Gas-Phase Ion Chemistry of Azomethane by Ion Cyclotron Resonance Spectroscopy

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Abstract: The ion–molecule reactions of azomethane, both pure and in binary mixtures with several other molecules, have been investigated by ion cyclotron resonance spectroscopy. Reaction pathways, product distributions, and rate constants have been determined for the parent and major fragment ions. Of particular interest are the formation and subsequent reactions of methyldiazonium ion, $CH_3N_2^+$, which accounts for the majority of the observed reaction products. Methyl cation transfer from this species to the parent neutral generates an intermediate trimethyldiazenium ion in a high state of internal excitation. Extensive hydrogen migration from carbon to nitrogen occurs in this intermediate prior to unimolecular decomposition, accounting for the relatively abundant protonated mono- and dimethylamine reaction products observed. Metastable transitions occurring in the mass spectrum of tetramethylhydrazine substantiate the proposed decomposition pathways of the reaction intermediate. Proton-transfer reactions observed in binary mixtures bracket the proton affinity of azomethane between ammonia and methylamine. Processes detected in the mixtures examined which involve nucleophilic displacement of nitrogen from methyldiazonium ion are discussed in light of recently proposed rules governing the occurrence of these reactions. Deprotonation reactions of the methyldiazonium ion yield a measure of the heat of formation of diazomethane, 64 kcal/mol $\leq \Delta H_f(CH_2N_2) \leq$ 73 kcal/mol.

Diazonium ions, RN_2^+, are frequently employed for the generation of carbonium ions in solution. Part of the controversy surrounding the liquid-phase reactivity of these species involves the frequent uncertainty as to whether the free carbonium ion, R^+, or the diazonium ion, RN_2^+, itself is subject to nucleophilic attack.[2] These latter processes are amenable to direct study in the gas phase. Recently we have demonstrated that methyldiazonium ions can be generated in a gas-phase nucleophilic displacement process, reaction 1.[3] While reaction 1 indicates that N_2

$$N_2 + CH_3FH^+ \longrightarrow CH_3N_2^+ + HF \qquad (1)$$

exhibits greater nucleophilicity toward methyl cations than HF, it can itself be displaced by a wide variety of attacking groups.[3-6]

Azo compounds are convenient sources of diazonium ions for studies of these gas-phase nucleophilic displacement reactions. In the case of azomethane ($CH_3N{=}NCH_3$), the methyldiazonium ion is 44% of the base peak of the mass spectrum at 70 eV.[7] In conjunction with the above investigation, we report in the present paper a detailed study of the gas-phase ion chemistry of azomethane, using the techniques of ion cyclotron resonance spectroscopy (icr). Included in this study are the identification of reaction pathways, determination of reaction rate constants at thermal ion energies, and a consideration of ion thermochemical properties, including the proton affinity (gas-phase basicity) of azomethane.

In previous publications,[8-10] we have examined the complementary information available from studies of ion–molecule reactions and mass spectral fragmentations when common intermediates are involved. In the present work we continue these correlative efforts, utilizing metastable transitions observed in the mass spectrum of tetramethylhydrazine to elucidate the mechanism of ion–molecule reactions occurring in azomethane. The relatively new technique of ion kinetic energy spectroscopy[11] is shown to be particularly useful in this application.

Experimental Section

Azomethane was prepared by a modification of the procedure of Renaud and Leitch.[12] Free 1,2-dimethylhydrazine was obtained from the dihydrochloride salt (Matheson Coleman and Bell) by treatment with aqueous NaOH and transferred to the HgO–water mixture by distillation on a vacuum line. The azomethane was distilled from the reaction mixture at −78° and passed through a Drierite column into a liquid nitrogen trap. A mass spectrum of the product showed impurities at masses 18 (H_2O^+), 31 ($CH_3NH_2^+$), 32 (O_2^+), and 45 [$(CH_3)_2NH^+$] to be less than 0.1% of the total ionization. Azomethane is somewhat photosensitive, and the bulb was wrapped in foil to minimize exposure to light. Nevertheless, it appeared that over a period of weeks the azomethane partially decomposed, yielding N_2 and C_2H_6.

Tetramethylhydrazine was obtained by pyrolysis[13] of tetramethyltetrazine at 300° and purified by glpc on a 0.375 in. × 10 ft UCC-W98 column. Tetramethyltetrazine was prepared by oxidation of 1,1-dimethylhydrazine with HgO.[14]

Mixtures used in the proton affinity measurements were prepared manometrically. Commercial samples of NH_3 (J. T. Baker, 99.99%) and CH_3NH_2 (J. T. Baker, 98.0%) were utilized as supplied except for degassing with freeze–pump–thaw cycles. Purities as ascertained by mass spectrometric analyses were acceptable.

The technique and instrumentation of ion cyclotron resonance spectroscopy have been described previously.[15-17] All measure-

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[1] (a) NDEA Predoctoral Fellow; (b) Alfred P. Sloan Fellow, 1968–1970.

[2] L. Friedman in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Wiley, New York, N. Y., 1970, Chapter 16.

[3] D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970).

[4] D. Holtz and J. L. Beauchamp, *Nature, Phys. Sci.*, **231**, 204 (1971).

[5] D. Holtz and J. L. Beauchamp, *Science*, **173**, 1237 (1971).

[6] J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Amer. Chem. Soc.*, in press.

[7] Z. Prášil and W. Forst, *ibid.*, **90**, 3344 (1968).

[8] J. L. Beauchamp and R. C. Dunbar, *ibid.*, **92**, 1477 (1970).

[9] T. A. Lehman, T. A. Elwood, J. T. Bursey, M. M. Bursey, and J. L. Beauchamp, *ibid.*, **93**, 2108 (1971).

[10] J. L. Beauchamp and M. C. Caserio, *ibid.*, in press.

[11] E. M. Chait and W. B. Askew, *Org. Mass Spectrom.*, **5**, 147 (1971), and references therein.

