

Contrasting Behavior in Azide Pyrolyses: An Investigation of the Thermal Decompositions of Methyl Azidoformate, Ethyl Azidoformate and 2-Azido-*N,N*-dimethylacetamide by Ultraviolet Photoelectron Spectroscopy and Matrix Isolation Infrared Spectroscopy

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Abstract: The thermal decompositions of methyl azidoformate (N_3COOMe), ethyl azidoformate (N_3COOEt) and 2-azido-*N,N*-dimethylacetamide ($\text{N}_3\text{CH}_2\text{-CONMe}_2$) have been studied by matrix isolation infrared spectroscopy and real-time ultraviolet photoelectron spectroscopy. N_2 appears as an initial pyrolysis product in all systems, and the principal interest lies in the fate of the accompanying organic fragment. For methyl azidoformate, four accompanying products were observed: HNCO , H_2CO , CH_2NH and CO_2 , and these are believed to arise as a result

of two competing decomposition routes of a four-membered cyclic intermediate. Ethyl azidoformate pyrolysis yields four corresponding products: HNCO , MeCHO , MeCHNH and CO_2 , together with the five-membered-ring compound 2-oxazolidone. In contrast, the initial pyrolysis of 2-azido-*N,N*-dimethyl acetamide, yields the novel imine intermediate $\text{Me}_2\text{NCOCH=NH}$, which

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subsequently decomposes into dimethyl formamide (HCONMe_2), CO , Me_2NH and HCN . This intermediate was detected by matrix isolation IR spectroscopy, and its identity confirmed both by a molecular orbital calculation of its IR spectrum, and by the temperature dependence and distribution of products in the PES and IR studies. Mechanisms are proposed for the formation and decomposition of all the products observed in these three systems, based on the experimental evidence and the results of supporting molecular orbital calculations.

Introduction

It is well known that azides release nitrogen very easily—often explosively—when heated, liberating a large amount of energy, and that they find application for practical purposes largely because of this characteristic. Recent studies^[1–3] on the thermal decomposition on organic azides by photoelectron spectroscopy (PES) and infrared matrix isolation spectroscopy have shown that two distinct decomposition pathways must be invoked to account for the experimental observations.

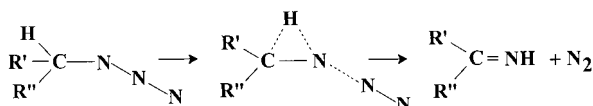
The first pathway—“Type 1”—is characterised by the initial liberation of nitrogen, and the formation of an imine. This is the route proposed by Bock and Dammel^[4–7] on the basis of the first PES studies of alkyl azide decompositions, and it has also been invoked to account for some of the products of azidoethanol or azidoacetone decomposition.^[2] Two different hypotheses have been proposed concerning

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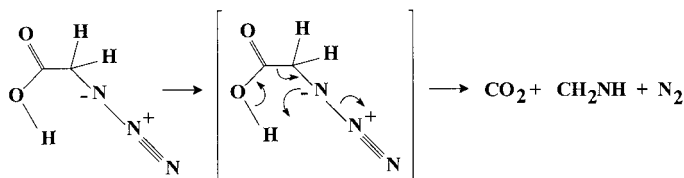
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imine formation. One suggestion is that the pyrolysis is step-wise, and that the initial products are N_2 and a nitrene, which subsequently isomerises to the imine. Alternatively, the imine may be formed by a 1,2-H shift *synchronous* with nitrogen elimination. At present, no nitrenes have been detected in the thermal decomposition of alkyl azides, so the mechanism for imine formation by the initial production of the nitrene cannot be regarded as firmly established.^[8–10] However, irrespective of the detailed mechanism, this reaction pathway involving imine formation essentially involves the transfer of one H atom from an adjacent C atom onto the electron-deficient N atom, following Scheme 1.



Scheme 1.

The second general pathway—“Type 2”—involves transfer of a proton, or more generally, an alkyl group, onto the electron-deficient N atom from a more remote site in the molecule, and may be envisaged as involving a cyclic transition state. It was first recognised in the decomposition of azidoacetic acid^[1] (Scheme 2) and has subsequently also been found to occur in the pyrolysis of ethyl azidoacetate.^[3] In both these molecules, “Type 1” behavior is also possible, but is evidently less favorable.



Scheme 2.

We are currently studying the mechanisms of decomposition of a number of selected organic azides, notably, azidoacetates, azidoamides, azidoformates and azidonitriles, with the overall aim of understanding the mechanisms of their decomposition, and of characterising any novel intermediates observed. Most recently, a study of the thermal decomposition of azidoacetamide^[11] determined the initial decomposition route as being of “Type 1”, and established for the first time the presence of the intermediate iminoacetamide. This intermediate was then shown subsequently to decompose via two alternative paths: one producing $HNCO$ and $CH_2=NH$ and the other producing HCN , CO and NH_3 .

As part of our continuing research in this field, a series of experiments was carried out designed firstly to investigate how pyrolysis might proceed in an azide system for which the “Type 1” route was *impossible*. Some of the simplest parent azides in which this constraint is present are azidoformate esters of general formula N_3COOR , and this paper

contains our results on the pyrolysis of methyl and ethyl azidoformate. In addition, we were interested in extending our previous work on 2-azidoacetamide by a study of the corresponding 2-azido-*N,N*-dimethylacetamide. Here, a point of importance would be whether the introduction of two additional methyl groups might significantly affect the possible decomposition pathway(s). The overall aim was therefore to establish the decomposition mechanisms of these azides, for which contrasting routes were anticipated, and to rationalise the results obtained.

This paper accordingly describes experiments in which the title compounds were thermally decomposed, and the products monitored by photoelectron spectroscopy (PES) and matrix isolation infrared (IR) spectroscopy at different stages of pyrolysis. This program of work also involved the synthesis and characterisation of the title compounds, and the use of *ab initio* molecular orbital calculations to assist in the assignment of the PE and IR bands. Finally, molecular orbital calculations were carried out on all three systems in an attempt to account for the various decomposition products observed and to establish the possible reaction pathways.

Experimental Section

Sample preparation and characterisation

Methyl azidoformate (N_3COOMe) is a colourless liquid at room temperature. It was prepared by the slow addition of methyl chloroformate to a solution of sodium azide (3 equiv) in distilled water. The mixture was stirred for 24 h in an oil bath at 50 °C. After cooling, the product was extracted with dichloromethane, dried over anhydrous sodium sulphate and the organic phase concentrated by evaporation. The methyl azidoformate was purified by distillation at reduced pressure (10 mbar; b.p. 20 °C). The compound was characterized in the vapour phase by UV-photoelectron spectroscopy and electron impact mass spectrometry, and in the liquid phase by 1H and ^{13}C NMR and by IR spectroscopy.

The 70-eV electron impact mass spectrum displayed a parent peak at 101 amu (0.9%) and a base peak at 59 amu ($COOCH_3^+$, 100%). Signals were also present at 70 (N_3CO^+ , 36.5%), 28 (N_2^+ , 17.9%), 29 (N_2H^+ , HCO^+ , 14.3%) and 42 (N_3^+ , NCO^+ , 12.3%) amu. In the 1H NMR spectrum, recorded in $CDCl_3$ solution, a single peak at $\delta = 3.84$ ppm relative to TMS is assigned to the methyl group. In the ^{13}C NMR spectrum, run in $CDCl_3$ solution, two peaks were observed: a peak at $\delta = 55.0$ ppm with respect to TMS due to the methyl carbon atom, and a second at $\delta = 157.9$ ppm assignable to the carbonyl carbon atom. The IR spectrum of the pure liquid recorded between KBr plates showed a weak peak at 2959 cm^{-1} , assigned to C–H stretching absorptions, strong bands at 1728 cm^{-1} (C=O stretching), 1241 cm^{-1} , and 905 cm^{-1} . The N_3 group was characterised by a complex, broad band with maxima at 2165, 2148 and 2134 cm^{-1} .

