processes then equalize. The rate of formation of β-alanine units subsequently begins to exceed the rate of radical polymerization, and then consumption of acrylamide is only due to nucleophilic addition with larger angles of rotation.

The polymer chains are destroyed in the second and especially in the third stages with large deformations (angles of rotation greater than 30°); condensation reactions accompanied by liberation of water take place to a marked degree. The water in turn participates in hydrolysis reactions, accompanied by splitting of peptide bonds and liberation of free β-alanine.

The results obtained illustrate the variety of chemical processes that can occur with mechanical loads on the substances, particularly on polymeric materials. We should emphasize that chemical reactions which were previously difficult to predict can occur in these conditions. The important role of water has been revealed in many different reactions; it very actively participates in hydrolysis reactions stimulated by conditions combining the effect of mechanical stresses and shear deformations.

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COMPOSITION OF PRODUCTS AND MECHANISM OF THE REACTION OF OZONE WITH 2,6-DI(*tert*-BUTYL)-4-METHYLPHENOL

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It was shown that two series of products with opening and with preservation of the aromatic nucleus are formed in the reaction of ozone with ionol, and a mechanism was proposed for the reaction.

Keywords: *ozone, phenols, 2,6-di(*tert*-butyl)-4-methylphenol.*

The reaction of ozone with phenol results in the formation of a set of products, of which more than 60% are the result of rearrangement of the initial complex and incorporation of ozone into the aromatic nucleus in the immediate vicinity of a phenol hydroxy group [1]. It was interesting to determine how the reaction takes place when the phenol has bulky substituents in positions 2, 4, and 6. The composition of products of the reaction of ozone with 2,6-di(*tert*-butyl)-4-methylphenol was investigated in the present study for this purpose.

EXPERIMENTAL

Chemically pure 2,6-di(*tert*-butyl)-4-methylphenol with a concentration of basic substance greater than 99% was used. Ozone was synthesized by passing O_2 through an electric discharge zone at a rate of 100 ml/min. The concentration of O_3 was measured spectrometrically. $[O_3]_0 = 1 \cdot 10^{-3}\text{-}1 \cdot 10^{-5}\ M$.

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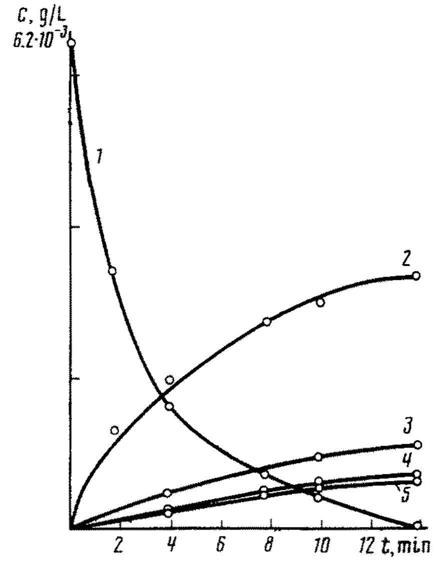


Fig. 1. Kinetics of consumption of ionol and formation of basic products of the reaction: 1) ionol; 2) **6**; 3) **8**; 4) **10**; 5) **11**.

The reaction of O_3 with ionol was conducted in a bubbling reactor at −100°C. The stoichiometric reaction coefficient was determined with the method in [2]. For determination of the composition of the products of the reaction, 1 g of ionol was dissolved in 100 ml of pentane, ozonized, and evaporated. The remaining dark oil was separated in a chromatographic column (silica gel μ 40/100, solvent: CCl_4:$CHCl_3$:C_3H_6O gradient). The yield of products from the column was monitored by TLC. The nature of the individual substances was established with the IR and PMR spectra and by chromatography−mass spectrometry. The kinetics of accumulation of products was investigated by GLC on a Tsvet 100 chromatograph, 2 m column, Chromosorb W, SE-30 phase, 3% helium, 175°C. The low-molecular-weight products were analyzed in a 1.5 m column, HMDS phase, helium, 50°C.

After separation of the products of the reaction, compounds **6**, **8**, **10**, and **11** were isolated and identified.

4-Methyl-6-*tert*-butyl-1,2-quinone (10). Yield of 8%. IR spectrum (ν, cm^{-1}): 1670 (C=O), 1600 (C=C). PMR spectrum (δ, ppm): 1.17 s ($C(CH_3)_3$); 1.21 s (CH_3); 4.7 s (C=CH); 6.2 (−CH=C).

6-Oxo-5-hydroxy-2,7,7-trimethyl-4-*tert*-butyl-2,4-octadienoic Acid (6). Yield of 50%. IR spectrum (ν, cm^{-1}): 1730 (C=O); 1690 (C=O); 3400-3500, 3550 (OH). PMR spectrum (δ, ppm): 1.5 s (CH_3); 1.12, 1.17 s ($C(CH_3)_3$); 3.8 s (C−OMe); 4.7 s (C=CH−).

