[CONTRIBUTION FROM THE MASS SPECTROMETRY LABORATORY, NATIONAL BUREAU OF STANDARDS]

Electron Impact Studies of Hydrazine and the Methyl-substituted Hydrazines[1]

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Relative abundances and appearance potentials are reported for the principal ions in mass spectra of hydrazine, monomethyl-, 1,1-dimethyl-, 1,2-dimethyl-, trimethyl- and tetramethylhydrazine. Heats of formation of the radical ions and probable ionization–dissociation processes are tabulated consistent with the calculated energetics. Molecular ionization potentials computed by the use of antisymmetrized orbitals are compared with experimental observations. Heats of formation of various hydrazyl and methyl amino radicals obtained from the appearance potential data permit a determination of bond strengths in the methylhydrazines and other nitrogen-containing molecules.

Introduction

Electron impact studies[3] have been reported for a variety of molecules containing one or more nitrogen atoms. Recently, a study of the ionization and dissociation of the volatile azides, hydrazoic acid and methyl azide, has been completed.[4] Another interesting series of nitrogen-containing molecules is the hydrazines. Harshman[5] has compiled physical and chemical properties of hydrazine and a number of alkyl-substituted hydrazines. The mass spectrum of hydrazine is given in the API tables[6] and a mass spectrometric study of hydrazine subjected to electrodeless discharge has been reported by Foner and Hudson.[7] Very little else is known or published concerning the behavior of such molecules under electron bombardment. Furthermore, the hydrazines, particularly 1,1-dimethylhydrazine, have proved to be of great interest and practical value as high energy fuels. Thus, as a matter of practical importance as well as theoretical interest, the present research was undertaken: *viz.*, to obtain fundamental information on ionization potentials, specific bond dissociation energies and heats of formation of the various products of the ionization–dissociation processes.

Experimental

Mass spectra and appearance potentials were obtained by means of a 6-inch radius of curvature, first order direction focusing mass spectrometer. General instrumental arrangement and provisions for adaptation to measure positive or negative ions or ions with excess kinetic energy have been described previously in some detail.[4] Briefly, ion source and collector were maintained near ground potential while the analyser tube was at -1000 v. for positive ions. Some measurements were made at 2000 v. ion accelerating potential. Mass spectra were obtained for nominal electron energies of 70 v. by varying the magnetic field at constant ion accelerating voltage. Ion currents were measured using a vibrating reed electrometer. Minimum ion currents of 10^{-15} amp. were measured reproducibly using a 10^{11} ohm input resistor. The ionizing voltage scale was calibrated by comparing the observed ionization potentials of argon and krypton with the known spectroscopic values.[8] Either of these gases was introduced simultaneously with the hydrazine. Appearance potentials were evaluated in a manner previously described.[4]

The hydrazine, monomethyl-, 1,1-dimethyl-, trimethyl- and tetramethylhydrazines were very kindly supplied by Dr. William McBride, U.S. Naval Ordnance Test Station, China Lake, California, through Dr. J. R. McNesby. These samples were received as purified materials sealed under their own vapor pressure in glass ampules. The 1,2-dimethylhydrazine was obtained from the Metalectro Corporation, Laurel, Maryland. The minimum purity of the latter was 98% as stated by the supplier. Mass spectra indicated only traces of impurities of higher molecular weight in any of the samples and with the possible exception of isomeric impurities in either of the dimethylhydrazines, we estimate total impurities to be less than 2% in any sample.

Results

The results of these studies are summarized in Tables I–VI. The principal ions and their relative abundances in the mass spectrum of each compound are given for 70 v. electrons in columns 1 and 2. The appearance potentials of various ions and our opinion as to the probable process by which each is formed appear in columns 3 and 4. Unless otherwise indicated, column 5 gives the heat of formation of the ion calculated from the appearance potential according to the process shown. In these thermochemical calculations we employed the following heats of formation of the compounds in the gas phase as given by Harshman[5]: N_2H_4, 22.7; $CH_3N_2H_3$, 22.3; 1,1-dimethylhydrazine, 19.7; 1,2-dimethylhydrazine, 21.6. All values are in kcal./mole. Heats of formation of trimethyl- and tetramethylhydrazine have not been determined and were estimated using the method of group equivalents[9] as follows:

