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SELECTIVE OXIDATION OF ANTHRACENE TO ANTHRAQUINONE IN ACETIC ACID WITH AIR IN PRESENCE OF NITRIC ACID

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Summary: The oxidation of anthracene in acetic acid with air in the presence of small proportions of nitric acid produces high quality anthraquinone with acceptable yields. A possible mechanism is suggested which explains the predominance of the oxidation reaction compared with that of nitration.

The oxidation of anthracene in liquid phase is of great interest as anthraquinone is obtained in operating conditions which are less exacting than those employed on industrial scale. Among the numerous oxidizing systems tested on acetic acid solutions, which are the most usual medium, these may be mentioned: cerium ammonium nitrate[1], tert-butylhydroperoxide[2], copper (II) chloro complexes[3], pyridinium fluorochromate[4], potassium bromate[5] and ammonium dichromate[6].

This work studies the oxidation of anthracene in acetic acid with air in the presence of small amounts of nitric acid. The experiments were carried out in a semibatch reactor open to the atmosphere, provided with heating, agitation and reflux condensation systems. The experimental procedure is the following: once the anthracene solution (28 mmol) in acetic acid (125 ml) reaches a temperature of 95ºC, the drip is begun of nitric acid 62.7% in weight (14 mmol) and the bubbling of the air stream (0.075 l/min) in the liquid phase. When the reaction time established is complete, the reaction product is precipitated by cooling the system to room temperature, separated by vacuum filtration, washed with warm water, dried at 105ºC, weighed and resolved in cyclohexanone. Afterward, the samples are analyzed by liquid chromatography (HPLC). An ODS-SilX-C-18, 10 μm, 25x4.6 cm reverse phase column was employed. The mobile phase consisted of 82% of methanol in water. The column temperature was held at 40ºC, with an eluent flow rate of 1.5 ml/min. The injection volume was 5 μl and a 254 nm wavelength UV detector was used.

The results contained in Table 1 show the influence of the proportion of nitric acid with regard to the substrate on the anthraquinone purity of the precipitated reaction product, as well as on the yield of anthracene to anthraquinone. For the molar ratio nitric acid/anthracene unit, 80% yield in anthraquinone is obtained. The precipitated solid contains 99.6% of anthraquinone. Below this nitric acid/anthracene ratio, the oxidation yield diminishes as the amount of nitric acid added is reduced. In these conditions the formation of 9-nitroanthracene is practically nul. When the ratio is greater than the unit, the nitration is favoured to the detriment of that from oxidation. This fact is more pronounced the greater the proportion of nitric acid tested.

In the reaction medium used the following equilibria, among others, are involved:

$$2\ HNO_3 \rightleftarrows NO_2 + H_2O + 1/2\ O_2 \qquad [1]$$

$$2\ HNO_3 + NO \rightleftarrows 3\ NO_2 + H_2O \qquad [2]$$

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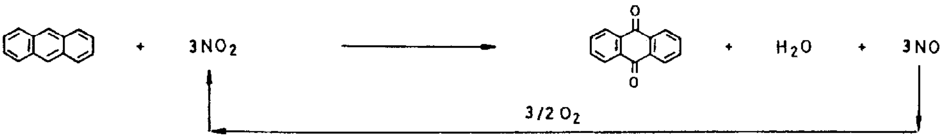
Table 1.- Anthracene oxidation. Experimental Results.

Run[a)]	Molar ratio HNO3/AN	Yield in AQ(%)	Purity(%)		
			AQ	9-NAN	AN
1	-	4.1	1.0	-	99.0
2	0.25	43.8	58.4	-	41.6
3[b)]	0.50	12.3	9.7	-	90.3
4	0.50	70.6	89.3	0.3	9.4
5	0.75	76.9	94.6	-	5.4
6	1.00	80.2	99.6	0.4	-
7	1.25	78.5	96.8	3.2	-
8	1.50	77.5	91.5	8.5	-
9	1.75	75.4	86.2	13.8	-
10	2.00	74.1	84.6	15.4	-

[a)] Conditions: 28mmol of AN, 125 ml AcOH 95%, 0.075 ml/mim of air, 95ºC, 2h.

