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SYNTHESIS AND REACTIONS OF QUINOLIDE PEROXIDES UNDER ACID-CATALYSIS CONDITIONS

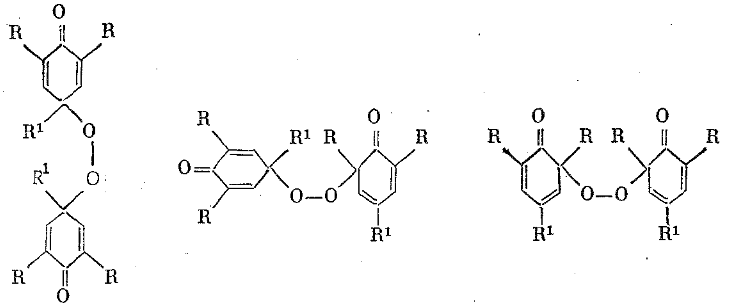
I. A. Batanov, G. A. Nikiforov,
and V. V. Ershov

UDC 542.943.7:547.56:541.459

Quinolide type peroxides are usually formed as intermediate compounds during inhibited oxidation of polymers and other organic materials if sterically hindered phenols and their derivatives are used for the inhibition. The chemical reactions of these peroxides, in particular the paths of their decomposition, can appreciably affect the character of the oxidation of the organic substrate.

The aim of the present work was to study the influence of the nature and the volume of para-substituents in 4-R^1-2,6-di-tert-butylphenols on the isomeric composition and mechanism of conversion under acid-catalysis conditions of quinolide peroxides formed in oxidation of the above phenols. The peroxides were obtained by the reaction between oxygen and the corresponding phenoxyl radicals, formed in the oxidation of 4-R'-2,6-di-tert-butylphenols by $K_3Fe(CN)_6$ in an alkaline medium. Three isomeric quinolide peroxides can be formed. The yields and the isomeric composition of the peroxides isolated are listed in Table 1.

The predominance of one or other isomer in the reaction mixture is determined by the nature and volume of the substituent at the 4-position of the initial phenol. As we have already shown [1], in the case of 2,4,6-tri-tertbutylphenol a mixture is formed consisting of two isomers (Ia) and (Ib) in a 3:1 ratio. Isomers of this type are also formed during the oxidation of 4-phenyl-2,6-di-tert-butylphenol, but isomer (IVb) predominates in the mixture (a:b=1:3). With decrease in the volume of R^1 (i-Pr and OMe), only the para-para isomers (IIa) and (IIIa) are formed. The introduction of an electronegative substituent (Bz) at the 4-position of the phenol gives the ortho-ortho isomer (Vc).



para-para (a) ortho-para (b) ortho-ortho (c) R = *t*-Bu.

The overall yield of the peroxides varies over wide limits and depends on their thermal stability and the possibility of competing reactions leading to the disappearance of the initial phenoxyl radicals. In general, structures (b) and (c) are less stable and decompose in the course of the reaction and during isolation of pro-

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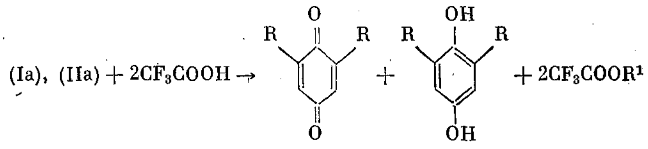
Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 359-364, February, 1982. Original article submitted June 23, 1981.

TABLE 1

Peroxide	R^1	Overall yield of peroxides, %	Relative yield of isomers, %		
			a	b	c
(I)	*t*-Bu	95	75	25	–
(II)	*i*-Pr	20	100	–	–
(III)	OMe	25	100	–	–
(IV)	Ph	87	25	75	–
(V)	Bz	8	–	–	100

ducts, with the formation of substituted 1,2- and 1,4-benzoquinones. It is this property of the above isomers which explains the low overall yield of peroxides (III) and (V). The overall yield of peroxides (IV) is high (87%), but in the course of chromatographic separation, isomer (IVb) decomposes, and only isomer (a) can be isolated in pure state. Due to the presence of an isopropyl group at the 4-position of phenol, the phenoxyl radical formed mainly disappears in a disproportionation reaction. Therefore, the yield of the peroxide is not higher than 20-25%.

