OXIDATION AND ALKOXYLATION OF 3,6-DI-TERT-BUTYL-PYROCATECHOL CATALYZED BY MANGANESE DIACETATE

from the stoichiometry of the two-electron reaction

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We have discovered that the oxidation of 3,6-di-tert-butylpyrocatechol (QH_2) by manganese triacetate in acetic acid and methanol under aerobic conditions with Mn(III): $QH_2 < 2$ departs

UDC 541.124:542.943.7:547.565.2

 $QH_2 + 2Mn(III) \rightarrow Q + 2Mn(II) + 2H^+$

where Q is 3,6-di-tert-butyl-o-benzoquinone, which is manifest in an enhanced yield of Q. QH₂ is stable in pure acetic acid and methanol. Thus, the observed disbalance is most likely explained by the oxidation of QH₂ by molecular oxygen catalyzed by Mn(II). This hypothesis is supported experimentally. The addition of Mn(OAc)₂ to a solution of QH₂ in methanol leads to the instantaneous appearance of a blue color characteristic for the semiquinone radical QH^{*} detected spectrally which is replaced by the red-brown color of Q upon the extensive conversion of QH₂. The readiness of oxidation in the presence of MN(II) is naturally related to the structure of QH₂, which is capable of acting as a chelating bidentate ligand. The mechanism for the catalytic oxidation of QH₂ apparently involves consecutive ligand exchange with the inclusion of QH₂ into the coordination sphere of the Mn(II) ion, the fixation of oxygen and the intrasphere oxidation of QH₂



$R = CMe_3$.

The oxidized Q ligand in methanol is capable of consecutive transformations. In addition to Q, a number of oxidation-alkoxylation products is found upon the prolonged contact of the reagents in the reaction system.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiva Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1. pp. 215-218, January, 1986. Original article submitted February 19, 1985.



Thin-layer chromatography permitted separation of 4-methoxy- and 4,5-dimethoxy-3,6di-tert-butyl-o-benzoquinone [MeO-Q and (MeO)₂-Q], their adducts with methanol with geminal arrangement of the MeO groups (I) and (II) and 2-hydroxy- and 2,4-dihydroxy-3,6-di-tertbutyl-p-benzoquinones [HO-Q and $(HO)_2-Q$], which corresponds to the hydrolytic loss of methanol from the methoxyquinones. Adducts (I) and (II) are in dynamic equilibrium with the related methoxyquinones, which permits the alkoxyl exchange realized in the following examples:



 $R' = CD_3$, Et.

The alkoxyl exchange and all the steps of the alternating alkoxylation—oxidation process are catalyzed by Mn(II). In the case of the $(MeO)_2-Q-(II)$ pair, this is especially clear: Pure $(MeO)_2-Q$ and (II) are stable while they are interconverted in the presence of Mn(II) with the establishment of equilibrium.

In order to develop a preparative method for the synthesis of alkoxylated derivatives, we studied the dependence of the alkoxylation process on the initial concentration of Q and the Q:Mn(II) ratio. The optimal values are: $[Q] = 0.5 \cdot 10^{-2}$ mole/liter and Q:Mn(II) = 2. The complete conversion of Q is more rapid at higher reagent concentrations, but the total yield of alkoxylation products decreases due to their binding in insoluble manganese complexes which separate as a dark-brown precipitate. The question of the structure of these complexes was not specifically studied. Their low solubility is apparently a consequence of the formation of planar or framework aggregates. Decomposition by the action of high pressure and shear deformation indicates the presence of MeO-Q and (MeO)₂-Q as ligands in these aggregates [1]. This is also in accord with the isolation of HO-Q and (HO)₂-Q upon the treatment of these complexes by dilute hydrochloric acid.

The determination of the structure of (II) deserves special consideration. The PMR signal for the tert-butyl group of this adduct appears as a singlet, which indicates molecular symmetry and the presence of intramolecular hydrogen bonding and a bridging OMe group (A). The alternative explanation involving oscillation of a hydrogen atom and O group between two adjacent positions (B) is less likely since two sharp discrete singlets correspond to the OMe groups in the PMR spectrum, i.e., if rearrangement B obtains, it proceeds at a rate insuf-



ficient for averaging of the OMe groups.

