Study of the Thermal Decomposition of 2-Azidoacetic Acid by Photoelectron and Matrix Isolation Infrared Spectroscopy

J. M. Dyke,[†] A. P. Groves,[†] A. Morris,[†] J. S. Ogden,[*,†] A. A. Dias,[†,§] A. M. S. Oliveira,[†,§] M. L. Costa,[‡] M. T. Barros,[‡] M. H. Cabral,[‡] and A. M. C. Moutinho[‡]

Contribution from the Department of Chemistry, The University of Southampton, Southampton SO17 1BJ, U.K., and CeFITec, Departamento de Fisica de Faculdade de Ciencas e Technologica, Universidade Nova de Lisboa, 2825, Monte de Caparica, Lisbon, Portugal

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Abstract: 2-Azidoacetic acid ($N_3CH_2CO_2H$) has been synthesized and characterized by a variety of spectroscopic techniques, and the thermal decomposition of this molecule studied by matrix isolation infrared spectroscopy and real-time ultraviolet photoelectron spectroscopy. The results are consistent with the vapor phase thermal decomposition following a pathway involving concerted ejection of molecular N_2 and the simultaneous formation of CO_2 and methanimine (CH_2NH). No evidence was found for the presence of intermediates such as the nitrene NCH_2CO_2H or the imine $HNCHCO_2H$. At higher temperatures, CH_2NH further decomposes to give HCN and H_2.

Introduction

Compounds containing the azido group ($-N_3$) have been recognized for many years as being potentially explosive, and experimental work on these compounds must therefore be carried out with care. Nevertheless, the thermal decomposition of azides is attractive as a synthetic method,[1−2] and there is considerable current interest in the mechanisms of such decompositions.

This interest has arisen[3−9] because of the potential use of these materials as high-energy storage sources in a number of industrial applications and as precursors for the preparation of single-crystal gallium and silicon nitride epitaxial layers on semiconductor substrates at relatively low temperatures. The dipolar character and relative instability of the azido group enables it to react in a variety of ways depending on the molecular structure, reagents, and experimental conditions.[10]

In general, the controlled thermal decomposition of azides releases molecular nitrogen and, it is believed in the first instance, a nitrene. This may subsequently undergo rearrangement, hydrogen abstraction, cyclization, dimerization, or addition to C−H or C=C bonds, and major research efforts have been made in an attempt to understand how singlet and triplet nitrenes interconvert and give rise to further products.[5−9]

In particular, the thermal decomposition of several alkyl azides (e.g., R_2HCN_3) has been studied extensively by Bock and Dammel[4−8] using photoelectron spectroscopy. Their work suggests that for these azides, N_2 evolution is accompanied by a 1,2 hydrogen atom shift to form the imine $R_2C{=}NH$, which in some systems can undergo further decomposition to produce simple hydrocarbons H_2 and HCN.

As part of a project designed to characterize and investigate more complex azides, this paper describes the characterization and thermal decomposition of azidoacetic acid. By analogy with the results obtained for decomposition of alkyl azides,[7] the thermal decomposition of $N_3CH_2CO_2H$ might be expected to yield the imine $HN{=}CHCO_2H$. Although it is possible to compute the essential features of its photoelectron (PE) spectrum, and thereby check for its formation, it is evident that a second characterization technique would be highly desirable. The possibility also exists that, in this more complex azide system, a quite different decomposition pathway leading to new products might be favored.

In addition to employing real-time gas phase ultraviolet photoelectron spectroscopy (PES), our studies on azidoacetic acid have also incorporated matrix isolation infrared (IR) spectroscopy. This is a well-established technique for the stabilization and detection of vapor phase intermediates and offers not only the possibility of an alternative fingerprint identification but also the potential for definitive characterization of any new chemical species *via* extensive C/H/N/O isotope labeling.