The more stable para-para isomers of peroxides (Ia), (IIa), and (IIIa) were selected as models for studying the kinetics and the mechanism of decomposition of the quinolide peroxides by the action of acids. In these cases, simple mixtures are formed as the result of the reaction, which can easily be analyzed by spectral methods. Peroxides (Ia) and (IIa) in CCl_4 containing CF_3COOH convert quantitatively in the course of 15 min at room temperature into a mixture of 2,6-di-tert-butylhydroquinone (VII) and 2,6-di-tertbutyl-1,4-benzoquinone (VI) in a ratio of 1:1.* Besides the above compounds, tert-butyl or isopropyl trifluoroacetates were isolated from the reaction mixture. Alkaline titration of the reaction mixtures showed that 2 moles of these esters are formed from 1 mole of the peroxide. The overall process of acid decomposition of peroxides (Ia) and (IIa) can be thus represented by the following equation:



(VI) (VII)

Peroxide (IIIa) decomposes more readily and unequivocally under the action of acids. In this case, only quinone (VI) is formed in a quantitative yield as the end product. The reaction proceeds fairly vigorously, even during weak acidification of aqueous-alcoholic solutions of the peroxide by mineral acids (H_2SO_4, HCl).

To establish the mechanism of decomposition of the quinolide peroxide by the action of acids, we studied the kinetics of conversion of peroxide (IIIa) in 50% methanol in the presence of 0.1 N H_2SO_4, and of peroxide (Ia) in a CCl_4 solution in the presence of CF_3COOH. Figure 1 shows the kinetics of consumption of peroxide (IIIa) and accumulation of quinone (VI), and also the semilogarithmic anamorphosis of the kinetic curve in $\log [(D - D_0)/(D_\infty - D_0)]$ vs t coordinates, where D is current optical density; D_0 is optical density of initial peroxide at $t = 0$; D_∞ is final optical density of quinone at wavelength of 252 nm. It can be seen that stable isobestic points are retained in the spectra of the reaction mixture up to the end of the reaction. This indicates that only two absorbing components are present in the reaction mixture, each of which passes into another. The kinetic curves become satisfactorily rectified in the above coordinates up to high degrees of conversion of peroxide (IIIa). From the slopes of the lines, effective rate constants (k_{ef}) were obtained at different contents of 0.1 N H_2SO_4 in the reaction mixture. The dependence of k_{ef} on the acid concentration is linear (Fig. 2).

From the chemical data and analysis of the kinetics of decomposition of peroxide (IIIa) by the action of acids, the mechanism for this process on the following page can be suggested.

According to kinetic data, the limiting stage of the process is clearly the formation of complex (VIII), which decomposes into a semiacetal of quinone (IX) and cation (X). In the presence of an acid, the former converts into quinone (VI) with splitting of CH_3OH, and the latter becomes stabilized with elimination of CH_3O^+. Thus, k_1, k_2, and $k_3 \gg K$, and $K[H_2SO_4] \approx k_{ef}$.

A more complex pattern is observed in the decomposition of peroxide (Ia) in CCl_4 solution by the action of CF_3COOH. In CCl_4 solution, where CF_3COOH is practically undissociated, the reaction proceeds at appreciable rates only in the presence of larger amounts of the acid. Therefore, the course of the reaction can be

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*Similar results were obtained in [2] in the study of the action of CF_3COOH on peroxide (Ia).

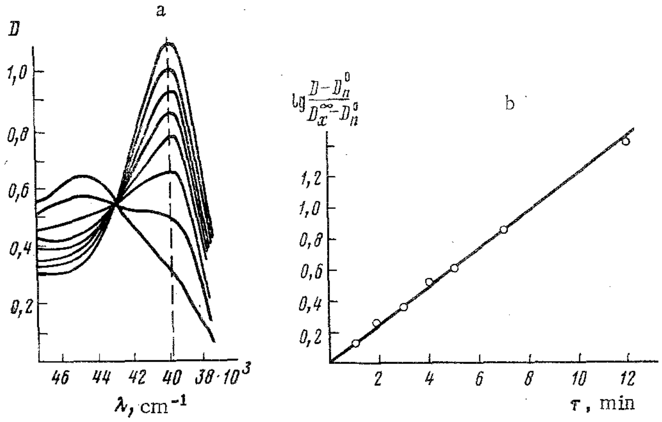


Fig. 1. Kinetics of consumption of peroxide (IIIa) and accumulation of quinone (VI) (a), and rectification of kinetic curve in log $[(D - D_0)/(D_\infty - D_0)]$ vs t coordinates (b) ($[IIIa] = 2.8 \cdot 10^{-5}$, $[H_2SO_4] = 0.5 \cdot 10^{-3}$ mole/liter).