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

[13] J. S. Watson, *J. Chem. Soc.*, 3677 (1956).

[14] W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **80**, 2516 (1958).

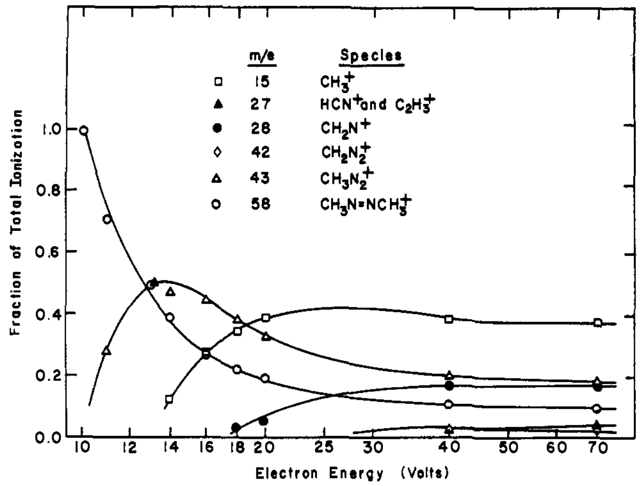

Figure 1. Variation of ion abundance with electron energy at 6 × 10^{-7} Torr for the seven most prominent species in the mass spectrum of azomethane.

ments were performed at ambient temperature (25–35°). Spectral intensities reported in tables and figures have as indicated been corrected to approximate ion abundances by dividing the single-resonance peak height by ion mass.[18] All data are also corrected for natural-abundance ^{13}C. Rate constants were calculated using a computer program employing an iterative procedure based on the analyses of Buttrill[18] and Buttrill and Marshall.[19] Reaction pathways were elucidated by double-resonance techniques.[15-17] The ion kinetic energy and pure metastable[20] spectra of tetramethylhydrazine were obtained on a CEC Type 21-492 mass spectrometer.[21]

Results and Discussion

(A) Mass Spectrum and Fragmentation of Azomethane. The single-resonance icr spectrum of azomethane taken with 70-eV electron energy at 6.7 × 10^{-7} Torr agrees well with recent mass spectrometry results.[7,22] The variation of ion abundance with electron energy at 6.7 × 10^{-7} Torr is illustrated in Figure 1. The major ions, including in particular the parent ion and the methyldiazonium ion, have appearance potentials sufficiently different to allow their ion chemistry to be interpreted separately as they appear in the spectrum with increasing electron energy.

(B) Ion Chemistry of Azomethane. At 9.2 eV the only species present at low pressure is the parent ion (Figure 1). With increasing azomethane pressure the parent ion reacts to form *m/e* 73, with empirical formula $C_3H_9N_2^+$. Most likely this species corresponds to the trimethyldiazenium ion (reaction 2). No other reaction products are observed at this electron energy.

$$CH_3N{=}NCH_3^+ + CH_3N{=}NCH_3 \longrightarrow (CH_3)_2N{=}NCH_3^+ + CH_3 + N_2 \quad (2)$$

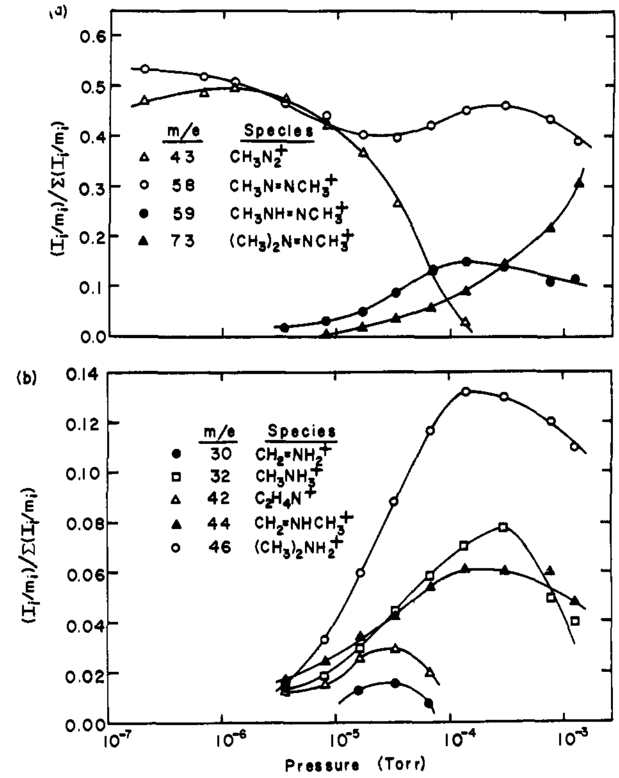

Figure 2. Variation with pressure of ion abundance for azomethane at an electron energy of 13.0 eV: (a) major ions, (b) minor ions. The decline of *m/e* 59 at high pressure may be due to inaccuracy in the deconvolution of the *m/e* 58 and 59 peaks, which are completely overlapped at the two highest pressures, or to collisional stabilization of the *m/e* 73 intermediate, which would be reflected in a decrease in the amount of *m/e* 59 formed by secondary reactions (see text). The amount of proton-bound dimer observed at 10^{-3} Torr was <1% of the total ionization.

