A Study of the Thermal Decomposition of Azidoacetone by Photoelectron and Matrix Isolation Spectroscopy

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2-Azidoacetone ($N_3CH_2COCH_3$) has been synthesized and characterized by a variety of spectroscopic techniques, and the thermal decomposition of this molecule at temperatures in the region 300−1150 K has been studied by matrix isolation infrared spectroscopy and real-time ultraviolet photoelectron spectroscopy. The results show the effectively simultaneous production of six prominent decomposition products: CH_2NH, CH_2CO, HCN, CO, N_2, and CH_3CHO, and several reaction pathways are proposed to account for their formation. Results of ab initio molecular orbital calculations indicate that the primary reaction intermediate is the imine $HNCHCOCH_3$, with the nitrene NCH_2COCH_3 being a transition state. No experimental evidence was found for the presence of the imine $HNCHCOCH_3$, but mechanistic considerations, and the existence of several weak unassigned IR bands point to the presence of a further decomposition product, which may be CH_2NCH_3.

Introduction

Organic azides are important industrially because they have applications in a number of areas, notably in the manufacture of seismic explosives,[1] semiconductors,[2] and photoresistors.[3] They are also a possible rapid source of gas for air bags in vehicles and they have biochemical applications.[4] Because of the intrinsic instability of many organic azides, their properties are difficult to measure. The mechanisms of their decomposition and the intermediates formed are largely unknown although there is general agreement in the literature that the initial step involves loss of molecular nitrogen. As a consequence, control of their decompositions is difficult to achieve and there is a need to characterize such decomposition in detail. Pyrolyses of alkyl azides in the gas phase have been studied by Bock and Dammel[5−8] using the technique of UV photoelectron spectroscopy (pes). The effect of substituent groups on the photoelectron spectra of the parent molecules and their decomposition pathways was studied. However, no studies on azidocarbonyl compounds were reported. From the results of the work of Bock and Dammel, it was suggested that the decomposition of alkyl azides is driven by the loss of nitrogen to form an imine ($R_2C{=}NH$), which may be formed via a nitrene intermediate or by simultaneous loss of nitrogen and a 1,2 hydrogen shift. Further heating may produce simple hydrocarbons, molecular hydrogen, and hydrogen cyanide.

The UV photoelectron spectrum of azidoacetone has been published previously,[9] and spectral band assignments were achieved by ab initio molecular orbital calculations using a 4-31G basis set. However, inspection of this work shows the ionization energy scale to be approximately 0.3 eV too high (from the position of known calibrant bands in the spectrum). This error was corrected in a later paper,[10] on the basis of results obtained in this present work, where only the first two vertical ionization energies are reported.

In a recent study,[11] we reported the thermal decomposition of 2-azidoacetic acid ($N_3CH_2CO_2H$) by matrix isolation infrared spectroscopy and real time ultraviolet photoelectron spectroscopy. The results were shown to be consistent with a decomposition pathway involving the ejection of N_2 and the simultaneous formation of CO_2 and methanimine (CH_2NH). At higher temperatures, HCN was produced.

In this present paper, we report parallel studies on the pyrolysis of azidoacetone ($N_3CH_2COCH_3$), where the mode of decomposition is similarly explored using photoelectron and matrix isolation infrared spectroscopic measurements. These studies are 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 the parent azide and its possible decomposition products.

Experimental Section

Sample Preparation. Azidoacetone was prepared from chloroacetone (95% Aldrich) and NaN_3 (99% Aldrich) mixed in a molecular ratio of 1:2. Typical quantities used were 5 g of NaN_3 and 3.1 mL of $ClCH_2COCH_3$ ($d = 1.15$ g.cm^{-3}). A solvent (Analar acetone) (10 mL) was added to homogenate the mixture, and sufficient distilled water was then added to dissolve the NaN_3 (about 10 mL). The reaction was carried out in a round-bottom flask with a $CaCl_2$ drying tube fitted. The mixture was stirred for 72 h in an ice bath. After 48 h, the acetone was removed from the mixture by rotary evaporation. The product $N_3CH_2COCH_3$ was then extracted with diethyl ether

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and dried over anhydrous magnesium sulfate. Final purification to remove the volatile solvents and unreacted $ClCH_2COCH_3$ required prolonged pumping under high vacuum (10^{-6} mbar) at room temperature. Sample purity was estimated to be greater than 97% on the basis of ^1H NMR and electron impact mass spectrometric results, a summary of which is included in the Results section.

Care was 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 Studies. Matrix isolation infrared studies on this system followed a pattern very similar to that described in our previous account of the azidoacetic acid system.[11] The inlet and pyrolysis parts of the apparatus were identical, as were the low temperature Displex and IR spectrometers. The only significant difference was that the lower vapor pressure of azidoacetone (compared with azidoacetic acid) removed the necessity to precool the sample prior to deposition. Spectra of the parent azide and its decomposition products were obtained in nitrogen matrices, and supporting experiments were also carried out on CH_3CHO/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. Matrix ratios were estimated to be well in excess of 1000:1.

