Title
FORMATION OF POLLUTION PARTICULATE NITROGEN COMPOUNDS BY NO-SOOT AND NH3-SOOT GAS-PARTICLE SURFACE REACTIONS

Permalink
https://escholarship.org/uc/item/1vj9z9zw

Authors
Chang, S.G.
Novakov, T.

Publication Date
1974-06-01
FORMATION OF POLLUTION PARTICULATE NITROGEN COMPOUNDS BY NO-SOOT AND NH$_3$-SOOT GAS-PARTICLE SURFACE REACTIONS

S. G. Chang and T. Novakov

June 1974

Prepared for the U. S. Atomic Energy Commission under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks.
For a personal retention copy, call Tech. Info. Division, Ext. 5545
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
FORMATION OF POLLUTED PARTICULATE
NITROGEN COMPOUNDS BY
NO-SOOT AND NH₃-SOOT GAS-PARTICLE
SURFACE REACTIONS

S. G. Chang and T. Novakov
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

June 1974

*Work supported by National Science Foundation - RANN and by U. S.
Atomic Energy Commission.
ABSTRACT

Three reduced forms of nitrogen are associated with ambient air pollution particulates: volatile ammonium (an ammonium compound other than, and in addition to ammonium nitrate or ammonium sulfate), and two additional species assigned to amine and/or amide and to nitrile. Nitrogen species of the same type and behavior can be synthesized in soot (or graphite) interactions with NO or NH$_3$. Volatile hydroxyl and/or carboxyl ammonium salts are produced in soot-NO and soot-NH$_3$ reactions at ambient temperatures, while amines, amides and nitriles are produced at higher temperatures. The proposed mechanism is in qualitative agreement with the field observations. The experiments were performed with the aid of x-ray photoelectron spectroscopy, ESCA.
I. INTRODUCTION

Using x-ray photoelectron spectroscopy (ESCA) Novakov et al. (1972) have observed, in addition to commonly occurring nitrate and ammonium, two unsuspected reduced nitrogen species in pollution aerosol particles. ESCA spectra indicate that these species possess a nitrogen net charge which is more negative than the corresponding nitrogen charge in the ammonium ion. Based on core electron binding energies, these nitrogen species were tentatively assigned to organic compounds of the amino- and pyridino-type. The diurnal concentration variations indicate that these compounds could be primary pollutants coming directly from sources, such as the automobile, rather than by way of atmospheric reactions.

Since the time when these nitrogen species, which we shall for the moment denote by $N_x$ were first observed they have been consistently found in every ambient particulate sample which we have analyzed by ESCA. In all cases $N_x$ was found to be either dominant or at least major component of the total particulate nitrogen. In spite of their abundance, the nature and origin of $N_x$ has remained unclear, however.

In the course of our work on the chemical characterization of pollution particles by ESCA, we have found evidence that a substantial fraction of ammonium ion is present in a chemical form other than ammonium nitrate, ammonium sulfate or other common ammonium salts. This particular ammonium ion is characterized by its
high volatility in vacuum at room temperature.

In this paper we show that reduced nitrogen species identical to those observed in ambient particulate, i.e. $N_x$ and volatile ammonium species, can be produced by surface reactions of common pollutant gases such as ammonia and nitric oxide with soot particles. Nitrogen species produced in these reactions at elevated temperature occur in the form of surface complexes such as amines, amides and nitriles. We will also show that ammonium ions may be associated with soot particles in the form of carboxyl-ammonium and/or hydroxyl-ammonium salts produced by soot-$NH_3$ and soot-NO reactions at ambient temperature.

Surface reactions of NO and $NH_3$ to be discussed involve soot particles, which are the unavoidable by product of even seemingly complete combustion of fossil fuels. Soot particles are basically a form of finely divided carbon with graphite-like structure (Gaydon and Wolfhard, 1959; Palmer and Cullis, 1965). Soot particle surface contains many exposed defects, dislocations and discontinuities in the layer planes, which constitute the active sites. Namely, surface carbon atoms located at these sites, because of residual valencies, show strong tendency to chemisorb other molecules, giving rise to stable non-stoichiometric surface functional groups such as carboxyls, carbonyls, hydroxyls, etc. The surface reactivity of soot is also manifested through high concentration of unpaired electron spin centers (Donnet, 1965).
Some soot microcrystallites are so small, having diameters less than 100Å that they consist on only a few unit cells of graphite structure and as such posses extremely large effective surface area.

