ON THE NATURE OF THE INSOLUBLE PRODUCT FORMED DURING THE RADIOLYTIC OXIDATION OF BENZENE IN WATER

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Abstract

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ON THE NATURE OF THE INSOLUBLE PRODUCT FORMED DURING THE RADIOLYTIC OXIDATION OF BENZENE IN WATER

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Although reactions involving the interaction of organic substances with the products of water radiolysis are of great interest, these reactions have as yet been little studied. One of the principal difficulties here is the isolation and identification of the products formed, since the yields of radiation-chemical reactions are usually small.

Among the most important reactions of this type is the oxidation of benzene during the radiolysis of its aqueous solutions, first studied in detail by Stein and Weiss (^1), who concluded that the principal products arising during radiolysis are phenol and diphenyl. These authors believed that both products are formed simultaneously, with diphenyl predominating in an atmosphere of inert gas, while in an oxygen atmosphere an increase in the concentration of phenol is observed, accompanied by some decrease in the diphenyl content of the system.

However, in later works devoted to the oxidation of benzene by the products of water radiolysis (^2), and also by Fenton's reagent (^3), it was found that, when the process is carried out in an oxygen atmosphere, diphenyl is not detected at all. It was also shown that, in the absence of oxygen, the introduction into the system of ions of variable valence can sharply reduce the yield of diphenyl. Ions of variable valence simultaneously cause an increase in the yield of phenol, and this occurs both in the absence (^4) and in the presence of oxygen (^5). The question of the formation of diphenyl remained not entirely clear. If appreciable amounts of diphenyl were formed, it should have precipitated under the experimental conditions.*

Despite the considerable number of works devoted to the oxidation of benzene by the products of water radiolysis, in none of them was the chemical nature of the water-insoluble substance formed investigated; in essence, the investigators assumed *a priori* that it was diphenyl.

The present communication is devoted to a description of our experiments, in which we investigated the conditions of formation and the nature of the precipitate formed during the oxidation of benzene in the absence of oxygen.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

This question is of not only theoretical but also practical interest, since our experiments showed that precipitate formation not only lowers the useful yield of phenol, but also complicates its isolation, because this precipitate forms in solutions a sparingly soluble, highly stable suspension.

The source of γ-radiation was Co^60 with an activity of approximately 1400 g-eq. The dose rate, measured by the ferrosulfate method, was 180 r/sec.

* Weiss (^6), for example, in his latest work considers the absence of a precipitate during oxidation in an oxygen atmosphere to be evidence for the absence of diphenyl.

The volume of the irradiated aqueous phase with benzene dissolved in it was 18 cm^3; the volume of the benzene layer above the aqueous phase was 1 cm^3. Before irradiation the solution was thoroughly degassed in vacuum. The milky-white suspension arising in the course of irradiation was separated from the bulk of the solution by prolonged centrifugation. To remove entrained phenol, the precipitate was thoroughly washed with 1 N sodium hydroxide solution and then with water to neutral reaction. The precipitate was dried under vacuum to constant weight. The molecular weight of this product was determined cryoscopically—from the depression of the freezing point of trimethylcarbinol (whose cryoscopic constant is 12.8; m.p. $-25.4°$). To establish the elemental composition of the precipitate, the microanalytical combustion method was used (^{7}). The ultraviolet spectra of alcoholic solutions of the precipitate were studied with an SF-4 spectrophotometer, and colorimetric analysis of these solutions, based on coupling with *p*-nitroaniline, was also carried out.

Fig. 1. Formation of an insoluble substance upon irradiation of an aqueous benzene solution as a function of dose

Fig. 2. Absorption spectra in the ultraviolet: **1** —solution of the precipitate in alcohol, **2** —*p*-hydroxydiphenyl, **3** —diphenyl

The solution separated from the precipitate, the alkaline extract, and the wash waters were analyzed for phenol content from the ultraviolet absorption spectrum.

In aqueous solutions the absorption maximum of phenol is observed at $\lambda = 270$ mμ; at this wavelength phenol absorbs approximately 330 times more strongly than benzene, so that phenol can be determined in the presence of benzene dissolved in water, whose absorption maxima lie in the region 245-260 mμ (^{2}). In alkaline solutions the absorption maxima of phenol shift to 286 mμ, and the sensitivity, as our measurements show, increases by approximately 1.5 times.

As is seen from the curve in Fig. 1, the amount of substance precipitated increases linearly with the irradiation dose.

In the spectrum of the precipitate dissolved in ethyl alcohol, only one maximum was found, in the wavelength region $\lambda = 250$–255 mµ (Fig. 2, curve 1), and the appearance of the spectrum proved to differ markedly from that of the spectrum of diphenyl (curve 3), recorded on the same instrument.

It also turned out that the molar extinctions of the substance obtained and of diphenyl at the absorption maxima differ sharply from one another (ε of diphenyl $= 17800$, ε of the precipitate $= 2200$).

It was further established that, unlike diphenyl, solutions of the precipitate, on coupling with *p*-nitroaniline, give a coloration characteristic of phenolic compounds ($\lambda_{\max} = 520$ mµ). The melting point of the precipitate proved to be $160 \pm 5°$, which coincides, within the experimental error, with the melting point of *p*-hydroxydiphenyl (160–165°) or 2,4-dihydroxydiphenyl (162–163°), but is much higher than the melting point of diphenyl. Elemental analysis of the precipitate showed: C 74.4%, O 16%, H 7-8% (the determination of hydrogen was not sufficiently accurate); this is closest to the empirical formula $C_6H_{7(8)}O$.