Photoelectron Spectroscopy. All of the photoelectron spectra recorded in this work were obtained using He(I) (21.22 eV) radiation. A single detector photoelectron spectrometer designed for high-temperature studies and described elsewhere[12,13] was employed.

The vapor pressure of the parent material ($N_3CH_2COCH_3$) was sufficient at room temperature to allow photoelectron spectra with good signal-to-noise ratio to be obtained by direct pumping on a liquid sample via the inlet system of the spectrometer. In thermal decomposition experiments the azide vapor was passed in a continuously flowing effusive beam through a stainless steel furnace, heated by radio frequency (rf) induction heating,[12,13] in the ionization chamber of the spectrometer. The furnace was heated to approximately 1200 K (as estimated from chromel−alumel thermocouple measurements, with the thermocouple in contact with the furnace) and the rf supply switched off. Photoelectron spectra were then recorded as the furnace cooled, removing the need for gated detection electronics, resulting in spectra with improved signal-to-noise ratios. The thermal isolation of the furnace resulted in slow cooling, allowing spectra of $N_3CH_2COCH_3$ to be obtained at varying degrees of pyrolysis, over a period of ≈30 min. The onset of decomposition was clearly marked by the appearance of characteristic bands of N_2 and CO.

The operating resolution of the photoelectron spectrometer (typically 30−35 meV as measured for argon $(3p)^{-1}$ fwhm ionized with HeI_α radiation) was found to be unaffected by this heating system even at the highest temperatures used (ca 1200 K).

Spectral calibration was achieved by reference to the known ionization energies of molecular nitrogen, methyl iodide, and traces of water present in the system.[14,15] He(I) photoelectron spectra were also obtained for $ClCH_2COCH_3$, used in the preparation of $N_3CH_2COCH_3$, and were in good agreement with that reported previously.[16] The second and third bands of this molecule at 11.43 and 11.91 eV ionization energy were the most intense. Photoelectron spectra of purified samples of $N_3CH_2COCH_3$ showed no evidence of $ClCH_2COCH_3$.

TABLE 1: Significant IR Bands (cm^{-1}) Observed in Matrix Isolation Studies on the Pyrolysis of Azidoacetone[a]

N_2 matrix (letter in Figure 1)	previous studies	assignment
2117 (A), 1740 (B)		$N_3CH_2COCH_3$
1419 (C), 1360 (D)		
1282 (E), 1170 (F)		
2138 (I)	2138	CO (ref 20)
3033, 2920	3033, 2930	CH_2NH (ref 11)
1637, 1450	1637, 1450	
(1352[b]) (K), (1128[c]) (S)	1353, 1128	
1065 (L)	1065	
3287 (G), 747/727 (M)	3287, 747/737	HCN (ref 11)
3159, 3065	3155, 3062	CH_2CO (ref 21a)
2142 (H), 1382 (O)	2142, 1381	
(1125[c]), 978	1125, 978	
2845, 2735	2845, 2735	CH_3CHO (ref 22)
1735 (J), 1431, (N)	1735, 1431	
(1352[b]), 1122 (T)	1352, 1122	
1663, 1360 (P),		unassigned features
1305 (Q), 1210 (R)		unassigned features appearing on pyrolysis

[a] Frequency accuracy, ± 1 cm^{-1}. [b] Overlap between CH_2NH and CH_3CHO bands. [c] Overlap between CH_2NH and CH_2CO bands.

Results

Characterization of $N_3CH_2COCH_3$. Purified samples of azidoacetone were characterized in the vapor phase by mass spectrometry and ultraviolet photoelectron spectroscopy and in the liquid phase by ^1H NMR, Raman, and ir spectroscopy. The 70 eV electron impact mass spectrum showed a parent ion peak at 99 amu (10%) and fragment peaks at 28 amu (45%, N_2^+), 43 amu (100%, $COCH_3^+$), and 71 amu (5%, $NCH_2COCH_3^+$). Two signals were observed in the 300 MHz ^1H NMR spectrum of azidoacetone in $CDCl_3$ solution. These were at 2.1 and 3.1 ppm relative to TMS, and their relative positions and integrated intensities are consistent with their assignment as methyl and methylene protons, respectively.

