A Study of the Thermal Decomposition of 2-Azidoethanol and 2-Azidoethyl Acetate by Ultraviolet Photoelectron Spectroscopy and Matrix Isolation Infrared Spectroscopy[†]

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The thermal decompositions of 2-azidoethanol and 2-azidoethyl acetate have been studied by matrix isolation infrared spectroscopy and real-time ultraviolet photoelectron spectroscopy. The products that were detected in a flow system at different temperatures (CH_2NH, H_2CO, N_2, CO, and HCN from $N_3CH_2CH_2OH$ and C_2H_4, CH_2NH, HCN, CO_2, and N_2 from $N_3CH_2COOCH_2CH_3$) allowed mechanisms for decomposition to be proposed. The experimental evidence obtained is consistent with 2-azidoethyl actetate decomposing via a concerted mechanism, similar to that found previously for azidoacetic acid, whereas the 2-azidoethanol decomposition is consistent with a stepwise decomposition mechanism as observed previously for azidoacetone.

Introduction

The intrinsic instability of organic azides makes their properties difficult to measure, and experimental work has to be carried out with care. Nevertheless, the study of the mechanisms of their decomposition is of considerable interest both from a fundamental viewpoint and because azides play important roles in heterocycle synthesis,[1−3] biological and pharmaceutical processes,[4−6] the preparation of semiconductor materials,[7,8] and as high-energy density materials used in solid propellants.[9,10] It is generally believed that the initial stage in the thermal decomposition of an organic azide such as R_2CHN_3 is the release of molecular nitrogen and the formation of a nitrene, R_2CHN.

The thermal decompositions of a number of alkyl azides, including CH_3N_3, have been studied several years earlier in the gas phase by Bock and Dammel[11−15] using UV photoelectron spectroscopy (PES). The conclusion from this work is that, for the azides studied, N_2 evolution is accompanied by a 1,2-hydrogen shift to form an imine $R_2C{=}NH$, which can undergo further decomposition to produce simple hydrocarbons, HCN and H_2.

More recently, Dianxun et al.[16] reported the UV photoelectron spectrum of CH_3N obtained by pyrolysis of CH_3N_3. In Dianxun's work, CH_3N was produced by passing CH_3N_3 mixed with NO through a heated plug of molecular sieve positioned 1−2 cm above the photon source of the spectrometer. CH_3N photoelectron spectra were observed at a molecular sieve temperature of 145 °C. It is clear from the conditions used that CH_3N was not produced in this work from a gas-phase decomposition but from decomposition of methyl azide on the surface of the molecular sieve in the presence of NO.[16]

The work presented here is part of a series of studies[17,18] on organic azides performed to investigate the mechanisms of their thermal decomposition. In these two previous studies,[17,18] the thermal decomposition of azidoacetic acid and azidoacetone were investigated using ultraviolet photoelectron spectroscopy and matrix isolation infrared spectroscopy. In the case of azidoacetic acid,[17] the results were shown to be consistent with a single decomposition pathway involving the ejection of N_2 and the simultaneous formation of methanimine (CH_2NH) and CO_2. At higher temperatures, HCN was produced. These results were supported by later ab initio and DFT calculations,[19] which showed that decomposition occurs via a concerted reaction that proceeds via a five-membered transition state leading to the products (N_2, CH_2NH, and CO_2). The decomposition of azidoacetone was found to be more complicated,[18] producing not only the products expected from the analogous pathway (N_2, CH_2NH, HCN, and ketene, CH_2CO) but also significant yields of CO and acetaldehyde. It was suggested that alternative radical pathways might be responsible for the observed distribution of products.

This present paper describes related studies on the pyrolysis of 2-azidoethanol and 2-azidoethyl acetate using the techniques of real-time ultraviolet photoelectron spectroscopy and matrix isolation infrared spectroscopy, supported by ab initio molecular orbital calculations. The main aim is to investigate the mechanism of thermal decomposition of these azides through the observation of the reactants, intermediates, and products at different pyrolysis temperatures. Also included in this study is the measurement of other spectroscopic properties for both parent azides.

Experimental Section

Sample Preparation. Samples of 2-azidoethanol and 2-azidoethyl acetate were prepared as follows: 2-Azidoethanol was prepared from 2-bromoethanol (95%, Aldrich) and sodium azide (99%, Aldrich), mixed in a molar ratio of 1:2.5. Solid sodium azide (2.05 g) was added slowly to a vigorously stirred solution of 2-bromoethanol (2.62 g) in distilled water (10 mL) at 0 °C. The solution was then allowed to warm to room temperature and was stirred for 4 h. More solid sodium azide was then added (1.05 g), and stirring was continued overnight at 80 °C. The

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solution was then cooled, and the azidoethanol was extracted with diethyl ether (3 × 10 mL), after which the combined ether layers were dried (over $MgSO_4$) and filtered. The filtrate was concentrated by vacuum distillation, first at room temperature and then finally at 105 °C to yield a colorless oil. In a very similar preparative procedure, 2-azidoethyl acetate was prepared from the reaction of ethyl bromoacetate (98%, Aldrich) with sodium azide (99%, Aldrich) mixed in the molar ratio of 1:2.5. To a vigorously stirred solution of ethyl bromoacetate (1.51 g) in acetone (10 mL) at 0 °C, was slowly added a solution of sodium azide (1.47 g) in water (10 mL). The mixture was allowed to warm to room temperature and then heated overnight at 60 °C. The resulting solution was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed first with 10% aqueous sodium bicarbonate solution and then with water and dried over magnesium sulfate and filtered. The filtered solution was concentrated by vacuum distillation, and the residue was distilled at 115 °C to yield a colorless oil.