In particular, the protonated parent ion is not observed. Reaction 2 is exothermic by 62 kcal/mol.[23]

At 13.0 eV (Figure 2), in addition to the parent ion,[24] only *m/e* 43 ($CH_3N_2^+$) is present to a significant extent at low pressure (Figure 1). With increasing pressure, $CH_3N_2^+$ reacts to yield *m/e* 30, 32, 42, 44, 46, 59, and 73 (Figure 2). A typical single-resonance spectrum showing these products is displayed in Figure 3a. The protonated parent ion (*m/e* 59) is likely formed by the simple proton-transfer reaction 3. The probable

$$CH_3N_2^+ + CH_3N{=}NCH_3 \longrightarrow CH_3NH{=}NCH_3^+ + CH_2N_2 \quad (3)$$

mechanism of the other $CH_3N_2^+$ reaction involves the exothermic methyl cation transfer reaction 4, forming

$$CH_3N_2^+ + CH_3N{=}NCH_3 \longrightarrow (CH_3)_2N{=}NCH_3^+ + N_2 \quad (4)$$
$$\Delta H = -75 \text{ kcal/mol}$$

the trimethyldiazenium ion (*m/e* 73), which subsequently partially decomposes, yielding the other reaction prod-

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(15) D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970), and references cited therein.

(16) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(17) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968).

(18) S. E. Buttrill, Jr., *J. Chem. Phys.*, **50**, 4125 (1969).

(19) A. G. Marshall and S. E. Buttrill, Jr., *ibid.*, **52**, 2752 (1970). For a more refined treatment, see M. B. Comisarow, *ibid.*, **55**, 205 (1971).

(20) K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davies, Ed., United Trade Press, London, 1967, p 105, and references cited therein.

(21) We are grateful to Dr. Fred Abramson of CEC Division of Du Pont for making these measurements.

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

(23) Thermochemical data used in this and all subsequent calculations are summarized in Table I.

(24) The peculiar behavior of the *m/e* 58 curve at intermediate pressures results essentially from the normalization procedure used to construct the figure. That is, at the magnetic field strengths used to observe the lower mass ions, transit times, and hence reaction times, are shorter than at the higher field of the *m/e* 58 resonance. Thus, when the spectrum is normalized, the abundances of the lower mass ions are enhanced relative to that of *m/e* 58. The result is a dip in the *m/e* 58 curve at the intermediate pressures where this effect is active.

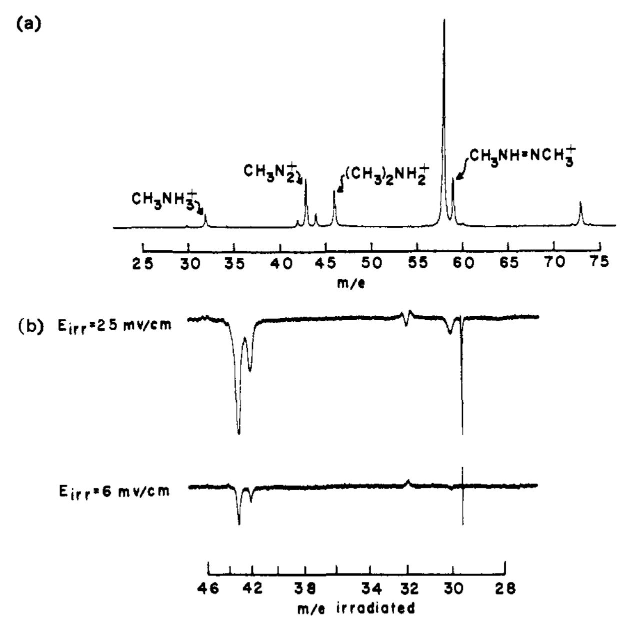


Figure 3. (a) Single-resonance spectrum of azomethane at 5 × 10^{-5} Torr with an electron energy of 12.0 eV. Several of the ionic species pertinent to the discussion in the text are indicated. (b) Double-resonance spectrum of azomethane protonated parent ion (*m/e* 59) at two irradiating field strengths. The conditions for obtaining the spectrum are as shown in (a). The feature at *m/e* 29.5 results from interaction of the irradiating and observing oscillators.

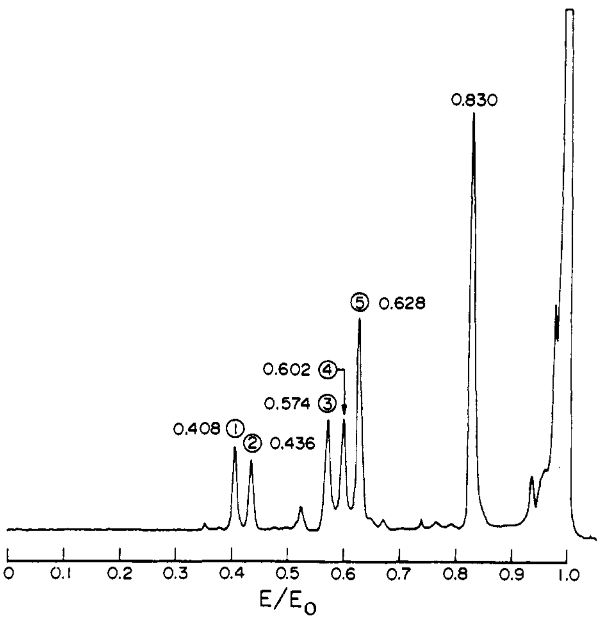


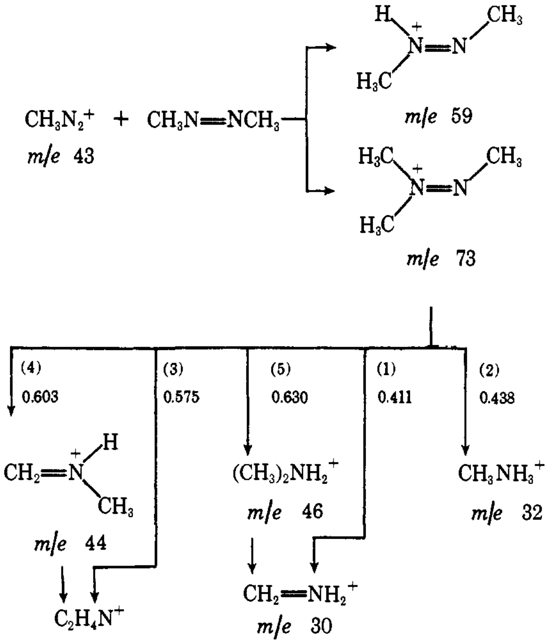
Figure 4. Ion kinetic energy spectrum of tetramethylhydrazine at 70 eV. E is the energy of ions transmitted by the electrostatic analyzer and E_0 is the energy of the main beam. The spectrum is obtained by sweeping the electrostatic analyzer voltage.

ucts, *m/e* 30, 32, 42, 44, and 46.[25] The product ions corresponding to *m/e* 32 and 46 most probably are the even electron species $CH_3NH_3^+$ and $(CH_3)_2NH_2^+$, respectively, since all other possible products are radical ions, unlikely to be formed in the ion–molecule reaction of two even-electron species. These two products suggest that extensive migration of hydrogen from carbon to nitrogen occurs in the postulated trimethyldiazenium ion intermediate.

