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The Electronic Structure of the $(CH_3)_2N$ Radical and the Pyrolysis Mechanism of Dimethylnitrosamine: A HeI Photoelectron Spectroscopic Study

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A continuous dimethylamino $(CH_3)_2N$ ± (DMA) radical beam is produced in situ by the pyrolysis of dimethylnitrosamine $(CH_3)_2NNO$ at 850 (0.5 ° C) in a double-heater inlet system on a double-chamber UPS machine-II which was built specifically to detect transient species. The HeI photoelectron spectrum (PES) of the $(CH_3)_2N$ radical is recorded for the first time. To assign the PES bands of the $(CH_3)_2N$ radical, the improved density functional theory (DFT) calculation based on the Amsterdam density functional (ADF) program package has been carried out according to C_{2v} symmetry for the ground state of the neutral $(CH_3)_2N$ radical and the equilibrium geometries of several ionic states of the cationic species. A sharp peak with the lowest ionization energy at 9.01 ± 0.02 eV comes from electron ionization of the HOMO($2b_1$) of the $(CH_3)_2N$ radical, corresponding to the ionization of the $(CH_3)_2N$ ($X\ ^2B_1$) to $(CH_3)_2N^+$($X\ ^1A_1$). The second band with vibration spacing 1980 ± 60 cm^{-1} comes from electron ionization of $1a_2$ orbital which is a strongly bound state for the $(CH_3)_2N$ radical, corresponding to ionization of $(CH_3)_2N$ ($X\ ^2B_1$) to the $^3B_1$ state of $(CH_3)_2N^+$ cation. The PES bands of the NO molecule clearly appears in the PE spectrum of the products pyrolyzed of the compound. The pyrolysis mechanism of the $(CH_3)_2NNO$ compound is shown as follows: $(CH_3)_2NNO \xrightarrow{850 \pm 0.5\ ^\circ C} (CH_3)_2N + NO$.

Introduction

It is well-known that *N*-nitroso compounds may have a significant role in human carcinogenesis. The ubiquity of their precursors leads to the ready formation of nitrosamines and other *N*-nitroso compounds in the human micro- and macroenvironment. Therefore, there is a continuing need to understand the extent and mechanisms of *N*-nitroso compound formation, as well as to understand the mechanisms of their bioactivation and detoxification. Recent discoveries have demonstrated several pathways for the endogenous formation of *N*-nitroso compounds. Ingested or endogenous nitrogenous substrates can react with nitrous acid in the stomach or be nitrosated either there or elsewhere by nitrosating agents arising from the endogenous formation of NO or the bacterial reduction of nitrate.[1−3]

To promote understanding of the mechanisms of the bioactivation and detoxification of nitrosamine compounds, a study of HeI photoelectron spectroscopy (PES) on the electronic structure of alkyl nitrosamines has been reported by us.[4]

It is also known that alkyl- and arylamidogen radicals are important intermediates in organic chemistry[5] and have also been invoked as ligands in organometallic chemistry,[6] The family of alkyl- and arylamidogen radicals has been involved in cancer formation.[7] Much work has been performed to try to establish the first ionization energy of the simplest members of alkylamidogen group. But the disagreement in the first ionization energy calculated for $(CH_3)_2N$ radical (DMA) is very clear,[8−11] and there is no experimental report on ionization energies of different orbitals for the $(CH_3)_2N$ radical until now.

Recently, during our PES study for transient species, NO_3 radical was also obtained in situ through the pyrolysis of N_2O_5.[12] In this paper, we would like to report the PES study on the electronic structure of $(CH_3)_2N$ radical which is in situ produced through the pyrolysis of $(CH_3)_2NNO$ compound. The assignment of the PES bands is done with the aid of the band shapes and that of the improved density functional theory (DFT) calculation based on the Amsterdam density functional (ADF) program package[13−15] for the ground state of $(CH_3)_2N$ radical and the ground and several ionic states of $(CH_3)_2N^+$ cation.[16] From the PES result, the pyrolysis mechanism of dimethylnitrosamine compound is also inferred.

Experiment

1. Synthesis of Dimethylnitrosamine. Dimethylnitrosamine was prepared from corresponding pure dimethylamine hydrochloride and nitrous acid.[17] The PE spectrum of dimethylnitrosamine obtained is the same as the spectra reported in refs 4−18.

2. UPS Measurement. PES experiments are performed on a double-chamber UPS machine-II which was built specifically to detect transient species as described elsewhere.[19] A continuous $(CH_3)_2N$ radical beam is produced in situ through the pyrolysis of dimethylnitrosamine at 850(±0.5) °C in a guartz tube using a double-heater inlet system and the temperature up to 1200.[12] The PE spectrum of $(CH_3)_2N$ radical is measured in the condition of about 25−30 meV operational resolution for the $^2P_{3/2}$ peak of argon(Ar^+). Experimental ionization energies (I_v in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide into the sample.

