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On the Mechanism of Air Nitrogen Fixation on Activated Carbon Surface in Water

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Abstract—High-performance liquid chromatography and gas chromatography were used to reveal formation of hydroxyl radicals in air–saturated water containing activated carbon. Probable mechanisms of $OH^{\cdot}$ formation are considered. The role of $OH^{\cdot}$ radicals in the formation of carbene centers on the activated carbon surface is discussed. For interpreting the experimental data on atmospheric nitrogen fixation on activated carbon surface, probable mechanisms of nitrogen activation are explored by quantum–chemical methods. Highly reactive $OH^{\cdot}$ radicals are unable to react with molecular nitrogen under mild conditions. A high reactivity of singlet and triplet carbenes of different nature on activated carbon surface with respect to N_2 molecules was revealed by density functional theory methods.

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The structure of activated carbon is macroscopically isotropic, but at the nano level it consists of 2D- and, in part, 3D-order fragments. At this ordering level activated carbon can be considered as a graphite-like material [1]. Nitrogen fixation on graphite surface on high-temperature reactions of graphite with various nitrogenous compounds is well documented. Plasma treatment of graphite under a pure nitrogen atmosphere gives rise to gaseous dicyan and surface nitrogenous carbon compounds [2]. X-ray photoelectron spectroscopy allowed to detect on the surface of graphite after such treatment pyridine (N-6) and pyrrole-like (N-5) groups, as well as fragments containing quaternary nitrogen (N–Q)[1] and cyano and amino groups [3].

At high temperatures activated carbon and its fibers form similar surface compounds on contact with NH_3, HCN, and nitrogen oxides N_yO_x. Ammonia and hydrogen cyanide exhibit reductive activity toward surface oxygen carbon, whereas nitrogen oxides can oxidize the carbon matrix. Upon treatment of activated carbon fibers with ammonia at 723–1073 K, nitrogen (1–4%) as amino and amido groups [4], as well as pyridine- and pyrrole-like fragment was found on the surface. Treatment of activated carbons with NH_3 and HCN at 873–1173 K results in formation of surface amino, cyano, and pyridine-like fragments [5]. Upon reactions of activated carbons with NO in the presence of oxygen under the same temperature conditions (873 K), nitroso, nitro, and nitrogen-containing groups like N-6, N-5, and N–Q were fixed on the carbon matrix [6]. Plasmochemical treatment of carbons with a mixture of N_2 with NO or NO with argon yielded surface pyridine- and pyrrole-like compounds N-6 and N-5, as well as NO_2 and NO_3 groups [2]. The reaction of activated carbon with N_2O at 773 K, too, gave a little surface nitrogen, but the nature of the resulting nitrogen-containing groups was not established [7].

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[1] According to [2], the nitrogen atoms having E_bN1s values reported in the cited work belong to a pyridine-like, rather than to an N–Q group.

It was previously shown that contact of activated carbon or its fibers with air in distilled water at room temperature gives rise to various redox reactions to form on the surface of carbon materials of not only oxygen carbon complexes, but also some nitrogen-containing fragments covalently bound with the carbon matrix [8]. These fragments are similar in nature to the surface nitrogen-containing compounds that are formed by treatment of carbons with ammonia, hydrogen cyanide, and nitrogen oxides under the above-described severe conditions. In our opinion, such oxygen- and nitrogen-containing fragments are formed by the reaction of carbon surface defects with water-dissolved oxygen molecules, involving charge transfer to give $O_2^{\cdot-}$ radical anion as a primary species. Evidence for the existence of this species was obtained by the nitro blue tetrazolium test [8]. Further reactions in solution near the activated carbon surface can provide various secondary reactive oxygen species, such as $HO_2^{\cdot}$, $^1O_2(^1\Delta_g)$, H_2O_2, or $OH^{\cdot}$ [8]. Under normal conditions in air the carbon surface is protected from corrosion by oxygen carbon complexes and surface compounds with a terminal C–H bond. Reactive oxygen species can oxidize these protective groups to form fragments of the juvenile surface of the carbon matrix, which are carbene centers. We consider reactions of certain such centers with water-dissolved molecular nitrogen responsible for the fixation of nitrogen in the carbon matrix. It is quite probable that similar surface carbene centers can also be formed by the above-mentioned high-temperature redox reactions with NH_3, HCN, and N_yO_x.

Let us now consider the probable mechanisms of primary reactions of active species with molecular nitrogen. On the one hand, the above oxygen species can oxidize water-dissolved N_2 molecules to form, for instance, N_2O. Actually, the direct gas-phase reaction of N_2 with an excited ($A_2\Sigma^+$) hydroxyl radical gives rise to N_2O [9]. Two-electron reductants are able, from the thermodynamic viewpoint, to convert N_2O into ammonia via an H_2N_2O intermediate [10]. Further reduction of the latter can provide NH_2OH molecules and other NH-containing species or radicals. Quite obviously, reactions of unsaturated 1,5- and 1,4-dicarbonyl compounds with ammonia or hydroxylamine on the activated carbon surface can give rise to surface pyridine- and pyrrole-like compounds and their derivatives [8]. Evidence for this suggestion comes from the results of Arraigada and co-workers [11–13] who revealed partial fixation of nitrogen-containing compounds on the surface of carbon contacting with aqueous solutions of ammonia [11, 12] and methyl- and diemthylamine [13], both under normal conditions and under elevated temperatures and pressures. According to [11–13], ammonia and amines are fixed on surface carboxy, lactone, and anhydride groups. Furthermore, the formation of ammonia from N_2 molecules under normal pressure in aqueous solutions containing a 1:2 clathrate complex of fullerene C_{60} with γ-cyclodextrin and $Na_2S_2O_4$ reductants was reported [14]. This reaction was shown to be favored by slight heating (60°C), stirring, and illumination with scattered visible light.