Consistent with the existence of this intermediate, Dibeler, Franklin, and Reese[26] report the nine most prominent fragment ions and their relative abundances in the mass spectrum of tetramethylhydrazine, $(CH_3)_2NN(CH_3)_2$: *m/e* 42 (100.0), 73 (95.0), 44 (85.5), 43 (50.6), 15 (50.4), 46 (40), 28 (26.9), 30 (26), and 32 (17). Hence, all of the above $CH_3N_2^+$ reaction products appear in the mass spectrum and could result in part from the unimolecular decomposition of *m/e* 73, which should have the trimethyldiazenium structure when derived by electron impact from tetramethylhydrazine.

To confirm these suggestions, the metastable transitions in the mass spectrum of tetramethylhydrazine were examined. Figure 4 shows the ion kinetic energy spectrum of $(CH_3)_2NN(CH_3)_2$; each peak corresponds to at least one metastable transition, the most intense being *m/e* 88 → *m/e* 73 (E/E_0 = 0.830). The five largest peaks at $E/E_0 < 0.7$ result from the decomposition of *m/e* 73 to *m/e* 30, 32, 42, 44, and 46. These peaks are designated by (1)–(5) and by the experimental (mass of daughter ion)/(mass of parent ion) ratio. Examination of pure metastable spectra of the daughter ions confirms these assignments and also shows the transitions *m/e* 46 → *m/e* 30 and *m/e* 44 → *m/e* 42. These results substantiate the existence of a trimethyldiazenium ion intermediate in the reaction of $CH_3N_2^+$ with azomethane and confirm the occurrence of extensive hydrogen migration prior to decomposition. Scheme I summarizes the reactions of $CH_3N_2^+$ as determined from the icr and metastable studies. The reactions producing the five products discussed above are labeled with a number corresponding to its metastable transition in Figure 4 and by the exact ratio of daughter ion mass to parent ion mass.

Scheme I



At higher pressures (Figure 2), the ionic products from Scheme I at *m/e* 30, 32, 42, 44, and 46 disappear,

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[25] Ion ejection experiments show that at 5 × 10^{-5} Torr, $\geq$87% of the *m/e* 73 ion product present is derived from *m/e* 43 in reaction 4, the remainder being formed in reaction 2.

[26] V. H. Dibeler, J. L. Franklin, and R. M. Reese, *J. Amer. Chem. Soc.*, 81, 68 (1959).

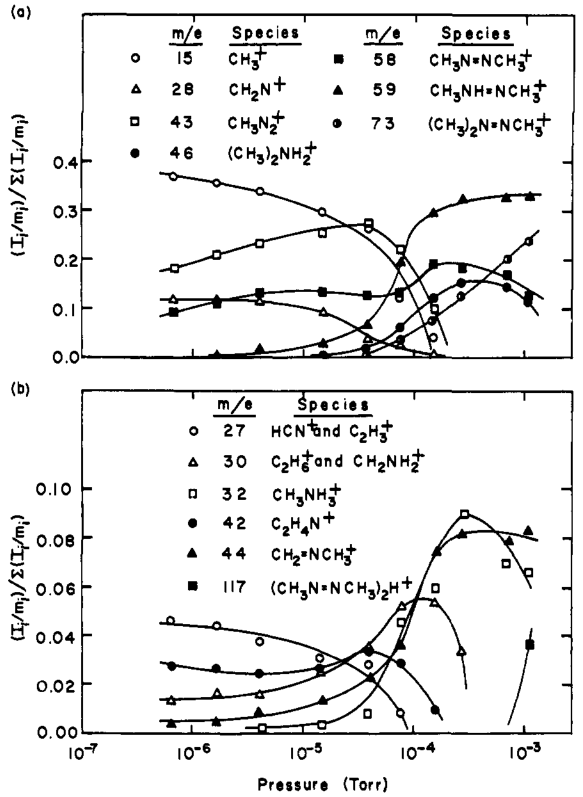

Figure 5. Variation with pressure of ion abundance for azomethane at an electron energy of 70 eV: (a) major ions, (b) minor ions. For an explanation of the behavior of *m*/*e* 58, see ref 24.

reacting by proton transfer to generate the protonated parent, *m*/*e* 59, as discussed further in the following section.

As shown in Figure 1, numerous primary ions are produced at 70 eV, the most important in order of decreasing abundance being CH_3^+ (*m*/*e* 15), $CH_3N_2^+$ (*m*/*e* 43), CH_2N^+ (*m*/*e* 28), $CH_3N{=}NCH_3^+$ (*m*/*e* 58), $CH_2N_2^+$ (*m*/*e* 42), and HCN^+ and $C_2H_3^+$ (both *m*/*e* 27).[7] The variation of ion abundance with pressure is depicted for azomethane at 70 eV in Figure 5. Note that the majority of the ionic species observed at 13.0 eV, including *m*/*e* 73, 59, 46, 44, 42, 32, and 30, behave similarly at 70 eV (*cf.* Figure 2).