Both products were characterized by a variety of spectroscopic methods as described below. Care was taken to minimize the effect of possible explosions at all stages in the preparation and handling of the azide samples, but no untoward occurrences were experienced during this work.

Thermal decomposition of the two azides prepared in this work was studied at different pyrolysis temperatures and hence different degrees of decomposition using matrix isolation infrared spectroscopy and gas-phase photoelectron spectroscopy.

Matrix Isolation Studies. Matrix isolation infrared studies on these azides followed a very similar pattern to those described in our recent studies on the pyrolysis of azidoacetic acid and azidoacetone.[17,18] The inlet and pyrolysis parts of the apparatus were identical, as were the low-temperature Displex and infrared (IR) spectrometers. Spectra of each parent azide and its decomposition products were obtained in nitrogen matrices, and supporting experiments were also carried out on H_2CO/N_2, CH_3NH_2/N_2, C_2H_4/N_2, C_2H_6/N_2, and CH_4/N_2 mixtures to aid spectral identification. Deposition times were typically 30−60 min at a particular superheater temperature, and any changes occurring during this period were monitored by spectral subtraction. The pressure in the pyrolysis region during a typical experiment was estimated as 10^{-4} Torr, and matrix ratios were estimated to be well in excess of 1000:1.

Photoelectron Spectroscopy. All photoelectron spectra recorded in this work were obtained using HeI (21.22 eV) radiation. The two spectrometers used, which were very similar and have been described elsewhere,[20,21] were single detector instruments designed for high-temperature pyrolysis studies. For each azide, photoelectron spectra of the parent compound and its decomposition products were obtained by passing the azide vapor through a heated furnace positioned inside the ionization chamber of the spectrometer, several centimeters above the photon source.

The vapor pressures of the parent materials ($N_3CH_2CH_2OH$ and $N_3CH_2COOCH_2CH_3$) were sufficient at room temperature to allow photoelectron spectra to be obtained with good signal-to-noise ratios by direct pumping on a liquid sample held in a small flask through a needle valve outside the spectrometer ionization chamber, rather than having to place sample vials on the ledge of the heated inlet system inside the ionization chamber of the spectrometer as was done for the less-volatile azidoacetic acid.[17] The operating resolution of each spectrometer (typically 35 meV fwhm as measured for the argon $(3p)^{-1}$ signal obtained with He(I) radiation) was unaffected when the heating system was in operation, even at the highest temperature used.

Photoelectron spectra were recorded in real time as the furnace temperature was changed. For each azide, the onset of decomposition was marked by the appearance of photoelectron bands associated with molecular nitrogen. Spectral calibration was achieved by reference to known ionization energies of methyl iodide added to the chamber and traces of nitrogen and water[22,23] present in the ionization chamber. In the PES work, the pressure in the pyrolysis region is estimated from previous pressure measurements as ca. 10^{-4} Torr and the flow time between the pyrolysis region and the photoionization region is estimated at ca. 5 ms.

The photoelectron spectrum was also recorded for $BrCH_2CH_2OH$ used in the preparation of the 2-azidoethanol, and it was in good agreement with that reported previously.[24] The first and second bands of the 2-azidoethanol, at vertical ionization energies of 9.90 ± 0.01 and 11.01 ± 0.01 eV, respectively, were the most intense, and photoelectron spectra recorded for $N_3CH_2CH_2OH$ showed no evidence of $BrCH_2CH_2OH$. Similarly, the photoelectron spectrum was recorded for $BrCH_2COOCH_2CH_3$, used in the preparation of $N_3CH_2COOCH_2CH_3$, and the photoelectron spectrum of the 2-azidoethyl acetate showed no evidence of bands associated with bromoethyl acetate.

The pyrolysis system used for the azidoethanol experiments consisted of a resistively heated furnace, which was made of molybdenum wire wrapped around an inner glass tube connected to a power supply via tungsten feed-throughs. The operating temperature of the furnace in the heated section was measured by a chromel−alumel thermocouple, and the maximum operating temperature recorded was 550 °C.

The pyrolysis experiments carried out for the 2-azidoethyl acetate were carried out on a spectrometer of similar design. The heating method used on this instrument was radio frequency (rf) induction heating. This could achieve much higher temperatures (>2000 °C) than the resistively heated system used for azidoethanol. It consisted of a tantalum cylinder (the rf susceptor) positioned inside the rf heating coils a few centimeters above the photon source. The sample vapor was then passed through an alumina tube, which was positioned in the center of the tantalum susceptor. As in the 2-azidoethanol experiments, photoelectron spectra were recorded as a function of heater temperature.

Results

Characterization of $N_3CH_2CH_2OH$. 2-Azidoethanol was characterized in the vapor phase by mass spectrometry and ultraviolet photoelectron spectroscopy, and also in the liquid phase by ^1H NMR, ^{13}C NMR, Raman, and infrared spectroscopy. The 70 eV electron impact mass spectrum showed a parent peak at 87 (10%), together with two intense fragments at 28 (40%, N_2^+ or NCH_2^+) and 31 (100%, CH_2OH^+) amu. Weaker signals were also observed at 45 (5%, $CH_2CH_2OH^+$), 43 (5%, N_3H^+), 29 (15%, COH^+), and 27 (5%, NCH^+) amu. No signals were seen that could be attributed to unreacted $BrCH_2CH_2OH$, and the mass spectrum was in good agreement with that reported previously.[25]

Two signals were observed in the 300 MHz ^1H NMR spectrum of 2-azidoethanol in $CDCl_3$ solution. These were at 3.41 and 3.77 ppm relative to TMS with integrated relative intensities of 0.4:0.6, respectively. After expansion, it could be seen that both peaks were triplets, but the band at 3.77 ppm had a much more intense central band; this was due to the −OH proton appearing in exactly the same place as one of the $-CH_2$ groups of protons. Two signals were also observed in the ^{13}C NMR spectrum at 53.7 and 61.5 ppm with integrated relative