On the other hand, carbene carbon centers formed by redox reactions on the activated carbon surface can react, in principle, with dissolved molecular nitrogen to form diazo compounds as intermediate products [15]. Such reactions, too, can fix nitrogen on the carbon surface.

Electron transfer to the oxygen molecule imparts a positive charge to the carbon matrix. Further C^+ reaction with a water molecule can provide atomic oxygen [16], but the latter can scarcely react with water-dissolved N_2 molecules under the conditions in question. This suggestion is supported by the results of quantum-chemical calculations [17] which show that the primary reaction leading to $NNH^{\cdot}$ radical formation is endothermic (ΔH 3.8 ± 0.5 kcal mol^{-1}), and, even having a fairly low energy barrier of 10.0 ± 1.0 kcal mol^{-1}, this reaction cannot compete with other exothermic and almost barrierless reactions of atomic oxygen.

In the present work we have studied the nature of reactive oxygen species formed in the system activated carbon–water-dissolved oxygen and performed a theoretical analysis of the possible mechanisms of fixation of atmospheric nitrogen on the activated carbon under these conditions.

The appearance of active oxygen species in the solution was detected by chromatographic analysis of their reaction products with traps: propan-1-ol and benzoic acid.

High-performance liquid chromatography of compounds formed on contact of a Busofit T-055 activated carbon fiber or a Norit SXG activated carbon with an air-bubbled aqueous solution of propan-1-ol revealed formation of propanal in both cases. At equal samples of carbon material, the yields of propanal differed about 2 times (1.0 mg l^{-1} with Norit SXG and 2.1 mg l^{-1} with Busofit T-055).

Analysis of products formed on contact of benzoic acid with atmospheric oxygen dissolved in distilled water in the presence of activated carbon was performed by GC–MS. Bezoic acid and its hydroxy derivatives formed were trimethylsilylated and analyzed in the SIM mode using 3-fluorobenzoic acid as a surrogate standard.

The analyzed samples were labeled as follows: (1) a solution of benzoic acid bubbled with purified air in the presence of activated carbon; (2) a 0.1 M NaOH eluate of the activated carbon from sample no. 1; (3) chemical grade benzoic acid recrystallized from water. Treatment of activated carbon with a solution of NaOH (sample no. 2) was applied to desorb benzoic acid and its hydroxy derivatives.

The assessed concentrations of hydroxybenzoic acids in the samples (mg l^{-1}) are listed below.

Compound	Sample no. 1	Sample no. 2
2-Hydroxybenzoic acid	0.1	1.5
3-Hydroxybenzoic acid	0.1	1.0
4-Hydroxybenzoic acid	0.06	0.4

Let us consider the resulting data in terms of the reactive oxygen intermediates formed in water and their possible reactions both with carbon surface and dissolved molecular nitrogen. In an elementary redox act, superoxide radical anion $O_2^{\cdot-}$ can in principle act as a one- or two-electron oxidant or reductant. The reaction mechanism (one- or two-electron) depends on the nature of both the oxidant or reductant, since thermodynamically allowed noncomplementary reactions are kinetically hindered. In the case of one-electron transfer, $O_2^{\cdot-}$ exhibits redultive properties under standard conditions, but acts as a one-electron oxidant only in the presence of very strong reductants, such as As(III) [18]. The reported standard one$^-$ $^{\cdot}$electron redox potentials, V, in aqueous solutions for $O_2/O_2^{\cdot-}$ and $O_2^{\cdot-}/O_2^{2-}$ pairs are –0.284 [19] (–0.563 at pH 14 [20]) and < –1.70. Two-$^{\cdot}$electron oxidation of the $O_2^{\cdot-}$ radical anion would be expected to provide dioxygenyl cation $O_2^{\cdot+}$; this requires for a very strong oxidant to be involved in reaction, which is impossible in our case. Presumably, $O_2^{\cdot-}$ can act as a two-electron oxidant with respect to propan-1-ol. However, this species is known to fails to oxidize 2-methylpropan-2-ol either by the one- and two-electron mechanism [18]. As judged from the detected reaction products, no two-electron oxidation of benzoic acid with $O_2^{\cdot-}$ occurs.

The standard potential of the $^1O_2/O_2^{\cdot-}$ pair is 0.79 V. Singlet molecular oxygen can form in the system in hand in several ways, including disproportionation of the hydroperoxyl radical formed by hydrolysis of the $O_2^{\cdot-}$ radical anion or reaction of $HO_2^{\cdot}$ with hydrogen peroxide [21]. In the latter case, hydroxyl radical $OH^{\cdot}$ is formed in the solution, along with $^1O_2$. According [22], the $^1O_2$ molecule does not react with propan-1-ol or this reaction is very slow and cannot compete with reactions of the alcohol with other, such as hydroxyl radical. Singlet oxygen $^1O_2$ does not react, at an appreciable rate, with benzoic acid [23] and with molecular nitrogen [24, 25] to form nitrogen oxides. However, $^1O_2$ can oxidize certain fragments of the carbon matrix. It is known [26] that the $^1O_2(^1\Delta_g)$ molecule reacts with fused aromatic compounds to form transannular peroxides, and its addition across conjugated double bonds gives rise to epiperoxide compounds. It should be noted that classical reviews on surface functional groups of activated carbons [27, 28] touch upon no of the above types of peroxides; at the same time, epiperoxides which are most frequently named cyclic peroxides are fairly frequently mentioned in the literature on activated carbons [29, 30]. The appearance of H_2O_2 molecules cannot be associated with hydrolysis of epiperoxide organic fragments on the carbon surface.