Ethyl azidoformate (N_3COOEt) is also a colourless liquid. It was prepared by reacting ethyl chloroformate, with sodium azide under conditions identical to those described above for the methyl ester, and similarly characterized.

The 70-eV electron impact mass spectrum displayed a parent peak at 115 amu (0.1%), (and 114 amu, 0.4%). The base peak was at 29 amu (N_2H^+ , $CH_2CH_3^+$, 100%), and signals were also present at 70 (N_3CO^+ , 34.5%), 27 (CH_3C^+ , 17.5%), 43 (N_3H^+ , 6.8%), 73 ($CH_3CH_2OCO^+$, 5.3%), 42 (N_3^+ , NCO^+ , 5.1%) and 100 ($N_3COOCH_2^+$, 3.4%) amu. In the 1H NMR spectrum, recorded in $CDCl_3$ solution, a triplet peak centred at $\delta = 1.32$ ppm relative to TMS corresponds to the methyl group,

while a quartet centred at $\delta=4.27$ ppm is assigned to the methylene group. In the ^{13}C NMR spectrum, run in CDCl_3 solution, three peaks were observed: a peak at $\delta=13.9$ ppm with respect to TMS due to the methyl carbon atom, a peak at $\delta=64.6$ ppm assigned to the methylene carbon, with the third at $\delta=157.3$ ppm assigned to the carbonyl carbon atom. The IR spectrum of the pure compound recorded between KBr plates showed peaks at 2986 cm^{-1} , assigned to C–H stretching absorptions, and strong bands at 1724 cm^{-1} (C=O stretching), 1220 cm^{-1} , and 1021 cm^{-1} . A doublet at $2179/2132\text{ cm}^{-1}$ was assigned to the N_3 group.

2-azido-*N,N*-dimethylacetamide was similarly prepared from the chloro derivative. In a typical preparation, 2-chloro-*N,N*-dimethylacetamide (FW 121.57) was added slowly to a solution of sodium azide (FW 65.01; 3 equiv) in water, and the mixture stirred for 2 h in an oil bath at 60°C . After cooling, the product was extracted with ethyl acetate, and the organic phase dried over anhydrous sodium sulfate. The solvent was then removed using a rotary evaporator, and the desired product purified by distillation at reduced pressure.

At room temperature, 2-azido-*N,N*-dimethylacetamide ($\text{N}_3\text{CH}_2\text{CONMe}_2$) is a viscous liquid with a low vapor pressure. It was characterized in the vapour phase by UV-photoelectron spectroscopy and electron impact mass spectrometry, and in the liquid phase by ^1H and ^{13}C NMR and by IR spectroscopy. The nitrogen matrix IR spectrum was also recorded.

The 70-eV electron impact mass spectrum displayed a parent peak at 128 amu (3.4%) and prominent peaks at 28, (N_2^+ , CH_2N^+ , 100%); 72, (CONMe_2^+ , 100%), 43, (HNCO , MeN_2 , MeCH_2N , 22.2%), (42, 18.9%), and 99, ($\text{NCH}_2\text{CONMeCH}_2^+$, 28.9%). Signals were also present at 15 (Me^+) and 85 (CHCONMe_2^+) amu. As found previously for azidoacetamide,^[11] the 20 eV electron impact mass spectrum showed enhanced intensities for most of the above ions with respect to the N_2^+ signal. The ^1H NMR spectrum, recorded in CDCl_3 solution showed a partially resolved doublet at $\delta=2.69$ ppm (relative to TMS) which was assigned to two chemically inequivalent methyl groups; and a singlet at $\delta=3.68$ ppm due to the methylene protons. The intensity ratio between the two groups was 3:1, consistent with the relative intensity expected for $(\text{CH}_3)_2$ and CH_2 protons. In the ^{13}C -[H] NMR spectrum, (also in CDCl_3) solution, a doublet peak at $\delta=35.6$ and 36.3 ppm (relative to TMS) is assigned to the methyl groups; a peak at $\delta=50.4$ ppm to the methylene carbon, and a feature at $\delta=167.3$ ppm to the carbonyl carbon.

The IR spectrum of the liquid recorded between KBr plates showed a relatively broad band with peaks at 2934 cm^{-1} and 2925 cm^{-1} , (C–H stretch), 2107 cm^{-1} (N_3 stretch), 1660 cm^{-1} (C=O stretch), 1403, 1284 and 1147 cm^{-1} .

Matrix isolation IR studies

The methodology of our matrix isolation infrared experiments followed a very similar pattern to that described in previous studies on organic azides.^[1–3,11] The inlet and pyrolysis parts of the apparatus were identical, as were the low temperature Displex and IR spectrometers. Spectra of the parent azides and of their decomposition products were obtained in nitrogen matrices, and supporting N_2 matrix experiments were also carried out on 2-oxazolidone, MeNCO , Me_2NH and HCONMe_2 to augment our N_2 matrix infrared data bank of known molecular vibration frequencies. Matrix ratios were estimated to be well in excess of 1000:1. Deposition times were typically 30 mins at a particular superheater temperature, and any changes occurring during this period were monitored by spectral subtraction. Spectral subtraction was also employed to remove the three (weak) IR bands of matrix-isolated H_2O , which were routinely observed in all experiments, and which are believed to arise from (variable) traces of water adsorbed on the inner walls of the sample inlet system.

Photoelectron spectroscopy

The PE spectrometer used a HeI photon source, and its mode of operation has been discussed elsewhere.^[12] However, although the azidoformates studied here have sufficient vapour pressure to be introduced directly into the ionisation chamber via a needle valve, 2-azido-*N,N*-dimethylacetamide is a liquid which does not have a sufficiently high vapour pressure at room temperature to allow PE spectra with sufficient signal-to-noise to be obtained in this way.

For studies on this compound, the sample was contained in two small glass vials placed in a region immediately above the pyrolysis zone on a small pad of glass wool, where the temperature is high enough to give a suitable vapour pressure. The inlet system itself consisted of two coaxial quartz tubes, and pyrolysis took place in the final few centimetres of the inner tube of this inlet system, above the photoionisation region in the spectrometer. With this arrangement, run times of about 30 min could be achieved, and it was possible to reach a temperature of 550°C without any major loss of resolution. The distance between the end of the pyrolysis region and the photoelectron beam was between 1 and 2 cm, which at the typical pressure of about 10^{-4} mbar normally achieved in the experiments, corresponds to a flight time between the centre of the pyrolysis region and the photoelectron beam of about 5–10 ms.

Calibration of the vertical ionisation energies (VIEs) of the parent azide photoelectron bands was achieved by introducing methyl iodide and argon into the ionisation chamber together with the parent azide. The release of N_2 and other clearly identifiable pyrolysis products also served to provide internal spectral calibrants.

The absence of detectable impurities arising from the starting materials used in the preparation was confirmed by running PE spectra of the volatile reagents used, and, in order to assist assignment of the bands appearing on pyrolysis, PE spectra were acquired for 2-oxazolidone and HCONMe_2 .

