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Chemical Processes on Active Carbon Surface: A New Example of Nitrogen Fixation

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Abstract—The behavior of activated carbon fibers (ACF) and activated carbon (AC) in water and aqueous solutions of H_2O_2, NaOH, NaCN and KI_3 in the presence of atmosperic air is studied by physicochemical methods: X-ray photoelectron spectroscopy (XPS), ESR, and attenuated total reflectance IR (ATR-IR) and Fourier Transform IR (FT–IR) spectroscopy. The superoxide radical anion $O_2^{-\bullet}$ is shown to exist on the ACF surface in aqueous solutions, whose formation is explained by reaction of molecular oxygen with radical active centers of surface defects. It is found that in aqueous solutions of inorganic compounds, both possessing (H_2O_2, KI_3) and not possessing (NaOH, NaCN) pronounced oxidative properties, the ACF surface is oxidized more rapidly than on aging in air. Evidence for fixation of atmospheric nitrogen on contact of ACF and AC with H_2O or aqueous solutions of NaOH, NaCN, and KI_3 is obtained. Possible conjugate redox reactions resulting in fixation of N_2 molecules and oxidation of the surface of carbon materials are discussed.

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Activated carbon (AC) and activated carbon fibers (ACF) are widely used in chemical technology, mostly as sorbents. They generally contact with air or air-saturated aqueous solutions. However, it is well known that graphite and some of its forms with disordered turbostrate structure (AC, carbon black, ACF) undergo slow surface oxidation (aging) on storage in air [1]. The reaction of the carbon material with air results in formation on the surface of oxygen-containing functional groups known as surface oxides or surface oxide carbon complexes. When the fresh graphite surface formed on grinding contacts with oxygen, gaseous products, such as CO and CO_2, are also evolved [2].

Surface oxides are also formed on contact of graphite and AC with deaerated water in the absence of air [3–6]. At ambient temperature or on slight heating, their formation is accompanied by evolution of gaseous compounds, the most abundant of which are H_2, CO, and CO_2 [3, 4]. It is noteworthy that H_2CO_2 are formed with high rate and yield in the system of C–H_2O at high-temperature synthesis of water gas or (in the presence of air) of air–water vapor mixture. Among the functional groups embraced by the term "surface oxides" are phenolic, etheric, xanthonic, quinonic, lactonic, lactolic, carboxy, and anhydride groups [1], as well as alcoholic, aldehydic, and ketonic [7].

The samples of carbon with turbostrate structure, such as AC, are paramagnetic (the concentration of paramagnetic centers is 10^{18}–10^{20}/1 g carbon [8]. Therefore, they can be considered as stable macroradicals. Paramagnetic centers are defects in the graphite structures: slit pore edges and layers themselves [1, 5, 6]. Paramagnetic oxygen [9] and water [5, 6] molecules are first adsorbed on paramagnetic centers, after which slow carbon oxidation takes place to form surface oxides [1].

In this work we studied the processes on the interface of AC (ACF) and aerated water or aqueous electrolyte solutions. We estimated the effect on the ACF surface of water and aqueous solutions of H_2O_2, NaOH, NaCN and KI_3. Changes on the sample surface (layer thickness 3–10 nm) were monitored my means of XPS. The relative surface concentrations of C, O and N (at %) was considered as a criterion of chemical processes in the systems studied. The total content of C, O and N atoms was taken as 100%. The results of a series of experiments with ACF are listed in Table 1.

As follows from Table 1, the surface concentration

Table 1. Study of ACF samples by X-ray photoelectron spectroscopy

Sample no.	Binding energy, eV/Content in the sample, %			Surface atomic concentration, at%
	Cls	Ols	Nls	
1	287.1/0.3 285.9/15.2 284.5/84.5	533.9/59.0 531.8/41.0	Not found	C 95.7, O 4.3
2	287.1/2.5 285.9/15.8 284.5/81.8	533.3/69.2 531.9/30.8	400.5	C 90.9, O 7.4, N 1.7
3	285.9/8.1 284.5/91.9	533.8/51.8 532.4/48.3	Not found	C 90.3, O 9.7
4	284.5	532.8	399.8	C 87.4, O 11.1, N 1.5
5	287.1/3.2 285.9/15.4 284.5/81.4	533.8/43.8 532.1/56.2	399.5	C 92.5, O 5.7, N 1.8
6	287.1/5.1 285.9/13.9 284.5/81.0	533.8/66.8 532.0/33.2	400.0	C 93.8, O 5.7, N 0.5
7	292.3/3.3 290.9/5.1 289.5/5.9 288.0/5.8 286.7/9.0 285.5/14.0 284.5/54.9	533.8/59.0 531.7/41.0	402.0/30.9 400.1/48.4 398.2/20.7	C 93.9, O 5.7, N 0.4

of oxygen in the starting ACF sample *1* is minimal, while the concentration of carbon is maximal.

The C1s band in the XPS spectrum of sample *1* is unsymmetrical and can be resolved into three bands: 284.5 (84.5%), 285.9 (15.2%), and 287.1 eV (0.3%). According to published data [7, 10, 11], the first band belongs to polyconjugated carbon atoms constituting the aromatic system of graphite. The second C1s band is assignable to carbon atoms bonded with oxygen by a single bond (phenolic group).

As to the third band [E_b(C1s) 287.1 eV], its assignment is controversial. Some authors [7, 11] suggest that bands in this region relate carbon bonded with oxygen by a double bond (carbonyl group) or to carbon in an O–C–O group. Other researchers, based on an abundant published evidence [10], assign the band with the same E_b(C1s) value to carbon incorporated in a xanthonic or an etheric C–O–C group.