Computational Details

To assign the PES bands of $(CH_3)_2N$ radical, the density functional theory (DFT) calculations have been performed on the $^2B_1$ ground state of the $(CH_3)_2N$ radical and the ground and

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several ionic states of the $(CH_3)_2N^+$ cation, because this DFT calculation was applied successfully to the assignment of the PES bands of NO_3 radical.[12] The calculation is carried out with the ADF program package,[13−15] in which a density fitting procedure[13] is used to obtain the Coulomb potential, and an elaborate three-dimensional numerical integration technique[14,15] is employed to calculate the Hamilton matrix elements. The Vosko−Wilk−Nusaair parametrization[20] of uniform electron gas data is used for the exchange-correlation energy and potentials, which is usually called the local spin density approximation (LSDA). The gradient correction of exchange energy due to Beck[21] and that of correlation energy developed by Perdew[22] have been performed in a post manner. The molecular orbitals were expanded in an uncontracted triple-ξ STO basis set augmented by two polarization basis functions for both the carbon and nitrogen atoms.

To assign the PES bands of the $(CH_3)_2N$ radical, the vertical ionization energies (E_v in eV) computed are obtained from the total energy difference of the resulting cation/neutral species in this study. To calculate the total energies of the singlet states described by multideterminantal wave function, the sum method proposed by Ziegler−Rauk−Baerends[23] is used. The geometries used in the calculation for the neutral $(CH_3)_2N$ radical are taken from the results of Huang et al.,[16] at the UMP2/6-31G** level of theory.

To identify the true ground state (X $^1A_1$) of $(CH_3)_2N$ radical, these DFT calculations on the ground state of NH_2 radical and several ionic states of NH_2+ cation were also performed. The ground state of NH_2^+ cation is X $^3B_1$ state, corresponding to the computed vertical ionization energy 12.098 eV, and comes from the electron ionization of ($3a_1$) orbital of NH_2 radical. The electron ionization of HOMO ($1b_1$) which is consisted essentially of the nitrogen $2P_\pi$ nonbonding orbital perpendicular to the H−N−H plane for the NH_2 radical, leads to the $^1A_1$ state corresponding to the computed vertical ionization energy 12.635 eV. These results shows that the DFT calculation for the assignment of the PES bands of NH_2 radical is better than ab initio ΔSCF,[24] because the results of DFT calculation are much close to PES experimental values for the NH_2 radical.[24]

Results and Discussion

1. Pyrolysis Mechanism of the $(CH_3)_2NNO$ Compound. From the results of the PES study of electronic structure for alkyl nitrosamines,[5] it is thought that if the $(CH_3)_2NNO$ molecule is pyrolyzed, the bond between the $(CH_3)_2N$ group and NO group will first broken, because the bond strength for this bond is weakest. During the pyrolysis process of $(CH_3)_2NNO$ compound, it is found that if the pyrolysis temperature is lower than 830 °C, there is no change for the PE spectrum of $(CH_3)_2$-NNO. If the pyrolysis temperature is higher than 830 °C, the changing PE spectra associated with the change of pyrolysis temperature are appeared. In fact, they are the PE spectra mixed of both $(CH_3)_2NNO$[5] and NO[25] species. A constant PE spectrum which is full different with the PE spectrum of $(CH_3)_2NNO$ molecule is obtained at 850(±0.5) °C. The Figure 1 gives the HeI photoelectron PE spectrum of the products pyrolyzed of $(CH_3)_2NNO$ molecule at 850(±0.5) °C. An expanded (PE) spectrum of the products pyrolyzed of $(CH_3)_2NNO$ molecule at the low ionization energy region (<11.00 eV) is given in Figure 2

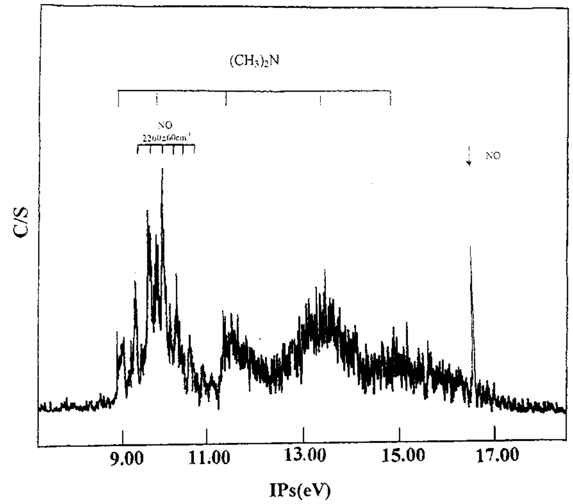

Figure 1. The HeI photoelectron spectrum (PES) of the products pyrolyzed from the $(CH_3)_2NNO$ compound.