TABLE I

MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF HYDRAZINE

m/e	Rel. abundance (%)	A.P.(e.v.)	Process	ΔH_f(ion) (kcal./mole)
32	100.0	$9.0_0 \pm 0.1$	$N_2H_4 \rightarrow N_2H_4^+$	229
31	32.8	$11.3 \pm .1$	$\rightarrow N_2H_3^+ + H$	230
30	19.6	$11.9 \pm .2$	$\rightarrow N_2H_2^+ + H_2$	297
30		$16.6 \pm .1$	$\rightarrow N_2H_2^+ + 2H$	300
29	16.2	$14.8 \pm .3$	$\rightarrow N_2H^+ + H_2 + H$	311
28	2.7	$16.2 \pm .1$	$\rightarrow N_2^+(A^2\Pi_u?) + 2H_2$	396
17	9.0			
16	4.8			
15	0.5			
14	0.1			

Taking the value of the $-NH_2$ group as 11.4 kcal./mole from N_2H_4 we determine the value of CH_3NH and $(CH_3)_2N-$ to be, respectively, 10.9 and 8.3

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[3] For a compilation of such studies through 1955, see: F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957.

[4] J. L. Franklin, V. H. Dibeler, R. M. Reese and M. Krauss, THIS JOURNAL, **80**, 298 (1958).

[5] R. C. Harshman, *Jet Propulsion*, **27**, 398 (1957).

[6] A.P.I. Tables of Mass Spectral Data, Serial No. 1110.

[7] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958).

[8] C. E. Moore, "Atomic Energy Levels," Natl. Bur. Standards (U. S.) Circ. 467.

[9] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

TABLE II

MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF MONOMETHYLHYDRAZINE

m/e	Relative abundance (%)	A.P.(e.v.)	Process	ΔH_f(ion) (kcal./mole)
46	100	8.63 ± 0.1	$CH_3N_2H_3 \rightarrow CH_3N_2H_3^+$	221
45	66.5	10.2 ± .1	$\rightarrow CH_5N_2^+ + H$	204
44	2.6	10.4 ± .2	$\rightarrow CH_4N_2^+ + H_2$	263
43	7.4	11.9 ± .3	$\rightarrow CH_3N_2^+ + H_2 + H$	242
43		14.8 ± .3	$\rightarrow$? ?	
42	4.4	15.2 ± .2	$\rightarrow CH_2N_2^+ + H_2 + 2H$	267
41	1.2	....		
31	42.2	10.7 ± .3	$\rightarrow N_2H_3^+ + CH_3$	237
30	15.7	11.2 ± .2	$\rightarrow N_2H_2^+ + CH_4$	298
29	23.3	13.3 ± .3	$\rightarrow N_2H^+ + CH_3 + H_2(?)$	296
28	58.0	13.2 ± .3	$\rightarrow N_2^+ + CH_4 + H_2(?)$	305
27	4.0	....	$\rightarrow (HCN^+ + ?)$	
15	5.1	14.1 ± .3	$\rightarrow CH_3^+ + N_2H_3$	87[a]

[a] ΔH_f radical.

TABLE III

MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF 1,1-DIMETHYLHYDRAZINE

m/e	Relative abundance (%)	A.P.(e.v.)	Process	ΔH_f(ion) (kcal./mole)
60	100.0	8.12 ± 0.1	$(CH_3)_2N_2H_2 \rightarrow (CH_3)_2N_2H_2^+$	207
59	40.2	10.2 ± .2	$\rightarrow C_2H_7N_2^+ + H$	202
45	39.3	9.7 ± .2	$\rightarrow CH_3N_2H_2^+ + CH_3$	211
44	9.7	10.9 ± .2	$\rightarrow (CH_3)_2N^+ + NH_2$	44[a]
43	19.2	12.5 ± .2	$\rightarrow C_2H_5N^+ + NH_2 + H(?)$	214
43		13.5 ± .2	? ?	
42	55.7	12.8 ± .2	$\rightarrow (CH_2)_2N^+ + NH_2 + H_2(?)$	274
41	3.6	....		
32	2.0	....		
31	2.3	....		
30	22.2	12.9 ± .1	$\rightarrow N_2H_2^+ + C_2H_4 + H_2(?)$	304
29	6.1	14.2 ± .5	?	
28	24.3	13.2 ± .1	$\rightarrow N_2^+ + 2CH_4\ (?)$	358
27	1.8	....		
15	12.7	14.5 ± .3	$\rightarrow CH_3^+ + CH_3NNH_2$	94[a]

[a] ΔH_f radical.