Deconvolution of the O1s band in the XPS spectrum of sample *1* gives two bonds. The band with E_b(O1s) 531.8 eV is commonly assigned to phenolic and/or etheric and xanthonic C–O–C oxygen [10]. At the same time, for the surface carbonyl group oxygen, E_b(O1s) ranging from 530.4 to 530.8 eV is reported [10]. Therefore, comparing these data with the XPS spectrum of sample *1* in the E_b(C1s) range we assume that sample *1* contains no carbonyl groups or bound nitrogen on its surface. Furthermore, we obtained no evidence, within the sensitivity of the method, for the presence of surface carboxy groups. This conclusion is consistent with the results for other types of ACF, obtained by means of special XPS techniques [12].

Treatment of sample *1* with distilled water at room temperature increases the concentrations of oxygen and nitrogen on its surface (sample *2*). The complex structure of the C1s band points to a decrease in the content of “free” carbon on the surface of sample *2* [E_b(C1s) = 284.5 eV] and an increase in the content of “oxidized” [arbon (E_b(C1s) = 287.1 eV]. These results are interesting to compare with those obtained after treatment of sample *1* with aqueous hydrogen peroxide (sample *3*). Activated carbon is known to catalyze H_2O_2 decomposition which involves intermediate formation of OH radicals [13]. At the same time, under aerobic conditions, hydrogen peroxide is formed in water contacting with activated carbon [13, 14]. As compared with sample *2* obtained by treatment with water, sample *3* contains on its surface more chemisorbed oxygen, less carbon, and no bound nitrogen. The highest content of chemisorbed oxygen is observed in sample *4* obtained by treatment of sample 1with 0.1 N aqueous NaOH. Therewith, unlike parent sample *1* and sample *3*, sample *4* contains 1.5% of chemisorbed nitrogen on its surface.

Treatment of sample *1* with aqueous NaCN (sample *5*) or KI_3 (sample *6*) gives similar results in terms of the surface concentrations of carbon and chemisorbed oxygen, but the surface concentration of bound nitrogen in sample *5* is three times higher than in sample *6*. On the other hand, those in sample *5* and sample *2* treated with water are coinciding.

As we noted, according to [7, 11], the band with E_b(C1s) 287.1 eV can be contributed by carbonyl groups. Aliphatic aldehydes and ketones are highly reactive toward nucleophilic addition of CN^- and HCN. The reactions provide α-hydroxy nitriles whose hydrolysis affords α-hydroxy acids. Aromatic aldehydes in the presence of CN^- undergo condensation to form α-hydroxy ketones while aromatic ketones do not react with CN^- at all, although aryl alkyl ketones form the corresponding cyanhydrines [15]. However, judging from the C : O : N ratio and E_b(C1s) and E_b(N1s) for samples *2* and *4* we can conclude that even if the signal has E_b(C1s) corresponding to carbonyl, it can only be a ketonic carbonyl, like in benzophenone. However, this conclusion contradicts the XPS data in the E_b(O1s) region. The E_b(O1s) value of 532.1 eV is closer to the reported range for oxygen bound with partners by two single bonds [10] (532.4–533.1 eV).

Interesting changes were found in sample *1* stored in air for 1.5 years (sample *7*). In its XPS spectrum, a appeared in the region of high E_b(C1s) values. Deconvolution of the spectrum gave evidence for the presence on the surface of sample *7* of alcoholic or etheric (286.7 eV), carbonyl (288.0 eV), and carboxy (289.5 eV) groups. Bands at E_b(C1s) 291.2–292.1 eV are commonly assigned to π–π^* electron transfer in an aromatic system [7, 10, 11]. In the E_bN1s region, the spectrum of sample *7* acquired an unsymmetrical band with its maximum at 400.1 eV. This band was resolved into three bands peaking at 398.2, 400.1, and 402.0 eV. The total and "free" surface carbon [E_b(C1s) 284.5 eV] carbon contents in sample *7* are lower, while those of oxygen and nitrogen are higher than sample *1*, but the changes are less significant than those produced by treatment of sample *1* with water or aqueous electrolyte solutions. In terms of the oxidation of the ACF surface, this result is consistent with the known phenomenon of aging of carbon materials. The ACF surface is much faster oxidized on contact with water and electrolyte solutions, such as aqueous NaOH, than on exposure to moist air.

Let us consider in more details the oxidation processes than may occur on the ACF and AC surfaces on their contact with water. It is known that AC exhibits formal redox dualism in water and aqueous-organic solvents. As to oxidative properties, carbon can be considered as catalysts in reactions of reducing agents with air oxygen [16, 17]. On the other hand, abundant evidence for reductive properties of AC and ACF is also available [7, 11, 16, 18, 19]. Unsaturated valence carbon atoms of graphite structural defects and other functional groups on the AC (ACF) surface can act as reductive centers. Depending on the nature of neighboring groups and their steric position, carbon atoms of the defects can enter either π-donor or π-acceptor interactions with the delocalized π-electron system of graphite. The resulting structures are close in their properties to carbocations or carbanions, respectively. Terminal carbon atoms are not involved in such electronic interactions and can be considered as carbene-like [9, 20]. They can be present in a diamagnetic singlet state which is close to carbanions or in a paramagnetic triplet state which is close to biradicals whose presence in graphite and AC was confirmed by ESR [8, 13, 20–22]. Although carbenes are commonly highly reactive, they can be very stable under certain conditions [23].

Reaction of carbon defects of the radical type with gaseous oxygen can lead to formation of peroxyl groups C–O–O$^{\bullet}$ which then convert in part to saturated valence oxygen complexes [2]. As noted in [17, 24], molecular oxygen adsorbed on the AC surface can convert into the superoxide radical anion $O_2^{-\bullet}$. Similar processes take place when oxygen is adsorbed on the Pt (*111*) surface [17]. The Further desorption of the radical anion $O_2^{-\bullet}$ from the AC surface can occur under the action of polar solvents [21, 22]. On the other hand, $O_2^{-\bullet}$ can also be formed in solution near the AC surface on contact of $O_{2(aq)}$ with radical-type defects, as it is in aerated aqueous solutions containing gold nanoparticles [25].

