Mass Spectrometry of Azomethane[1]

Z. Prášil and W. Forst[2]

Contribution from the Department of Chemistry, Université Laval, Quebec 10, Canada. *Received December 22, 1967*

Abstract: The conventional mass spectrum of azomethane with 75-V electrons, as well as the appearance potentials of ions at masses 15, 28, 43, and 58, has been redetermined. A high-resolution mass spectrum has shown peaks at masses 14, 27, 28, and 29 to be composite. This information is used to trace the decomposition mechanism of the azomethane ion. It proceeds principally by simple bond ruptures, $CH_3N_2CH_3^+ \longrightarrow CH_3^+$, $CH_3N_2CH_3^+ \longrightarrow CH_3N_2^+$, and by the more complicated rearrangement process $CH_3N_2CH_3^+ \longrightarrow CH_2N^+$. The three fragment ions plus the parent ion account for 85% of the mass spectrum. Three appearance potentials were found at mass 28, corresponding to the three species contributing to this peak (CH_2N^+, $C_2H_4^+$, N_2^+). Two appearance potentials were found for CH_3^+ at mass 15, the lower corresponding to formation of CH_3^+ directly from the azomethane ion, and the higher to formation of CH_3^+ from $CH_3N_2^+$. Within experimental error, the new appearance potential data are in good agreement with thermochemical data from other sources, notably the activation energy for the pyrolysis of azomethane. Previous appearance potential data for ions at masses 15 and 43 are shown to be in error due to instrumental effects.

The mass spectrum of azomethane has been determined a number of times in the past[3-6] in order to obtain the fragmentation pattern for analytical purposes. Gowenlock, Majer, and Snelling[7] (GMS) determined appearance potentials of some of the ions in the azomethane mass spectrum and used this information for thermochemical calculations. We have examined the azomethane mass spectrum in somewhat more detail in order to obtain information about the decomposition mechanism of the azomethane ion and its implications for the thermochemistry of azomethane.

Experimental Section

Two samples of azomethane were prepared by the method of Renaud and Leitch[8] and were purified by gas chromatography. This procedure removed all organic impurities, in particular CH_3Cl. The only impurities likely to be present in the sample actually introduced into the mass spectrometer were small amounts of water vapor, air, and carbon dioxide, the latter probably originating from the helium carrier gas used in the gas chromatograph. The contributions of these impurities to the azomethane mass spectrum were ~2% at mass 18 (H_2O^+), ~1% of CO^+ (from CO_2^+), and about the same amount of N_2^+ from air at mass 28, 0.2% at mass 32 (O_2^+ from air), and ~10% at mass 44 (CO_2^+), all relative to peak 15 = 100%. The azomethane mass spectrum shown in Table I was corrected for the contribution of these impurities.

The mass spectra were taken with a Hitachi Perkin-Elmer mass spectrometer at 75 V; high-resolution runs were done on the same instrument with suitably reduced slit widths, which increased the resolution to about 2500. Appearance potentials were obtained from a semilogarithmic plot of ionization efficiency curves *vs.* energy, with Xe^+ as reference standard. The distance between practically parallel linear parts of these curves was read at 0.1% of peak height, where 100% corresponds to peak height at 30 eV. Since electrons with a thermal spread of energies were used, the estimated accuracy of these measurements is about ±0.3 eV.

Results

Table I summarizes the results of the various determinations extant of the mass spectrum of azomethane (all normalized to 100). Only the most important peaks are listed, but they account for over 95% of the whole mass spectrum. It is worthwhile to mention that among the minor peaks omitted in Table I is a metastable peak we have observed at mass 31.9 (about 0.1% of the peak at mass 15).

In a general way, there is a fairly good agreement among the various azomethane mass spectra except that Gowenlock and Majer's[5] shows an unusually low abundance of higher mass peaks and a very high abundance of peak 15. (The same is true to a lesser extent of the mass spectrum of Stief and Ausloos.[4]) This markedly higher abundance of peak 15 is reflected in the significantly lower appearance potential (AP) found for this peak by GMS as compared with our results (*cf.* Table I). On the other hand, the two determinations of the AP of peak 43 are only 0.5 eV apart and identical results are obtained for the AP of the parent ion at mass 58 (except for our less optimistic estimate of the error limits).

GMS did their work on the MS-2 mass spectrometer. This machine has an enclosed ion source, and the filament region cannot be readily pumped out.[9] As a result, pyrolysis occurs on the filament, which can readily account for the discrepancy between our results and theirs.

