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Investigation of 2-ethylanthraquinone degradation on palladium catalysts

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Abstract

The hydrogenation of 2-ethylanthraquinone (eAQ) was performed over alumina, silica and carbon supported palladium catalysts. Present research is concentrated on the process of eAQ degradation and especially a role of the type of catalyst is examined. Degradation of eAQ in the catalytic experiments has been discussed on the basis of reaction pattern reported for the reduction of carbonyl groups in anthraquinone by standard procedures (Zn, Sn, $NaBH_4$). Various by-products formed by degradation of hydroquinone ($eAQH_2$) have been identified by GC–MS. They are the product of C─O hydrogenolysis such as 2-ethylanthrone (eAN, two isomers), 2-ethylanthracene (eANT) and the products of eAN hydrogenation (H_4eAN, two isomers). Tautomerization of partially and fully saturated hydroquinones produces OXO-isomers [two isomers OXO-H_4(1,2) and OXO-H_8(1,2)]. Reduction of eAQ with $NaBH_4$ gives 2-ethyl-9,10-dihydroxy-9,10-dihydroanthraquinone, intermediate product in the consecutive reactions occurring during the hydrogenolysis of C─O and resulting in eAN. A difference in performance of 0.5% Pd/C, 0.5% Pd/SiO_2 and 0.5% Pd/Al_2O_3 catalysts is related with their reactivity in degradation of $eAQH_2$. Much higher reactivity in the whole degradation process and especially in the formation of intermediate product exhibits alumina-supported catalyst.

Keywords: 2-Ethylanthraquinone; Palladium catalysts; Hydrogenation

1. Introduction

The hydrogenation of 2-ethylanthraquinone (eAQ) into 2-ethylanthrahydroquinone ($eAQH_2$) is one of the key steps in the industrial synthesis of H_2O_2 [1]. In this method eAQ is catalytically hydrogenated (Scheme 1) to yield 2-ethylanthrahydroquinone. Oxidation of the latter produced hydrogen peroxide with the regeneration of the starting eAQ. Al_2O_3, SiO_2, silica–alumina-supported Pd catalysts are commonly used in the hydrogenation process. However, even on the most selective catalyst, the hydrogenation of quinone to hydroquinone is accomplished due to a slow hydrogenation of desirable $eAQH_2$ to various side products.

Two reaction pathways have been suggested for the consumption of $eAQH_2$. One consists of the successive saturation of phenyl ring $eAQH_2 \rightarrow H_4eAQH_2 \rightarrow H_8eAQH_2$, the second route is the hydrogenolytic cleavage of C–O bonds [2,3]. In the former H_4eAQH_2, active quinone is produced, whereas hydrogenolysis-deriving products like 2-ethyloxanthrone (OXO-E), 2-ethylanthrone (eAN) and 2-ethylanthracene (eANT) are formed in the latter. All of these products as well as H_8eAQH_2 are termed as "degradation products" [1]. They are not oxidized to form H_2O_2 and thus represent a loss of starting eAQ. Slow deactivation of palladium catalysts is frequently correlated with their reactivity in degradation of $eAQH_2$ [4–6]. To the best of our knowledge, however, little work is done to investigate the hydrogenolytic reactions leading to degradation of $eAQH_2$ [2,5]. Here, to discuss this problem the reaction pattern (Scheme 2) established during the reduction of carbonyl groups in anthraquinone by means of classical methods (Sn, Zn in acidic medium, $NaBH_4$ in methanol) is adopted [7]. These methods of reduction are widely studied because they are commonly used to prepare anthrone and anthracenes. As Scheme 2 shows the first step of C–O reduction is the transformation of quinone system in AQ (I) to aromatic hydroquinone (II) which tautomerizes to OXO (III) isomer. The tautomers exist

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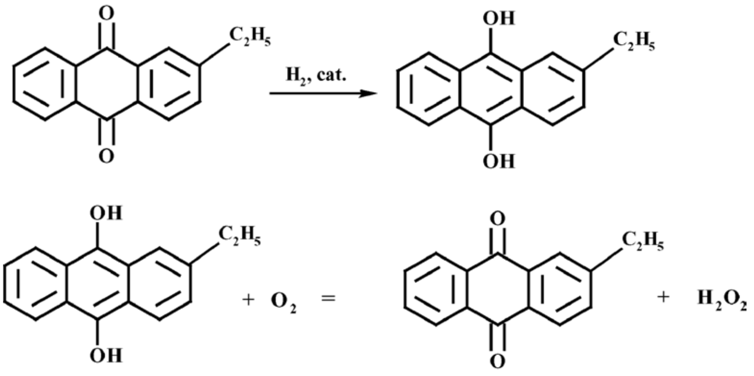
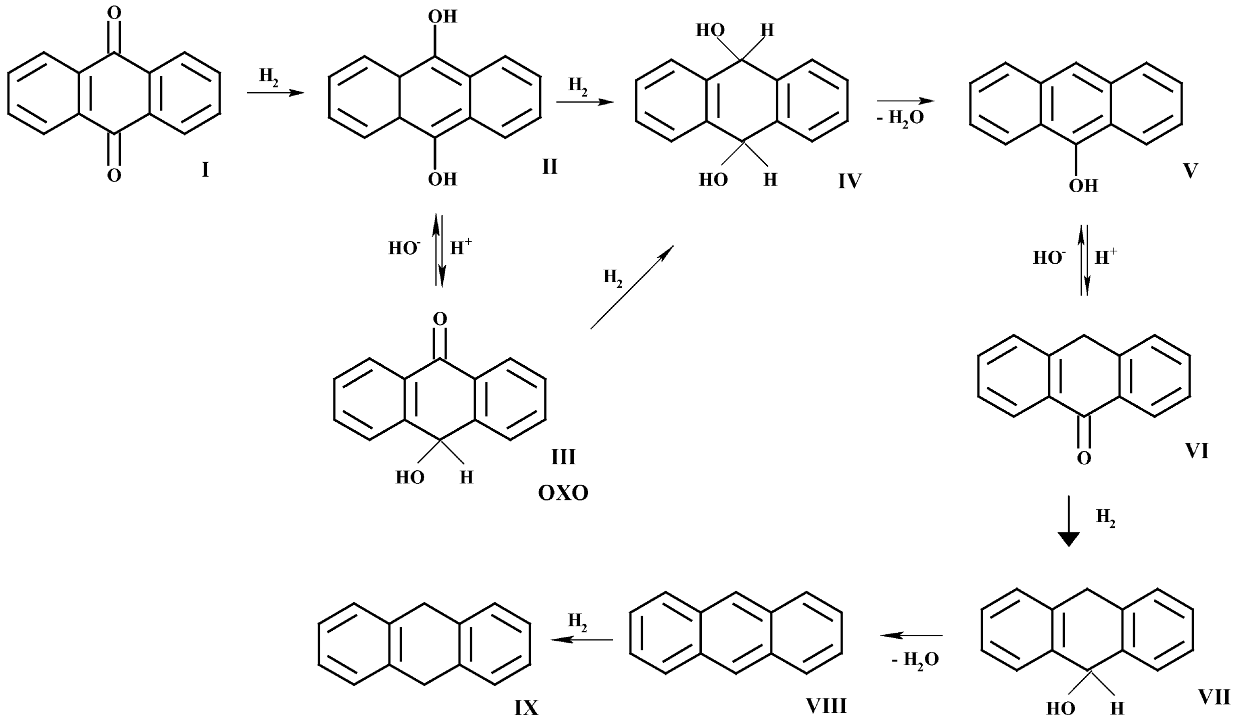