EXPERIMENTAL

The chromatographic separation was carried out on Silufol UV-254 using 6:1 hexane-ether as the eluent.

Oxidation of QH_2 by Mn(III). a) A sample of 2.68 g (10 mmoles) $Mn(OAc)_3 \cdot 2H_2O$ was added to a solution of 1.11 g (5 mmoles) QH_2 in 100 ml methanol or acetic acid and stirred for 30 min at about 20°C. The solvent was distilled off and quinone Q was extracted with hot hexane to give 1.06 g (96%) product, mp 197°C (from hexane) [2].

b) Upon using conditions analogous to those for procedure a and 1.34 g (5 mmoles) Mn(III) quinone Q was separated from unreacted QH₂ chromatographically to yield 0.86 g (77%) product.

Oxidation of QH_2 in Methanol in the Presence of Mn(II). A sample of 2.5 mmoles Mn(OAc)₂. 4H₂O was added to a solution of 5 mmoles QH_2 in 100 ml methanol in an open vessel. A strong blue color appeared instantaneously which is characteristic for the semiquinone chromophore (λ_{max} 750 nm). The color of the solution gradually became red-brown corresponding to Q. After 10 h, methanol was distilled off and the products were extracted with hot hexane. Q was separated by cooling of the hexane adducts to 0.97 g (89%) product. The mother liquor was subjected to chromatography to give 0.02 g Q (R_f 0.6) and 0.12 g (9%) MeO-Q (R_f 0.2), mp 99°C (from hexane) [3], which was identical to a sample obtained by the oxidation of 4methoxy-3.6-di-tert-butylpyrocatechol.

Oxidative Alkoxylation of QH_2 in Methanol in the Presence of $Mn(OAc)_2$. A sample of 5 mmoles $Mn(OAc)_2 \cdot 4H_2O$ was added to a solution of 10 mmoles QH_2 in 200 ml methanol and left for 5 days at about 20°C in contact with the atmosphere. During this time, the solution became red-brown and a shiny dark brown precipitate formed in the bottom of the flask (0.25 g). The solution was decanted and the precipitate was washed with methanol. The solvent was distilled off, and the residue was subjected to chromatography to give 0.88 g (35%) MeO-Q ($R_f 0.2$), mp 99°C (from hexane), 0.7 g (24%) (MeO)_2-Q ($R_f 0.4$) as dark-brown crystals, mp 70°C. The spectral data for these products correspond to the literature values [3].

During chromatographic separation, colorless adduct (I) (R_f 0.55) loses methanol to form Me-Q. The yield is 0.1 g (<5%).

Adduct (II) (R_f 0.70) was obtained as colorless crystals, mp 99°C (from hexane). Found: C 65.40; H 9.01%. Calculated for $C_{17}H_{28}O_5$: C 65.38; H 8.97%. PMR spectrum (δ , ppm, CCl₄): 1.37 s (18H), 3.25 s (6H). 4.16 s (3H), 7.75 s (1H). IR spectrum (KBr): 1600 (CO), 2925 cm⁻¹ (OH). HO-Q was obtained as yellow crystals with mp 84°C (from hexane) which was identical to an authentic sample obtained by the acid-catalyzed hydration of Q according to our previous procedure [2]. This compound has pH-chromism and becomes raspberry red above pH 7.

(HO)₂Q (R_f 0.9) was obtained at bright-yellow crystals, mp 140°C (from hexane). Found: C 66.70; H 8.01%. Calculated for C₁₄H₂₀O₄: C 66.66; H 7.93%. At pH > 7, the compound becomes pink.

<u>Alkoxyl Exchange for $(MeO)_2-Q$ and Adduct (II)</u>. A sample of 0.14 g (0.5 mmole) $(MeO)_2-Q$ or 0.16 g (0.5 mmole) (II) was dissolved in 10 ml CD₃OD and than 0.12 g (0.5 mmole) Mn(OAc)₂·4H₂O was added and maintained for 24 h. The contents were subjected to chromatography, and layers were separated which corresponded in their R_f values to $(MeO)_2-Q$ and (II). The substance was washed with hexane, and hexane was evaporated. The residue was dissolved in CCl₄ and analyzed by PMR spectroscopy. The spectra of both compounds showed the absorption of only tert-butyl groups (1.25 and 1.37 ppm, respectively).