Molecular orbital calculations

Molecular orbital calculations were carried out with the Gaussian98 program on methyl azidoformate, ethylazidoformate, 2-azido-*N,N*-dimethylacetamide and dimethyliminoacetamide, $\text{Me}_2\text{NCOCH=NH}$, at the MP2/6–31G** level to establish equilibrium geometries, and subsequently to calculate vertical ionisation energies (VIEs) and infrared frequencies and intensities. For the VIEs, Koopmans' theorem was applied to the SCF orbital energies obtained at the MP2/6–31G** geometry and the values obtained were scaled^[13,14] by a factor of 0.92. Harmonic vibrational frequencies were calculated at the MP2/6–31G** level by second-derivative calculations. These frequencies are expected to be higher than the experimental values not only because no anharmonicity correction was introduced but also because in the method used only partial allowance was made for electron correlation.

Results and Discussion

Calculated equilibrium geometries: assignment of PE spectra

Methyl azidoformate: For methyl azidoformate, four minimum-energy conformers were located for the closed-shell singlet state, depending on the relative positions of the carbonyl, methyl and azide groups. The three most stable structures lie within 4.3 kcal mol^{-1} , whilst the fourth lies $12.7\text{ kcal mol}^{-1}$ higher in energy than the most stable conformer. Because of the small differences in energy between the three lowest conformers, it is likely that all three structures contribute to the experimental PE spectrum. The experimental photoelectron spectrum was assigned by applying Koopmans' theorem to the computed orbital energies for the lowest energy conformer, although the valence VIEs computed for the three lowest energy structures were found to be very similar.

Ethyl azidoformate: For the ethyl azidoformate, seven minimum-energy conformers were located for the closed-shell singlet state, depending on the different relative positions of the carbonyl, methyl, methylene and azide groups. The

lowest five lie within $4.25 \text{ kcal mol}^{-1}$, whilst the two others lie at 12.4 and $17.8 \text{ kcal mol}^{-1}$ above the ground-state conformer. As in the methyl azidoformate case, the experimental PE spectra could be assigned by using computed VIEs for the lowest energy structure. Again, the computed VIEs for the next four structures were found to be very similar.

2-Azido-*N,N*-dimethylacetamide: Four minimum-energy conformers were computed for $\text{N}_3\text{CH}_2\text{CONMe}_2$. Three lie within $1.1 \text{ kcal mol}^{-1}$, whilst the fourth lies $3.7 \text{ kcal mol}^{-1}$ higher than the most stable *cis-trans* conformer. The computed VIEs for all four conformers differed by only 0.1 – 0.2 eV . Calculations were also carried out to predict the appearance of the IR spectrum of this species, and hence to assess the reliability of such a procedure by comparing the results with the experimental spectrum.

Dimethyliminoacetamide: Dimethyliminoacetamide was the only imine intermediate observed in this work, and in order to confirm the identity of this species, it was important to obtain satisfactory agreement between the experimental and computed IR spectra. The extent of agreement between the

calculated and experimental frequencies and intensities was expected to be comparable to that for the parent azide. IR frequency and intensity calculations were accordingly carried out for this imine at the same level as described above.

Observed and calculated VIEs: For each azide, the photoelectron spectra were recorded, and experimental vertical ionisation energies (VIEs) were obtained by averaging the VIEs of the bands from several different spectra. Typical PE spectra of these parent azides are shown in Figure 1a, Figure 2a and Figure 3a, and the experimental and calculated VIEs are summarised in Table 1.

Calculated IR spectrum of 2-azido-*N,N*-dimethylacetamide: Molecular orbital calculations were initially carried out on 2-azido-*N,N*-dimethyl acetamide to assign its PE spectrum, but were extended to rationalise the appearance of its IR spectrum. Comparison with the observed IR spectrum provides a way of testing the method prior to use in related calculations to support the identification of a possible imine intermediate. This strategy was shown to work well in previous studies on the pyrolysis of 2-azidoacetamide.^[11]

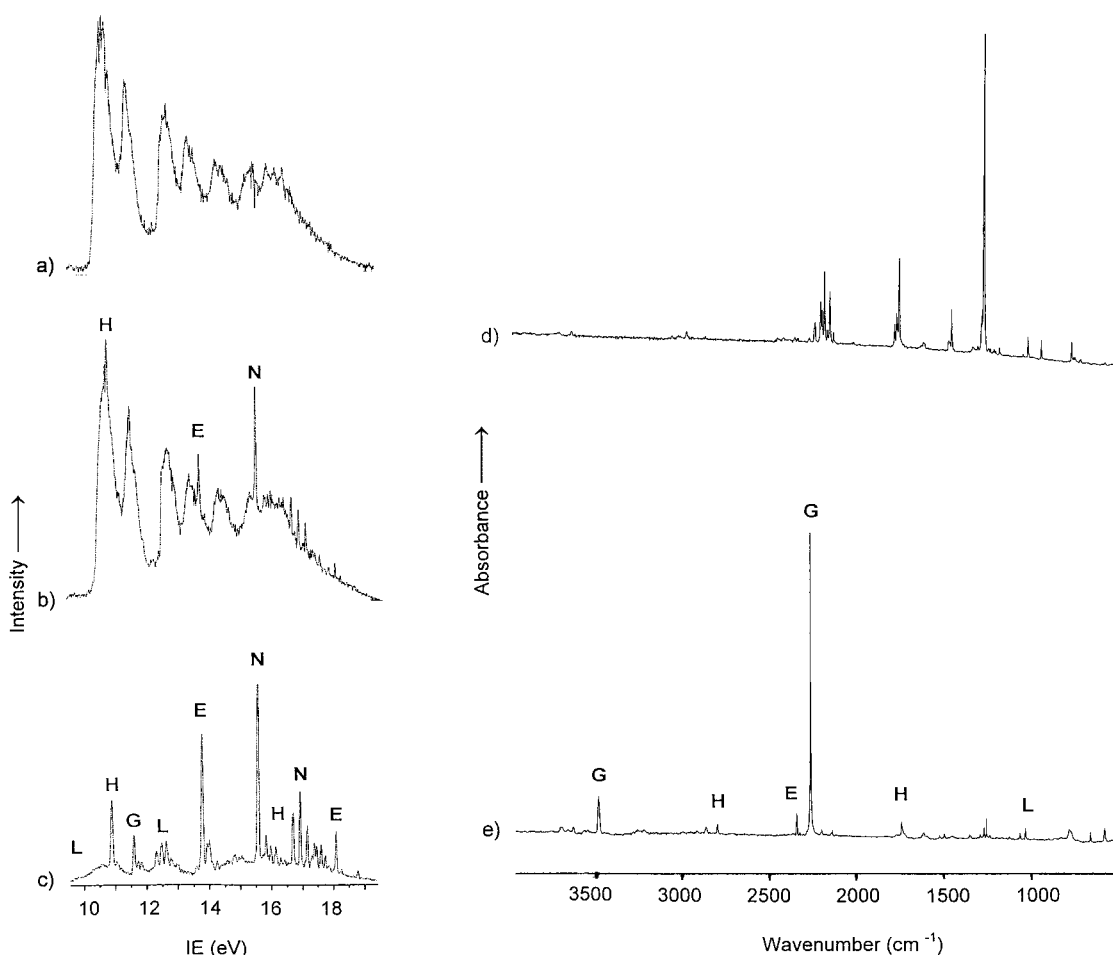


Figure 1. Spectra obtained during pyrolysis studies on N_3COOMe : a) PE spectrum of parent azide, before pyrolysis, b) PE spectrum after pyrolysis at about 170°C , c) PE spectrum after pyrolysis at about 420°C , d) N_2 matrix IR spectrum of parent azide, e) N_2 matrix IR spectrum after pyrolysis at about 280°C .