Soot particles have been found to efficiently catalyze SO$_2$ oxidation (Novakov et al., 1974) and with the evidence about the role of soot particles in the formation of nitrogen species, that we present in this paper it becomes clear that the role of soot in the chemical processes of polluted air cannot be neglected.

II. EXPERIMENTAL RESULTS

Experiments described in this paper were performed with the aid of x-ray photoelectron spectroscopy. This technique has been extensively discussed and reviewed in the literature and therefore will not be discussed here. (For a general review see for example: Hollander and Jolly, 1970; for applications of ESCA to the chemical characterization of pollution particulates see: Novakov, 1973).

In this section we will present the results of ESCA measurements on ambient air particulates which demonstrate that most of the reduced nitrogen species is found in the form of volatile ammonium and N$_x$. We will also describe laboratory experiments which show that soot-NO and soot-NH$_3$ surface reactions lead to the formation of reduced nitrogen species chemically equivalent to those observed in the polluted air.
The relative concentrations of different nitrogen species typically associated with pollution particulates can be visualized with the aid of ESCA spectra such as the one in Figure 1a. Individual peaks corresponding to NO$_3^-$, NH$_4^+$ and N$_x$ are indicated in the figure. The peak areas are proportional to the relative atomic concentrations (i.e. as N) of these species. Obviously most of the nitrogen is found as NH$_4^+$ and as N$_x$.

A more detailed analysis of such spectra reveals the presence of a hitherto unrecognized form of ammonium component characterized by its relatively high volatility in vacuum. This is achieved by the following procedure. The spectrum in Figure 1a is taken with the sample (collected on 8/29/73 in West Covina, CA.) at -150°C. The sample was kept at low temperature in order to prevent volatile losses because of the vacuum in ESCA spectrometer. In Figure 1b we show the same spectral region of the same sample after its temperature was raised to 25°C, which is the normal operating temperature. This spectrum reveals only a trace of the original nitrate and a decrease of about 60% in the ammonium peak intensity. The amount of ammonium nitrogen lost by volatilization between -150°C and 25°C is much greater than the original nitrate nitrogen as observed at -150°C. Actually at most about 15% of the total ammonium ion present in the sample at low temperature could be associated with nitrate as NH$_4$NO$_3$. We conclude therefore that the volatile ammonium component is not associated with volatilization of
ammonium nitrate.

We have furthermore found that the ammonium sulfate compound will exhibit no change in either ammonium or sulfate peak intensity between -150°C and 25°C. Actually we found ammonium sulfate to be stable in vacuum at 25°C for time intervals normally used to complete the analysis of ambient samples. Also, in the case of ambient samples no detectable decrease in the sulfate peak, as measured at -150°C and 25°C, was observed.

Based on these results the decrease in the ammonium peak intensity observed between -150°C and 25°C can not be adequately explained by the volatile losses of either ammonium nitrate or ammonium sulfate. The limited volatility of ammonium salts and the behavior of the ambient samples suggests that a major fraction of ammonium ion pollution aerosol particles is present in a previously unrecognized volatile form. The apparent inconsistencies between ammonium concentrations as determined by ESCA (in vacuum) and by wet chemical techniques caused by the volatility effects, were recently discussed by Appel et al. (1974).

In the remainder of this section we will describe the results of our laboratory experiments, dealing with surface interactions of soot and graphite with NO and NH₃, which lead to the formation of both volatile ammonium and Nₓ species. We will furthermore demonstrate that the synthetic and ambient Nₓ species are chemically analogous.
Soot particles for these experiments were generated by a premixed propane-oxygen flame. The exposure of soot particles to NO and NH\textsubscript{3} was done under two different experimental conditions: In a static regime, with propane soot precollected on a (silver) membrane filter, which is then subsequently exposed to the reactant gas (insert in Figure 2) at ambient temperature; and, in a flow system with the propane-oxygen flame on, by introducing the reactant gas downstream from the flame (insert in Figure 3), i.e. while the soot particles are still at high temperature.