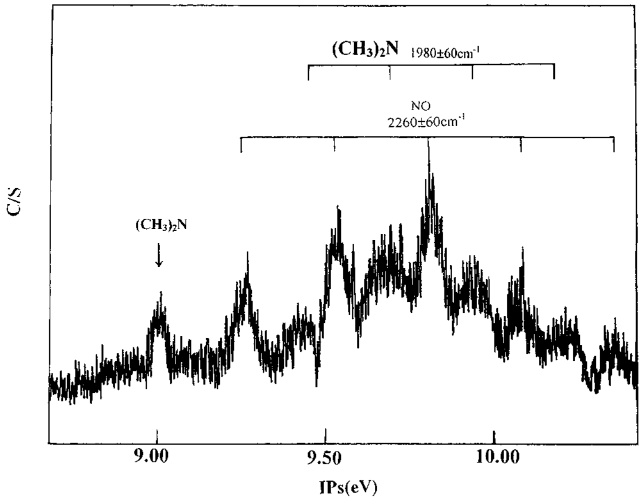

Figure 2. The expanded PE spectrum of the $(CH_3)_2N$ radical for the first peak and second band with vibration fine structure.

From the Figure 1 and 2, it is clearly seen that the five peaks with 2260 ± 60 cm^{-1} vibration spacings is the same as those of the first band of the NO molecule.[25] The ionization energy 9.26 eV corresponding to the first vibrational peak in these five peaks is also the same as the adiabatic ionization energy of the first PES band of NO molecule.[25] A more clear evidence in the PE spectrum of the products pyrolyzed of $(CH_3)_2NNO$ molecule is that a sharp peak at 16.56 eV is also characteristic of generation of NO molecule. The high intensity of the peak at 9.82 eV can be explained by the overlapping of third vibration peak for the first band of NO molecule on the second band of new species pyrolyzed of $(CH_3)_2NNO$ molecule, because the highest intensity peak for the first band of NO molecule is the second vibration peak at 9.54 eV. Therefore, the pyrolysis of $(CH_3)_2NNO$ molecule yields the $(CH_3)_2N$ radical via NO loss:

$$(CH_3)_2NNO \xrightarrow{850 \pm 0.5\ °C} (CH_3)_2N + NO$$

That is to say, the pyrolysis mechanism of $(CH_3)_2NNO$ molecule seems to be consistent with the suggestion for the detoxification mechanism of the $(CH_3)_2NNO$ molecule.[27,28]

2. Assignment of PES Bands for the $(CH_3)_2N$ Radical. From the Figure 1, it is clearly seen that the peak at 9.01 eV is a very sharp peak and that there is no vibrational progression in the peak. This shows that there is no geometry change in going from the ground state of $(CH_3)_2N$ neutral radical to the ground state of $(CH_3)_2N^+$ cation in the photoionization process, because the vertical ionization energy (I_v) is equivalent to the

TABLE 1: Experimentally Determined Vertical Ionization Energies (I_v in EV) and Ionization Energies Computed (E_v in eV) According to the C_{2v} Symmetry for the $(CH_3)_2N$ Radical by Using DFT Calculation for Several Ionic States of the $(CH_3)_2N^+$ Cation

experimental I_v(eV)	DFT energies E_v(eV)	cationic states
9.01	9.256	$^1A_1$
9.65	9.678	$^3B_1$
11.25	10.778	$^1B_1$
13.40	12.618	$^3A_2$
	12.750	$^1A_2$
14.87	13.170	$^3B_2$
	13.468	$^1B_2$

adiabatic ionization energy (I_a). That is to say, the ionization corresponding with this peak comes from the result of the electron ionization of the nonbonding orbital. This assignment for the peak at 9.01 eV is also consistent with the reported[28] in which an unpaired electron occupies the nitrogen P-orbital perpendicular to the C−N−C plane.

According to the C_{2v} symmetry and assuming a $^2B_1$ ground state for the neutral $(CH_3)_2N$ radical, the molecular orbitals would be in the following order of increasing energy: ...$(4a_1)^2$ $(1b_1)^2$ $(5a_1)^2$ $(3b_2)^2$ $(6a_1)^2$ $(4b_2)^2$ $(1a_2)^2$ $(2b_1)^1$. The removal of an electron from the HOMO will leave the ion in the singlet state $^1A_1$. The removal of an electron in turn from each of the other valence shell orbitals can leave both the triplet and singlet states of the ion. Therefore, the first PES peak at the lowest ionization energy (9.01 eV) for the $(CH_3)_2N$ radical should be expected to originate from electron ionization of the HOMO $(2b_1)^1$. That is to say, the first peak at 9.01 eV for the $(CH_3)_2N$ radical comes from electron ionization of nonbonding orbital, because the vertical ionization energy (I_v) is equivalent to the adiabatic ionization energy (I_v) in the peak. This assignment for the first peak is also supported by the results of the DFT calculation for the $(CH_3)_2N$ radical and the $(CH_3)_2N^+$ cation in their ground electronic state, because the DFT calculation shows that the HOMO ($2b_1$) of the neutral $(CH_3)_2N$ radical is a formally nonbonding nitrogen p_π-orbital perpendicular to the C−N−C plane, and the ground state of $(CH_3)_2N^+$ cation is formed due to the ionization of the HOMO ($2b_1$) electron of neutral $(CH_3)_2N$ radical. According to the Franck−Condon principle, the computed ionization energy (E_v) corresponding to this sharp peak should be obtained from the resulting cation/neutral total energy difference 9.256 eV (See Table 1), which is close to the PES experimental value (9.01 ± 0.02 eV).