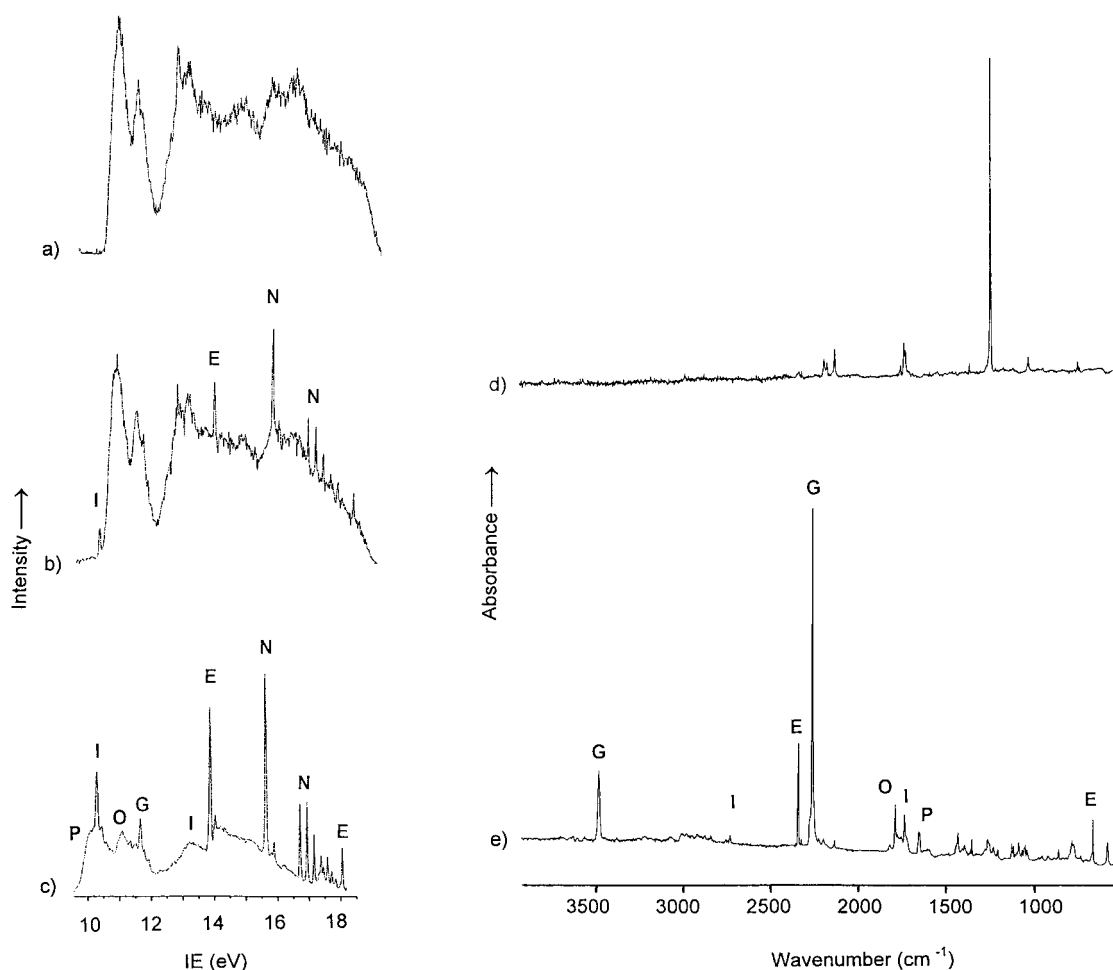


Figure 2. Spectra obtained during pyrolysis studies on N_3COOEt : a) PE spectrum of parent azide, before pyrolysis, b) PE spectrum after pyrolysis at about 190 °C, c) PE spectrum after pyrolysis at about 410 °C, d) N_2 matrix IR spectrum of parent azide, e) N_2 matrix IR spectrum after pyrolysis at about 280 °C.

Table 1. Experimental and computed VIEs (eV) for methyl azidoformate, ethyl azidoformate and 2-azido-*N,N*-dimethylacetamide.

Methyl azidoformate		Ethyl azidoformate		2-Azido- <i>N,N</i> -dimethylacetamide	
Calcd ^[a]	Exptl	Calcd ^[a]	Exptl	Calcd ^[a]	Exptl
10.53	10.84	10.49	10.72	9.25	
11.41	11.55	11.34		9.47	9.19
12.01	12.79	11.79	11.36	10.74	9.85
13.10	13.47	12.67	12.89	11.67	11.36
13.87	14.36	13.15		13.27	
14.30	15.43	13.57	13.50	13.45	13.31
15.51	16.41	13.86	14.68	14.09	
		14.74	15.64	14.16	
		15.89	16.32	14.44	14.22
				14.79	
				16.21	
				16.48	16.03

[a] Value from Koopmans' Theorem, scaled by factor of 0.92.

Figures 4a and b compare the experimental matrix isolation IR spectrum of 2-azido-*N,N*-dimethylacetamide with that calculated for the lowest energy *cis-trans* conformer. The

agreement between the two spectra is acceptable, taking into account the neglect of anharmonicity and the limited inclusion of electronic correlation in the calculations. These effects are more marked for the higher frequencies, for example, the C–H, N–H and N_3 stretches. The intensity pattern in particular is satisfactory, reproducing quite well the intensity ratios of the experimental bands. Even better agreement may be obtained by allowing a contribution from the next lowest energy conformer (the *trans-trans*), but even without this refinement, the agreement is satisfactory.

Thermal decomposition studies

Methyl azidoformate: Typical spectra showing various stages in the pyrolysis of N_3COOMe are shown in Figure 1, with Figure 1a and d showing PE and IR spectra, respectively, for the parent azide (i.e. no pyrolysis).

Photoelectron spectroscopy: Figures 1b and c show PE spectra obtained from N_3COOMe at increasing pyrolysis temperatures, and reflect an increasing degree of decomposition

