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Quantum-Chemical Simulation of the Synthesis of Structural Fragments of Humic Substances Analogs

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Abstract—Semiempirical calculations by the PM3 method were used to optimize the structural fragments of the precursors of synthetic humic and fulvic acids. Changes in the thermodynamic parameters (enthalpy of formation, entropy, and Gibbs energy) were determined and a conclusion was drowm if the postulated processes are thermodynamically possible.

Keywords: humic acids, fulvic acids, quantum-chemical simulation, enthalpy of formation, entropy, Gibbs energy

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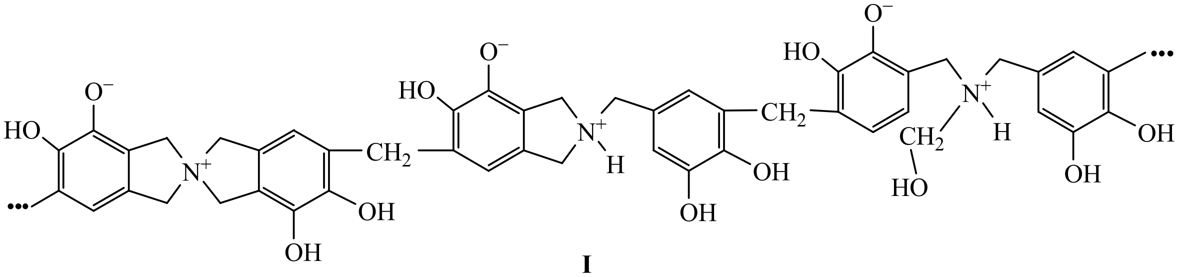
Natural humic substances include humic and fulvic acids. The former have a higher molecular weight and are insoluble at pH < 2, and the latter are relatively low-molecular compounds soluble at any pH. The interest in synthetic analogs of humic acids is expaplained by the possibility to synthesize preparations with specified properties, which makes it possible to avoid difficulties associated with standardization of natural humic substances. The problem of standardizetion arises when such substances are suggested to be used in medicine and veterinary.

In this connection gaining insight in to the mechanisms of reactions leading to formation of such complex supramolecular associates as humic and fulvic acids takes significance. Successful syntheses of these compounds and detailed investigation of their physicochemical properties were published in [1–3]. In the present work we undertook an attempt of simulating initial stages for consecutive oxidation of structural elements of a certain precursor, leading to a product containing protogenic groups with widely varying p*K* values. It is noteworthy that in the experiment the initial phase of active oxygen absorption was followed by a quasi-equilibrium state, when no oxygen absorption was observed. The carbonate detected in the reaction mixture contained up to 40% of carbon which initially was incorporated in the organic precursor.

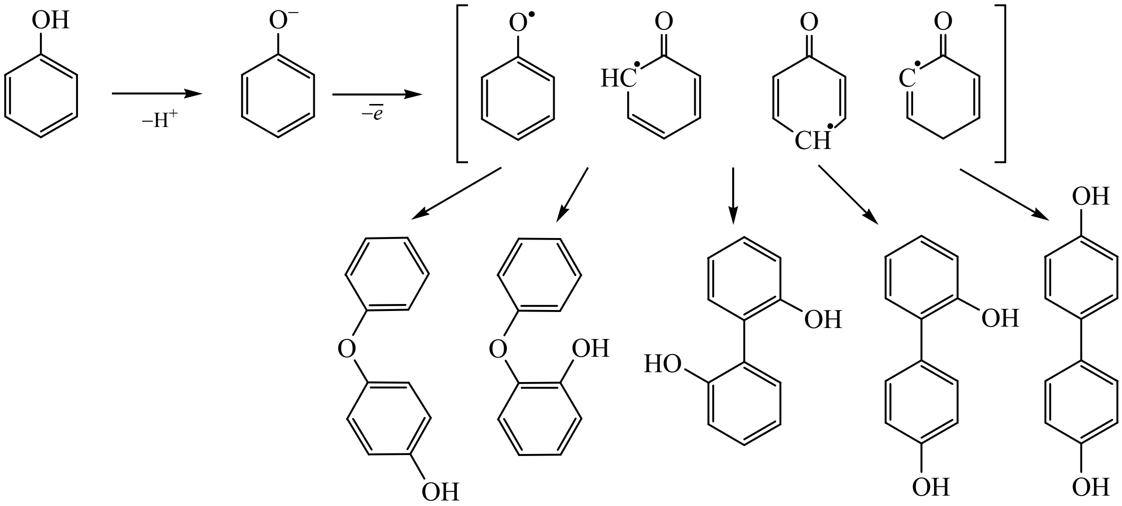
Synthetic humic acids were prepared by the oxidation of the nitrogen-containing amphoteric polyelectrolyte **I** obtained as described in [3] with a pure electrolytic oxygen (Scheme 1). Treatment of the reaction mixture with concentrated HCl at pH < 2 results in precipitation of a water-insoluble product, namely, a synthetic humic acid.