This project is also supported by *ab initio* molecular orbital calculations of different degrees of sophistication in order to compute the electronic structures and valence ionization energies of parent azides and their possible decomposition products.[11]

Experimental Section

Sample Preparation. Azidoacetic acid was prepared from the reaction between bromoacetic acid ($BrCH_2CO_2H$, Aldrich, 95%) and sodium azide (NaN_3, Aldrich 99%). In a typical synthesis, a 1:2 mixture of $BrCH_2CO_2H$ and saturated aqueous NaN_3 was stirred continuously in an ice bath for 24 h and subsequently acidified with aqueous HCl

* To whom correspondence should be addressed.
† The University of Southampton.
‡ Universidade Nova de Lisboa.
§ Praxis XXI Scholarship holders, Lisbon.
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(1:1) to pH = 5. The product, $N_3CH_2CO_2H$, was then extracted with diethyl ether and dried over anhydrous $MgSO_4$. Final purification to remove diethyl ether and the last traces of water required prolonged pumping under vacuum (10^{-6} mbar) at room temperature. Sample purity was estimated to be >99% on the basis of ^1H NMR and mass spectrometric data, a summary of which is included in the Results.

Routine precautions were taken to minimize the effect of possible explosions at all stages in the preparation and handling of azide materials, but no untoward occurrences were experienced during this work.

Matrix Isolation IR Spectroscopy. Matrix isolation studies on the thermal decomposition of azidoacetic acid were based around a conventional closed-cycle cooling unit (APCI "Displex", model CSW202) as described elsewhere.[12] For these particular studies, the parent azidoacetic acid vapor was admitted to the system via a PTFE needle valve at a pressure monitored by a Pirani gauge. The vapor then passed through a 15 cm length of 5 mm i.d. silica tubing connected directly to the housing of the Displex. This provided a direct line-of-sight to a central CsI deposition window, which was maintained at ca. 12 K. Vapors passing through this silica tube could be superheated to ca. 1000 K, by a concentric cylindrical furnace, and subsequently co-condensed on the central cooled window[12] with a large excess (>×1000) of matrix gas.

In a typical experiment, a sample of azidoacetic acid was pre-cooled to ca. 281−283 K prior to admission to provide better flow control and was subsequently co-condensed with nitrogen as the inert matrix gas. This host was chosen in preference to argon, in order to provide a more uniform environment for any trapped species, as it was expected that molecular nitrogen would be *generated* during thermal decomposition.

The initial deposition was usually carried out with the superheater switched off, in order to record the matrix IR spectrum of the parent azidoacetic acid and to establish a suitable flow rate. Several spectra were then recorded after periods of deposition with the superheater set at increasingly higher temperatures, in the anticipation that at some stage new features arising from decomposition products would be isolated in the matrix. From time to time, the superheater temperature was reduced to room temperature to check that the flow of parent azidoacetic acid remained unchanged. Typical deposition times between spectra varied from 30 to 90 min.

Matrix IR spectra were recorded over the frequency range 4000−300 cm^{-1} using either a Perkin-Elmer 983G or a Bio-Rad FTS60 spectrometer equipped with routine spectral subtraction procedures, and any spectral changes taking place as a result of changes in the inlet temperature or sample flow rate could readily be detected.

In addition to monitoring changes in IR band intensity during deposition, it was also possible to investigate the effect of controlled diffusion on the trapped species. During these studies, the temperature of the matrix was cycled within the temperature range ca. 12−35 K.

Separate matrix isolation studies were also carried out to confirm the positions of the IR bands of H_2O, CO, CO_2, HCN, and HCOOH in N_2 matrices and to establish, for the purpose of elimination, the matrix IR spectra of $BrCH_2CO_2H$ and the Et_2O solvent used in the preparation of the azidoacetic acid.

Photoelectron Spectroscopy. All photoelectron spectra recorded in this work were obtained using He(I) (21.22 eV) radiation. The spectrometer used was a single-detector instrument designed for high-temperature work[13,14] with a modified inlet system capable of superheating a vapor species immediately prior to photoionization. The vapor pressure of the parent material, $N_3CH_2CO_2H$, was insufficient at room temperature to allow photoelectron spectra to be recorded with acceptable signal-to-noise. Samples were therefore preheated to ca. 373−423 K in order to generate a greater partial pressure to allow spectra with greater signal-to-noise ratio to be recorded.

