

Studies on Humic Acids

V*. The Reaction of *p*-Benzoquinone with Alkali

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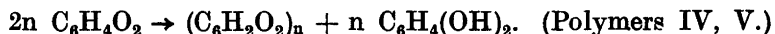
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p-Benzoquinone, treated with alkali yields hydroquinone and amorphous "quinone humic acids". The amount of hydroquinone increases with increasing alkalinity. With weak alkali polyhydroquinones are probably formed, *e. g.* $[\text{C}_6\text{H}_4(\text{OH})_2]_n$ which are oxidised by quinone to partly quinonoid products with formation of hydroquinone (15–30 %). Investigations of the humic acid itself seems to support this theory. With strong alkali over 50 % hydroquinone is formed and the polymeric acid should correspondingly be more highly oxidised. The results obtained with these products were, however, inconsistent.

Many quinones when treated with alkali undergo disproportionation leading to the corresponding hydroquinones and amorphous polymerisation products, "quinone humic acids". The nature of these acids is obscure, but they are obviously related to the "humic acids" formed on alkaline oxidation of the corresponding phenols and, according to Eller¹, also to the natural humic acids obtained from soil, peat and brown coal. Eller suggested that all these products are polymeric hydroxyquinones and one of us (H. E.), that the polymerisation essentially involves the formation of diphenyl linkages². There are numerous examples of the facile formation of diphenyl derivatives from simple phenols and quinones.

In a very simplified manner the polymerisation of *p*-benzoquinone in the absence of other oxidising substances, *e. g.* air, may be discussed in the following way.

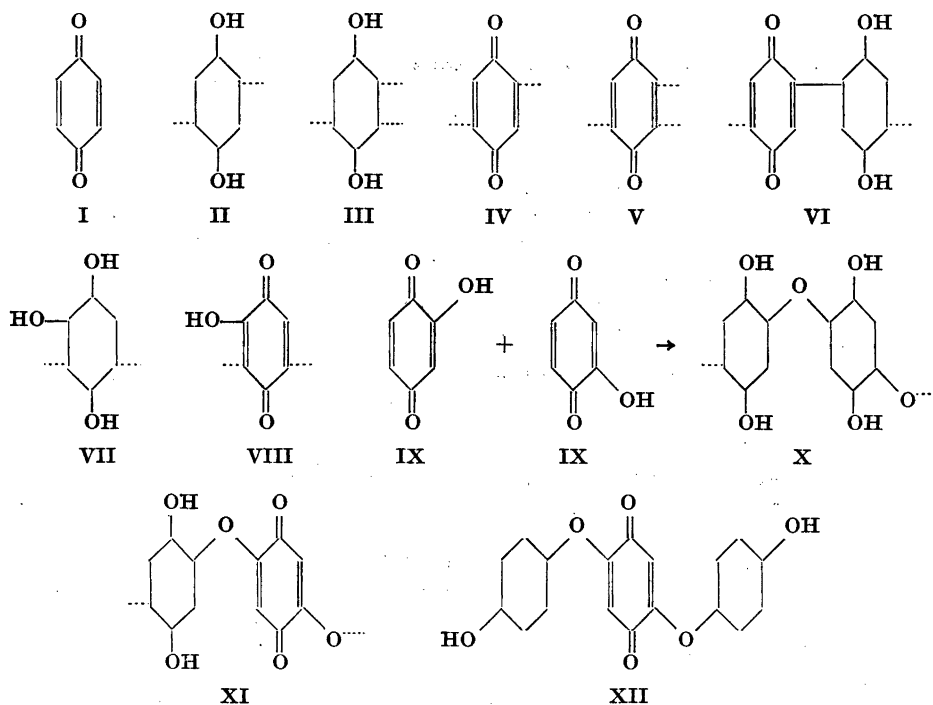
Quinone ($\text{C}_6\text{H}_4\text{O}_2$) (I) may be transformed into a linear polymer II (or more probably into a three dimensional polymer containing elements of type III) without formation of hydroquinone: $n \text{C}_6\text{H}_4\text{O}_2 \rightarrow (\text{C}_6\text{H}_4\text{O}_2)_n$. Dehydrogenation of such polymers to a more or less quinonoid stage by unchanged quinone would require the simultaneous formation of up to 50 % hydroquinone:



* Continuing the series *Studies on the Formation of Complex Oxidation and Condensation Products of Phenols*, *Proc. Roy. Soc. (London)*, A 143 (1933) 177, 191, 223, 228.