Scheme 1.

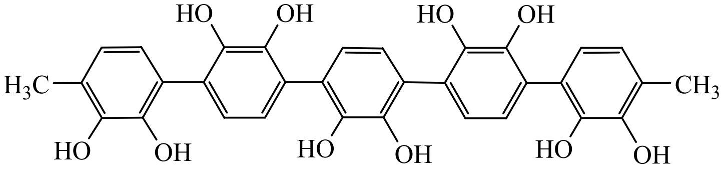


I

Scheme 2.



Scheme 3.



II

Naturally, the presented structure of the amphoteric polyelectrolyte is simplified, because here we leave out the probability of chain branching. The present work is an attempt of quantum-chemical simulation of some structural fragments of the intermediate products to elucidate their electronic structure and evolution during synthesis. For simulation we chose short fragments of the polymeric chain with free valences terminated by CH_3 groups.

Radical oxidation of phenols can leads to the condensed products (Scheme 2) [4].

Oxidation of phenols is an intricate multistage process, and its mechanism is still scarcely understood. One thing which is clear right now is that this mechanism can significant vary depending on the nature of one- or two-electron oxidant.

According to [5], the oxidative condensation of pyrocatechol in the course of the synthesis of fulvic acids will occur in the same way by forming chains of polyhydroxypolyphenylene **II** [6] (Scheme 3).

The condensation products can be not only linear, but also branched, and also contain bridging oxygen atoms in the chain. However, in the present work we restricted ourselves to oxidation in a linear structure with C–C bonds.

The quantum-chemical calculations were per-formed by the semiempirical PM3 method [7] for a singlet ground state using the Pollack−Rebiry procedure for geometry optimization in the closed-shell systems (RHF). All calculations were performed using the GAMESS package [7–10].

Since the synthetic fulvic acids were obtained by oxidative polycondensation of pyrocatechol [5], to simulate the process of synthetic fulvic acid formation we chose for the starting structure a linear fragment of the polyphenylene chain containing *ortho*-hydroxy groups in the benzene rings.

In the case of humic acids, we chose for the starting structure a fragment of the chain of polyelectrolyte **I** [3]. On the basis of this structure we simulated stronger oxidized structures which are the components of synthetic analogs of natural humic acids.

The possible consecutive oxidation stages of phenolic nuclei in the starting fragments are shown in Scheme 2.

The oxidation process was simulated by stepwise changing the structure of the starting fragments according to Scheme 4. Full optimization of the electronic structure and geometry was performed at every

Scheme 4.