As known [31], alcohols, including propan-1-ol, fail to react at an appreciable rate with hydrogen peroxide and molecular oxygen under normal conditions. Addition of benzoic acid to aqueous solutions of hydrogen peroxide allows the titer of the latter to be maintained for over 1 year, which provides evidence for the stability of this system [32] and, at least, for the lack of hydroxylation of the aromatic ring. Thus, no one of the above-considered compounds can alone form propanal or an isomeric mixture of hydroxybenzoic acids. At the same time, hydrogen peroxide which is always present in water over activated carbons in a low but constant concentration [29] can oxidize both the carbon surface [33] and, in principle, N_2 to N_2O even at room temperature [24, 25]. There is experimental evidence showing that the latter process occurs fairly fast at high temperatures [34].

The standard redox potential for the $HO_2^{\cdot}/HO_2^{-}$ pair is –0.744 V [19], implying a weak oxidative capacity of the hydroperoxyl radical in a one-electron reaction in standard conditions. The hydroperoxyl radical takes part in liquid-phase oxidation of alcohols [35]. The oxidative process involving atmospheric oxygen and the organic peroxyl radicals formed provides carbonyl compounds as final products.

Hydroxyl radicals fast oxidize primary alcohols into corresponding aldehydes [36]; along with aldehydes, more profound destruction products are formed. Under the action of $OH^{\cdot}$ radicals, 2-methylpropan-2-ol forms formaldehyde with a fairly high yield [37]. In this connection we would like to mention that, as found in [5], ethanolic sodium ethylate over activated carbon in air converts into a mixture of at least 6 compounds, including acetaldehyde and glyoxal. Under argon instead of air, no such compounds are formed in the same system.

Benzoic acid scarcely reacts with hydroperoxyl radical [38]. With hydroxyl radical, a mixture of compounds is formed [39], that contains 2-, 3-, and 4-hydrobenzoic acids as major components, di- and trihydroxybenzoic acids as minor components, and phenol and hydroquinone as traces. Di- and trihydroxybenzoic acids are formed by the reaction of corresponding isomers of salicylic acid with hydroxyl radicals [40]. Quantitative analysis of the mixture showed that the relative amount of isomeric hydroxybenzoic acids depend on the mode of generation of hydroxyl radicals and the pH of the solution. As shown in [39], the maximum isomer ratio is 1:1:1, but, depending on experimental conditions, the fractions of the 3-hydroxy and, especially, 4-hydroxy isomer can be slightly smaller.

Certain authors [34, 41] have suggested formation of NO in the reaction of molecular nitrogen with hydroperoxyl radical, but we consider such process hardly probable.

The reaction of $OH^{\cdot}$ with graphite in a gas flow at 298 K gives CO and CO_2 in roughly equivalent amounts [42].

It is known [43] that hydroxyl radical is a conjugate acid (pK_a 11.9 ± 0.2) of the radical anion of atomic oxygen O^{-}. The WSC-208C-GR activated carbon used in experiments with benzoic acid belongs to H^{-}carbons. The concentration of hydroxide anions near the surface of H^{-} carbons can be quite high [29], and, therefore, one cannot exclude formation of hydrated O^{-} according to Eq. (1).

$$OH^{\bullet} + OH^{-} \rightleftarrows O^{-\bullet} + H_2O. \qquad (1)$$

The primary products of the reaction of O^{-} radical anion with benzoic acid derivatives are phenoxyl-type radicals [44]. In aqueous alkaline solutions, O^{-} reacts with N_2O to form molecular nitrogen and NO_2^{-} anion [45].

Theoretical research [10] shows that O^{-} radical anion, having π-donor orbitals, can act with respect to molecular nitrogen as an isolobal analog of a transition metal ion. As a result, $[N_2O]^{-}$ and $[N_2ON_2]^{-}$ complexes can form is principle, and, therewith, N_2O^{-} bond energy in the first species is 41.8 kJ mol^{-1} [10]. Thus result, together with data in [45], gives certain grounds for explaining the formation of NO_2^{-} in γ-radiolysis of air-saturated aqueous alkaline solutions [46]. However, it is known that in the absence of solvent the N_2O^{-} species at 77 K in the solid phase gives one electron to oxygen molecule to convert it to O_2^{-} radical anion [47], while in aqueous solutions N_2O^{-} decomposes according to Eq. (2).

$$N_2O^{-\bullet} \rightarrow N_2 + OH^{\bullet} + OH^{-}. \qquad (2)$$

The lifetime of N_2O^{-} in alkaline solutions can be longer than 10^{-8} s; some evidence for intermediate formation of $N_2OH^{\cdot}$ radical anion is available (cf. [48] and references therein). Molecular nitrogen and hydroxyl radical can also be formed by the reaction of N_2O with atomic hydrogen [49].

Singlet atomic oxygen $^1O(^1D)$ is known to be a strong electrophile, since it has a vacant *p* orbital (LUMO). According to [50], $^1O(^1D)$ reacts with molecular nitrogen to form N_2O, and in aqueous solutions $^1O(^1D)$ readily reacts with solvent [51] whose is concentration is incommensurable higher that the concentration of dissolved nitrogen [Eq. (3)].

$$^1O(^1D) + H_2O = 2OH^{\bullet}. \qquad (3)$$

By this reason, $^1O(^1D)$ was impossible to distinguish from $OH^{\cdot}$ in our present work. However, even if $^1O(^1D)$ species still form in any way in solutions, then, in force of the above-mentioned reasons, we consider its reaction with N_2 molecules unlikely.

Finally, formation of secondary intermediates and such species as H_2O_3 and O_3 [52–54] [Eq. (4)], as well as radical ozone reduction products: O_3^{-} and $HO_3^{\cdot}$ [55, 37].

$$^1O_2 + yH_2O \begin{array}{l} \rightarrow [H_2O_3(H_2O)_{y-1}] \\ \\ \rightarrow O_3 \end{array} \qquad (4)$$

Ozone much slower reacts with benzoic acid in aqueous solutions than $OH^{\cdot}$ radicals generated in the O_3–H_2O system [55]. Alcohols, too, much slower react with ozone in aqueous solutions than are oxidized with hydroxyl radicals [37]. By this reason, the reaction of ozone with $C_6H_5COOH^{\cdot}$ is masked by oxidation of the latter with $OH^{\cdot}$ radicals [23, 54], which is likely to be also the case with propan-1-ol oxidation.

