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Abstract

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COUPLED DECARBOXYLATION DURING THE AUTOOXIDATION OF ISOPROPYLBENZENE IN A MIXTURE WITH FATTY ACIDS

It was shown earlier by us ([1,2]) that low-temperature autooxidation of resin acids is accompanied by coupled decarboxylation of these acids. In this connection, it was of interest to determine whether coupled decarboxylation of carboxylic acids is possible in a mixture with a hydrocarbon undergoing autooxidation. Experiments carried out for this purpose showed that the autooxidation of isopropylbenzene in a mixture with acetic, butyric, isobutyric, and stearic acids is indeed accompanied by coupled decarboxylation of the added acids. Thus, in the case of autooxidation of mixtures of hydrocarbons with carboxylic acids, in accordance with the terminology introduced by N. A. Shilov ([3]), oxidation of the hydrocarbon induces the coupled process of decarboxylation of the acid.

Since autooxidation of hydrocarbons, especially at higher temperatures, can lead to the formation of acids which, in the course of further autooxidation, are capable of undergoing coupled decarboxylation, establishing this phenomenon is of definite interest for understanding the chemistry of hydrocarbon oxidation in general.

It should be noted that spontaneous decarboxylation of fatty acids occurs only at considerably higher temperatures than the coupled decarboxylation discovered by us.

Thus, Hurd ([4]) indicates that acetic acid does not decompose below the temperature of dark-red heat. According to Bamford and Dewar ([5]), acetic acid vapors decompose at a measurable rate above 500°. Sanderson and Abulenk ([6]) found that butyric, isobutyric, propionic, and isovaleric acids are stable up to a temperature of 460°. In the presence of animal charcoal, noticeable decomposition of these acids begins at 330–340°. According to Korshak and Rogozhin ([7]), spontaneous decarboxylation of most dibasic acids, which decarboxylate more readily than monobasic acids, occurs only above 200°.

Before the experiments, isopropylbenzene (technical grade, produced by the Voikov Chemical Plant) was distilled four times over metallic sodium on a column with glass packing, after which it had the following constants: b.p. 149–

Fig. 1

Figure 1: Fig. 1

151.0°; d_4^{20} 0.860; n_D^{20} 1.4917. Acetic acid (chemically pure, Kharkov Chemical Reagents Plant) was additionally purified by freezing out (^{8}). Butyric, isobutyric, and stearic acids (“pure”) were distilled at atmospheric pressure for purification. Radioactive acetic acid (C^{14} in the carboxyl, obtained through Soyuzreaktivsb) had an activity of 1 mCu/ml. In the experiments, acetic acid diluted with ordinary acid 100.9 times was used. Thus, the activity of the acetic acid used directly was 0.0099 mCu/ml. Cobalt acetate, used as the autooxidation initiator (“pure,” Krasny Khimik plant), was not subjected to additional purification. According to analysis, it contained 4 molecules of water of crystallization.

The rate of autoxidation of mixtures of isopropylbenzene with acids was studied by the previously described method in a static system $^{(9)}$ at a temperature of 80.5°. The content of CO_2 in the gas phase above the reaction products was determined by purging the system with a stream of oxygen and trapping the carbon dioxide formed in barium water. In addition, the composition of the gas phase above the oxidation products was analyzed with a VTI apparatus.

The presence of radioactive CO_2 in the gaseous oxidation products was determined by absorbing it in barium water and measuring the radioactivity of the barium carbonate precipitate on a type B apparatus. Fig. 1 shows the course

Fig. 1. Kinetic curves of the oxidation of isopropylbenzene with additions of fatty acids. Temperature 80.5°; initiator—cobalt acetate ($2.1 \cdot 10^{-3}$ mole per mole of isopropylbenzene); 1—pure isopropylbenzene, 2—32.8 mol.% acetic acid, 3—9.0 mol.% stearic acid, 4—31.4 mol.% butyric acid, 5—31.1 mol.% isobutyric acid

of oxygen absorption as a function of time in experiments with isopropylbenzene without an additive and with additions of acetic, butyric, isobutyric, and stearic acids. The amount of added acids ranged from 9.0 to 32.8 mol.%. The amount of cobalt acetate was $2.1 \cdot 10^{-3}$ mole per mole of isopropylbenzene. As is seen from Fig. 1, in the presence of acids the rate of autoxidation of isopropylbenzene increases by approximately the same number of times (the amount of oxygen absorbed in 5 hours in the presence of any of the acids studied is more than 4 times greater than in the absence of acid). In all experiments the initial rate was the greatest and decreased as oxidation proceeded.

To determine the influence of acid concentration on the rate of oxidation of isopropylbenzene, experiments were carried out with various concentrations of isobutyric acid; the results are given in Table 1.