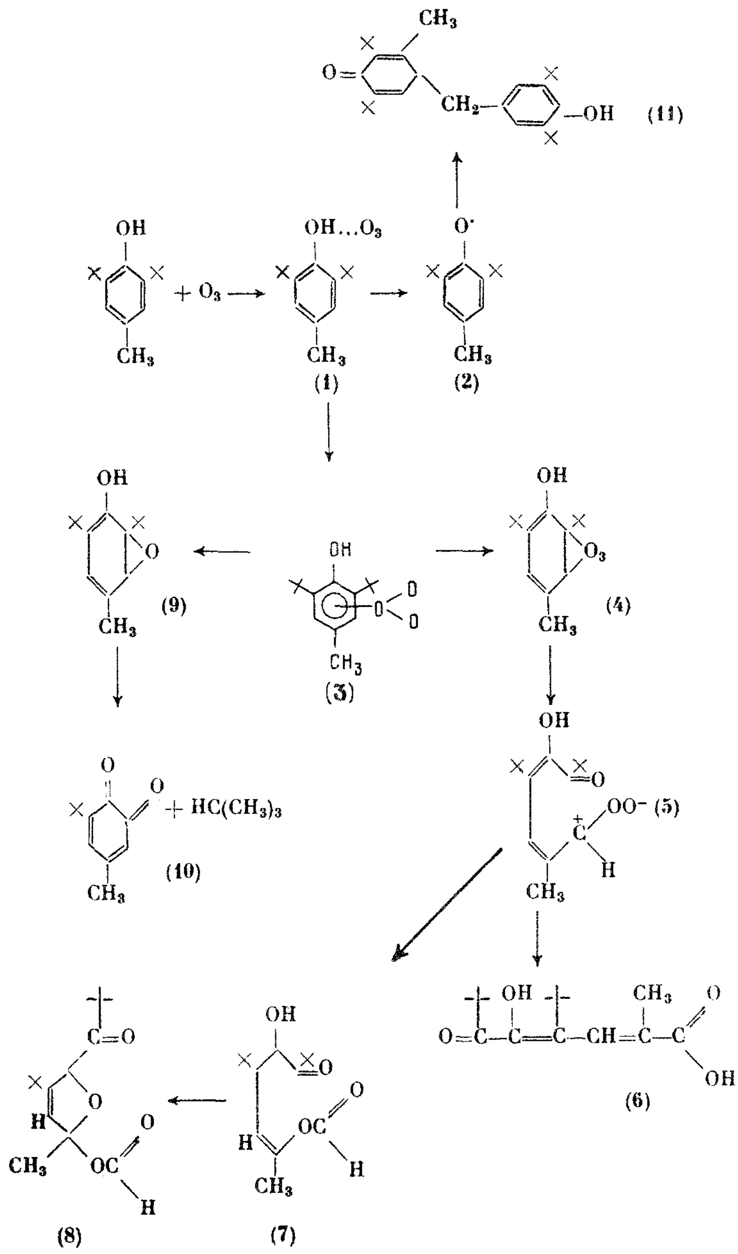
4-(4′-Hydroxybenzyl)-2,6-di(*tert*-butyl)-4-methyl-2,5-cyclohexadien-1-one (11). Yield of 17%. IR spectrum (ν, cm^{-1}): 1670 (C=O); 3400 (OH); 1600, 1490 (C=C). PMR spectrum (δ, ppm): 1.2 s (CH_3); 1.12 s (18 H, $C(CH_3)_3$); 3.8 s ($-CH_2-$); 7.8 s (OH); 7.2 s (2H(CH arom); 4.9 s (C=CH−); 4.7 s (C=C−).

5-Trimethylacetyl-4-*tert*-butyl-2-methyl-2-formylhydroxy-2,5-dihydrofuran (8). Yield of 15%. IR spectrum (ν, cm^{-1}): 1700 (C=O); 1780 (C=O); 1250 (C−O−C). PMR spectrum (δ, ppm): 1.12, 1.17 s ($C(CH_3)_3$); 1.7 s (CH_3); 7.6 s (OCHO); 4.7 s (C=CH); 6.2 s (C−CH).

DISCUSSION OF THE RESULTS

As demonstrated in [3], ionol reacts with ozone at −100°C much more rapidly than the products of the reaction, and after absorption of 1 mole of ozone per 1 mole of ionol, the reaction almost stops. According to the GLC data, in the early stages of the reaction, all products accumulate parallel in the system, beginning with low degrees of conversion of ionol (Fig. 1).

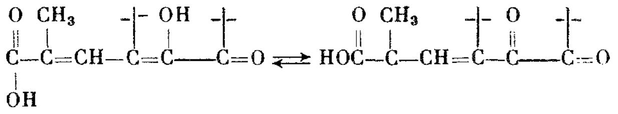
Interpretation of the structure of the compounds formed showed that two series of products of the reaction are present in the reaction mixture: with opening of the aromatic nucleus (corresponding to incorporation of ozone in the *meta* position with respect to the hydroxy group) and with its preservation (scheme).