In initial thermal decomposition experiments, a sample of liquid $N_3CH_2CO_2H$ was placed in a small stainless steel furnace inside the spectrometer. A short length of cylindrical ceramic tube with a thin tantalum inner liner was placed approximately 2 cm beneath the furnace but above the photon beam. The tantalum insert was heated to ca. 1000 K by radiofrequency induction heating,[13,14] and the stainless steel furnace containing the azidoacetic acid was heated by radiation from the ceramic insert. Although this system provided a high enough temperature to obtain full pyrolysis of the parent azide, it was found that sufficiently controlled pyrolysis could not be achieved.

A new pyrolysis system using a resistively heated furnace was therefore developed to allow controlled superheating over longer times. In this inlet system, molybdenum wire was wrapped around an inner glass tube and connected via tungsten feedthroughs in an outer glass tube to a 15 V dc power supply with a maximum operating current of 2 A. Above the heating wire, the glass tube widened and sample vials were placed on a ledge in this section which was not heated directly. It was found that the maximum operating temperature reached by this system was 850 K in the heated section (as measured by a chromel−alumel thermocouple). The upper region of the furnace containing vials of azidoacetic acid was heated by conduction, and the temperature reached was found to be high enough to generate vapor pressures of azidoacetic acid which gave photoelectron spectra with good signal-to-noise ratios. Furthermore the operating resolution of the photoelectron spectrometer (typically 30−35 meV as measured for argon $(3p)^{-1}$ fwhm ionized with He Iα radiation) was found to be unaffected by this heating system even at the highest temperature available (ca. 850 K).

Photoelectron spectra were recorded in real time as the furnace temperature was varied in the temperature range 300−850 K. The onset of decomposition was marked by the appearance of characteristic PES bands associated with molecular N_2 and CO_2. Spectral calibration was achieved at low ionization energy (9.0−11.0 eV) by CH_3I and at higher energies by reference to the known ionizations of (added) Ar or traces of H_2O present in the system.[15,16]

PE spectra were also obtained for $BrCH_2CO_2H$, used in the preparation of $HCO_2CH_2N_3$. The lowest energy ionization of this molecule consists of an intense, closely spaced doublet at 10.61 and 10.95 eV. This feature is assigned to spin−orbit coupling, and the separation (0.34 eV) is typical of a Br-localized ionization.[17] However, no evidence for $BrCH_2CO_2H$ was found in photoelectron spectra recorded for purified samples of azidoacetic acid.

Results

Characterization of $N_3CH_2CO_2H$. Samples of purified azidoacetic acid were characterized in the vapor phase by mass spectrometry and UV photoelectron spectroscopy and in the condensed phase by ^1H NMR, Raman, and IR spectroscopy. The 70 eV electron impact mass spectrum showed a prominent parent ion peak at 101 amu (55%), together with two intense fragments at 28 (97% N_2^+) and 45 (100%, CO_2H^+) amu. The other signals observed were all significantly less intense but included a very weak doublet at 138/140 amu (ca. 1%) arising from unreacted $BrCH_2CO_2H$.

Only two signals of any significance were observed in the 300 MHz ^1H NMR spectrum of azidoacetic acid in $CDCl_3$ solution. These were observed at 4.0 and 10.3 ppm relative to TMS, and their relative positions and integrated intensities (ca. 1.7:1) are consistent with their assignment as methylene and hydroxyl protons, respectively.

