

The Isotope Effect of Hydrogen on the Oxidation of Benzene to Phenol¹⁾

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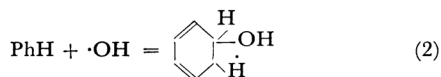
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Benzene is oxidized to phenol in a good yield in an oxygenated aqueous solution of iron or copper sulfate at elevated temperatures (above 150°C). The various facts concerning the oxidation support that the main reaction of the propagation process is the abstraction reaction of hydrogen from benzene by phenyl peroxide^{2,3)}:



On the other hand, it has been confirmed that the formation of phenol in an aqueous solution of benzene at room temperature, by radiation⁴⁾ and by the use of Fenton's reagent,⁵⁾ may be attributed to the addition reaction of the hydroxyl radical to benzene:



Since the oxidation is a non-chain reaction at room temperature and a chain reaction at elevated temperatures, the mechanism of the phenol formation should be different at lower and higher temperatures. In order to prove this assumption, the oxidation has been carried out for an equimolar mixture of C₆H₆ and C₆D₆, and the isotope effect of hydrogen or the rate constant ratio of the reaction, $k_{\text{H}}/k_{\text{D}}$, has been estimated from the isotopic composition of the phenol produced, using the equation:

$$\frac{k_{\text{H}}}{k_{\text{D}}} = \frac{(\text{C}_6\text{D}_6)}{(\text{C}_6\text{H}_6)} \times \frac{(\text{C}_6\text{H}_5\text{OH})}{(\text{C}_6\text{D}_5\text{OH})} \quad (3)$$

where (C₆D₆)/(C₆H₆) is the initial mole ratio of the benzene mixture. The observed values were about 1.2 between 150°C and 200°C.²⁾ The abstraction reaction usually gives a higher value than this.

Equation (3) can give the true value of $k_{\text{H}}/k_{\text{D}}$ on the assumption that the concentration of benzene in the aqueous phase is in excess of that of the oxidant, for example, phenyl peroxide in reaction (1), and that the concentration is constant throughout the reaction. If benzene does not satisfy this

assumption because of its low solubility or because of the fast oxidation rate, the value of $k_{\text{H}}/k_{\text{D}}$ calculated equation (3) approaches an unity, that is, it gives a lower value. However, it is difficult to control the oxidation conditions in the reactor using the previous method.²⁾

In the present study, the oxidation was initiated by Fenton's reagent at 20°C and 70°C, and the concentration of the initiator (the hydroxyl radical) was changed in order to control the ratio (benzene)/(initiator), so as to examine the above circumstances. In spite of the wide change of reaction conditions, which will be ascribed in Experimental, the values of $k_{\text{H}}/k_{\text{D}}$ from Eq. (3) ((C₆D₆)/(C₆H₆)=1.09) were 1.25 ± 0.02 at 20°C, and 1.37 ± 0.02 at 70°C. The difference between 20°C and 70°C is only 0.12, but even this is distinct beyond the range of experimental error.

Since acetone was added only at 20°C in order to increase the solubility of benzene in the aqueous phase, benzene is sufficiently in excess, at least at 20°C, to satisfy the assumption of Eq. (3). Furthermore, the isotope effect would decrease with an increase in the temperature. Therefore, the higher value at 70°C than at 20°C indicates that the oxidation process at 70°C contains a reaction which gives a higher isotope effect than that at 20°C (reaction 2). In fact, the yield of phenol indicates that the oxidation is apparently a non-chain reaction at 20°C, while it is a chain reaction at 70°C. These facts regarding the value of $k_{\text{H}}/k_{\text{D}}$ and the yield of phenol at both temperatures support implicitly the abstraction reaction (reaction (1)), assumed at elevated temperatures, instead of the addition reaction (reaction (2)) at room temperature.

The lower value in the previous paper²⁾ (1.2) may be due to the concentration of benzene being too low in the previous study, for the estimation of the $k_{\text{H}}/k_{\text{D}}$ using Eq. (3).

Experimental

An aqueous solution of hydrogen peroxide (10 cc) was added, drop by drop, to a suspension of benzene at 20°C and 70°C in a 300 cc flask open to the air. The benzene was an approximately equi-molar mixture of C₆H₆ and C₆D₆, the latter of which was obtained from Merck, Sharp & Dohme of Canada, Ltd. It was determined to be chemically pure by gas chromatography, and to be isotopically pure by mass spectrometry. Benzene (1 cc) was suspended, using a magnetic

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stirrer, in 0.4 N sulfuric acid containing 0.01 M ferrous sulfate. As the aqueous phase, 100 cc of this acidic solution was used at 70°C, but acetone (50 cc) was added to this acidic solution (50 cc) at 20°C.

The concentration of the initiator (the hydroxyl radical) was controlled by changing the concentration of hydrogen peroxide (0.5—3.0%), the addition rate (10—100 sec), and the stirring conditions.

After the mixture had been stirred for 5 min and then cooled, the phenol produced was extracted in ether, as in the previous study,⁷⁾ separated by gas chromato-

graphy, and analyzed by mass-spectrometry.²⁾

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