0.48	70
	Unknown	0.38_0	—	—	—	70
	β-Phenyl ethyl alcohol	—	0.21_3	0.0006	—	70

* See Ref. 2.

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4) D. Samuel and B. L. Silver, *Advances in Phys. Org. Chem.*, **3**, 123 (1965).

$$RH + R'OO\cdot \rightarrow R\cdot + R'OOH \qquad (2)$$

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

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

$$ROOH + Fe^{2+} \rightarrow RO\cdot + OH^- + Fe^{3+} \qquad (5)$$

$$ROOH + Fe^{3+} \rightarrow ROO\cdot + H^+ + Fe^{2+} \qquad (6)$$

$$ROO\cdot + ROO\cdot \rightarrow ROOR + O_2 \rightarrow 2\,RO\cdot \qquad (7)$$

where R· represents phenyl, benzyl or α-methyl benzyl radical. Reaction (1) represents that hydroxyl radicals give some peroxide in the presence of oxygen as the result of either the hydrogen abstraction from RH or the addition to RH.

From the above findings, the following process independent of the water oxygen is assumed for the formation of benzaldehyde and acetophenone, that is, the elimination process of proton from the oxyradical catalyzed by ferric ion;

$$C_6H_5CH_2O\cdot + Fe^{3+} \rightarrow C_6H_5CHO + H^+ + Fe^{2+} \qquad (8)$$

and

$$C_6H_5\dot{C}HOCH_3 + Fe^{3+} \rightarrow C_6H_5COCH_3 + H^+ + Fe^{2+} \qquad (9)$$

This is supported by the fact that the content of ferrous ion in the iron ion increases with the production of these products.[3]

For the hydroxylation compounds, *i. e.*, phenol, benzyl alcohol and methyl phenyl carbinol, their oxygen-18 atom percentages in Table 1 are

$$1.64_5 > x > x_0$$

This means that the oxygen of these products is donated partly by water and partly by molecular oxygen dissolved. The fraction of the product, to which oxygen is donated by water, is estimated as F_w in Table 1 by equation

$$F_w = \frac{x' - 0.20_4}{1.64_5 - 0.20_4} \qquad \text{(ii)}$$

$$x' = x - \alpha(x_0 - 0.20_4) \qquad \text{(iii)}$$

where the oxygen exchange with water after the product formation is corrected by α, which is put tentatively as 0.5.

The reaction

$$RO\cdot + H^+ + Fe^{2+} \rightarrow ROH + Fe^{3+} \qquad (10)$$

is assumed as the process by which molecular oxygen is donated to the product after reactions (5) and (7). On the other hand, the reaction

$$R\cdot + OH^- + Fe^{3+} \rightarrow ROH + Fe^{2+} \qquad (11)$$

is assumed as the transfer process for the oxygen of water. Reaction (11) is consistent with the reduction of iron ion at the oxidation of benzene to phenol. Reaction (11), which is competitive with reaction (3), postulates the formation of carbonium cation as the intermediate from the radical without oxidation to the peroxide. Such probability is in the order of

$$\text{phenyl} > \alpha\text{-methyl benzyl} > \text{benzyl} \qquad (12)$$

from the value of F_w in Table 1. α-Methyl benzyl cation is assumed as the intermediate for the oxygen exchange of methyl phenyl carbinol with water in the acidic solution in comparing the rate with the rate of the racemization.[5] It is acceptable that α-methyl benzyl carbonium cation is more probable than benzyl one. The highest ionization probability of phenyl radical to the carbonium cation without oxidation to phenyl peroxide gives a new subject for us. The less reactivity of phenyl radical towards oxygen is suggested by some investigators.[6,7] The electron affinity of phenyl radical is larger than that of benzyl radical.[8]

The unknown product from ethylbenzene in Table 1 could not be identified. This product has a retention time of gas chromatography close to that of β-phenyl ethyl alcohol, and gives the same highest mass number of the mass spectrum with this alcohol, but the NMR spectrum is quite different from this alcohol.

For phenol in Table 1, the present values, obtained in the 0.4 N acidic solution at 70°C, is higher than the previous value, obtained in the 0.01 N acidic solution at 150°C and 180°C.[2] If the value of F_w increases with an increase of temperature as seen between 150°C and 180°C, the high value of F_w at 70°C suggests the promotion of the carbonium cation formation by hydrogen ions.

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

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[6] G. A. Russell and R. F. Bridger, *J. Am. Chem. Soc.*, **85**, 3765 (1963).

[7] D. F. DeTar, *ibid.*, **89**, 4058 (1967).

[8] A. F. Gaines and F. M. Page, *Trans. Faraday Soc.*, **59**, 1266 (1963).