Evidence for the high adsorptive capacity of the ACF surface toward radical species was obtained be means of spin labeling with the stable radical 4-amino-2,2,6,6-tetramethylpiperidinyloxyl (radical **I**). In aerated aqueous solutions with no ACF at room temperature, the spin label at concentrations of 1–5 mM gave well-resolved ESR spectra with a typical triplet structure (a_N 16.89 G) [26]. Under the experimental conditions, the ESR spectra showed no intrinsic paramagnetic carbon signals. On addition of ACF to solutions containing radical **I**, the signal of the label sharply diminished without changing shape and position. The decrease was 10–20 times and depended on the quantity of the radical label radical and the adsorbent added. Washing off the ACF from the adsorbed radical did not lead to regeneration of the ESR signal. The binding of radical **I** with ACF surface centers differ in its nature from ordinary ion–ion or hydrophobic interactions. On spin probing of gel sulfo cationites with specific surface areas comparable with those of ACF, anisotropic broadening of ESR signals was observed, explained by attenuated translation–rotation motion of the probe in the vicinity of adsorption centers [27]. Therewith, no evidence for probe adsorption on the surface was obtained. The absence of changes in the shape of the ESR signals of the spin label in the solution with ACF added points to chemisorption interaction of ACF paramagnetic centers with nitroxyl radicals, resulting in immobilization of the radical on the sorbent surface. The reaction pattern of radical **I** with the ACF surface is specific and differs from that for gold nanoparticles [25].

To detect the superoxide anion radical, we made use of the property of 2,2-di(*p*-nitrophenyl)-5,5'-diphenyl-3,3'-(dimethoxy-4,4'-diphenylene)-2*H*-tetrazolium chloride (Nitrotetrazolium Blue, dye **II**) to form different reduction products under different conditions. In aqueous solutions, dye **II** is known [28] to be colored yellow and can be reduced under the action of solvated electron and $O_2^{-\bullet}$ to form a brightly colored reddish-brown poorly soluble diformazan. Other particles which could in principle be detected in the system $C\|H_2O\|O_{2(aq)}$ ($H^\bullet$, H_2O_2, $OH^\bullet$, H^+, OH^-, and H_2) do not show such property. However, the reduction of dye **II** to diformazan under the action of e_{solv} or $O_2^{-\bullet}$ can be recognized in view of the fact that this reaction is decelerated by superoxide dismutase (molecular weight ~35 kD) [29].

On contact of ACF with a 0.2% solution of dye **II** in water, the dye was appreciably consumed, since the intensity of color of the solution decreased. After 1 h the fiber was separated from the solution, dried with filter paper, and treated with anhydrous chloroform. The chloroform fast colored to reddish-brown, indicating reduction of dye **II** to diformazan. The color intensity of the chloroform solution was higher, when the solution of dye **II** was kept with the fiber for 1 h at 4°C rather than at 20°C.

Addition of superoxide dismutase to a solution of dye **II** ($t = 37.0 \pm 0.1$ °C, pH = 7.4), followed by addition of ACF to the solution under the same conditions did not lead to coloration of chloroform. This result points to the presence in the solution near the activated carbon surface of $O_2^{-\bullet}$ radical anions formed by one-electron reduction of oxygen molecules dissolved in water or those adsorbed on the AC surface before its contact with solutions.

Superoxide anion radical is a reactive species with clearly pronounced reductive properties $\{E^0(O_2/O_2^{-\bullet}) = -0.284$ V [30]; –0.33 V [31]}. In aqueous solution, it behaves as a conjugate base of an acid, the hydroperoxyl radical $HOO^\bullet$ ($pK_a = 4.88$), and takes up proton or disproportionates [Eqs. (1) and (2)] [31]:

$$O_2^{-\bullet} + H_2O \rightleftarrows HOO^\bullet + OH^-, \tag{1}$$

$$2O_2^{-\bullet} + H_2O \rightleftarrows O_2 + OH^- + OOH^-. \tag{2}$$

The hydroperoxyl radical $HOO^\bullet$ can also appear in reaction of the air oxygen dissolved in water with atomic hydrogen [31]:

$$O_2 + H^\bullet \longrightarrow HO_2^\bullet. \tag{3}$$

Indirect evidence for reaction (3) is provided by the liberation of hydrogen on contact of graphite with water under anaerobic conditions at room temperature [3, 4] and quantum-chemical calculations [32] of the assumed behavior of water molecules in the complexes $[C(H_2O)]$ and $[C(H_2O)]^+$.

The hydroperoxyl radical $HO_2^\bullet$ is capable of further redox transformations [29, 33, 34]:

$$2HO_2^\bullet \longrightarrow {}^1O_2 + H_2O_2, \tag{4}$$

$$H_2^\bullet + H_2O_2 \longrightarrow {}^1O_2 + OH^\bullet + H_2O. \tag{5}$$

Reaction of the radical anion $O_2^{-\bullet}$ with hydrogen peroxide formed in reactions (2) and (4) can result in formation of a strong one-electron oxidizer, the hydroxyl radical $OH^\bullet$ [31]:

$$O_2^{-\bullet} + H_2O_2 \longrightarrow O_2 + OH^\bullet. \tag{6}$$

Reactions (1)–(6) are typical for γ-radiolysis of water saturated with oxygen. The yield of reaction products in the system AC–aerated water should be fairly low, and their high reactivity results in that the above reactions occur near the AC or ACF surface. The reactive species formed in reactions (1)–(6), specifically singlet oxygen, hydroxyl, and hydroperoxyl radicals, and hydrogen peroxide can promote deeper oxidation of the AC or ACF surface.

