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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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STEPWISE PATHWAY OF RADIATION-CHEMICAL PROCESSES OF COMPOUNDS OF AROMATIC NATURE IN AN AQUEOUS MEDIUM

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In the present work we set ourselves the goal of giving a general mechanism for the radiolysis of dilute aqueous solutions of compounds of aromatic nature –thiophene, pyridine, furan, benzene, pyrrole–on the basis of the experimental results obtained and an analysis of certain literature data on the radiolysis of the benzene-water system. In published works on the radiolysis of benzene-water there are serious disagreements concerning the question of the nature and quantity of the products formed ([1–5]). For example, in works ([2,4]) the mechanism of formation of a "dimer" by combination of $\dot{C}_6H_6OD$ and $\dot{C}_6H_6D$ radicals is not in agreement with the data of ([4]), according to which the deuterium content in the COD and CD groups of the "dimer" is respectively 7.4 and 3.8 at. %.

Irradiation of the systems RH_2 (compound of aromatic nature)–water was carried out with γ-rays from Co^{60} at pH 7. The products were analyzed by nephelometry and by ultraviolet and infrared spectroscopy.

Fig. 1. Accumulation of the concentration of α-oxythiophene *(1)* and "dimer-1" *(2)* as a function of absorbed dose at a dose rate of 0.6975 W/kg and a thiophene concentration of $1.27 \cdot 10^{-2}$ M.

The kinetics of accumulation of products in an inert atmosphere can in general be represented as follows. Two products mainly accumulate–oxy products (α-oxythiophene, γ-oxypyridine, and phenol) and "dimers-1" *. For the thiophene-water system this dependence is shown in Fig. 1. In addition to them, molecular hydrogen is evolved. A similar course of the curves is also observed for the other systems. Experimental curves obtained at different dose rates (from 0.176 to 5.19 W/kg) show that formation of "dimer-1" does not occur immediately, but after an induction period, the magnitude of which depends on the dose rate. Evidently, this fact and the influence of the error of the gravimetric method were reflected in the results of earlier published works, in which the induction period was not detected ([1,2–4,8]).

As can be seen from Fig. 1, at the beginning of irradiation a relatively rapid

increase in the concentration of the oxy product is observed, and with a decrease in the rate of formation of the oxy product there occurs an increase in the rate of formation of "dimer-1."This circumstance, as well as the presence of an induction period, indicates that, first, formation of "dimer-1" is not directly connected with transformation of the starting substances; second, "dimers-1" are formed by further radiation-chemical condensation of oxy products. The curves obtained for dilute aqueous solutions of the indicated substances (10^{-2} M) correspond to two consecutive reactions and obey the equation of a first-order chemical reaction.

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* The word "dimer-2" in the present work denotes the resinification products in an oxygen medium, while "dimer-1" denotes the substance precipitating in cases with thiophene and benzene, and the product remaining after removal of α-oxyfuran and γ-oxypyridine in an inert atmosphere.

Taking into account that some dihydrogenated derivatives of benzene readily split off hydrogen ([6,7]), again passing into the benzene system, it may be assumed that, since addition products of the type $\dot{R}H_2OH$ and $\dot{R}H_3$ ([3,4]) exist, the following reactions are probably not excluded when they encounter one another:

$$\dot{R}H_2OH + \dot{R}H_3 \rightarrow 2RH_2 + H_2O,$$

$$\dot{R}H_2OH + \dot{R}H_2OH \rightarrow RH(OH) + RH_2 + H_2O,$$

$$2\dot{R}H_3 \begin{cases} \nearrow & 2RH_2 + H_2, \\ \searrow & RH_2 = RH_2 + H_2 \end{cases}$$

since the aromatic structure, of all hydrogenated and similar systems, has the smallest energy reserve. Since "dimer-1" is formed through an induction period, after formation of the oxy product the following radiation-chemical processes are possible, for example in D_2O

$$\left\{ \begin{array}{c} RH(OD) + D \rightarrow \dot{R}H(OD)D, \\ RH(OD) + OD \rightarrow \dot{R}H(OD)_2, \\ \dot{R}H(OD)D + \dot{R}H(OD)_2 \rightarrow DHO + RD(OD) = RH(OD) \end{array} \right\}.$$

The proposed mechanism for formation of "dimer-1" is consistent with the existence of an induction period, which until now had not been known; with data on the deuterium content in the COD (7.4 at. %) and CD (3.8 at. %) bonds ([4]), and with qualitative data on the products: IR and UV spectra, molecular

weights, etc., which indicate the existence of OH groups and saturated units ([1–5,8]).