Scheme 1. Reactions of the anthraquinone process.

in an equilibrium, which could be to some extent influenced by acid–base medium. Reduction of both, hydroquinone and OXO tautomers produces an intermediate product (IV) which is transformed to anthrone in enol (V) and/or keto (VI) forms and finally to anthracene (VIII) and 9,10-dihydroantracene (IX).

In the present research, the type of compounds considered as degradation products and the reactions leading to their formation are discussed. In order to identify these products eAQ was reduced by means of classical methods [8–10]. The reduction was performed with metals (Zn, Sn) in acidic medium [9] and with $NaBH_4$ in methanol [10]. This latter procedure was used by Criswell and Klanderman [10] for the reduction of anthraquinone and its various derivatives among them 2-methyl-9,10-anthraquinone. The successive reductions of anthraquinone (AQ) produced at first 9,10-dihydroxy-9,10-dihydroanthracene (intermediate product IV, Scheme 2) and finally anthrone. This method was successfully adopted in the present work to prepare 2-ethyl-9,10-dihydroxy-9,10-dihydroanthracene (IV-E) as well as 2-ethylanthrone.

Catalytic hydrogenation of eAQ was performed in batch slurry reactor on 0.5% Pd/C, 0.5% Pd/SiO_2 and 0.5% Pd/Al_2O_3 with the aim to get more light on the problem of “degradation products”. Various by-products are identified as well as experimental evidences showing the formation of OXO-tautomers of partially and fully saturated hydroquinones (H_4eAQH_2 and H_8eAQH_2, respectively) are reported. It is also observed that the course of hydrogenolytic reactions is affected by the type of catalyst. 0.5% Pd/Al_2O_3 exhibits the highest ability to hydrogenolytic reactions and especially to the formation of intermediate product, a precursor of eAN.



Scheme 2. Reaction pattern during the reduction of anthraquinone by classical methods.

2. Experimental

2.1. Preparation of catalysts

Pd/C, Pd/SiO_2 and Pd/Al_2O_3 catalysts were prepared using commercial (Aldrich) materials, silica gel (156.4 m^2/g), γ-Al_2O_3 (155 m^2/g) and active carbon (760 m^2/g).

0.5% Pd/Al_2O_3, support (dried for 16 at 120 °C) was treated at room temperature with Pd^{2+} solution ($PdCl_2$ concentration 0.023 mol/dm^3 and NaCl 0.28 mol/dm^3, pH ∼3–4) up to the complete sorption of palladium ions confirmed by colorimetric method.

0.5% Pd/SiO_2, a well-established procedure commonly used to prepare the catalysts for anthraquinone process was used. In this procedure palladium hydroxide (or hydrated oxide) is precipitated on silica support pre-impregnated with alkaline reagent. In this work, silica (dried for 16 h at 120 °C) was at first pre-impregnated with Na_2CO_3 solution (0.05 mol/dm^3, 60 ml of solution per 10 g of support). Then, the obtained material was treated with Pd^{2+} solution ($PdCl_2$ concentration 0.023 mol/dm^3 and NaCl 0.28 mol/dm^3, pH ∼3–4) up to the complete precipitation of palladium ions on silica support.

0.5% Pd/C and 2% Pd/C, support (dried for 16 at 120 °C) was treated with appropriate volume of $PdCl_2$ solution ($PdCl_2$ concentration 0.0154 mol/dm^3, NaCl 0.0092 mol/dm^3 and HCl 0.033 mol/dm^3) to obtain 0.5 wt.% and 2 wt.% Pd in the final catalysts. The suspension was stirred at room temperature up to the complete sorption of palladium ions.

After the preparation, the catalysts were washed with water until the elimination of Cl^- ions and dried for 16 h at 120 °C.

The reduction of catalysts was performed with dihydrogen in the reactor (“in situ”, 30 min at 62 °C) immediately before the hydrogenation test.

2.2. Hydrogenation experiments

The catalytic test was carried out in agitated glass reactor at atmospheric pressure of hydrogen and temperature 62 °C [3]. A mixture of xylene–octanol-2 (volume ratio 1:1) was used as the solvent and the concentration of quinone was 20 g/dm^3. The course of hydrogenation was followed by measuring hydrogen uptake as a function of reaction time. In a typical hydrogenation experiment 0.28 g of catalyst in 20 cm^3 of solution was used and the reaction was carried out up to the consumption of ca. 2–3 mol of H_2 per 1 mol of quinone initially present in the reactor. The hydrogenation experiments were reproducible with ca. 5% over two to three catalysts batches.

