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Abstract

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ON THE CAUSES OF THE INCREASED YIELD OF PHENOL IN THE RADIOLYSIS OF SULFURIC-ACID AQUEOUS SOLUTIONS OF BENZENE CONTAINING FERROUS IONS AND OXYGEN

(Presented by Academician V. I. Spitsyn, January 20, 1965)

It is known ([1]) that the yield of phenol in irradiated aerated sulfuric-acid solutions of benzene containing Fe^{2+} ions is substantially higher ($\sim$ 6 molecules/100 eV) than in their absence. The opinion has been expressed ([1–3]) that this effect is due to the reaction of Fe^{2+} ions with HO_2 radicals and to the consequent formation of an additional quantity of OH radicals. However, by analogy with the radiolysis of aqueous solutions of other organic substances in the presence of Fe^{2+} ions and oxygen, for which the presence of chain reactions has been shown ([4–9]), one may expect a chain process to occur in the system under consideration as well. Moreover, it is known ([6,10]) that $G(Fe^{3+})$ in ferrous sulfate solutions saturated with air increases markedly upon the addition of benzene.

In this connection we undertook a detailed study of the radiolysis of sulfuric-acid aqueous solutions of benzene in the presence of oxygen and Fe^{2+} ions. The yields of ferric iron, phenol, and carbonyl compounds were measured as functions of the concentrations of Fe^{2+} ions and benzene.

We used Co^{60} γ-radiation and electrons with an energy of 0.9 MeV generated in a Cockcroft–Walton accelerator. The absorbed dose was determined by the ferrous sulfate method. In the case of Co^{60} γ-radiation, the solutions were irradiated in glass ampoules. In work with electrons, a glass membrane cell with a sealed-in quartz spectrophotometric cuvette was used.

The solutions were prepared with twice-distilled water. Mohr' s salt (chemically pure grade) was used without preliminary purification. Sulfuric acid was twice distilled in vacuum. Benzene ("for cryoscopy" grade) was distilled on a rectification column (50 theoretical plates); its purity was checked chromatographically.

Ferric iron was determined spectrophotometrically from the light absorption at a wavelength of 304 mμ. The decrease in ferrous iron was measured by the *o*-phenanthroline method. Phenol was analyzed colorimetrically from the color of the dye formed on coupling with diazotized *p*-nitroaniline ([11]). Carbonyl compounds were analyzed by the method described in ([12]), using a procedure improved for our purposes ([13]). It was assumed that the only carbonyl com-

pound formed both in the radiolysis of the given system and in the radiolysis of aqueous benzene solutions saturated with air is muconic dialdehyde, $C_6H_6O_2$.* The extinction coefficient of the 2,4-dinitrophenylhydrazone of this aldehyde under the condi–

* The formation of muconic dialdehyde in the radiolysis of aqueous aerated benzene solutions has been observed in a number of works ([12,14–16]). In the system investigated by us, the possibility of this substance is confirmed by the identical spectra of the 2,4-dinitrophenyl- and *p*-nitrophenylhydrazones, by the absence of quinones and monoaldehydes of composition C_1-C_6, as was found by paper chromatography ([17]), and by elemental analysis of the 2,4-dinitrophenylhydrazone.

analyses (alkaline medium) at a wavelength of 550 mμ, as we found, is equal to $3.5 \cdot 10^4$. On the basis of this value of the coefficient, the aldehyde concentrations in the irradiated solution were calculated.

In all experiments, 0.4 M sulfuric-acid solutions saturated with air were used. The yields were determined at doses of $\sim 1.5 \cdot 10^{17}$ eV/ml. The dose rate was $\sim 2.5 \cdot 10^{15}$ eV/ml $\cdot$ sec.

Figure 1 shows the dependence of the optical density* of Fe^{3+} ions at 304 mμ on the time after irradiation of the solutions with electrons (exposure was 1 min) at various concentrations of Fe^{2+} ions and at a constant

[Figure 1 and Figure 2 graphs]

Fig. 1. Dependence of the optical density of Fe^{3+} ions at 304 mμ on the time after irradiation (solutions in 0.4 M H_2SO_4, saturated with benzene and air, irradiation with electrons, dose $1.5 \cdot 10^{17}$ eV/ml, dose rate $2.55 \cdot 10^{15}$ eV/ml $\cdot$ sec):
1 –$2.55 \cdot 10^{-4}$ M Fe^{2+},
2 –$5 \cdot 10^{-4}$ M Fe^{2+};
3 –$7.5 \cdot 10^{-4}$ M Fe^{2+};
4 –10^{-3} M Fe^{2+}, and
5 –$2.5 \cdot 10^{-3}$ M Fe^{2+}

Fig. 2. Dependence of the yields of phenol (1) and muconic dialdehyde (2) on the time after irradiation for a $2.5 \cdot 10^{-4}$ M solution of Fe^{2+} in 0.4 M H_2SO_4, saturated with benzene and air (irradiation with electrons, dose $1.47 \cdot 10^{17}$ eV/ml, dose rate $2.44 \cdot 10^{15}$ eV/ml $\cdot$ sec)

benzene concentration (benzene-saturated solution). As can be seen, the process of post-radiation oxidation of ferrous iron, depending on the concentration of Fe^{2+}, lasts from several to 50-70 min. The increase in the optical density of Fe^{3+} ions due to the post-effect is greater, the lower the concentration of Fe^{2+} ions. A similar dependence for post-effects was observed earlier in the case of aqueous solutions of ethyl alcohol containing Fe^{2+} and oxygen ([9]).