ESCA spectra of the nitrogen (1s) region of soot samples prepared in these ways are shown in Figures 2 and 3. It is evident from Figure 2 that interaction of NO and NH\textsubscript{3} with "cold" soot particles results in ammonium like species. On the other hand, as seen from Figure 3, both NO and NH\textsubscript{3} interacting with "hot" soot particles produce species with ESCA peaks of binding energies corresponding to N\textsubscript{x} species. Ammonium species still seen in these samples is probably produced on soot particles after they have been collected on the filter and cooled down.

That soot particles are equivalent to graphite with respect to NO and NH\textsubscript{3} surface reactions was demonstrated in experiments which we describe next. The main surface chemical difference between soot and graphite is in the nature and amount of surface carbon-oxygen complexes. Soot particles surface is always covered with surface oxygen complexes, the amount and nature of which depends on the
history of soot formation and in particular on temperature. To achieve suitable oxygen coverage on graphite a piece with dimensions of about 0.1 x 0.5 x 1.5 cm$^3$ was placed inside a quartz tube which was inserted in an electric furnace (insert in Figure 4), one end of which was connected to a conventional vacuum system. The system was evacuated to about 15 torr and the graphite was heated for about 30 minutes at a temperature of about 1000°C. The temperature was then gradually brought down to between 300 and 600°C when the graphite specimen was exposed to particle free, high humidity air at one atmosphere for about 15 minutes. After that the tube was again evacuated and the pretreated graphite was exposed to about 30 - 50 torr of NH$_3$ or NO for 15 minutes. The nitrogen ESCA peaks of graphite specimens exposed to NH$_3$ and to NO at 400°C are shown in Figure 4. Obviously the photoelectron peaks of graphite exposed to NH$_3$ and NO at elevated temperature appear at the same binding energy as the $N_x$ peak observed in ESCA spectra of ambient particulates and of specimens produced by interaction of hot soot particles with either NO or NH$_3$.

The described experiments demonstrate that the nitrogen species produced synthetically and the ambient $N_x$ species have the same core electron binding energy. An inspection of Figures 1, 3, and 4 also shows that both synthetically produced and ambient $N_x$ species result in relatively broad photoelectron peaks of about 3 eV (measured at half-maximum), i.e. wider than the N (1s) photoelectron peaks from
well defined nitrogen compounds, indicating that the $N_x$ species, both ambient and those produced in surface reactions in the laboratory, may contain more than one distinct chemical state with slightly different binding energy.

That the nitrogen species produced by surface reactions of NO and NH$_3$ with carbon are chemically equivalent to the ambient $N_x$ species is demonstrated by studying their behavior as function of the sample temperature. The experimental procedure involves ESCA measurements at gradually increasing sample temperatures. The sample remains in vacuum during the entire measurement sequence. The results of such measurements of one ambient particulate sample, collected in Pomona, CA during a moderate smog episode (October 24, 1972) and for a sample prepared by NH$_3$ - hot soot interaction are shown in Figure 5 and 6.

The spectrum of the ambient sample (Figure 5) shows again the presence of NO$_3^-$, NH$_4^+$ and $N_x$. In contrast to the situation shown in Figure 1a, this time the sample was at 25°C (in vacuum) during the measurement. Therefore, most of the ammonium peak is not due to the volatile ammonium compound (at 25°C in vacuum). At 80°C the entire nitrate peak is lost accompanied with a similar loss in ammonium peak intensity. The shaded portion of the ammonium peak in the 25°C spectrum represents the ammonium fraction volatilized between 25°C and 80°C. It appears therefore that the nitrate in this sample is mainly in the form of ammonium nitrate. At 150°C the only nitrogen
species remaining is $N_x$. The ammonium fraction still present at 80°C but absent at 150°C is associated with some ammonium compound more stable than NH$_4$NO$_3$, possibly ammonium sulfate.