The most intense absorption in the (liquid) ir spectrum was found at 2109 cm^{-1} and is assigned to a vibration of the N_3 group. Other prominent bands were present at 1728 (C−O str.), 1421, 1360, 1285, and 1189 cm^{-1}. The liquid Raman spectrum exhibited counterparts to all of the above bands, with notably intense bands at 2108, 1728, 1421, and 1285 cm^{-1}. In addition, the Raman spectrum showed significant features in the C−H stretching region (at 2968, 2924 cm^{-1}) compared with a weak feature at 2904 cm^{-1} in the infrared. The ir bands in a nitrogen matrix were shifted only slightly from the liquid-phase values. Their positions and relative intensities appear in Figure 1a and Table 1 below and are discussed in the context of the pyrolysis results.

The HeI PES of azidoacetone is shown in Figure 2a, and our assignment of this spectrum is made with reference to the results of ab initio molecular orbital calculations. An estimate of the equilibrium geometry was obtained at the MP2/6-31G* level using the Gaussian 94 code.[17] 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. Other conformers were found to be higher in energy. The three highest occupied molecular orbitals in the ground state (orbitals 26, 25, and 24) are essentially non bonding or weakly antibonding, whereas orbital 23 is essentially a π(C−O) bonding orbital. Deeper orbitals are less easily described in such terms because they are more delocalized. Table 3 compares our experimental vertical ionization energies (VIEs) with calculations resulting from the application of Koopmans'

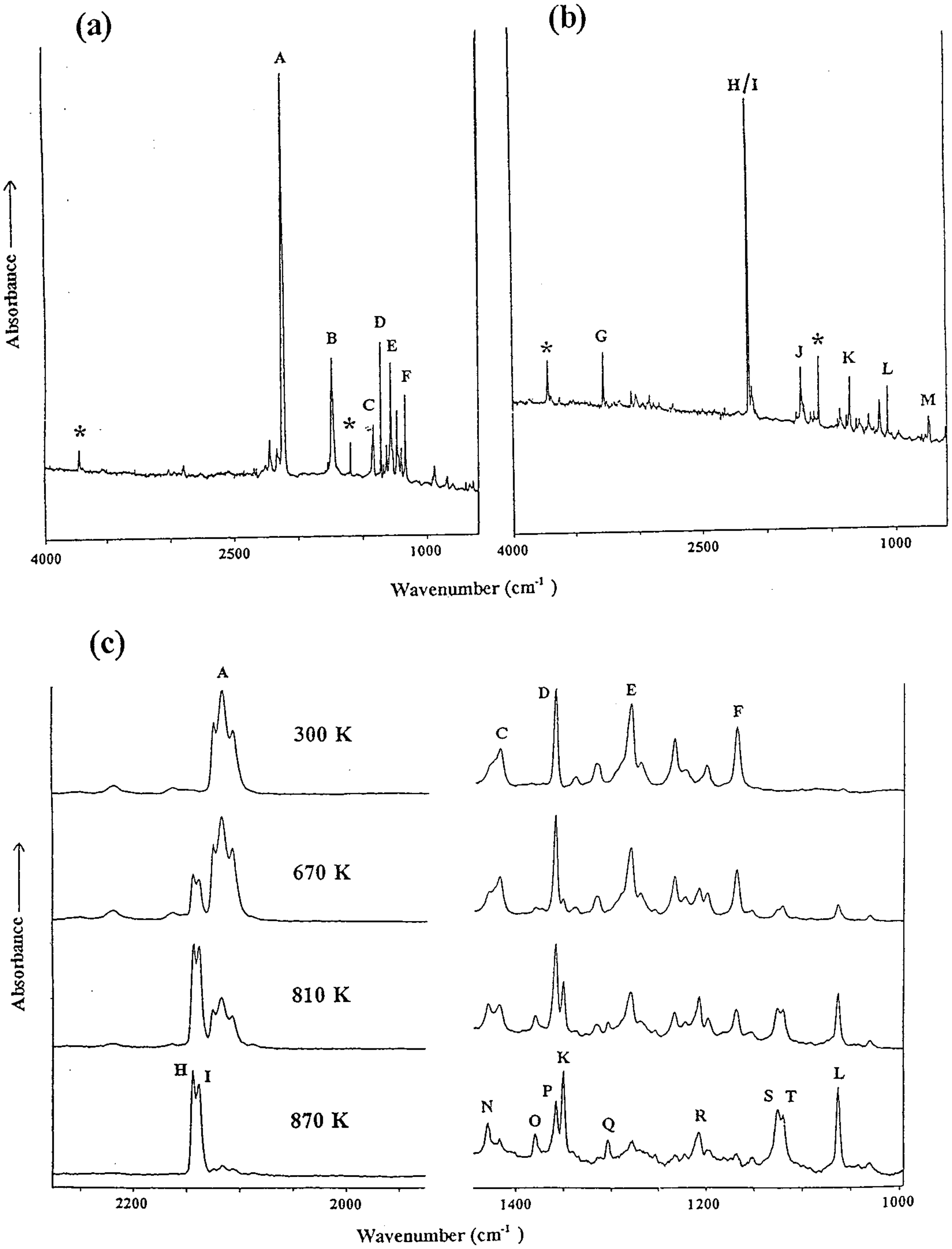


Figure 1. Nitrogen matrix IR bands observed during pyrolysis studies on azidoacetone. Band identification is shown in Table 1. (a) Spectrum with no superheating (effectively azidoacetone subliming at 300 K). (b) Spectrum obtained after passage through superheater at 870 K. (c) Series of spectra obtained with superheater temperatures in the range 300−870 K. Bands in the region 1400−1000 cm^{-1} are shown with enhanced intensity in comparison with those between 2200 and 2000 cm^{-1}.