Figure 2 presents the dependence of the yields of phenol and muconic dialdehyde on the time after irradiation at constant concentrations of Fe^{2+} ($2.5 \cdot 10^{-4}$ M)

and benzene (10^{-2} M). The influence of the initial concentration of Fe^{2+} ions on the final yields of phenol, muconic dialdehyde, and Fe^{3+} ions is illustrated by Fig. 3, from which it follows that the final yields of all the products studied, at a constant benzene concentration, decrease with increasing Fe^{2+} concentration. Finally, Fig. 4 shows the dependence of the final product yields on the benzene concentration. As can be seen, these yields, at a constant Fe^{2+} concentration, increase with increasing benzene concentration.

From Figs. 2–4 it is seen that the yields of the radiolysis products of this system are characterized by high values. Thus, at Fe^{2+} and benzene concentrations equal, respectively, to $2.5 \cdot 10^{-4}$ and 10^{-2} M, $G(Fe^{3+}) = 65$, $G(C_6H_5OH) = 14$, and $G(C_6H_6O_2) \approx 8$ molecules/100 eV. $G(H_2)$ for the system under consideration is substantially higher than in the case of an aerated solu-

* In these experiments, for convenience, the optical density of the irradiated solutions was measured at 304 mμ. It should be noted that in these solutions, besides Fe^{3+}, some other substance is formed (apparently muconic dialdehyde), which absorbs in the same spectral region. The concentration of Fe^{3+}, measured from the decrease of Fe^{2+} with *o*-phenanthroline, is approximately 10% less than that determined directly from the absorption of light at 304 mμ.

benzene solution. According to our preliminary data, $G(H_2)$ for a solution containing 0.4 M H_2SO_4, $2.5 \cdot 10^{-3}$ M Fe^{2+}, 10^{-2} M C_6H_6, and saturated with air exceeds 2 molecules/100 eV. At the same time, as the Fe^{2+} concentration decreases, $G(H_2)$ increases.

Undoubtedly, such large product yields indicate the occurrence of a chain process. An important role in this process is played by peroxycyclohexadienyl radicals, formed as a result of reactions ([18,19]):

$$C_6H_6 + OH \rightarrow C_6H_6OH, \tag{1}$$

$$C_6H_6OH + O_2 \rightarrow O_2C_6H_6OH. \tag{2}$$

The rate constant of reaction (1), according to ([19]), is $4.3 \cdot 10^9$ l/mol · sec. According to ([20]), $k_{Fe^{2+}+OH}$ is $\sim 3 \cdot 10^8$ l/mol · sec. Therefore, at any of the investigated concentrations of Fe^{2+} and benzene, all OH radicals are consumed in reaction (1). Hence it may be concluded that the observed dependences are explained by competition between C_6H_6 and Fe^{2+} for certain secondary radicals.*

Fig. 3. Dependence of the final yields of Fe^{3+} (1), phenol (2), and muconic dialdehyde (3) for 0.4 M H_2SO_4 saturated with benzene and air on the concentration of Fe^{2+} ions (γ-radiation from Co^{60}, dose $1.5 \cdot 10^{17}$ eV/ml, dose rate $2.5 \cdot 10^{15}$ eV/ml · sec).

Fig. 4. Dependence of the final yields of Fe^{3+} (1), phenol (2), and muconic dialdehyde (3) for a $2.5 \cdot 10^{-4}$ M solution of Fe^{2+} in 0.4 M H_2SO_4, saturated with

air, on the benzene concentration (γ-radiation from Co^{60}, dose $1.5 \cdot 10^{17}$ eV/ml, dose rate $2.5 \cdot 10^{17}$ eV/ml $\cdot$ sec).

Apparently, the radicals $O_2C_6H_6OH$ can both decompose and interact with Fe^{2+} ions:

$$O_2C_6H_6OH \rightarrow HO_2 + C_6H_5OH, \tag{3}$$

$$H^+ + Fe^{2+} + O_2C_6H_6OH \rightarrow Fe^{3+} + HOOC_6H_6OH, \tag{4}$$

$$HOOC_6H_6OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OC_6H_6OH, \tag{5}$$

$$H^+ + Fe^{2+} + OC_6H_6OH \rightarrow H_2O + Fe^{3+} + C_6H_6 + {}^1/_2O_2. \tag{6}$$

Since the yields of the products at constant Fe^{2+} concentration increase with increasing benzene concentration, it may be assumed that reaction (6) is competed with by the reaction:

$$OC_6H_6OH + C_6H_6 \rightarrow C_6H_6OH + C_6H_5OH. \tag{7}$$

* It is interesting to note that addition of Fe^{3+} ions (up to $1.25 \cdot 10^{-3}\,M$) to a $2.5 \cdot 10^{-4}\,M$ solution of ferrous sulfate in $0.4\,M$ H_2SO_4, saturated with benzene and air, has no effect on the product yields. This indicates that the Fe^{3+} ions formed upon irradiation of the system under study do not enter into reverse reactions.

Obviously, Fe^{2+} ions are also oxidized by HO_2 radicals and by hydrogen peroxide,

$$H^+ + Fe^{2+} + HO_2 \rightarrow Fe^{3+} + H_2O_2, \tag{8}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-. \tag{9}$$

According to the scheme presented, chain propagation occurs through reactions (3) and (7).

It is not excluded that, upon irradiation of this system, some other reactions also take place (for example, decomposition of $HOOC_6H_6OH$, decomposition of $O_2C_6H_6OH$ radicals with formation of OH and muconic dialdehyde, recombination of $O_2C_6H_6OH$ radicals, etc.). Obviously, for a final solution of the question of the mechanism, additional experimental material is required (in particular, it is necessary to investigate the effect of dose rate and pH of the medium on

the yields of products, and to study in detail the radiolysis of aqueous aerated benzene solutions in the absence of Fe^{2+}, etc.).

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