At mass 15, GMS were getting a significant contribution from methyl radicals formed by pyrolysis; since the ionization potential (IP) of CH_3 (9.83 eV[10]) is of necessity lower than the AP of CH_3^+ formed from the molecular ion of azomethane, the AP of peak 15 determined under such conditions will yield an artificially low result for the AP of CH_3^+ formed from $CH_3N_2CH_3^+$, and the relative abundance of the peak 15 will be unusually high. The fragment at mass 43 corresponds to $CH_3N_2^+$. The neutral counterpart (CH_3N_2) will also be formed by pyrolysis on the filament, but according to

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[1] Work done with financial assistance from the National Research Council of Canada.

[2] Author to whom correspondence should be addressed.

[3] R. D. McCoy, Ph.D. Thesis, University of Oregon, 1956, p 23.

[4] L. J. Stief and P. Ausloos, *J. Phys. Chem.*, 65, 877 (1961).

[5] B. G. Gowenlock and J. R. Majer, University of Birmingham, personal communication, 1965.

[6] F. P. Lossing, National Research Council, personal communication, 1965.

[7] B. G. Gowenlock, J. R. Majer, and D. R. Snelling, *Trans. Faraday Soc.*, 58, 670 (1962).

[8] R. Renaud and L. C. Leitch, *Can. J. Chem.*, 32, 545 (1954).

[9] We are grateful to Professor A. G. Harrison, University of Toronto, for this information.

[10] R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 301 ff.

Table I. Conventional and High-Resolution Mass Spectra of Main Peaks in Azomethane Mass Spectrum and Their Appearance Potentials

	Abundances (normalized to 100)										
				Lossing[6]		This work		High-resolution mass spec		IP and AP, eV	
				Hitachi RMU6-D, 75 eV							
m/e	McCoy[8] 70 eV	Ausloos[4] CEC 21-101, 70 eV	Gowenlock[5] MS-2, 70 eV	*a*	*b*	*a*	*b*	Species	%	Gowenlock[5]	This work
14	3.10	4.72	...	3.20	2.58	3.17	3.23	CH_2^+	97		
								N^+	3		
15	43.23	47.29	49.99	40.97	39.58	42.02	42.97	CH_3^+	100	11.5	12.2 ± 0.3[c]
26	...	0.77	2.76	0.77	0.59	0.67	0.62	$C_2H_2^+$	100		
27	5.97	6.05	8.46	5.74	4.88	5.18	5.01	$C_2H_3^+$	30		
								HCN^+	70		
28	19.67	13.48	17.50	16.47	13.79	13.99	13.57	$C_2H_4^+$	5		12.9 ± 0.3
								CH_2N^+	86		14.7 ± 0.3
								N_2^+	9		16.3 ± 0.3
29	...	0.85	1.15	1.05	1.07	0.87	0.88	$C_2H_5^+$	50		
								CH_3N^+	50		
30	...	1.27	1.67	1.86	1.88	1.59	1.55	$C_2H_6^+$	100		
42	2.39	2.63	3.59	2.95	3.30	2.95	2.94	$CH_2N_2^+$	100		
43	15.39	16.13	8.78	18.31	20.79	18.55	18.29	$CH_3N_2^+$	100	9.0	9.5 ± 0.3
57	...	0.72	1.05	0.93	1.15	1.08	1.04	$C_2H_5N_2^+$	100		
58	10.25	6.10	5.05	7.74	10.39	9.94	9.90	$C_2H_6N_2^+$	100	8.65	8.65 ± 0.2

[a] Sample I. [b] Sample II. [c] There is a higher AP at 15.75 ± 0.3 eV.

the commonly accepted thermochemical argument (*cf.* further below) the decomposition of this neutral fragment is exothermic and hence very rapid; thus only few CH_3N_2 fragments will survive long enough to diffuse from the filament region into the ionization chamber and so ultimately contribute to ions of mass 43. The majority of the latter will be therefore "legitimate" $CH_3N_2^+$ fragments formed from $CH_3N_2CH_3^+$. Since obviously $IP(CH_3N_2) < AP(CH_3N_2^+$ from azomethane ion), GMS's experimental conditions should yield an AP for mass 43 that, although lower, should be considerably closer to the "true" AP than in the case of mass 15, and this is exactly what is observed (*cf.* Table I). Finally, regardless of pyrolysis on the filament, GMS should have obtained the correct result for the IP at mass 58, but pyrolysis should have caused its relative abundance to be lower than normal. Since the ion of mass 43 is formed practically only from ion 58, the relative abundance of ion 43 in GMS's experiments should have been likewise lower than normal. All these conclusions are borne out by the results shown in Table I.

