Soviet-era science, translated into English

L. I. Kartasheva, Z. S. Bulanovskaya, E. V. Barelko,

Ya. M. Varshavsky, and M. A. Proskurnin

1961

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196101.82864

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Physical Chemistry

L. I. Kartasheva, Z. S. Bulanovskaya, E. V. Barelko,
Ya. M. Varshavsky, and M. A. Proskurnin

Investigation of the Radiation Oxidation of Benzene in Aqueous Solution by the Tracer-Atom Method

(Presented by Academician V. A. Kargin, July 16, 1960)

The available experimental data ($^{1-4}$) indicate that the primary action of radiation in the radiation oxidation of benzene in aqueous solution is the absorption of radiation by water molecules. Such an "indirect" action of radiation on benzene may be either the result of the direct action on benzene molecules of active particles—radicals and excited molecules—formed during the radiolysis of water and diffusing in the solution until they encounter molecules of the dissolved substance, or a consequence of the transfer of excitation energy to the benzene molecule by migration of the corresponding energy quanta through the water.

There is reason to believe that in the benzene-water system both mechanisms of such "indirect" action are manifested. In favor of the first mechanism are the composition of some isolated products, the possibility of an effect of molecular oxygen on the yield (at low temperatures), and also a noticeable, though not very strong, effect of temperature on the yield (^{5}). In favor of the second mechanism is the formation of muconic aldehyde in the presence of oxygen (^{6,7}).

The possibility of a mechanism involving the addition of hydrogen atoms and hydroxyl radicals, formed during the radiolysis of water, to benzene molecules (and also to chlorobenzene) was indicated in studies (^{2,8}) devoted to the radiolysis of aqueous solutions of these substances, as well as in a recently published work (^{9}).

As shown by the study of the water-insoluble substance formed, along with phenol, during irradiation of the benzene-water system in vacuum, its composition corresponds to the gross formula $C_{12}H_{14[16]?}O_2$, and the infrared spectrum of this substance indicates the presence in it of aliphatic and aromatic C=H bonds, as well as OH bonds (^{9}). Thus, the precipitate contains oxyhydrodiphenyls and possibly dioxydiphenyls. It follows from this that the primary products in the radiolysis of benzene in aqueous solution are not phenyl radicals formed as a result of hydrogen abstraction from the benzene ring according to the schemes

$$C_6H_6 + OH^\bullet \rightarrow C_6H_5^\bullet + H_2O$$

or

$$C_6H_6 + H^\bullet \rightarrow C_6H_5^\bullet + H_2,$$

which underlie the currently accepted scheme of Stein and Weiss (^{12}), but rather radicals that are products of the addition of $OH^\bullet$ and $H^\bullet$ radicals to benzene molecules, i.e. $C_6H_7^\bullet$ and $C_6H_6OH^\bullet$, whose recombination leads to the formation of molecules of the water-insoluble substance under investigation.

New possibilities for investigating the mechanism of formation of the product of benzene oxidation and for testing the indicated assumptions are opened by the stu-

study of the radiolysis of benzene in the presence of heavy water (D_2O, to which the present work is devoted. The idea of the experiments is as follows. If the addition mechanism is valid for both $H^\bullet$ and $OH^\bullet$ radicals, then in the substance formed deuterium should be contained not only in the OH groups (the hydrogen atoms of which freely exchange with water molecules), but also in the $C-H$ bonds, in which hydrogen isotope exchange, in the absence of irradiation, as is known, does not occur (^{10}). By treating the precipitate obtained in the radiolysis of benzene in the presence of heavy water with a solvent containing a hydroxyl group of normal isotopic composition with respect to hydrogen, i.e., by “washing out”deuterium from the OH groups of the precipitate and determining its content after treatment, one can establish the amount of deuterium introduced into the CH bonds of the reaction product and, by difference, determine the deuterium content in the OH bonds. The ratio between the deuterium concentrations in the OH and CH bonds can characterize the ratio of the probabilities of addition, respectively, of $OH^\bullet$ and $H^\bullet$ radicals to the ring in the realization of the addition mechanism postulated above. On the other hand, if in the course of the reaction a phenyl radical is formed in the system, then deuterobenzene should also be formed, as a result of recombination of the phenyl radical with hydrogen atoms. Therefore, by measuring the deuterium content in the unreacted benzene, one can directly judge the possibility of realization of the Stein and Weiss scheme.

Method

Irradiation of the benzene—heavy-water mixture was carried out using a γ-radiation source Co^{60} with a dose rate of 170 r/sec; the irradiation time was 250 h; the deuterium concentration in the water was 26.7 at. %. Before use, the benzene and water were carefully purified. The volume of the irradiated aqueous phase with benzene dissolved in it was 95 ml, and the volume of the benzene layer above the aqueous phase was 15 ml. The experiments were carried out in glass ampoules. Before irradiation, the solution was thoroughly degassed in vacuum by repeated freezing and thawing. The white product formed, together with phenol, in the aqueous phase during irradiation was separated from the bulk of the solution by prolonged centrifugation according to the procedure described previously (2). After drying in a vacuum desiccator, the isolated substance (1.0-1.2 g) was divided into three portions. The first portion was used to determine the deuterium content without any chemical treatment; the second portion was weighed and subjected to repeated (14 times, in 5-mm portions) dissolution in alcohol followed by evaporation, in order to "wash out" deuterium from the O — H groups by isotopic exchange with the alcohol. The completeness of the "washing out" was verified by the absence of changes in the deuterium content upon further washing. The substance remaining after distillation of the alcohol was weighed, and the concentration of deuterium remaining in it (in CH bonds) was determined. The third portion was repeatedly treated with an aqueous solution of soda, after which it was washed with water. Such treatment of the reaction product was intended to ensure removal of small amounts of phenol that could have been adsorbed on the precipitate (the bulk of the phenol remains in the aqueous solution). In addition, in this case, as with the second portion, "washing out" of deuterium from OH groups took place. The powder obtained after such treatment was weighed, and the content of deuterium remaining in it was determined.

