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N-Nitrosamines Formation from Secondary Amines by Nitrogen Fixation on the Surface of Activated Carbon

Lokesh P. Padhye,^{†,‡} Benjamin Hertzberg,[§] Gleb Yushin,[§] and Ching-Hua Huang^{*,†}

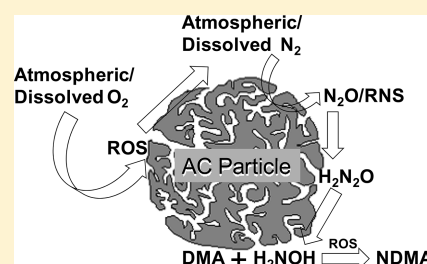
[†]School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[‡]Geosyntec Consultants, Kennesaw, Georgia 30144, United States

[§]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

 Supporting Information

ABSTRACT: Our previous study demonstrated that many commercial activated carbon (AC) particles may catalyze transformation of secondary amines to yield trace levels of *N*-nitrosamines under ambient aerobic conditions. Because of the widespread usage of AC materials in numerous analytical and environmental applications, it is imperative to understand the reaction mechanism responsible for formation of nitrosamine on the surface of ACs to minimize their occurrence in water treatment systems and during analytical methods employing ACs. The study results show that the AC-catalyzed nitrosamine formation requires both atmospheric oxygen and nitrogen. AC's surface reactive sites react with molecular oxygen to form reactive oxygen species (ROS), which facilitate fixation of molecular nitrogen on the carbon surfaces to generate reactive nitrogen species (RNS) likely nitrous oxide and hydroxylamine that can react with adsorbed amines to form nitrosamines. AC's properties play a crucial role as more nitrosamine formation is associated with carbon surfaces with higher surface area, more surface defects, reduced surface properties, higher O₂ uptake capacity, and higher carbonyl group content. This study is a first of its kind on the nitrosamine formation mechanism involving nitrogen fixation on AC surfaces, and the information will be useful for minimization of nitrosamines in AC-based processes.



INTRODUCTION

N-Nitrosamines are a group of water contaminants with rising concerns due to their widespread detection in water and wastewater treatment systems^{1,2} as well as due to their higher carcinogenic risks.³ In the data from the second cycle of Unregulated Contaminant Monitoring Regulation (UCMR2) recently released by the U.S. EPA,¹ the most frequently detected compound was *N*-nitrosodimethylamine (NDMA), which was detected in approximately 26% of the 1200 public water systems (PWS) analyzed for nitrosamines. Concentrations of NDMA ranged as high as over 600 parts per trillion (ng/L), with the median detection of 4 ng/L and an average detection of 9 ng/L. This frequency of detection is significantly higher than the 5% frequency of detection for perchlorate (most frequently detected unregulated contaminant) in the first UCMR1⁴ or any other unregulated contaminant in the UCMR2.¹ Other nitrosamines detected in the UCMR2 included *N*-nitrosodiethylamine (NDEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodi-*n*-butylamine (NDBA), and *N*-nitroso-*n*-methylethylamine (NMEA).

As noted above, the median and average NDMA concentrations detected in PWS in UCMR2 are approximately an order of magnitude higher than its 10^{−6} cancer risk level of 0.7 ng/L.⁵ Similarly, NDEA's (frequency of detection = 2%)¹ median detection value of 23 ng/L is 2 orders of magnitude higher than its 10^{−6} cancer risk level of 0.2 ng/L.⁵ The Ontario Ministry of the Environment has a maximum allowable concentration (MAC) of 9 ng/L for NDMA,⁶

whereas the California Department of Public Health has established a notification level of 10 ng/L for NDMA, NDEA, and NDPA and a public health goal (PHG) of 3 ng/L for NDMA.⁷

Because of their low target levels, nitrosamine analysis in water requires preconcentration by solid-phase extraction (SPE) or liquid–liquid extraction (LLE) followed by GC/MS or LC/MS analysis. Of the SPE procedures for nitrosamines, most favorable results are with activated carbon (AC) adsorbents, including synthetic, coconut shell-based and charcoal-based carbonaceous particles. EPA's Method 521⁸ for nitrosamine analysis uses charcoal-based carbonaceous adsorbent. Several other carbonaceous adsorbents^{8–16} have been reported for SPE of nitrosamines in water as well as foods and beverages. For many years, Ambersorb 572 (Rohm and Haas, Philadelphia, PA) particles had been the preferred choice for SPE of nitrosamines by numerous studies.^{17–23} However, production of Ambersorb 572 was discontinued in 2007,²⁴ leading to a growing demand for alternate carbonaceous SPE materials including coconut shell-based¹¹ and charcoal-based carbons²⁵ for nitrosamine extraction.

While evaluating various commercial AC materials for SPE of nitrosamines, it was discovered in our previous study²⁶ that AC

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materials can promote transformation of secondary amines to yield trace levels of *N*-nitrosamines under ambient aerobic conditions. Because AC materials are used widely not only in nitrosamine analytical methods but also in water and wastewater treatment systems for removal of small molecular weight organic compounds, the potential of AC materials to promote nitrosamine formation could lead to nitrosamine analytical errors and may even pose environmental risks if secondary amines are present at high concentrations. While important from the analytical standpoint, the implications on water treatment operations are less considering that most surface waters contain only low concentrations of secondary amines, the typical contact time during AC processes (in powder or granular AC mode) is rather short, and the formation of nitrosamines was significantly higher during the drying phase of AC particles than in the solution.

