REDOX REACTIONS OF 3,6-DI-TERT-BUTYL-ORTHO-BENZOQUINONE, CATALYZED BY TETRAFLUOROSILANE

A. K. Chekalov, N. G. Gvazava, V. B. Vol'eva T. I. Prokof'eva, A. I. Prokof'ev, and V. V. Ershov

UDC 542.97:543.422.27:547.567

Tetrafluorosilane-catalyzed redox reactions of 3,6-di-tert-butyl-ortho-benzoquinone have been examined. From the EPR spectroscopic data and a study of the reaction products, a mechanism for these reactions is proposed involving the formation of a quinone-tetrafluorosilane complex which has strong oxidizing properties, and which enables the original quinone to undergo further reactions.

EPR spectroscopy has been used to identify an ortho-seimiquinolate complex of tetrafluorosilane (I) [1], formed by reaction of SiF_4 with 3,6-di-tert-butyl-ortho-benzoquinone.

$$\begin{array}{c} \stackrel{+}{\underset{+}{\overset{}}} \stackrel{0}{\underset{+}{\overset{}}} \stackrel{+}{\underset{+}{\overset{}}} \stackrel{1}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{+}{\underset{+}{\overset{}}} \stackrel{0}{\underset{+}{\overset{}}} \stackrel{+}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{+}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}{\overset{}}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}}{\underset{+}} \stackrel{-}} \overset{-}} \overset{-}} \overset{-}} \overset{-}} \overset{-} \overset{-}}$$

Our studies of this reaction (1a) have shown that the complex (I) is an intermediate in the redox reactions of the original quinone, the final products of which, isolated by TLC, are 3,6-di-tert-butylpyrocatechol (II), 2-hydroxy-3,6-di-tert-butyl-para-benzoquinone (III), and 2,5-dihydroxy-3,6-di-tert-butyl-para-benzoquinone (IV).

Protonic acids and Lewis acids form complexes with ortho-benzoquinones which are stronger oxidizing agents than the starting quinones (activating complexation [2 3]). With this in mind, the formation of the pyrocatechol (II) may be rationalized as a two-electron reduction of the tetrafluorosilane—quinone complex, followed by dissociation of the reduced form:

$$\begin{array}{c} + & 0 \\ + & \mathrm{SiF}_{4} \rightarrow \begin{array}{c} + & 0 \\ + & 0 \end{array} \\ & + & 0 \end{array} \end{array} \overset{\mathsf{F}_{4} \xrightarrow{\tilde{e}_{1} \operatorname{H}^{+}}}{\overset{\mathsf{F}_{1} \operatorname{H}^{+}}{\overset{\mathsf{F}_{1} \operatorname{H}^{+}}{\overset{\mathsf{F}_{2} \operatorname{H}^{+}}{\overset{\mathsf{F}_{3} \operatorname{H}^{+}}{\overset{\mathsf{F}_{4} \operatorname{H}^{+}}}{\overset{\mathsf{F}_{4} \operatorname{H}^{+}}}{\overset{\mathsf{F}_{4} \operatorname{H}^{+}}}}}}}} (2)$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1105-1108, May, 1990. Original article submitted July 27, 1989.

This route (2) is confirmed by the observation that the reaction of pyrocatechol (II) with tetrafluorosilane under aerobic conditions results in the formation of the complex (I), as shown by EPR, and also by the synthesis of 2,5-dimethylpyridinium 3,6-di-tert-butyl-pyrocatechatetetrafluorosilicate (V), oxidation of which gave rise to the spectrum of (I) [4].

$$\begin{bmatrix} + & 0 \\ + & 0 \\ (V) \end{bmatrix}^{2^{-}} \begin{pmatrix} H \\ N \\ - & 0 \end{pmatrix}_{2}^{+} \xrightarrow{PbO_{2}} (I)$$
(3)

In addition to (II), which is the principal product of reaction (1b) (yield 80-90% on starting quinone, depending on ROH), TLC showed the presence of the hydroxyquinones (III) and (IV), the formation of which may be due to the catalyzed methoxylation of the quinone, followed by protolytic cleavage of the alkoxyquinones thus obtained [5].