2.3. Analytical procedure

In the course of reaction the samples of solution were taken at appropriate time intervals (15–20 min) and the composition of solution was analysed by HPLC and GC–MS methods. The hydroqinone forms ($eAQH_2$, H_4eAQH_2) present in the solution taken from the reactor are not stable in contact with air because they react spontaneously and quantitatively with atmospheric oxygen, thus forming hydrogen peroxide and regenerating quinones eAQ and H_4eAQ, respectively. In the oxidized solution normally used for analyses the hydroquinones are absent and only the corresponding quinones are present.

The content of reagents (number of moles of eAQ $\{n^t(\mathrm{eAQ})\}$ and H_4eAQ $\{n^t(H_4\mathrm{eAQ})\}$ at time t) was analysed in a re-oxidized solution by high-performance liquid chromatography (HPLC) using a chromatograph (Knauer) with UV detector (254 nm), 10 cm long, 1 mm in diameter column filled with SiO_2 fraction 5 μm, eluent: 2% isopropyl ether + 0.2% diglyme in heptane. The sum of eAQ and H_4eAQ moles was smaller that the initial content of eAQ. This difference is assumed as a cumulative content of degradation products (n_D) given by mass balance

$$N_D = n^0(\mathrm{eAQ}) - n^t(\mathrm{eAQ}) - n^t(H_4\mathrm{eAQ})$$

Compounds termed “degradation products” were analysed by GC–MS method using Perkin-Elmer Auto System XL, column PE-5 MS, 0.25 μm × 0.25 mm × 30 m long, isothermal run 200 °C, flow rate of He gas 1 ml/min. GC–MS method was also used to determine the products formed on eAQ reduction with classical methods. Reproducibility of the chromatographic analysis was ca. 5%.

3. Results and discussion

The hydrogenation experiments performed on 2% Pd/C catalyst provided most of data enabling identification of compounds, commonly considered as degradation products. A role of the type of catalyst is studied using 0.5% Pd/C, 0.5% Pd/Al_2O_3 and 0.5% Pd/SiO_2.

The hydrogenation of eAQ was carried out up to the consumption of ca. 2–3 mol of H_2 per 1 mol of eAQ. After the consumption of first equivalent of hydrogen a break on the hydrogen uptake curves appeared thus evidencing almost complete hydrogenation of quinone (eAQ) form to the hydroquinone ($eAQH_2$) one (Fig. 1). Further hydrogenation occurring at relatively low rate resulted in a slow consumption of hydroquinone $eAQH_2$, primary and desirable product. Present study focuses on this latter process.

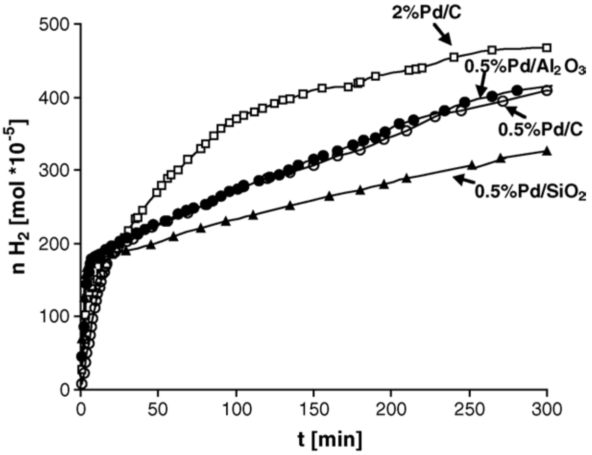


Fig. 1. Hydrogen consumption curves for hydrogenation of eAQ (conditions: 0.28 g of catalyst; 20 ml of eAQ solution; $n^0(\mathrm{eAQ}) = 167 \times 10^{-5}$ mol).

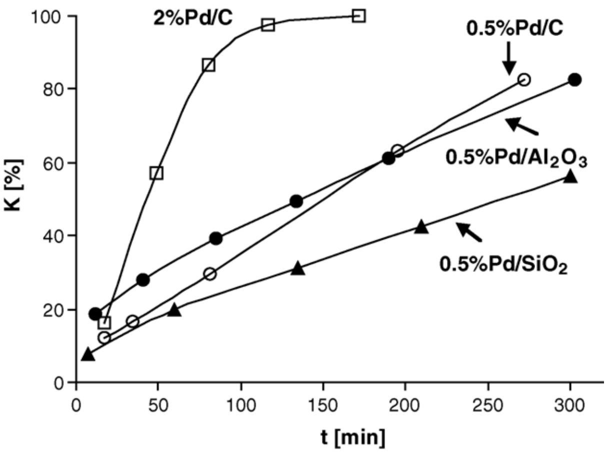


Fig. 2. Conversion of $eAQH_2$ as a function of reaction time.

The conversion of $eAQH_2$ against reaction time is plotted in Fig. 2. The contents of H_4eAQ and degradation products against the conversion of $eAQH_2$ are given in Fig. 3. In the present research, however, apart from the cumulative content of degradation products also the content of 2-ethylanthrone is studied. eAN in the form of two isomers eAN(1) and eAN(2) is detected in this work. Similarly to our previous observation [12] these isomers are attributed to enol and/or keto forms of 2-ethylanthrone. The sum of isomers [eAN(1) + eAN(2)] is plotted in Fig. 3.

Hydrogenation experiments on highly active 2% Pd/C catalyst makes possible the identification of various products formed before as well as after the complete conversion of hydroquinone $eAQH_2$.