Our previous study²⁶ found that the AC-catalyzed nitrosamine formation is strongly influenced by the carbon properties, the amine properties, and the reaction conditions such as pH and exposure to the atmospheric oxygen. The NDMA yield at pH 7.5 ranged from 0.001% to 0.01% of initial amount of aqueous dimethylamine (DMA) concentration but at 0.05–0.29% of the amount of adsorbed DMA by AC. Nitrosamine yield increased with higher pH and for higher molecular weight secondary amines. ACs with adsorbed secondary amines dried under air for a longer period of time exhibited significantly higher nitrosamine yields. Hence, it was hypothesized that the nitrosamine formation from amines is a catalyzed oxidation of amine by AC surfaces on the basis that AC materials are common catalysts because of their high surface areas, porous structures, and reactive oxygenated surface groups.^{27,28} However, the reaction mechanism responsible for the nitrosamine formation on the AC surfaces was not fully elucidated.

Evidently, it is critical to properly evaluate the catalytic impact of ACs on promoting nitrosamine formation from amines and understand the involved mechanism in order to minimize analytical errors and undesirable nitrosamine formation during AC-based water analysis and treatment processes. Since nitrosamine yield was not found to be consistent among different ACs,²⁶ surface properties of ACs were termed critical for evaluating nitrosamine formation mechanism. Consequently, four different ACs were examined in this study to determine whether there is a correlation of surface properties with that of nitrosamine formation. In addition, with the use of labeled compounds, efforts were made to determine the source of nitrogen in the nitrosamine formation to better understand the reaction mechanism. Results of this study will be highly useful for the water industry to minimize analytical artifacts associated with nitrosamine analysis and develop strategies to reduce nitrosamine formation under water treatment conditions that employ ACs.

MATERIALS AND METHODS

Chemicals. Sources of chemicals and reagents are provided in Supporting Information Text S1.

Activated Carbons and Modifications. The four types of AC particles used in this study were coconut-shell based Siemens Aquacarb carbon (AqC) from Siemens Water Technologies (Warrendale, PA), coconut-shell based Prominent Systems carbon (PSC) from Prominent Systems Inc. (City of Industry, CA), a bituminous coal-based carbon, F400, from Calgon Corporation (Pittsburgh, PA), and synthetic Carboxen 572 (Ambersorb 572 equivalent) from Sigma-Aldrich (St. Louis, MO). These materials

were selected because they represent ACs with high (AqC), medium (PSC), and low (F400 and Carboxen 572) NDMA yield (NDMA formed/DMA adsorbed), respectively, based on our previous study.²⁶ For experiments carried out to understand the reaction mechanism, AqC particles were used due to their higher yield of NDMA formation. Since Carboxen 572 particles were expensive and available in limited supply, those were used only for selected experiments. PSC particles were pretreated with ozone or were baked at 600 °C to modify their surface characteristics²⁶ for surface functional group determination.

Experimental Setup and Nitrosamine and Amine Analyses. Batch experiments were conducted in deionized (DI) water matrices using amber borosilicate bottles with Teflon-lined caps. Experiments followed procedures common for nitrosamine extraction as described previously.²⁶ AC particles (150–200 mg) were added to 100–125 mL of DMA or ¹⁵N-DMA solution (at 222 μM), which were buffered at desired pH using 5 mM phosphate buffer. Unless specified otherwise, most experiments were conducted at pH 7.5. Selected experiments (e.g., drying of AC particles in pure oxygen and experiments involving ¹⁵N-DMA) were conducted at pH 9.2 to obtain easily measurable nitrosamine formation since NDMA formation on the AC increases with higher pH.²⁶ The amine+AC solution was shaken on a platform shaker at 250 rpm for 1–2 h at room temperature (22–23 °C) and filtered through a glass-fiber filter (Millipore, Jaffrey, NH). The collected carbon particles were air-dried for 1–3.5 h and transferred to a GC vial, and 0.5 mL of dichloromethane (DCM) was added to desorb nitrosamines from the particles. Then, the DCM layer was analyzed for nitrosamines by GC/MS.

Details of NDMA analysis and GC/MS conditions are described previously.²⁶ In the previous study, the amount of NDMA formed was quantified with and without correction for extraction efficiency using NDMA-d₆.²⁶ In this study the presented results for NDMA were not corrected by extraction efficiency of NDMA-d₆. This approach is appropriate since most (>90%) of the nitrosamine formation on the surface of AC occurs during drying of AC particles²⁶ and thus is presented in the mass units of NDMA (nanomoles) and without isotope dilution correction.

For experiments with N₂O, ¹⁵N-isotope labeled N₂O was generated in the laboratory through reaction of 200 mg of ¹⁵NH₄Cl with 10 mL of HNO₃ (1:1) and with continuous heating.²⁹ It was assumed that the reaction yielded predominantly ¹⁵N–N₂O (one N is labeled)²⁹ without direct monitoring of the generated N₂O gas. Since the yield of NDMA formation from dibutylamine (DBA) is higher than the yield of NDMA formation from DMA,²⁶ DBA was selected for this study as a source of secondary amine to generate easily measurable quantity of labeled NDMA. Two sets of AqC particles, weighing 200 mg each, were deposited with 767 μmol of pure DBA stock. One set was used as a control, and particles were air-dried for 1 h, while particles in the second set were dried under the ¹⁵N–N₂O gas. Afterward, the particles were added with DCM prior to GC/MS analysis for nitrosamines.