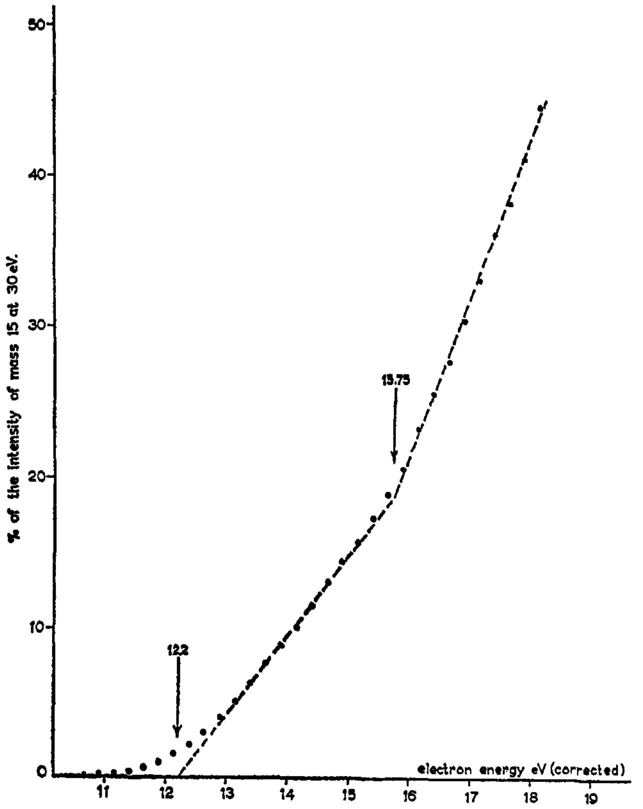

Figure 1. Ionization efficiency curve at m/e 15.

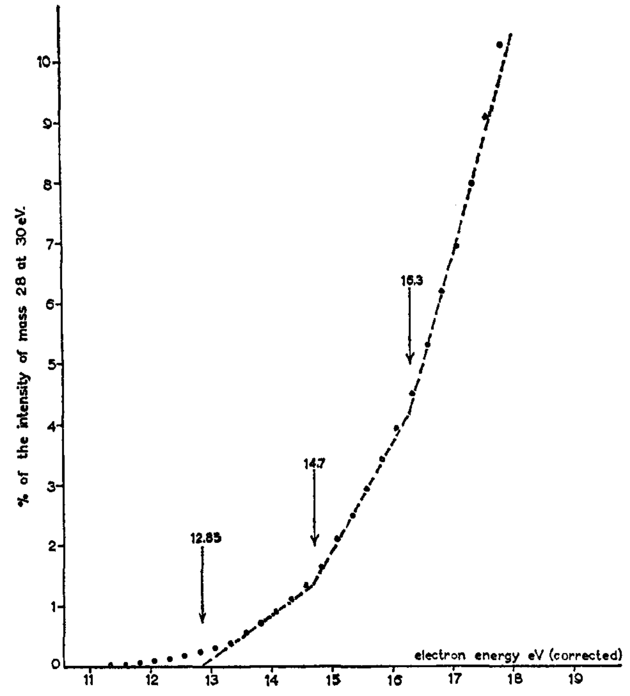

Figure 2. Ionization efficiency curve at m/e 28.

Figures 1 and 2 present the ionization efficiency curves of peaks 15 and 28, respectively. The distinct breaks in these curves are discussed below.

Decomposition Mechanism of the Azomethane Ion

The highest occupied orbital in the neutral azomethane molecule is the n_+ orbital formed essentially from the nonbonding orbitals on the nitrogens;[11] therefore the electron lost on ionization will be removed from this orbital; *i.e.*, the charge will be located principally on the nitrogens. The weakest bond in azomethane is the C–N bond, and this will be roughly true also of the azomethane ion since we would not expect the nonbonding orbitals from which the electron was lost to be involved in an important way in the bonding between nitrogen and carbon. We can therefore anticipate that the fragmentation requiring the least energy will be a process where this weakest bond is broken and the charge remains on the nitrogens.

$$CH_3N_2CH_3^+ \longrightarrow CH_3N_2^+ + CH_3 \qquad (1)$$

This process gives rise to the metastable peak we have observed at mass 31.9. Table I shows that the fragment $CH_3N_2^+$ does have the lowest appearance potential, but it is only 0.85 eV higher than the ionization potential of azomethane. Since the dissociation energy of the C–N bond in neutral azomethane is ~2.28 eV (*cf.* further below), it is obvious that the C–N bond energy in ionized azomethane is substantially lower, so that the process of ionization affects fairly profoundly the entire azomethane molecule and it is only a very rough approximation to say that the charge is located principally on the nitrogens. Theoretical calculations[11] on the hypothetical diimide HN=NH show in fact that the $n_\pm$ molecular orbital wave functions have nonzero H-atom contribution.