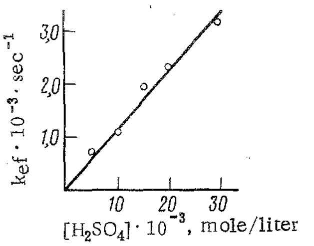


Fig. 2

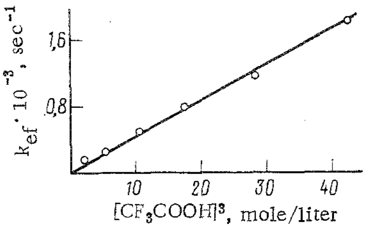
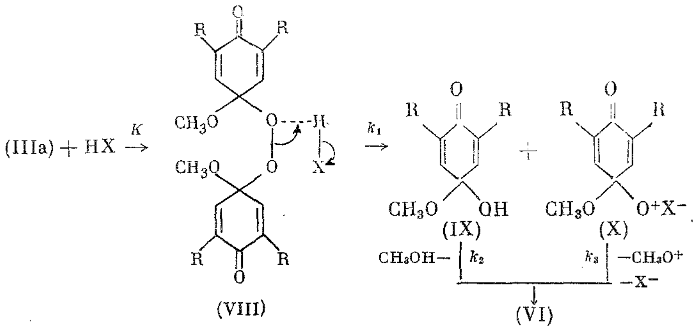


Fig. 3

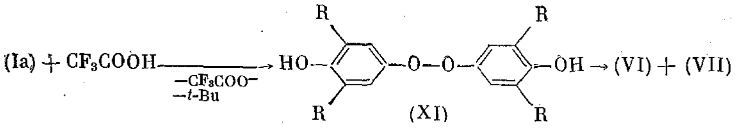
Fig. 2. Dependence of k_{ef} of peroxide (IIIa) decomposition on concentration of H_2SO_4.

Fig. 3. Dependence of k_{ef} of peroxide (Ia) decomposition on concentration of CF_3COOH.



followed only from the accumulation of quinone at the wavelength of 340 nm, the second maximum of quinone (VI), where the absorption of the initial peroxide (Ia) and hydroquinone (VII) is inappreciable. The isobestic point on the spectral curves of the mixture becomes dislocated towards the end of the process. Therefore, a satisfactory rectification in the first-order reaction coordinates is attained only up to 60-65% conversion of the initial peroxide. The k_{ef} values obtained from the slope of the lines are linearly dependent on the cube of the acid concentration (Fig. 3).

This indicates the complex character of the process. Nevertheless, without specifying the initial stages of the process, from the data of chemical analysis of the reaction mixtures, we can assume that tert-butyl fragments are split from the peroxide molecule in the form of carbocations with formation of an intermediate peroxide (XI), which rapidly converts into the end products (VI) and (VII). In reaction with CF_3COO^- anions, the tert-butyl cations give the corresponding ester:



In conclusion, we should note that a ready and selective conversion of the quinolide peroxides into the corresponding quinones and hydroquinones by the action of acids can be used as a very convenient method for the preparation of these compounds. It is clear that in carrying out the process there is no need to isolate the quinolide peroxides. We tested the possibilities of this method using as an example 2,4,6-tri-tert-butylphenol, a side product in the production of the widely known inhibitor Ionol. As already mentioned, when oxidized in an alkaline medium by $K_3Fe(CN)_6$, this phenol quantitatively gives a mixture of two isomeric peroxides (Ia) and (Ib) (3 : 1). Subsequent treatment of the organic phase of the reaction mixture with CF_3COOH, and then with a mixture of CH_3COOH and zinc dust, made it possible to obtain a mixture of hydroquinone (VII) (88%) and 3,5-di-tert-butylpyrocatechol (12%) in a quantitative yield. The substituted hydroquinone is readily separated from pyrocatechol by crystallization from hydrocarbons.

EXPERIMENTAL

The UV spectra were recorded on the Specord UV-VIS spectrophotometer, using hexane as solvent. The PMR spectra were run on the Varian-100 spectrometer with HMDS as external standard. The purity of the products was controlled by TLC on Silufol UV 254.

Preparation of Quinolide Peroxides. A 0.01 mole portion of the initial phenol was dissolved in 200 ml of benzene, and the solution was stirred for 30 min with 250 ml of water containing 0.1 mole of $K_3Fe(CN)_6$ and 0.2 mole of KOH. The benzene solution of the phenoxyl radical was separated, washed with water, and purged with air to decolorization. After removal of benzene, the quinolide peroxide was recrystallized from hexane or alcohol.

(Ia), mp 130-131°C (from hexane); cf. [1]; λ_{max} 239 nm. PMR spectrum (CCl_4, δ, ppm): 0.77 m (18H), 1.19 s (36H), 6.42 s (4H).