A different picture is observed upon irradiation of the system $R\mathrm{H}_2$—O_2—$\mathrm{H}_2\mathrm{O}$. Here the initial products are oxy products (phenol, α-oxythiophene ([9]), γ-oxypyridine ([10]), α-oxyfuran ([9]), etc.) and hydrogen peroxide. The yield of products depends on the concentration of the starting substances; as the content of the latter increases, the G of the oxy products rises. Of interest is the observance of a balance in the radiolysis of the system $R\mathrm{H}_2$ (3.5%)–$\mathrm{H}_2\mathrm{O}$—O_2 (30 atm.), between the G of the oxy products ([9]) and hydrogen peroxide, where $G_{R\mathrm{HOH}} \cong G_{\mathrm{H2O_2}} \cong 2.3\ \frac{\text{molec.}}{100\ \text{eV}}$ (Fig. 2,2), which points to equal beginnings of the reactions taking place:

$$\begin{cases} \mathrm{H} + \mathrm{O}_2 \rightarrow \mathrm{HO}_2, \\ 2\mathrm{HO}_2 \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2, \end{cases}$$

$$\begin{cases} R\mathrm{H}_2 + \mathrm{OH} \rightarrow \dot{R}\mathrm{H}_2\mathrm{OH}, \\ 2\dot{R}\mathrm{H}_2\mathrm{OH} \rightarrow \mathrm{HROH} + R\mathrm{H}_2 + \mathrm{H}_2\mathrm{O}. \end{cases}$$

It should be taken into account that such a balance pertains to the initial period of radiolysis of the system at a dose rate of 1.89 W/kg. Formation of other products is not observed in this interval; for their appearance, either an increase in the amount of dissolved substance or an increase in the absorbed dose is necessary; this is equivalent to what would be caused by an increase in the concentration of the oxy products formed, which, in the radiation zone, interacting with the oxidative or reductive components of water radiolysis, are converted into side products. Such processes, as is known, are secondary reactions. Consequently, with an increase in absorbed energy, various secondary radiation-chemical reactions begin, in which the radiolysis products and such active substances as oxy products (as compared with $R\mathrm{H}_2$) and hydrogen peroxide participate with one another and with each other.

As an example of a sharp decrease in G, the accumulation of the concentration of $\mathrm{H}_2\mathrm{O}_2$ and $G_{\mathrm{H2O_2}}$ is shown as a function of absorbed dose, at a dose rate of 1.89 W/kg for the system thiophene (3.5%)–$\mathrm{H}_2\mathrm{O}$—O_2 (30 atm.) (Fig. 2). The accumulation curve of "dimer-2" (the resinification product) under the same conditions is shown in Fig. 3. Comparison of these curves shows that the drop in $G_{\mathrm{H2O_2}}$

is accompanied by the formation of "dimer-2." However, such a coincidence does not mean that "dimer-2" is a product of the reaction of $\mathrm{H}_2\mathrm{O}_2$ and RH_2.

On the basis of the facts indicated, and also of the established regularities (in particular cases), it has been suggested that the various observed products (for example, in experiments with benzene, the formation of ortho- and para-dioxybenzenes, "dimer-2," quinones, CO_2) are the results of secondary radiation-

Figure 2 graph

Figure 2: Figure 2 graph

Figure 3 graph

Figure 3: Figure 3 graph

chemical transformations, i.e., reactions in which the organic radicals formed, oxyproducts, hydrogen peroxide, and the products of radiolysis of water enter:

$$\begin{cases} \mathrm{HROH} + \mathrm{OH} \rightarrow \dot{\mathrm{H}}\mathrm{R(OH)_2}, \\ 2\dot{\mathrm{H}}\mathrm{R(OH)_2} \rightarrow \mathrm{R(OH)_2} + \mathrm{HROH} + \mathrm{H_2O}, \end{cases}$$

$$2\dot{\mathrm{H}}\mathrm{R(OH)_2} \rightarrow \mathrm{H(OH)R} - \mathrm{O} - -\mathrm{R(OH)H} + \mathrm{H_2O}.$$

The existence of C–O–C bonds has been proved by the infrared spectra of "dimers-2" ; for example, in the case of thiophene, bands at 800-1250 cm^{-1} are present in the infrared spectra. Ideas about the cause of the formation of by-products and quantitative characterization of the mechanisms of these complex radiation-chemical transformations encounter a number of difficulties, since these processes are judged mainly from the final products, and the multitude of final products does not give a clear idea of the sequence of these reactions. For example, the following reactions may also play a role in the formation of dioxyproducts:

Fig. 2. Dependence of the concentration of $\mathrm{H_2O_2}$ (1) and $G_{\mathrm{H_2O_2}}$ (2) on the absorbed dose at a dose rate of 1.897 W/kg

$$\dot{\mathrm{R}}\mathrm{H_2(OH)} + \mathrm{HO_2} \rightarrow \mathrm{R(OH)_2} + \mathrm{H_2O}, \qquad \mathrm{RHOH} + \mathrm{H_2O_2} \rightarrow \mathrm{R(OH)_2} + \mathrm{H_2O},$$

since, besides a number of reasons (oxidation of phenol and α-oxythiophene by hydrogen peroxide to dioxybenzene, dioxythiophene, etc.), this is also supported by the fact that their accumulation occurs nonproportionally to the absorbed dose.

