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Abstract

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ON THE PRINCIPAL POSSIBILITY OF THE LIQUID-PHASE OXIDATION OF BENZENE TO PHENOL

(Presented by Academician N. N. Semenov, 15 V 1957)

Recently one of us (^{1}) raised the question of the expediency of transferring a number of high-temperature gas-phase oxidation processes to regimes of low-temperature liquid-phase oxidation, using the principle of gas initiation to stimulate the reaction.

The effectiveness of this proposal was illustrated by the example of the oxidation of *n*-butane in the liquefied state at temperatures close to the critical temperature. There exist, however, many other processes in which the deep destructive oxidation characteristic of high-temperature reactions in the gas phase is the principal obstacle to obtaining valuable oxygen-containing products by direct oxidation. Among such processes, undoubtedly, is the reaction of oxidation of benzene to phenol. Benzene is one of the hydrocarbons most difficult to oxidize. The resistance of benzene to oxidation by molecular oxygen is associated above all with the great strength of the C—H bonds in the molecule of this hydrocarbon (102 kcal/mole). Oxidation in the gas phase proceeds at an appreciable rate only at temperatures of 600-700°. At the same time, along with the formation of small amounts of phenol, resins and very large amounts of products of deep combustion—CO, CO_2, and water—are obtained (^{2}, ^{3}).

A similar situation was also encountered in the oxidation of *n*-butane in the gas phase. To carry out the process, a temperature of about 400° was required, at which deep, useless combustion of the hydrocarbon was also observed. The situation changed substantially when the oxidation reaction of liquefied butane was carried out. In this case the process developed already at 130-150°, with the formation exclusively of products of "mild" oxidation—acetic acid and methyl ethyl ketone.

It could be hoped that an attempt to carry out the oxidation of benzene in the liquid phase at temperatures close to the critical temperature would likewise lead

Fig. 1

Figure 1: Fig. 1

to positive results. Since for benzene $t_{\text{cr}} = 288°$, $p_{\text{cr}} = 48$ atm., we attempted to register the oxidation of benzene at temperatures of 230–270° and at a pressure of 50 atm.

The experiments were carried out in an autoclave apparatus for the oxidation of hydrocarbons in the liquid phase under pressure. In each experiment, 200 ml of benzene was charged into the reactor. Oxidation was carried out with oxygen from a nitrogen-oxygen mixture of composition 1 : 1, at a rate of passage of 20 l/hr. During the course of the process, samples of the oxidized benzene were withdrawn and analyzed for phenol content. With the aid of a photocolorimeter, the optical density of the oxidized benzene was also measured; this characterized the accumulation of resins.

The experiments showed that at 250° the oxidation of benzene in the liquid phase proceeds at an appreciable rate. As a result of the oxidation, phenol and resins are formed. The kinetic curve of phenol accumulation has an S-shaped cha-

character. However, the maximum concentration of phenol in this process is small and amounts to only 0.16 mol.%. The kinetic curve for the accumulation of phenol in this experiment is shown in Fig. 1 (curve 3).

An experiment with cobalt stearate, taken as a catalyst, led to an unexpected result. It is known that this catalyst accelerates the oxidation of many hydrocarbons. However, the oxidation of benzene with cobalt stearate at 250° showed that in this case this catalyst directs the reaction toward condensation of benzene with the formation of soot, while phenol is formed in a small amount. The maximum concentration of phenol during oxidation in the presence of cobalt stearate is 0.11 mol.%, i.e., less than in the uncatalyzed oxidation (Fig. 1, curve 1).

Experiments on the oxidation of benzene in the presence of small amounts of such readily oxidizable substances as cyclohexane and cyclohexanone showed their accelerating effect on the oxidation of benzene. These processes are a coupled oxidation of two substances, in which the readily oxidized substance induces the oxidation of benzene. Fig. 2 shows the kinetic curves for the formation of phenol and adipic acid during the oxidation of benzene with the addition of 1 mol.% cyclohexanone. In this case a much higher maximum phenol concentration is attained, amounting to 0.5 mol.%. The course of the kinetic curves for the formation of adipic acid and phenol is practically parallel, and inhibition of the formation of both products occurs simultaneously.

Fig. 1. Oxidation of benzene at 250° in the presence of 0.15 mol.% St_2Co and 2% cyclohexane. 1 –kinetic curve for the accumulation of phenol; 2 –change in

optical density; 3 —kinetic curve for the accumulation of phenol in an experiment without catalyst at 250°

It is interesting to note that the "dying out" of this process is connected not with consumption of the inducer additive (by the end of the reaction 0.3 mol.% unreacted cyclohexanone remains), but with self-inhibition of the reaction by the products of benzene oxidation. The best yields of phenol were obtained in experiments with gas initiation of the process by nitrogen dioxide. In these experiments, before entering the reactor, air enriched with oxygen was passed through a trap with liquid nitrogen dioxide, where it became saturated with NO_2. The NO_2 content was 2 vol.%.