There are two ways in which $CH_3N_2^+$ can, in principle, decompose further.

$$CH_3N_2^+ \longrightarrow CH_3^+ + N_2 \qquad (2)$$

$$CH_3N_2^+ \longrightarrow N_2^+ + CH_3 \qquad (3)$$

Since IP(N_2) = 15.58 eV,[10] and IP(CH_3) = 9.83 eV,[10] process 3 will be more endothermic than process 2 by 5.75 eV, and their activation energies will differ by a similar order of magnitude, so that process 3 is unlikely compared with (2). This is essentially what could be deduced from Stevenson's rule.[12] In agreement with these considerations, we have found very little N_2^+ at mass 28 (see Table I). However, we cannot exclude the possibility that the N_2^+ might also be formed in the one-step process $CH_3N_2CH_3^+ \rightarrow N_2^+ + 2CH_3$.

It is useful to note that $CH_3N_2^+$ is isoelectronic with CH_3CN so that this fragment will be particularly stable. In agreement with this, peak 43 is the second largest peak in the mass spectrum of azomethane (Table I), unlike the thermal decomposition of azomethane[13] where the fragment CH_3N_2 decomposes almost immediately into CH_3 and N_2. In view of the high stability of $CH_3N_2^+$, one might wonder if process 2 is the only principal pathway for the formation of CH_3^+ which is the most abundant species in the mass spectrum of azomethane (Table I). It is well known that the dissociation energies (*D*) of isoelectronic diatomic species are nearly the same; for instance, $D(N_2^+) \sim 8.8$ eV,[14] while D(C–N) ~ 8.2 eV.[15] Using these correlations as a very rough guide, and fully aware that the extrapolation may be quantitatively uncertain, it can be assumed that the energy required to dissociate $CH_3N_2^+$ into $CH_3^+ + N_2$ will be of the same order of magnitude as the dissociation energy of the C–C bond in CH_3CN, *i.e.*, 4.5 eV,[16] plus, loosely speaking, whatever energy is required to transfer the charge from the nitrogens in $CH_3N_2^+$ to CH_3^+. Thus the appearance potential of CH_3^+ from $CH_3N_2^+$ is likely to be some 4 or 5 eV higher than AP($CH_3N_2^+$), *i.e.*, about 14.5 eV. The ionization efficiency curve for CH_3^+ (Figure 1) yields one AP (CH_3^+) = 12.2 eV and another, higher AP(CH_3^+) = 15.75 eV. We suppose therefore that the higher AP is due to process 2; the lower energy pathway can be only

$$CH_3N_2CH_3^+ \longrightarrow CH_3^+ + CH_3N_2 \longrightarrow CH_3^+ + CH_3 + N_2 \qquad (4)$$

Since necessarily IP(CH_3N_2) < AP($CH_3N_2^+$), it follows that IP(CH_3N_2) < IP(CH_3), and the simultaneous occurrence of processes 1 and 4 constitutes a violation of Stevenson's rule, but this is understandable because of the great disparity between the stabilities of $CH_3N_2^+$ and CH_3N_2. The actual contribution of processes 2 and 4 to the measured total abundance of CH_3^+ produced by 75-eV electrons depends on the distribution function for the internal excitation energy of the molecular ion. In the two cases (propane and butane) where this function was determined experimentally,[17] it turned out that the function had an appreciable value only up to 4 or 5 eV above threshold and dropped asymptotically to zero at higher energies. In azomethane, CH_3^+ begins to be formed (assuming our conclusions are correct) by process 4 at 12.2–8.65 = 3.55 eV above threshold, and by process 2 at 15.75–8.65 = 7.10 eV above threshold. If the azomethane distribution function has the same general shape as in the two cases cited, most of the CH_3^+ in the 75-eV mass spectrum of azomethane would be formed by process 4.

The presence of a peak at mass 57 implies the formation of fragment $CH_3N_2CH_2^+$ by the process

$$CH_3N_2CH_3^+ \longrightarrow CH_3N_2CH_2^+ + H \qquad (5)$$

This fragment can then decompose in two ways

$$CH_3N_2CH_2^+ \longrightarrow CH_3^+ + CH_2N_2 \qquad (6)$$

$$CH_3N_2CH_2^+ \longrightarrow CH_2N_2^+ + CH_3 \qquad (7)$$

The fragments CH_2N_2 and $CH_2N_2^+$ very likely have a linear carbon–nitrogen skeleton and would thus be essentially neutral and ionized diazomethane, respectively. Since IP(CH_2N_2) = 9.03 eV,[18] while IP(CH_3) = 9.83 eV, process 7 will be more probable and only few ionized methyl radicals would be formed in process 6. The diazomethane fragment can then decompose further according to

$$CH_2N_2^+ \longrightarrow CH_2^+ + N_2 \qquad (8)$$

Again, since IP(CH_2) = 10.39 eV[19] and IP(N_2) = 15.58 eV, CH_2 will be the charged species rather than nitrogen,

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[11] M. B. Robin, R. R. Hart, and N. A. Keubler, *J. Am. Chem. Soc.*, **89**, 1564 (1967).