As Fig. 3d shows on 2% Pd/C catalyst the cumulative content of degradation products is close to or only slightly higher than that of eAN up to ca. 80% of $eAQH_2$ conversion. As the reaction progresses the content of ethylanthrone passes through the maximum, whereas cumulative content of degradation products increases slowly during the whole hydrogenation experiment.

In the chromatogram of solution (Fig. 4a) registered before the maximum on eAN curve (at ca. 40% of $eAQH_2$ conversion) the peaks of eAQ + H_4eAQ (no. 1), two isomers of eAN (nos. 2 and 3) and a small one of iso-H_4 (no. 4) can be seen. The latter product, iso-H_4 (2-ethyl-1,2,3,4-tetrahydroanthraquinone) has already been observed in previous studies [11,12]. The products formed due to 2-ethylanthrone consumption by C–O hydrogenolysis as well as by the saturation of aromatic ring are detected at the end of experiments (Fig. 4b) only. In the former reaction 2-ethylanthracene (eANT, peak no. 8) and H_2eANT (peak no. 9), the product of eANT hydrogenation are formed, in the latter reaction two isomers of H_4eAN (peaks nos. 10 and 11) are produced.

Very interestingly, the saturation of aromatic ring in eAN is started even if $eAQH_2$ is present in the solution. On the other hand, the non-active H_8eAQH_2 was formed only after complete consumption of the starting hydroquinone $eAQH_2$ (Fig. 4b and c). This effect is in agreement with the observation of other authors [2] suggesting that the presence of not reacted $eAQH_2$ prevents the formation of fully saturated H_8eAQH_2.

Hence, degradation products formed from the beginning up to the maximum on eAN-curve predominantly contains eAN. Other degradation products (eANT, H_2eANT, H_4eAN, H_8eAQ) are formed only when almost all $eAQH_2$ is reacted.

It is clearly observable in Fig. 3a–c that 0.5% Pd/C, 0.5% Pd/SiO_2 and 0.5% Pd/Al_2O_3 catalysts differ in reactivity for individual reactions in which $eAQH_2$ is consumed. This difference in reactivity is especially evident in the initial stage of $eAQH_2$ conversion. Although the cumulative content of degradation products exceeds that of H_4eAQ on all three catalysts, domination of degradation reactions is the highest on 0.5% Pd/Al_2O_3. The formation of H_4eAQH_2 is observed from the very

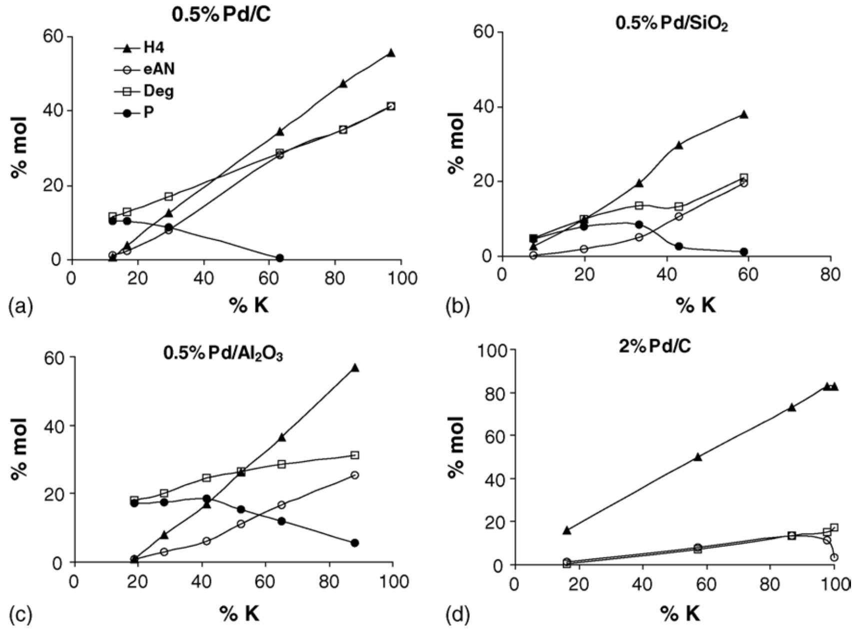


Fig. 3. The contents of H_4eAQ, degradation products (Deg), 2-ethylanthrone (eAN) and intermediate product (P) (mol%) as a function of $eAQH_2$ conversion (% K).