Carbon Characterization. (1) *BET Measurements* of carbons were conducted by a TriStar II 3020 surface area and porosity measurement system (Micromeritics Inc., GA). (2) *Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) Measurements* of the AC particles were conducted using a LEO 1530 SEM microscope (LEO, Japan, now Nano Technology Systems Division of Carl Zeiss SMT, USA). (3) *X-ray Photoelectron Spectroscopy (XPS) Measurements* were performed using a Thermo K-Alpha XPS system (Thermo Scientific, USA). Details of procedures are provided in Text S2.

Table 1. NDMA Formation Potential and Surface Properties of Four Activated Carbons^b

carbon	pH _{pzc}	S _{BET} (m ² /g)	S _{BJH} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso+macro} (cm ³ /g)	DFT pore surface area (m ² /g)						NDMA (nanomoles)	NDMA yield (%)
							total	<1 nm	>1 nm	1–2 nm	2–3 nm	>3 nm		
AqC	9.6	1202	109	0.519	0.404	0.115	900	688	212	200	9	3	1.65 ± 0.10	0.29
PSC	9.7	1114	153	0.509	0.339	0.170	838	624	214	180	23	11	0.56 ± 0.07	0.10
F400 ^a	9.2	1035	-	0.553	0.404	0.149	803	595	208	166	-	-	0.54 ± 0.06	0.05
Carboxen 572	7.0	858	130	0.756	0.460	0.296	-	-	132	102	1	29	0.07 ± 0.02	0.00

^a Properties of F400 were obtained from the literature.⁵⁵ ^b NDMA formation experiments were conducted at pH 7.5, using 222 μM DMA, 150 mg carbon, 3 h particle drying time; instrument detection limit for NDMA = 2 picomoles; mean ± standard deviation (*n* = 3). - = not available. NDMA yield was calculated by normalizing nanomoles of NDMA formed by nanomoles of DMA adsorbed on the AC particles.

(4) *Boehm Titration.* The acidic (i.e., carboxyl, lactone, phenolic hydroxyl, and carbonyl) and basic (e.g., pyrone-type and chromene-type structures) oxygen-containing surface functional group content was evaluated by adopting Boehm's titration method as described by Tessmer et al.³⁰ Five AC particles were chosen for this part of the study: untreated PSC, ozonated PSC representing oxidized surfaces, PSC particles baked at 600 °C representing reduced surfaces, AqC, and F400 particles. Two grams of each of the above five AC samples were equilibrated in 70 mL of each 0.05 N NaOH, NaHCO₃, and Na₂CO₃ and 0.25 N NaOH solutions individually for 3 days. At the end of the 3 days, filtrate was titrated against 0.25 N H₂SO₄ to determine the carbonyl, carboxyl, lactone, and phenolic hydroxyl group contents for each AC. Similarly, 0.05 N HCl was used to determine the total basic group contents of the above ACs; the amount of acid consumed by the basic groups was determined by using 0.05 N NaOH to titrate HCl solutions to pH 11.5.

(5) *Trace Metal Analysis.* AqC, PSC, and F400 particles were analyzed for surface elemental composition by subjecting those to acid digestion protocol as described in U.S. EPA's Method 3050B. A total of 10 mL of 1:1 HNO₃ was added to 1 g of AC particles, and the sample was heated for 15 min at 90 °C. Subsequently, 5 mL of concentrated HNO₃ was added to the sample, and it was heated for 2 h at 90 °C. Two mL of water and 3 mL of 30% H₂O₂ was added, and the mixture was heated for 15 min at 90 °C before an addition of 10 mL of concentrated HCl and heating it for 15 min at 90 °C. Lastly, the carbon particles were filtered out, and the filtrate was collected for elemental composition analysis by Optima 7300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES) with Scott Spray Chamber (PerkinElmer, Waltham, MA).

(6) *Oxygen Uptake.* The capability of the ACs to chemisorb oxygen was measured by modifying the protocol described by Vidic and Suidan.³¹ AC particles weighing 1 g were immersed in 10 mL of DI water and were bubbled with nitrogen gas for 48 h to physically eliminate surface oxygen contents. Afterward, the purged carbons were immersed into 20 mL of DI water with saturated dissolved oxygen (DO) level. After 30 min of contact time, depletion of DO content was measured by a VWR SympHony SP80PD DO probe (VWR, Radnor, PA).