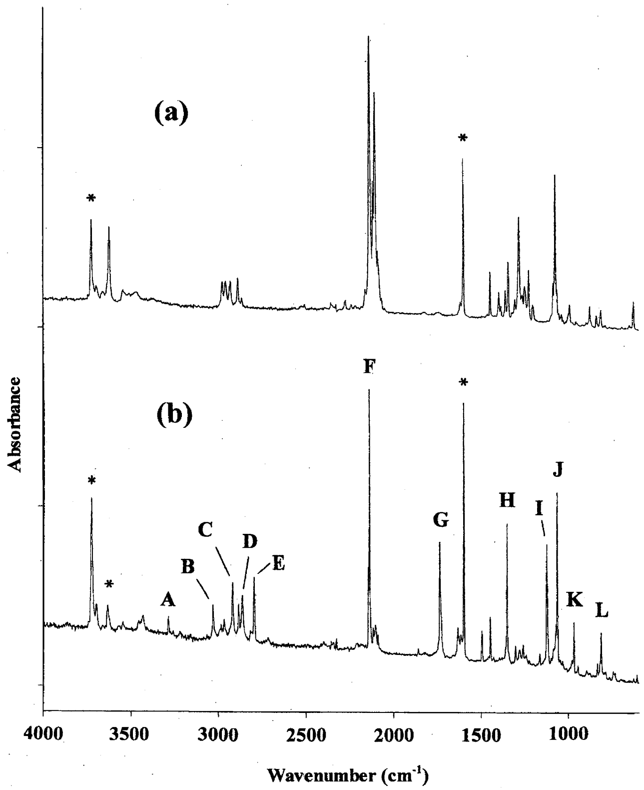


Figure 1. Nitrogen matrix infrared bands observed during pyrolysis studies on 2-azidoethanol. Absorptions denoted by an asterisk are assigned to H_2O. Band identification is shown in Table 1. Spectrum a was obtained with no superheating (parent 2-azidoethanol sublimed at room temperature). Spectrum b was obtained after passage through superheater at 570 °C.

TABLE 1: Significant IR Bands (cm^{-1}) Observed in Matrix Isolation Studies on the Pyrolysis of 2-Azidoethanol and 2-Azidoethyl Acetate

N_2 matrix (letter in Figures 1 and 3)[a]	previous studies	assignment
3623, 2977, 2958, 2930, 2888, 2137, 2105, 1282, 1074		$N_3CH_2CH_2OH$
2116, 1753, 1373, 1351, 1293, 1199, 1034		$N_3CH_2COOCH_2CH_3$
2139(F)	2139	CO (ref 30)
2347(O), 662(S)	2347, 662	CO_2 (ref 31)
3032(B), 2919(C), 1637, 1450, 1352(H), 1127(I), 1065(J)	3033, 2920, 1637, 1450, 1353, 1128, 1065	CH_2NH (ref 29)
3287(A), 747/727	3287, 747/737	HCN (refs 29 and 34)
2864(D), 2800(E), 1738(G), 1497, 1245, 1169	2865, 2800, 1740, 1499, 1244, 1167	H_2CO (ref 33)
3106(M), 3077, 2988(N), 1888(P), 1437(Q), 947(R)	3107, 3077, 2989, 1889, 1438, 947	C_2H_4 (ref 32)
1306	1306 (most intense)	CH_4 (ref 35)
2967, 2885, 1263, 816(L), 970(K)		unassigned features appearing on pyrolysis

[a] Wavenumber accuracy = ±1 cm^{-1}.

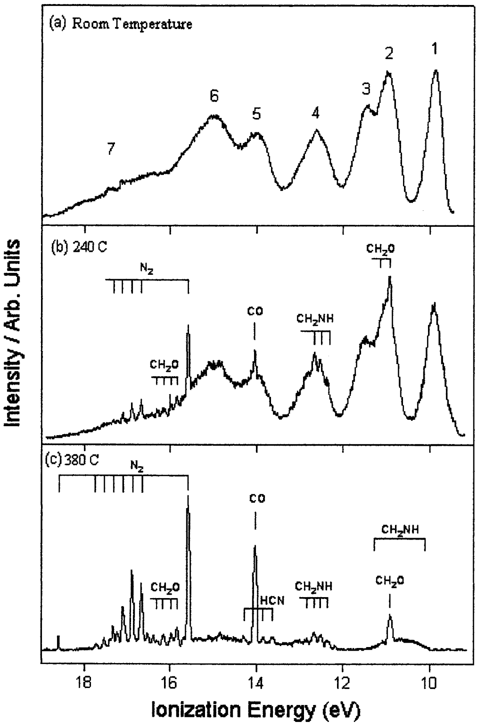


Figure 2. He(I) photoelectron spectrum recorded for 2-azidoethanol at different stages of pyrolysis. Panel a shows the photoelectron spectrum of the parent 2-azidoethanol. The numbered bands are listed in Table 3. Panel b shows the photoelectron spectrum obtained on pyrolysis of 2-azidoethanol at a temperature of 240 °C. Panel c shows the photoelectron spectrum obtained for complete pyrolysis of 2-azidoethanol at 380 °C.

intensities of 1:1. H−C correlation was also carried out, and good correlation was found between the two sets of peaks indicating that the 3.77 ppm (^{1}H NMR) peak and the carbon at 61.5 ppm (^{13}C NMR) were from the same group ($-CH_2OH$) and the 3.41 ppm (^{1}H NMR) and the signal at 53.7 ppm (^{13}C NMR) were from the other group (N_3-CH_2-).

