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Abstract

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Investigation of the Mechanism of Benzene Oxidation by Isotopic and Mass-Spectrometric Methods

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In our previous works (1) it was shown that reactions proceeding with the participation of phenyl radicals in a benzene medium $C_6D_6 + C_6H_6$ lead to the appearance in the solvent of a new isotopic variety of benzene, C_6H_5D (as a result of abstraction by the radicals $C_6H_5\cdot$ of deuterium from the medium), and to the formation of diphenyl of characteristic isotopic composition.

In the present work, for the purpose of indicating phenyl radicals and studying the mechanism, we investigated the oxidation of benzene $C_6D_6 + C_6H_6$ (also containing benzenes d5, d4, d3, and d2, but not d1) by Fenton' s reagent, pernitrous acid, potassium permanganate in an acidic medium, ammonium persulfate in the presence of Ag^+ ions, and also the radiolysis of a mixture of this benzene with water and of dry benzene. Some of the experiments were carried out with benzene C_6H_5D. From it two isotopic varieties of phenyl radicals, $C_6H_5\cdot$ and $C_6H_4D\cdot$, can be formed. Abstraction of deuterium from the medium by the latter gives benzene $C_6H_4D_2$, the appearance of which should serve, in these experiments, as an indicator of the participation of phenyl radicals in the reaction. Another sign of the participation of phenyl radicals in reactions with C_6H_5D may be the appearance of diphenyl d3 in the diphenyl formed. This isotopic variety should be obtained as a result of disproportionation of hydrodiphenyl radicals (1,2) containing two deuterium atoms (formed by addition of $C_6H_4D\cdot$ radicals to benzene C_6H_5D), for example:

$$\mathrm{C_6H_4D{-}}\text{[[structural formula]]} + \mathrm{C_6H_4D\cdot{-}}\text{[[structural formula]]} \longrightarrow \mathrm{C_6H_4D{-}C_6H_5} + \mathrm{C_6H_4D{-}}\text{[[structural for}$$

$$\mathrm{C_6H_4D{-}}\text{[[structural formula]]} \xrightarrow{\text{oxid.}} \mathrm{C_6H_4D{-}C_6H_3D_2}$$

Oxidation of benzene by Fenton' s reagent (13), pernitrous acid (11), and persulfate (12) was carried out according to known procedures. Oxidation with permanganate acidified with sulfuric acid was conducted at boiling. Radiolysis was carried out by irradiating carefully degassed preparations for 500 hr with γ-rays of Co^{60} (dose $1.4 \cdot 10^{22}$ eV/ml). The conversion of benzene ranged from 10–15 to 90% and only in the radiolysis of dry benzene was it very small (about

0.1%). Table 1 presents typical results of isotopic analysis of unreacted benzene, and Table 2 presents results of analysis of some products of the reactions studied.*

The data of Table 1 show that the benzene from experiments Nos. 1-5 does not contain the variety C_6H_5D, while the benzene from experiments Nos. 6-7 does not contain the variety $C_6H_4D_2$. This indicates the nonparticipation of phenyl radicals in all the reactions studied, with the exception of the radiolysis of dry benzene. In the latter process the participation of phenyl radicals apparently leaves no doubt (4) and has been confirmed by us by analysis of the diphenyl formed (see below). It nevertheless remained undetected from the benzene analysis data, because of the low percentage conversion and the insignificant yield of phenyl radicals and of the product of their transformation—benzene C_6H_5D.

In the oxidation of benzene $C_6D_6 + C_6H_6$ by Fenton' s reagent and $KMnO_4$, the unreacted benzene contains considerably less deuterium than the initial benzene, chiefly because of an increase in the fraction of the light variety C_6H_6. This observation could be explained by assuming that the heavy varieties of benzene are oxidized faster than the light ones (there is a negative isotope effect of deuterium in these reactions). Such an explanation seems doubtful,

Table 1

Analysis of benzene from the experiments (contents of varieties in percent)

* Isotopic analysis was performed by the method of low-voltage mass spectrometry (3).