Water-dissolved ozone effectively oxidizes the surface of coal granules, thus increasing the concentration of oxygen atoms on it [33]. Ozone generates all types of oxygen carbon complexes on the surface, but the content of hydroxy, carbonyl, and carboxy groups increases to the greatest extent [33].

From the thermodynamic viewpoint, ozone can convert molecular nitrogen into nitrogen(I) oxide [25], whereas, as known, this process does not actually occur.

Hydroxyl radicals effect nonregioselective hydroxylation of benzoic acid, whereas short-lived hydro–ozonyl radicals $HO_3^{\cdot}$ selectively oxidize benzoic acid exclusively to 4-hydroxybenzoic acid [23]. The yield of this isomer is lower than the yields of 2 and 3-hydroxybenzoic acids, from which it follows that the oxidant $HO_3^{\cdot}$ contributes nothing or very little in the overall process.

As judged from our present results, the existence of hydroxyl radical in the system in question can be considered proven, but this radical can be formed in the solution in several ways.

Not excluded that the above-considered reactive oxygen species, first of all hydroxyl radicals, take part in the well-documented [29, 56] catalytic oxidation of various organic and inorganic compounds with atmospheric oxygen in the presence of activated carbon. The most characteristic example of this property of activated carbon is the methodology of waste water purification by means of catalytic wet air oxidation (CWAO), which is presently being actively developed. In cases of our interest, either activated carbon itself or its particles with deposited platinum metals or inorganic compounds are used as catalysts [57]. The oxidant here is formally atmospheric oxygen, and the process is accomplished at elevated temperatures and pressures [57]; therewith, such compounds as ammonia and methyl- and diethylamines, too, are oxidized in these conditions [12, 13]. The oxidation products are N_2 and H_2O (with NH_3 at 130–190°C) or a mixture of N_2, H_2O, and CO_2 [with NH_2CH_3 and $NH(CH_3)_2$ at 195°C]. With NH_2CH_3 and $NH(CH_3)_2$, traces of nitrite and nitrate ions were also detected [13]. As known, hydroxyl radicals oxidize ammonia in aqueous solutions into molecular nitrogen and water [58]. Both primary and secondary amines can behave in a similar way, and, therewith, the oxidation of NH_2CH_3 and $NH(CH_3)_2$ in aqueous solutions with $OH^{\cdot}$ radicals begins with hydrogen elimination from the NH and/or CH_3 groups, which is determined by the pH of the system [59].

The catalytic oxidation of NH_3, NH_2CH_3, and $NH(CH_3)_2$ is best performed on carbon preliminarily treated with hydrogen [12, 13]. This treatment frees the carbon surface from oxygen-containing fragments which protect, to a certain extent, the surface from further oxidation and reaction with water with its dissolved oxygen and other reactive species. The reduction process is accompanied by formation of new defects capable of reacting with molecular oxygen dissolved in water. Thus, the probability of generation of superoxide radical anions is increased. The latter, in their turn, favor formation of hydroxyl radicals [8] that oxidize amines. The unusual reactivity of carbene centers was exemplified by Liu et al. [60] by the reaction of NO with defects on walls of carbon nanotubes.

Analysis of the primary processes involving N_2 and high-reactivity species on or at the carbon surface on its contact with air-saturated water prompted us to consider the possibility of reaction of the N_2 molecule with hydroxyl radical. To this end, we calculated the structure of the possible products N_2OH and the energies of their formation in the reaction between N_2 and $OH^{\cdot}$. The calculations were performed by methods of density functional theory (B3LYP), fourth-order perturbation theory (MP4SDTQ), and coupled clusters (CCSD) in the 6-311++G basis using the GAUSSIAN-98 software [61]. The optimized geometries of these compounds are shown in Fig. 1.

Below we present the calculated energies of the reactions between N_2 and $OH^{\cdot}$ (kJ mol^{-1}), forming compounds **I–IV**.

Compound	B3LYP	MP4SDTQ	CCSD
I	365.2	512.5	527.1
II	148.9	375.7	330.9
III	39.3	245.2	225.9
IV	65.3	261.9	250.6

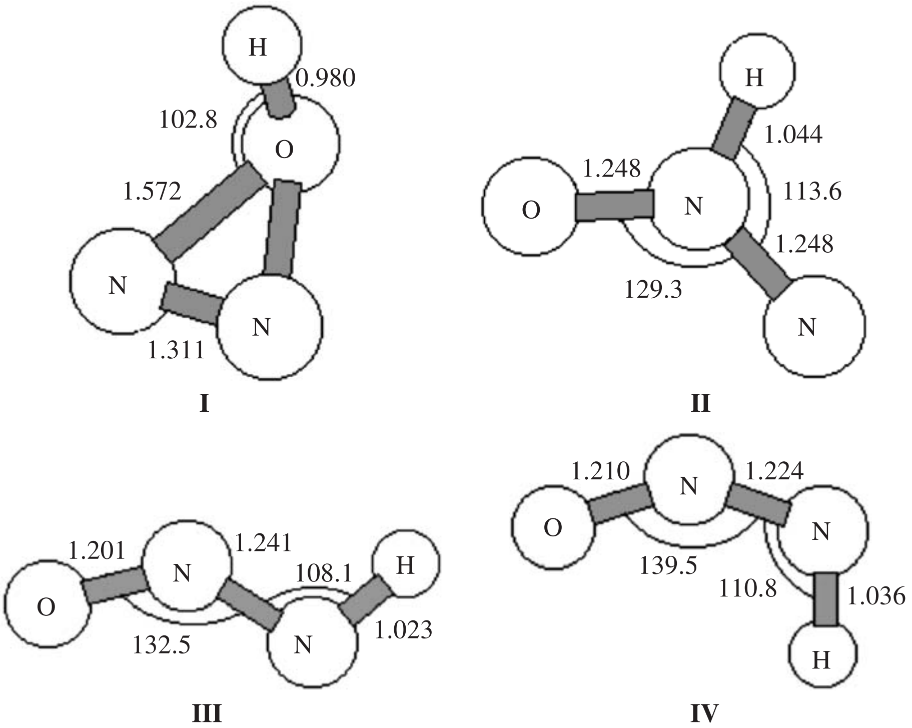
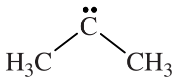