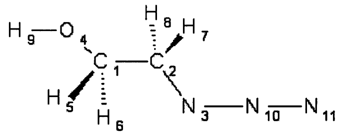
The most intense absorption band in the liquid infrared spectrum was found at 2123 cm^{-1}, which was assigned to the N_3 group. Other prominent bands were present at 3442 cm^{-1} (OH stretch), 2988 and 2928 cm^{-1} (CH stretch), and 1296 and 1066 cm^{-1}. The infrared bands in a nitrogen matrix were in general shifted only slightly from the liquid-phase values, and their positions and relative intensities are shown in Figure 1a and in Table 1. The only significant differences between the liquid and matrix infrared spectra were in the position of the O−H stretching band, which was significantly higher (3623 cm^{-1}) for the isolated molecule, and in the multiplet structure observed for the N_3 absorption at ca. 2120 cm^{-1}. This band is quite broad in the liquid spectrum, and the resolution of at least two components in this band in the matrix spectrum perhaps reveals the existence of more than one conformer.

The liquid Raman spectrum exhibited counterparts to all of the above bands except for the OH stretch.

The He(I) photoelectron spectrum of 2-azidoethanol is shown in Figure 2a. Assignment of this spectrum is achieved with reference to ab initio molecular orbital calculations carried out as part of this study. The computed minimum energy geometry of $N_3CH_2CH_2OH$ was obtained at the MP2/6-31G** level using the Gaussian 94 code. The geometrical parameters listed in Table 2 from the MP2/6-31G** calculations correspond to a stationary point on the potential energy surface with all real vibrational frequencies.

The highest occupied molecular orbital in the ground state (orbital 23) is weakly antibonding between the terminal nitrogen atoms of the N_3 group, nonbonding between the adjacent nitrogen atoms, and weakly antibonding in the C−N direction. Orbital 22 is π-bonding in the terminal N−N bond, weakly antibonding between the other N−N group, and weakly C−N antibonding. Orbital 21 consists of a π(C−O) bonding orbital,

TABLE 2: Computed Structural Parameters of Azidoethanol at the MP2/6-31G Level Showing the Atom Numbering**[a]



bond	length (Å)	angle	value (deg)
C_1-C_2	1.5134	$C_1-C_2-N_3$	106.94
C_1-O_4	1.4221	$C_2-C_1-O_4$	105.73
C_2-N_3	1.4781	$H_9-O_4-C_1$	107.81
O_4-H_9	0.9635	$C_2-N_3-H_{10}$	115.39
N_3-N_{10}	1.2449	$C_1-C_2-H_{7/8}$	109.58
$N_{10}-N_{11}$	1.1633	$C_2-C_1-H_{5/6}$	109.32
$C_1-H_{5/6}$	1.094	$N_3-N_{10}-N_{11}$	180.00
$C_2-H_{7/8}$	1.092		

[a] One minimum energy structure was found at the MP2/6-31G** level.

TABLE 3: Comparison of Experimental and Computed Vertical Ionization Energies (VIEs) of 2-Azidoethanol

					ΔSCF values MP2/6-31G**	
MO	band no.	exptl VIE (eV)	KT VIE (eV)	KT × 0.92 eV	AIE (eV)	VIE (eV)
23	1	9.90	10.18	9.37	9.94	9.99
22	2	11.01	11.93	10.98	10.64	11.30
21	3	11.47	12.38	11.38		
20	4	12.64	13.80	12.70		
19	5	14.06	15.23	14.01		
18	6	15.03	15.67	14.42		
17			17.82	16.39		
16			17.86	16.43		
15	7	17.42	18.26	16.80		

and orbital 20 is bonding between the two carbon atoms and C−O antibonding.

Table 3 compares the experimental vertical ionization energies (VIEs) with VIEs obtained from application of Koopmans' theorem to the SCF/6-31G** molecular orbital energies obtained at the MP2/6-31G** computed minimum energy geometry (Table 2). The values computed were, as expected, higher than the experimental values, but scaling by a factor of 0.92[26,27] afforded much better agreement with the experimental VIEs. This result was similar to the azidoacetic acid[17] and azidoacetone cases[18] in which a factor of 0.9 was used. Also included in Table 3 are the first two adiabatic ionization energies (AIEs) and VIEs for 2-azidoethanol calculated by the ΔSCF method using the optimized geometries of the cation obtained at the MP2/6-31G** level. These show good agreement with experimental values.

Thermal Decomposition Experiments: IR Matrix Isolation Spectroscopy. Figure 1a shows a typical nitrogen matrix infrared spectrum obtained from a sample of $N_3CH_2CH_2OH$ deposited from the vapor phase without superheating. The absorptions denoted by the asterisk (∗) indicate the most intense infrared absorptions of matrix-isolated H_2O and arise from traces of water in the system. The most intense parent absorption consists essentially of a doublet at 2137/2105 cm^{-1}, one component of which exhibits weaker shoulders. These absorptions are assigned to the N_3 unit, and the complex appearance is attributed to different conformers trapped in the matrix. Our previous study on azidoacetone[18] also showed a multiplet structure in this spectral region. Other prominent features were noted at 1282 and 1074 cm^{-1}, which are in similar positions to those found in the neat liquid, and a relatively high OH stretch at 3623 cm^{-1}, which owes its position to the absence of hydrogen bonding.

Pyrolysis experiments were carried out in the range ca. 100−600 °C, and even at the lowest temperatures, there was evidence for some decomposition, with the generation of new products. However, traces of the parent azide could still be detected up to 500 °C.