theorem to the SCF/6-31G* molecular orbital energies. Values computed at this 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[18,19] afforded much better agreement with the experimental VIEs, as was also the case for azidoacetic acid.

Inspection of Table 3 shows that the four-band maxima observed in the 9.0−11.0 eV ionization energy region cannot be assigned to four one-electron ionization processes on the basis of Koopmans' theorem and must be assigned to only three one-electron ionizations, with the second band of azidoacetone consisting of two vibrational components (at 10.34 and 10.65 eV) with a spacing, as averaged over 11 spectra, of (2500 ± 50) cm^{-1}. As the second highest occupied molecular orbital is weakly N−N−N antibonding in nature and the experimental N_3 stretching mode in the neutral molecule has been measured as 2108 cm^{-1} in this work, an increase of vibrational frequency of ≈400 cm^{-1} on ionization is reasonable.

Matrix Isolation Studies: Thermal Decomposition and Spectral Assignment. Figure 1a shows a typical nitrogen matrix ir spectrum obtained from a sample of $N_3CH_2COCH_3$ deposited from the vapor phase without superheating. The absorptions denoted by the asterisk (*) indicate the two most intense ir absorptions of matrix isolated H_2O and arise from minute traces

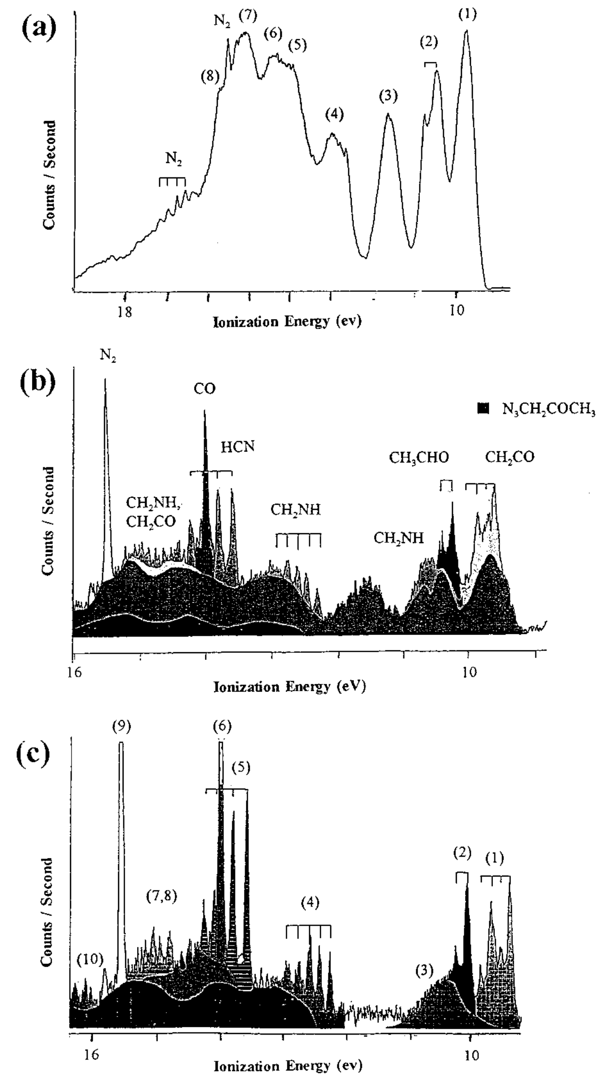


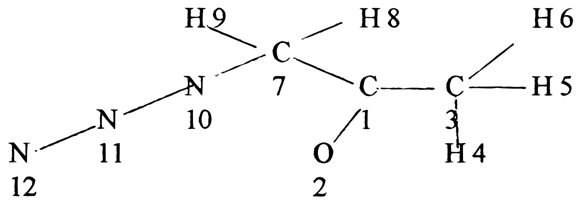
Figure 2. HeI photoelectron spectra recorded for azidoacetone at different stages of pyrolysis. (a) PE spectrum of the unpyrolyzed azidoacetone. Numbered bands identified in Table 3. (b) PE spectrum obtained on pyrolysis at a temperature of 700 K. (c) PE spectum obtained for complete pyrolysis at 800 K. Bands are identified as follows: (1), CH_2CO; (2), CH_3CHO; (3), CH_2NH; (4), CH_2NH; (5), HCN; (6), CO; (7 and 8), CH_2NH and CH_2CO; (9), N_2; (10), CH_2CO.