When the reaction of tetrafluorosilane with 3,6-di-tert-butyl-ortho-benzoquinone is carried out in acetone, the pyrocatechol (II) is again one of the main products. In addition to (II), there were isolated from the reaction mixture by TLC the hydroxyquinone (III), the condensation product of (II) with acetone, viz., 2,2-dimethyl-4,7-di-tert-butyl-1,3-benzdioxolane (VI), and the isopropylidene ether of 3,8-dihydroxy-1-methyl-4,7-di-tert-butyl-7,8-dihydrobenzofuran (VII)



The product (VII), an adduct of the ether (IV) with dehydroacetone, has not previously been reported in the chemistry of ortho-benzoquinones and their derivatives. Its formation in the reaction of the quinone and tetrafluorosilane in acetone is the key to the interpretation of the redox behavior of this system, since it is evidence of the involvement of a strong oxidant in the reactions taking place. It is natural to assume that it is the tetrafluorosilane-quinone complex which has these oxidizing properties. As already mentioned, examples have been reported in the literature of activating complexation resulting in changes in the redox behavior of quinones. For example, reaction of quinones with halides (chlorides and bromides) of group III elements MX_3 results in the formation of the ortho-semiquinolates of the corresponding halide, and atomic halogen, rationalized as an intracomplex redox reaction [2]. In the case of tetrafluorosilane and the fluorides of the elements, cleavage of atomic fluorine is energetically disfavored, thus excluding the intracomplex route for redox reactions. The behavior observed for the quinone-tetrafluorosilane system therefore leads to the conclusion that the complexation of quinones with the fluorides of various elements may be regarded as a novel principle in the design of molecular systems with strong oxidizing properties.

In addition to (II), (III), (VI), and (VII), from the mixture obtained in reaction (4) there was isolated the product of the oxidative polycondensation of the starting quinone (37% yield on starting quinone), as the paramagnetic polymer (VIII) with a concentration of paramagnetic centers of 10^{18} spin/g and a molecular mass up to 15,000 atomic units.



EXPERIMENTAL

Tetrafluorosilane was obtained by decomposition of sodium hexafluorosilicate with sulfuric acid [6].

The reactions of 3,6-di-tert-butyl-ortho-benzoquinone in the presence of tetrafluorosilane were examined in 250 ml ampuls, in which were placed 3 g (15 mmoles) of the quinone, 50 ml of solvent, and 4 g (38 mmoles) of tetrafluorosilane, condensed into the ampul by cooling in liquid nitrogen. The ampuls were sealed and kept for three days. After opening the ampuls, the solvent was distilled off, and the reaction mixtures washed with hexane until the washings were colorless. The residues were then separated by TLC on Silufol UV-254 plates in the system hexane:ether, 6:1. The products (II)-(VI) were identified by comparing their R_f values and melting points with those of previously synthesized compounds [5, 7]. By TLC there was isolated 0.3 g (10% on starting quinone) of (VII) as bright yellow crystals from hexane, R_f 0.7 (hexane:ether, 6:1). Found: C 75.22; H 9.62%. $C_{20}H_{30}O_3$. Calculated: C 75.47; H 9.43%. Mass spectrum, m/z: 318 M⁺, 303 (M-Me⁺, 275 (M-MeCO)⁺, 261 (M-Bu)⁺, 245 (M-MeCHCO)⁺, 233 (M-BuCO)⁺, 218 (M-BuMeCO)⁺, 203 (M-BuMe₂CO). PMR spectrum ((CD₃)₂CO, external standard TMS, δ , ppm): 1.16 s (CH₃), 1.32 s (C₄H₉), 1.39 s (C₄H₉), 1.42 s (CH₃), 1.65 s (CH₃), 5.61 s (CH), 6.87 d (CH, J = 8.3 Hz). After removal of the hexane-soluble fraction, there remained 1.1 g (37% on starting quinone) of the polymer (VIII) as a black film of elemental composition: C 68.75, H 7.88%; IR spectrum (ν , cm⁻¹): 3200-3400 sh (OH), 2900-3000 (C-H_{arom}, C-H_{tert-butyl}). The concentration of paramagnetic centers in the polymer was determined by EPR on a Varian E-12A instrument, and the molecular mass by GLC on a Waters ALC/GPC-244.

LITERATURE CITED

- 1. A. K. Chekalov, A. I. Prokof'ev, N. N. Bubnov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1037 (1983).
- 2. G. A. Abakumov, Organometallic Compounds and Radicals [in Russian], Nauka, Moscow (1985), pp. 85-109.
- 3. The Chemistry of Quinoid Compounds, Part 1, Wiley, New York (1974), p. 335.
- 4. A. K. Chekalov, Dissertation of Candidate of Chemical Science [in Russian], Moscow (1986).
- 5. V. B. Vol'eva, I. A. Novikova, E. V. Ivanova, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 215 (1986).
- 6. M. G. Ryss, The Chemistry of Inorganic Fluorides [in Russian], Goskhimizdat, Moscow (1954).
- 7. I. S. Belostoikaya, E. V. Dzhuaryan, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2808 (1973).