Figure 1b shows the spectrum obtained at a superheater temperature of 570 °C. An intense feature is still present close to the original N_3 doublet at 2137/2105 cm^{-1}, but closer examination shows that this now appears as a sharp feature at 2139 cm^{-1} with a shoulder at 2146 cm^{-1}. This new band (labeled F) is assigned to CO. Apart from a weak residual N_3 feature near 2100 cm^{-1}, all other bands corresponding to parent absorptions are clearly absent, having been replaced by numerous new features. However, despite the complexity of these matrix infrared spectra, many of these new features can be assigned from previous studies,[17,18] on the basis of a consideration of expected reaction products. The results are summarized in Table 1.

CH_2NH is unequivocally identified by at least five characteristic peaks: B, C, H, I, and J, while band A indicates the formation of HCN. A fourth prominent pyrolysis product is identified as H_2CO (bands D, E, and G) both by comparison with previously published work and also as a result of supporting matrix infrared experiments. The identification of these four products accounts for the majority of the new features produced on pyrolysis, but six additional weak features were routinely observed at 2967, 2885, 1306, 1263, 970, and 816 cm^{-1}, the assignment of which was unknown. In an attempt to establish their identity, supporting matrix infrared experiments were carried out on CH_3NH_2, CH_4, C_2H_4, and C_2H_6 isolated separately in nitrogen matrixes, with the aim of obtaining a suitable match for at least two frequencies for each compound. In practice, only the most intense feature of CH_4 gave a positive match for the frequency at 1306 cm^{-1}.

Thermal Decomposition Experiments: Photoelectron Spectroscopy. The He(I) photoelectron spectrum obtained for azidoethanol is shown in Figure 2a, and the photoelectron spectrum obtained upon partial pyrolysis is shown in Figure 2b. The temperature of the furnace under these conditions was approximately 240 °C as estimated from chromel−alumel thermocouple measurements. The He(I) photoelectron spectrum recorded for complete pyrolysis is shown in Figure 2c, recorded at a furnace temperature of approximately 380 °C.

Signals arising from N_2, CO, and HCN are clearly observed on pyrolysis (Figure 2b,c). In addition, pyrolysis also produced four further features: a broad band with a VIE of 10.65 eV, which is associated with the vibrationally resolved band at 12.66 eV (VIE), and a sharp feature at 10.90 eV (VIE), which is associated with the vibrationally resolved band at 15.84 eV (VIE). These can be attributed to the first two bands of CH_2NH and the first two bands of CH_2O, respectively, by comparison with known spectra of methanimine[15,28] and formaldehyde.[22]

No spectral features were observed that indicated the possible formation of an imine intermediate ($HN{=}CHCH_2OH$, first VIE computed at the ΔSCF QCISD/6-31G** level for the X^1A' state is 9.96 eV) or a nitrene intermediate (NCH_2CH_2OH, first VIE computed at the ΔSCF QCISD/6-31G** level for the X^3A'' state is 10.59 eV). Also, it is significant that the bands assigned to N_2, H_2CO, CH_2NH, CO, and HCN appear together on pyrolysis and show the same temperature profiles. No spectral features were observed associated with CH_4, indicating that if it is produced it is a very minor product.

Characterization of $N_3CH_2COOCH_2CH_3$. 2-Azidoethyl acetate was characterized in the vapor phase by mass spec-

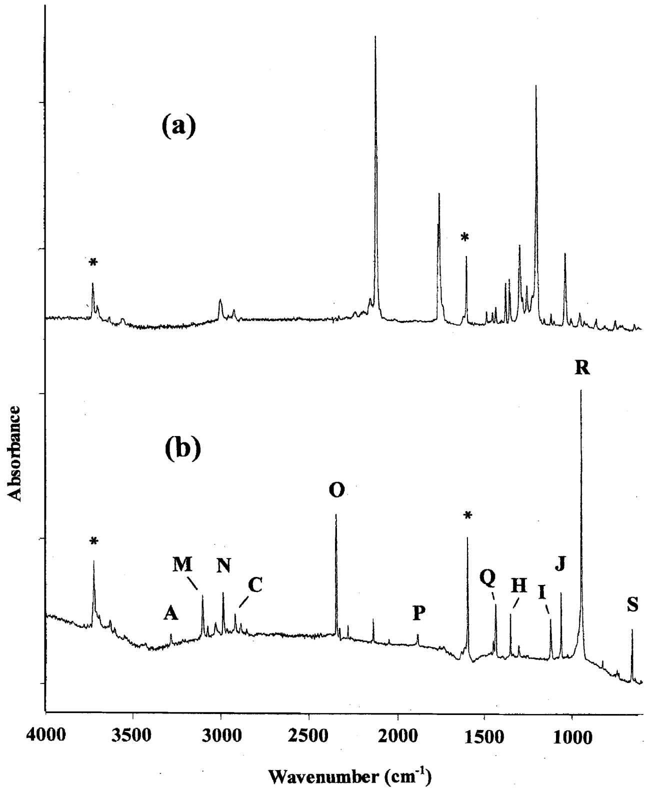


Figure 3. Nitrogen matrix infrared bands observed during pyrolysis studies on 2-azidoethyl acetate. Absorptions denoted by an asterisk are assigned to H_2O. Band identification is shown in Table 1. Spectrum a was obtained with no superheating (parent ester sublimed at room temperature). Spectrum b was obtained after passage through superheater at ~500 °C.

trometry and ultraviolet photoelectron spectroscopy, and also in the liquid phase by ^{1}H NMR, ^{13}C NMR, Raman, and infrared spectroscopy. The 70 eV electron impact mass spectrum showed an intense parent peak at 129 amu (100%) together with the following fragments: 73 (20%, $CO_2CH_2CH_3^+$), 56 (55%, N_3-CH_2^+), 45 (25%, $OCH_2CH_3^+$), 42 (20%, N_3^+), and 29 amu (45%, $CH_2CH_3^+$). No signals were seen that could be attributed to unreacted $BrCH_2COOCH_2CH_3$.