Double-resonance experiments at 70 eV verify the principal reactions 5–9 of the new primary ions. The two processes 8 and 9 account for the pressure dependence of *m*/*e* 43 and *m*/*e* 58 at 70 eV as compared to the behavior observed at 13.0 eV (Figure 2). Both reactions 8 and 9 exhibit reaction rate constants which

$$C_2H_3^+ + CH_3N{=}NCH_3 \longrightarrow C_2H_2 + CH_3NH{=}NCH_3^+ \qquad (5)$$
$$\Delta H = -61 \text{ kcal/mol}$$

$$HCN^+ + CH_3N{=}NCH_3 \longrightarrow CN + CH_3NH{=}NCH_3^+ \qquad (6)$$
$$\Delta H = -97 \text{ kcal/mol}$$

$$CH_2N^+ + CH_3N{=}NCH_3 \longrightarrow HCN + CH_3NH{=}NCH_3^+ \qquad (7)$$
$$\Delta H = -42 \text{ kcal/mol}$$

$$CH_3^+ + CH_3N{=}NCH_3 - \begin{cases} \longrightarrow CH_3N{=}NCH_3^+ + CH_3 & (8) \\ \qquad \Delta H = -28 \text{ kcal/mol} & \\ \longrightarrow CH_3N_2^+ + 2CH_3 & (9) \\ \qquad \Delta H = -15 \text{ kcal/mol} & \end{cases}$$

increase with increasing ion energy. This is usually characteristic of charge-transfer processes and is expected in the case of reaction 8.[17] On this basis the neutral products in reaction 9 are formulated as two methyl radicals rather than ethane, which would be produced in a more complex reaction process. The recombination energy of CH_3^+ is 9.8 eV,[27] which is 0.6 eV above the appearance potential of $CH_3N_2^+$ from azomethane. Charge transfer from CH_3^+ can thus deposit sufficient excitation in the azomethane parent ion to induce decomposition to the methyldiazonium ion. The double-resonance spectrum of *m*/*e* 58 also exhibits a contribution from *m*/*e* 28, which could be due to any one of the three species comprising this mass peak at 70 eV.[7] At the highest pressures examined, the protonated parent ion and trimethyldiazenium ion are the most abundant species. Although the proton-bound dimer is observed (Figure 5), the tendency of protonated azomethane to cluster with azomethane neutrals is much less than is the case for other aliphatic nitrogen species.

(C) Proton Affinity of Azomethane. The enthalpy change for the gas-phase reaction 10 is known as the

$$MH^+ \longrightarrow M + H^+ \qquad (10)$$

proton affinity (PA) of the species M and is a quantitative measure of the basicity of M. The observation of reaction 11 proceeding in the direction shown is inter-

$$M_1H^+ + M_2 \longrightarrow M_2H^+ + M_1 \qquad (11)$$

preted as indicating that $PA(M_2) \geq PA(M_1)$, *provided that both neutrals are present.* Ion cyclotron resonance is ideally suited for identifying the occurrence and direction of reaction 11.[15,28] By examining suitable binary mixtures, it is possible to establish a self-consistent sequence of relative proton affinities. With suitable standards, absolute proton affinities can be assigned with an estimated accuracy of ±5 kcal/mol.[15]

The variation of ion abundance with pressure for a mixture of ammonia and azomethane in the mole ratio 4:1 at 70 eV is shown in Figure 6. A point of particular interest, discussed in detail later, is the dramatic increase in the abundance of $CH_3NH_3^+$ relative to the azomethane system. Note that at high pressure the ammonia ion declines in abundance relative to protonated azomethane. Double-resonance studies demonstrate that reaction 12 occurs only in the direction indicated.

$$NH_4^+ + CH_3N{=}NCH_3 \longrightarrow NH_3 + CH_3NH{=}NCH_3^+ \qquad (12)$$

The results of a similar study with a mixture of methylamine and azomethane in the mole ratio 3:2 are shown in Figure 7. At high pressure, protonated azomethane decreases relative to protonated methylamine, implying reaction 13. Double-resonance experiments again ver-

$$CH_3NH_2 + CH_3NH{=}NCH_3^+ \longrightarrow CH_3NH_3^+ + CH_3N{=}NCH_3 \qquad (13)$$

ify that reaction 13 proceeds only in the direction indicated.

The above results indicate that the relative ordering of proton affinities is $PA(NH_3) < PA(CH_3N{=}NCH_3) < PA(CH_3NH_2)$. The proton affinity of ammonia has

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[27] Lindholm reports a wide variety of values for the recombination energy of CH_3^+, ranging from 9.0 to 10.5 eV [E. Lindholm, *Advan. Chem. Ser.*, No. 58, 1 (1966)]. The value employed in the text is the adiabatic ionization potential of CH_3.

[28] J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, 48, 1783 (1968).

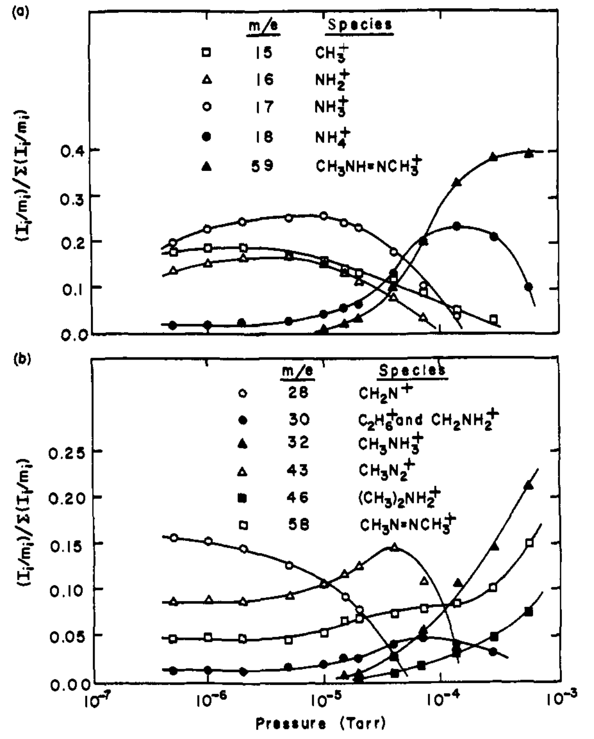

Figure 6. Variation of ion abundance with pressure for a 4:1 mixture of ammonia and azomethane at an electron energy of 70 eV: (a) major ions, (b) minor ions.