(Ib), mp 129-130°C (from hexane); cf. [1]; λ_{max} 240. PMR spectrum (CCl_4, δ, ppm): 0.72 m (18H); 1.10 s (9H), 1.16 s (18H), 1.22 s (9H), 6.21 d (1H), 6.40 d (1H), 6.52 s (2H).

(IIa), mp 125-126°C (from hexane); cf. [3]; λ_{max} 240 nm. PMR spectrum (CCl_4, δ, ppm): 0.75 d (J = 6 Hz, 12H), 1.24 s (36H), 1.80 quart. (1H), 6.40 s (4H).

(IIIa), mp 115-116°C (from hexane); cf. [4]; λ_{max} 230 nm. PMR spectrum (CCl_4, δ, ppm): 1.20 s (36H), 3.29 s (6H), 6.48 s (4H).

(IV), mp 140-142°C (from hexane); cf. [6]; λ_{max} 230 nm, 278 nm. PMR spectrum (CCl_4, δ, ppm): 1.28 s (36H), 6.64 s (4H), 7.24 m (10H).

(Vc), mp 134-135°C (from ethanol), cf. [5]; λ_{max} 262, 317 nm. PMR spectrum (CCl_4, δ, ppm): 0.87 s (18H), 1.30 s (18H), 7.29 d (J = 3 Hz, 4H), 7.80 m (10H).

Conversion of Quinolide Peroxides (Ia), (IIa), and (IIIa) by the Action of Acids. a) A solution of 0.01 mole of (Ia) in 3 ml (0.04 mole) of CF_3COOH was stirred for 15 min at ~20°C, and then 50 ml of octane were added. The solution was washed with water, dried over $CaCl_2$, and $CF_3COOC(CH_3)_3$ was distilled. Yield 2 g (75%), bp 45°C, cf. [7].

The octane solution was evaporated in vacuo, and the residue partitioned on a column with silica gel to yield 2.2 g (40%) of quinone (VI), mp 68°C, cf. [4], and 2.2 g (40%) of hydroquinone (VII), mp 114-115°C, cf. [4].

To determine the consumption of CF_3COOH, the aqueous extracts from the reaction mixture were titrated with NaOH using phenolphthalein as indicator.

b) The reaction with peroxide (IIa) was carried out similarly.

c) A mixture of 0.55 g of (IIIa) and 0.5 ml of CF_3COOH was held for 5 min at ~20°C, and 20 ml of hexane were added. The solution was washed with water, and hexane was evaporated in vacuo. The yield of quinone (VI) was quantitative.

Kinetics of Conversion of Peroxides (Ia) and (IIIa) by the Action of Acids. The kinetics were studied spectrophotometrically in a quartz cuvette (1 cm) at 21 ± 2°C on the Specord UV-VIS spectrophotometer.

A mixture of CCl_4 and CF_3COOH was added to 1 ml of a solution of (Ia) in CCl_4 so that the overall volume was 3 ml, and the concentration of the initial peroxide did not exceed $7.5 \cdot 10^{-3}$ mole/liter. The concentration of CF_3COOH varied from 1.3 to 3.5 mole/liter. The course of the reaction was followed from the change in the optical density at 340 nm wavelength. The kinetic curves are rectified in first-order reaction coordinates: $-\log (1 - D/D_\infty)$ vs t.

Water and 0.1 N H_2SO_4 were added to 1 ml of solution of (IIIa) in methanol, so that the overall volume of the solution was 2 ml, and the optical density of the solution of the initial peroxide at wavelength 241 nm was within 0.5-0.6. The H_2SO_4 concentration varied from 0.5 to $3 \cdot 10^{-3}$ mole/liter. The course of the reaction was followed from the change in the optical density at 252 nm wavelength (the first maximum of the quinone). The kinetic curves were rectified in first-order reaction coordinates: $\log [(D - D_0)/(D_\infty - D_0)]$ vs t.

CONCLUSIONS

1. The isomeric composition and structure of quinolide peroxides, formed in the oxidation of 4-R^1-2,6-di-tert-butylphenols, are determined by steric and electronic effects of substituent R^1.

2. By the action of acids, the quinolide peroxide derivatives of 4-R^1-2,6-di-tert-butylphenols convert selectively in high yields into 2,6-di-tert-butyl-1,4-benzoquinone and 2,6-di-tert-butylhydroquinone. The rates of the reaction depend on the nature of substituent R^1 and on the acidity of the medium.

3. The mechanism of conversion of the quinolide peroxides derived from 4-R^1-2,6-di-tert-butylphenols in the presence of acids has been proposed and confirmed.

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