The most intense absorption in the (liquid) IR spectrum was found at 2117 cm^{-1}, and this was assigned to a vibration of the N_3 group. Other prominent bands were present at 1700−1800 (br, C−O stretch), 1421, 1285, and 1250−1150 (br) cm^{-1}. The liquid Raman spectrum exhibited counterparts to all the above bands (2116, 1730 (br), 1422, 1285, and 1225 cm^{-1}) and in addition showed intense features of 2921 (C−H stretch), 947, 880, 236, and 171 cm^{-1}. The O−H stretching region showed

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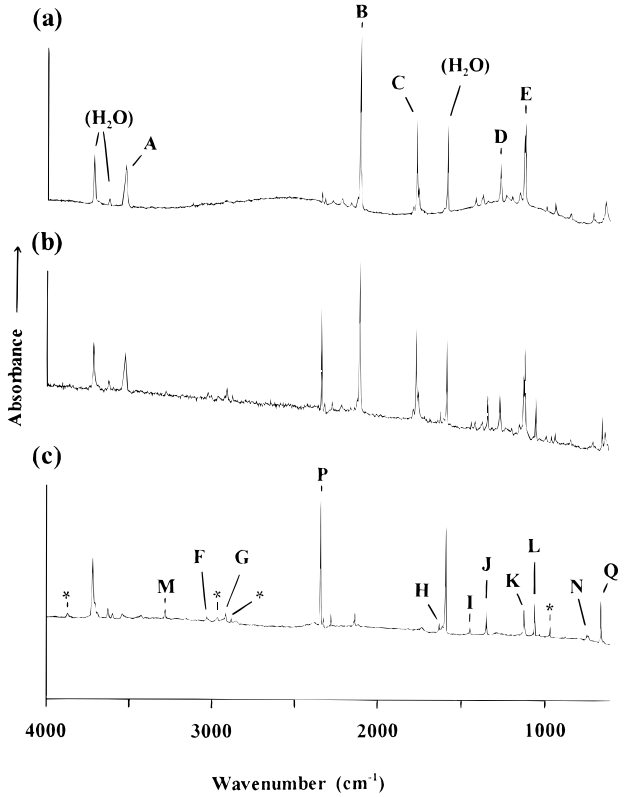

Figure 1. Nitrogen matrix IR spectra obtained during pyrolysis studies on 2-azidoacetic acid. (a) Spectrum of parent material: bands A−E listed in Table 1. (b) Spectrum obtained after pyrolysis at ca. 600 K. (c) Spectrum obtained after pyrolysis at ca. 900 K: new bands F−Q identified in Table 1.

Table 1. Principal IR Bands (cm^{-1}) Observed in Matrix Isolation Studies on the Pyrolysis of Azidoacetic Acid[a]

N_2 matrix (band letter)	previous matrix studies	assignment
3534 (**A**)		N_3CH_2COOH
2118 (**B**)		
1782 (**C**)		
1279 (**D**)		
1138/1131 (**E**)		
3033 (**F**)	3032	CH_2NH (ref 24)
2920 (**G**)	2920	
1637 (**H**)	1639	
1450 (**I**)	1452	
1353 (**J**)	1354	
1128 (**K**)	1129	
1065 (**L**)	1065	
3287 (**M**)	3287	HCN (refs 23 and 24)
747/737 (**N**)	748/738	HCN
2347 (**P**)	2347	CO_2 (ref 25)
662 (**Q**)	662	CO_2

[a] Wavenumber accuracy ±1 cm^{-1}.

few distinctive features. In the IR, two very broad absorptions centered at ca. 3500 and 3050 cm^{-1} were present but the Raman showed no discernable features in this region apart from a very broad, ill-defined band.

Figure 1a shows a typical nitrogen matrix IR spectrum obtained from a sample of $N_3CH_2CO_2H$ deposited from the vapor phase without superheating. The absorptions at 3726, 3633, and 1597 cm^{-1} are due to matrix-isolated H_2O arising from traces of water in the system, but additional intense features are also present at 3534, 2118, 1782, 1279, and 1138 cm^{-1}. The agreement between the positions of these absorptions and the values listed above for liquid phase azidoacetic acid is very satisfactory. The results are summarized in Table 1, and it is found that the only significant difference is to be found in the