been estimated by Haney and Franklin at 207 kcal/mol.[29,30] They also report PA(CH_3NH_2) as 211 kcal/mol.[30] However, based on new data for the heat of formation of methylamino radical, $\Delta H_f(CH_3NH)$ = 42 kcal/mol,[31] this value is recalculated to be 216 kcal/mol. Based on these data, we assign PA($CH_3N{=}NCH_3$) = 212 ± 5 kcal/mol, corresponding to $\Delta H_f(CH_3NH{=}NCH_3^+)$ = 199 ± 5 kcal/mol.

Of interest are the thermochemical changes attending proton transfer reactions 14–17 from *m/e* 30 ($CH_2NH_2^+$), *m/e* 32 ($CH_3NH_3^+$), *m/e* 44 ($CH_2{=}NHCH_3^+$), and *m/e* 46 [$(CH_3)_2NH_2^+$] to azomethane. While reaction 14 is exothermic, the latter three processes (15–17) are calculated to be endothermic and yet proceed

$$CH_2NH_2^+ + CH_3N{=}NCH_3 \longrightarrow CH_3NH{=}NCH_3^+ + CH_2NH \qquad \Delta H = -10 \text{ kcal/mol} \quad (14)$$

$$CH_3NH_3^+ + CH_3N{=}NCH_3 \longrightarrow CH_3NH{=}NCH_3^+ + CH_3NH_2 \qquad \Delta H = +4 \text{ kcal/mol} \quad (15)$$

$$CH_2{=}NHCH_3^+ + CH_3N{=}NCH_3 \longrightarrow CH_3NH{=}NCH_3^+ + CH_2{=}NCH_3 \quad (16) \qquad \Delta H = +6 \text{ kcal/mol}$$

$$(CH_3)_2NH_2^+ + CH_3N{=}NCH_3 \longrightarrow CH_3NH{=}NCH_3^+ + (CH_3)_2NH \quad (17) \qquad \Delta H = +12 \text{ kcal/mol}$$

in the direction indicated. Since *m/e* 32, 44, and 46 are formed in highly exothermic reactions, as indicated in Table II, it is possible that they retain sufficient internal excitation to overcome the endothermicity of reactions 15–17. In addition, these processes can proceed only to the right owing to the negligible concentrations of neutrals required for the reverse processes to occur. The occurrence of reaction 15 in the azomethane system is thus attributed to the absence of methylamine. In contrast, when the appropriate neutral is present in abundance, as in the azomethane–methylamine mixture, the reaction preferentially proceeds in the opposite direction (Figure 7). The double-resonance spectrum of the protonated parent ion presented in Figure 3b indicates in the limit of low irradiating power a positive response for reaction 15, implying a reaction rate constant which increases with increasing ion energy. This is consistent with an endothermic reaction.[28] The double-resonance results for reactions 16 and 17 are somewhat uncertain. Only the pressure dependence of these species as illustrated in Figures 2 and 5 is evidence for the suggested processes. The negative responses observed in Figure 3b for *m/e* 30, 42, and 43 contributing to the protonated parent ion are consistent with previous observations of exothermic proton-transfer reactions.[17,28]

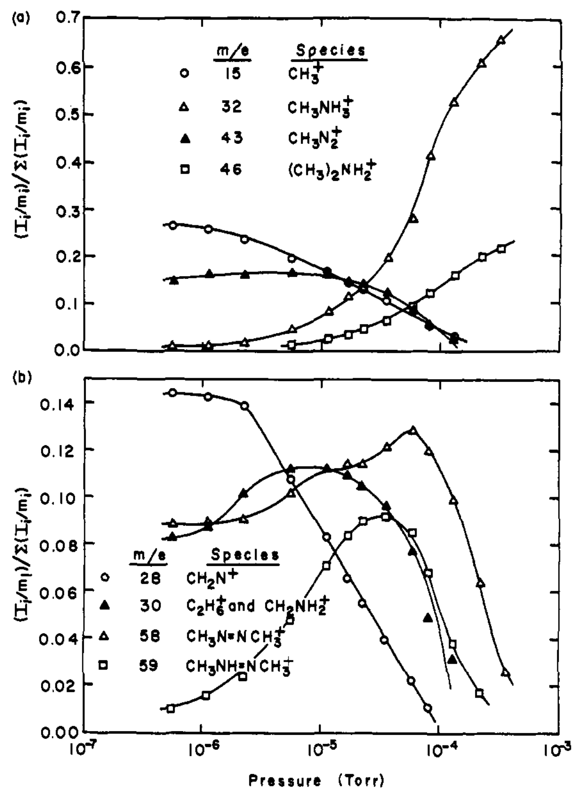

Figure 7. Variation of ion abundance with pressure for a 3:2 mixture of methylamine and azomethane at an electron energy of 70 eV: (a) major ions, (b) minor ions.

(D) Nucleophilic Displacement Reactions. We have put forth two criteria to decribe the occurrence of gas-phase nucleophilic displacement reactions (*e.g.*, reaction 1).[3] Simply stated, these criteria require that (1) the displacement process be exothermic and (2) proton transfer from the substrate to the nucleophile be endothermic.

The expected behavior is observed in the case of ammonia. Proton transfer from the methyldiazonium ion to ammonia could not be detected using double-resonance techniques in the mixture of ammonia with

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(29) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, 50, 2028 (1969).