In the 400 MHz ^{1}H NMR spectrum of 2-azidoethyl acetate in $CDCl_3$, three signals were observed at 4.25, 3.86, and 1.30 ppm with integrated relative intensities of 2:2:3, respectively. These three signals were assigned as follows: The signal at 4.25 ppm was a quartet corresponding to the two protons on the CH_2 in the $-OCH_2CH_3$ group, the signal at 3.86 ppm was a singlet corresponding to the N_3CH_2- group, and the signal at 1.30 ppm corresponds to the protons on the terminal methyl group. In the ^{13}C NMR of the 2-azidoethyl acetate four strong signals were observed at 14.20, 50.44, 61.96, and 168.4 ppm. Good ^{1}H$-^{13}$C correlation was found between the two sets of NMR signals, indicating that the signal at 14.20 ppm corresponds to the terminal methyl group, the signal at 50.44 ppm corresponds to the N_3CH_2- group, and the signal at 61.96 ppm corresponds to the CH_2 in the $-OCH_2CH_3$ group. The final signal at 168.4 ppm is due to the carbon in the carbonyl group.

In the liquid infrared spectrum, intense absorptions were observed at 1749, 2110, 2935, and 2993 cm^{-1}. These were assigned to the C=O stretch, the N_3 group, and the C$-$H stretches (2935 and 2993 cm^{-1}), respectively. The liquid Raman spectra exhibited counterparts to each of these bands observed in the infrared spectrum.

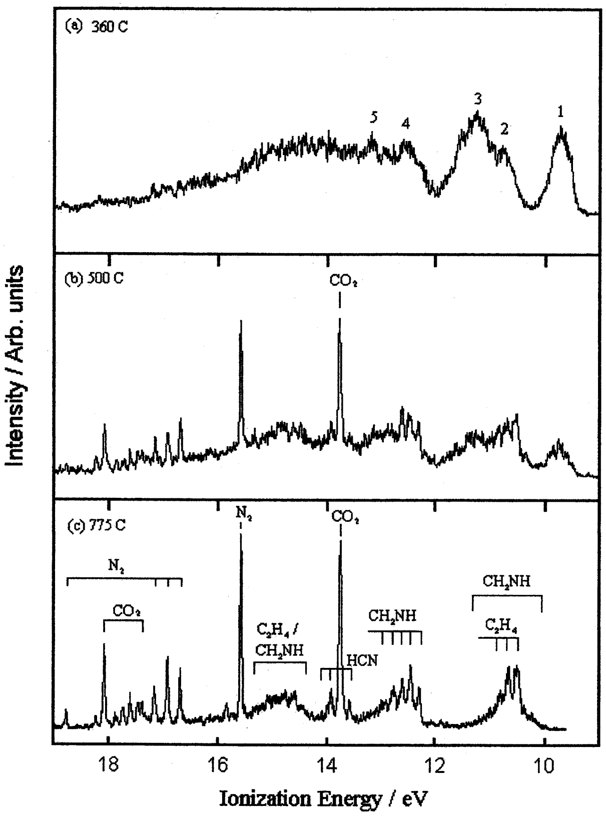


Figure 4. He(I) photoelectron spectrum recorded for 2-azidoethyl acetate at different stages of pyrolysis. Panel a shows the photoelectron spectrum of the parent 2-azidoethyl acetate. The numbered bands are listed in Table 5. Panel b shows the photoelectron spectrum obtained on pyrolysis of 2-azidoethyl acetate at a temperature of 500 °C. Panel c shows the photoelectron spectrum obtained for complete pyrolysis of 2-azidoethyl acetate at 775 °C.

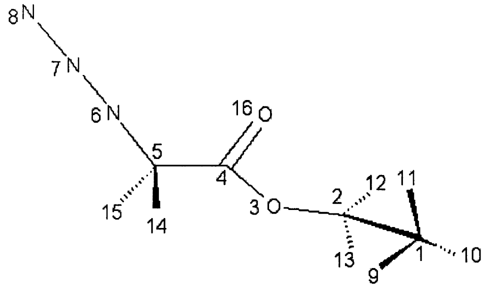
The infrared spectrum recorded in a nitrogen matrix is shown in Figure 3a, and the main absorptions are summarized in Table 1.

The He(I) photoelectron spectrum of 2-azidoethyl acetate is shown in Figure 4a. As in the azidoethanol case, assignment of the spectrum is made by use of ab initio molecular orbital calculations with the Gaussian 94 code. The minimum energy structure at the MP2/6-31G** level is shown in Table 4. This was the lowest energy conformer. The highest occupied molecular orbital (orbital 34) is antibonding between the terminal nitrogens on the N_3 group. Orbital 33 is delocalized over the $N_3CH_2CO_2-$ grouping and is antibonding between each pair of bonded atoms. Orbital 32 has a major contribution from the lone pair on the oxygen on the C$-$O group and a minor bonding contribution from the C$-$N group. Orbital 31 is localized on the two oxygens and is mainly O2p antibonding in character.

The experimental VIEs have been compared with VIEs obtained from application of Koopmans' theorem to the SCF/6-31G** molecular orbital energies obtained at the MP2/6-31G** computed minimum energy geometry (see Tables 4 and 5). The Koopmans' theorem values are, as expected, higher than the experimental values, but scaling by 0.92 gives much better agreement with experiment, as in the azidoethanol case. Also included in Table 5 is the first AIE and VIE computed by the ΔSCF method using optimized geometries of the cationic states obtained at the MP2/6-31G** level. The ΔSCF first VIE shows good agreement with the experimental value.