RESULTS AND DISCUSSION

Comparison of NDMA Formation for Four ACs. The four ACs (AqC, PSC, F400, and Carboxen 572) focused on in this study were evaluated for their potential to catalyze NDMA formation from DMA under similar conditions. DMA at 222 μM

in 100 mL of aqueous solution (pH 7.5) was subject to SPE by 150 mg of each AC with 1.5 h shaking time and 3 h particle drying time. Table 1 summarizes the NDMA formation results and some surface properties of the carbons including pH of point of zero charge (pH_{pzc}) and carbon's specific areas and pore volumes (S_{BET} and S_{BJH}). Although both PSC and F400 formed the similar amounts of NDMA, DMA mass adsorbed on the F400 particles was found to be higher and hence the NDMA yield, calculated by normalizing the amount of NDMA formed by the amount of DMA adsorbed, was lower for the F400 particles than for the PSC particles (Table 1). Secondary amine adsorbed on the surface of carbon was determined based on the difference between the initial and the final (after shaking the carbon suspension and removing the carbon particles by filtration) amine concentrations in the solution.²⁶

Note that NDMA was not present as an impurity in any of the carbon samples nor was formed in the control experiments where carbons were absent. Previous study²⁶ also shows that the majority (>90%) of NDMA formation occurs during the particle drying stage. While no linear correlation between NDMA formation and any of the carbon's surface properties could be established, Carboxen with the lowest pH_{pzc} had the lowest NDMA formation, consistent with the previous finding that overall more NDMA formation occurred with carbons that had more reduced (or basic) surface (i.e., higher pH_{pzc})²⁶ AqC with the largest surface area showed the most NDMA formation, while Carboxen with the least surface area had the lowest NDMA formation, indicating a possible role of availability of surface sites for the transformation of secondary amines to nitrosamines.

Investigating Source of Nitrogen in NDMA Formation. The results in Table 1 and our previous study²⁶ clearly show that ACs can catalyze nitrosamine formation from amines. Next, the source of nitrogen atoms in the formed NDMA was probed in this study by the following experiments.

Study with Isotope-Labeled Nitrite. Because ACs have been reported to catalyze nitrosation of secondary amines with nitrite to yield nitrosamines,¹⁶ the potential role of nitrite in contributing to the observed NDMA formation needs to be evaluated. First, nitrite was measured using a colorimetric method^{26,32} and found to be below the method detection limit (MDL ~ 70 nM) in the deionized water used in the experiments and in DMA stocks. Then, ¹⁵N-labeled nitrite was spiked at various amounts in DMA solution that was subject to SPE by carbons. It was found that ¹⁵N-NDMA formation compared to ¹⁴N-NDMA formation was not significant at least until nitrite concentration reached 1000 nM (0.046 mg/L) (Table S1). These results confirmed that nitrite at concentrations below the MDL, if existed in the reaction

Table 2. Summary of NDMA Formation from AqC under Different Conditions

samples	reaction conditions	NDMA (nanomoles)	¹⁵ N-NDMA (nanomoles)	¹⁵ N, ¹⁵ N-NDMA (nanomoles)
DMA	^a	6.85 ± 0.71	ND	ND
¹⁵ N-DMA	^a	ND	6.47 ± 0.43	ND
AqC dried in air	^b	1.79 ± 0.15	-	-
AqC dried in pure oxygen	^c	0.19 ± 0.01	-	-
DMA (suspension)	^d	0.07 ± 0.01	-	-
DMA + TBA (suspension)	^d	0.04 ± 0.00	-	-
DMA	^e	1.62 ± 0.01	-	-
DMA + TBA	^e	0.62 ± 0.06	-	-
DMA + NH ₂ OH	^f	232 ± 7.43	-	-
DMA	^f	1.62 ± 0.01	-	-

^aExperiments were conducted at pH 9.2, using 222 μM DMA/¹⁵N-DMA, 200 mg AqC carbon, 3.5 h particle drying time. ^bExperiments were conducted at pH 9.2, using 222 μM DMA, 200 mg AqC carbon, dried in pure oxygen gas at a flow rate of 12 L/min for the duration of 1.5 h. ^cSame as “b” except air-dried for 1.5 h. ^dExperiments were conducted at pH 7.5, using 222 μM DMA, 200 mg AqC carbon, no drying. ^eSame as “d” except 2 h of drying. ^fExperiments were conducted at pH 7.5, using 222 μM DMA, 200 mg AqC carbon, 3 h particle drying time; instrument detection limit for NDMA = 2 picomoles; mean ± standard deviation (*n* = 3). ND = not detected; - = not applicable.

solution, was not a contributing factor to the observed NDMA formation and were consistent with findings from the previous study.²⁶

Study with Isotope-Labeled DMA. Experiments were conducted by spiking ¹⁵N-labeled DMA at 222 μM in 100 mL of aqueous solution for SPE by 200 mg AqC particles. After 1.5 h of shaking, particles were filtered and then air-dried for 3.5 h. Afterward, the NDMA formed was quantified. Control experiments were carried out simultaneously with unlabeled DMA. The solution pH of the control and isotope experiments was at 9.2 by phosphate buffer. Results showed that 6.47 ± 0.43 nanomoles of ¹⁵N-NDMA (*m/z* = 75) was formed in the experiments with ¹⁵N-DMA, while no regular NDMA (*m/z* = 74) or ¹⁵N,¹⁵N-NDMA (*m/z* = 76) were detected. The amount of ¹⁵N-NDMA formed was similar to the amount (6.85 ± 0.71 nanomoles) of regular NDMA formed in the experiments with unlabeled DMA (Table 2). The above results indicate that DMA is responsible for yielding only one nitrogen in NDMA formation, and the source of second nitrogen of the nitroso group of NDMA is either atmospheric, dissolved, or through carbon.