TABLE IV

MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF 1,2-DIMETHYLHYDRAZINE

m/e	Relative abundance (%)	A.P.(e.v.)	Process	ΔH_f(ion) (kcal./mole)
60	80.3	7.75 ± 0.1	$(CH_3)_2N_2H_2 \rightarrow (CH_3)_2N_2H_2^+$	200
59	4.4	9.3 ± .2	$\rightarrow C_2H_7N_2^+ + H$	184
45	100.0	9.1 ± .2	$\rightarrow CH_3N_2H_2^+ + CH_3$	200
44	41.0	9.7 ± .3	$\rightarrow CH_3N_2H^+ + CH_4$	264
43	9.3	9.7 ± .5	$\rightarrow CH_3N_2^+ + CH_3 + H_2$	213
42	8.5	12.1 ± .5	$\rightarrow (CH_2)_2N^+ + NH_2 + H_2(?)$	259
41	0.5	....		
32	3.8	....		
31	6.8	10.2 ± .2	$\rightarrow N_2H_3^+ + C_2H_5$	233
30	63.0	11.0 ± .2	$\rightarrow N_2H_2^+ + C_2H_6$	295
30		13.0 ± .2	$\rightarrow N_2H_2^+ + C_2H_4 + H_2(?)$	309
29	19.2	11.7 ± .2	? ?	
28	71.2	12.5 ± .2	$\rightarrow N_2^+ + 2CH_4(?)$	345
27	5.0	....		
15	12.1	13.9 ± .3	$\rightarrow CH_3^+ + CH_3NHNH$	82[a]

[a] ΔH_f radical.

kcal./mole from the heats of formation of methylhydrazine and 1,1-dimethylhydrazine. From these the heats of formation of gaseous trimethyl- and tetramethylhydrazines are estimated readily to be 19.2 and 16.6 kcal./mole., respectively.

Omitted from the tabulated spectra but discussed in a following section are a number of ions, the abundances of which were dependent on the pressure and thus assumed to be formed by secondary processes. Also omitted from the tables are ions ob-

TABLE V

MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF TRIMETHYLHYDRAZINE

m/e	Relative abundance (%)	A.P.(e.v.)	Process	ΔH_f(ion) (kcal./mole)
74	64	7.93 ± 0.1	$(CH_3)_3N_2H \rightarrow (CH_3)_3N_2H^+$	202
73	7.5	8.9 ± .1	$\rightarrow C_3H_9N_2^+ + H$	173
72	30	8.2 ± .1	$\rightarrow C_3H_8N_2^+ + H_2$	207
71	11.1	10.7 ± .1	$\rightarrow C_3H_7N_2^+ + H_2 + H$	214
59	100.0	9.4 ± .1	$\rightarrow (CH_3)_2N_2H^+ + CH_3$	203
58	3.0	....		
57	15.0	11.1 ± .4	$\rightarrow (CH_2)_2N_2H^+ + CH_3 + H_2$(?)	242
45	1.5	....		
44	28	11.1 ± .2	$\rightarrow (CH_3)_2N^+ + CH_3NH$	48[a]
43	32.2	10.7 ± .3	$\rightarrow$ S-$C_3H_7^+ + N_2H_3$(??)	76[a]
42	100.5	11.7 ± .2	$\rightarrow (CH_2)_2N^+ + NH_2 + CH_4$	268
41	8.6	12.1 ± .2	? ?	
40	6.0	....		
39	1.8	....		
32	11.7	11.9 ± .2	$\rightarrow N_2H_4^+ + C_2H_2, CH_4$ (?)	256
31	9.4	11.7 ± 1.0	$\rightarrow N_2H_3^+ + C_2H_4 + CH_3$ (?)	244
30	13.3	11.9 ± 1.0	$\rightarrow N_2H_2^+ + C_2H_4 + CH_4$ (?)	298
29	11.9	12.4 ± 1.0	? ?	
28	66.3	13.2 ± 0.2	$\rightarrow N_2^+ + CH_4 + C_2H_6$ (?)	361
27	14.4	....		
15	45.0	14.0 ± 0.5	$\rightarrow CH_3^+ + (CH_3)_2N_2H$	81[a]

[a] ΔH_f radical.