of water in the system. The most intense parent absorption consists of a central peak at 2117 cm^{-1} flanked by weaker shoulders, and this structure is shown more clearly in the uppermost trace of Figure 1c. This absorption arises from the N_3 unit, and its triplet appearance could perhaps be attributed to different conformers trapped in the matrix. Other prominent features may be noted at 1740, 1419, 1360, 1282, and 1170 cm^{-1} (bands B−F), all of which are very similar in position to those found in the neat liquid.

Figure 1b shows the spectrum obtained at a superheater temperature of 870 K. An intense feature is still present near 2100 cm^{-1}, but closer examination shows that this now appears as a doublet centered at ca. 2140 cm^{-1} and that all of the other features B−F have disappeared. Figure 1c shows the spectral changes observed over a range of superheater temperatures, and in particular, the growth of a doublet at 2142/2138 cm^{-1} at the expense of the parent azide band at 2117 cm^{-1}. These dramatic intensity changes near 2100 cm^{-1} are matched by equally significant changes at lower frequencies, notably in the range 1400−1000 cm^{-1}, and all of the significant bands identified in Figure 1 are listed in Table 1.

TABLE 2: Computed Structural Parameters of Azidoacetone at the Hartree−Fock MP2/6-31G* Level

Atom Numbering Scheme for Azidoacetone



Structural Parameters of Azidoacetone (MP2/6-31G*)

bond lengths	angstroms	bond angles	degrees
C1−O2	1.224	O2−C1−C3	123.24
C1−C3	1.510	C1−C3−H4	109.36
C3−H4	1.090	C1−C3−H5	111.08
C3−H5	1.095	H4−C3−H5	110.05
C3−H6	1.095	C1−C3−H6	109.50
C1−C7	1.528	O2−C1−C7	120.85
C7−H8	1.102	C3−C1−C7	115.90
C7−H9	1.094	C1−C7−H8	108.15
C7−N10	1.460	C1−C7−H9	110.24
N10−N11	1.249	C1−C7−N10	113.54
N11−N12	1.162	C7−N10−N11	115.84
		N10−N11−N12	170.81

TABLE 3: Comparison of Experimental and Computed Vertical Ionization Energies of Azidoacetone

band M. O.	exptl IE (eV)	Koopmans' theorem (eV)[a]	Koopmans' theorem × 0.9 (eV)
(1) 26	9.59	10.12	9.11
(2) 25	10.34	11.50	10.35
(2) 25	10.65		
(3) 24	11.53	12.46	11.21
(4) 23	13.03	13.69	12.32
(5) 22	14.04	15.49	13.94
(6) 21	14.42	15.74	14.16
(7) 20	15.13	16.60	14.94
(8) 19	15.84	17.19	15.47

[a] Obtained from a single point calculation at the HF/6-31G* level at the MP2/6-31G* geometry specified in Table 2.

Despite the complexity of these matrix ir spectra, many of the features which appear as a result of superheating can readily be assigned from previous studies.[11] Bands G and M indicate the formation of HCN, and CH_2NH is similarly unequivocally identified by at least five characteristic peaks, including L (Table 1). The bands at 2138 and 2142 cm^{-1} (H, I) showed parallel growth patterns over a wide range of conditions and were initially assigned to the same (unknown) species. However, the PES studies indicated the possible presence of both CH_2CO and CO as decomposition products, with the result that bands H and I could then be assigned to these different species with considerable confidence. CO in a nitrogen matrix has a characteristic absorption at 2138 cm^{-1},[20] and although ketene (CH_2CO) has not apparently been studied in a nitrogen matrix, prominent ir bands have been reported[21] in argon and oxygen matrices at 3062, 2142, and 1381 cm^{-1} (argon), and 3060, 2142, and 1382 cm^{-1} (oxygen), in excellent agreement with the bands assigned in this work.

A fifth pyrolysis product is identified as CH_3CHO as a result of PES evidence and supporting matrix experiments[22] on the pure material (Table 1), but it is evident from Figure 1c that at least three new bands P, Q, and R still remain to be assigned. As with all of the features produced on pyrolysis, the intensities of these bands are found to correlate well, and at this stage they must provisionally be assigned to the same species. The identity of this pyrolysis product remains unknown at the present time,

TABLE 4: Assignment of Bands Observed in the HeI Photoelectron Spectrum Recorded for Fully Pyrolyzed Azidoacetone

band[a]	vertical IE (eV)	assignment
(1)	9.63, 9.73, 9.91, 10.05	ketene first band 4 components
(2)	10.23, 10.38	acetaldehyde first band 2 components
(3)	10.62	methanimine first band
(4)	12.49	methanimine second band
(5)	13.62	hydrogen cyanide first band
(6)	14.01	carbon monoxide first band
(7,8)	ca. 14.7	ketene second band methanimine third band (unresolved)
(9)	15.58	nitrogen first band
(10)	ca. 16.1	ketene third band

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

and further experimental and theoretical work is in progress in an attempt to account for these bands. However, on the basis of mechanistic arguments (see below), we suggest that they could arise from the imine CH_2NCH_3.