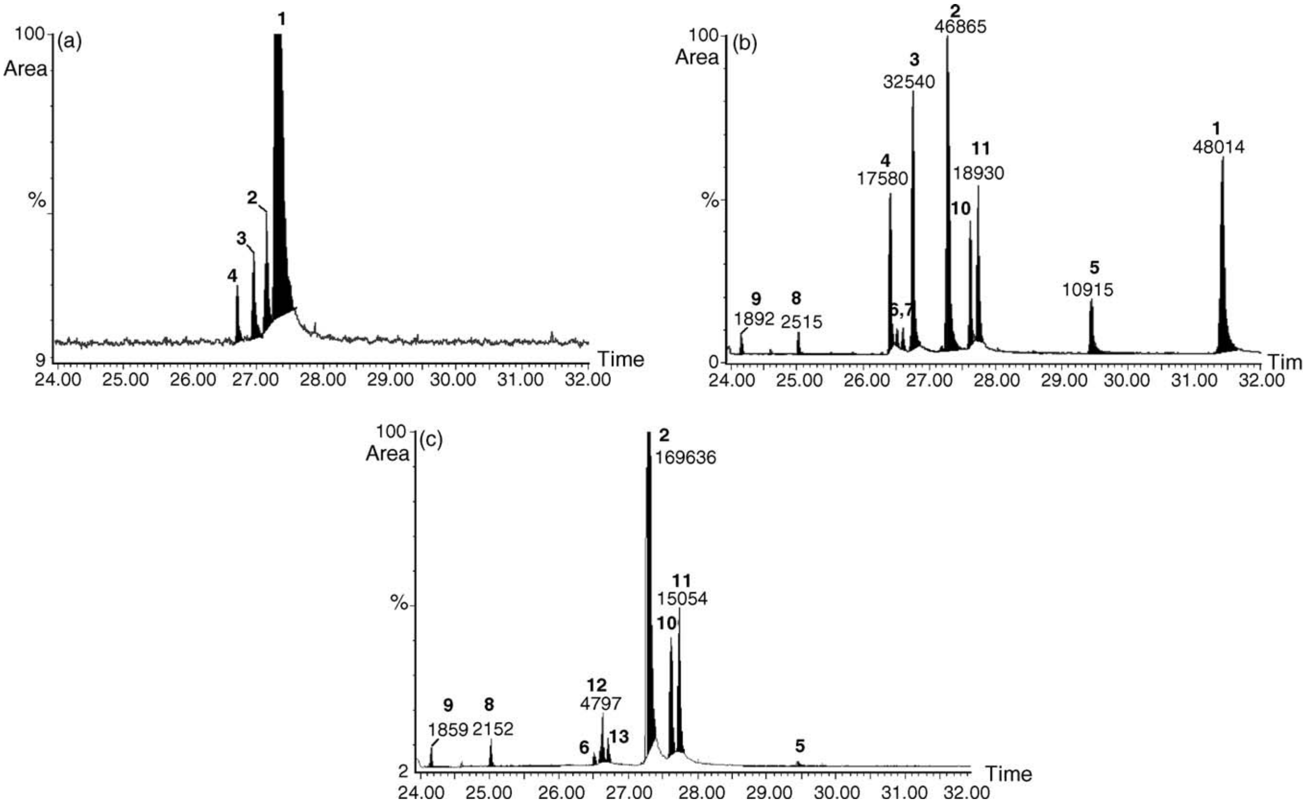


Fig. 4. The chromatograms (GC–MS) of solution, hydrogenation of eAQ in the presence of 2%Pd/C catalyst (conditions: 0.28 g of catalyst, 20 ml of eAQ solution, n^0(eAQ) = 167 × 10^{-5} mol). (a) Hydrogention carried out up to 40% conversion of $eAQH_2$, re-oxidized solution, peak no. 1, not separated eAQ and H_4eAQ; nos. 2 and 3, two isomers of eAN (1 + 2); no. 4, iso-H_4eAQ; (b) and (c) hydrogenation carried out up to the complete conversion of $eAQH_2$, (b) chromatogram registered immediately after taken the solution from reactor, (c) chromatogram registered after re-oxidation of solution. Peak no. 1, H_4eAQH_2; no. 2, H_4eAQ; nos. 3 and 4, two isomers of OXO-H_4, no. 5, H_8eAQH_2; nos. 6 and 7, two isomers of OXO-H_8; no. 8, eANT; no. 9, H_2eANT; nos. 10 and 11, two isomers of H_4eAN; no. 12, H_8eAQ; no. 13, iso-H_4eAQ.

beginning on 0.5% Pd/SiO_2 and 0.5% Pd/C catalysts, whereas this reaction is almost fully suppressed on 0.5% Pd/Al_2O_3 (up to ca. 20% conversion of $eAQH_2$). Such a difference in catalysts behaviour can be related with their reactivity in consecutive reactions (Scheme 2) in which $eAQH_2$ is reacted.

In view of Scheme 2 it is interesting to discuss relationships between the cumulative content of degradation products (Deg) and that of 2-ethylanthrone [eAN(1) + eAN(2)].

In the presence of all catalysts the cumulative content of degradation products is much higher than that of eAN in the initial stage of $eAQH_2$ consumption. As the reaction progresses such predomination slowly decreases and finally, almost all degradation products are transformed to eAN. This observation is well confirmed by the GC–MS analysis showing two strong peaks of 2-ethylanthrone [eAN(1) and eAN(2)] only. Besides eAN, very small peaks of H_4eAN, the products formed by the saturation of phenyl ring in eAN are also observed. The formation of eANT and other side products like fully saturated H_8eAQ was found to be negligible. Hence, “degradation products” formed from the very beginning of $eAQH_2$ consumption contains not only eAN but also intermediate products, because they are almost fully transformed to 2-ethylanthrone (eAN). The content of such intermediate products (P) calculated as the difference between the cumulative content of degradation products and that of eAN is plotted in Fig. 3. From this figure, it can be seen that the maximum on P-curves is reached. Very interestingly, the highest content of P is formed on 0.5% Pd/Al_2O_3 catalyst.

Scheme 2 shows that as hypothetical intermediate products preceding the formation of eAN both reagents OXO-E, the tautomerized form of $eAQH_2$ and 2-ethyl-9,10-dihydroxy-9,10-dihydroanthracene (IV-E) can be taken into consideration.

It is well known that hydroquinone ($eAQH_2$) is spontaneously and quickly oxidized with air to the quinone (eAQ) form. On the other hand, it has been reported that OXO-E, the tautomerized form of $eAQH_2$ is stable in contact with air (in solid state) [1,9]. Transformation of OXO-E to the starting hydroquinone $eAQH_2$ in benzene or methanol solutions is a very slow process. In an atmosphere of nitrogen and at 20 °C after 180 h only 50% of OXO-E was transformed back to $eAQH_2$, at 60 ° this process was completed after 6 h [9].

In the present studies, OXO-E was only occasionally detected by GC–MS analysis. Two peaks (retention time 28.15 and 28.26 min) of $m/z = 238$ corresponding to molecular formula $C_{14}H_9O_2C_2H_5$ detected in the chromatograms suggest two isomers OXO-E(1) and OXO-E(2). No rational arguments can be given with respect to conditions favouring the formation of OXO-E. However, it cannot be excluded that the content of OXO-E was too small to be detected in the conditions used in the present GC analysis.