Fig. 3 shows the kinetic curves for the accumulation of phenol in oxidizing benzene in an experiment without initiation at 250° (curve 3) and in experiments with initiation at different temperatures (curves 1 and 2). It is evident from the figure that the use of gas initiation makes it possible to accelerate the formation of phenol and to increase its maximum concentration from 0.16 to 0.8% at 250° and to 1.1% at 267°. Along with phenol, formation of nitrobenzene was observed in the experiments with gas initiation.

The experimental data obtained on the oxidation of benzene indicate that the process is a chain, distinctly branched (4), self-inhibiting reaction. The kinetic data agree well with the following mechanism. Chain initiation in the reaction is effected as a result of the action of the initiator at a rate w_0, and as a result of pronounced branching at the intermediate product P at a rate $k_3[P]$. Chain termination occurs as a result of recombination of free radicals at a rate $k_4 n^2$. By the method of stationary concentrations, the total concentration of free radicals is equal to

$$n = \sqrt{\frac{w_0 + k_3[P]}{k_4}}.$$

Let the intermediate product be converted by a chain pathway into the final product K. The final product, reacting with radicals, leads to the replacement of part of the active radicals by less active ones, capable of reacting with the intermediate product but not interacting with the initial hydrocarbon. Analysis of such a scheme gives the following differential equations (in dimensionless variables) for the rates of accumulation of the intermediate and final products:

$$\frac{d\pi}{d\tau} = \frac{\omega_0 + \pi}{\sqrt{\omega_0 + \pi + \alpha\xi}} - \pi\sqrt{\omega_0 + \pi}$$

$$\frac{d\xi}{d\tau} = \pi\sqrt{\omega_0 + \pi},$$

where

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

$$\pi = \frac{[\mathrm{P}]}{p_{\max}}; \quad p_{\max} = \frac{k_1[\mathrm{RH}]}{k_2}; \quad \xi = \frac{[\mathrm{K}]}{p_{\max}};$$

$$\omega_0 = \frac{w_0}{k_3 p_{\max}}; \quad \tau = k_2\sqrt{\frac{k_3 p_{\max}}{k_4}}\, t; \quad \alpha = \frac{k_5 p_{\max}}{k_4}$$

k_1 is the rate constant of the reaction of active radicals with the hydrocarbon; k_2 is the rate constant of the reaction of radicals with the intermediate product; k_5 is the rate constant of active radicals with the final product.

Fig. 2. Kinetic curves for the accumulation of phenol (1), the formation of dicarboxylic acids from cyclohexanone (2), and the change in the optical density of the reacting mixture (3) during oxidation of benzene with an addition of 1 mol.% cyclohexanone at 250°.

Fig. 3. Kinetic curves for the accumulation of phenol in experiments on the oxidation of benzene under continuous gas initiation by nitrogen dioxide at different temperatures: 1 –267°; 2 –250°; 3 –kinetic curve for the accumulation of phenol at 250° in an experiment without initiation.

The term

$$\frac{\omega_0 + \pi}{\sqrt{\omega_0 + \pi + \alpha\xi}}$$

in the first equation characterizes the rate of formation of the intermediate product as a result of the reaction of active radicals with the hydrocarbon. It is evident that, in the course of the reaction, as the concentration of the final product increases, this rate decreases. The term $\pi\sqrt{\omega_0 + \pi}$ characterizes the consumption of the intermediate product. It is evident that the maximum concentration of the intermediate product is the greater, the greater the rate of chain initiation ω_0. If $w_0 \gg k_3[\mathrm{P}]$ and, consequently, $\omega_0 \gg \pi$, so that $\sqrt{\omega_0 + \pi} \approx \sqrt{\omega_0}$, then

$$\pi_{\max} = \frac{\sqrt{\omega_0}}{\sqrt{\omega_0 + \alpha\xi}}.$$

Such a qualitative dependence was also obtained by us in experiments with gas initiation, the use of which makes it possible to increase severalfold the maximum concentration of phenol in the reaction. The kinetic curves π, constructed by graphical integration of the system of two differential equations obtained by us, have an S-shaped form with a clearly expressed maximum.

It is precisely this form that the kinetic curves for the accumulation of phenol have in our experiments.

Thus, as a result of the present study, the fundamental possibility has been demonstrated of oxidizing benzene to phenol in the liquid phase at temperatures close to the critical temperature, using the principle of gas-phase initiation, which gives the best results. At the same time, the prospects for further research become clear—it is necessary to find ways of eliminating the effects of self-inhibition of the process.

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