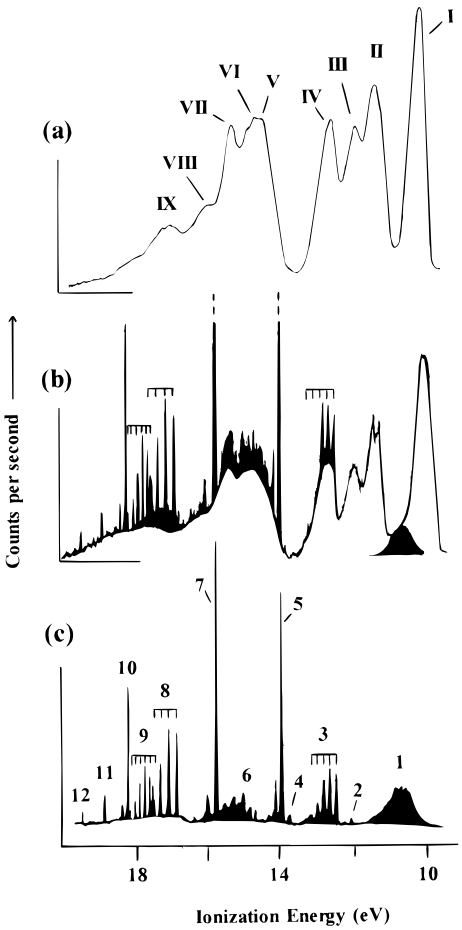

Figure 2. Vapor phase PE spectra obtained during pyrolysis studies on 2-azidoacetic acid. (a) Spectrum of parent material: bands I−IX listed in Table 3. (b) Spectrum obtained after pyrolysis at ca. 680 K. (c) Spectrum obtained after pyrolysis at ca. 750 K: new bands 1−12 identified in Table 4.

O−H stretching region. In the neat liquid, only broad absorptions are observed, indicative of extensive hydrogen bonding, but in the matrix-isolated sample, a prominent feature is found at 3534 cm^{-1}. Under matrix isolation conditions, there is little possibility of intermolecular hydrogen bonding, and this absorption is assigned as the O−H stretch in *monomeric* $N_3CH_2CO_2H$.

The HeI PES of azidoacetic acid is shown in Figure 2a, and our assignment of this spectrum was made with reference to the results of *ab initio* molecular orbital calculations. An estimate of the equilibrium geometry was obtained both at the MP2/6-311G** Hartree−Fock level and at the VWN/TZPP DFT level using the Gaussian 94 code[18] and the Amsterdam Density Functional code,[19,20] respectively. The parameters listed in Table 2 from the MP2/6-311G** calculations correspond to a stationary point on the potential energy surface with all real vibrational frequencies. Other conformers were found to be higher in energy. The three highest occupied molecular orbitals in the ground state of this molecule (orbitals 26, 25, and 24) are essentially nonbonding, whereas orbital 23 is essentially a π(C−O) bonding orbital. Deeper orbitals are less easily

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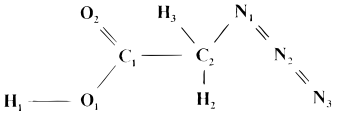
Table 2. Computed Structural Parameters of Azidoacetic Acid at the Hartree−Fock MP2/6-311G** Level



bond lengths (Å)		bond angles (deg)	
$d(C_1{=}O_2)$	1.20	$\angle(O_1{-}C_1{=}O_2)$	124.5
$d(C_1{-}O_1)$	1.35	$\angle(C_1{-}O_1{-}H_1)$	105.7
$d(O_1{-}H_1)$	0.97	$\angle(O_1{-}C_1{-}C_2)$	110.0
$d(C_1{-}C_2)$	1.52	$\angle(C_1{-}C_2{-}H_2)$	109.3
$d(C_2{-}H_2)$	1.09	$\angle(C_1{-}C_2{-}H_3)$	107.7
$d(C_2{-}H_3)$	1.10	$\angle(C_1{-}C_2{-}N_1)$	112.7
$d(C_2{-}N_1)$	1.46	$\angle(C_2{-}N_1{=}N_2)$	115.2
$d(N_1{=}N_2)$	1.24	$\angle(N_1{=}N_2{=}N_3)$	171.5
$d(N_2{=}N_3)$	1.15	dihedral $(N_2{=}N_1{-}C_2{-}C_1)$	63.9
		dihedral $(N_1{-}C_2{-}C_1{-}O_1)$	164.3