On the other hand, OXO-tautomers of partially (H_4eAQH_2) and fully (H_8eAQH_2) saturated hydroquinones are easily detected during the catalytic experiments. It is well known that such hydroquinones forms, both are much more stable in contact with air than is $eAQH_2$. Longer time is required to transform these hydroquinones to the corresponding quinones (H_4eAQ and H_8eAQ, respectively). Consequently, the peaks of hydroquinones as well as quinones forms of partially and fully saturated eAQ are detected in the chromatogram. Fig. 4b shows the chromatogram of solution registered immediately after withdrawing from the reactor and Fig. 4c, the one registered after re-oxidation of solution (20 h in contact with air). In the former, except the intensive peaks of hydroquinone H_4eAQH_2 (no. 1) and quinone H_4eAQ (no. 2) (formed on partial re-oxidation of hydroquinone) also two peaks of OXO-H_4 tautomers (nos. 3 and 4) can be seen. Their molecular peaks at $m/z = 242$ (molecular formula $C_{14}H_{13}O_2C_2H_5$) and fragmentation pathways very well correspond to the OXO-H_4 tautomers. Practically identical fragmentation pathways of both OXO-H_4(1) and OXO-H_4(2) make difficult the discrimination between two isomers from the MS analysis only. The peaks of fully saturated hydroquinone H_8eAQH_2 (no. 5) and its OXO-H_8 tautomers (nos. 6 and 7) can also be seen in this chromatogram. The peaks of hydroquinones and OXO-tautomers of partially saturated H_4eAQ completely vanished as the expense of that of quinone form (no. 2) in the re-oxidized solution (Fig. 4c). Oxidation of fully saturated H_8eAQH_2 and its OXO-tautomers also proceeds but to lower extent compared to that of H_4eAQ forms. It is interesting to note that the intensity of both OXO-H_4 peaks evidently exceeds that of hydroquinone form. Hence, hydroquinone H_4eAQH_2 tautomerizes very easily and the equilibrium in the H_4eAQH_2-OXO-H_4 system is strongly shifted to the OXO-tautomers. This equilibrium is also shifted to the OXO-tautomers in the case of H_8eAQH_2, fully saturated hydroquinone. Hence, both hydroquinones, H_4eAQH_2 and H_8eAQH_2 tautomerize to the corresponding OXO-forms and in both cases the hydroquinone-OXO equilibrium is shifted to the OXO forms.

To identify 2-ethyl-9,10-dihydroxy-9,10-dihydroanthracene (IV-E), the second intermediate product preceding eAN (Scheme 2) the reduction of carbonyl groups in eAQ was performed with classical methods [9,10]. Reduction of eAQ with Sn or Zn in acidic ($HCl + CH_3COOH$) medium produces a mixture composed mainly of 2-ethylanthrone (eAN) and 2-ethylanthracene (eANT). Intermediate product, 2-ethyl-9,10-dihydroxy-9,10-dihydroanthracene (IV-E) was prepared by the reduction of eAQ with sodium borohydride in methanol [10]. A white precipitate of IV-E was formed (m.p. 162–167 °C, elemental analysis 79.88% C, 6.64% H) with very high yield (∼95%). FTIR spectrum of the obtained IV-E product was very similar to the one reported for the 2-methyl-derivative of IV [10]. The most characteristic spectral features of IV-E structure, a strong C–O stretching band at $1031\ cm^{-1}$ and the strong peak attributed to intramolecular hydrogen bond at about $3280\ cm^{-1}$ appeared in the IR spectrum of our IV-E product. The GC–MS analysis showed the molecular peak at $m/z = 240$ ($C_{14}H_{11}O_2C_2H_5$) ($t = 27.70$ min) as well as the fragmentation pathway well confirming the proposed IV-E molecular structure. IV-E is only slightly dissolved in less polar organic solvents like *n*-heptane, xylene, better dissolved in ocatnol-2 and easily dissolved in ethanol and methanol. FTIR confirms that IV-E (in solid state) is stable in contact with air (1 month).

The retention time of chromatographic peak characteristic of IV-E (Fig. 5, peak no. 1, $t = 27.70$ min) is very near to that of non-separated peak of eAQ ($t = 27.38$ min) and H_4eAQ ($t = 27.28$). Therefore, the peak of IV-E can be detected only when the content of quinones, eAQ + H_4eAQ is very low and that of IV-E high. However, in a typical analysis carried out during the catalytic hydrogenation, the content of quinones is much higher than that of IV-E. As a consequence, non-separated peak of quinones (eAQ + H_4eAQ) is very intensive and wide. It strongly overlaps with that of IV-E. From Fig. 3 it can be seen that the maximum content of P is equal to ca. 18 mol% only and it is reached in the initial stage of hydrogenation when the content of quinones (especially eAQ) is distinctly higher. Therefore, detection of IV-E peak at this high content of quinones is practically impossible in the conditions used in the present analysis.