Fig. 1. Structures of compounds **I–IV**.

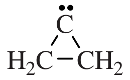
As follows from the presented data, the formation of compounds **I–IV** is an endothermic process, structure **I** being the most thermodynamically favorable. The N=N–OH structure is not realized, since it is a weakly bound van der Waals complex. Structures **II–IV** are more favored by energy. Quantum–chemical calculations [62] suggest that structures **II–IV** can be formed as intermediates in fuel combustion in air via oxidation of NNH radical with atomic oxygen. The decomposition of these intermediates along several independent pathways is considered to be responsible for the appearance of such compounds as NO and N_2O among the combustion products [62]. However, according to our calculations, the nitrogen molecule is almost impossible to oxidize with $OH^{\cdot}$ radicals under mild conditions.

Analysis of published data shows that the reactions of valence–saturated carbon atoms on the surface of activated carbon with $OH^{\cdot}$ radical may well form carbene centers which are potentially capable of fixing nitrogen. To check this suggestion, we performed DFT/PBE simulation of addition of molecular nitrogen to carbenes **V–XI** in the singlet and triplet states.



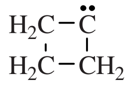
$C(CH_3)_2$

V



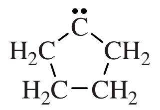
$C(CH_2)_2$

VI



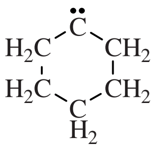
$C(CH_2)_3$

VII



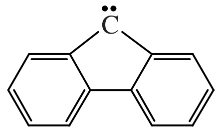
$C(CH_2)_4$

VIII



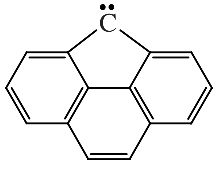
$C(CH_2)_5$

IX



$C(C_6H_4)_2$

X



$C(C_{14}H_8)$

XI

Energy gains (ΔE, kJ mol^{-1}) and energy barriers ($\Delta E^{\neq}$, kJ mol^{-1}) for nitrogen addition to carbenes, obtained by the DFT/PBE method (the indices S and T relate to the singlet and triplet states, respectively)

Characteristics	Carbene[a]						
	$C(CH_3)_2$*	$C(CH_2)_2$	$C(CH_2)_3$*	$C(CH_2)_4$	$C(CH_2)_5$*	$C(C_6H_4)_2$*	$C(C_{14}H_8)$*
ΔE_S	–130.9	–109.6	–136.87	–115.9	–121.3	–161.5	–128.0
ΔE_T	–28.9	–24.3	–40.6	–56.1	–19.2	–23.8	–25.5
$\Delta E^{\neq}_T$	24.7	32.2	29.3	45.2	24.3	30.1	30.1
Singlet–triplet splitting energy, ΔE_{ST}	13.4	–40.6	6.7	–30.1	14.6	36.4	43.9
Imaginary vibration frequency, w_i, cm^{-1}	307.5	352.5	326.5	303.1	298.9	268.7	265.6
∠CCC, deg	120.6	66.8	93.1	115.4	133.1	116.0	115.7
∠CCN, deg	122.1	118.9	131.1	115.5	107.6	123.9	121.3
∠CNN, deg	128.2	120.3	125.8	119.3	110.6	109.4	109.1
C–N bong length r(C–N), Å	1.96	1.95	1.97	1.96	1.96	2.51	2.50
N–N bong length r(N–N), Å	1.13	1.13	1.13	1.13	1.13	1.10	1.10

[a] Star-labeled are carbenes triplet in the ground state.

The table lists the energy characteristics of these reactions and structural characteristics of transition states. The calculations were performed using the PRIRODA program [63] with the SBK pseudopotential and an extended basis.

Figure 2 shows as an example the structures of a model surface active center with the greatest number of carbon atoms and its reaction products with molecular nitrogen.

Different carbenes show similar reactivities toward molecular nitrogen. A singlet reaction product always has a linear C–N=N group and is formed with the greatest energy gain. Therefore, it has the lowest energy irrespective of what carbene state, singlet or triplet, is lower by energy. Moreover, the formation of a singlet adduct with N_2 is a barrierless process.

The triplet state is the principal state of carbene centers, and singlet–triplet splitting is prevailing in most aromatic carbene structures. Conjugation effects decrease energy expenses for their formation. It is quite remarkable that reactions of triplet carbene complexes with nitrogen always occur with an energy gain, though not too large, and have low activation barriers.

Thus, our study led us to suggest that carbene centers of different types, arising on the surface of activated carbon, are highly reactive toward molecular nitrogen. It is very important that nonlinear triplet adducts of molecular nitrogen bear an appreciable spin density on the N_2 fragment. This creates prerequisites for further recombination reactions with radical species present in the system or for addition to unsaturated bonds, which can result in further weakening and possible cleavage of the nitrogen–nitrogen bond to form structures containing one nitrogen atom. Since carbenes are highly reactive species and can readily enter in diverse reactions, their quasisteady-state concentration controls fixation of molecular nitrogen.