Under ambient conditions (T 293 K, relative humidity ~60%) in air, the walls of AC and ACF pore defects are covered mostly with a monomolecular water film [35]. Unlike to bulk aqueous solution, particle exchange, in particular H_2O substitution for $O_2^{-\bullet}$ or disproportion of the radical anion in the monomolecular film on the surface of ACF pore defects, can be hindered. This fact probably explains

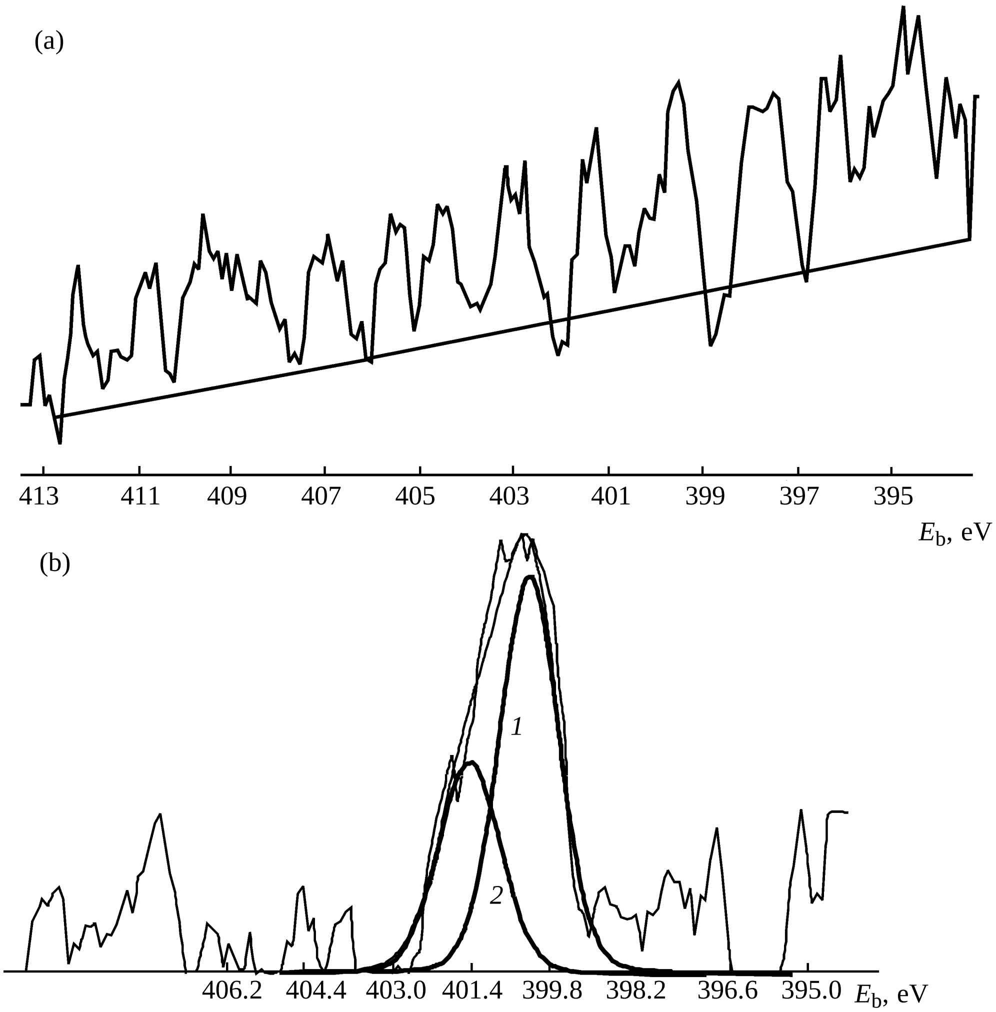


Fig. 1. XPS spectra of samples (a) *8* and (b) *9* in the E_b(N1s) region. For *1* and *2*, see text.

the above-mentioned faster oxidation of the ACF surface with oxygen dissolved in water than with air oxygen. However, as shown in [36], saturation with water vapor does not passivate a freshly prepared graphite surface completely with respect to O_2 adsorption [36].

We have to explain also the appearance of bound nitrogen in samples *2* and *4–7*. As noted above, according to XPS data, nitrogen does not occur in samples *1* and *3*. No nitrogen was detected in sample *1* by Dumas analysis. However, it is not excluded that the appearance of nitrogen in samples *2* and *4–7* might be associated with adsorption of nitrogen containing admixtures in air, water, or dissolved reagents. Moreover, nitrogen might be contained in the analyzed material in trace amounts spread irregularly on the surface or be incorporated in ACF during graphitization of organic materials (purified cellulose), performed under nitrogen. In the latter case, nitride groups might appear on the ACF surface [37]. The appearance of bound nitrogen on the surface of activated carbon was recently observed by Simanova et al. [18] who studied sorption of gold from aqueous solutions of $H[AuCl_4]$.

For a more detailed study we synthesized AC from sucrose of chemical grade. The sample was carbonized under CH_4 and then activated by water vapor under argon. The sample was divided into two portions: One was left as reference (sample *8*) and the other was placed to ` Drechsel vessel filled with 0.1 N NaOH (chemical grade) prepared with freshly distilled water (sample *9*). The outlet of the vessel was protected with a water seal, and a flow of air purified by passing through Drechsel vessels with 10% aqueous solutions of H_2SO_4 and NaOH was fed to the inlet for 24 h.