[b)] No oxygen uptake. AN = Anthracene; AQ = Anthraquinone; 9-NAN = 9-Nitroanthracene

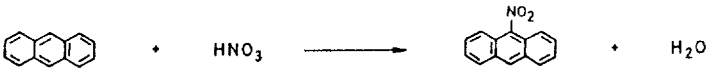
The oxidation reaction takes place due to the action of the nitrogen dioxide in the following way:



[3]

The presence of air is therefore indispensable in order to regenerate the nitrogen dioxide consumed. As is revealed in Table 1 the use of air or nitric acid separately in the oxidation of anthracene does not provide interesting results. However the joint use of both of oxidizing agents does prove satisfactory.

In an excess of nitric acid the nitration reaction,



[4]

is significant compared with that oxidation and it comes about through the action of the nitronium ion[7]. Thus, the predominance of one reaction over another is a function of the concentration of nitric acid in the medium with regard to that of the substrate.

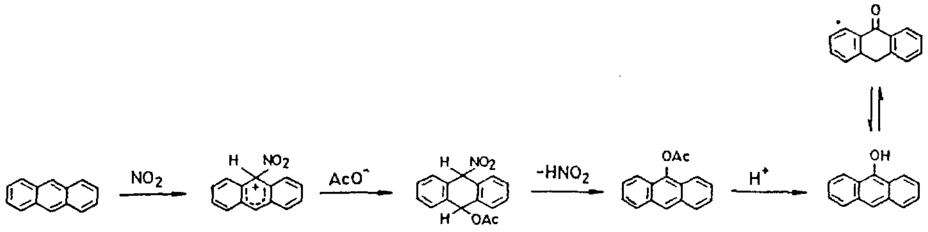


Figure 1.- Oxidation mechanism scheme.

In the reaction product precipitated intermediate oxidation compounds are not found. Analyses of the liquid phase indicates the presence of 9-acetoxyanthracene and anthrone, in a proportion which is greater the shorter the reaction time is. The anthracene oxidation mechanism to anthraquinone by means of nitrogen dioxide is not clearly established. Thus, in order to explain this reaction path, an electron-transfer was proposed[8]. However, the oxidation of anthracene and related hydrocarbons with nitrogen dioxide by electron transfer has recently rejected as a result of the standard electrode potentials involved[9]. In this work an oxidation mechanism of anthracene to anthrone with nitrogen dioxide in acetic acid by aromatic electrophilic substitution is suggested (Figure 1). The anthrone oxidation mechanism to anthraquinone is yet to be established.In its initial stage, the mechanism can be considered as normal aromatic electrophilic substitution. In this is formed, from the anthracene, the 9-nitro-9,10-dihydroanthracene cation (characteristic Wheland intermediate). This cation can react with the nucleophilic species acetate anion in order to give 9-nitro-10-acetoxy- 9,10-dihydroanthracene[10]. This compound can lose one nitrous acid molecule[10], turning by aromatization into 9-acetoxyanthracene, which is easily hydrolyzed in acetic acid medium in order to give 9-anthranol, according to the experimental results obtained by Gronowska and Dzielendziak[11] for referable compounds. The 9- anthranol is in equilibrium with its tautomeric form, the anthrone.

The presence of 9-nitroanthracene is justified by the classic aromatic electrophilic susbstitution mechanism[7]. Given the characteristics of the Wheland intermediate proposed, which is susceptible of aromatization or stabilizing, its participation in the formation of 9-nitroanthracene cannot be neglected.

The oxidation and nitration mechanisms suggested demand the following equilibria:

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+ \tag*{[5]}$$

$$2\,HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O \tag*{[6]}$$

$$NO_2^+ + CH_3COO^- \rightleftarrows CH_3COONO_2 \tag*{[7]}$$

The first equilibrium represents the dissociation of the acetic acid necessary in order to have available the nucleophilic species, the acetate anion, whose participation is basic in the oxidation of anthracene to 9-acetoxyanthracene. The following equilibrium justifies the presence of the nitronium ion, responsible for nitration. The last equilibrium allows the abstraction of the nitronium ion, thus reducing nitration.

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