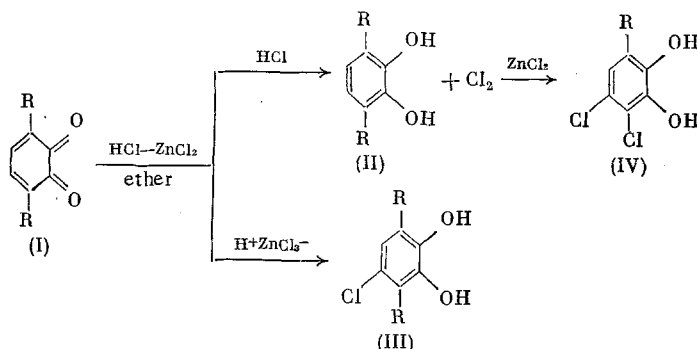


REACTION OF 3,6-DI-*tert*-BUTYL-*o*- BENZOQUINONE WITH ACIDS

I. A. Novikova, V. B. Vol'eva,
N. L. Komissarova, I. S. Belostotskaya,
and V. V. Ershov

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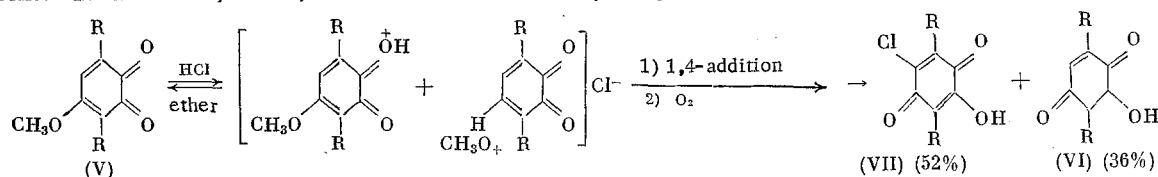
It has already been shown [1] that in the reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone (I) with HCl in ether, instead of the electrophilic 1,4-addition, usual for quinones, an oxidation-reduction process takes place with the formation of 3,6-di-*tert*-butylpyrocatechol (II) and chlorine. The unusual character of the reaction of (I) with HCl induced us to study this reaction depending on the nature of the acid (HCl, HCl-ZnCl₂, HCl-H₂O, H₂SO₄, H₂SO₄-H₂O) and solvent (ether, CH₃OH, C₂H₅OH, hexane, benzene, CCl₄). From the data obtained we can conclude that the most important stage in the transformation of (I) in acids is the formation of a protonated form of quinone, which, depending on the closest environment, can exhibit the properties of an oxidizing agent or electrophile. The redox process in the (I)-HCl-ether system probably proceeds with participation of undissociated form of HCl. An increase in the degree of dissociation of the acid should increase the probability of the usual 1,4-addition. In fact, in the (I)-HCl-ZnCl₂-ether system, besides the pyrocatechol (II) (70%), a product of ionic 1,4-addition of HCl is formed, 4-chloro-3,6-di-*tert*-butylpyrocatechol (III) (20%). 5,6-Dichloro-3-*tert*-butylpyrocatechol (IV) was also isolated in a yield of 7%, which according to the literature data [2], is formed during an electrophilic halogenation of (II). The overall yield of (II) and (IV) and the yield of (III) characterize the relative contribution of the two possible paths of transformation of (I) in the HCl-ZnCl₂-ether system.



Here and below R = C(CH₃)₃.

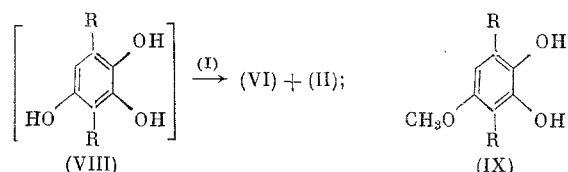
The reaction of (I) with concentrated H₂SO₄ in ether leads to (II). In this case the protonated form of (I) should transform into (II) as the result of hydride splitting from the molecule of the solvent. Examples of such ionic hydrogenation of quinones are known [3].

The introduction of a methoxy group (quinone (V)) changes the character of the reaction of the quinone with HCl in ether. The presence in (V) of a center of a competing O-protonation decreases the concentration of the form protonated at the carbonyl group, whose oxidation potential is lowered by the action of the methoxy substituent. In this case, the 1,4-addition of HCl and hydrolytic splitting of the methoxy group take place.