[12] D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

[13] W. Forst and O. K. Rice, *Can. J. Chem.*, **41**, 562 (1963).

[14] K. E. Shuler, T. Carrington, and J. C. Light, *Appl. Opt., Suppl.*, 2, 81 (1965).

[15] H. B. Gray, "Electrons and Chemical Bonding," W. A. Benjamin, Inc., New York, N. Y., 1964, p 83.

[16] C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

[17] W. A. Chupka and M. Kaminsky, *J. Chem. Phys.*, **35**, 1991 (1961).

[18] G. S. Paulett and R. Ettinger, *ibid.*, **39**, 825 (1963).

[19] G. Herzberg, *Can. J. Phys.*, **39**, 1511 (1961).

and mass 14 (CH_2) is indeed the largest peak in the diazomethane mass spectrum.[18] In the mass spectrum of azomethane, peaks 57 ($CH_3N_2CH_2^+$), 42 ($CH_2N_2^+$), and 14 (CH_2^+) constitute only minor components, in agreement with the fact that the C–H bond rupture in process 5 is energetically less favorable than C–N bond breakage in processes 1, 2, or 4.

A process that is even less energetically favorable is the N–N bond rupture

$$CH_3N_2CH_3^+ \longrightarrow CH_3N^+ + CH_3N \tag{9}$$

A peak at mass 29 is indeed found in the azomethane mass spectrum (Table I), but, as expected, it is of very low intensity and the high-resolution run revealed that only one-half of it corresponds to CH_3N^+, the remainder being $C_2H_5^+$.

No simple bond rupture can account for the peak at mass 28, the third most important peak in the azomethane mass spectrum, unless it is N_2^+. The high-resolution mass spectrum reveals that peak 28 actually consists of three components (Table I), the most important of which is CH_2N^+. Figure 2 shows the ionization efficiency curve for mass 28 near threshold. Three distinct appearance potentials can be discerned, corresponding to the three components of peak 28; the assignment was confirmed by taking the high-resolution mass spectrum near threshold.

Thus the third most important species in the mass spectrum of azomethane is CH_2N^+. Clearly some sort of fairly drastic rearrangement of the azomethane ion is necessary to produce this kind of fragment, which is not likely to be formed from CH_3N^+ whose abundance is negligible. Müller and Rundel[20] have found that in ether solution azomethane reacts with $LiCH_3$ as if present in the tautomeric form $CH_2{=}NNHCH_3$. Presumably the excited azomethane ion can rearrange to $CH_3NHN{=}CH_2^+$ which then decomposes according to

$$CH_3NHN{=}CH_2^+ \longrightarrow CH_2N^+ + NHCH_3 \tag{10}$$

It seems reasonable that the fragment having the multiple bond should be the charged species; in agreement with this, the high-resolution mass spectrum shows no $HNCH_3^+$ at mass 30 (Table I).

The ion CH_2N^+ formed in (10) could then decompose further to give HCN^+.

$$CH_2N^+ \longrightarrow HCN^+ + H \tag{11}$$

Since IP(H) = 13.59 eV,[10] and IP(HCN) = 13.73 eV,[10] the charge should be located on the H atom. However, the difference between the two ionization potentials is small enough to make it reasonable to suppose that process 11 could nevertheless produce appreciable amounts of HCN^+. (No H^+ was found in the azomethane mass spectrum.) If this reasoning is correct, the azoethane ion, for example, should decompose according to

$$C_2H_5NHN{=}CHCH_3^+ \longrightarrow CH_3CHN^+ + NHC_2H_5$$

followed by

$$CH_3CHN^+ \longrightarrow CH_3CN^+ + H$$

where there can be little doubt about CH_3CN^+ as the charged species since IP(CH_3CN) = 12.52 eV.[16] One would therefore expect peaks at masses 42 and 41 to be fairly important in the mass spectrum of azoethane. This has been in fact found by Clark.[21] It is impossible to exclude completely the direct formation of HCN^+ from the azomethane parent ion (or the direct formation of CH_3CN^+ from the azoethane parent ion) in a more drastic rearrangement process

$$CH_3N_2CH_3^+ \longrightarrow HCN^+ + CH_3NH_2 \tag{12}$$

$$CH_3CH_2N_2CH_2CH_3 \longrightarrow CH_3CN^+ + CH_3CH_2NH_2 \tag{13}$$

Since the ionization potentials of the product alkylamines are much lower than those of HCN^+ and CH_3CN^+ [IP(CH_3NH_2) = 8.97 eV,[10] IP($C_2H_5NH_2$) = 8.86 eV[10]], the amines should be the charged species and (12) and (13) should not occur as written, unless HCN^+ and CH_3CN^+ do not have the structure of hydrocyanic acid and methyl cyanide, respectively, and possess, in addition, lower ionization potentials. This question cannot be decided with the information on hand. We might mention in this connection that in more complicated organic nitrogen-containing compounds, such as arylsulfonylhydrazones[22] and aniline,[23] HCN (or HNC) is eliminated as a *neutral* fragment, presumably because of a lower ionization potential of the remaining large fragment.