EXPERIMENTAL

Propanal was determined by HPLC on a Waters LCM–module-1 instrument with a UV detector (λ 254 nm) on a Symmetry C18 3.9×150 mm (particle size 5 mm), mobile phase flow rate 1 ml min^{-1}, injection volume 30 μl. Mobile phase acetonitrile–deionized water (1:1 v/v).

Gas chromatography–mass spectrometry was performed on a Shimadzu QP 2010 instrument (for conditions, see below).

Sample preparation. As activated carbon materials we used a Busofit T-055 activated carbon fiber or a Norit SXG activated carbon in experiments with propan-1-ol and a WSC-208C GR carbon (6–12 mesh) in experiments with benzoic acid.

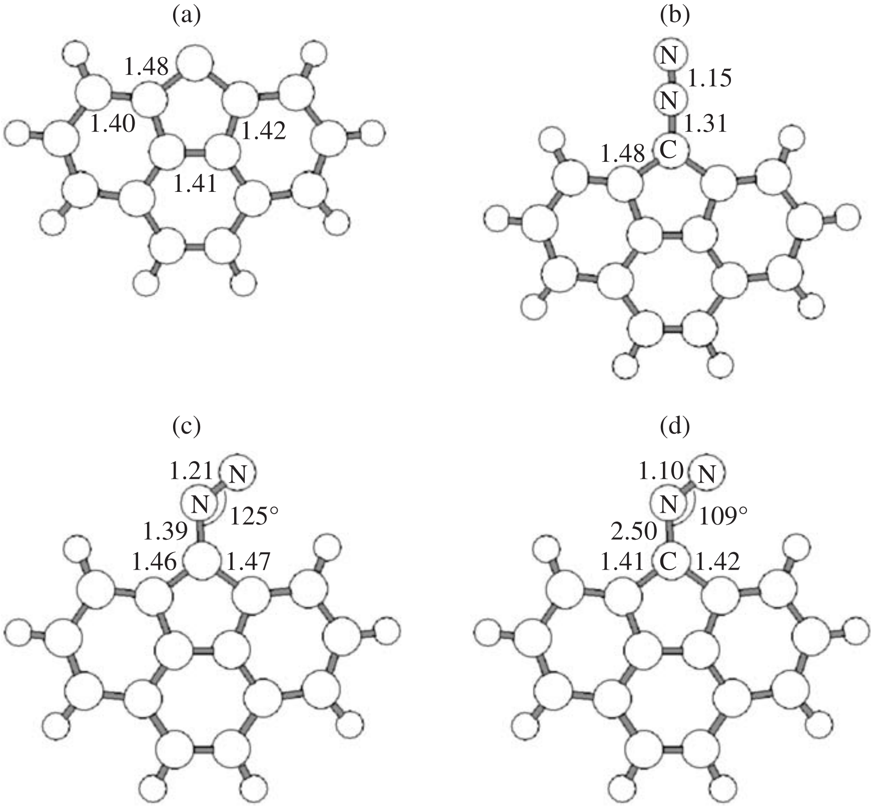


Fig. 2. Optimized structures and geometric parameters of (a) singlet carbene $C(C_{14}H_8)$ and its complexes with nitrogen $N_2C(C_{14}H_8)$: (b) singlet, (c) triplet, and (d) triplet transition state of addition of molecular nitrogen, obtained by the DFT PBE method.

Propan-1-ol, 5 g, of chemical grade or 1 g of benzoic acid was dissolved in a freshly distilled water (100 ml) in a two-necked flask. Benzoic acid of chemical grade was preliminarily recrystallized from hot water. Activated carbon or carbon fiber, 250 mg, was added to the solution, and preliminarily purified (by passing through Drexel's flasks containing concentrated H_2SO_4 and 20% NaOH).

Determination of propanal by HPLC. The aqueous solution of propan-1-ol in the flask was filtered to remove carbon, and 4 ml of a 5 mM solution of 2,4-dinitrophenylhydrazine in DMSO was added to the filtrate. The mixture was allowed to stand for 1 h and then subjected to analysis. In a blank experiment, 2 μl propanal was added to 10 ml of a 5% aqueous solution of propan-1-ol. The retention times of 2,4-dinitrophenylhydrazine and propanal 2,4-dinitrophenylhydrazone were 5.1 and 19.2–19.7 min, respectively.

Determination of isomeric hydroxybenzoic acids by GLC. After completion of the experiment with $C_6H_5COOH^{\cdot}$, the flask content was filtered through a glass frit. The filtrate, 1 ml, was taken with a pipette and evaporated to dryness in a vacuum concentrator. An alkaline sample (sample no. 2) was preliminarily neutralized to pH 6 with 0.1 M HCl. Acetonitrile, 200 μl, and a solution of internal reference were added to the residue, and the solution was unltrasonicated for 5 min. The acetonitrile solution was transferred with a syringe into another vial. The procedure was repeated with a new portion of acetonitrile. The acetonitrile solution was reduced to 20 μl under a stream of argon, 20 μl of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was added, and the mixture was heated for 30 min at 60°C with intermittent shaking, cooled, and analyzed by GC–MS (injection volume 1 μl).

Conditions of chromatographic separation: injector temperature 250°C; splitless mode (0.2 min); HP-5 MS (30 m × 0.2 mm × 0.25 μm) capillary column; temperature program: initial temperature 50°C (1 min), heating rate 10 deg min^{-1}, final temperature 270°C; carrier gas helium, flow rate 0.9 mm^3 min^{-1}. Interface and detector temperatures 250°C.