All intermediate degrees of oxidation (e.g. VI) are possible and yields of hydroquinone varying between 0 and 50 % would therefore be theoretically possible.

Complications due to nuclear hydroxylation may be expected and for the formation of polymer VII, $(C_6H_4O_3)_n$, (which is equivalent to IV as regards degree of oxidation) we have the following balance: $2n C_6H_4O_2 + n H_2O \rightarrow (C_6H_4O_3)_n + n C_6H_4(OH)_2$ requiring the formation of 50 % hydroquinone. Complete oxidation to polymer VIII would increase the quantity of hydroquinone, to a possible maximum yield of about 67 %.



Flaig³ assumed that the oxidation of hydroquinone in alkali to a humic acid proceeds *via* hydroxyquinone (IX) which is polymerised in a way "resembling the Thiele acetylation" to X. We have no reason to believe that the humic acids produced by oxidation of phenols and decomposition of quinones in alkali have fundamentally different structures. The polymer X has the same composition as polymer VII and if obtained by anaerobic polymerisation of quinone would require the simultaneous formation of about 50 % hydroquinone (if completely oxidised to XI, 60 %). As will be shown below quinone actually may be polymerised by weak alkali with formation of only about 15–20 % hydroquinone and this makes Flaig's mechanism of humic acid formation improbable. Moreover polymer XI would presumably not be capable of existence in alkaline solution but would suffer hydrolysis with formation of

2,5-dihydroxyquinone, a compound which has never been observed as a product of the alkaline decomposition of quinone. Diels and Kassebart's interesting quinone trimeride (XII) obtained from quinone by the action of pyridine is easily hydrolysed by alkali to hydroquinone and 2,5-dihydroxyquinone⁴. The success of this trimerisation is due to the specific participation of pyridine in the process, as recognised by Diels.

It is true that *p*-xyloquinone and thymoquinone on treatment with alkali do not yield typical humic acids but undergo some other type of reaction. Di-, tri- and tetra-quinone, however, yield typical humic acids when treated with alkali (Erdtman, Granath and Schultz, forthcoming publication).

From the above discussion it is evident that the yields of hydroquinone actually obtained on alkaline polymerisation of quinone are of importance for the understanding of the polymerisation process and the structure of the polymers. Consequently we have studied this problem in some detail and some of the results are recorded in Table 1.

Table 1. Per cent hydroquinone formed from quinone on polymerisation with alkali. In all experiments 0.01 mole quinone was added to 10 ml sodium hydroxide solution.

Normality of sodium hydroxide solution	Time of reaction	Per cent hydroquinone
15	120 min	63
10	15 »	52
10	24 hours	51
5	24 »	39
2	15 min	35
1	15 »	28
1	24 hours	25
0.5	15 min	23
0.5	24 hours	21
0.25	24 »	20
0.1	24 »	— *
NaAc	20 days	14 **

* Solution almost neutral. Partial decomposition only.

** Details see below.

As seen from Table 1 the yield of hydroquinone varies greatly. Strongly alkaline media favour the formation of hydroquinone (increase the degree of oxidation of the polymerisation product). The yield of hydroquinone is independent of the amount of alkali used in the experiments, except at low alkali concentrations when the effect of the neutralisation of the alkali by the humic acid is noticeable.

Reaction of quinone with methanolic sodium hydroxide also furnishes hydroquinone, e.g. with 2 *N* sodium hydroxide 34 % as compared with 35 % obtained with aqueous sodium hydroxide.

It was of course of interest to see whether the formation of hydroquinone could be depressed below 20 %, (the minimum reached in our experiments with sodium hydroxide) by employing still weaker alkali, and quinone was therefore treated with a saturated sodium acetate solution in the presence of

undissolved sodium acetate. Under these conditions the reaction was slow. A yield of only 14–15 % hydroquinone was obtained and in this case the hydroquinone was contaminated with a little 2,5,2'5'-tetrahydroxydiphenyl (about 1–2 % of the quinone). This observation provides an interesting indication of the probable route of polymerisation.