Further heating of the sample to 250°C results in the appearance of another peak labels $N_x$ in Figure 5. This peak continues to grow at the next temperature setting of 350°C. The total peak areas of spectra recorded at 150°C, 250°C and 350°C remain constant, meaning that the $N_x$ component is transformed into $N'_x$ under the action of heating in vacuum. This temperature dependent behavior can be taken as characteristic of ambient $N_x$ species.

$N_x$ species produced by surface reactions of hot soot (or graphite) with NH$_3$ (or NO) have the same kind of temperature dependence as the ambient samples. This is illustrated in Figure 6. The spectrum taken at room temperature shows that the only species found in this particular sample are of the $N_x$ type. Heating the sample in vacuum to 150°C does not influence the line shape or intensity. At 250°C, however, the formation of $N'_x$ is evident. Further transformation of $N_x$ to $N'_x$ occurred at 350°C.

$N'_x$ species, produced by heating in vacuum, will remain present in both ambient and synthetically produced samples even if the temperature is lowered back to room temperature, provided that the sample has remained in vacuum. However, if the sample containing $N'_x$ species is taken out of vacuum and exposed to moisture, $N'_x$ will be transformed back to the original $N_x$ compound. It can be concluded that $N'_x$ species
are produced from $N_x$ when the latter looses water by heating in vacuum.

III. DISCUSSION

The outlined results indicate that reduced nitrogen species of the $N_x$ and $N'_x$ type, observed in ambient pollution particulates are chemically analogous to the reduced nitrogen species produced by surface reactions at elevated temperature, of ammonia and nitric oxide with finely divided carbon or soot. In addition the same reactants at room temperature produce surface ammonium compounds.

The question remaining to be answered deals with the chemical form of $N_x$ and $N'_x$ which thus far have been identified only through their manifestations on the chemical shift. A comparison of the chemical shifts of known nitrogen compounds with the chemical shifts of the ambient and synthetic samples shows that the $N_x$ binding energy is compatible with amides and/or amines, while the $N'_x$ binding energy may correspond to nitriles. The results of the temperature dependent ESCA studies of ambient and laboratory produced samples suggest that $N_x$ is at least in part an amide, because amides became nitriles when they dehydrate. Because we were unable to achieve complete conversion of $N_x$ to $N'_x$ at temperature employed, the possibility that a considerable fraction of $N_x$ species are amines can not be ruled out at this time.

An understanding of the formation of these nitrogen species can be gained by consideration of the possible interactions of surface oxygen complexes on carbon with $NH_3$ and NO. For the reasons
of simplicity we shall first consider in some detail the interactions of soot with NH$_3$, after which we shall broaden the discussion to include the case of NO.

The interaction of oxygen with carbon surfaces has been the subject of many studies in the past.

Nearly every type of oxygen-containing functional group known in organic chemistry has been postulated to exist on the carbon surface as the result of these interactions. The functional groups most often suggested are carboxyl groups, phenolic hydroxyl groups, and quinone carbonyl groups (Boehm, 1966; Coughlin and Ezra, 1968; Puri, 1966, 1970; Puri and Bansal, 1964; Puri et al. 1961; Smith, 1959; Zarif'yang et al., 1967). Less often suggested are ether, peroxide, and ester groups in the forms of normal and fluorescein-like lactones (Garten et. al., 1957), carboxylic acid anhydrides (Boehm et al., 1964; Mattson and Mark, 1969), and cyclic peroxide (Puri, 1962).

The relative amounts of these complexes and their structure depends on the thermal history of carbon particles (Hart et al., 1967; Laine et al., 1965; Puri, 1970; Weller et al., 1948). For example, it has been shown that carbon outgased at high temperature and subsequently exposed to oxygen between 200° and 700°C, will have acidic oxygen functional groups. The temperature needed for the development of maximum acidic groups has been found to be close to 400°C. On the other hand, outgased carbon exposed to oxygen either below 200 or above 700°C will have basic character and will adsorb acids. In
reality, however, there is no sharp transition temperature which separates the formation of acidic from basic groups. Instead there is a certain degree of overlap in these temperature ranges.

