KINETICS AND MECHANISM OF THE REACTION OF OZONE WITH 3,6-DI-*tert*-BUTYLPYROCATECHOL

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*The reaction of ozone with 3,6-di-*tert*-butylpyrocatechol at ~20°C was investigated, and it was found that the main reaction product was 3,6-di-*tert*-butylquinone, while the reaction rate was proportional to the concentrations of the reagents. A reaction scheme explaining the mechanism of formation of the main and side products is proposed.*

Keywords: *Ozone, 3,6-di-*tert*-butylpyrocatechol.*

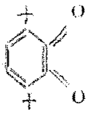
The reaction of ozone with phenols has been the subject of a series of investigations [1-3], directed mainly at the search for optimum methods of breaking down the phenols present in natural and waste water. The reaction products include dihydroxybenzenes, dicarboxylic acids, and quinones, with the latter at impurity levels [3].

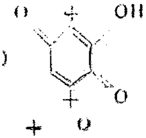
The mechanisms of the possible transformations of dihydroxybenzenes and quinones during the breakdown of phenols have been studied little, and reaction schemes involving their participation have been discussed at the hypothetical level. However, it is this stage in the degradation of phenols by the action of ozone that is the most important.

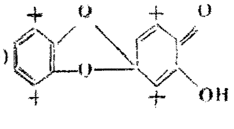
We found that the reaction of ozone with 3,6-di-*tert*-butylpyrocatechol is accompanied by the formation of 3,6-di-*tert*-butylquinone with a high yield. Below we give the results from an investigation of the composition of the products, the kinetics, and the mechanism of the reaction.

EXPERIMENTAL

In the experiments we used 3,6-di-*tert*-butylpyrocatechol (**1**) and its isopropylidene ether (**5**), synthesized by the methods in [4] and [5] respectively. The ozone was obtained by passing oxygen through an electric discharge. The O_3 concentration was measured by spectrometry at $\lambda = 254$ nm, $[O_3]_0 = (1\text{-}5) \cdot 10^{-3}$ *M*. The rate constants for the reaction of O_3 with compounds **1** and **5** were determined by the method in [6], and the stoichiometric coefficient of the reaction was determined according to [7]. The kinetics of the formation of the products were studied in a bubble-type reactor ($V_{sol} = 15$ ml, chloroform, $[1]_0 = 0.227$ g). As the reaction proceeded we took samples and analyzed them on a liquid chromatograph (eluant C_6H_{14}:i-C_3H_7OH, Separon SGXNH$_2$ column). At the end of the reaction the solvent was evaporated, and the reaction products were separated on a column (silica gel μ 40/100, gradient elution, $CDCl_3$:$CHCl_3$). The emergence of the products from the column was monitored by TLC. During separation of the products the following substances were isolated and identified by comparison with standard samples on a liquid chromatograph:

(2)  Yield 85 wt. %, mp 197°C [8]

(3)  Yield 5 wt. %, mp 84°C [9]

(4)  Yield 10 wt. %, mp 253°C [10].

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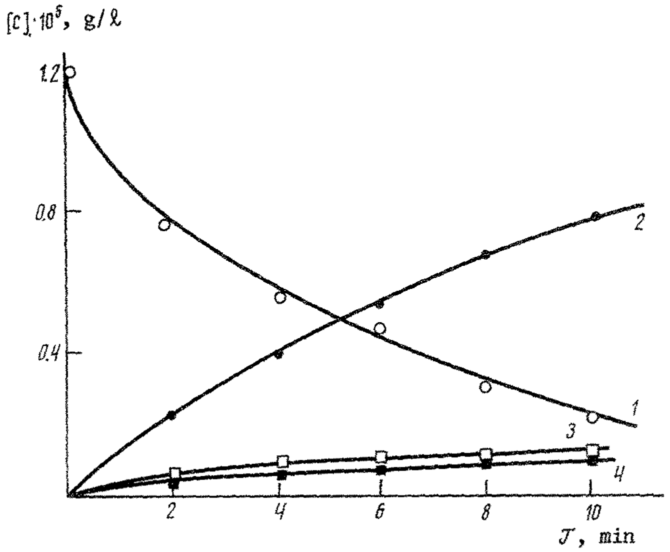


Fig. 1. Kinetics of the consumption of 3,6-di-*tert*-butylpyrocatechol and formation of the main reaction product: 1) 3,6-di -*tert*-butylpyrocatechol; 2) 3,6-di-*tert*-butyl-1,2-quinone; 3) 2-hydroxy-3,6-di-*tert*-butyl-1,4-quinone; 4) 3,6-di-*tert*-butyl-5-hydroxy-3,6-di-*tert*-butyl-p-benzophenone 1,2-phenylene acetal.