Another drastic rearrangement process would be the direct formation of the diazomethane ion in the process

$$CH_3N_2CH_3^+ \longrightarrow CH_2N_2^+ + CH_4 \tag{14}$$

Because of the high ionization potential of methane [IP(CH_4) = 12.98 eV[10]], there is little doubt that $CH_2N_2^+$ would be the charged species. If the configuration of the azomethane ion is *trans*, as in the neutral molecule, reaction 14 would probably require a *trans–cis* isomerization as a first step in order to facilitate the formation of CH_4. It is claimed[24] that the *trans* → *cis* isomerization of azomethane in solution takes place photochemically at 3650 Å (but not at 3430 Å), which implies a barrier height hindering internal N–N rotation of some 3.4 eV; by comparison, the barrier height in ethylene is 2.66 eV.[25] A barrier of this order of magnitude would presumably render process 14 energetically unfavorable compared with 7. However, it is by no means certain that the barrier height is the same in the ion and in the molecule; in fact, there are reasons to believe that in the ion it might be considerably less.[26] In the absence of appearance potential measurements at mass 42 the question whether $CH_2N_2^+$ is formed by process 7 or 14 or both remains open.

The formation of the ethane ion at mass 30 in the azomethane mass spectrum represents no doubt another sort of rearrangement process

$$CH_3N_2CH_3^+ \longrightarrow C_2H_6^+ + N_2 \tag{15}$$

It is interesting in this connection that molecular elimination of ethane has been recently detected in the photolysis of azomethane.[27,28] Those ethane ions

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[20] E. Müller and W. Rundel, *Chem. Ber.*, **90**, 1307 (157).

[21] W. D. Clark, Ph.D. Thesis, University of Oregon, 1958, p 17.

[22] A. Bhati, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc., C*, 358 (1966).

[23] P. N. Rylander, S. Meyerson, E. L. Eliel, and J. D. McCollum, *J. Am. Chem. Soc.*, **85**, 2723 (1963).

[24] R. F. Hutton and C. Steel, *ibid.*, **86**, 745 (1964).

[25] B. S. Rabinovitch, J. E. Douglas, and F. S. Looney, *J. Chem. Phys.*, **20**, 1807 (1952).

[26] R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

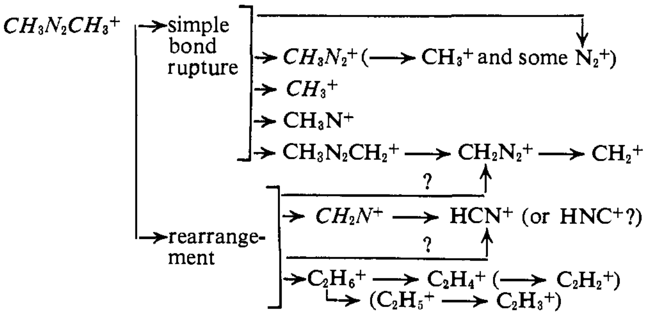
[27] R. E. Rebbert and P. J. Ausloos, *J. Phys. Chem.*, 67, 1925 (1963).

[28] S. Toby and J. Nimoy, *ibid.*, **70**, 867 (1966).

which contain sufficient excitation energy will decompose further, yielding mostly $C_2H_4^+$ which is the most important fragment in the mass spectrum of ethane.[29,30] Other, less abundant fragments attributable to the decomposition of the ethane ion are $C_2H_5^+$, $C_2H_3^+$, and $C_2H_2^+$, all of which are in fact present as minor constituents in the mass spectrum of azomethane (Table I). CH_3^+ is only a very minor constituent of the ethane mass spectrum, so that $C_2H_6^+$ produced in reaction 15 will make only a negligible contribution to peak 15 of the azomethane mass spectrum.

In summary, the principal modes of decomposition of the azomethane ion can be represented by Scheme I,

Scheme I



where the species that contribute more than 5% to the total mass spectrum are in italics and minor decomposition pathways are shown in parentheses. All told, the four italicized species represent about 85% of the total mass spectrum.

Thermochemistry of Azomethane Decomposition

Following GMS, we will define the first and second bond dissociation energies, D_1 and D_2, as the endothermicities of reactions a and b, respectively. We will

$$CH_3N_2CH_3 \longrightarrow CH_3 + CH_3N_2 \quad (a)$$

$$CH_3N_2 \longrightarrow CH_3 + N_2 \quad (b)$$

also use their value $D_1 + D_2 = 21$ kcal/mole $= 0.91$ eV. The most recent results on the thermal decomposition of azomethane[31] give for the critical energy $E_a = 18{,}374$ cm^{-1} $= 2.28$ eV. Very likely E_a measures the activation energy of (a); assuming, in addition, that the activation energy of the back-reaction

$$CH_3 + CH_3N_2 \longrightarrow CH_3N_2CH_3 \quad (a')$$

is small, as would be reasonable for a reaction between two radicals, we will have $E_a \simeq D_1$, and hence $D_2 \sim -1.37$ eV, so that process b is exothermic.