Figure 1 shows the XPS spectra of samples *8* and *9* in the region of 395–407 eV. Starting sample *8* (Fig. 1a) does not contain bound nitrogen on its sur-

Table 2. Assignment of peaks in the E_b(N1s) region of the XPS spectra of carbon surface (published data)

Peak	E_b(N1s), eV	Assignment	Reference
1	395.6–396.7	Nitrogen in nitride-like species or aromatic imines	[10]
	397.8		[38]
2	398	Nitrogen in pyridine-like or cyano groups	[17]
	398.0–399.0	Nitrogen in pyridine- or acrydine-like groups (N-6)	[1]
	398.4–399.0	Nitrogen in pyridine-like groups	[39]
	398.4–398.8		[10]
3	400	Nitrogen in amino groups	[1]
	400–401	Nitrogen in amino or amido groups	[17]
	400.0–400.6	Nitrogen in pyrrole- or pyridone-like group (N-5)	[39]
	400.1–400.4	Nitrogen in pyrrol-like or amino groups	[10]
4	400.9–401.9	Nitrogen substituting carbon in the aromatic graphene system (N-Q)	[39]
5	~401.5	Nitrogen in pyridone-like groups	[40]
6	402.1–402.6	Nitrogen in pyridine *N*-oxides	[10]
	402–405	Nitrogen in terminal N–O (N–X) groups	[39]
7	404.9–405.6	Nitrogen in chemisorbed oxides	[10]

face. By contrast, the spectrum of sample *9* (Fig. 1b) treated with aerated aqueous NaOH contains a peak corresponding to nitrogen. Deconvolution of this peak gives two peaks with E_b(N1s) 400.3 (64.2%) and 401.4 eV (35.8 %). The total surface concentration of nitrogen is 0.8 at%.

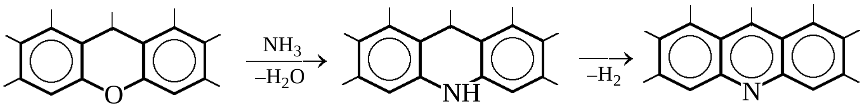
The resulting data suggest that the only source of nitrogen on the AC surface is the air dissolved in distilled water. At 20°C, the equilibrium concentrations of nitrogen and oxygen in water contacting with air are ~0.54 and ~0.22 mM.

The nature of nitrogen on the AC and ACF surface was revealed by means of XPS and AIP-IR spectroscopy. The E_b(N1s) bands in the XPS spectra of some nitrogen-containing samples were unsymmetrical and could be resolved into several components that were assigned by comparison with published data (Table 2).

It follows from the XPS data (Table 2) that samples *2*, *4*, *5*, and *6* contain nitrogen incorporated in amino or imido groups or pyrrol- or pyridone-like compounds (peak type *3*). In sample *7* obtained by prolonged keeping of starting sample *1* in air we can detect nitrogen incorporated in a pyridine(acrydine)-like group [E_b(N1s) 398.2 eV, peak type 2], fragments with E_b(N1s) 400.1 eV (peak type 3), and a pyridine *N*-oxide group (E_b(N1s) 402.0 eV, peak type 6). In sample 8 treated with aerated aqueous NaOH (sample *9*) we detected bound nitrogen of two types: with E_b(N1s) 400.3 (peak type 3) and 401.4 eV. The last value can formally be assigned to type 4 compounds (quaternary nitrogen N–Q, according to the classification in [39]). However, the intercalation of nitrogen to the bulk graphene system via substitution of carbon atoms in the graphite aromatic system seems unlikely. More realistic, in keeping with published data [40], is to assign this band to pyridone-like fragments.

The AIP-IR spectra of samples *1*, *3* and *5* show no bands near 3490 or 3425 cm^{-1}, characteristic of free and H-bonded NH groups in coals [34]. We also did not detect bands assignable to ν(NH) in the FT-IR spectrum of sample *9*. The main differences between the AIP-IR spectra of starting sample *1* and samples *3* and *5* are as follows. The spectra of ACF samples treated with solutions of NaOH or NaCN acquire methyl and methylene ν(CH) bands at 2915 and 2844 cm^{-1}, respectively. Their respective δ(CH) bands were found in the spectrum of sample *5* only (1449 and 1378 cm^{-1}). The AIP-IR spectra of samples *3* and *5* contain broad bands with their maxima at 1608 and 1612 cm^{-1}, which were not fond in the spectrum of sample *1*. From [10, 41] it follows that this region contains overlapping bands related to –HC=N– and –HC=C– vibrations in pyridine-like structures and cyclic amides. Furthermore, as compared to sample *1*, the spectra of samples *3* and *5* contain additional peaks at 1306 and 1295 cm^{-1}, respectively, commonly assigned to etheric, epioxide, and phenolic groups in various structural environment [10].

From the XPS and IR data we assume that nitrogen in sample *9* exists mainly in the form of pyridine-like and pyridone-like fragments. The pyridine-like and analogous fragments are formed on high-temperature treatment of AC and ACF with gaseous ammonia [10, 17, 42]. In [17], the formation of the pyridine-like fragment is explained by nitrogen substitution for an oxine oxygen atom.



On the other hand, it is known that pyridines and their derivatives can be formed on condensation of unsaturated 1,5-dicarbonyl compounds with ammonia or hydroxylamine [43]. A similar condensation of 1,4-dicarbonyl compounds leads to pyrroles and *N*-hydroxypyrroles [43]. However, this brings up the question: What is the source of ammonia or hydroxylamine in the considered systems?