Photoelectron Studies: Thermal Decomposition and Spectral Assignment. The He(I) photoelectron spectrum obtained for azidoacetone is shown in Figure 2a and the PE spectrum obtained upon partial pyrolysis is shown in Figure 2b. The temperature of the furnace under the conditions used for Figure 2b was approximately 700 K, as estimated from chromel−alumel thermocouple measurements. Figure 2c shows a He(I) photoelectron spectrum recorded for complete pyrolysis at a furnace temperature of approximately 800 K. Tabulated vertical ionization energies for the photoelectron bands in Figure 2c are shown in Table 4. Spectral calibration was achieved using the known ionization energies of nitrogen and carbon monoxide.[14]

The experimental He(I) photoelectron spectrum, shown in Figure 2c, is quite complex. Bands associated with molecular nitrogen are readily identifiable with vertical ionization energies of 15.57 and 16.98 eV.[14] Also, a sharp, intense band at 14.01 eV VIE is assigned to the first band of carbon monoxide.[14] The second band of carbon monoxide, not shown in Figure 2c, was visible in the experimental spectra but was partially overlapped by the second band of nitrogen. Two sharp features at 13.64 and 13.82 eV VIE in this figure are assigned to the first two components of the first band of hydrogen cyanide.[14] The most interesting part of the spectrum is between 9.0 and 11.0 eV where six sharp features and one broad band are seen. The four lowest ionization energy components are part of two vibrational progressions and are assigned to the first band of ketene at 9.64 eV VIE.[14] The sharp feature at 10.62 eV and the weaker feature at 10.44 eV are assigned to the first band of acetaldehyde.[23] The broad band at 10.62 eV VIE is associated with the vibrationally resolved band at 12.49 eV (VIE) (vibrational separation 1300 cm^{-1}). These bands are the first two bands of methanimine (CH_2NH).[5,8,24] Spectra recorded at temperatures between 300 and 800 K showed partial degrees of pyrolysis, but all spectra could be assigned to unpyrolyzed $N_3CH_2COCH_3$ or to CH_2CO, CH_3CHO, CH_2NH, CO, HCN, and N_2.

The minimum energy geometry of the possible imine intermediate $HNCHCOCH_3$ was computed at the MP2/6-31G* level, and VIEs were obtained by applying Koopmans' theorem to the orbital energies obtained at the 6-31G* level at the MP2/6-31G* optimized geometry. These calculations formed a basis for the prediction of the positions of the PES bands in this compound, but no bands that could possibly be associated with $HNCHCOCH_3$ were observed experimentally. Furthermore, the bands associated with CH_2NH, CH_3CHO, CH_2CO, HCN, CO, and N_2 all retained the same intensity ratios as the furnace temperature was changed.

Possible Mechanisms of Gas-Phase Thermal Decomposition of Azidoacetone. *Single-Step Processes.* From the results of the earlier study on azidoacetic acid,[11] it was anticipated that N_2, CH_2CO, and CH_2NH would be observed on pyrolysis, and these were indeed found, but the observation of CH_3CHO and CO was not anticipated. In addition, HCN was formed in much greater abundance, relative to the other decomposition products, and at lower temperatures compared with the pyrolysis of azidoacetic acid, and its appearance was found to correlate with that of the other decomposition products. This suggests that this is a primary decomposition product, whereas in the pyrolysis of azidoacetic acid we have presented evidence[11] that HCN was observed only at higher temperatures (>850 K) as a decomposition product of methanimine (CH_2NH). If the initial fragmentation of azidoacetone to produce N2 and HCN is considered, it is clear, from mass balance, that acetaldehyde could also be formed, and two overall reactions may therefore be taking place:

$$CH_3COCH_2N_3 \rightarrow H_2C{=}C{=}O + HN{=}CH_2 + N_2 \quad (1)$$

$$\rightarrow CH_3CHO + HCN + N_2 \quad (2)$$

If HCN were produced primarily as a decomposition product of CH_2NH and not via reaction 2, molecular hydrogen should also be produced. No hydrogen was observed during these experiments, but it is known that H_2 has a relatively low photoelectron cross-section at the He(I) photon energy and it would not be observed in the ir. Failure to detect its presence during these experiments is not therefore completely conclusive.