Conditions of mass spectral analysis: ionizing electron energy 70 eV, ion source temperature 250°C, registration mode SCAN (*m*/*z* 33–500, choice of analysis conditions) or SIM (analysis). Since hydroxybenzoic acids were determined in the presence of high concentrations of benzoic acid, the following registration conditions were used. In window 1 (*RT* 9.2–10.3 min), a peak of 3-fluorobenzoic acid (internal reference) was registered (*RT* 10.2 min, *m*/*z* 197). In window 2 (*RT* 10.3–12.0 min), the mass-selective detector was turned off (the *RT* of benzoic acid is 10.5 min). In window 3 (*RT* 12.0–22.0 min), peaks of bistrimethylsilyl esters of 1,2-, 1,3-, and 1,4-hydroxybenzoic acids were registered (*RT* 14.32, 14.97, and 15.75 min, respecively; *m*/*z* 267). After each analysis the column was treated in succession with a 5% methanolic solution of trime-thylanilinium hydroxide, acetonitrile, and BSTFA, since the analyzed conditions possess a high sorption capacity.

REFERENCES

1. Fenelonov, V.B., *Poristyi uglerod* (Porous Carbon), Novosibirsk: Inst. Kataliza Sib. Otd. Ross. Akad. Nauk, 1995.
2. Hueso, J.L., Espinus, J.P., Caballero, A., Cotrino, J., and Gonzalez-Elipe, A.R., *Carbon*, 2007, vol. 45. no. 1, p. 89.
3. Zhu, Q., Money, S.L., Russel, A.E., and Thomas, K.M., *Langmuir*, 1997, vol. 13, no. 7, p. 2149.
4. Dimotakis, E.D., Cal, M.P., Economy, J., Rood, M.J., and Larson, S.M., *Environ. Sci. Technol*., 1995, vol. 29, no. 7, p. 1876.
5. Stohr, B., Boehm, H.P., and Schlogl, R., *Carbon*, 1991, vol. 29, no. 6, p. 707.
6. Suzuki, T., Kyotani, T., and Tomita, A., *Ind. Eng. Chem. Res*., 1994, vol. 33, no. 11, p. 2840.
7. Velasquez, J.J.D., Suarez, L.M.C., and Figueiredo, J.L., *Carbon*, 2007, vol. 45, no. 1, p. 212.
8. Vorob'ev-Desyatovskii, N.V., Ibragimova, R.I., Gordeev, S.K., and Nikolaev, B.P., *Zh. Obshch. Khim.,* 2006, vol. 76, no. 6, p. 988.
9. Estupinan, E.G., Stickel, R.E., and Wine, P.H., *Chem. Phys. Lett*., 2001, vol. 336, nos. 1–2, p. 109.
10. Shestakov, A.F. and Shilov, A.E., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2001, no. 11, p. 1963.
11. Soto-Garrido, G., Aguilar, C., Garcia, R., and Arraigada, R., *J. Chil. Chem. Soc*., 2003, vol. 48, no. 3, p. 65.
12. Aguilar, C., Garcia, R., Soto-Garrido, G., and Arraigada, R., *Appl. Catal. B: Environ*., 2003, vol. 46, no. 2, p. 229.
13. Aguilar, C., Garcia, R., Soto-Garrido, G., and Arraigada, R., *Top. Catal*., 2005, vol. 33, nos. 1–4, p. 201.
14. Nishibayashi, Y., Saito, M., Uemura, S., Takekumura, S., Takekumura, H., and Yoshida, Z., *Nature*, 2004, vol. 428, no. 6980, p. 279.
15. Shilov, A.E., Shteinman, A.A., and Tjabin, M.V., *Tetrahedron Lett*., 1968, no. 39, p. 4177.
16. Panin, A.I. and Tulub, A.V., *Int. J. Quant. Chem*., 2000, vol. 77, no. 2, p. 580.
17. Gu, J., Xie, Y., and Schaefer H.F., III, *J. Chem. Phys.,* 1998, vol. 108, no. 19, p. 8029.
18. Xu, T., Kamat, P.V., and O'Shea, K.E., *J. Phys. Chem. A*, 2005, vol. 109, no. 40, p. 9070.
19. Tur'yan, Ya.I., *Okislitel'no–vosstanovitel'nye reaktsii i potentsialy v analiticheskoi khimii* (Redox Reactions and Potentials in Analytical Chemistry), Moscow: Khimiya, 1989.
20. Bard, A.J., Parsons, R., and Jordan, J., *Standard Potentials in Aqueous Solution*, New York: Marcel Dekker, 1990.
21. Sawyer, D.T. and Gibian, M.J., *Tetrahedron,* 1979, vol. 35, no. 12, p. 1471.
22. Lemp, E., Pizarro, N., Encinas, M.V., and Zanocco, A.L., *Phys. Chem. Chem. Phys*., 2001, vol. 3, no. 23, p. 5222.
23. Wentworth, P., Jr., Wentworth, A.D., Zhu, X., Wilson, I.A., Janda, K.D., Eschenmoser, A., and Lerner, R.A., *Proc. Natl. Acad. Sci. USA*, 2003, vol. 100, no. 4, p. 1490.
24. 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.
25. Gekhman, A.E., Stolyarov, I.P., Ershova, N.V., Moiseeva, N.I., and Moiseev, I.I., *Kinet. Katal*., 2004, vol. 45, no. 1, p. 45.
26. Kearns, D.R., *Chem. Rev*., 1971, vol. 71, no. 4, p. 395.
27. Boehm, H.P., *Carbon*, 1994, vol. 32, no. 5, p. 759.
28. Boehm, H.P., *Carbon*, 2002, vol. 40, no. 2, p. 145.
29. Garten, V.A. and Weiss, D.E., *Rev. Pure Appl. Chem.,* 1957, vol. 7, no. 1, p. 69.
30. McDougall, G.J. and Fleming, C.A., *Extraction of Precious Metals on Activated Carbon. Ion Exchange and Sorption Processes in Hydrometallurgy*, Streat, M and Naden, D., Eds., Chichester: Wiley, 1987, vol. 19, p. 57.
31. Carey, F.A. and Sundberg, R.J., *Advanced Organic Chemistry*, New York: Plenum, 1977. Translated under the title *Uglublennyi kurs organicheskoi khimii,* Moscow: Khimiya, 1981, vol. 2, p. 312.
32. *Perekis' vodoroda i perekisnye soedineniya* (Hydrogen Peroxide and Peroxide Cpmpounds), Pozin, M.E., Moscow: Goskhimizdat, 1951, p. 257.
33. Langley, L.A. and Fairbrother, D.H., *Carbon*, 2007, vol. 45, no. 1, p. 47.
34. Nagiev, T.M., Zokhrabbekov, S.Z., and Shakh-

