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Oxidation of 3,5,3',5'-Tetra-*tert*-butyl-4,4'-dihydroxybiphenyl with Atmospheric Oxygen in the Absence of Base Catalysts

S. V. Bukharov, L. K. Fazlieva, N. A. Mukmeneva,
R. M. Akhmadullin, and V. I. Morozov

Kazan State Technological University, Kazan, Tatarstan, Russia

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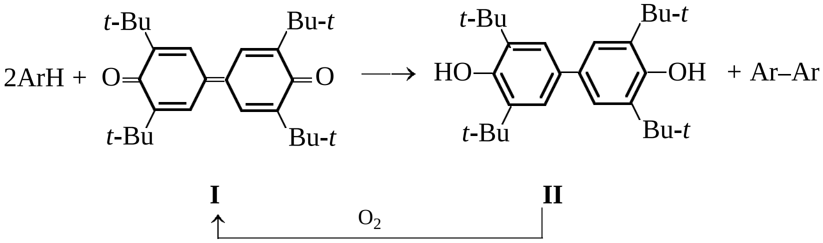
Abstract—Use of dimethylformamide as solvent and preliminary addition of 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone allow oxidation of 3,5,3',5'-tetra-*tert*-butyl-4,4'-dihydroxybiphenyl with atmospheric oxygen to be efficiently performed in the absence of base catalysts.

The use of oxidants capable of regeneration by oxidation of their reduced forms with atmospheric oxygen shows promise in industrial oxidations. Such oxidants can be used repeatedly without accumulation of their reduced forms, which often form the main body of production waste.

One of such oxidants is a mild dehydrogenating agent, 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone **I** [1]. Its reduced form, 3,5,3',5'-tetra-*tert*-butyl-4,4'-dihydroxybiphenyl **II**, can be readily oxidized with atmospheric oxygen in the presence of base catalysts [2] [scheme (1)].



(2)

The use of alkalis as ionizing agents catalyzing oxidation of phenols has a significant drawback: The spent alkalis should be neutralized, with the formation of waste. At the same time, dipolar aprotic solvents [3] forming hydrogen bonds with sterically hindered phenols [4] facilitate to some extent their ionization.

We found that, with dimethylformamide or its mixture with water as solvent, oxidation of **II** with atmospheric oxygen can be performed at relatively low temperatures in the absence of base catalysts. Since it is known that quinones can both catalyze [5, 6] and inhibit [7] autooxidation of sterically hindered phenols, we also examined the effect of quinone **I** on oxidation of **II**. We found that addition of **I** in amounts comparable with those of **II** appreciably accelerates oxidation of **II** (see table).

Redox reactions between sterically hindered phenols and quinones with the formation of phenoxyl radicals were reported in [8–11]. Such a transformation in the system phenol **II**–quinone **I** was discussed in [12], and formation of phenoxyl radical **III** [scheme (2)] was presumed.

Oxidation of phenol **II** with atmospheric oxygen in various solvents (6 h, 90–100°C, c_{II} 0.25 M)

Solvent	c_{I}, M[a]	Yield of quinone **I**, %[b]
DMF	0	18
DMF	0.025	20
DMF	0.25	60
Toluene	0.25	15
DMF–H_2O, 20 : 1	0.25	70
DMF–H_2O, 10 : 1	0.25	80

[a] In the initial mixture. [b] After subtraction of the amount of **I** initially added to the solution.

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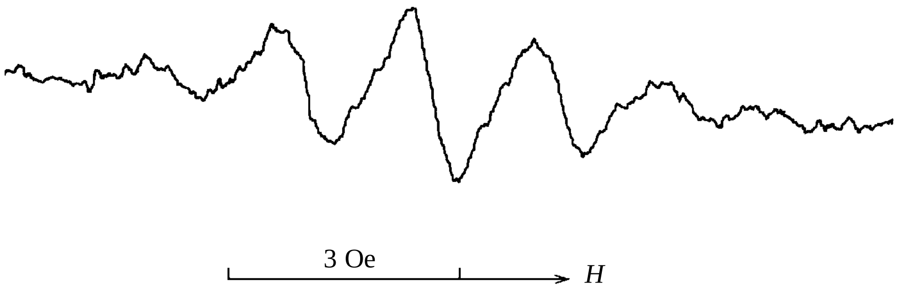
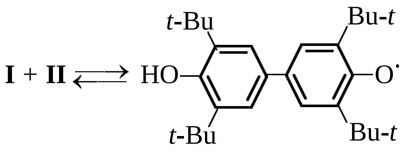


ESR spectrum of phenoxyl radical **III** (323 K, $c_{\mathbf{I}} = c_{\mathbf{II}} = 5 \times 10^{-3}$ M).



(2)

III

This equilibrium can account for the effect of **I** on oxidation of **II**. Namely, in the first stage, radicals **III** are generated by relatively fast dehydrogenation of the substrate, whereas in the absence of **I** radicals **III** are generated by slow [13] oxidation of un-ionized phenol **II** with atmospheric oxygen [scheme (3)]. This is follower by reactions (4) and (5).

$$\mathbf{II} + O_2 \longrightarrow \mathbf{III} + HO_2^-, \qquad (3)$$

$$\begin{array}{l} \mathbf{III} + HO_2^- \longrightarrow \mathbf{I} + HOOH \qquad (4) \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad H_2O + 1/2O_2, \end{array}$$

$$\mathbf{III} + O_2 \longrightarrow \mathbf{I} + HO_2^-. \qquad (5)$$

The fact that, for significant acceleration of the oxidation of **II**, the amount of **I** should be comparable with that of **II**, and not catalytic, counts in favor of such a mechanism. Furthermore, we detected radicals **III** in toluene solutions containing equimolar amounts of **II** and **I** by ESR spectroscopy (see figure). The multiplicity of the signal (1 : 4 : 6 : 4 : 1) and its parameters (hyperfine coupling constant 1.67 Oe, *g*-factor 2.004) coincide with the published data [14]. The low intensity of the signal, decreasing with temperature, shows that the concentration of radicals **III** is low and is determined by the equilibrium constant of reaction (2).

Oxidation of **II** in the presence of **I** can be regarded as a self-conjugated process in which oxidation of **II** with atmospheric oxygen is conjugated with its dehydrogenation under the action of **I**.

Thus, regeneration of quinone **I** from its reduced form **II** can be efficiently performed with atmospheric oxygen in DMF in the absence of base catalysts. Preliminary addition of quinone **I** results in noticeable acceleration of the reaction owing to the occurrence of a self-conjugated process.

EXPERIMENTAL

The ESR spectra of **III** were recorded on a Radiopan SE/X-2544 spectrometer. The solution was deaerated by threefold freezing–pumping–thawing.

Oxidation of 3,5,3',5'-tetra-*tert*-butyl-4,4'-dihydroxybiphenyl II. A solution of 1 g of phenol **II** and 1 g of quinone **I** in 10 ml of dimethylformamide was placed in a reactor equipped with an efficient reflux condenser and an adapter for air bubbling. Through the reaction mixture heated to 90–100°C, air was bubbled for 6 h at a rate of 39 l h^{-1}. Then the mixture was cooled to room temperature, and the precipitate of **I** was filtered off.

Oxidation of **II** in other solvents and without addition of **I** was performed similarly.

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