Table 1 gives the PES experimental determined ionization energies (I_v in eV) and corresponding computed ionization energies (E_v) for different ionic state of the $(CH_3)_2N$ radical. The energies of the ionic states for the $(CH_3)_2N$ radical are given using the vertical ionization energy (E_v), chosen as the maxima of the bands in the PE spectrum.

The ionization of electron for the $1a_2$ orbital of neutral $(CH_3)_2N$ radical leads to both $^3B_1$ triplet and $^1B_1$ singlet states. The $^3B_1$ triplet state should has lower ionization energy which corresponds to the band centered near 9.65 eV, and the $^1B_1$ singlet state corresponds to the band centered near 11.25 eV, also because the observed intensity being approximately three times high as for the 9.65 eV band as for the third band at 11.25 eV gives some confirmation for this assignment.

From the expanded PE spectrum of the $(CH_3)_2N$ radical (see Figure 2), it is seen that the second band of the PE spectrum displays vibrational fine structure (1980 ± 60 cm^{-1}). This fact shows that the ionization which leads to the second band of the PE spectrum comes from electron ionization of a strongly bound state, because the orbital electron ionization of a strongly bound state always leads to a PES band with a long vibrational progression. With the aid of the result of the DFT calculation, the second band centered at 9.65 eV can be attributed to the ionization of electron for the $1a_2$ orbital of the $(CH_3)_2N$ radical, because the experimental ionization energy associated with the ionization is in good agreement with the computed value (9.678 eV). And the DFT calculation of $(CH_3)_2N$ radical shows that the $1a_2$ orbital is a bonding orbital for whole molecule. Therefore, the electron ionization of the $1a_2$ orbital should lead to the band with long vibration progression, maybe corresponding to the bending mode of the radical $(CH_3)_2N$.

The third PES band of the $(CH_3)_2N$ radical located at 11.25 eV is designated to the $^1B_1$ singlet state of the $(CH_3)_2N^+$ cation, because this experimental value is also close to the computed ionization energy (10.778 eV), and the intensity of the third band is also weaker. A further survey in the third of the $(CH_3)_2N$ radical at 11.25 eV seems to be the band associated with some fine vibration structure, but the vibration spacing on the band is smaller than that (1980 ± 60 cm^{-1}) of the second band.

The band centered near 13.40 eV can be assigned to ionization of electrons of the $4b_2$ orbital leading to both triplet $^3A_2$ and singlet $^1A_2$ states, because the band is very broad and the computed ionization energies 12.618 and 12.750 eV for the two ionic states are very close. Similarly the band centered near 14.87 eV can be considered as the ionization to both triplet $^3B_2$ and Singlet $^1B_2$ states, because the computed ionization energies 13.170 eV and 13.469 eV for the two ionic states are also very close.

In short, the assignment of the PES band for the $(CH_3)_2N$ radical is supported by the DFT calculation.

Conclusion

The HeI PE spectrum of the $(CH_3)_2N$ radical has been obtained in situ by pyrolysis of the $(CH_3)_2NNO$ compound. The sharp peak with the lowest ionization energy (9.01 ± 0.02 eV) shows that the HOMO ($1b_1$) of the neutral $(CH_3)_2N$ radical is a nonbonding orbital corresponding to ionization of $(CH_3)_2N$ (X $^2B_1$) radical to $(CH_3)_2N$ (X $^1A_1$). The second band with the vibration fine structure 1980 ± 60 cm^{-1} associated with the vertical ionization energy 9.65 eV comes from electron ionization of a strong bound state leading to the $^3B_1$ state of the $(CH_3)_2N^+$ cation.

The improved density functional theory (DFT) calculation based on the Amsterdam density functional (ADF) program package enables the PES bands of the $(CH_3)_2N$ radical to be assigned.

The PES experimental results seems to be consistent with the suggestion for detoxification mechanism of the $(CH_3)_2NNO$ compound which is the formation of the $(CH_3)_2N$ radical via NO loss.

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