Effect of Atmospheric and Dissolved Nitrogen. It was observed in the previous study²⁶ that significantly less amount of nitrosamine formed when drying of AC particles was conducted under pure nitrogen gas instead of air. Also, the presence of oxygen was identified to be critical for the AC-catalyzed nitrosamine formation.²⁶ However, NDMA formation in the case of drying of the AC particles under pure oxygen was only 20–30% of the NDMA formation when the particles were air-dried.²⁶ There can be two possible reasons to explain this result; either insufficient amount of oxygen was provided during the experiment of drying particles in pure oxygen or exclusion of nitrogen gas limited NDMA formation.

Hence, to evaluate the above two potential reasons, experimental protocol was modified to completely eliminate the presence of external nitrogen source altogether and to ensure sufficient oxygen flow rate. To achieve this objective, DMA was spiked at 222 μM in a solution previously purged with pure oxygen at the rate of 5 L/min for 15 min to remove dissolved nitrogen, and 200 mg AqC particles were added for SPE. The total volume of solution was 125 mL with no head space. After 2 h of shaking, particles were filtered and then transferred to a 500-mL gas-washing cylinder with an inlet and outlet for oxygen circulation.

The particles were dried in pure oxygen gas at a flow rate of 12 L/min for the duration of 1.5 h after which NDMA formed was quantified. A control experiment was also carried out in a similar way except that the aqueous solution was not purged with oxygen and drying of particles was conducted in the flow of air. This experiment differs from the previous study²⁶ in two major ways. First, the presence of dissolved nitrogen in the aqueous solution was mostly eliminated for the current study which was not the case previously. Second, the oxygen flow rate was increased by nearly 2 orders of magnitude to ensure that oxygen was not a limiting factor responsible for low yield of NDMA observed previously.

Results of this experiment show that NDMA formation decreased by an order of magnitude for particles dried under pure oxygen and in the near absence of dissolved nitrogen. Only 0.19 ± 0.01 nanomoles of NDMA was formed compared to the control in which 1.79 ± 0.15 nanomoles of NDMA formation was observed (Table 2). These findings highlight the importance of external nitrogen source in the formation of NDMA and demonstrate that atmospheric and dissolved nitrogen is likely contributing to one nitrogen atom for NDMA formation. Overall, the results discussed above show that AC surfaces can catalyze oxidative transformation of amines to nitrosamines with the presence of oxygen and nitrogen. Molecular oxygen is the source of oxidant while molecular nitrogen is the external nitrogen source in addition to amine for nitrosamine formation.

Carbon Characteristics and Impact on NDMA Formation. In this section, further characterization of the four ACs materials was conducted to obtain more insight to the impact of carbon properties on the catalytic activity to promote nitrosamine formation.

Oxygen-Containing Surface Functional Groups. While surface reaction rates are expected to increase with carbon's specific surface area, more often the carbon's surface chemistry plays an even greater role.³³ Hence, the activity of AC is determined by a number of factors including the nature, concentration, and accessibility of AC's active sites and the presence of functional groups of heteroatoms (O, N, S). Oxygen and nitrogen functional groups, which are incorporated into the carbon materials during activation process or by a variety of chemical and thermal methods, play an important role in this context.^{34–41} Common oxygen containing surface functional groups observed on the surface of ACs include carboxyl, phenolic, quinonoid, lactone,