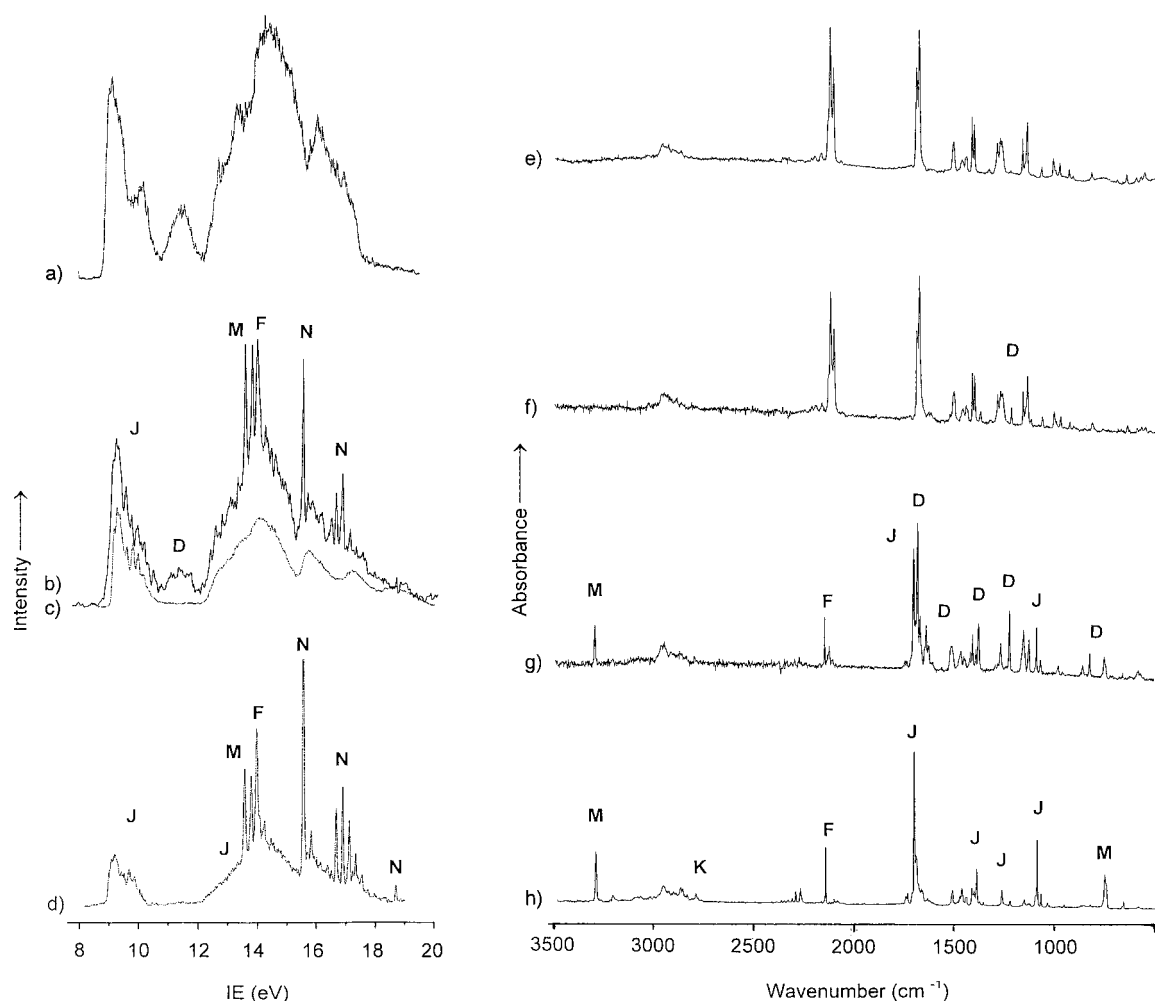


Figure 3. Spectra obtained during pyrolysis studies on 2-azido-*N,N*-dimethylacetamide. a) PE spectrum of parent azide, before pyrolysis, b) PE spectrum after pyrolysis at about 350°C, c) PE spectrum of dimethyl formamide, d) PE spectrum after pyrolysis at about 510°C, e) N_2 matrix IR spectrum of parent azide, f) N_2 matrix IR spectrum after pyrolysis at about 160°C, g) N_2 matrix IR spectrum after pyrolysis at about 280°C, h) N_2 matrix IR spectrum after pyrolysis at about 400°C.

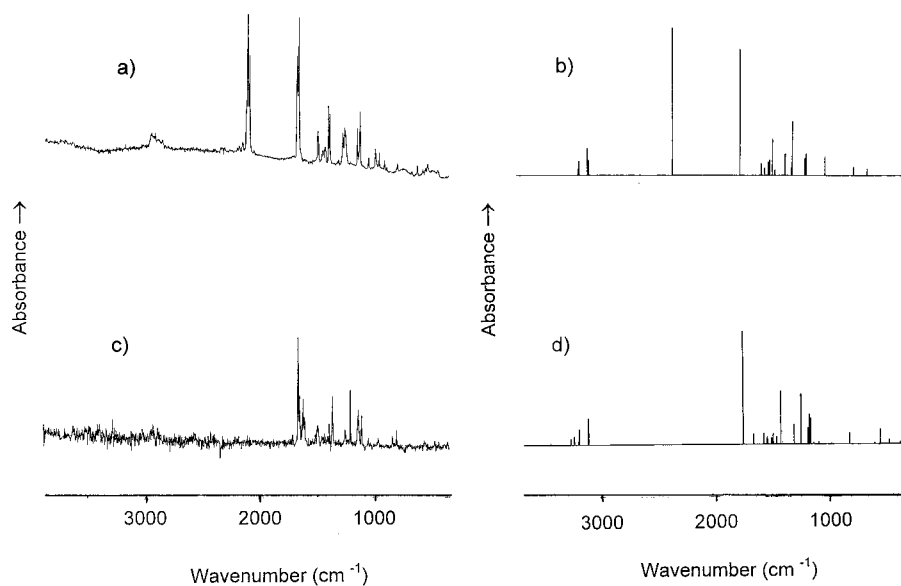


Figure 4. Comparison of observed and calculated IR spectra: a) observed spectrum of 2-azido-*N,N*-dimethylacetamide, b) calculated spectrum of 2-azido-*N,N*-dimethylacetamide, c) observed spectrum of iminodimethylacetamide, d) calculated spectrum of iminodimethylacetamide.

from about 10% at 170°C to essentially 100% at 420°C. The first evidence of pyrolysis occurred at a temperature of about 150°C, when the first band of N₂ (species **N**) at 15.58 eV (VIE) could be observed.^[15] At the same time, peaks at 10.88 and 13.78 eV were also clearly visible. Their position and appearance fit the well-known first bands of H₂CO (species **H**) and CO₂ (species **E**), respectively.^[15] With increasing temperature, the parent bands decrease, and bands of other products appear: notably a broad band at 10.50 eV (VIE) and two vibrationally resolved bands at 11.61 and 12.50 eV (VIE). The bands at 10.50 and 12.50 eV are both attributed^[5] to CH₂NH (species **L**), and the vibrationally resolved band at 11.61 eV (VIE equal to AIE) is attributed^[16] to HNCO (species **G**). At 420°C, pyrolysis was found to be essentially complete. A further band of H₂CO (vibrationally resolved, with AIE = 15.85 eV, VIE = 16.0 eV) was now visible, (see e.g., Figure 1c) together with additional bands of N₂ and CO₂.

Matrix isolation IR studies: Figure 1d shows a typical nitrogen matrix IR spectrum of methyl azidoformate. In contrast to many previously studied azides, the most intense feature in this spectrum is associated not with the N₃ group at ca 2100–2200 cm⁻¹, but instead lies at 1260 cm⁻¹. The positions of the most significant N₃COOMe bands appear in Table 2.

The first new feature to appear on pyrolysis was the characteristic 2265 cm⁻¹ band^[11] of HNCO, (species **G**) which was first observed at a temperature of ca 160°C. As the temperature was raised, bands due to the parent azide decreased, and additional features grew in, and pyrolysis was essentially complete at a temperature of ca 360 °C. At this stage the matrix spectrum showed IR bands characteristic of CO₂, (**E**), H₂CO (**H**), and CH₂NH, (**L**) together with additional bands of HNCO. Figure 1e shows a typical spectrum obtained at a pyrolysis temperature of 280°C. The band positions associated with species **E**, **G**, **H** and **L** are listed in Table 2.

Table 2. Significant IR bands (cm⁻¹) observed in matrix isolation studies on the pyrolysis of methyl azidoformate, ethyl azidoformate and 2-azido-*N,N*-dimethylacetamide.