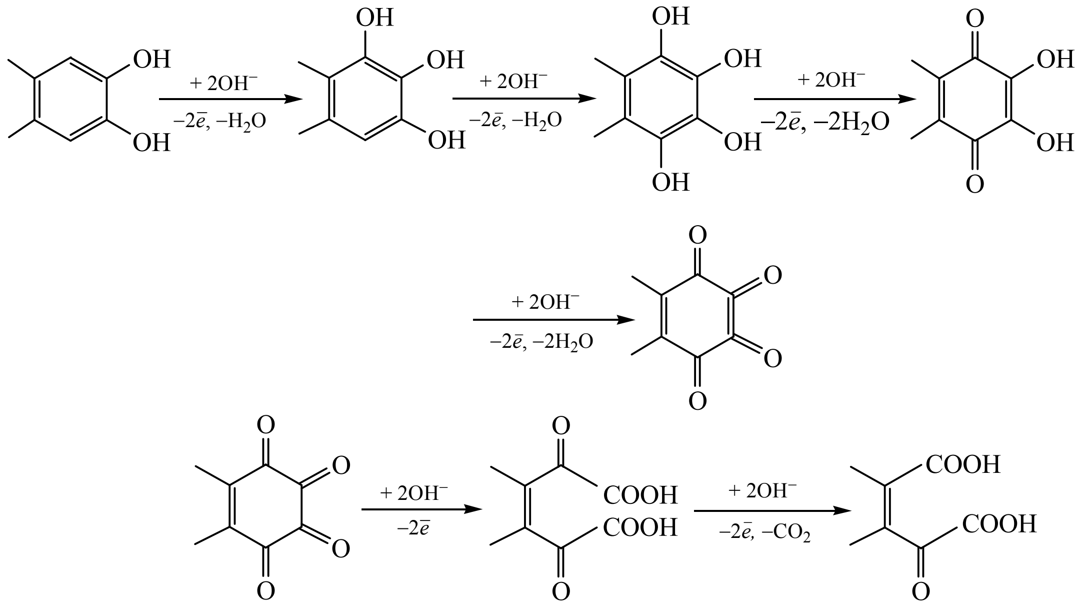
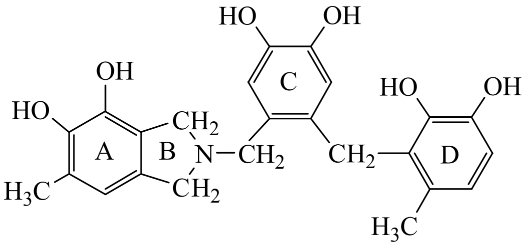
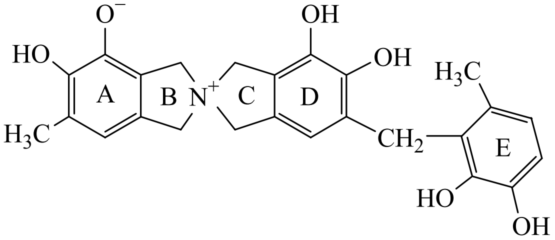


Table 1. Oxidation stages of the fragment of polyelectrolyte **I** with a tertiary nitrogen atom in ring B



Stage	Process	Δ*H*, kcal/mol	Δ*S* × 10^4, kcal/mol	Δ*G*, kcal/mol
1	Hydroxylation of ring D	–61.59	3.31	–61.69
2	Formation of a quinoid structure in ring D	–39.01	–0.78	–38.99
3	Formation of a quinoid structure in ring C	–35.97	–0.42	–35.96
4	Hydroxylation of ring A	–61.31	2.89	–61.40
5	Formation of a quinoid structure in ring A	–35.94	–0.25	–35.94
6	Opening of ring A to form carboxy groups	–81.82	5.67	–81.99
7	Oxidation of the methine group in ring B	–85.95	1.55	–85.99
8	Opening of ring D to form carboxy groups	–81.40	4.74	–81.55
9	Formation of a quinoid structure in ring C	–62.60	1.39	–62.64
10	Hydroxylation of ring C	–58.20	0.42	–58.21
11	Formation of a quinoid structure in ring C	–125.00	1.03	–25.03
12	Decarboxylation of ring A	91.26	–6.41	91.45

Table 2. Oxidation stages of the fragment of polyelectrolyte **I** with a tertiary nitrogen atom in the bridge for ring A



Stage	Process	Δ*H*, kcal/mol	Δ*S* × 10^4, kcal/mol	Δ*G*, kcal/mol
1	Hydroxylation of ring A	–62.27	2.57	–62.35
2	Formation of a quinoid structure in ring A	–35.73	–0.27	–35.72
3	Opening of ring A to form carboxy groups	–79.48	5.74	–79.65
4	Decarboxylation of ring A	144.79	–7.26	145.00

stage. Along with oxidation, the process involved conformational changes. Spontaneous nature of the oxidation process was controlled by analyzing the Gibbs energies at every stimulation stage.

The iteration process in the self-consistent PM3 method in fact stimulates self-organization of the substance during formation of an oxidized structure, because every iteration step involves calculation of electron interaction and total energy gradient which controls the direction of nuclear motion in the course of self-organization.

Table 1 lists the oxidation steps of the chosen fragment of polyelectrolyte **I**, which contains a tertiary nitrogen atom in ring B.

Oxidation at every stage of the synthesis process was simulated in accordance with the localization of the highest occupied molecular orbital (HOMO), because oxidation consists in electron withdrawal from the HOMO. The choice of the oxidation site is exemplified in Fig. 1a which shows that the HOMO of the starting fragment is localized on ring D. Therefore, the next oxidation stage is simulated to involve formation of a quinoid structure of ring D (Table 1, stage 2). After geometry optimization of the resulting structure (Fig. 1b) it becomes evident that the HOMO has shifted to ring C.