One of the referees has remarked that compared with $D(CH_3\text{-}NH_2) \sim 3.5$ eV (80 kcal/mole), our $D_1 = 2.28$ eV implies that (i) the CH_3N_2 radical has a large delocalization energy, or (ii) we must have $D_1 > E_a$ and hence there must be a large activation energy for process a′. Since neither of these possibilities can be easily explained away, there appears to be a difficulty about the C–N bond dissociation energy in azomethane. It seems to us, however, that methylamine may be a poor choice for a reference molecule, since the bonding is different: in CH_3NH_2 the nitrogen can be thought of as sp^3 hybridized, while in azomethane the hybridization is sp^2. In addition, we are not at all sure that the "other" half of the molecule can be ignored, *i.e.*, the fact that in methylamine the nitrogen is bonded to two hydrogens, while in azomethane it is bonded to NCH_3. For all these reasons we are inclined to think that methylamine and azomethane are not quite comparable molecules and that it might be unwise to compare directly their C–N bond dissociation energies (witness the difference in D(C–N) for neutral and ionized azomethane mentioned earlier in this paper).

Taking the lower of the two measured AP(CH_3^+)'s as that of methyl ions formed in reaction 4, for reasons discussed in the previous section, we should have

$$AP(CH_3^+) \simeq IP(CH_3) + D_1$$

provided the activation energy of the reverse process

$$CH_3^+ + CH_3N_2 \longrightarrow CH_3N_2CH_3^+ \quad (4')$$

is small, which is likely to be the case for a reaction between a radical ion and a radical. With IP(CH_3) = 9.83 eV and $D_1 = 2.28$ eV, the measured appearance potential of CH_3^+ should be 12.11 eV; experiment gives 12.2 ± 0.3 eV, so that the two values are identical within experimental error. The uncertainty in the experimental value would at the same time take care of any small activation energy for the reverse process a′ or 4′ or both. It should be noted that their smaller measured AP(CH_3^+) forced GMS to assume that the activation energy of (a′) is 10–20 kcal/mole, which is inordinately large for this type of process.

By a similar argument, we will have for process 1

$$AP(CH_3N_2^+) \simeq IP(CH_3N_2) + D_1$$

which leads to a value of 7.2 ± 0.3 eV for the ionization potential of the radical CH_3N_2, if the activation energy of the process reverse to (1) does not exceed the uncertainty in the appearance potential of $CH_3N_2^+$. In view of the high stability of the later ion, this assumption may be suspect.

With respect to ground-state azomethane, the minimum activation energy of reaction 2 is

$$IP(CH_3) + D_1 + D_2 = 10.74 \text{ eV}$$

If we have correctly assigned the higher AP(CH_3^+) = 15.75 eV to the CH_3^+ formed in process 2, this would imply an activation energy of 5.01 eV for the reverse process

$$CH_3^+ + N_2 \longrightarrow CH_3N_2^+ \quad (2')$$

Since, roughly speaking, in reaction 2′ an electron must be transferred from nitrogen to carbon, we can reasonably anticipate the activation energy of this process to be of the order of the difference between the ionization potentials of N_2 and CH_3, which is 15.58–9.83 = 5.75 eV. It would thus appear that the assignment of the two appearance potentials of CH_3^+ is borne out by the thermochemistry of the system.

Similarly, the minimum activation energy for reaction 3, with respect to ground state azomethane, is

$$IP(N_2) + D_1 + D_2 = 16.49 \text{ eV}$$

and this is identical within experimental error with the appearance potential found for N_2^+ (Table I), so that the activation energy for the reverse process

$$N_2^+ + CH_3 \longrightarrow CH_3N_2^+ \quad (3')$$

must be less than 0.3 eV. Since N_2^+ is isoelectronic

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(29) API Catalog of Mass Spectral Data, Serial No. 2 and 61.

(30) Z. Prášil and W. Forst, *J. Phys. Chem.*, 71, 3166 (1967).

(31) W. Forst, *J. Chem. Phys.*, **44**, 2349 (1966).

with CN, reaction 3′ is more like a reaction between two radicals and a low activation energy can be expected. It should be noted that if N_2^+ is formed directly in a three-fragment decomposition of $CH_3N_2CH_3^+$, the thermochemistry remains the same and there is no way to distinguish between a two-fragment and a three-fragment formation of N_2^+.