Along with investigation of the insoluble product, the deuterium content in the unreacted benzene was also determined. To determine the deuterium content, the substance was burned in an excess of oxygen over copper oxide; the water obtained was purified, and its isotopic analysis was carried out by the drop method (11). Each sample was analyzed three times, and the average result was taken. The accuracy of determining the deuterium concentration was 0.02 at. %.

Results and Discussion

The results of the experiments are presented in Table 1. The data obtained show that the insoluble product of the radiation oxidation of benzene formed together with phenol in the presence of heavy water contains

Table 1

Results of experiments on the radiolysis of benzene in the presence of heavy water

Substance	Deuterium content, at. %	Weight of substance, g before treatment	Weight of substance, g after treatment
Solid product, isolated directly from the irradiated mixture	11.2	1.1585	–

Substance	Deuterium content, at. %	Weight of substance, g before treatment	Weight of substance, g after treatment
Solid product treated with alcohol*	3.8	0.3762	0.3766
Solid product treated with sodium carbonate solution	3.8	0.3941	0.405
Benzene**, isolated from the irradiated mixture	0.0	–	–

* After an additional sixfold treatment of part of this sample, the deuterium concentration in it remained 3.8 at. %.
** Before combustion, the benzene was dried and purified.

deuterium both in OH groups and in the C—H bonds of the aromatic rings. After repeated treatment of the product with alcohol (with subsequent evaporation), leading to complete "washing out" of deuterium from the OH groups, the concentration of deuterium in the product falls, as is evident from Table 1, by approximately a factor of three. It follows from this that the ratio between the amounts of deuterium in OH and CH bonds is approximately $\sim 2:1$.

The absence of deuterium in the benzene remaining in the irradiated mixture indicates, above all, that under the conditions of the experiment and, in particular, at the radiation doses used, isotopic exchange between benzene and water does not occur directly. Consequently, deuterium atoms cannot be incorporated into the aromatic C—H bonds of the benzene oxidation product directly as a result of isotopic exchange between benzene and water with subsequent conversion of deuteriobenzene. The presence of deuterium in the aromatic C—H bonds of the reaction product can be explained by the addition of deuterium atoms, formed as a result of the radiolysis of water, to benzene molecules and by the subsequent conversion of deuteroradicals $C_6H_6D^\bullet$. The presence of hydroxyl groups in the reaction product is a consequence of an analogous process of addition of $OD^\bullet$ radicals to benzene molecules, with the formation of radicals $C_6H_6OD^\bullet$, which, like the radicals $C_6H_6D^\bullet$, participate in further transformations leading ultimately to the formation of phenol and an insoluble precipitate.

The absence of deuterium in benzene indicates that, under the experimental conditions, formation of a phenyl radical does not occur, since such a radical would inevitably have had to recombine with the deuterium atoms present in the system, forming deuteriobenzene.

The data obtained in this work unambiguously confirm the mechanism according to which (2) the products of the radiation oxidation of benzene in aqueous solution arise as a result of recombination of the radicals $C_6H_7^\bullet$ and $C_6H_6OH^\bullet$, formed by the addition of hydrogen atoms and OH radicals to benzene molecules. Moreover, the result obtained in this work

the ratio of the deuterium concentrations in the $O = H$- and C—H-bonds of the product, equal to approximately $2 : 1$, indicates that the C_6H_6OD radicals are formed about twice as often as the C_6H_6D radicals, which, in turn, may be explained by the easier formation of hydrogen molecules from atoms in comparison with the formation of hydrogen peroxide molecules from OH radicals.

Physicochemical Institute
named after L. Ya. Karpov

Received
11 VII 1960

REFERENCES CITED

1. M. A. Proskurnin, E. V. Barelko, Collection of Works on Radiation Chemistry, Publishing House of the Academy of Sciences of the USSR, 1955, p. 99.
2. E. V. Barelko, L. I. Kartasheva, M. A. Proskurnin, DAN, **116**, 74 (1957).
3. I. Stein, J. Weiss, J. Chem. Soc., 1949, 3245.
4. P. Phulla, M. Burton, Radiation Res., **1**, 199 (1957).
5. E. V. Barelko, L. I. Kartasheva, P. D. Novikov, M. A. Proskurnin, Proceedings of the First All-Union Conference on Radiation Chemistry, Publishing House of the Academy of Sciences of the USSR, 1958, p. 89.
6. M. A. Proskurnin, Ya. M. Kolotyrkin, Proceedings of the Second Conference on the Peaceful Uses of Atomic Energy, 1958, p. 211.
7. I. Loeff, G. Stein, Nature, **19**, 901 (1959).
8. N. P. Krushinskaya, M. A. Proskurnin, ZhFKh, **33**, 1954 (1959).
9. Masao Matsui, Sci. Papers Inst. Phys. Chem. Res., **53**, 82 (1959).
10. A. I. Brodsky, Chemistry of Isotopes, Publishing House of the Academy of Sciences of the USSR, 2nd ed., 1958.
11. A. I. Shatenshtein, Ya. M. Varshavsky, ZhAKh, **11**, 746 (1956).

SovietRxiv

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.