Finally, determination of the molecular weight gave a value of 183 ± 3, exceeding the molecular weight of diphenyl (154) by an amount considerably greater than the error of determination. This value of the molecular weight is very close to the molecular weight of dioxydiphenyl (186), with which the results of the elemental analysis are also in agreement to some extent. This sum of facts led us to suppose that the substance obtained is not diphenyl, but its oxy derivative. In Fig. 2 it can be seen that the spectrum of our substance is rather close to the spectrum of *n*-oxydiphenyl (curve 2). However, it cannot be asserted that oxydiphenyl is the sole component of the precipitate. In fact, in the infrared spectrum of the precipitate* along with absorption bands at 3310 cm^{-1} (OH) and 3020 cm^{-1} (aromatic CH), confirming the presence of phenolic groups in the precipitate, there is also a band characteristic of an aliphatic CH bond (2900 cm^{-1}).

Fig. 3. Spectra of phenol formed in solution (irradiation dose $4.4 \cdot 10^{20}$ eV/cm^3), 1 —sodium extract of the precipitate, 2 —aqueous solution separated from the precipitate, 3 —alcoholic solution of the precipitate

Taking into account the elemental-analysis data, it should therefore be thought that complex oxy compounds containing CH or CH_2 bonds of nonaromatic character could have entered into the composition of the precipitate.

This is probably also connected with the very low value of the molar extinction of the precipitate in comparison with the extinctions observed for diphenyl, *n*-oxydiphenyl, etc.

As can be seen from Fig. 3, in the absorption spectrum of the aqueous phase there is only one maximum at $\lambda = 270$ mμ, characteristic of phenol. The sodium extract of the precipitate also contains a phenolic product. Thus, upon irradiation of aqueous benzene solutions under vacuum conditions, mainly two types of phenolic compounds are formed: ordinary phenol, readily soluble in water, and a high-molecular-weight oxy compound that precipitates.

In Table 1 the distribution of the yields of these products (calculated per molecule of benzene) is shown as a function of the radiation dose. It is seen from the table that the total consumption of benzene in this case is on average 2.0–2.5 mol per 100 eV. Under vacuum conditions the consumption of benzene for phenol thus does not exceed 25%.

In an oxygen atmosphere, condensation products are not found, and the yield of phenol, as is already known, reaches 2.3–2.5 mol per 100 eV.

Table 1

Dose in eV/cm^3 · 10^{-20}	Yield in mol of benzene per 100 eV: phenol	Yield in mol of benzene per 100 eV: oxy derivatives of diphenyl	Total yield in mol per 100 eV
0.69	0.5	2.3	2.8
2.1	0.5	2.1	2.6
4.4	0.5	1.8	2.3
8.4	0.5	1.5	2.0
11.4	0.45	1.6	2.1
14.5	0.3	1.9	2.2

The investigation carried out of the properties of the precipitate formed shows that the latter consists not of diphenyl, as had been assumed earlier, but of its oxy derivative or, most probably, of a dioxy derivative.

This result is of fundamental importance, since it compels one to revise as a whole or, at least, substantially to supplement the scheme of the radiolytic oxidation of benzene in aqueous solution proposed by Stein and Weiss ([1]). In this scheme one of the main roles is played by phenyl radicals formed in the reaction of free hydroxyl with benzene. Depending on whether the phenyl radicals recombine, colliding with free hydroxyl or with one another, according to Weiss, phenol or diphenyl is formed. On the basis of this scheme, the formation of oxydiphenyls or their derivatives cannot be understood. We see a possible way of explaining the formation of such compounds in the fact that the free oxyhexadienyl radical (C_6H_6OH), formed upon collision of a benzene molecule with free hydroxyl, is a sufficiently long-lived compound for recombination of two such radicals with one another, or of one such radical with the C_6H_7 radical or with a benzene molecule, to become possible.

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* Kindly recorded at our request by N. A. Slovokhotova.

If the participation of the hexadienyl radical in the reaction is assumed, then in this case the following scheme for the formation of the substance precipitating from water is possible:

$$C_6H_7^{\bullet} + C_6H_6OH^{\bullet} \longrightarrow C_6H_8 - C_6H_5OH.$$

This variant, it seems to us, is in better agreement with the facts we have found concerning the presence of aliphatic bonds in the molecule of the precipitate. The failure to detect diphenyl also leads one to suppose that the formation of phenol may proceed not through the stage of formation of free phenyl. It may be imagined, for example, that in the reaction of two oxyhexadienyl radicals, along with coupling of the rings, a parallel process may also occur—the formation of phenol.

$$\text{oxyhexadienyl radical} + \text{oxyhexadienyl radical} \longrightarrow HO{-}C_6H_4{-}C_6H_4{-}OH + H_2$$

$$\text{oxyhexadienyl radical} + \text{oxyhexadienyl radical} \longrightarrow C_6H_{11}OH + H_2O + C_6H_6.$$

The results of the investigation carried out suggest that polymeric compounds formed upon irradiation of pure benzene may also contain hydrogenated units; if this is accepted, the small radiation-chemical yield of hydrogen in this case is readily explained.

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Note: Figure translations are in progress. See original paper for figures.