Thermal Decomposition Experiments: IR Matrix Isolation Spectroscopy. Figure 3a shows a typical nitrogen matrix

TABLE 4: Computed Structural Parameters of 2-Azidoethyl Acetate at the MP2/6-31G Level Showing the Atom Numbering**[a]



bond	length (Å)	angle	value (deg)
C_1-C_2	1.5127	$C_1-C_2-O_3$	110.7
C_2-O_3	1.4544	$C_2-O_3-C_4$	115.05
O_3-C_4	1.3498	$O_3-C_4-C_5$	109.7
C_4-C_5	1.5202	$C_4-C_5-N_6$	112.56
N_6-C_5	1.4609	$C_5-N_6-N_7$	115.49
N_7-N_6	1.2493	$N_6-N_7-N_8$	171.07
N_8-N_7	1.1616	$O_{16}-C_4-O_3$	125.68
C−H	~1.09	C−C−H	~110
$C_4=O_{16}$	1.2173		

[a] Six minimum energy structures were found at both the HF/6-31G** and MP2/6-31G** levels corresponding to different rotational conformers about the C_5 and C_1 centers. They all have very similar bond lengths and angles. At the 6-31G**/MP2 level, their total energies were found to be within 0.65 kcal mol^{-1}. The ΔSCF computed first and second VIEs and AIEs are all within 0.05 eV, and hence for simplicity, only the results obtained for the lowest energy minimum (that shown in the diagram above) are included in the text.

TABLE 5: Comparison of Experimental and Computed Vertical Ionization Energies (VIEs) of 2-Azidoethyl Acetate

					ΔSCF values	
MO	band no.	exptl VIE (eV)	KT VIE (eV)	KT × 0.92 eV	AIE (eV)	VIE (eV)
34	1	9.74	10.27	9.45	9.76	9.94
33	2	10.82	11.87	10.93		
32	3	11.33	12.68	11.66		
31	4	12.60	12.82	11.80		
30	5	13.20	13.77	12.66		
29			14.57	13.41		
28			14.71	13.53		
27			15.60	14.35		
26			16.09	14.80		
25			16.71	15.38		
24			17.91	16.47		

infrared spectrum obtained from a sample of $N_3CH_2COOCH_2CH_3$ deposited from the vapor phase without superheating. The absorptions arising from matrix-isolated H_2O are again denotedby an asterisk (∗), and the intense N_3 mode in the parent azide now lies at 2116 cm^{-1}. Other prominent features are to be found at 1753 and 1199 cm^{-1} and are in similar positions to those found in the neat liquid. A list of the more significant bands is given in Table 1.

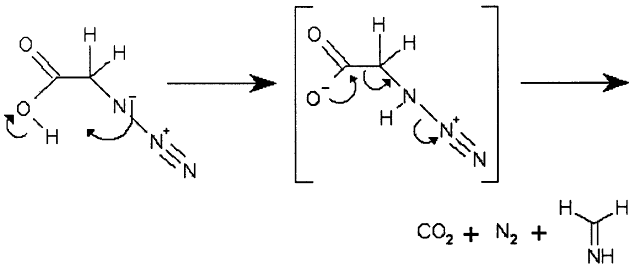
Pyrolysis experiments were carried out in the range ca. 100−550 °C, and Figure 3b shows the spectrum obtained at a superheater temperature of ca. 500 °C. At this temperature, all of the parent absorptions are effectively absent, but several ofthe new features that have appeared can be assigned from previous studies.

Both CH_2NH (bands C, H, I, and J) and HCN (band A) are again present, and the very intense new band labeled R is identified as being due to C_2H_4 by comparison with previously published work (Table 1). Closer inspection reveals that a further four bands (M, N, P, and Q) may also be assigned to C_2H_4. CO_2 is unequivocally identified by bands O and S, leaving only very weak features unidentified.

Thermal Decomposition Experiments: Photoelectron Spectroscopy. The He(I) photoelectron spectrum obtained for 2-azidoethyl acetate is shown in Figure 4a. The photoelectron spectra obtained on partial and complete pyrolysis are shown in Figure 4b,c recorded at furnace temperatures of 500 and 775 °C, respectively. The bands associated with the parent azide decrease, as expected, as the furnace temperature increases, and bands associated with C_2H_4, CH_2NH, HCN, CO_2, and N_2 appear. The temperature profiles of these product bands are, within experimental error, the same, all reaching a maximum intensity at the same furnace temperature. No photoelectron bands associated with an imine intermediate ($HNCHCOOCH_2CH_3$, X^1A', first VIE computed at the ΔSCF MP2/6-31G** level 10.57 eV) or a nitrene intermediate ($NCH_2COOCH_2CH_3$, X^3A'', first VIE computed at the ΔSCF MP2/6-31G** level 10.03 eV) were observed in these pyrolysis experiments.

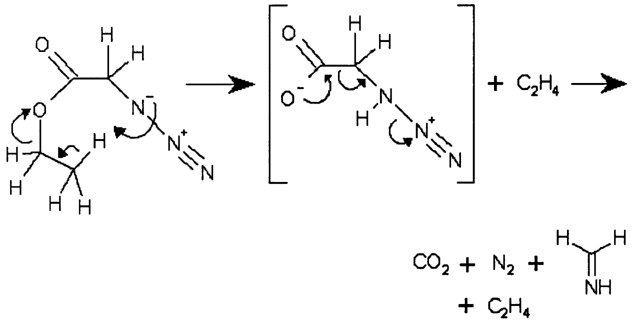
Mechanisms of Gas-Phase Decomposition. To present mechanisms for the gas-phase thermal decomposition of 2-azidoethanol and 2-azidoethyl acetate that are consistent with the experimental photoelectron and matrix infrared spectroscopic evidence, it is valuable to make a comparison with the earlier results obtained for 2-azidoacetic acid and 2-azidoacetone. The available evidence obtained for these organic azides showed that decomposition occurred via a concerted mechanism leading to formation of molecular nitrogen and the final reaction products or occurred in a stepwise manner with loss of molecular nitrogen and a proton transfer to form an imine, which subsequently decomposes.