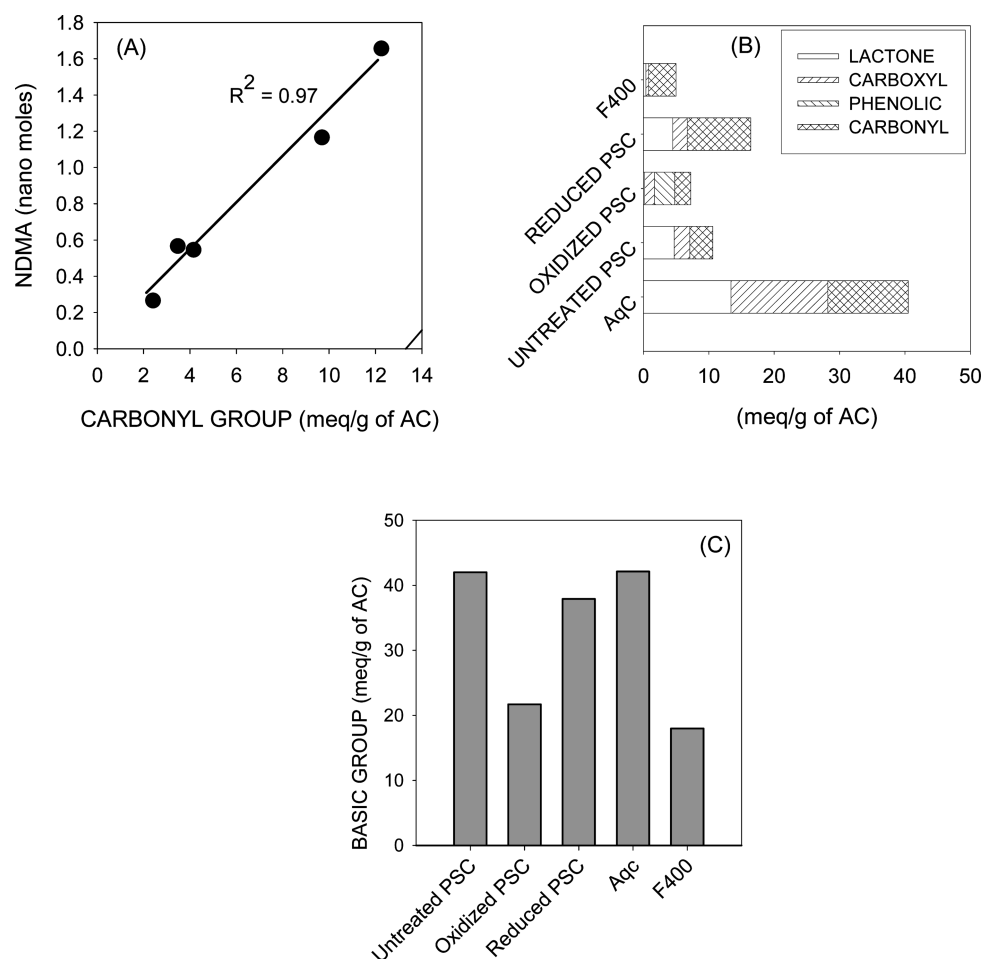


Figure 1. Surface functional groups of five different activated carbon samples (untreated PSC, oxidized PSC, reduced PSC, AqC, and F400) and their effects: (A) relationship between the amounts of NDMA formation and the surface carbonyl group content, (B) surface acidic functional group content, and (C) surface basic functional group content. Oxidized: pretreated by ozone; reduced: prebaked at 600 °C.²⁶

and anhydride groups.⁴² The influence of oxygen or nitrogen surface functional groups on AC's catalytic activity varies in different types of oxidation or reduction reactions.^{35,38–41,43,44}

Aguilar et al.⁴⁵ studied the AC-catalyzed catalytic wet air oxidation (CWAO) of methylamine and DMA and reported that the catalytic activity was related to ACs' oxygenated surface functional groups. Methylamine and DMA were oxidized to nitrogen, water, and carbon dioxide under the employed conditions (195 °C and 16 atm). The authors proposed that the quinone surface groups on ACs were responsible for the catalytic activity, while carboxylic, lactone, and anhydride groups were responsible for catalytic activity inhibition, despite that the latter groups appeared to exhibit stronger adsorption of methylamine and DMA. In a recent study,⁴⁶ the oxidized AC surface was found to be responsible for increased DMA chemisorption due to oxygen-containing surface functional groups. These findings were consistent with our results from the previous study²⁶ where we found that ACs treated with HNO₃ showed an increase in DMA adsorption though their NDMA formation yield decreased.

It should also be noted that for ACs tested in this study, especially AqC, NDMA yield was observed to decrease over time. Experimental studies with AqC revealed that NDMA yield of AqC gradually decreased over time and was reduced by ~40% at the end of first year of its arrival in the laboratory. One primary

reason listed in the literature is formation of surface oxides or surface oxide carbon complexes due to reaction of the AC surface with air and moisture which in turn shield the active carbon sites from participating in redox reactions.⁴⁷ This aging of AqC surface is assumed to be a reason for the observed decrease in NDMA formation potential of AC over time.

For the five types of ACs tested in these experiments, there was a significant correlation ($R^2 = 0.97$) between the amount of NDMA formed and the carbonyl group content on the surfaces of ACs (Figure 1A). The higher the carbonyl group content on the AC surfaces, the higher the NDMA formation potential. No significant correlations could be established between NDMA formed and the other functional group concentrations. When NDMA formation was normalized by the amount of amine adsorbed on the carbons, there was still a strong correlation to the surface carbonyl content, indicating that the carbonyl group may not necessarily enhance the secondary amine adsorption on the AC surface. The exact role of how carbonyl groups enhance the transformation of DMA to NDMA on the AC surfaces is still unclear and requires further research to elucidate the mechanism.

Figure 1B shows the surface acidic functional group composition of the five carbons. Note that the reduction of PSC particles was carried out by heating the particles to 600 °C. The carbonyl groups are resistant to thermolysis at this temperature and

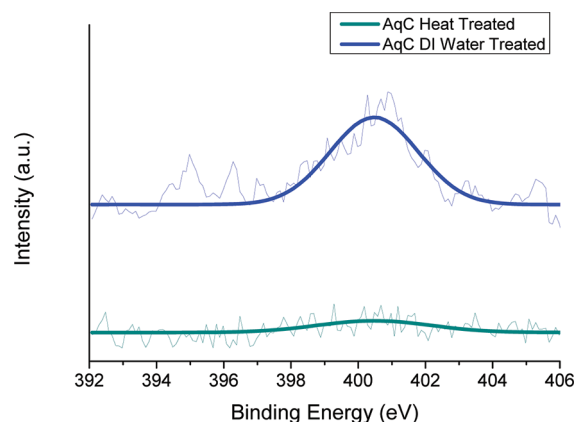


Figure 2. Comparison of XPS peaks for nitrogen (at ~ 400 eV) for AqC particles that were only heat treated and for AqC particles that were heat pretreated and then also exposed to DI water.

require 1200°C or higher for their complete removal from the AC surface.³⁰ In the study by Tessmer et al.,³⁰ the authors found that after heating AC to 500°C , surface carbonyl content was increased, possibly due to conversion of more acidic surface functional groups (e.g., carboxylic) to carbonyl. While no strong correlation was found between total basic surface functional groups and NDMA formed, overall more NDMA was formed for carbons with higher basic group content (Figure 1C).