Nitrogen molecules are known to be inert, and, therefore, the Haber–Bosch synthesis of ammonia requires extremely rigid conditions. On the other hand, N_2 can enter redox reactions at room temperature and atmospheric pressure on surface defects of carriers or catalysts. For example, in the presence of O_2, molecular nitrogen reacts with 3,5-di-*t*-butylpyrocatehol deposited on silica gel [44] to form a mixture of compounds, among which 1*H*-2,4,6,8-tetra-*t*-butylphenoxazin-1-one and a derivative of the corresponding quinone with an *N*-(3,5-di-*t*-butyl-4-hydroxy)-3,5-di-*t*-butylphenyliminyl radical as a substituent. In the absence of oxygen or silica gel, this process fails to occur. The reduction of N_2 to NH_3 also occurs on the surface of TiO_2 containing 0.2% of Fe_2O_3 [45] or Ta_2O_5 doped with Fe(III) ions [46], as well as on the surface of an $Fe_2Ti_2O_7$ film [47, 48] or a composite consisting of TiO_2 and an organic conductor film [49]. In all the mentioned works [45–49], to fix nitrogen required UV irradiation, and H_2O or ethanol vapors were involved as a reducing agents. Along with ammonia, Schrauser and Guth [45] registered traces of hydrazine. The intermediates in this process are, naturally, oxygen-containing compounds and hydrogen formed from H_2O, and the role of the surface is likely to consist in providing defects where water molecules are activated. It is shown that the primary intermediates formed on photolysis of water on the TiO_2 surface are $OH^{\cdot}$ radicals [50]. In this respect, the AC or ACF surface with numerous defects and exhibiting metal rather than semiconductor (like TiO_2) conductivity, too, can activate N_2 molecules.

Katakis and Taube [51] found that the atomic singlet oxygen O(1P) formed on photolysis of an O_3–N_2 mixture binds N_2 molecules to form N_2O. The referees also showed that the contact of carbonyl complexes of platinum metals with a gas mixture containing CO, N_2, and H_2O gives rise to ammonia, and with a mixture of CO and air nitrogen, N(I) and N(II) oxides are formed. According to Fedoseev [52], these products can be formed due to the appearance of singlet oxygen $O(^1P)$ in the reaction of CO with air oxygen in the presence of carbonyl complexes of platinum metals. As noted above, the contact of AC (ACF) with oxygen and water even at room temperature leads to liberation of CO and CO_2 in small amounts, which, too, leaves room for intermediate formation of $O(^1P)$ atoms followed by their reaction with N_2 molecules dissolved in water.

The evolution of N_2O was also registered at 0–20°C from aqueous solution containing H_2O_2, vanadium(V) acetylacetonate complex, and CF_3COOH [53]. Gekhman et al. [53] assumed that N_2 is oxidized by singlet atomic oxygen $O(^1P)$. The formation of N_2O and $H_2N_2O_2$ was registered in the reaction of N_2 with H_2O_2 under homogeneous conditions at 400–650°C [54–57]; the hydroperoxide radical $HO_2^{\cdot}$ was suggested to be the oxidant here. Noteworthy is that the hydroxyl radical $OH^{\cdot}$ formed on thermal decomposition of H_2O_2 [58] can, from the thermodynamics viewpoint, too oxidize N_2 molecules. The formation of NO_2^- was detected on γ-radiolysis of aqueous alkaline solutions saturated with nitrogen and oxygen, whose yield was 0.2 atom of bound nitrogen per 100 eV of imparted energy [59]. According to [59], the primary act of oxidation of molecular nitrogen is its reaction with the $OH^{\cdot}$ radical generated by radiolysis, and nitroxyl $NOH^{\cdot}$ is an intermediate product.

We suggest that the reaction of nitrogen dissolved in water with products formed on contact of AC or ACF with water saturated with air oxygen [O_2, $HO_2^{\cdot}$, $OH^{\cdot}$, and, possibly, $O(^1P)$] can yield $N_2OH^{\cdot}$, $N_2O_2H^{\cdot}$, N_2O, or N_2O_2H. Their reduction at/on the AC (ACF) surface with solvated electron, radical anion $O_2^{-\cdot}$, or atomic hydrogen can afford NH_3 or NH_2OH, which further give pyridine-, pyridone-, or pyrrole-like fragments. Evidence for such process was provided by Shestakov and Shilov [60], who showed the principal possibility of obtaining NH_3 from N_2 by a conjugated redox reaction involving N_2O and H_2N_2O intermediates.

Introduction of oxidants to the system of AC(ACF)||(water or electrolyte solution saturated with oxygen and oxygen) inactivates the AC (ACF) surface. As a result, the redox processes are suppressed completely (with H_2O_2, sample *3*) or to a great extent (sample *6* treated with KI_3 solution), and nitrogen either not fixed at all or to a much lesser extent than on treatment of the same AC (ACF) with water only.

In the case of KI_3, this is indirectly confirmed by the known fact of HI formation from water and I_2 in the presence of AC [61].

Thus, the use of classical titration methods [1, 11] for qualitative and, especially, for quantitative determination of functional groups on AC surface under aerobic conditions can in some cases provide incorrect results.

In conclusion we note that the processes described in this work might be one of the possible routes to formation of complex organic molecules, a source of life on the Earth.

EXPERIMENTAL

The ATR-IR spectra were registered on a Bruker IFS-88 spectrometer. The Fourier transform IR spectra were obtained a Bruker IFS-113 instrument in KBr pellets.

The ESR spectra were registered on a Bruker BER-420 instrument with 4-amino-2,2,6,6-tetramethylpiperidinyloxyl as reference (Sigma, USA).

The XPS spectra were registered on a Perkin–Elmer PHI-5400 spectrometer with a MgK_a source (E 1253.6 eV). The residual pressure in the spectrometer was no higher than 2.10–8 mm Hg. Calculation of atomic concentrations and deconvolution of selected in the XPS spectra was performed standard Perkin–Elmer procedures. The accuracy in measuring the binding energies was 0.1 eV and in quantitative analysis, 10% . The spectra were calibrated against the C1s band of the hydrocarbon fraction of impurities.

