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The Isotope Effect of Hydrogen on the Autoxidation of Benzene and Toluene in Aqueous Solutions*[1]

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As the result of studies of the autoxidation of benzene[1] and toluene[2] in aqueous solutions catalyzed by metal ions at elevated temperatures, it has been assumed that the main reaction of the propagation process is the abstraction reaction of hydrogen by peroxides:

$$\mathrm{ROO\cdot + RH \rightarrow ROOH + R\cdot} \qquad (1)$$

where R represents the phenyl or benzyl radical. As an extension of this work, the autoxidation, initiated by Fenton's reagent, was carried out for an equimolar mixture of C_6H_6 and C_6D_6 and one of $C_6H_5CH_3$ and $C_6D_5CD_3$ in a previous work.[2] The isotope effect of hydrogen or the rate constant ratio of this reaction, k_H/k_D, was then estimated from the isotopic composition of the products at a low reaction conversion by using the equation:

$$\frac{k_H}{k_D} = \frac{(\mathrm{RD})}{(\mathrm{RH})} \times \frac{(\mathrm{Product})}{(\mathrm{d\text{-}Product})} \qquad (2)$$

where (RD)/(RH) is the initial mole ratio of the

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*[1] The Autoxidation of Aromatic Hydrocarbons in Aqueous Solutions. XII.

[1] H. Hotta, N. Suzuki and T. Abe, This Bulletin, **39**, 417 (1966).

[2] N. Suzuki and H. Hotta, *ibid.*, **40**, 1361 (1967).

deuterated reactant to the normal reactant, which was unity, while (Product)/(d-Product) is the mole ratio of the normal product to the deuterated product. This method should give the value of k_H/k_D, when the concentration of the reactant (RH or RD) in the aqueous phase is always high in comparison with that of ROO· in reaction (1).[3] For this purpose, acetone was added in the aqueous phase in order to increase the solubility of aromatic hydrocarbons.

The values in the previous work[2] (*i. e.*, *ca.* 1.4), however, seemed to be rather low for the confirmation of reaction (1). Recently, it has been found that direct mass spectrometry is not a good method for measuring the isotopic composition of the products, since the isotope effect of vaporization during sampling sometimes becomes effective for products with such low vapor pressures.[4] Therefore, the isotopic measurements were carried out by an entirely different procedure in the present work. Namely, the products, separated by gas chromatography, were converted to hydrogen and deuterium prior to the mass spectrometry. The present method is definitely a better way for the isotopic measurement, since it avoids the inherent error due to the above isotope effect of vaporization. The values of the present work, estimated by Eq. (2), are listed in Table 1.

TABLE 1. ISOTOPE EFFECT OF HYDROGEN

Reactant	Product	Temp., °C	k_H/k_D
Benzene	Biphenyl	20	1.9
	Phenol	70	2.4±0.2
Toluene	Benzyl alcohol	70	4.6±0.3
	Dibenzyl	70	4.8

The values (4.5—4.8) obtained for toluene are similar to the values for the propagation process (reaction (1)) of the autoxidation of aromatic hydrocarbons, that is, 5.5 for cumene at 60°C[5] and 5.1 for diphenylmethane at 30°C.[6] Meanwhile, similar values (4.5—5.1) have also been reported for the oxidation of *p*-methoxytoluene by manganic acetate in acetic acid,[7] which involves the detachment of the hydrogen atom by an electron-transfer process.

As for the oxidation of benzene, Smith and Norman suggested, after a qualitative experiment, that there is no kinetic isotope effect on the hydroxylation of benzene to phenol by Fenton's reagent at room temperature.[8] Meanwhile, the addition of the hydroxyl radical to benzene has been confirmed as the primary process in the formation of phenol in the pulse radiolysis of an aqueous solution of benzene at room temperature.[9]

Contrary to the above observations of Smith and Norman, however, the present value for benzene at 70°C (2.4) appears somewhat unexpectedly high. In our previous preliminary study,[3] too, it was a general tendency for the value of k_H/k_D, obtained at 70°C to be relatively larger than that at 20°C. Since the kinetic isotope effect usually decreases with an increase in the temperature, the higher value at 70°C seems to suggest that the process at 70°C includes a different reaction route, which has a higher isotope effect. A few possible pathways have already been proposed as examples in reference (8). However, none of these mechanisms can explain the fact that more than one half of the oxygen in the produced phenol is originated from water.[4] Further investigation is necessary, for the mechanism is rather complicated for the case of benzene.

Experimental

The oxidation procedure was almost the same as an earlier one.[3] That is, 0.4 cc of benzene was dissolved in 75 cc of a 0.4N sulfuric acid solution containing 0.01M ferrous sulfate and 25 cc of acetone at 20°C, while 0.5 cc-portions of benzene and toluene were dissolved in 80 cc of the above ferrous solution and 20 cc of acetone at 70°C. Benzene or toluene was almost an equimolar mixture with the respective deuterated reagent, Benzene-d_6 and toluene-d_8, obtained from Merck, Sharp & Dohme of Canada, Ltd , were proved extremely pure chemically and isotopically by gas chromatography and mass spectrometry, 10 cc of 1.5% hydrogen peroxide were added, drop by drop, over a period of about 90 sec, to the above solutions in a 300 cc flask opened to the air.

After the mixture had been stirred for 10 min and then cooled, the products were separated by gas chromatography (PEG 6000). Then they were converted to water by being passed through cupric oxide pellets at 500°C with dry oxygen. This water was again reduced to hydrogen gas by passing it through zinc pellets at 370°C. The ratio of hydrogen to deuterium in this gas was determined by mass spectrometry.

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3) H. Hotta, This Bulleın, **40**, 687 (1967).

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

5) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

6) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **44**, 1119 (1966).

7) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

8) J. R. L. Smith and R. O. C. Norman, *J. Chem. Soc.*, **1963**, 2897.

9) L. M. Dorfman, I. A. Taub and R. E. Bühler, *J. Chem. Phys.*, **36**, 3051 (1962).