takhtinskii, T.N., *Dokl. Akad. Nauk SSSR*, 1987, vol. 292, no. 6, p. 1392.

35. Denisov, E.T. and Denisova, T.G., *Neftekhimiya*, 2006, vol. 46, no. 5, p. 333.
36. Lindsey, M.E. and Tarr, M.A., *Chemosphere*, 2000, vol. 41, no. 3, p. 409.
37. Flyunt, R., Leitzke, A., Mark, G., Mvula, E., Reisz, E., Schick, R., and von Sonntag, C., *J. Phys. Chem. B.,* 2003, vol. 107, no. 30, p. 7242.
38. Kwon, B.G. and Lee, J.H., *Bull. Korean Chem. Soc.,* 2006, vol. 27, no. 11, p. 1785.
39. Oturan, M.A. and Pinson, J., *J. Phys. Chem*., 1995, vol. 99, no. 38, p. 13948.
40. Cao, Yu., Chu, Q., and Ye, J., *Anal. Bioanal. Chem.,* 2003, vol. 376, no. 5, p. 691.
41. Nagiev, T.M., Zokhrabbekov, S.Z., and Shakhtakhtinskii, T.N., *Azerb. Khim. Zh*., 1978, no. 1, p. 3.
42. Mulcahy, M.F.R. and Young, B.C., *Carbon*, 1975, vol. 13, no. 2, p. 115.
43. Lee, J. and Grabowski, J.J., *Chem. Rev*., 1992, vol. 92, no. 7, p. 1611.
44. Kishore, K. and Mikherjee, T., *Radiat. Phys. Chem.,* 2006, vol. 75, no. 1, p. 14.
45. Dainton, F.S. and Peterson, D.B., *Proc. Royal Soc. London, Ser. A*., 1962, vol. 267, no. 1331, p. 443.
46. Proskurikhin, M.A., Orekhov, V.D., and Barelko, E.V., *Usp. Khim*., 1955, vol. 24, no. 5, p. 584.
47. Anpo, M., Aikawa, N., and Kubokawa, Y., *J. Chem. Soc., Chem. Commun*., 1984, no. 10, p. 644.
48. Anbar, M., *Quart. Rev*., 1969, vol. 22, no. 4, p. 578.
49. Castillo, J.F., Aoiz, F.J., Basares, L., and Collins, M.A., *J. Phys. Chem. A*., 2004, vol. 108, no. 32, p. 6623.
50. Katakis, D. and Taube, H., *J. Chem. Phys*., 1962, vol. 36, no. 2, p. 416.
51. Katakis, D. and Gordon, G., *Mechanisms of Inorganic Reactions*, New York: Wiley, 1987, p. 338.
52. Wentworth, P., Jr., McDunn, J.E., Wentworth, A.D., Takeuchi, C., Nieva, J., Bautista, C., Ruedi, J., Guttierrez, A., Janda, K.D., Babior, B.M., Eschenmoser, A., and Lerner, R.A., *Science*, 2002, vol. 298, no. 5601, p. 2195.
53. Wentworth, P., Jr., Nieva, J., Takeuchi, C., Wentworth, A.D., Dilley, R.B., DeLaria, G.A., Saven, A., Babior, B.M., Janda, K.D., Eschenmoser, A., and Lerner, R.A., *Science*, 2003, vol. 302, no. 5647, p. 1053.
54. Lerner, R.A. and Eschenmoser, A., *Proc. Natl. Acad. Sci. USA*, 2003, vol. 100, no. 6, p. 3013.
55. Beltran, F.J., *Ozone Reaction Kinetics for Water and Wastewater Systems*, Washington: Lewis, 2003.
56. Tarkovskaya, I.A., *Okislennyi ugol’* (Oxidized Carbon), Kiev: Naukova Dumka, 1981.
57. Stuber, F., Font, J., Fortuny, A., Bengoa, C., Eftaxias, A., and Fabregat, A., *Top. Catal*., 2005, vol. 33, nos. 1–4, p. 3.
58. Lee, J., Park, H., and Choi, W., *Environ. Sci. Technol.*, 2002, vol. 36, no. 24, p. 5462.
59. Mossoba, M.M., Rosenthal, I., and Riesz, P., *Can. J. Chem.*, 1982, vol. 60, no. 12, p. 1493.
60. Liu, L.V., Tian, W.Q., and Wang, Y.A., *J. Phys. Chem. B*, 2006, vol. 110, no. 5, p. 1999.
61. Frisch, J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E, Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Jr., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al–Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head–Gordon, M., Replogle, E.S., and Pople, J.A., *Gaussian 98*, Revision A.7, Pittsburgh, PA: Gaussian, 1998.
62. Haworth, N.L., Mackie, J.C., and Bacskay, G.B., *J. Phys. Chem. A*, 2003, vol. 107, no. 35, p. 6792.
63. Ustynyuk, Yu.A. and Laikov, D.N., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2005, no. 3, p. 804.