Fig. 3. Dependence of the accumulation of the resinification product on the absorbed dose at a dose rate of 1.8228 W/kg

Many similar hypothetical schemes can also be proposed to explain the causes of the formation of other by-products ($\mathrm{CO_2}$, $\mathrm{SO_2}$, oxyacids, quinones, etc.), but in formulating them it is necessary to take into account that all these products are formed in subsequent reactions in which the primary products participate.

The processes described show that, both in an oxygen medium and in an inert one, in addition to the conditions and the nature of the starting substances, in

all cases the qualitative and quantitative aspects of the radiolysis process of the system are significantly affected by the reactivity of the products formed, even if the concentration of the latter is very low in comparison with the concentration of the starting products. An example is the process of hydrogenation of the oxyproducts formed, whereas the original aromatic nuclei are not hydrogenated. Apparently, these reasons may explain the small magnitude or practical absence of a rectilinear segment in the dependence of the amount of primary products on the absorbed dose during radiolysis of aqueous solutions of certain other organic substances.

The proposed mechanisms are based also on the following experimental facts: a) in an inert medium in the stationary state, G "di-

"measure-1" amounts to half the yield of the oxyproduct (Fig. 1); b) in an inert medium, the established value of the concentration of oxyproducts depends almost not at all on the dose rate for a given content of the starting substance and is reached the sooner, the higher the dose rate; c) in an oxygen medium, under optimal conditions, a balance is reached between the oxidizing and reducing products of water radiolysis. A similar comparable balance is maintained at elevated temperatures and pressure, where a chain process proceeds, and the yield of oxyproducts amounts to half of all the other reaction products[11].

As can be seen, the primary radiation-chemical transformations are divided into two directions (fronts) and proceed stepwise. In an inert medium, along with the formation of oxyproducts, there is a parallel process of accumulation of molecular hydrogen, while in the presence of oxygen the reactions develop in the directions of formation of hydrogen peroxide and oxyproducts.

An analysis of works on the radiolysis of dilute aqueous solutions of organic substances shows that the frontal-stepwise pathway of transformations is valid also in other cases, both for primary and for secondary processes.

In our opinion, the existence of a frontal-stepwise mechanism in the radiolysis of aqueous solutions of organic substances is connected with the fact that, first, the complete reaction of oxidation or reduction of one molecule of an organic substance in one act of interaction, in most cases, requires an even number of oxidizing and reducing equivalents, whereas the products of water radiolysis have one equivalent each (H, OH, HO_2); second, in radiation oxidation-reduction transformations there occur odd-electron transitions, the confirmation of which is the formation of radical products detected by various indirect and direct methods; third, the parent substance reacts mainly either with the oxidizing or with the reducing components of water radiolysis, i.e., the interaction of molecules proceeds selectively, according to their mutual affinities, in parallel in two or more directions, thereby creating the frontality of the process.

The appearance of radicals during the oxidation of phenols has recently received experimental proof by various methods[12], including the ESR method. The radicals in these cases were obtained by oxidation of phenols in various solvents, including water.

The idea of the present work concerning the role of secondary processes also finds its proof in the above-mentioned ESR data, in which it was found that after a certain time the primary radicals are replaced by secondary ones, and that even for a number of phenols it was not possible at all to detect primary radicals, while the spectra recorded at the moment of radical formation correspond to the spectra of secondary radicals.

For the practical application of the indicated results it should be taken into account that the formation of oxyproducts has also been observed in the radiolysis of aqueous solutions and emulsions of other aromatic systems (benzothiophene, benzofuran, quinoline, acridine, and the like).

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CITED LITERATURE

1. G. Stein, J. Weiss, J. Chem. Soc., 1949, 3245.
2. E. V. Barelko, M. A. Proskurnin, *Collection of Works on Radiation Chemistry*. Publishing House of the Academy of Sciences of the USSR, 1955, p. 99.
3. M. Matsui, Sci. Papers Inst. Phys. Chem. Res., 53, 82 ((1959).
4. L. I. Kartasheva et al., DAN, 136, No. 1, 143 (1961).
5. M. A. Bertolaccini-Manzitti et al., Energia nucl., 8, No. 7, 445 (1961).
6. Baeyer, Lieb. Ann., 258, 1 (1890).
7. Baeyer, Lieb. Ann., 269, 145 (1892).
8. S. A. Safarov et al., DAN, 140, No. 6, 1345 (1961).
9. S. A. Safarov, M. A. Proskurnin, Dokl. AN AzSSR, 17, No. 10, 887 (1961).
10. S. A. Safarov, *Kinetics and Catalysis*, 3, No. 3, 449 (1962).
11. M. A. Proskurnin et al., *Problems of Physical Chemistry*, vol. 2, Moscow, 1959, p. 177.
12. N. M. Emanuel, Yu. N. Lyaskovskaya, *Inhibition of the Oxidation Processes of Fats*, Moscow, 1961.

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