Table 3. Comparison of Experimental and Computed Vertical Ionization Energies (IEs) of Azidoacetic Acid

MO	experimental IE band no.	(eV)	VWN/TZPP (eV)	KT × 0.9 (eV)[a]	KT VIE (eV)[a]
26	I	(9.95)	10.01	9.63	10.47
25	II	(11.17)	10.70	10.91	12.12
24	III	(11.79)	11.85	11.81	13.12
23	IV	(12.38)	12.95	12.31	13.68
22	V	(14.31)	13.58	14.30	15.89
21	VI	(14.65)	13.71	14.76	16.40
20	VII	(15.16)	14.58	15.83	17.59
19	VIII	(15.96)	15.17	16.39	18.21
18	IX	(17.15)		17.70	19.67

[a] Obtained from a single-point calculation at the HF/6-311G** level.

described in such simple terms because they are more delocalized. Table 3 compares our experimental vertical ionization energies (VIEs) with calculations resulting from the application of Koopmans' theorem (KT) to the SCF/6-311G** molecular orbital energies. Values computed at the HF/6-311G** level were, as expected, higher than the experimental values because of the use of the Koopmans' approximation, but scaling by a factor of 0.9[21,22] afforded much better agreement with the experimental values. The VWN/TZPP/DFT VIE values, obtained by the transition-state method also show good agreement with experiment.

Matrix Isolation Studies. Thermal Decomposition and Spectral Assignment. Figure 1, parts b and c, shows matrix IR spectra obtained after passing azidoacetic acid vapor through the superheater maintained at *ca.* 600 and 900 K, respectively. At the lower temperature, the most intense absorptions of the parent acid are still present, but several new features may be observed, notably at 2347, 1353, 1065, and 662 cm^{-1}, and the positions of the new absorptions appearing on superheating are summarized in Table 1.

With the superheater temperature at *ca.* 900 K, the parent absorptions have essentially disappeared (Figure 1c), indicating that almost complete thermal decomposition of the azide has taken place.

The assignment of some of these new IR bands is relatively straightforward. Firstly, on the basis of the earlier work by Bock *et al.*,[4−8] one might anticipate that at the highest superheater temperatures HCN would be present as a final decomposition product. The most intense bands in the nitrogen matrix spectrum of HCN[23,24] lie at *ca.* 3287, 747, and 737 cm^{-1}, and these correspond within experimental error to three of the new bands found here (see Table 1). The intense band at 2347 cm^{-1} is due to CO_2. This molecule has been observed many times during the course of matrix IR studies, and its assignment is confirmed[25] by the accompanying ^{13}C feature at 2283 cm^{-1}, the bending mode at 662 cm^{-1}, and combination bands at 3607 and 3712 cm^{-1}.

All other major features that are present after pyrolysis are assigned to CH_2NH. Table 1 compares the frequencies observed in these experiments with the nitrogen matrix data previously obtained by Jacox and Milligan.[24] The agreement is very satisfactory and leaves no room for ambiguity. Four minor absorptions remain unassigned, and these are identified by asterisks in Figure 1c. They lie at 3878, 2969, 2887, and 970 cm^{-1} and are not unique to this azidoacetic acid system. In particular, they are routinely present in blank experiments, where no sample is passing through the superheater, and are attributed to small traces of organic material desorbed from the walls of the superheater over the prolonged period of deposition.