	N ₂ matrix ^[a]	Previous studies	Assignment
A	2174, 2143, 1743, 1260		N ₃ COOMe
B	2204, 2143, 1740, 1250		N ₃ COOEt
C	2118/2104, 1685/1672		N ₃ CH ₂ CONMe ₂
D	1673, 1630, 1371, 1217		Me ₂ NCOCHNH
E	2345, 662	2347, 662	CO ₂ ^[20]
F	2139	2139	CO ^[11,21]
G	3483, 2265, 780, 581	3483, 2265	HNCO ^[b]
H	2864, 2799, 1739, 1497	2864, 2800, 1738, 1497	H ₂ CO ^[22]
I	2734, 1737, 1431, 1121	2735, 1735, 1431, 1122	MeCHO ^[2]
J	1694, 1384, 1082	1694, 1384, 1082	HCONMe ₂ ^[c]
K	2828, 2786, 1148, 1021	2828, 2786, 1148, 1021	Me ₂ NH ^[c]
L	1352, 1127, 1065	1353, 1128, 1065	CH ₂ NH ^[23]
M	3285 747/737	3287, 747/737	HCN ^[24]
O	1791, 1226, 1201, 1081	1791, 1226, 1201, 1081	2-oxazolidone ^[c]
P	1654	1652 (most intense)	MeCHNH ^[d]

[a] Wavenumber accuracy ±1 cm⁻¹. [b] Reference [11]; (bands at 780 and 581 cm⁻¹ were also seen in reference [11], but not tabulated). [c] This work: independent experiments. [d] Reference [25], argon matrix data.

Ethyl azidoformate: Typical spectra showing various stages in the pyrolysis of N₃COOEt are shown in Figure 2, with Figures 2a and d showing PE and IR spectra respectively for the parent azide (i.e. no pyrolysis).

Photoelectron spectroscopy: Figures 2b and c show photoelectron spectra of ethyl azidoformate at different degrees of pyrolysis, from about 20% at 190°C to about 100% at 410°C. The first evidence of pyrolysis was detected at about 170°C, as shown by the appearance of N₂, and at this stage, sharp bands associated^[17] with MeCHO (species **I**) and CO₂ (**E**) were also clearly visible at 10.26 and 13.78 eV (VIE) respectively. At higher temperatures, the parent bands continued to decrease, whilst bands of new products appeared, and gained intensity. A broad band at about 10.17 eV (VIE) and a partially resolved band at around 11.43 eV (VIE) were attributed^[18] to CH₃CH=NH (species **P**), and the vibrationally resolved band (Figure 2b) at 11.61 eV (VIE equal to AIE) arises from HNCO (**G**). In addition, there was evidence of a broad band at ca 11.05 eV, which did not correlate with the other pyrolysis products so far considered. At about 410°C, (Figure 2c) when pyrolysis was essentially complete, a second band of MeCHO (broad, VIE = 13.24 eV) could be identified, and there was also clear evidence of additional bands due to N₂ and CO₂. The 14.0–16.0 eV ionisation energy region now consisted of a relatively broad plateau as a result of overlap between the bands of MeCHO and MeCH=NH, but the band at 11.05 eV was still present, indicating the formation of a pyrolysis product with significant thermal stability. After some consideration, this band was attributed to the cyclic compound, 2-oxazolidone (species **O**). In the 10.0–13.0 eV region, the PE spectrum of this compound^[19] shows bands at 10.21, 10.71, 11.07 (most intense) and 12.82 eV. The first two are likely to be obscured by the envelope of the first MeCH=NH band, but the third is provisionally identified in these spectra.

Matrix isolation IR studies: Figure 2d shows a typical nitrogen matrix IR spectrum of ethyl azidoformate. As noted previously for the methyl ester, the most intense IR band is associated not with the N₃ group but lies at 1250 cm⁻¹. The positions of the most significant N₃COOEt bands are given in Table 2. The first new feature to appear on pyrolysis was again the characteristic 2265 cm⁻¹ band of HNCO (species **G**), and as the temperature was raised, bands due to the parent azide decreased, and additional features grew in. Ultimately, the matrix spectrum showed bands characteristic of CO₂ (**E**) and MeCHO

(I), together with the weaker fundamentals of HNCO. Prominent features at 1791 and 1654 cm^{-1} identified with new species **O** and **P** respectively were also observed at this stage. Figure 1e shows a typical spectrum obtained at a pyrolysis temperature of ca. 280 °C, and the band positions associated with species **E**, **G**, **I**, **O** and **P** are listed in Table 2.

2-Azido-*N,N*-dimethylacetamide: Figure 3 summarises the effect of pyrolysis as observed by the PE and IR techniques, with Figures 3a and e respectively showing spectra of the parent azide.

Photoelectron spectroscopy: Here, the onset of pyrolysis was again marked by the appearance of characteristic bands of N_2 —at temperatures close to 250 °C. As the pyrolysis temperature increased, bands due to the parent azide generally decreased as expected, but the “parent” band centred at 11.36 eV proved to be surprisingly persistent, and only fully disappeared above 480 °C. This anomalous behaviour was subsequently interpreted as indicating the presence of a reaction intermediate (**D**) with one of its bands at the same ionisation energy as one of the parent bands. Calculations of the VIEs of the imine intermediate indicate that this band corresponds its third VIE. At about 350 °C, (Figure 3b), HCN (species **M**) could be detected from its well-established^[15] band at 13.60 eV (VIE), together with the first sharp band of CO (**F**, VIE 14.01 eV). At the same time, a vibrationally resolved band appeared at ca 9.75 eV, indicating^[15] the formation of HCONMe₂ (**J**). The PE spectrum of this latter compound consists of several rather broad features which were found to dictate the underlying spectral envelope, and Figure 3c reproduces the PE spectrum obtained for a pure sample of HCONMe₂ to illustrate this. Above about 500 °C only bands associated with N_2 , HCN, CO and HCONMe₂ could positively be identified, and Figure 3d shows a typical spectrum recorded at a pyrolysis temperature of about 510 °C.

Matrix isolation IR studies: A typical IR spectrum of the parent azide is shown in Figure 3e, where it is evident that the most intense features (at 2118/2104 and 1685/1672 cm^{-1}) can be assigned as stretching modes of the N_3 and C=O groups, respectively. On heating to about 160 °C (Figure 3f), relatively few changes could be detected, apart from the appearance of a weak feature at 1217 cm^{-1} denoted **D**. Further heating to about 280 °C resulted in the continued growth of this band, and the appearance of bands characteristic of HCN (species **M**); CO, (species **F**) and HCONMe₂, (species **J**), together with three further prominent bands associated with **D** at 1673, 1630, and 1371 cm^{-1} (Figure 3g). At temperatures above ca 300 °C, bands **D** began to decrease in intensity, whilst bands **M**, **F** and **J** remained prominent. Above about 400 °C, **D** had effectively disappeared (Figure 3h), but in addition to **M**, **F** and **J**, a weak feature at 2786 cm^{-1} (labelled **K**) was also visible, and traces of HNCO and MeNCO could also be detected via their characteristic band positions (2265 and 2288 cm^{-1} , respectively). **K** was subse-

quently identified as Me₂NH, by comparison with independent supporting experiments.

One of the more significant features of this system is that species **D** is clearly an intermediate in the pyrolysis process, and that Figure 3f shows that it is formed prior to the appearance of HCN (**M**) and CO (**F**).

Characterisation of the imine intermediate Me₂NCO-CH=NH: Both PES and IR matrix isolation data indicate that an intermediate is produced on the decomposition of 2-azido-*N,N*-dimethylacetamide. In the PES spectra, a band at 11.36 eV nominally associated with the parent compound persists under conditions where one would anticipate very little parent to remain, whilst in the matrix isolation IR experiments, the sequence of spectra recorded at increasing temperatures clearly shows the formation and decay of an intermediate (denoted **D** in Figure 3). By analogy with previous studies on the pyrolysis of 2-azidoacetamide, this intermediate was provisionally identified as dimethyliminoacetamide (Me₂NCOCH=NH). Supporting calculations were therefore carried out on this molecule in order to establish its lowest energy conformer, and to predict the appearance of its IR spectrum.