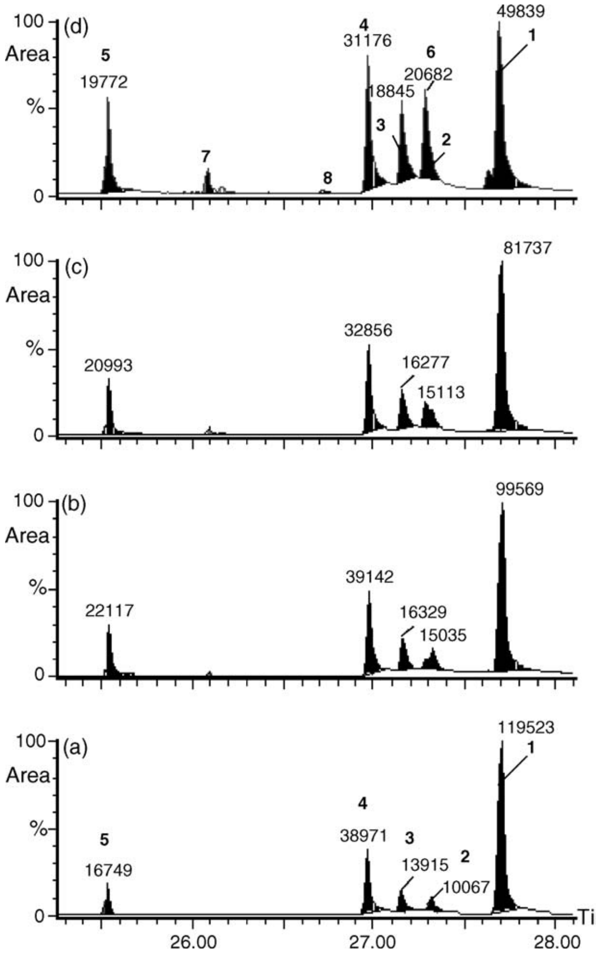
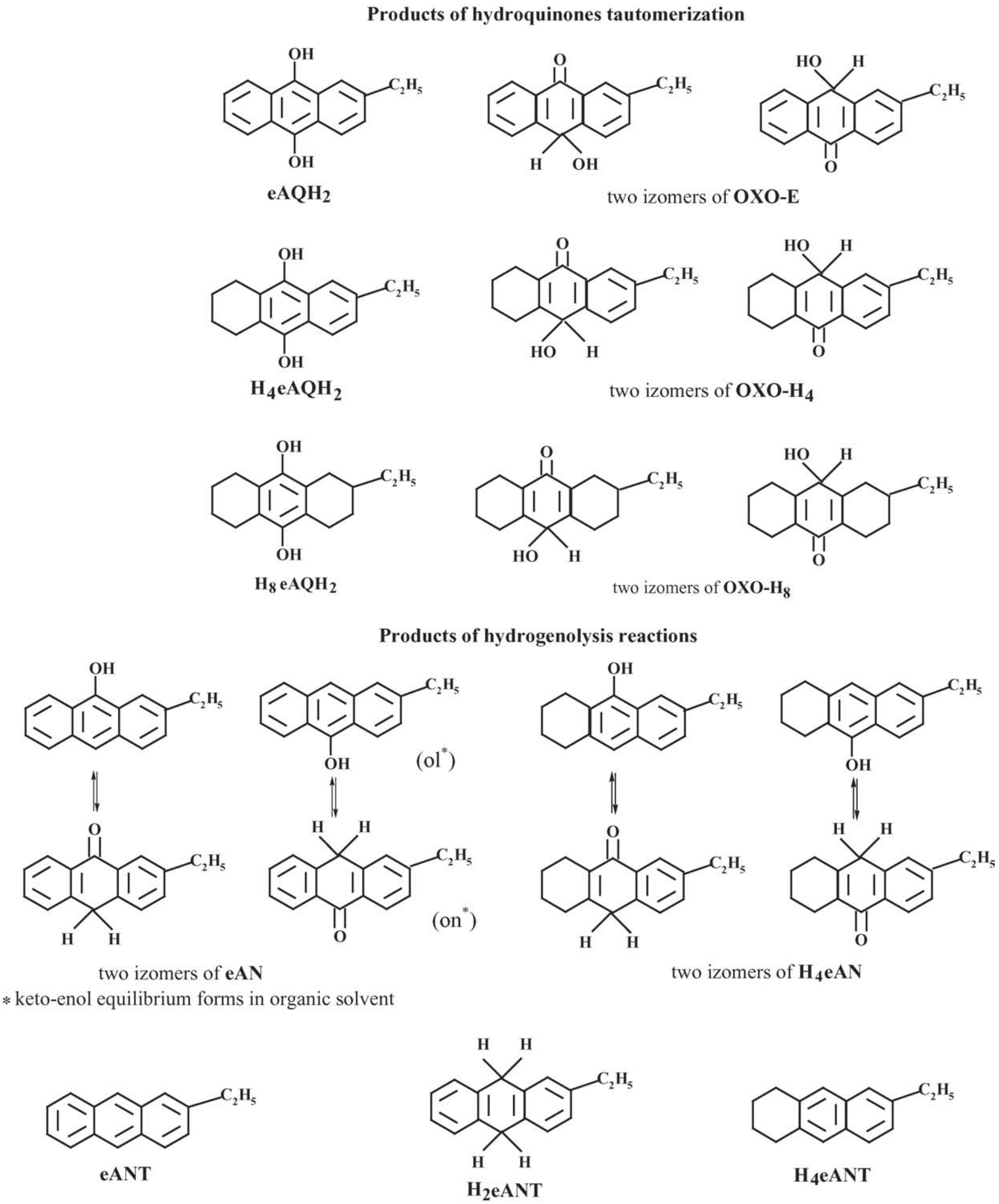


Fig. 5. Hydrogenation of IV-E carried out in conditions: 0.28 g of 0.5%Pd/SiO_2 catalyst, 30 ml of IV-E solution, concentration of IV-E equal to 13 g/dm^3. The chromatograms (GC–MS) of solutions; initial solution (a), conversion of IV-E equal to 17% (b) 32% (c) and 59% (d). Peak no. 1, IV-E; no. 2, eAQ; nos. 3 and 4, two isomers of eAN; no. 5, eANT; no. 6, H_4eAQ; nos. 7 and 8, unidentified compounds.

Fig. 5 shows the chromatograms registered during the hydrogenation of IV-E (0.5% Pd/SiO_2, xylene–octanol-2 mixture as solvent, 62 °C). In order to better recognize the changes of reagents contents, the areas of individual peaks are given in the chromatograms. Decrease in the content of IV-E (peak no. 1) is accompanied by the slow increase in intensity of peaks characteristic of eAN-1 (no. 4) and eANT (no. 5). Formation of these products reveals the hydrogenolytic cleavage of C–O in the IV-E reagent.

Although the starting solution of IV-E contains very low amount of eAQ (peak no. 2) (contamination after the preparation), the peak of eAQ does not decrease during the hydrogenation experiment, whereas slowly increases the peak of H_4eAQ (no. 6), the product formed by hydrogenation of aromatic ring.