TABLE VI

MASS SPECTRUM AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF TETRAMETHYLHYDRAZINE

m/e	Relative abundance (%)	A.P.(e.v.)	Process	ΔH_f(ion) (kcal./mole)
88	105.0	7.76 ± 0.05	$(CH_3)_4N_2 \rightarrow (CH_3)_4N_2^+$	196
73	95.0	9.1 ± .1	$\rightarrow (CH_3)_3N_2^+ + CH_3$	196
72	3.1	8.9 ± .1	$\rightarrow C_3H_8N_2^+ + CH_4$ (?)	242
71	5.5	10.7 ± .1	$\rightarrow C_3H_7N_2^+ + CH_3 + H_2$	233
58	6.0	10.5 ± .1	$\rightarrow C_2H_6N_2^+ + C_2H_6$ (?)	279
58		13.3 ± .5	$\rightarrow C_2H_6N_2^+ + 2CH_3$ (?)	262
57	5.2	12.4 ± .2	$\rightarrow C_2H_5N_2^+ + CH_3 + CH_4$(?)	289
46	40	10.9 ± .2	?	
46		12.3 ± .2	?	
45	8.1	9.7 ± .2	?	
44	85.5	11.2 ± .2	$\rightarrow (CH_3)_2N^+ + (CH_3)_2N$	51[a]
43	50.6	10.9 ± .2	$\rightarrow$ S-$C_3H_7^+ + CH_3N_2H_2$ (?)	78[a]
43		13.2 ± .3	$\rightarrow$ S-$C_3H_7^+ + CH_3 + N_2 + 2H$(?)	187
42	100.0	12.2 ± .2	$\rightarrow (CH_2)_2N^+ + NH_2 + C_2H_6$(?)	277
41	7.2	~13		
40	4.5	....		
32	17	12.3 ± .1	$\rightarrow N_2H_4^+ + C_3H_5 + CH_3$ (?)	238
30	26	11.9 ± .2	$\rightarrow N_2H_2^+ + C_2H_6 + C_2H_4$(?)	299
28	26.9	13.1 ± .2	$\rightarrow N_2^+ + 2C_2H_6$	360
27	4.2	....		
15	50.4	14 ± 1	$\rightarrow CH_3^+ + (CH_3)_3N_2$	79[a]

[a] ΔH_f radical.

served at *m/e* = 14, 16, 17 and 18. Appearance potentials of these ions gave strong evidence that they originated from small amounts of NH_3 and H_2O either desorbed from the interior surfaces of the sample introductory system or formed by chemical reaction in the ion source.

No negative ions were observed in the spectra of these hydrazines. It is estimated that the maximum abundance relative to the most abundant positive ion in each case is less than 0.001.

Several selected ions of low *m/e*, *e.g.*, *m/e* = 44 and *m/e* = 15, were examined for evidence of excess kinetic energy. Although no excess energy was observed, an unusually large uncertainty of 0.3 v. is associated with the "zero" energy determination. This was probably the result of deposits accumulating in the slit systems.

Discussion

Mass Spectra.—The partial spectrum of hydrazine given in Table I is generally in agreement with that previously obtained on a 180° mass spectrometer and published in the A.P.I. tables of mass spectral data.[6] The reported abundances in the

N_1-group were obtained after correcting our spectrum for water, assuming that all of the observed $m/e = 18$ was the H_2O^+ ion. However, we observed no unaccountable ions at $m/e = 12$ and 27 as previously reported,[6] although at unusually high pressures, the $m/e = 33$ ion was pressure dependent.

Spectra of the methyl-substituted hydrazines have not been reported previously. The tabulated spectra are mutually consistent, generally demonstrating the expected relation between successive methyl substitution and dissociation probability. The spectra of the dimethylhydrazines show significant differences that are again consistent with molecular structure.

Appearance Potentials. Parent Ions.—The parent ions are formed, of course, by a vertical transition process as required by the Franck-Condon rule. Hall[10] and Franklin[11] have shown that the use of antisymmetrized orbitals permits a ready semiempirical calculation of ionization potentials if there are known ionization potentials sufficient to provide the necessary empirical parameters. Taking the ionization potential of methane as 13.12 v.[3] and those of hydrazine and monomethylhydrazine from this study, and neglecting second-order interactions, ionization potentials of the remaining methylhydrazines were calculated. The results given in Table VII show generally satisfactory agreement. However, the measured value for the symmetrical dimethylhydrazine is considerably lower than either the calculated value or the measured ionization potential of the unsymmetrical dimethyl compound, suggesting that a different process may be occurring here.