Three closely separated minimum energy structures were located from these calculations. The most stable structure may be described as *trans-trans*, with structures *cis-cis* and *cis-trans* lying at energies higher by 1.4 and 2.8 kcal mol⁻¹, respectively. IR spectra were subsequently calculated for all three conformers, and compared with the IR spectrum corresponding to the intermediate.

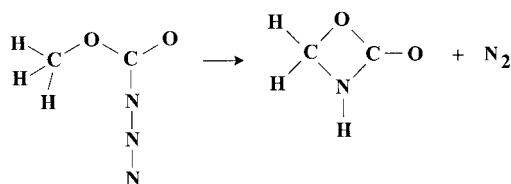
Detailed comparison between these observed and calculated spectra indicated that *two* structures, the *trans-trans* and the *cis-cis* both contribute to the observed spectrum. This *cis-trans* notation reflects the relative positions of the C-H proton in the NH=CH group to the O atom, and to the N-H proton respectively. Either one of these two lowest energy structures provides an acceptable fit to the observed spectrum, and Figures 4c and d compare the observed and calculated spectra for the intermediate, assuming the lowest energy *trans-trans* conformer. The level of agreement here is similar to that found for the parent azide (Figures 4a and b), and also for the previously characterised iminoacetamide.^[11] Furthermore, the thermal decomposition of this species can account for all the major spectral features subsequently observed at higher pyrolysis temperatures.

Suggested mechanisms for gas-phase decomposition

Methyl azidoformate: The experimental evidence from PES suggest that the onset of pyrolysis occurs with nitrogen release and the almost simultaneous formation of CO₂ and CH₂=NH, whilst in the parallel IR studies, the first species to be clearly detected are CO₂ and HNCO. This apparent dichotomy arises solely as a result of the relative cross-sec-

tions/extinction coefficients in PE and IR spectroscopy for the various products. As the concentration of reaction products builds up, all the observed products (CO_2 , CH_2NH , HNCO , H_2CO) are typically identified using both techniques.

This variety of pyrolysis products implies at least two independent decomposition pathways, both of which result in proton transfer to a nitrogen atom. The “Type 1” decomposition route is not available for this azide, but if one assumes that the product distribution is dictated initially by the transfer of a methyl proton, as indicated in Scheme 3, it turns out that the resulting cyclic intermediate could act as a precursor for two such pathways, consistent with the observed products.

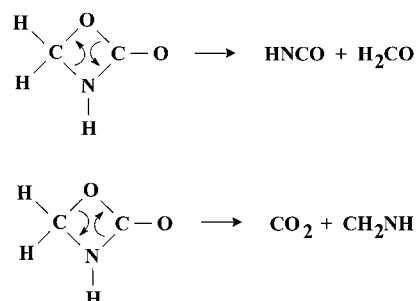


Scheme 3.

Ab initio calculations show that this proposed cyclic intermediate has all-real vibrational frequencies and the structure is predicted to be relatively very stable (the relative energy diagram is reported in Figure 5). By applying Koopmans' theorem to the orbital energies obtained at the SCF level, the first VIE is predicted at 11.85 eV, and furthermore, its IR spectrum simulation predicts a very intense $\text{C}=\text{O}$ stretching mode at 1969 cm^{-1} . However, this four-membered-ring species was not detected experimentally. This may be due to the high excitation energy with which such an intermediate is formed, resulting in an extremely short lifetime, and in this event, it should be possible to account for the formation of all the observed products by consider-

ing two possible modes of decomposition for this ring (Scheme 4).

As in Scheme 4, these alternative modes of ring cleavage give two pairs of products: $\text{HNCO} + \text{H}_2\text{CO}$, and $\text{CO}_2 + \text{CH}_2\text{NH}$, consistent with experiment. Ab initio calculations



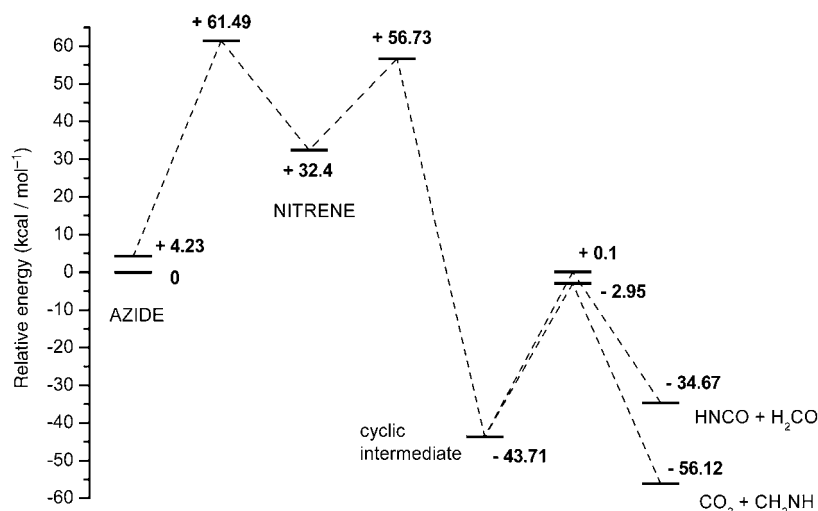
Scheme 4.

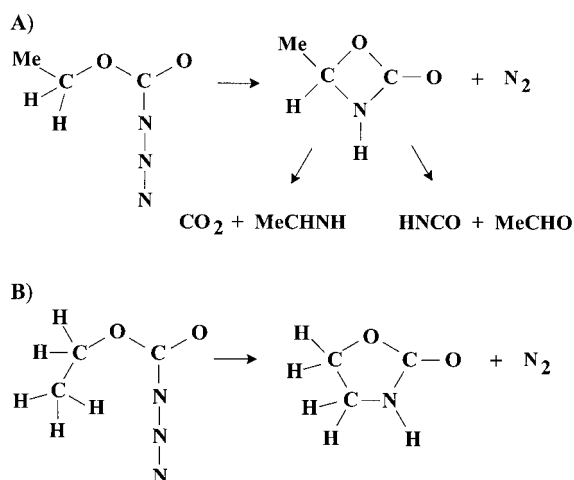
were accordingly carried out at the MP2/6-31G** level to investigate these two pathways, and the results are shown in Figure 5. In energy terms, there is a preference for the latter route, but experimentally, all the product bands were judged to maintain the same intensity ratio throughout the temperature range studied, indicating little distinction between the competing reaction channels.

Ethyl azidoformate: The pyrolysis of ethyl azidoformate presents a similar situation, in that the “Type 1” mechanism is impossible. Here, however, the presence of an additional methylene group provides an additional possible source of protons for transfer, as indicated in the Scheme 5.

Capture of a methylene proton (Scheme 5 A) would create a four-membered ring analogous to that formed in the thermal decomposition of methyl azidoformate, and assuming facile rupture of the ring, the predicted products would be $\text{CO}_2 + \text{MeCH}=\text{NH}$ and $\text{HNCO} + \text{MeCHO}$. If, on the other hand, a methyl proton is transferred, (Scheme 5 B), the result would be the formation of the five-membered-ring species 2-oxazolidone. This latter structure would be expected to be less strained than the isomeric four-membered ring, and might therefore not undergo further rupture quite so easily.

Experimentally, the two pairs of products predicted from Scheme 5 A were readily identified, and corresponding ab initio calculations predicted the most stable products to be $\text{CO}_2 + \text{MeCHNH}$, with $\text{HNCO} + \text{MeCHO}$ lying at somewhat higher energy

Figure 5. Pathway energetics for the pyrolysis of N_3COOMe .



Scheme 5.