Scheme 3. Products formed during the catalytic hydrogenation of eAQ.

Hence, IV-E is an intermediate product also for the formation of H_4eAQH_2. This finding confirms very well previous assumption [3] that both reactions, the hydrogenation of phenyl ring and the hydrogenolysis of C–O in $eAQH_2$ proceed via the same intermediate product, which is identified in the present work as IV-E reagent.

It is evident from the catalytic results that $eAQH_2$, the hydroquinone form of parent quinone participates in the phenyl ring saturation and hydrogenolytic cleavage of C–O. In contrast, the hydroquinone form of H_4eAQ participates only in the hydrogenation of aromatic ring.

When H_4eAQ is catalytically hydrogenated (0.5% Pd/SiO_2, xylene–octanol-2 mixture as solvent, 62 °C) besides the hydroquinone H_4eAQH_2 and OXO-H_4(1,2) tautomers, fully saturated H_8eAQH_2 and OXO-H_8 tautomers are formed as the only products. No hydrogenolysis-deriving products are then produced. This observation is very consistent with the literature data suggesting that hydrogenolysis-deriving products are formed due to the consumption of $eAQH_2$ only [1].

The obtained results clearly show that degradation of $eAQH_2$ yields various products. The kind of theses products strongly depends on the conversion of $eAQH_2$. In the initial stage of $eAQH_2$ consumption, intermediate product P and eAN are formed as the only degradation products. Although analytical difficulties with the identification of this intermediate product P exist, in view of Scheme 2, the compounds IV-E and OXO-E are the only products which can be fully transformed to eAN identically to the observation in the present studies (Fig. 3).

As the reaction progresses, almost all intermediate products (P) are transformed to eAN and the latter is slowly reacted to other by-products. The hydrogenolysis of C–O in eAN produces 2-ethylanthracene (eANT), which is slowly hydrogenated to H_2eANT. Other process consuming eAN is the saturation of phenyl ring giving two isomers of H_4eAN (1, 2). All of the products identified in this work are collected in Scheme 3. The products known from the literature (H_4eAQH_2, H_8eAQH_2, OXO-form of $eAQH_2$, eAN, eANT) are also given there.

It should be pointed out, that identical by-products are observed on all studied catalysts. The catalysts 0.5% Pd/C, 0.5% Pd/SiO_2 and 0.5% Pd/Al_2O_3 differ, however, in reactivity towards consecutive reactions in which intermediate product P and eAN are formed. Such a difference is evidenced by the products distribution curves in Fig. 3. Similarly, to the previous findings [9] much higher reactivity in the whole process of $eAQH_2$ degradation is observed for 0.5% Pd/Al_2O_3. At the same conversion of $eAQH_2$ evidently lower content of H_4eAQ is formed on 0.5% Pd/Al_2O_3 compared with those on 0.5% Pd/C and 0.5% Pd/SiO_2 catalysts. On both 0.5% Pd/C and 0.5% Pd/SiO_2 catalysts almost all content of P is transformed to eAN up to ca. 40–50% conversion of $eAQH_2$. On the other hand, this transformation is not complete even at 90% conversion of $eAQH_2$ in the case of 0.5% Pd/Al_2O_3. It is also clearly observable in Fig. 3 that the intermediate product P reaches the highest content on alumina-supported catalyst.

In conclusion, reactivities of 0.5% Pd/C and 0.5% Pd/SiO_2 catalysts in the transformation of hydroquinone $eAQH_2$ to intermediate products P and subsequently to eAN are comparable. Such reactivities differ, however, from that of 0.5%Pd/Al_2O_3 which exhibits much higher ability to the formation of intermediate product (IV-E and/or OXO-E).

A difference between alumina and silica supported palladium catalysts with respect to the formation of degradation products has already been reported [6]. Degradation of eAQ dominated on Pd/Al_2O_3, while Pd/SiO_2 favoured the hydrogenation of aromatic rings resulting in H_4eAQ. The results obtained in this work are very consistent with these observations. Moreover, from the present results it can be concluded that the observed high reactivity of Pd/Al_2O_3 in degradation of eAQ is in fact a high ability of this catalyst to the formation of intermediate product, precursor of eAN and H_4eAQ.

At the present stage of the investigation, no further explanation can be given with respect to the role of the type of catalyst. To discuss the observed difference in catalysts performance more data with regard to the characterization of catalysts properties are needed, before we can speculate further.

4. Conclusions

The obtained results show that degradation process is concentrated on hydroquinone $eAQH_2$ and various products are then formed. They differ substantially depending on the conversion of $eAQH_2$. In the initial stage of $eAQH_2$ consumption besides the active quinone H_4eAQH_2/OXO-H_4 (1, 2), as the only degradation products, intermediate product P and eAN are observed. As the reaction progresses, almost all intermediate product is transformed to eAN which is slowly reacted to other by-products. The hydrogenolysis of C–O in eAN results in 2-ethylanthracene (eANT) and subsequently in H_2eAN, the saturation of phenyl ring in eAN produces two isomers of H_4eAN (1, 2). The transformation of eAN to by-products proceeds even before the complete consumption of $eAQH_2$, whereas the hydrogenation of second aromatic ring producing fully saturated non-active H_8eAQH_2/OXO-H_8 is observed only after complete consumption of hydroquinone $eAQH_2$. eAN is formed in a consecutive reaction via an intermediate product P, which is most probable composed of OXO-E (tautomer of hydroquinone) and 2-ethyl-9,10-dihydro-9,10-dihydroxyanthraquinone (IV-E). This latter product was prepared by reduction of eAQ with $NaBH_4$. The catalysts 0.5% Pd/C, 0.5% Pd/SiO_2 and 0.5% Pd/Al_2O_3 differ in performance and especially in reactivity towards consecutive reaction in which intermediate products and eAN are formed. Pd/Al_2O_3 exhibits much higher reactivity in the whole degradation process as well as in the formation of intermediate product.

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