Surface Elemental Composition. Some previous studies^{28,48} have reported that ACs' catalytic activity is related to trace metals (ash content) on the surface of ACs, while others found that metals and metal oxides on the surface of ACs were not important for catalyzing irreversible adsorption of phenolic compounds.³⁰ For the latter, the AC surfaces are known to catalyze oxidation of adsorbed phenols in the presence of oxygen.⁴⁹ To determine if surface elemental composition can play a significant role in NDMA formation, three AC particles, AqC, PSC, and F400, were subjected to trace metal analysis with results shown in Table S2. Higher amounts of surface sodium, aluminum, and potassium on ACs were found to be linked to higher NDMA yield. However, their role in NDMA formation is uncertain, and further research is needed to understand their contribution to the NDMA yield.

SEM, EDS, and XPS. The ability of activated carbon surfaces to react with oxygen is well documented.⁵⁰ Since generation of reactive oxygen species on the surface of carbon is found to be related to surface defects,⁴⁷ SEM images were taken of the surfaces of AqC, PSC, F400, and Carboxen 572 (Figure S1). As can be seen, Carboxen 572 had the smoothest surface with the least amount of surface defects, while AqC and PSC particles showed considerable microdefects on their surfaces which may interact with dissolved oxygen to generate ROS.⁴⁷ Since these two carbons have higher NDMA yield than F400 or Carboxen 572, carbon surface defects may indeed be responsible for reactions involved in nitrosamine formation.

Evaluating the nitrogen content of AC surfaces was then conducted to assess the interactions of N_2 with carbon surfaces. Since EDS results failed to reveal nitrogen content on the surface of ACs due to a high detection limit (Figure S2), XPS analysis was performed on two differently treated AqC particles. For the first set of the AqC particles, untreated AqC particles were pretreated at 700°C under argon gas for 1 h and then cooled under argon and later air. The other set of the AqC particles

received similar heat treatment and cooling but was followed by contact with DI water for 2 h and then dried in air. An increase in the nitrogen peak (~ 400 eV) for AqC particles that were exposed to DI water was evident compared to AqC particles that were not in contact with DI water (Figure 2). This observation confirmed that nitrogen fixation indeed occurred on the AqC surfaces when the particles were exposed to both water and air. Such phenomenon of nitrogen fixation on AC surfaces when exposed to oxygen and moisture has been previously reported, albeit limitedly.⁴⁷

Oxygen Uptake. Vidic⁴⁹ discovered that the amount of irreversibly adsorbed phenolic compounds on the surfaces of ACs was directly proportional to the amount of molecular oxygen consumed. Chemisorption of oxygen on the surface of AC may lead to the formation of acidic, neutral, or basic functional groups.³⁰ Further, consumed O_2 may lead to formation of ROS on the surface of AC which may participate in fixation of atmospheric nitrogen in the carbon matrix.⁵¹ Dissolved oxygen uptake experiments were conducted as described in the Materials and Methods section. Among the 3 carbons tested in this study, AqC consumed the most DO (4.73 mg/L), followed by PSC (4.29 mg/L), and last F400 (2.09 mg/L). Thus, oxygen uptake capacity of ACs was found to be directly related to its NDMA formation yield, suggesting a possible relationship between consumed oxygen, ROS generation, and NDMA formation.

Reaction Mechanism for Carbon-Catalyzed Nitrosamine Formation from Amines. *Role of Hydroxyl Radicals.* Previous studies have suggested that interaction between oxygen and AC surface reactive sites can generate ROS such as superoxide radical anion (which can lead to other secondary ROS including hydroxyl radical and hydrogen peroxide) and even superoxo anion via charge transfer from carbon to the adsorbed oxygen.^{47,51,52} The ability of activated carbons to interact with nitrogen was discussed by a few studies.^{47,51} In those studies, the authors observed formation of oxygen- and nitrogen-containing fragments on the surfaces of carbons when the carbons were in contact with water that was saturated with air at room temperature. The reaction between oxygen and carbon surfaces in generating ROS was suggested to be critical in the redox reaction of nitrogen fixation.

Based on the above reports, formation of NDMA from DMA on AC surfaces likely involves radical reactions. Therefore, experiments were conducted to evaluate the importance of ROS in NDMA formation using radical scavengers. Experiments were conducted using a similar protocol described above that spiked $222\text{ }\mu\text{M}$ DMA into 100 mL of pH 7.5 solution and added 200 mg of AqC particles for SPE. *Tert*-butanol (TBA) at 10 mM was added as a scavenger of hydroxyl radical. Control experiments without addition of radical scavengers were also carried out simultaneously. After 1.5 h of shaking, one set of samples was analyzed for NDMA formation in the suspension state with no drying of particles. The amount of nitrosamine formed while in the suspension state was determined by decanting the water in the amine+AC aqueous suspension and collecting the carbon particles; DCM was immediately added to the carbon particles in a centrifuge tube followed by centrifugation; afterward, the DCM layer was analyzed for nitrosamines by GC/MS. The second set of samples was filtered, and the particles were air-dried for 2 h and NDMA formation was measured at the end of drying. As shown in Table 2, samples amended with TBA showed lower NDMA formation than controls for both sets. In the suspension state, 0.07 ± 0.01 nanomoles of NDMA was formed in the controls while only 0.04 ± 0.00 nanomoles of NDMA formed in the