Table 4. Assignment of Bands Observed in the He I Photoelectron Spectrum Recorded for Fully Pyrolyzed Azidoacetic Acid[a]

band no.	vertical ionization energy (eV)	assignment
1	10.62	methanimine first band
2	11.92	CO_2 first band recorded with HeIβ
3	12.49	methanimine second band
4	13.60	HCN first band (HeIβ, N_2)
5	13.79	CO_2 first band
6	14.77	methanimine third band
7	15.58	N_2 first band
8	16.94	N_2 second band
9	17.56	CO_2 second band
10	18.08	CO_2 third band
11	18.76	N_2 third band
12	19.40	CO_2 fourth band

[a] The experimental error on the vertical ionization energies is ±0.02 eV.

Photoelectron Studies. Thermal Decomposition and Spectral Assignment. The He I photoelectron spectrum obtained for azidoacetic acid is shown in Figure 2a, and the PE spectrum obtained upon partial pyrolysis is shown in Figure 2b. The temperature of the superheater under these conditions was approximately 680 K as estimated from chromel−alumel thermocouple measurements. Figure 2c shows a He I photoelectron spectrum obtained on complete pyrolysis of azidoacetic acid, recorded at a furnace temperature of approximately 750 K. Tabulated vertical ionization energies for the photoelectron bands observed in Figure 2c are shown in Table 4. Calibration of these spectra was achieved using the known ionization energies of nitrogen, water, and carbon dioxide.

Signals arising from nitrogen, hydrogen cyanide, and carbon dioxide are clearly observed in the experimental photoelectron spectra recorded for the pyrolysis products (Figure 2a,b), being readily identified by comparison with published spectra.[15,16] But in addition, pyrolysis produces three further features: a broad band with a vertical ionization energy of 10.62 ± 0.02 eV, a vibrationally resolved band at 12.49 ± 0.02 eV showing structure with a mean separation 1280 ± 30 cm^{-1}, and a weak band at approximately 14.80 eV. The relative intensity of these three bands remained constant when experimental conditions were varied, and comparison with literature PE spectra of methanimine[5,8,26] shows that these bands correspond to the three

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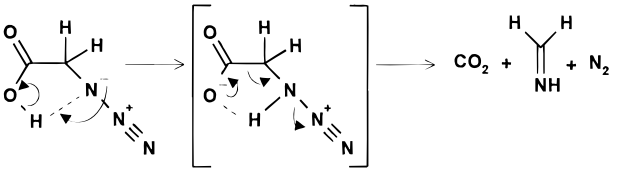
lowest energy ionizations of this species. The band centered at 10.62 eV is the first band of methanimine and is reported[5] to show a vibrational progression with a mean separation of 500 cm^{-1}. This corresponds to excitation of the CNH bending mode. This structure was not resolved in this work. However, the second band of methanimine has a vertical ionization energy of 12.49 eV,[5,8,26] and for this feature, the expected structure was resolved. This band has a vibrational spacing of *ca.* 1280 cm^{-1} corresponding to the excitation of the C═N stretching mode in the cation. This compares with a vibrational frequency of 1638 cm^{-1} for the C═N stretching mode in the neutral,[27] indicating that ionization has occurred from a bonding C═N orbital. The third band of methanimine has a vertical ionization energy of 14.77 eV.[5] This band was found previously to exhibit a complex vibrational pattern, corresponding to excitation of the C—H and C═N stretching modes in the ion. The experimental spectra in this work are not sufficiently resolved to identify all the components of this band; however, most components are seen and the overall band profile is in excellent agreement with that in the literature.[5,8,26] Thus by comparison of our experimental photoelectron spectra with those recorded by Peel and Willett[26] and Dammel and Bock[5,8] for CH_2NH, methanimine is positively identified in the photoelectron spectrum recorded for the pyrolysis products of azidoacetic acid.

Spectral features indicating the possible formation of an intermediate nitrene or imine were not observed, and it is perhaps significant that, in these PES studies, the features assigned to N_2 and CO_2 routinely appeared *together*.