Despite the large number of products of the reaction, its mechanism fits within the scheme of the reaction of ozone with phenol in [1], with several important differences: addition of ozone in positions 2, 4, and 6 does not take place, probably due to steric hindrances, and most of the products of the reaction are formed because of incorporation of ozone in positions 3 and 5. We note that these positions are the least active in unsubstituted phenol.

Formation of complex **1** is the first stage of the reaction [3]; it decomposes into phenoxyl radical **2** or is isomerized into **3**. The probable structure of **3** and its ability to be isomerized and decomposed was examined in detail in [1]. Complex **3** can be converted into primary ozonide **4** or decomposed with formation of **9** and O_2.

Formation of primary ozonide **4**, which is isomerized with rupture of the ring and formation of a bipolar ion and keto group **5** at the terminal carbon atoms at the site of the rupture, is the most probable direction of the reaction. As demonstrated in [4], the bipolar ion is easily isomerized into an acid with formation of 6-oxo-5-hydroxy-2,7,7-trimethyl-4-*tert*-butyl-2,4-octadienic acid (**6**). This compound can be considered key, since it constitutes approximately 50%. We predicted that **6** exists in two tautomeric forms:

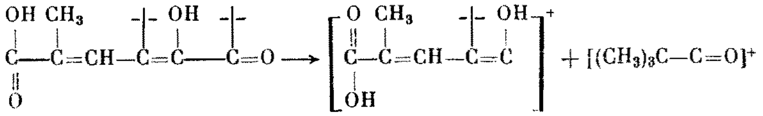


$$\underset{OH}{\overset{O}{C}}-\overset{CH_3}{C}=CH-\overset{-|-}{C}=\overset{OH}{C}-\overset{-|-}{C}=O \rightleftarrows HO\overset{O}{C}-\overset{CH_3}{C}-CH=\overset{-|-}{C}-\overset{O}{C}-\overset{-|-}{C}=O$$

(6a) **(6b)**

However, judging by the characteristics obtained, the equilibrium is shifted toward enol, which is probably stabilized by electronegative terminal groups and the steric hindrances of neighboring *tert*-butyl substituents.

All of the spectral data support structure **6a**: the UV spectra contain an absorption band with $\lambda = 235$ nm, indicative of the presence of a conjugation system, and the IR spectra contain an absorption band in the 3400-3500 cm^{-1} region with a narrow shoulder at 3550 cm^{-1} corresponding to a free hydroxyl group. The mass spectra exhibit fragmented ions, which is in good agreement with the most probable paths of decomposition of **6a** on electron impact (70 eV) [5].



$$\underset{\underset{O}{\|}}{\overset{OH}{\overset{|}{C}}}-\overset{CH_3}{\overset{|}{C}}=CH-\overset{-|-}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}-\overset{-|-}{\overset{|}{C}}=O \longrightarrow \left[\underset{\overset{|}{OH}}{\overset{O}{\overset{\|}{C}}}-\overset{CH_3}{\overset{|}{C}}=CH-\overset{-|-}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}\right]^{+} + [(CH_3)_3C-C=O]^{+}$$

(6a) m/z 85

One argument in support of structure **6a** is that 2 moles of ozone are consumed per mole of **6** in the reaction of ozone with **6** at 20°C (the reaction subsequently takes place much more slowly), which confirms the presence of two double bonds.

In contrast to **6**, compound **7** easily passes into tautomeric cyclic form **8**.

We previously showed that phenoxyl radicals are formed in the system in the reaction of ozone with 2,6-di(*tert*-butyl)-4-methylphenol [6]. The yield is insignificant, ~5%. Dimerization of phenoxyl radicals results in the formation of 4-(4′-hydroxybenzyl)-2,6-di(*tert*-butyl)-4-methyl-2,5-cyclohexadien-1-one (**11**).

In addition to the products listed above, 4-methyl-6-*tert*-butyl-1,2-quinone (**10**) was also detected in the reaction mixture. There are several possible paths of its formation. First, a radical path in which the phenoxyl radical **2** reacts with O_2, forming quinolide peroxide, which subsequently decomposes into two molecules of **10**. In this case, 2,6-di(*tert*-butyl)-1,4-quinone, isobutane, and isobutylene should be formed in the system together with **10** [7]. In our case, 2,6-di(*tert*-butyl)-1,4-quinone and isobutylene were not detected in the reaction mixture. Of the low-molecular-weight products, only isobutane was found. These data did not support the radical path of formation of **10**. 4-Methyl-6-*tert*-butyl-1,2-quinone can also be formed in decomposition of complex **3** into O_2 and **9** with subsequent isomerization of **9** into **10**. Reactions of this type are known for olefins [8] and aromatic hydrocarbons. Compound **9** is unstable due to perturbation of aromatic conjugation and is rapidly isomerized. 2,3-Epoxy-2,3-dihydroionol **9** could not be recorded in the reaction mixture probably for this reason, and only products of isomerization and decomposition of **9** were detected: isobutane and 4-methyl-6-*tert*-butyl-1,2-quinone. The above suggests that **10** is probably formed by the path **1—3—9—10**.

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