In the case of azidoacetic acid, CO_2, CH_2NH, and N_2 were observed at the same time on pyrolysis, with HCN being produced from CH_2NH at higher temperatures. The results are consistent with a concerted mechanism which can be written as



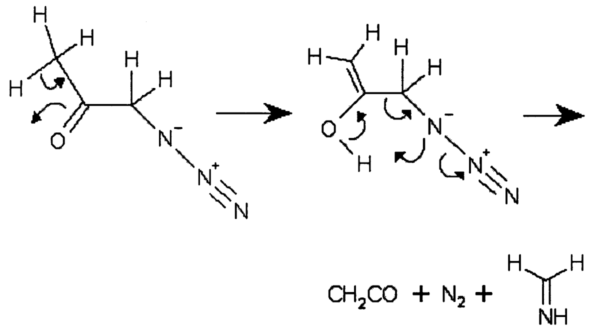
This mechanism is consistent with results of DFT and ab initio molecular orbital calculations performed by Cordeiro et al.[19] on the stepwise and concerted dissociation processes of 2-azidoacetic acid.

The results obtained in this work for 2-azidoethyl acetate, from which C_2H_4, CH_2NH, CO_2, and N_2 are produced at the same time with the same concentration profile as a function of temperature, are also consistent with such a concerted mechanism, which can be written as

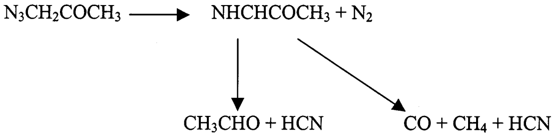


This mechanism would explain the production of C_2H_4, CO_2, CH_2NH, and N_2 at the same temperatures (as is observed) with HCN being produced by subsequent pyrolysis of CH_2NH. However, the temperatures used for the 2-azidoethyl acetate pyrolyses were greater than those used for the azidoacetic acid pyrolysis and are probably sufficient to lead to some decomposition of CH_2NH to HCN in the heated flow tube. Hence, it is felt that the results obtained for 2-azidoethyl acetate are consistent with a concerted mechanism with C_2H_4, CO_2, CH_2NH, and N_2 being the major products.

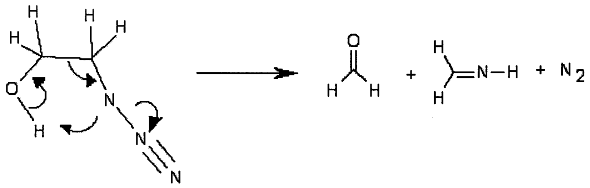
In the case of the azidoacetone, the simultaneous production of CH_2NH, H_2CO, HCN, CO, N_2, and CH_3CHO meant that, although a concerted mechanism of the type



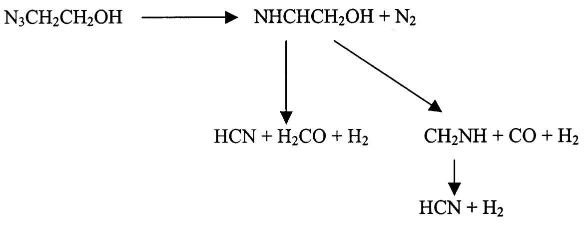
which gives rise to $H_2C{=}C{=}O$, CH_2NH, N_2, and HCN, is possible, a stepwise pathway, possibly involving radicals, had to be invoked to explain production of CH_3CHO and CO simultaneously with the other products. For example,



For 2-azidoethanol, it was expected that N_2, H_2CO, and CH_2NH would be observed on pyrolysis from the following reaction:



The observation of CO and HCN at the same time as N_2, H_2CNH, and H_2CO was not anticipated if the above mechanism was taking place. The experimental evidence provided by PES and matrix isolation infrared experiments showed that CO, N_2, H_2CO, CH_2NH, and HCN are observed at the same time with the same concentration profile as a function of temperature within experimental error. Therefore, the following stepwise mechanism is put forward to explain the decomposition:



This is very similar to the stepwise mechanism put forward for the decomposition of azidoacetone, and as in the azidoacetone case, it is also possible that this multistep process proceeds via a radical mechanism.

Conclusions

2-Azidoethanol and 2-azidoethyl acetate have been synthesized and characterized by a range of techniques, including matrix isolation infrared and UV photoelectron spectroscopy. The photoelectron spectra of azidoethanol and azidoethyl acetate consist of seven and five resolved bands in the 9.0−21.0 eV ionization energy region, respectively. Ab initio calculations have been performed for these azides, and application of Koopmans' theorem to the computed orbital energies yields vertical ionization energies that are in satisfactory agreement with experimental values.

The results of this pyrolysis study of 2-azidoethanol and 2-azidoethyl acetate, as well as the results from earlier studies on the thermal decomposition of 2-azidoacetic acid and 2-azidoacetone, indicate that *two* main mechanisms of decomposition of organic azides of the type considered are beginning to emerge. 2-Azidoacetic acid and 2-azidoethyl acetate decompose via a concerted process through a cyclic transition state to give the products, whereas 2-azidoethanol and azidoacetone decompose via a stepwise mechanism through imine intermediates, which decompose to give the products via two possible pathways.

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