In an attempt to demonstrate that these two separate reaction channels exist, experiments were carried out to try and favor one channel over the other. Two variables were altered, namely the pyrolysis time and the pyrolysis temperature. In the PES studies, the reaction time scale was extended by moving the furnace higher above the photon beam (from approximately 1 to 4 cm). This had the effect of reducing the overall photoelectron signal, but the relative intensities of the ketene and acetaldehyde first photoelectron bands remained constant within experimental error. Also, a higher furnace temperature was used (1150 K) to try and favor one reaction channel over the other. However, it was found that the relative amounts of ketene and acetaldehyde were not altered on increasing the furnace temperature to 1150 K. Parallel experiments in the matrix ir studies led to the same conclusion. Hence, the branching ratio between the two reaction channels 1 and 2 could not be altered by changing the experimental conditions.

One final observation that was difficult to rationalize was that the photoelectron intensity and ir band intensity of the CO formed were both high, and that CO and N_2 both appear, together with the other decomposition products, at the onset of pyrolysis. If CO were formed as a decomposition product of either acetaldehyde or ketene, it would be expected that as the CO photoelectron intensity increases, the intensity of bands due to acetaldehyde or ketene would decrease. This *was not found to be the case.* The relative intensities of the carbon monoxide, acetaldehyde, and ketene photoelectron bands remained approximately constant as the experimental conditions changed, and precisely the same conclusion was evident from the matrix ir studies. The only way in which these observations can be rationalized is to postulate a third reaction channel in which CO is a primary product. From mass balance considerations, this can be achieved in a number of ways, e.g.,

$$CH_3COCH_2N_3 \rightarrow CO + N_2 + \text{“}C_2NH_5\text{”} \quad (3a)$$

with one possibility being

$$\rightarrow CO + N_2 + HCN + CH_4 \quad (3b)$$

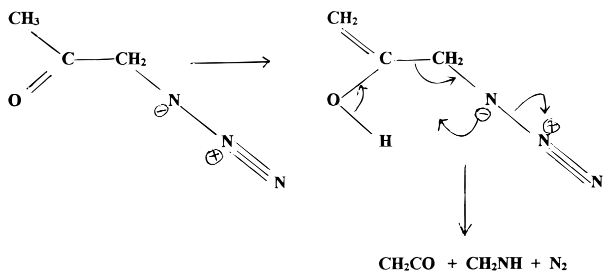
As already described, HCN, CO, and N_2 are observed as decomposition products with constant relative band intensities. Methane is known to have a broad photoelectron spectrum in the ionization energy region 12.5−14.5 eV[14] and would therefore be difficult to detect as it would be masked by other more structured bands (see Figures 2b and 2c). However, if reaction 3b were a significant pathway, one would expect to find evidence for matrix isolated CH_4 in the ir experiments.

The ir spectrum of methane in a nitrogen matrix has been studied relatively recently by Nelander.[25] The two ir allowed T_2 modes each appear as prominent doublets, accompanied by weaker features, and these doublets lie at 3027.4/3031.4 cm^{-1} (C−H stretch) and 1306.3/1307.3 cm^{-1} (H−C−H bend). Careful examination of our ir spectra in light of this possible product showed that there were no prominent bands at either of these positions, although a weak feature was present at 1305 cm^{-1} which grew on pyrolysis in parallel with the product bands discussed above. Its intensity was always considerably less than that of the CO band at 2138 cm^{-1}.

Reaction 3 therefore remains most probable, but confirmation would be dependent on supporting PES and matrix ir spectra on an authentic sample of the second product “C_2NH_5”. Work is currently in progress to explore the various geometries and energies expected for molecules of this stoichiometry in an attempt to justify reaction 3. One probable candidate would be the substituted imine CH_2NCH_3, and although the PES studies found no evidence for this product, there remain several unassigned ir bands from the pyrolyzed product which might be assigned to such a species.

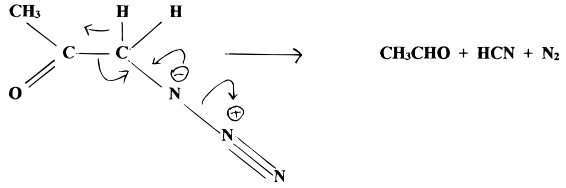
On the basis of the experimental evidence provided by PES and matrix isolation infrared experiments, together with the results of ab initio calculations on both this system and on azidoacetic acid [11], we conclude that if single-step processes are operating, then the decomposition of azidoacetone must proceed via at least three separate reaction channels.