The data in Table 1 show that, while the addition of 1.04 mol.% isobutyric acid (see experiment 2) causes an increase in the rate of autoxidation—

Fig. 2

Figure 2: Fig. 2

Table 1

Effect of the concentration of isobutyric acid on the rate of autoxidation of isopropylbenzene
(amount of isopropylbenzene in the experiments 14.3×10^{-3} *mole; cobalt acetate* -0.9×10^{-3} *mole per mole of isopropylbenzene)*

Experiment No.	Added isobutyric acid (mol.%)	Absorbed O_2 (in moles per 360 min.)	CO_2 formed (in moles per mole of oxygen)	Experiment No.	Added isobutyric acid (mol.%)	Absorbed O_2 (in moles per 360 min.)	CO_2 formed (in moles per mole of oxygen)
1	–	0.078	0.0080	4	3.76	0.272	0.0185
2	1.04	0.364	0.0119	5	7.00	0.346	0.0242
3	1.51	0.337	0.0125	6	27.34	0.344	0.0759

of isopropylbenzene oxidation by more than 4 times in comparison with the experiment without isobutyric acid; a further increase in the amount of acid added (to 27.34 mol.%) practically does not change the amount of oxygen absorbed).

At the same time, increasing the concentration of isobutyric acid in the mixture leads to a considerable increase in the amount of carbon dioxide formed. As is seen from Table 1, and also from Fig. 2, increasing the isobutyric acid content from 1 to 27 mol.% leads to an increase in carbon dioxide formation by more than 6 times (with the amount of oxygen absorbed remaining practically unchanged).

Fig. 2. Dependence of the amount of carbon dioxide evolved during the oxidation of isopropylbenzene with additions of isobutyric acid on the concentration of the latter in the mixture. Temperature 80.5°; initiator—cobalt acetate ($0.9 \cdot 10^{-3}$ mole per mole of isopropylbenzene)

The results of experiments on the oxidation of isopropylbenzene in a mixture with radioactive acetic acid (labeled in the carboxyl) confirm that the carbon dioxide evolved is formed (at least in part) from the carboxyl group of the added acid. Indeed, as Fig. 3 shows, the radioactivity of the barium carbonate precipitate formed as a result of absorption of CO_2 increases with increasing acetic acid content in the mixture, and the observed dependence is close to linear. Experiments on the oxidation of acetic, butyric, isobutyric, and stearic acids, carried out under analogous conditions (80.5°, addition of $0.9 \cdot 10^{-3}$ mole

Fig. 3

Figure 3: Fig. 3

of cobalt acetate), but in the absence of isopropylbenzene, showed that in the case of acetic and butyric acids neither absorption of oxygen nor formation of carbon dioxide occurs.

Fig. 3. Change in the radioactivity of the $BaCO_3$ precipitate as a function of the content of $CH_3C^{14}OOH$ in the mixture with isopropylbenzene. Temperature 80.5°; initiator—cobalt acetate ($0.9 \cdot 10^{-3}$ mole per mole of isopropylbenzene)

A small amount of carbon dioxide evolved in experiments on the autoxidation of pure isobutyric and stearic acids apparently represents a process coupled with the autoxidation of these acids. To explain the coupled process of decarboxylation of organic acids during the simultaneous autoxidation of hydrocarbons, the following scheme may be proposed.

1. Formation of the isopropylbenzene hydroperoxide radical:

$$C_6H_5{-}\underset{\text{I}}{C^\bullet}(CH_3)_2 + O_2 \rightarrow C_6H_5{-}C(\underset{\text{II}}{CH_3})_2{-}OO^\bullet$$

2. Interaction of the isopropylbenzene hydroperoxide radical (II) with an organic acid, with formation of the acid radical (V):

$$\underset{\text{II}}{C_6H_5{-}C(CH_3)_2{-}OO^\bullet} + \underset{\text{III}}{R{-}COOH} \longrightarrow \underset{\text{IV}}{C_6H_5{-}C(CH_3)_2{-}OOH} + \underset{\text{V}}{R{-}COO^\bullet}$$

3. Decarboxylation proper:

$$\underset{\text{V}}{R{-}COO^\bullet} \rightarrow \underset{\text{VI}}{R^\bullet} + CO_2.$$

4. Abstraction of a hydrogen atom from isopropylbenzene at the tertiary group as a result of interaction with the formed radical $R^\bullet$:

$$R^\bullet + C_6H_5{-}CH(CH_3)_2 \rightarrow RH + \underset{\text{I}}{C_6H_5{-}C^\bullet(CH_3)_2}$$

This reaction leads to regeneration of the initial radical (I) and thereby ensures continuation of the principal chain process. It is, of course, also necessary to take into account the possibility of oxidation of the radical $R^\bullet$ with formation of a hydroperoxide radical:

$$R^\bullet + O_2 \rightarrow R{-}OO^\bullet,$$

which then reacts with a molecule of isopropylbenzene, likewise regenerating the initial radicals (I)

$$R{-}OO^{\bullet} + C_6H_5{-}CH(CH_3)_2 \rightarrow R{-}OOH + \underset{\text{I}}{C_6H_5{-}C^{\bullet}(CH_3)_2}$$

Thus, according to the scheme presented, reactions 2–4 are, in essence, chain-transfer reactions and therefore should not exert either an inhibiting or an accelerating effect on the course of the entire chain process. In fact, however, small additions of acid cause an increase in the oxidation rate; a further increase in the amount of added acid does not noticeably affect the rate of autoxidation.

The absence of a dependence of the autoxidation rate on the acid concentration in the region of 1–27 mole % of the latter is a fact confirming the indicated scheme. The increase in the autoxidation rate at small acid additions indicates the existence also of other pathways by which the acid influences the reaction rate.

Thus it has been shown that, during autoxidation of mixtures of isopropylbenzene with fatty acids, oxidation of the hydrocarbon induces the decarboxylation process, coupled with it, of the added acids.

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