The results recorded in Table 1 support our assumption that quinone humic acids are formed by nuclear C-C-coupling. In weak alkali (low yields of hydroquinone) the polymeric product appears to contain mainly elements of types II and III with relatively small amounts of structures IV, V, VII and VIII.

In stronger alkali when high yields of hydroquinone are obtained the polymers probably possess a higher degree of oxidation. This may be due to a higher percentage of quinonoid nuclei and/or structures of the types VII and VIII.

As already mentioned, pure phenol ether structures (X, XI) are improbable but diphenyleneoxide groups may well be formed especially after the acidification of the reaction mixtures. The observation that humic acids which have been dried in air or even stored under water for some time exhibit a decreased reactivity may perhaps be explained by such complications.

The amorphous nature of the humic acids and their derivatives is easily understood on the basis of the above considerations. They obviously possess a very complex and irregular structure and the number of possible atropisomerides is very great.

The humic acids dissolve in alkali giving green or brown solutions which absorb oxygen with the greatest of ease yielding deep brown solutions. This phenomenon is particularly pronounced with the "sodium acetate humic acid" and is probably due to the oxidation of the primary polymers to products containing a larger percentage of quinonoid nuclei.

In our studies on the chemistry of the polymeric products we encountered all the hardships inherent in humic acid research. Strictly reproducible results could never be obtained, especially with the products obtained with strong alkali. However, as expected, the product obtained with sodium acetate gave less confusing results, some of which are therefore recorded.

Methylation with dimethyl sulphate and alkali in the absence of oxygen yielded products containing 20–25 % methoxyl increased by further methylation with diazomethane to 24–25 %. (A polymer of type VI with OCH_3 instead of OH requires 25.5 % methoxyl.) The analytical data for hydrogen and carbon give little information. A methylated polymer II requires 70.6 % C and 5.9 % H and methylated VI 69.4 % C and 4.1 % H. Most of our products had 66.2–68 % C and 4.1–4.5 % H.

Similar result were obtained on reductive acetylation with zinc and acetic anhydride. The light coloured products contained 50–51 % acetoxy increased to 56 % on renewed reductive acetylation. (An acetylated polymer II requires 61.4 % acetoxy, 62.5 % C and 4.2 % H. A "monoacetate" of II requires 39.3 % acetoxy, 64.0 % C and 4.0 % H. Found: 62.1–62.6 % C and 4.4–4.7 % H.)

When hydrolysed with alkali in the absence of air, solutions were obtained which absorbed oxygen with the development of a green colour soon changing to brown.

The results obtained with these humic acid preparations are at least qualitatively in harmony with the view that they consist essentially of partly oxidised polymers of the types II and III.

EXPERIMENTAL

Reaction of p-benzoquinone with alkali: Quinone (1.1 g) was very finely powdered and added under hydrogen to oxygen free sodium hydroxide solutions (10 ml) of varying concentrations and the mixture vigorously shaken. After the decomposition of the quinone the solutions were acidified with 2 N sulphuric acid allowing no contact with air as long as the solution was alkaline. If necessary, the humic acid suspension was boiled briefly in order to facilitate filtration. The precipitate was carefully washed with 1 % sulphuric acid and the filtrate and washings exhaustively extracted with ether. The light brown ether solution was dried (Na_2SO_4), filtered through a short column of aluminium oxide to remove a small amount of brown impurities and the ether evaporated. The residue was almost pure hydroquinone as shown by the melting point and mixed melting point with an authentic specimen. The experiments were run in duplicate, the results varying within one or two per cent. Compare further Table 1.

Reaction of quinone with sodium acetate: Finely powdered quinone (1.1 g) was mixed with powdered anhydrous sodium acetate (8.2 g) and water (10 ml). The mixture was shaken vigorously under hydrogen and then allowed to stand for twenty days, and worked up as described above. The hydroquinone did not appear to be quite pure and the experiment was run on a larger scale employing 55 g quinone. The hydroquinone fraction was acetylated and the acetate distilled in a vacuum. A residue was obtained which on trituration with methanol crystallized. After recrystallization the product was obtained pure (m. p. 168–169°) and was identified as dihydroquinone tetraacetate by mixed m. p. with an authentic specimen as well as by conversion to diquinone.