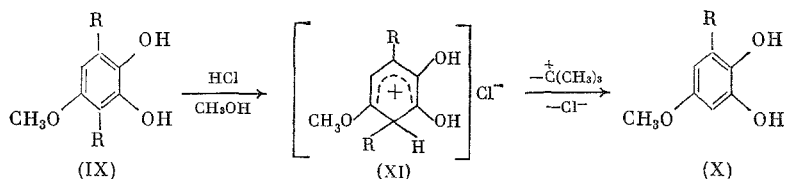
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The reactions of (I) with acids in hydroxy-containing solvents (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, binary mixture $\text{CH}_3\text{OH}-\text{H}_2\text{O}$) proceed exclusively as the stepwise addition of a proton and the nucleophilic part of the solvent molecule. The reaction of (I) with HCl and H_2SO_4 in aqueous methanol leads to the formation of 2,5-di-*tert*-butyl-6-hydroxy-*p*-benzoquinone (VI) and (II) in an equimolar ratio

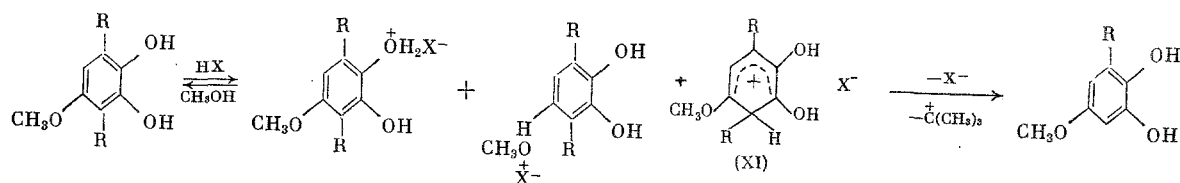


Pyrocatechol (VIII) (or its tautomeric form), formed as the result of the 1,4-addition of water, takes part in the oxidation-reduction reaction with the initial (I) to form (II) and (IV).

In the reaction of (I) with $\text{CH}_3\text{OH}-\text{H}_2\text{SO}_4$, 4-methoxy-3,6-di-*tert*-butylpyrocatechol (IX) is formed. Because of the presence of traces of water in the system, (II) and (VI) are also formed in a low yield. The reaction of (I) with $\text{CH}_3\text{OH}-\text{HCl}$ does not stop at the stage of the formation of (IX), which can be isolated only if special precautions are observed. Under these conditions, (IX) splits off the *tert*-butyl group, and converts into methoxy-mono-*tert*-butylcatechol (X)



The results obtained for the (I)-HX- CH_3OH system can be interpreted by the concepts of hard and soft acids and bases. The preliminarily formed (IX) can undergo a competing O- and C-protonation; the O-protonation with the formation of an oxonium ion (hard cation) is preferred at $\text{X} = \text{HSO}_4^-$ (hard anion). The softer Cl^- favors the formation of a soft cation (the C-protonated form - the arenonium ion (XI))



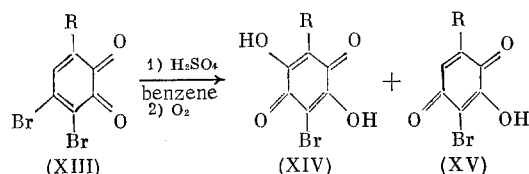
For ion (XI), not only the reversible deprotonation, but also the irreversible splitting of the *tert*-butyl cation is possible (soft acid, splitting is most favorable at $\text{X} = \text{Cl}^-$).

On the transition from methanol to the more basic ethanol, no fragmentation of (IX) is observed. In the $\text{C}_2\text{H}_5\text{OH}-\text{HX}$ -pyrocatechol system, compound (IX) is stable irrespective of the nature of the solvent, which shows that the debutylation process is sensitive to the basicity of the solvent used.

The reaction of (I) with acids in nonsolvated and weakly solvated media has several characteristic features. In system (I)- HCl -hexane, the reversible formation of a complex of (I) with HCl , leading to the disappearance of the quinone color, is possible. The decoloration of the solution is not related to any chemical reaction, and (I) is completely regenerated after removal of the solvent. But prolonged passing of HCl through a solution of (I) in hexane leads to the formation of products of the oxidation-reduction reaction (II) and (III). In this case, the formation of (III) is probably the result of an intercellular recombination of the radical pair formed during the redox process and not due to the ionic 1,4-addition of HCl . It is clear that in the absence of solvation, the degree of probability of such a recombination increases. The reaction of (I) with HCl in benzene and CCl_4 proceeds similarly. The oxidation-reduction transformations of (I) in benzene or CCl_4 also proceed in the presence of H_2SO_4 , as indicated by the presence of (II) in the reaction products.

The above discussed reactions are strictly specific for *o*-quinone (I), its analogs 3,5-di-*tert*-butyl-*o*-benzoquinone (XII) and 5,6-dibromo-3-*tert*-butyl-*o*-benzoquinone (XIII) cannot undergo acid-initiated oxidation-

reduction transformations. The 1,4-addition reactions are characteristic of quinones (XII) and (XIII). In the system (XIII)–H₂SO₄–benzene, p-quinones (XIV) and (XV) are formed



All the data obtained indicate that symmetric steric screening of the carbonyl groups of o-quinone is manifested in the characteristic features of its chemical behavior.

EXPERIMENTAL

Reactions of (I) with HCl. A current of dry HCl was passed through a solution of (I) ($5 \cdot 10^{-3}$ M) in 50 ml of the corresponding solvent to decoloration. The reaction mixture was analyzed by TLC on Silufol UV-254. The reaction products were isolated by fractional crystallization of the residue after evaporation of the solvent and in several cases by preparative TLC.