Isotopic variety	Initial benzene	Benzene: from experiment no. 1 —oxidation with $H_2O_2 + Fe^{2+}$	Benzene: from experiment no. 2 — radiolysis of a mixture of benzene with water	Benzene: from experiment no. 3 — radiolysis of dry benzene	Benzene: from experiment no. 4 —oxidation with $KMnO_4$	Benzene: from experiment no. 5 —oxidation with $(NH_4)_2S_2O_8 + Ag^+$	Initial benzene	Benzene: from experiment no. 6 —oxidation with $H_2O_2 + Fe^{2+}$	Benzene: from experiment no. 7 —oxidation with ONOOH
C_6D_6	29.4 (59.0)*	26.9 (58.5)	29.5	29.3	25.4 (59.6)	30.1	–	–	–
C_6D_5H	12.2 (24.5)	11.3 (24.6)	12.4	11.9	10.5 (24.6)	12.3	–	–	–
$C_6D_4H_2$	5.7 (11.4)	5.4 (11.7)	5.6	5.5	4.7 (11.3)	5.8	–	–	–
$C_6D_3H_3$	2.1 (4.2)	2.0 (4.3)	2.0	1.9	1.8 (4.2)	2.1	–	–	–
$C_6D_2H_4$	0.38 (0.77)	0.43 (0.93)	0.43	0.38	0.22 (0.47)	0.60	–	–	–
C_6DH_5	–	–	–	–	–	–	93.6	93.6	93.8
C_6H_6	50.2	54.0	50.1	51.0	57.4	49.1	6.4	6.4	6.2
At. %D	44.6	41.0	44.3	43.9	38.3	45.3	15.6	15.6	15.6

* The percentages of the amounts of the varieties from $-d_1$ to $-d_6$ are given in parentheses.

since only a few cases of a negative isotope effect have been described, and its very existence is uncertain. But we found no other explanation. The data presented on the nonparticipation of phenyl radicals in these reactions are of great importance for understanding their mechanism.

In the oxidation of organic compounds by permanganate (5) and persulfate (see, for example, (6)), there are grounds for expecting the intermediate formation of radicals. It is now clear that in the oxidation of benzene these radicals cannot be $C_6H_5\cdot$ radicals. Oxidation of benzene by Fenton' s reagent and radiolysis of its mixtures with water are often represented (see, for example, (7,8)) by schemes involving phenyl radicals:

$$\begin{array}{ll} \text{a)} & C_6H_6 + HO\cdot \to C_6H_5\cdot + H_2O; \\ \text{b)} & C_6H_5\cdot + HO\cdot \to C_6H_5OH; \qquad (1) \\ \text{c)} & C_6H_5\cdot + C_6H_5\cdot \to C_6H_5{-}C_6H_5. \end{array}$$

Sometimes (1b) is replaced by the reaction

$$C_6H_5\cdot + Fe^{3+} + H_2O \to C_6H_5OH + Fe^{2+} + H^+. \tag{2}$$

The formation of diphenyl, in addition to (1c), is represented by the reaction

$$C_6H_5\cdot + C_6H_6 \xrightarrow{-H\cdot} C_6H_5{-}C_6H_5, \tag{3}$$

which, as is now known (^{1,2}), should be specified in detail as follows:

$$\begin{array}{ll} \text{a)} & C_6H_5\cdot + C_6H_6 \longrightarrow \text{cyclohexadienyl-type adduct;} \\ & \text{cyclohexadienyl-type adduct} + X\cdot \longrightarrow C_6H_5{-}C_6H_5 \quad (X = C_6H_5,\ OH\cdot,\ \text{etc.}); \\ \text{b)} & 2\,\text{cyclohexadienyl-type adduct} \longrightarrow C_6H_5{-}C_6H_5 + \text{cyclohexadienyl-type adduct;} \\ & \text{cyclohexadienyl-type adduct} \xrightarrow{\text{oxid.}} C_6H_5{-}C_6H_5. \end{array} \tag{4}$$

Our data show that schemes (1)–(4) do not express the course of the reactions under consideration.