(30) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969).

(31) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, U. S. Government Printing Office, Washington, D. C., 1969, p 35.

azomethane. Furthermore, NH_4^+ is *not* observed below the ionization potential of NH_3, even though $CH_3N_2^+$ remains relatively abundant. Protonated methylamine in this mixture rises to a maximum of 22% of the total ionization at 70 eV, to be compared with a maximum of 9% in azomethane alone at the same electron energy (Figures 5 and 6). This suggests reaction 18, which is calculated to be 74 kcal/mol exothermic. This was confirmed using double-resonance techniques by examination of a mixture of ammonia-d_3 and azomethane. The product of reaction 18 shifts to *m/e* 35, corresponding to $CH_3ND_3^+$.

$$CH_3N_2^+ + NH_3 \rightarrow CH_3NH_3^+ + N_2 \tag{18}$$

$$CH_3N_2^+ + NH_3 \not\rightarrow NH_4^+ + CH_2N_2 \tag{19}$$

The methyldiazonium ion, however, contradicts the pattern of substrate reactivity usually observed in that *both* proton transfer and methyl cation transfer occur competitively with azomethane, reactions 3 and 4. In this respect, the methyldiazonium ion comprises an unusual substrate in that it can deprotonate to yield a relatively stable neutral species, diazomethane. Analogous behavior is observed in the case of the acyl cation which readily deprotonates to yield ketene.[32]

Similarly in the case of methylamine, competition between methyl cation transfer (reaction 20) and proton transfer (reaction 21) is again observed. Reaction 20 is 81 kcal/mol exothermic. Double-resonance studies of a mixture of CD_3NH_3 and azomethane confirmed the occurrence of reactions 20 and 21, the corresponding products shifting to *m/e* 49 ($CH_3NH_2CD_3^+$) and *m/e* 35 ($CD_3NH_3^+$), respectively.

$$CH_3N_2^+ + CH_3NH_2 \rightarrow (CH_3)_2\overset{+}{N}H_2 + N_2 \tag{20}$$

$$CH_3N_2^+ + CH_3NH_2 \rightarrow CH_3\overset{+}{N}H_3 + CH_2N_2 \tag{21}$$

Nucleophilic displacement reactions involving the methyldiazonium ion are currently under active scrutiny and will be reported in detail in a future publication.

(E) Heat of Formation of Diazomethane. The above experiments suggest that diazomethane can be included in the experimentally determined order of proton affinities in accordance with expression 22 considering

$$PA(NH_3) < PA(CH_2N_2) < PA(CH_3N{=}NCH_3) < PA(CH_3NH_2) \tag{22}$$

carbon as the site of protonation. The heat of formation of methyldiazonium can be calculated from the appearance potential for this species derived from azomethane. There are two literature values for this quantity, 9.0[22] and 9.5[7] eV. Using icr detection, we have determined an appearance potential of 9.2 eV for $CH_3N_2^+$ from azomethane by the extrapolated voltage difference method.[33,34] This corresponds to a heat of formation of $CH_3N_2^+$ of 223 kcal/mol, which has been utilized in all thermochemical calculations in the present study. Since the proton affinity of azomethane itself is known only to be between ammonia and methylamine, the same limits apply to the proton affinity of diazomethane for carbon protonation, giving the result 64 kcal/mol $\leq \Delta H_f(CH_2N_2) \leq$ 73 kcal/mol. The lower limit results from failure to observe proton transfer to NH_3. The upper limit corresponds to the observation of proton transfer to methylamine.

Setser and Rabinovitch present evidence based on kinteic studies which suggests that $\Delta H_f(CH_2N_2) \geq$ 67 kcal/mol.[35] An examination of the thermochemical changes attending hydrogen halide addition to diazomethane leads to the limits 64 kcal/mol $\leq \Delta H_f(CH_2N_2) \leq$ 77 kcal/mol.[36] These thermochemical studies are hence in good agreement with the limits which we have derived from a study of proton-transfer reactions, and the value $\Delta H_f(CH_2N_2) \cong$ 71 kcal/mol quoted in Table I appears reasonable.

Table I. Thermochemical Data

Species	$\Delta H_f°$, kcal/mol
CN	100[a]
$CH_2{=}NH$	17[b]
$CH_2{=}N{-}CH_3$	17[c]
CH_2N_2	71[d]
$CH_3N{=}NCH_3$	45[d]
CH_3	34[n]
NH_4^+	148[e]
H_2CN^+	228[f]
CH_3^+	261[n]
$CH_2{=}NH_2^+$	178[a]
$CH_3NH_3^+$	145[g]
$CH_2{=}NHCH_3^+$	165[h]
$(CH_3)_2NH_2^+$	138[i]
$CH_3N_2^+$	223[j]
$CH_3N{=}NCH_3^+$	244[k]
$CH_3NH{=}NCH_3^+$	199[l]
$(CH_3)_2N{=}NCH_3^+$	193[m]

[a] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. Heats of formation not listed will be found in this reference. [b] W. T. Huntress, Jr., and J. L. Beauchamp, unpublished results. [c] Based on $\Delta H_f(CH_2{=}NH)$ = 17 kcal/mol and the fact that *N*-methyl substitution, as in the three methylamines, has little effect on the heat of formation. [d] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [e] Based on $PA(NH_3)$ = 207 kcal/mol, ref 29 and 30. [f] Based on PA(HCN) = 170 kcal/mol, ref. 30. [g] Based on $PA(CH_3NH_2)$ = 216 kcal/mol; see text. [h] Based on appearance potential of $C_2H_6N^+$ from $(CH_3)_2$-NH of 9.6 eV: D. Holtz and J. L. Beauchamp, unpublished results. [i] Based on $PA[(CH_3)_2NH]$ = 224 kcal/mol: J. L. Beauchamp, unpublished results. [j] Determined from $AP(CH_3N_2^+)$ = 9.2 eV from azomethane (see text). [k] References 7 and 22. [l] See text. [m] Reference 26. [n] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

Contradicting the above results is the somewhat lower heat of formation for diazomethane obtained from mass spectral studies by Paulett and Ettinger.[37] Measurement of the appearance potential of CH_2^+ from CH_2N_2 leads to an estimate of 49 kcal/mol for $\Delta H_f(CH_2N_2)$. More recently, Laufer and Okabe[38]

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(32) D. Holtz and J. L. Beauchamp, unpublished results.