Reaction 1:



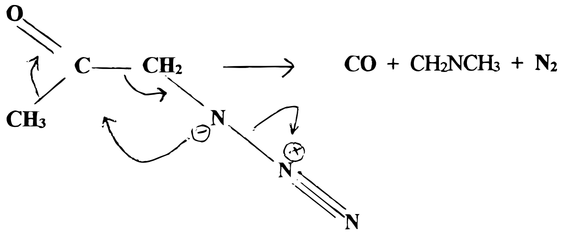
After an initial keto−enol transformation, this reaction is precisely analogous to the formation of CO_2 and CH_2NH (and N_2) proposed previously[11] for the azidoacetic acid system. Molecular N_2 is evolved at the same time as a hydrogen atom is transferred from the other end of the molecule to the remaining nitrogen atom, giving rise to a simultaneous generation of the three products.

Reaction 2:



Here, the product species CH_3CHO and HCN can be realized by single-stage hydrogen atom transfer to generate all of the reaction products simultaneously.

Reaction 3:

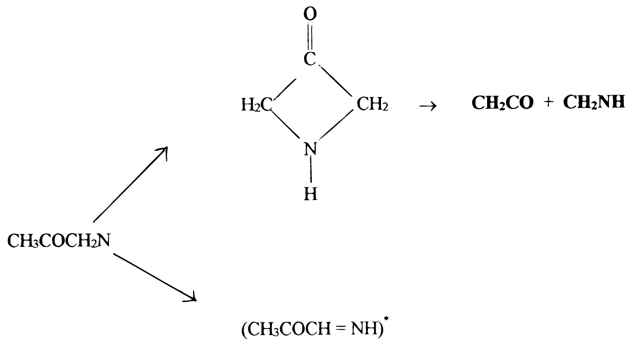


Carbon monoxide could be generated by a concerted route directly from the azide.

Multistep Processes − Radical Pathways. In addition to the single-step mechanisms discussed above, one may also envisage multistep processes in which the initial step is rate-determining. Previous work[11] has indicated that nitrene formation is a feasible initial reaction:

$$CH_3COCH_2N_3 \rightarrow CH_3COCH_2N + \mathbf{N_2}$$

This could then either decompose via a (strained) cyclic intermediate into ketene and methanimine or rearrange to form the imine $CH_3COCHNH$



This imine could then act as the source of a sequence of radical chain reactions which produce all of the remaining observed products:

Initiation: $(CH_3COCHNH)^* \rightarrow CH_3CO + HCNH$

Propagation: $CH_3CO \rightarrow CH_3 + \mathbf{CO}$

$HCNH \rightarrow \mathbf{HCN} + H$

$CH_3COCHNH + H \rightarrow \mathbf{CH_3CHO} + HCNH$

$\rightarrow \mathbf{CH_2NH} + CH_3CO$

Termination: *(e.g.)* $H + H \rightarrow H_2$

$CH_3 + H \rightarrow CH_4$

Summary and Conclusions

Azidoacetone has been synthesized and characterized by a range of techniques, including UV photoelectron spectroscopy and matrix isolation infrared spectroscopy. The He(I) photoelectron spectrum of azidoacetone consists of nine bands in the 9.0−21.0 eV ionization energy range. The second band shows two resolved vibrational components with a separation of (2500 ± 50) cm^{-1}. Inspection of the character of the second highest occupied molecular orbital suggests that it is weakly N_3 antibonding in character. The experimental value for the N_3 stretching mode in neutral azidoacetone has been measured as 2109 cm^{-1} in this work. Hence, ionization from an antibonding orbital results in an increase in vibrational frequency in the ionic state as expected. Ab initio molecular orbital calculations have been performed on azidoacetone, and application of Koopmans' theorem to the computed orbital energies yields vertical ionization energies which show adequate correlation with the experimental values. The characters of the four uppermost occupied molecular orbitals in this molecule are essentially N_3 nonbonding, N_3 weakly antibonding, O2p (lone pair), and π(CO) bonding in nature, as derived from the SCF molecular orbitals at the HF/6-31G* level.

Two experimental methods, matrix isolation infrared spectroscopy and real-time ultraviolet photoelectron spectroscopy, together with the results of ab initio molecular orbital calculations, have been used to explore the thermal decomposition of azidoacetone over a range of pyrolysis temperatures. Although the imine $CH_3COCH{=}NH$ was not detected, the reactive species ketene (CH_2CO) and methanimine (CH_2NH) were observed in high yield, in addition to the more stable molecules nitrogen, carbon monoxide, acetaldehyde, and hydrogen cyanide. The changes in relative band intensities of these products as a function both of time and pyrolysis temperature indicate several simultaneous decomposition routes, possibly involving radical intermediates. However, the lack of any evidence for the formation of CH_4 or the methyl radical, raises the possibility that a seventh, as yet unidentified reaction product may also be present. Further experimental and theoretical work is in progress in an attempt to confirm this and to estimate the activation energies associated with these proposed reaction schemes.

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