A Busofit T-055 fiber (Technical Standard 04056.104-97, Belarus) industrially produced from purified hydratocellulose was used as ACF. Its main characteristics measured at our laboratory are as follows: specific surface 1300–100 m^2 g, micropore specific surface 0.36 $cm^3\ g^{-1}$, mesopore specific surface 0.11 $cm^3\ g^{-1}$, and micropore half-width 0.73 nm. The ACF porous structure was calculated from adsorption isotherms obtained fwith benzene on a Carlo Erba Strumentazione Microstructure 85/02/04 instrument. The micro- and mesopore volumes were calculated by equations of the micropore volume filling theory of. Specific surface was calculated using the Brunauer–Emmet–Teller equation from data on low-temperature nitrogen adsorption measured on a Sorty 1750 Carlo Erba Strumentazione instrument.

Synthesis of activated carbon (sample *8*). A weighed sample of chemical grade sucrose, 1.5 g, was placed to a fused glass combustion boat and inserted to a fused glass flow reactor. The reactor was purged with methane for 10 min to remove air, after which the temperature was stepwise increased to 680°C within 20 min temperature. Carbonization was continued for 10 min, and the sample was then cooled in a closed air-proof vessel to room temperature. The yield of the carbonized product was 0.278 g (18.5%). Further treatment was performed using in the same fused glass reactor at 830 ± 10°C. For activation, argon (200 ml min^{-1}) was passed through a Drechsel bottle with distilled water heated to 60°C, and the resulting gas flow was passed through the reactor for 1 h. The reaction product was cooled under argon to room temperature. Yield 0.245 g (88% per carbonized sample).

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REFERENCES

1. Boehm, H.-P., *Carbon*, 1994, vol. 32, no. 5, p. 759.
2. Fedorov, G.G., Zarif'yants, Yu.A., and Kiselev, V.F., *Zh. Fiz. Khim.*, 1963, vol. 37, no. 7, p. 1619.
3. Pierce, C., Smith, R.N., Wiley, J.W., and Cordes, H., *J. Am. Chem. Soc.*, 1951, vol. 73, no. 10, p. 4551.
4. Smith, R.N., Pierce, C., and Joel, C.D., *J. Phys. Chem.*, 1954, vol. 58, no. 4, p. 298.
5. Miura, K. and Morimoto, T., *Langmuir*, 1986, vol. 2, no. 6, p. 824.
6. Miura, K. and Morimoto, T., *Langmuir.*, 1988, vol. 4, no. 6, p. 1283.
7. Moreno–Castilla, C., Lopez–Ramon, M.V., and Carrasco–Marin, F., *Carbon*, 2000, vol. 38, no. 14, p. 1995.
8. Grishina, A.D., *Dokl. Akad. Nauk SSSR*, 1971, vol. 199, no. 6, p. 1339.
9. Kiselev, V.F. and Nikitina, O.V., *Dokl. Akad. Nauk SSSR*, 1966, vol. 171, no. 2, p. 374.
10. Biniak, S., Szymanski, G., Siedlewski, J., and Swiatkowski, A., *Carbon*, 1997, vol. 35, no. 12, p. 1799.
11. Boehm, H.-P., *Carbon*, 2002, vol. 40, no. 2, p. 145.
12. Povstugar, V.I., Mikhailova, S.S and Shakov, A.A., *Zh. Analyt. Khim.*, 2000, vol. 55, no. 5, p. 455.
13. Garten, V.A. and Weiss, D.E., *Rev. Pure Appl. Chem.*, 1957, vol. 7, no. 1, p. 69.
14. Frumkin, A.N., *Usp., Khim.*, 1949, vol. 18, no. 1, p. 9.
15. *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1982, vol. 2.

