WATER AS A SENSITIZER OF THE RADIATION INITIATION OF THE BENZENE OXIDATION PROCESS

1958

SovietRxiv

Abstract

Full Text

Physical Chemistry

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WATER AS A SENSITIZER OF THE RADIATION INITIATION OF THE BENZENE OXIDATION PROCESS

(Presented by Academician V. N. Kondrat' ev, 15 III 1958)

The production of phenol by direct oxidation of benzene is one of the important problems to which a number of works have been devoted ([1–3]). The authors of the present communication have previously investigated the radiolytic oxidation of benzene to phenol in aqueous solution; moreover, at room temperature the catalytic influence of iron ions on this radiation-chemical reaction was discovered ([4]). When the experimental temperature was raised, autocatalytic acceleration of the reaction was observed, which argued in favor of the development of a chain mechanism of oxidation ([5]). Radiation initiation of branched chain processes has also been used, as is known, in the oxidation of saturated hydrocarbons ([6,7]).

The present communication is devoted to the oxidation of benzene in the aqueous phase, discovered by the authors, by a branched-chain mechanism and, in particular, to the study of the role of water as a sensitizer of the process of radiation initiation.

Co^{60}, with an activity of approximately 1400 g-equiv. of radium, was used as the radiation source. The experiments were carried out in an autoclave made of stainless steel of grade 1Kh18N9T, equipped with a special furnace for heating and a manometer for measuring pressure.

The average dose rate, determined in a glass vessel of the same geometric shape as the irradiation ampoule, was 140 r/sec. Calibration of the source was carried out by the ferrous sulfate method; the oxidation yield of divalent iron ions was taken to be 15.6 molecules per 100 eV. The ratio of the volumes of water and benzene in the autoclave was 32 : 1. Purified benzene and twice-distilled water were used for the experiments. All experiments were carried out at an initial oxygen pressure of 10 atm, in the temperature range 20-220°. Analysis for phenol was carried out by extracting the reaction mixture with benzene, which was then treated with a soda solution (1 N). Phenol was determined in the soda solution by ultraviolet absorption at $\lambda = 286$ mμ. The content of resinous products was determined by distilling the water-benzene mixture in vacuum and weighing the nonvolatile polymeric product remaining in the vessel.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Figure 1 gives curves for the dependence of phenol concentration on irradiation dose at different temperatures. For comparison, an analogous curve for the oxidation of benzene in the absence of water is given (curve 1). It can be seen that in aqueous solution, already at a temperature of 165°, the reaction has a clearly pronounced autocatalytic character. In parallel with the formation of phenol in the liquid phase, the formation of resins is observed (Fig. 2). The kinetics of formation of resin-like oxidation products is identical in character to the kinetics of phenol formation; in particular, the maxima of concentration on the concentration–dose curves are obtained in both cases simultaneously (Fig. 1, 5, 7; Fig. 2, 2, 3). Phenolic derivatives and polyphenyls were found in the composition of these products.

Another proof that the reaction under study is a branched chain process, in which radiation can be used as the initiating agent, is the kinetic curve for phenol formation in the case when irradiation was stopped 2 hours after the beginning of the experiment, while the reaction continued, accelerating by itself (Fig. 3)*. To the 8 molecules of phenol formed during the irradiation period per 100 eV of energy, 26 molecules are added during the aftereffect, and the total yield of phenol at a temperature of 190° is 15-20 times greater than the yield of phenol in the radiation oxidation of benzene in aqueous solution at room temperature (8).

Fig. 1. Dependence of the phenol yield on the radiation dose at different temperatures (dose rate 140 r/sec.). 1 –oxidation of pure benzene at $t = 165°$; 2-9 –oxidation of benzene in aqueous solution: 2 –at $t = 20°$, 3 –at 100°, 4 –at 115°, 5 –at 135°, 6 –at 165°, 7 –at 190°, 8 –at 200°, 9 –at 220°

At the same time, in the absence of water at temperatures up to 220°, under analogous irradiation conditions, it is not possible to observe a transition to a self-accelerating course of the reaction. The question of the reason for such an influence of water on radiation initiation appears to us fundamental for understanding oxidation processes. This reason, in our opinion, lies chiefly in the different radiation resistance of benzene and water. The yield of free radicals from benzene at room temperature, according to the data of Shapiro (9) and Weber (10), is 0.5-0.7 per 100 eV. Under the same conditions the yield from the decomposition of water is 3.66 molecules per 100 eV (11), which is equivalent to the formation of 7-8 H and OH radicals. Thus,

Fig. 2. Dependence of the yield of resin-like reaction products on the radiation dose. 1 –at $t = 135°$, 2 –at 165°, 3 –at 200°

Fig. 3

Figure 3: Fig. 3

Fig. 3. Aftereffect of irradiation

* An analogous course of the kinetic curve of the aftereffect was observed for resin formation.

one may consider that the number of free radicals and atoms formed under the action of radiation and ultimately responsible for the initiation of the chain process is, in the case of water, an order of magnitude greater.

We believe that the use, as sensitizers of the radiation initiation of branched chain processes, of substances that are chemically inert but radiation-unstable—of which water is a particular case—may have very broad significance. It should be noted, however, that in the present case the role of water need not be limited only to its influence on the initiation process. The presence of water may also affect the subsequent steps of the chain process. Thus, for example, the thermal decomposition of hydrogen peroxide formed during irradiation of water may be one of the elementary steps of pronounced branching. We have succeeded in inducing oxidation of benzene by introducing hydrogen peroxide into an aqueous solution and heating the mixture.

Scientific Research Physicochemical Institute
named after L. Ya. Karpov

Received
12 III 1958

CITED LITERATURE

1. I. I. Ioffe, Ya. S. Levin et al., *ZhFKh*, **28**, 1386 (1954).
2. H. Frank. Über die katalytische Oxidation von Benzol zu Phenol, Doctoral dissertation, Zurich, 1955.
3. N. M. Emanuel, E. M. Denisov, *DAN*, **117**, No. 3, 458 (1957).
4. M. A. Proskurnin, E. V. Barelko, Collection of papers on radiation chemistry, 1955, p. 99.
5. E. V. Barelko, L. I. Kartasheva, P. D. Novikov, M. A. Proskurnin, Collection of reports at the First All-Union Conference on Radiation Chemistry, 1957 (in press).
6. M. A. Proskurnin, Yu. L. Khmel' nitskii et al., *DAN*, **112**, No. 5, 886 (1957).

7. N. M. Emanuel, *DAN*, **111**, 6, 1286 (1956).
8. G. Stein, J. Weiss, *J. Chem. Soc.*, 1949, 3245.
9. L. Bouby, A. Shapiro, *J. Chem. Phys.*, **52**, 645 (1955).
10. E. Weber, P. Forsyth, R. Schuler, *Rad. Res.*, **3**, 68 (1955).
11. C. Hochanadel, G. Ghormley, *J. Chem. Soc.*, **21**, 880 (1953).

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