DISCUSSION OF RESULTS

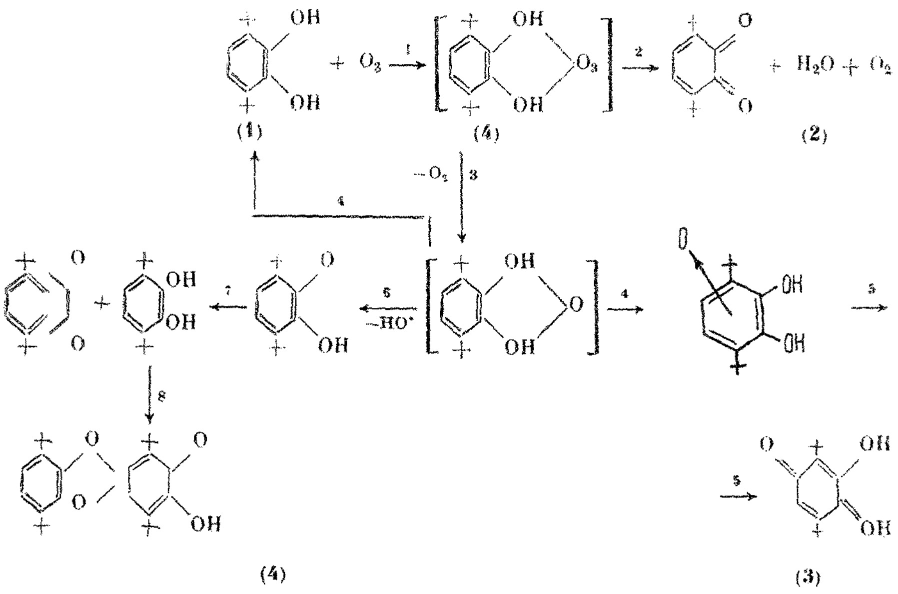
Investigation of the composition of the products from the reaction of O_3 with 3,6-di-*tert*-butylpyrocatechol showed that right up to complete disappearance of compound 1 the main reaction product was 3,6-di-*tert*-butylquinone (2) (Fig. 1). The stoichiometric coefficient of the reaction was 1:1. It should be mentioned that according to the data from various authors the stoichiometric coefficient for the reaction of ozone with phenol is appreciably higher and fluctuates in the range of about 3-4 [7].

The dependence of the reaction rate W_r on the concentration of O_3 and of compound 1 was studied (Fig. 2). It was found that the reaction is described by a bimolecular law $W_r = k_1[O_3][1]$, where $k_1 = 3 \cdot 10^2$ liter/mole·sec. Constancy in the obtained k_1 values is closely observed both with variation in the initial concentrations of the reagents and during the consumption of compound 1.

The observations given above make it possible to reach the following conclusions. First, the reaction of compound 1 takes place without involving the products in secondary interactions with the initial reagents, as observed in the case of phenol. Second, in contrast to phenol, the composition of the products indicates that ozone is not inserted into the aromatic ring.

In view of the foregoing it is possible to propose a reaction scheme that explains the mechanism of formation of the main and side reaction products.

Scheme 1



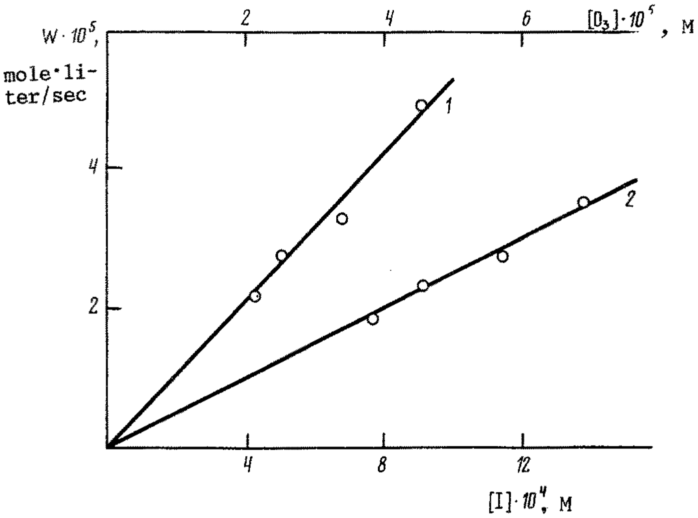
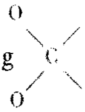


Fig. 2. Dependence of the initial reaction rate W_r on: 1) the concentration of 3,6-di-*tert*-butylpyrocatechol, $[O_3]_0 = 5.5 \cdot 10^5$ *M*; 2) the concentration of ozone, $[1]_0 = 4.7 \cdot 10^{-4}$ *M* at 20°C, solvent chloroform.

In Scheme 1 it is assumed that the first stage of the reaction is the formation of the intermediate complex **6**, and by analogy with phenols the hydroxy groups and not the aromatic ring participate in the formation of the complex [1]. This is favored by the reduction of more than two orders of magnitude in the reaction rate during combination of the OH groups into the ether grouping  . Complex **6** then dissociates in three different ways: 1–2 and 1–3–6–7 lead to similar reaction products and are kinetically indistinguishable. The predominant contribution of one or the other of them in the balance of transformations is probably more conveniently judged from the effect of the reaction conditions on the composition of the products. In particular, if n-C_6H_{14} is used as medium for the reaction it could be expected that the hydroxy radical would react preferentially with C_6H_{14}, forming alkyl and alkylperoxy radicals (in the presence of O_2). Here hexyl alcohols, hexanones, quinolide peroxides, and other products from destruction of the radicals should be formed in the system [11]. Accordingly, the yield of compound **2** would be reduced. The absence of an effect from the nature of the solvent on the composition of the reaction products makes it possible to consider that the contribution from the 1–3–6–7 path to the reaction is small.

An additional experiment was set up with the addition of isopropyl alcohol to the system (10% in relation to the solvent), since it is known that isopropyl alcohol is a good trap for OH˙ radicals [12]. However, even additions of isopropyl alcohol did not lead to appreciable changes in the composition or relative yields of the products. The search for traces of acetone in the reaction mixture, formed in the reaction of isopropyl alcohol with HO˙ radical, did not give a positive result. All these observations indicate that the reaction takes place predominantly by the 1–2 path.

The compound **3**, present in the mixture in relatively small amounts, is evidently formed as a result of dissociation of the O_3 combined into a complex, into an oxygen atom and molecule, followed by migration of the atom to the aromatic system, the formation of an unstable oxide, and subsequent isomerization (1–3–4–5).

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