Based on the most oftenly-mentioned surface oxygen-carbon functional groups (i.e. carboxyl groups and phenolic hydroxyl groups) and in analogy with organic chemistry we can describe some possible reactions of \( \text{NH}_3 \) and soot leading to the formation of amides, amines, nitriles and ammonium salt like compounds associated with soot or graphite particle surfaces.

\[
\begin{align*}
\text{H}_2\text{O} + \text{NH}_3 & \rightarrow \text{ONH}_4 \text{ complexes} \\
\text{ONH}_4 \text{ complexes} & \rightarrow \text{carboxyl ammonium complexes} \\
\text{ONH}_4 \text{ complexes} & \rightarrow \text{phenolic hydroxyl ammonium complexes} \\
\text{ONH}_4 \text{ complexes} & \rightarrow \text{amines} \\
\text{ONH}_4 \text{ complexes} & \rightarrow \text{amides} \\
\text{ONH}_4 \text{ complexes} & \rightarrow \text{nitriles}
\end{align*}
\]
At low temperature: soot particles or graphite covered with surface carboxyl or phenolic groups, may act as a Brønsted acid when interacting with NH$_3$. Carboxyl ammonium or phenolic ammonium salts will be formed as the result of proton exchange. At elevated temperature: the carboxyl group carbon is electrophilic and has the tendency to accept an electron pair from the basic species in the process of coordination. The nucleophilic substitution reaction of NH$_3$ with carboxylic acid yields an amide which may dehydrate and become a nitrile upon further heating. Carboxyl and phenolic hydroxyl ammonium salts may dehydrate at elevated temperature to produce amides and/or nitriles and amines respectively.

The outlined mechanism of the formation of amides, amines and nitriles is supported by the ESCA measurements which show that the oxygen concentration on graphite samples is substantially higher before interaction with NH$_3$, i.e. indicating the dehydration process during the reaction.

In the terms of photoelectron spectroscopic results obtained on ambient air samples the amides and amines correspond to the N$_x$ species. These, as we have already mentioned appear as broad peaks indicating the presence of more than one chemical species. Nitriles formed from amides by dehydration upon heating correspond to the N$_x$ species. We have already established the rever-
sibility of the $\frac{N_x}{2} + H_2 O N_x$ process. The carboxyl ammonium and phenolic hydroxyl ammonium salts produced by NH$_3$ chemisorption correspond to the volatile ambient ammonium species.

It is known that graphite has reducing properties. Soot, formed from combustion of hydrocarbon fuels, on the other hand, may exist as a partially pyrolysed carbonaceous material which contains residual hydrogen throughout its bulk. The hydrogen content is of the order of 1% by weight, corresponding to an atomic ratio of C to H of about 8 (Palmer and Cullis, 1965). It is therefore expected that soot has reducing properties.

From Figure 2b it is evident that NO can be reduced to an ammonium salt when interacting with soot, in the presence of moisture and air at room temperature. At elevated temperature soot - NO interaction will yield $N_x$ and $N'_x$ species. This evidence suggests that NO is first reduced by soot to NH$_3$ which will form ammonium salts, amines, amides and nitriles as the result of reactions with the surface carbon-oxygen functional groups.

Another possible mechanism may involve the nitration of soot followed by the reduction of nitro groups to amine. Since we did not detect the existence of nitro nitrogen in the photoelectron spectra, however, the latter mechanism seems less likely.

The described experiments and the outlined discussion can be summarized as follows:
1) Three reduced forms of nitrogen are associated with ambient pollution particulates: a volatile ammonium constituent (other than ammonium nitrate or ammonium sulfate) and two additional nitrogen species $N_x$ and $N'_x$.