- a) (I)–HCl–ether. Pyrocatechol (II) was isolated in a yield of 96%; mp 96–97°C (from hexane); comp. [4].
 - b) (I)–HCl–ZnCl₂–ether. Anhydrous ZnCl₂ (10^{-2} M) was used. Pyrocatechols (II), (III), and (IV) were isolated by preparative partition chromatography on Silufol in the hexane–ether system (6:1) in yields of 70, 20, and 7%, respectively [R_f (II) 0.45; R_f (III) 0.35; R_f (IV) 0.2]. Compounds (III) and (IV) were converted by the action of Ag₂O in benzene into quinones. 4-Chloro-3,6-di-tert-butylquinone: mp 50–51°C. UV spectrum: λ_{max} 390 nm (ϵ 2215) and λ_{max} 580 nm (ϵ 69.3). Found: C 66.40; H 7.65%. C₁₄H₁₉O₂Cl. Calculated: C 66.14; H 7.48%. 5,6-Dichloro-3-tert-butylquinone: mp 108–109°C. UV spectrum: λ_{max} 416 nm (ϵ 2215) and λ_{max} 580 nm (ϵ 36.8). Found: C 51.52; H 4.41%. C₁₀H₁₀O₂Cl₂. Calculated: C 51.50; H 4.29%.
 - c) (I)–HCl–CH₃OH. Pyrocatechol (X) was isolated in a yield of 69%, mp 96–97°C (from hexane). Found: C 67.38; H 8.06%. C₁₁H₁₆O₃. Calculated C 67.35; H 8.16%. UV spectrum: λ_{max} 290 nm (ϵ 1580). PMR spectrum (δ , ppm): 1.36 s (9H), 3.66 s (3H), 5.09 d (2H), 61.7 and 6.29 d.d. (2H, J = 3 Hz). Compound (IX) was identified by TLC. When the time of passing HCl was shortened and the mixture was cooled to 5°C, (IX) could be isolated on a preparative scale in a yield of 20%.
 - d) (I)–HCl–hexane. A current of HCl was passed through the solution of (I) in hexane for 12 h; yield of (II) 77%, of (III) 15%.
- (V)–HCl–Ether. Hydroxyquinone (VI) and hydroxychloroquinone (VII) were separated by TLC on Silufol UV 254 in the hexane–ether (5:1) system. Compound (VI), yield 36%; mp 83–84°C (from hexane). Found: C 71.00; H 8.57%. C₁₄H₂₀O₃. Calculated: C 71.15; H 8.53%. PMR spectrum (δ , ppm): 1.25 d (18 H), 6.3 s (1 H), 7.55 s (1 H). Compound (VII), yield 52%; mp 175–176°C (hexane–CHCl₃). Found: C 62.07; H 7.07%. C₁₄H₁₉O₃Cl. Calculated: C 62.09; H 7.07%.

Reactions of (I) with H₂SO₄. To a solution of (I) ($5 \cdot 10^{-3}$ M) in 50 ml of the corresponding solvent, 1 ml of concentrated H₂SO₄ was added. After decoloration, the reaction mixture was washed several times with water, and dried over MgSO₄. The solvent was removed, and the products were extracted from the residue by fractional crystallization, or partition by the TLC method.

- a) (I)–H₂SO₄–ether. Compound (II) was isolated in a yield of 89%.
- b) (I)–H₂SO₄–CH₃OH. Compound (IX) was isolated in a yield of 70%; mp 130–131°C (from hexane). Found: C 71.31; H 9.54%. C₁₅H₂₄O₃. Calculated: C 71.43; H 9.58%. UV spectrum: λ_{max} 288 nm (ϵ 2280). By oxidation with Ag₂O in benzene, (IX) was converted into quinone (V), identical with an authentic sample. Compounds (II) and (VI) were isolated in a yield of 7%.
- c) (I)–H₂SO₄–hexane. Compound (II) and its isomerization and dealkylation products: 3,5-di-tert-butylpyrocatechol, 3- and 4-tert-butylpyrocatechols, and the unsubstituted pyrocatechol were detected and identified by the TLC method, with standardization on Silufol.
- d) (I)–H₂SO₄–CCl₄. Products similar to those formed in hexane were obtained.

e) $(I) - H_2SO_4 - \text{benzene}$. First, (II) and all its isomerization and dealkylation products are formed. Seven hours after mixing of the reagents, (II) and other alkylpyrocatechols disappear from the reaction mixture. p -Di-*tert*-butylbenzene was isolated from the reaction mixture.

$(I) - H_2SO_4(HCl) - H_2O - CH_3OH$. A standard ratio between the reagents, and 5 ml of water are used. The composition of the reaction mixture was analyzed by TLC, with standardization. The products were separated after oxidation of (II) into (I) ; compounds (I) and (VI) were isolated in the same yield (42%), and identified by comparison with authentic samples.

CONCLUSIONS

In the reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with acids in different media, the protonated form of the quinone can exhibit the properties of an oxidizing agent or an electrophile, depending on the nature of the acid and solvent.

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