CONCLUSIONS

A catalytic effect was found for $Mn(OAc)_2$ in the oxidation and alkoxylation of 3,6-ditert-butylpyrocatechol. A mechanism was proposed entailing the formation of a metal complex with pyrocatechol and oxygen ligands. A preparative procedure was developed for the synthesis of alkoxylated derivatives of 3,6-di-tert-butyl-o-benzoquinone.

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RELATIVE HYDROCARBOXYLATION OF STYRENE IN CO AND SYNTHESIS GAS IN THE PRESENCE OF PALLADIUM COMPLEXES AT LOW PRESSURES

UDC 542.97:547.538.141

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The use of synthesis gas instead of CO in the carbonylation of olefins is an important industrial problem. In our previous work [1], we showed that the hydrocarboxylation of alkenes in dioxane in the presence of $PdCl_2(Ph_3P)_2$ (I) with $SnCl_2$ additive proceeds at 2.0 MPa synthesis gas to give a high yield (97%) and selectivity (80%) of the linear product. In the present work, the effect of the replacement of CO by synthesis gas was studied relative to the hydrocarboxylation of styrene.

The reaction was carried out in dioxane using (I) with added $Ph_P P$ or $SnCl_2$ as the catalyst. A steel autoclave with glass reactor and sample outlet device was employed. The volume of the reaction mixture was 10.6 ml and the concentration of (I) was $6.7 \cdot 10^{-3}$ mole/liter. The Pd/styrene mole ratio was 1:150. The reaction was monitored by gas-liquid chromatography on a Tsvet-110 chromatograph.

The reaction products were 2-phenyl- (II) and 3-phenylpropionic acids (III). The rates of accumulation of these regioisomers (r_{II} and r_{III}), given in Table 1, were evaluated using the initial (5-40% styrene conversion) linear segment of the kinetic curve taking account of the selectivity, which was constant during the entire reaction time

 $PhCH = CH_{3} \underbrace{co. H_{1}O}_{PhCH_{2}CH_{2}COOH} (II)$

The catalytic carbonylation of styrene in the presence of palladium complexes at 30-70 MPa CO in ethanol [2, 3] and 0.1 MPa in olefin solution [4] process with the predominant formation of the α -isomer. We have found that isomer (II) is the major reaction product in the case of the hydrocarboxylation of styrene in 2.0 MPa CO and a twofold excess of Ph_P relative to (I) (see Table 1). Replacement of dioxane by THF of DME has virtually no effect on the reaction rate and selectivity (experiments 2 and 3). In all three cases, the yield is almost quantitative. When the CO pressure is reduced to 1.0 MPa, the selectivity relative to the α -isomer is reduced (see experiments 1 and 4), which is a result both of the decrease in the rate of formation of this isomer r_{II} and the marked increase in the rate of accumulation of the β -isomer r_{III}. Going from pure CO to synthesis gas (1:1 CO-H_2) with 1.0 MPa partial CO pressure leads to even less selectivity relative to the α -isomer (experiment 5). This reduction is related to a further increase in the rate of formation of isomer (III) (the value for r_{II} is unchanged relative to the experiment with P_{CO} = 1.0 MPa).

A similar effect of pressure and gas composition on the reaction selectivity and rate of regionsomer formation is found when using the (1)/0.5 SnCl₂ catalytic system (experiments 6-8). The introduction of SnCl₂ instead of PPh₃ leads to a significant decrease in selectivity due to a sharp increase in r_{III} (see experiments 1, 4, 5, and 6-8).

A definite similarity is noted in the effect of the conditions on the direction of the hydrocarboxylation of styrene and alkenes [1, 5, 6]. In both cases, a decease in P_{CO} , the addition of hydrogen, and the introduction of SnCl₂ facilitate carbonylation at the terminal carbon atom of the vinyl group. However, while the linear product analogous to β -isomer (III) is the major product and going to synthesis gas increases the reaction selectivity in the case of alkenes [1], the use of synthesis gas in the case of styrene gives the opposite result.

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