2) Nitrogen species of the same type and behavior can be synthesized under laboratory conditions by soot-$\text{NH}_3$ and soot-$\text{NO}$ reactions. The three types of compounds are assigned to soot with carboxyl and/or hydroxyl ammonium surface complexes, amine and amide corresponding to $N_x$ and nitrile which correspond to $N'_x$.

3) The volatile hydroxyl and/or carboxyl ammonium salts are produced in soot-$\text{NH}_3$ or soot-$\text{NO}$ surface reactions at ambient temperatures.

4) Amine, amide and nitrile is produced in high temperature reactions between surface carbon-oxygen complexes on soot particles and $\text{NH}_3$ or NO.

As it is the case with other processes whose feasibility has been demonstrated under laboratory conditions, the assessment of the relevance of soot-$\text{NO}$ and soot-$\text{NH}_3$ surface reactions to the chemistry of aerosol air pollution has to be established by considering the available analytical and other field data. The process that we propose is based on abundant presence of finely divided, high surface area, soot particles in the polluted atmosphere. Experimental results obtained with ambient particulates
support this assumption, which is logical in view of the fact that most of urban air pollution originates in combustion and that even what seems to be complete combustion will, under realistic circumstances, produce significant amounts of soot.

Actually, photoelectron spectra (Figure 7) of ambient particulates reveal that carbon (1s) photoelectron peak appears essentially as a single peak with a binding energy corresponding to a neutral charge state, compatible with either elemental carbon or hydrocarbons or both. Chemically shifted carbon peaks, due to oxygen bonding are generally of low intensity as compared with the main hydrocarbon and elemental carbon peak.

Unfortunately, because of the nature of the chemical bonding in hydrocarbons, they cannot be distinguished from elemental carbon by core electron shift under realistic sample conditions. We have, therefore, employed other supplementary, although somewhat indirect, measurements to estimate the relative abundance of "elemental" carbon or soot. This was attempted in one series of experiments by comparing the carbon ESCA peak intensity with the sample at normal operating temperature of 25°C to the peak intensity obtained with the same sample at 350°C. The difference between the low temperature and high temperature runs should give the fraction of the volatile organic compounds, under assumption that organic compounds of interest to aerosol chemistry will have vapor pressures above at least $10^{-6}$ torr, i.e., considerably higher
than the pressure in the ESCA spectrometer. The result of one such measurement is shown in Figure 7, where the carbon (1s) peak of a sample collected on 8/24/73 in West Covina, CA as measured at 25° and at 350°C is reproduced. It is noticed that the slight decrease in intensity is practically confined to the chemically shifted carbon peaks. This result shows that most of the carbon is nonvolatile at 350°C in vacuum, i.e. that it is most likely soot. The decrease in the intensity of chemically shifted carbon peaks is expected for soot and it may reflect the "stripping" of soot surface of carbon oxygen complexes.

Our conclusion about the high nonvolatile carbon content could be erroneous if a large fraction of the particulate carbon volatiles even at 25°C in vacuum. This seems unlikely, however, because reasonably good agreement has been found between the total carbon concentration as measured by ESCA and by a combustion technique (Appel et al, 1974).

With these conclusions about particulate carbon in mind we can reasonably expect that the formation of amines and amides, i.e. the \( N_x \) species, may occur in the act of combustion where there are high concentrations of hot soot particles. This view is supported by the diurnal concentration variations an example of which is shown in Figure 8, where we show the diurnal plots of \( N_x \), total particulate carbon and lead obtained on twelve samples without particle size segregation, collected in downtown Los Angeles on 9/20/1972.
at a site adjacent to a freeway. We note, however, that because of the changes in the wind direction the freeway itself is not the only contributor of the particulates. Actually, much of the particles originate at places other than the freeway. The similarity between the carbon and $N_x$ pattern is obvious.