(Figure 6). In addition, both the PE and IR data also showed the *definite formation* of 2-oxazolidone, thus providing firm evidence for the mechanism in Scheme 5B.

Subsequent calculations confirmed that 2-oxazolidone would be a stable product in this system, and also that its thermal decomposition involved transition state(s) to the products $\text{CO}_2 + \text{MeCHNH}$ at considerably higher energy than those from the 4-membered ring. The results of these calculations are summarised in Figure 6.

Pyrolysis of 2-azido-*N,N*-dimethylacetamide: The experimental results from the PE studies show that the pyrolysis of 2-azido-*N,N*-dimethylacetamide proceeds via an early release of N_2 , whilst the PES and IR matrix studies indicate the early formation of a new species (**D**) which itself undergoes decomposition at higher temperatures (see Figure 3). Both techniques showed the presence of HCN, CO, Me_2NH and HCONMe_2 as final decomposition products.

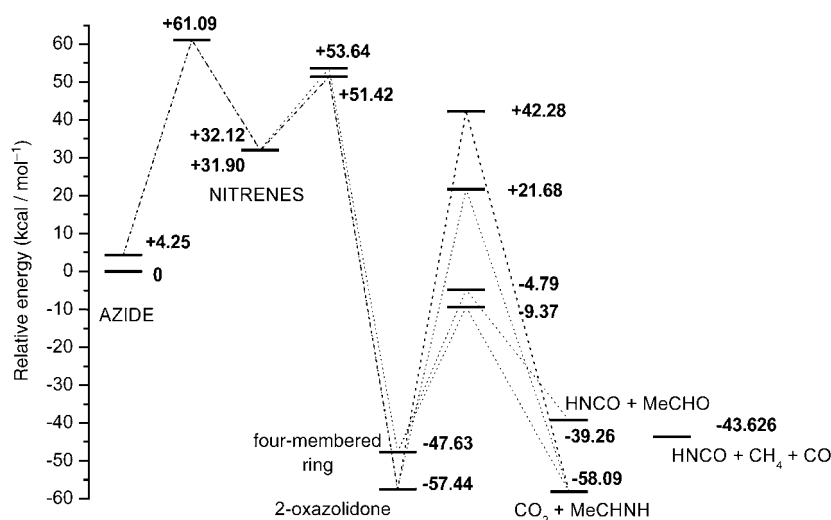
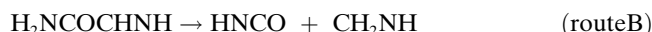
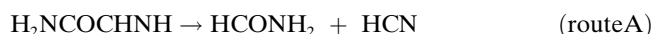
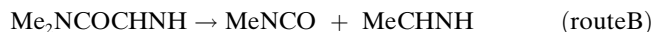


Figure 6. Pathway energetics for the pyrolysis of N_3COOEt .

These observations are entirely consistent with the initial formation of iminodimethyl acetamide, $\text{Me}_2\text{NCOCHNH}$, via the “Type 1” route, and so mirror the results of previous studies on the pyrolysis of 2-azidoacetamide.^[11] Support for the identification of this intermediate comes from the agreement between the IR spectral features assigned to intermediate **D** (Figure 4c), and the IR spectral simulation for the minimum energy conformer of this imine, shown in Figure 4d. The decomposition of iminodimethylacetamide (**D**) to give the four final observed products (HCN, CO, Me_2NH and HCONMe_2) may be regarded as being analogous to the previously reported decomposition of iminoacetamide,^[11] where three routes (A–C) were proposed to account for imine decomposition.



These routes accounted for the major high temperature pyrolysis products with one proviso: HCONH_2 was not observed, but rather it was suggested that at the reaction temperatures involved, this compound itself decomposed into $\text{HNCO} + \text{H}_2$. By analogy, the ultimate pyrolysis products of 2-azido-*N,N*-dimethylacetamide would arise from the pyrolysis of iminodimethylacetamide in three possible ways (A–C):



The spectra presented in Figure 4 show a clear preference for route A, based on band intensities in both the PE and IR spectra.

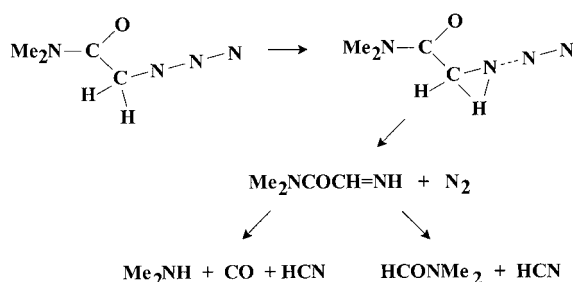
Route B predicts significant yields of MeNCO and MeCHNH , but no bands corresponding to MeCHNH were detected in either the PES or IR studies. The IR spectrum did, however, show a very weak feature at 2288 cm^{-1} at the position of the most intense IR fundamental of MeNCO . However, comparative spectral studies show that this absorption has a very high extinction coefficient, and that the MeNCO observed here is present in only very small concentrations. We do not believe that route B is a significant mechanism here.

Route C predicts the presence of CO and Me₂NH, both of which can be identified in the IR spectra of the final products, with CO being relatively prominent (Figure 3h). CO also appears in the PE spectra (Figure 3d), and this channel therefore seems to operate concurrently with route A. The production of Me₂NH was not confirmed in the PES studies, probably because the PE bands of this product are overlapped^[13,16] by more intense bands arising from HCONMe₂.

The only remaining species which could be identified was a trace of HNCO in the IR studies (at 2265 cm⁻¹, Figure 3h). Like the 2288 cm⁻¹ band of MeNCO, this band has a very high extinction coefficient,^[11] and its presence here corresponds to a very small concentration. At the present time, we have no straightforward explanation for its formation.

It is therefore proposed that Route A provides the dominant mechanism for imine decomposition, but that Route C also provides a viable channel. Both these routes, together with the initial stage of imine formation, were explored with the aid of ab initio calculations at the MP2/6-31G** level. These calculations showed that the intermediate was relatively stable, and that its subsequent decomposition into HCONMe₂ + HCN (route A) is thermodynamically more favored over route C by 2.68 kcal mol⁻¹.

The overall decomposition can therefore be represented as shown in Scheme 6.



Scheme 6.

Conclusion

Methyl and ethyl azidoformate have been synthesised and characterised by means of ¹H and ¹³C NMR, IR spectroscopy, mass spectrometry and PES. The thermal decomposition of these azides in the gas phase has been studied by PES and matrix isolation IR spectroscopy, and the experimental results supported by molecular orbital ab initio calculations. There is strong evidence that both compounds undergo pyrolysis via a four-membered-ring intermediate which itself can fragment in two distinct ways. In addition, ethyl azidoformate can also eliminate molecular N₂ and form the stable five-membered-ring compound 2-oxazolidone. For both compounds, the initial reaction step is the transfer of a

proton from a remote site in the molecule onto the nitrogen atom, distinctive of "Type 2" behavior.

2-Azido-*N,N*-dimethylacetamide has also been synthesized and characterised by routine spectroscopic methods. The thermal decomposition of this azide in the gas phase has similarly been studied by PES and matrix isolation IR spectroscopy, and the experimental results supported by molecular orbital ab initio calculations. In contrast to the azidoformates, the results here indicate that 2-azido-*N,N*-dimethylacetamide decomposes via a stepwise "Type 1" mechanism involving the initial formation of the novel imine, Me₂N-COCH=NH. This intermediate has been characterised by IR spectroscopy supported by ab initio calculations, and is shown subsequently to decompose preferentially into HCONMe₂ and HCN. A secondary channel results in the formation of Me₂NH, CO and HCN.

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