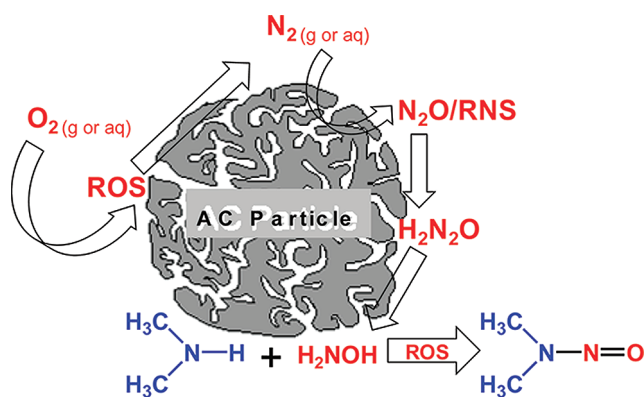


Figure 3. Proposed mechanism for formation of *N*-nitrosamine from secondary amine on the surface of AC particles. ROS = reactive oxygen species; RNS = reactive nitrogen species.

TBA-spiked samples. The overall (suspension plus drying phases) NDMA formation was 1.62 ± 0.01 nanomoles in the control but was only 0.62 ± 0.06 nanomoles in the TBA-spiked samples.

Furthermore, in another study, the effect of pretreatment of AC particles with TBA on NDMA formation was examined. Two hundred mg of AqC particles was suspended in aqueous solution of 135 mM of TBA and were shaken at 250 rpm for 2 h. After shaking was completed, particles were filtered and air-dried for one hour. When these pretreated particles were used for SPE in the similar experimental setup, NDMA formation was reduced by more than 50% compared to untreated AqC particles. These results indicate that hydroxyl radicals play a significant role in the formation of NDMA from DMA in the presence of carbon particles.

Nitrous Oxide and Hydroxylamine as Intermediates. Previous studies^{47,51} have suggested that the ROS generated or carbene centers created by reactions of ROS on carbon surfaces could be responsible for nitrogen fixation by reacting with dissolved N_2 to form reactive nitrogen species (RNS) like N_2O or diazo intermediates. From the thermodynamic viewpoint, two-electron reductants are able to convert N_2O into ammonia via an H_2N_2O intermediate.⁵³ Further reduction of the latter can provide hydroxylamine (NH_2OH) molecules and other NH-containing species. Since AC is known to exhibit both oxidant and reductant propensities,^{47,51} the above pathways are possible on the AC's active sites. Furthermore, it was shown earlier that NH_2OH can react with DMA in the presence of ROS through UDMH pathway to generate NDMA.⁵⁴

The generation of ^{15}N -NDBA (100 nanomoles) was observed for DBA-dosed AqC particles when the particles were dried under labeled (only 1 nitrogen atom) $^{15}N-N_2O$ gas. It was also found that an order of magnitude higher unlabeled NDBA (420 nanomoles) was formed when DBA-dosed AqC particles were dried under $^{15}N-N_2O$ gas than when dried under air (40 nanomoles). Results from these experiments confirmed that N_2O is a likely RNS intermediate that participates in nitrosamine formation on the surface of AC, and either of the two nitrogen atoms of N_2O can contribute to nitrosamine formation.

In another set of experiments, hydroxylamine was found to substantially enhance NDMA formation from DMA in the presence of AC particles but not in the absence of AC particles (Table 2). More than 2 orders of magnitude higher NDMA formation (232 ± 7 nanomoles) was observed for AqC particles

in contact with equimolar amounts of DMA and NH_2OH than for AqC particles in the presence of the same amount of DMA alone under similar reaction conditions (1.62 ± 0.01 nanomoles). Thus, it may be possible that hydroxylamine is an important intermediate product formed during nitrogen fixation on the surface of AC and may contribute to transformation of DMA to NDMA through reactions catalyzed by AC surfaces.

Proposed Reaction Mechanism. Based on the above results and discussion, the proposed mechanism for catalyzed NDMA formation from DMA on AC surfaces in the presence of oxygen and nitrogen is depicted in Figure 3. Reactive sites on the AC surfaces react with molecular oxygen to form ROS, particularly hydroxyl radicals. The ROS generated promote fixation of molecular nitrogen to form RNS such as N_2O , H_2N_2O , and NH_2OH . The subsequent reaction of NH_2OH with DMA can be catalyzed by AC's surface sites or ROS to yield NDMA. Our results that NDMA formation was lowered in the presence of TBA is consistent with the above mechanistic hypothesis since TBA quenches hydroxyl radical and, hence, may prevent formation of N_2O and thus hydroxylamine and NDMA. The pH trend of increase in nitrosamine formation with an increase in pH²⁶ can also be explained based on a longer lifetime of ROS and RNS at higher pH and thus increased formation of NH_2OH . For a carbon surface that is more reduced and with more defects and available surface sites, formation of ROS is more favorable, so is the formation of N_2O and conversion of N_2O to NH_2OH , and thus more NDMA can be formed. Although only demonstrated for NDMA in Figure 3, catalyzed formation of other *N*-nitrosamines from secondary amines on AC surfaces is expected to follow the same reaction mechanism.

■ ASSOCIATED CONTENT

S Supporting Information. Text S1–S2, Tables S1–S2, and Figures S1–S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 404-894-7694. Fax: 404-385-7087. E-mail: ching-hua.huang@ce.gatech.edu.

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