Because high temperature is required for the formation of amines and amide (via the surface interactions of soot and NO or NH$_3$) the obvious conclusion is that $N_x$ species, and implicitly particulate carbon, are primary pollutants. This conclusion is further supported by the fact that $N_x$ and $N_x^+$ (both ambient and laboratory synthesized) are not volatile in vacuum up to at least 400°C and that they do not dissociate in acidic solution. If they are formed from the homogeneous gas phase reactions, however, we would expect that the acid catalyzed hydrolysis of amide, nitrile or aromatic amine type stoichiometric organic compounds, will yield ammonium salts and carboxylic acids or aromatic alcohols. The formation of volatile ammonium compounds of the hydroxyl and/or carboxyl ammonium type, on the other hand, is expected to occur at ambient temperatures, that is along the pathways of carbon particles through the atmosphere.

The results described in this paper indicate the importance of carbon particles as sites for surface reactions with NO and NH$_3$. We have already pointed out (Novakov et al, 1974) the importance of soot particles as a probable catalyst in SO$_2$ oxidation to sulfate.
In so far as the catalytic oxidation of $\text{SO}_2$ on carbon particles is concerned, it is of interest to note that carbon particles on which amines and amides have been formed by one of the described reactions, seize to be catalytically active for $\text{SO}_2$ oxidation. These species are therefore poisoning the carbon catalyst, probably by engaging the same active sites. This finding further illustrates the importance of the surface conditions for the catalytic and surface activity of carbon particles.
REFERENCES


Novakov, T. (1973) Chemical Characterization of atmospheric pollution particulates by photoelectron spectroscopy, P. 197, 2nd Joint Conf. on sensing Envir. Pollutants, Washington, D.C.


FIGURE CAPTIONS

FIGURE 1
a) Nitrogen (1s) photoelectron spectrum of an ambient particulate sample taken with the specimen at -150°C. Individual peaks corresponding to NO$_3^-$, NH$_4^+$ and N$_x$ are indicated.
b) The same spectral region of the same sample at 25°C.

FIGURE 2
a) Nitrogen (1s) ESCA spectrum of cold soot particles exposed to NH$_3$.
b) Nitrogen (1s) spectrum of cold soot particles exposed to NO. Insert shows the setup used for exposure of cold soot to NH$_3$ and NO.

FIGURE 3
a) Nitrogen (1s) spectrum of hot soot particles exposed to NH$_3$.
b) Nitrogen (1s) spectrum of hot soot particles exposed to NH$_3$. Insert shows the experimental arrangement used for sample preparations.

FIGURE 4
a) Nitrogen (1s) spectrum of pretreated hot graphite exposed to NH$_3$.
b) Nitrogen (1s) spectrum of pretreated hot graphite exposed to NO. Insert shows the setup used for exposure of graphite to NH$_3$ and NO.
FIGURE 5

Nitrogen (1s) spectrum of an ambient sample as measured at 25°C, 80°C, 150°C, 250°C and 350°C.

FIGURE 6

Nitrogen (1s) spectrum of (hot) soot sample exposed to NH₅, as measured at 25°C, 150°C 250°C and 350°C.

FIGURE 7

Carbon (1s) spectrum of an ambient sample taken at 25°C and 350°C. The shaded area represents the volatile carbon fraction. The volatile loss is confined to the chemically shifted carbon.

FIGURE 8

Diurnal concentration variations of Nₓ, total particulate carbon and lead obtained on two of the 2 hour samples without particle size segregation, collected in Los Angeles.
Fig. 1
Cold soot + \(\text{NH}_3\) or \(\text{NO}\)

\[\text{NH}_4\text{H}^+\]

Fig. 2
(a) Hot soot + NH$_3$

![Diagram of chemical reaction]

(b) Flame Filter

![Diagram of experimental setup]

**Fig. 3**
Fig. 4

(a) Hot graphite + NH₃

(b) Hot graphite + NO

Intensity (arbitrary units)

Binding energy (eV)

Hot graphite + NH₃

Hot graphite + NO

XBL746-3528
Fig. 5
Hot soot + NH₃

Binding energy (eV)

Intensity

25°C
150°C
250°C
350°C

Fig. 6
Fig. 7

- Neutral C
- Chem. shifted C

Net counts vs Binding energy (eV)

- 350°C
- 25°C
Fig. 8
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.