Mechanism of Gas-Phase Thermal Decomposition of Azidoacetic Acid. On the basis of the experimental evidence provided by the PES and matrix IR experiments, we propose that the decomposition of 2-azidoacetic acid occurs via a concerted process involving the formation of a five-membered ring transition state which decomposes as shown below to form molecular nitrogen, carbon dioxide, and methanimine.



Further heating then results in the decomposition of methanimine to form hydrogen cyanide: the other product of this reaction step being almost certainly molecular H_2. The detection of this product by matrix isolation IR is precluded by selection rules, and hydrogen was not seen in the PES work, probably due to its low photoionization cross section and/or overlap with other bands. Indeed it has been reported[5] that the presence of molecular H_2 in PES studies on alkyl azide pyrolyses could only be observed after spectral subtraction. However, its formation in the matrix studies could be inferred from the otherwise inexplicable rise in pressure in the vacuum system at the highest pyrolysis temperatures employed.

Our results therefore indicate that the initial decomposition of azidoacetic acid can be written as

$$N_3CH_2CO_2H \rightarrow HN{=}CH_2 + CO_2 + N_2 \qquad (1)$$

and that at higher temperatures (>900 K)

$$HN{=}CH_2 \rightarrow HCN + H_2 \qquad (2)$$

The scheme summarized in the above equations not only accounts for all the species observed in the pyrolysis but also is consistent with the apparently *simultaneous* generation of CO_2, N_2, and CH_2NH and the subsequent formation of HCN only at the highest temperatures. The observation that N_2 and CO_2 appeared to be produced simultaneously in the PES studies effectively precludes stepwise reaction schemes involving the nitrene or imine, as might be envisaged in the possible reactions 3−8 below:

$$\underset{\text{parent azide}}{\underline{N_3CH_2CO_2H}} \rightarrow \underset{\text{nitrene}}{NCH_2CO_2H} + \underline{N_2} \qquad (3)$$

$$\underset{\text{nitrene}}{NCH_2CO_2H} \rightarrow \underset{\text{imine}}{HN{=}CHCO_2H} \qquad (4)$$

$$\text{nitrene } \textit{or} \text{ imine} \rightarrow \underline{HN{=}CH_2} + \underline{CO_2} \qquad (5)$$

$$\rightarrow \underline{HCN} + HCOOH \qquad (6)$$

$$\rightarrow \underline{HCN} + \underline{CO_2} + H_2 \qquad (7)$$

$$\rightarrow CO + H_2O + \underline{HCN} \qquad (8)$$

In the above equations, only those molecules which were observed are underlined.

Conclusions

Azidoacetic acid has been synthesized and characterized by a range of techniques, including IR and UV PE spectroscopy. In particular, the photoelectron spectrum of azidoacetic acid recorded with He I radiation consists of nine bands in the 9.0−21.0 eV ionization energy region. *Ab initio* calculations have been performed for azidoacetic acid, and application of Koopmans' theorem to the computed orbital energies yields vertical ionization energies which are in satisfactory agreement with experimental values. The characters of the four uppermost occupied molecular orbitals of azidoacetic acid are essentially N_3 nonbonding, N_3 nonbonding, and O 2p (lone pair), O 2p (lone pair), and π(CO) in nature as obtained from examination of the molecular orbitals calculated at the HF/6-311G** level of theory.

Thermal decomposition studies of azidoacetic acid reveal nitrogen, carbon dioxide, and methanimine as the only observable initial decomposition products, and a mechanism has been proposed which is consistent with these findings. In the flow system used in these experiments, significant decomposition was observed above 650 K which was essentially complete by 750 K. At temperatures above 900 K, there was evidence of methanimine decomposition, resulting in the formation of hydrogen cyanide and (probably) molecular hydrogen.

Previous studies have shown that, when heated alone under conditions similar to those used in this study, methanimine begins to decompose above 1200 K.[5] This difference in decomposition temperature is almost certainly due to CH_2NH being formed here with a high internal energy as a result of the initial pyrolysis of the azidoacetic acid.

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