Alternative schemes (^{8},^{9}), in which the radicals $HO^\bullet$ do not abstract hydrogen from benzene, but add to it, giving hydrohydroxyphenyl radicals, explain the formation of phenol and diphenyl as follows:

$$\begin{array}{l} \text{a) } C_6H_6 + HO^\bullet \longrightarrow \text{hydrohydroxyphenyl radical;} \\ \quad \text{hydrohydroxyphenyl radical} + X^\bullet \longrightarrow C_6H_5OH + XH \\ \qquad (X = OH;\ Fe^{3+}\ \text{etc.}) \end{array}$$

$$\begin{array}{l} \text{b) } 2\,\text{hydrohydroxyphenyl radicals} \longrightarrow C_6H_5OH + \text{hydrohydroxyphenyl radical;} \\ \quad \text{hydrohydroxyphenyl radical} \longrightarrow C_6H_6 + H_2O \end{array} \tag{5}$$

$$\text{c) } 2\,\text{hydrohydroxyphenyl radicals} \longrightarrow \text{intermediate} \longrightarrow C_6H_5{-}C_6H_5 + 2H_2O$$

d) hydrohydroxyphenyl radical$+C_6H_6 \xrightarrow{-H^\bullet}$ intermediate $\longrightarrow C_6H_5{-}C_6H_5+H_2O$

Recently M. A. Proskurnin and co-workers (^{10}) confirmed the occurrence of reactions of this type in the radiolysis of a benzene-water mixture.

In the oxidation of benzene with pernitric acid, transformations of the same kind are assumed (^{11}): phenol is formed according to (5a), and nitrobenzene and nitrophenol according to the reactions:

$$\text{hydrohydroxyphenyl radical}+NO_2^\bullet \longrightarrow \text{nitrohydroxycyclohexadienyl radical (d)} \underset{-H_2O}{\xrightarrow{-H_2}} \begin{cases} C_6H_5(NO_2)(OH) \\ C_6H_5NO_2 \end{cases} \tag{6}$$

Our data on the isotopic composition of the products of the transformations studied make it possible to refine schemes (5) and (6) and to discard some of the reactions included in them. In the mechanism of phenol formation, which we isolated in experiments Nos. 1 and 6, these data make it possible to reject the second stage of reaction (5b), since its occurrence would have led in experiment No. 1 to the appearance in benzene of species d_1, and in experiment No. 6 of species d_2, which were not present.

The isotopic composition of diphenyl from experiments Nos. 1 and 6 is close to that calculated for reactions (5c) or (5d) without a kinetic isotope effect (calculated percentage ratio of species for experiment No. 1: $d_{10} : d_9 : d_8 : d_7 : d_6 : d_5 : d_4 : d_3 : d_2 : d_1 : d_0 = 9.0 : 7.1 : 4.2 : 2.0 : 0.65 : 31.1 : 13.1 : 4.7 : 1.3 : 0.14 : 26.8$; for experiment No. 6: $d_2 : d_1 : d_0 = 60.7 : 34.4 : 4.9$) and does not correspond to that calculated for formation according to scheme (4b), especially for diphenyls d_6 and d_1 (calculated for experiment 1: $d_{10} : d_9 : d_8 : d_7 : d_6 : d_5 : d_4 : d_3 : d_2 : d_1 : d_0 = 7.9 : 7.6 : 4.4 : 1.8 : 2.4 : 28.4 : 14.2 : 4.6 : 1.2 : 2.9 : 24.0$). This once again confirms that scheme (4) is incorrect for the case of oxidation

Table 2

Analysis of reaction products (content of species in percent)