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Potential Functions and the Bonding in the XCO Free Radicals

James S. Shirk and George C. Pimentel

Contribution from the Chemistry Department, University of California, Berkeley, California 94720. Received January 3, 1968

Abstract: Careful normal coordinate analysis for the free radicals HCO, FCO, and ClCO reveals carbonyl stretching force constants of 13.7 ± 0.5, 14.3 ± 0.1, and 14.5 ± 0.5 mdyn/Å, respectively. These force constants suggest carbonyl bond orders near 2.3. This result and its relative insensitivity to the electronegativity of the attached atom contrast with the force constants in the XNO and XOO molecules. The bonding is discussed in terms of the Linnett quartet scheme and the (p–π^*) bond idea. An improved estimate of the HCO molecular geometry is derived: $r_{CH} = 1.16$ Å, $r_{CO} = 1.17$ Å, and $\angle HCO = 123.8°$.

The vibrational spectra of three triatomic carbonyl free radicals have been reported, HCO,[1,2] FCO,[3] and ClCO.[4] We have recently measured the carbonyl stretching frequency of the acetyl radical.[5] Normal coordinate analyses which fully exploit the wealth of isotopic data have not been reported earlier and are presented here. The resulting potential functions permit a consideration of the bonding in these related molecules.

Normal Coordinate Analyses

All available frequencies were considered in the least-squares determination of the best-fit potential function.[6] For each of the XCO molecules (X = H, F, Cl) a variety of valence bond potential functions was derived, extending from the most general, with six potential constants, to the simplest, with all off-diagonal force constants set equal to zero. In each case, the fit was evaluated in terms of average discrepancy $\bar{\epsilon}$ between calculated and observed frequencies.

FCO and ClCO. Normal coordinate analyses on FCO and ClCO were straightforward. In the absence of structural data, we follow Milligan, *et al.*,[3,4] who used bond lengths from the stable prototypes HFCO (C–F, 1.36 Å and C–O, 1.18 Å) and Cl_2CO (C–Cl, 1.75 Å and C–O, 1.18 Å) and two possible bond angles, 120° (in analogy with HCO) and 135° (in analogy with the isoelectronic NO_2).

Table I shows calculations for FCO using three principal force constants only, one off-diagonal constant, and three off-diagonal constants. With a single off-diagonal force constant and a 120° angle, $k_{1\alpha}$ gives the best fit to the observed frequencies, whereas with a 135° angle k_{12} is the most effective term. With either angle, the fit is better than the experimental error in the frequencies (±1 cm^{-1}). With six parameters, there was further and about the same improvement at 120 and 135° bond angles. Three conclusions can be drawn from Table I: (a) The data do not provide a basis for fixing the bond angle in the range 120–135°. (b) Without an accurate bond angle, the data do not suffice to determine the off-diagonal force constants. (c) Despite conclusions a and b, reasonable and useful limits can be placed on the principal force constants.

Table I. Force Constant Calculations for FCO. Eight Observed Frequencies

Isotopes F	Isotopes C	Isotopes O	Frequencies,[3] cm^{-1} ν_1	ν_2	ν_3
19	12	16	1855	1018	626
19	13	16	1814	995	620
19	12	18	1813	1016	...

FCO bond angle, deg	k_1, mdyn/Å	k_2, mdyn/Å	k_α, ergs/rad^2	k_{12}, mdyn/Å	$k_{2\alpha}$, mdyn	$k_{1\alpha}$, mdyn	$\bar{\epsilon}$, cm^{-1}
120	13.3	3.55	1.77	...	...	...	3.8
120	14.1	3.18	2.30	0.91	...	...	1.5
120	13.1	4.83	1.54	...	0.21	...	1.4
120	14.2	4.51	1.81	...	...	1.07	0.7
120	14.3	5.09	1.42	0.61	0.30	0.27	0.3
135	12.8	4.61	1.48	...	...	...	1.9
135	13.0	4.0	1.68	...	−0.37	...	2.0
135	14.3	4.51	1.40	0.79	...	...	0.6
135	14.2	5.13	1.34	1.16	0.10	−0.31	0.4

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(1) G. E. Ewing, W. Thompson, and G. C. Pimentel, *J. Chem. Phys.*, 32, 927 (1960).

(2) D. E. Milligan and M. E. Jacox, *ibid.*, 41, 3032 (1964).

(3) D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford, and D. E. Mann, *ibid.*, 42, 3187 (1965).

(4) D. E. Milligan and M. E. Jacox, *ibid.*, 43, 866 (1965).

(5) See J. S. Shirk, Ph.D. Thesis, University of California, Berkeley, 1966.

(6) The calculations were based upon the computer program by J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules, V and VI," Technical Report No. 231-64, Shell Development Co., Emeryville, Calif., 1964.