Preparation of "sodium acetate humic acid": Quinone (30 g) was treated as in the previous experiment with sodium acetate (250 g) and water (300 ml). The mixture was poured into water (4 l) containing concentrated hydrochloric acid (250 ml). As soon as possible the precipitated humic acid was filtered (no suction!) or centrifuged. The creamy material was suspended in dilute (1 %) hydrochloric acid and centrifuged, the process being repeated several times. Finally, the humic acid was washed once with distilled water. (Repetition causes considerable losses due to peptisation.) The humic acid was partly dehydrated on porous tile and used for further experiments in this state (containing 50–70 % water). When dry the humic acid dissolves slowly even in alkali.

Methylation of "sodium acetate humic acid": Fresh, moist humic acid (about 4 g) was dissolved in methanol (25 ml) and dimethyl sulphate (4 ml) added, followed by the dropwise addition (under hydrogen) of sodium hydroxide solution (4 ml, 40 %), with stirring and external cooling. After the completion of the reaction the mixture was acidified and the precipitate collected and carefully washed. The air-dried product was extracted with light petroleum in order to remove traces of hydroquinone dimethyl ether. Part of the preparation was dried *in vacuo* over phosphorous pentoxide at room temperature and analysed. The bulk of the material was dissolved in dioxan and treated with a large excess of diazomethane in ether. After 24 hours light petroleum was added to precipitate the humic acid which was then dried *in vacuo* over paraffin wax and phosphorous pentoxide.

The methoxyl content of the products obtained by methylation with dimethyl sulphate and alkali varied somewhat. Found: OCH_3 , 24.9, 23.4, 20.9, 20.4, 20.6, 22.0, 20.0, 20.3, 20.7 %. Remethylated (CH_2N_2) products (prior to remethylation 20.3, 20.7 % OCH_3) contained 24.7, 24.5 % OCH_3 .

Attempts were made to reduce the „sodium acetate humic acids” (prior to acidification) with sodium amalgam (under hydrogen). The colour decreased very considerably but colourless solutions were never obtained. Direct methylation of the reaction mixtures with dimethyl sulphate and alkali yielded alkali insoluble products which were extracted with petroleum ether to remove the hydroquinone dimethyl ether. The insoluble products were lighter coloured than the methylated nonreduced humic acids. Found: OCH_3 , 27.2, 27.6 %. This is far less than expected for a methylated polymer II and the result is difficult to explain. Possibly nuclear hydrogenation has occurred.

Samples of "sodium acetate humic acids" which had been stored for three months under water, in the presence of a little toluene to avoid microbial infection, on methylation with dimethyl sulphate and alkali gave products with a decreased methoxyl content (15–16 %).

Reductive acetylations: Fresh, moist "sodium acetate humic acid" (6 g) was suspended in acetic anhydride (300 ml), containing four drops of pyridine. The mixture (cooled externally) was stirred mechanically and zinc dust added until the colour of the resulting solution no longer decreased. The brown solution was filtered with stirring into a large volume of ice cold water. The light yellowish brown precipitate was filtered and washed carefully with water, dried in air and extracted with ether which dissolved only a very small amount of material. Part of the product was dried *in vacuo* over phosphorous pentoxide at room temperature and the residue subjected to two renewed acetylations. Found after the first acetylation 50.5, after the second 55.8 and after the third acetylation 56.1 % acetoxy. The products were not "homogeneous" and when the product containing 56.1 % acetoxy was dissolved in chloroform and fractionately precipitated with ether fractions were obtained containing between 48 and 57 % acetoxy. The acetoxy content increased with increasing solubility in the solvent mixture. Preparations made from humic acids which had been stored under water for 3–6 months had only 43–46 % acetoxy content. (One reductive acetylation only.)

A methylated "sodium acetate humic acid" containing 22.8 % OCH_3 was also subjected to reductive acetylation. The product was found to contain 23.0 % acetoxy and 13.3 % methoxyl a result which is not easy to interpret.

As mentioned in the introduction, humic acids prepared with strong alkali gave inconsistent results. As a rule methylation and reductive acetylation experiments yielded preparations containing less methoxyl and acetoxy than those obtained from the "sodium acetate humic acid".

The reaction of quinone with 10 N NaOH in the presence of methanol yielded a humic acid which after reductive acetylation contained methoxyl (5.5 % OCH_3 , 38.5 % OCOCH_3) indicating that some addition of methanol had taken place during the formation of the humic acid.

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