Isotopic species	Exp. No. 1	Exp. No. 6	Exp. No. 3	Isotopic species	Exp. No. 7
$C_{12}D_{10}$	11.3	–	5.2	$C_6D_3H_2NO_2$	–
$C_{12}D_9H$	8.4	–	4.4	$C_6D_2H_3NO_2$	–
$C_{12}D_8H_2$	4.8	–	2.8	$C_6DH_4NO_2$	82.3
$C_{12}D_7H_3$	1.9	–	1.1	$C_6H_5NO_2$	17.7
$C_{12}D_6H_4$	0.72	–	1.2		
$C_{12}D_5H_5$	31.8	–	28.0	$C_6D_3H(NO_2)(OH)$	–

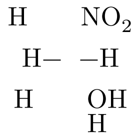
Isotopic species	Exp. No. 1	Exp. No. 6	Exp. No. 3	Isotopic species	Exp. No. 7
$C_{12}D_4H_6$	11.4	–	12.3	$C_6D_2H_2(NO_2)(OH)$	1.2(?)
$C_{12}D_3H_7$	4.4	–	4.6	$C_6DH_3(NO_2)(OH)$	65.7
$C_{12}D_2H_8$	1.3	62.1	1.8	$C_6H_4(NO_2)(OH)$	34.1
$C_{12}DH_9$	0.24	32.8	1.2		
$C_{12}H_{10}$	24.0	5.1	37.5		

benzene by Fenton' s reagent. It is also obvious that reaction (5d) proceeds without the intermediate stage of radical disproportionation (which might have been expected), since such a process would change the isotopic composition of diphenyl.

The diphenyl obtained in the radiolysis of dry benzene (experiment No. 3) has a completely different isotopic composition than in experiment No. 1. This is explained by the participation of the radicals $C_6H_5\cdot$ (4) in the reaction and by the formation of diphenyl according to scheme (4): the composition of diphenyl does not at all correspond to that calculated according to schemes (5c) or (5d) (calculated $d_{10} : d_9 : d_8 : d_7 : d_6 : d_5 : d_4 : d_3 : d_2 : d_1 : d_0 = 10.1 : 7.4 : 4.3 : 1.9 : 0.63 : 32.2 : 11.8 : 4.6 : 1.3 : 0.14 : 25.6$), but is close to that calculated according to scheme (4b), under the condition that the latter reaction proceeds with a kinetic isotope effect (approximately calculated for an isotope effect equal to five: $d_{10} : d_9 : d_8 : d_7 : d_6 : d_5 : d_4 : d_3 : d_2 : d_1 : d_0 = 4.9 : 6.1 : 3.8 : 1.8 : 1.2 : 28.7 : 14.3 : 5.3 : 1.4 : 1.3 : 31.7$.

The isotopic composition of the nitrobenzene obtained in experiment No. 7 is close to that calculated according to scheme (6), if the isotope effect of the reaction is taken as equal to 2 (approximately calculated $d_1 : d_0 = 85.0 : 15.0$). It follows from this that the limiting stage is the elimination of water from molecule (a), since only at this stage are the C—H bonds broken.

The isotopic composition of *o*-nitrophenol does not correspond to that calculated for reaction (6) (approximately calculated $d_1 : d_0 = 85.0 : 15.0$ for an isotope effect of elimination of the H_2 molecule equal to 2, and $d_1 : d_0 = 78.0 : 22.0$ in the absence of an isotope effect). Consequently, this generally accepted scheme is incorrect. Nitrophenol, apparently, is obtained by hydroxylation of nitrobenzene, since the composition calculated for such a mechanism ($d_1 : d_0 = 65.8 : 34.2$) satisfactorily corresponds to the composition found experimentally. It remains unclear, however, what causes the formation of some quantity of nitrophenol d_2. It is possible that it consists in disproportionation of radicals:



$$\begin{array}{cc} H & NO_2 \\ H- & -H \\ H & OH \\ & H \end{array}$$

formed by the addition of HO· radicals to nitrobenzene and serving as the source of formation of *o*-nitrophenol.

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