16. Tarkovskaya, I.A., *Okislennyi ugol'* (Oxidized Carbon), Kiev: Naukova Dumka, 1981.
17. Stohr, B., Boehm, H.-P., and Schlogl, R., *Carbon,* 1991, vol. 29, no. 6, p. 707.
18. Simanova, S.A., Lysenko, A.A., Burmistrova, N.M., Shchukarev, A.V., Astashkina, O.V. and Timoshenko, S.I., *Zh. Prikl. Khim.,* 1998, vol. 71, no. 1, p. 50.
19. Simanova, S.A., Burmistrova, N.M., Lysenko, A.A., Astashkina, O.V., and Khramkova, N.V., *Zh. Prikl. Khim.,* 1998, vol. 71, no. 3, p. 375.
20. Kiselev, V.F., *Surface Effects in Semiconductors and Dielectrics* (Poverkhnostnye yavleniya v poluprovodnikakh i dielektrikakh), Moscow: Nauka, 1970.
21. Grishina, A.D., *Elektrokhimiya,* 1974, vol. 10, no. 2, p. 291.
22. Grishina, A.D., *Dokl. Akad. Nauk SSSR,* 1976, vol. 229, no. 3, p. 651.
23. Borissou, D., Guerret, O., Gabbai, F.P., and Bertrand, G., *Chem. Rev.,* 2000, vol. 100, no. 1, p. 39.
24. Zawadzki, J., *Chemistry and Physics of Carbon,* Thrower, P., Ed., New-York: Dekker, 1988, vol. 21, p. 147.
25. Zhang, Z., Berg, A., Levanon, H., Fessenden, R.W., and Meisel, D., *J. Am. Chem. Soc.,* 2003, vol. 125, no. 26, p. 7959.
26. Kuznetsov, A.N., *Metod spinovogo zonda* (The Method of Spin Label), Moscow: Nauka, 1976, p. 210.
27. Ivanova, T. V., Nikolaev, B.P., Petrov, L.N., and Toropov, D.K., *Vysokomol. Soedin.,* 1985, vol. 27A, no. 11, p. 2281.
28. Pikaev, A.K., and Kriminskaya, Z.K., *Usp. Khim.,* 1998, vol. 67, no. 8, p. 745.
29. Fridovich, I., *Free Radicals in Biology,* Pryor, W.A., Ed., New York: Academic, 1976, vol. 1. Translated under the title *Svobodnye radikaly v biologii,* Moscow: Mir, 1979, vol. 1, p. 272.
30. Tur'yan, Ya.I., *Okislitel'no-vosstanovitel'nye reaktsii i potentsialy v analiticheskoi khimii* (Oxidation-Reduction Reactions and Potentials in Analytical Chemistry), Moscow: Khimiya, 1989.
31. Sawyer, D.T. and Gibian, M.J., *Tetrahedron.,* 1979, vol. 35., no. 12, p. 1471.
32. Panin, A.I. and Tulub, A.V., *Int. J. Quantum Chem.,* 2000, vol. 77, no. 2, p. 580.
33. Khan, A.U., *J. Am. Chem. Soc.,* 1981, vol. 103, no. 21, p. 6516.
34. Howard, J.A., *Free-Radical Chemistry,* Williams, G.H., Ed., London: Logos, 1972, vol. 4, p. 49.
35. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area and Porosity,* London: Academic, 1982, 2nd ed.
36. Zarif'yants, Yu.A., Kiselev, V.F., and Fedorov, G.G., *Zh. Fiz. Khim.,* 1963, vol. 37, no. 8, p. 1846.
37. Minus, M.I. and Kumar, S., *J. Minerals, Metals, Materials Soc.,* 2005, vol. 57, no. 2, p. 52.
38. Su, F., Zhao, X.S., Lu, L., and Zhou, Z., *Carbon,* 2004, vol. 42, no. 14, p. 2821.
39. Kapteijn, F., Moulijn, J.A., Matzner, S., and Boehm, H.-P., *Carbon,* 1999, vol. 37, no. 7, p. 1143.
40. Zhu, Q., Money, S.L., Russel, A.E., and Thomas, K.M., *Langmuir.,* 1997, vol. 13, no. 7, p. 2149.
41. Rus'yanova, N.D., *Uglekhimiya* (Coal Chemistry), Moscow: Nauka, 2003.
42. Cal, M.P., *Characterization of Gas Phase Adsorption, Capacity of Untreated and Chemically Treated Activated Carbon Cloths. Thesis, Univ. of Illinois at Urbana,* Champaign, 1995, p. 59.
43. *Comprehensive Organic Chemistry,* Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979. Translated under the title *Obshchaya organicheskaya khimiya,* Moscow: Khimiya, 1982, Vol. 8.
44. Vol'eva, V.B., Belostotskaya, I.S., Bundel', A.Yu., Komissarova, N.L., and Ershov, V.V., *Izv. Akad. Nauk, Ser. Khim.,* 1997, no. 2, p. 398.
45. Schrauzer, G.N. and Guth, T.D., *J. Am. Chem. Soc.,* 1977, vol. 99, no. 22, p. 7189.
46. Yue, Ch., Trudeau, M. L.and Antonelli, D., *Can. J. Chem.,* 2005, vol. 83, no. 4, p. 308.
47. Rusina, O., Eremenko, A., Frank, G., Strunk, H.P., and Kisch, H., *Angew. Chem., Int. Ed. Engl.,* 2001, vol. 40, no. 21, p. 3993.
48. Rusina, O., Linnik, O., Eremenko, A., and Kisch, H., *Chem. Eur. J.,* 2003, vol. 9, no. 2, p. 561.
49. Hoshino, K., *Chem. Eur. J.,* 2001, vol. 7, no. 13, p. 2727.
50. Turchi, C.S. and Ollis, D.F., *J. Catalysis,* 1990, vol. 122, no. 1, p. 178.
51. Katakis, D. and Taube, H., *J. Chem. Phys.,* 1962, vol. 36, no. 2, p. 416.
52. Fedoseev, I.V., *Zh. Neorg. Khim.,* 2003, vol. 48, no. 3, p. 426.
53. Gekhman, A.E., Stolyarov, I.P ., Shestakov, A.F., Shilov, A.E., and Moiseev, I.I., *Izv. Akad. Nauk, Ser. Khim.,* 2003, no. 3, p. 733.
54. Nagiev, M.F., Nagiev, T.M., Aslanov, F.A., Bairamov, V.M., and Iskanderov, R.A., *Dokl. Akad. Nauk SSSR,* 1973, vol. 213, no. 5, p. 1096.
55. Nagiev, T.M., Zokhrabbekov, S.Z., and Shakhtakhtinskii, T.N., *Azerb. Khim. Zh.,* 1978, no. 1, p. 3.
56. Nagiev, T.M. and Zokhrabbekov, S.Z., *Azerb. Khim. Zh.,* 1978, no. 6, p. 39.
57. Nagiev, T.M., Zokhrabbekov, S.Z., and Shakhtakhtinskii, T.N., *Dokl. Akad. Nauk SSSR,* 1987, vol. 292, no. 6, p. 1392.
58. Stefanič, I. and La Verne, J.A., *J. Phys. Chem.,* 2002, vol. 106, no. 2, p. 447.
59. Proskurikhin, M.A., Orekhov, V.D., and Barelko, E.V., *Usp. Khim.,* 1955, vol. 24, no. 5, p. 584.
60. Shestakov, A.F. and Shilov, A.E., *Izv. Akad. Nauk, Ser. Khim.,* 2001, no. 11, p. 1963.
61. Danil'chenko, P.T. and Ravich, M.I., *Zh. Russ. Fiz.-Khim. O—va.,* 1929, vol. 61, no. 1, p. 123.