(33) J. W. Warren, *Nature (London)*, **165**, 810 (1950).

(34) The appearance potential of $CH_3N_2^+$ was determined to be 0.57 eV above the ionization potential of azomethane, which is given as 8.65 eV in ref 7 and 22.

(35) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

(36) J. C. Hassler and D. W. Setser, *J. Amer. Chem. Soc.*, **87**, 3793 (1965).

(37) G. S. Paulett and R. Ettinger, *J. Chem. Phys.*, **39**, 825, 3534 (1963); **41**, 2557 (1964).

(38) A. H. Laufer and H. Okabe, *J. Amer. Chem. Soc.*, **93**, 4137 (1971).

Table II. Reactions of Primary Ions at 13.0 eV

Reaction		ΔH, kcal/mol[a]	Rate constant $\times 10^{11}$ cm^3 molecule^{-1} sec^{-1} [c]
$CH_3N_2^+ + CH_3N{=}NCH_3$	$\rightarrow CH_2{=}NH_2^+ + CH_3NC + H_2 + N_2$	−54	2.5 ± 1.0
	$\rightarrow CH_3NH_3^+ + CH_3NC + N_2$	−87	6.6 ± 1.2
	$\rightarrow C_2H_4N^+ + HCN + N_2 + 2H_2$		4.9 ± 1.8
	$\rightarrow CH_2{=}NHCH_3^+ + HCN + N_2 + H_2$	−71	8.5 ± 3.2
	$\rightarrow (CH_3)_2NH_2^+ + HCN + N_2$	−98	13.0 ± 3.0
	$\rightarrow CH_3NH{=}NCH_3^+ + CH_2N_2$	≤ 0[b]	12.2 ± 1.4
	$\rightarrow (CH_3)_2N{=}NCH_3^+ + N_2$	−75	3.0 ± 1.0
$CH_3N{=}NCH_3^+ + CH_3N{=}NCH_3$	$\rightarrow (CH_3)_2N{=}NCH_3^+ + CH_3 + N_2$	−62	0.38 ± 0.06[d]

[a] Neutral products are assumed. [b] Required because $PA(CH_2N_2) < PA(CH_3N{=}NCH_3)$; see text. [c] Rate constants refer to an ion kinetic energy of ~0.15 eV, attributable to the oscillatory motion of ions in the trapping field. [d] Determined from pressure data at 9.2 eV; see text.

have utilized a photodissociatiom method to determine the limit $\Delta H_f(CH_2N_2) \geq 51$ kcal/mol, which they believe is close to the true heat of formation. Even considering the many uncertainties involved in all of the measurements, it does not appear possible to resolve the discrepancy of ~20 kcal/mol between these results and those discussed above.

(F) Kinetics of Reaction. Rate constants, summarized in Table II, were calculated from the data of Figure 2 for the seven indicated reactions. The rate for *m/e* 73 production from *m/e* 43 was determined from data at pressures low enough to avoid significant contributions from *m/e* 58 (reaction 2). The rate constant for reaction 2 is the slowest of any observed in the azomethane system, $3.8 \pm 0.6 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. While the rate constants of the individual $CH_3N_2^+$ reactions are rather low for ion–molecule reactions in general, the total rate constant for the disappearance of *m/e* 43 is 5.1×10^{-10} cm^3 molecule^{-1} sec^{-1}. Rate constants for processes other than those listed in Table II could not be determined due to the complexity of the reaction scheme.

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Complex Equilibria Involving 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane. I. The Proton Magnetic Resonance Spectrum and Types of Complexation

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Abstract: The proton magnetic resonance spectrum of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (the pesticide *p,p'*-DDT) was obtained as a function of the concentration of several complexing agents and of temperature. Equilibrium constants and values of the standard free energy, $\Delta G°$, standard enthalpy, $\Delta H°$, and standard entropy change, $\Delta S°$, on complex formation were calculated. Two types of complexes were observed, one association involving primarily the benzhydryltrichloromethyl grouping of DDT with a polar complexing agent, and the other interaction of the DDT aromatic π-electron system with π electrons in the complexing molecule.

The extensive occurrence of the compound 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, also known as the para isomer of the pesticide DDT,[1] in the global environment makes the interactions of this compound very interesting. Their elucidation may well be an extremely important task. Considerable attention has been given to the interaction of DDT with biological systems.[2] Fewer studies have been undertaken to determine the types of interactions involved and their energies.

The possibility of formation of charge-transfer or other types of molecular complexes involving DDT has been indicated by studies with model systems.[3–5]

Evidence for charge-transfer interaction of DDT with tetracyanoethylene from the ultraviolet–visible spectra has been obtained.[6] The use of nuclear magnetic

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(1) The abbreviation DDT will be used throughout this article for the compound 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane.

(2) See, for example, T. Narahishi and H. G. Hass, *J. Gen. Physiol.*, **51**, 177 (1968); F. Matsumura and M. Hayashi, *Science*, **153**, 757 (1966); R. B. Koch, *J. Neurochem.*, **16**, 269 (1969); R. M. Welch, W. Levin, and A. H. Conney, *Toxicol. Appl. Pharmacol.*, **14**, 358 (1969).

(3) D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962).

(4) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 52–55.

(5) R. T. Ross and F. J. Biros, *Biochem. Biophys. Res. Commun.*, **39**, 723 (1970).