In the same way we simulate oxidation of the fragment of an amphoteric polyelectrolyte containing quaternary nitrogen atoms in the chain and for the polyhydroxyphenylene fragment (Tables 2 and 3).

As follows from experimental data, the reaction mixture after the synthesis of humic or fulvic acid contains much carbonate which might be formed by decarboxylation of COOH groups (Scheme 2). However, the calculated Gibbs energy of the decarboxylation reaction is positive, the last stage.

The resulting data give us grounds to state that the stepwise oxidation of amphoteric polyelectrolyte **I** can the products which contain both weakly acidic phenolic hydroxyls and carboxy groups. The same is true of the polyhydroxyphenylene fragment of the precursor of synthetic fulvic acid. This result can be explained by the neglect of solvent effects and some other factors which are impossible to include in the

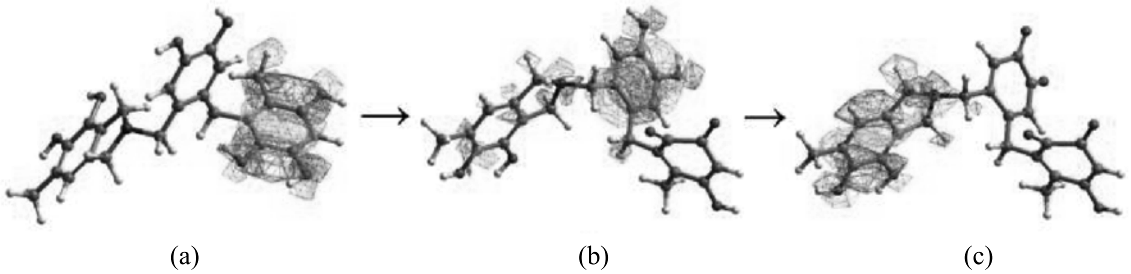
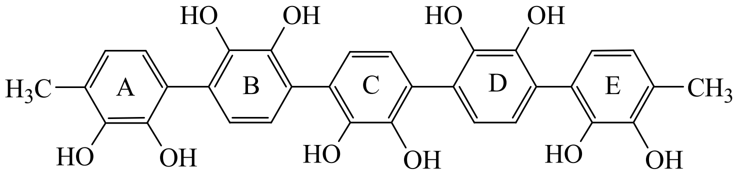

(a) (b) (c)

Fig. 1. Principles of the choice of further oxidation step, based on the HOMO localization on (a) ring D, (b) ring C, or (c) fragment AB (Table 1, stages 2 and 3).

Table 3. Oxidation stages of the polyhydroxypolyphenylene chain



Stage	Process	ΔH, kcal/mol	$\Delta S \times 10^4$, kcal/mol	ΔG, kcal/mol
1	Hydroxylation of ring C	–60.68	1.73	–60.73
2	Hydroxylation of ring C	–60.91	1.65	–60.96
3	Formation of a quinoid structure in ring C	–42.47	–0.25	–42.46
4	Hydroxylation of ring B	–60.94	1.97	–61.00
5	Hydroxylation of ring B	–60.82	1.52	–60.87
6	Formation of a quinoid structure in ring B	–41.80	–0.10	–41.80
7	Hydroxylation of ring D	–62.37	1.41	–62.41
8	Hydroxylation of ring D	–59.24	1.68	–59.29
9	Formation of a quinoid structure in ring D	–39.54	–0.23	–39.54
10	Hydroxylation of ring E	–61.74	2.51	–61.81
11	Hydroxylation of ring E	–60.78	1.79	–60.83
12	Formation of a quinoid structure in ring E	–40.43	–0.23	–40.43
13	Hydroxylation of ring A	–61.80	2.49	–61.87
14	Hydroxylation of ring A	–61.23	1.72	–61.28
15	Formation of a quinoid structure in ring A	–39.27	–0.22	–39.26
16	Opening of ring B to form carboxy groups	–77.81	4.25	–77.93
17	Opening of ring D to form carboxy groups	–75.81	3.35	–75.91
18	Opening of ring E to form carboxy groups	–83.27	4.45	–83.40
19	Opening of ring C to form carboxy groups	–79.97	2.99	–80.06

quantum-chemical calculation we used in the present work.

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