TABLE VII

MOLECULAR IONIZATION POTENTIALS OF THE HYDRAZINES

	Ionization potential (e.v.) calcd.	Ionization potential (e.v.) obsd.
N_2H_4	(9.00)	(9.00)
$CH_3N_2H_3$	(8.63)	(8.63)
$(CH_3)_2NNH_2$	8.3	8.12
$(CH_3NH)_2$	8.3	7.75
$(CH_3)_3N_2H$	8.0	7.93
$(CH_3)_4N_2$	7.75	7.76

Parameters: $e[I(CH_4)] = 13.12$ v.
$f[I(N_2H_4)] = 9.00$ v.
c(interaction constant) $= 1.29$ v.

m/e = **73.**—This ion is formed in both trimethyl- and tetramethylhydrazine and is undoubtedly $C_3H_9N_2^+$. The abundance of this ion from the former is rather small (7.5%) whereas that from the latter is quite large (95%). Consequently we place more reliance upon the appearance potential determined for $C_3H_9N_2^+$ from tetramethylhydrazine. Thus we consider the more probable value of $\Delta H_f(C_3H_9N_2^+)$ to be 193 kcal./mole.

m/e = **72.**—This ion is formed in considerable abundance from trimethylhydrazine. Its composition is unequivocal and, in view of the low appearance potential, there seems little doubt that H_2, rather than H atoms, is formed in the process. The corresponding ion from tetramethylhydrazine is found in very low abundance and hence the appearance potential is probably not very accurate. The ion could be either $C_3H_8N_2^+$ or $C_4H_{10}N^+$. We are inclined to favor $C_3H_8N_2^+$ although the heat of formation does not agree well with that obtained from trimethylhydrazine.

m/e = **71.**—Ions of this mass are formed in rather low abundance from the trimethyl and tetramethyl compounds. The ion from the trimethyl is $C_3H_7N_2^+$ formed by elimination of H_2 and H. The analogous reaction with tetramethylhydrazine involves elimination of H_2 and CH_3 (or CH_4 and H) and leads to a $\Delta H_f(C_3H_7N_2)^+$ which agrees poorly with that from trimethylhydrazine. The ion could, of course, be $C_4H_9N^+$, but we are inclined to prefer $C_3H_7N_2^+$ as this reaction requires less extensive rearrangement than does that for the formation of $C_4H_9N^+$.

m/e = **59.**—Large peaks at this mass were observed in 1,1-dimethyl- and trimethylhydrazine and a rather small peak (4%) was observed for the symmetrical dimethyl compound. In all cases the ion is undoubtedly $C_2H_7N_2^+$ and the heat of formation as determined from the appearance potentials of the ion from the 1,1-dimethyl- and trimethylhydrazine is 202 kcal./mole. The value obtained from the 1,2-dimethyl compound may be considered as only approximate because of the low abundance.

m/e = **45.**—The peak at $m/e = 45$ from methylhydrazine can be formed only by the removal of a hydrogen atom, the heat of formation of the ion being calculated as 204 kcal./mole. The ion of this mass from the dimethylhydrazines could be either $CH_3N_2H_2^+$ formed with the loss of CH_3, or $C_2H_7N^+$ formed with the loss of NH. The former mechanism gives values of 211 and 200 kcal., respectively, for the heat of formation of the ion from the two dimethylhydrazines. The heats of formation of $C_2H_7N^+$, calculated using $\Delta H_f(NH) = 81$ kcal./mole,[4] result in the values 162 and 151 kcal./mole. These do not correspond to known heats of formation of the ion of 203 to 213 kcal./mole. Thus we conclude that the mass 45 ion from the dimethylhydrazines is $CH_3N_2H_2^+$.

m/e = **44.**—The only ion of this mass that can be formed from methylhydrazine is $CH_4N_2^+$. The low value of the appearance potential implies that H_2 rather than 2H is ejected and the resulting value of $\Delta H_f(CH_4N_2^+)$ is 263 kcal./mole in reasonable concordance with the 297 kcal./mole found for the analogous $N_2H_2^+$ ion.

With the higher methylhydrazines the mass 44 ion may be either $C_2H_6N^+$ or, in the case of the tri- and tetramethyl compounds, $C_3H_8^+$. The simplest reaction for producing an ion of mass 44 from the 1,2-dimethylhydrazine would seem to be one involving elimination of CH_3 and H or CH_4. If one assumes, by analogy to the reaction producing this ion (ΔH_f = 263 kcal./mole) from methylhydrazine, that CH_4 is eliminated, one obtains a value of 264 kcal./mole for $\Delta H_f(CH_4N_2^+)$. This excellent agreement is somewhat fortuitous.

The 1,1-dimethyl-, trimethyl- and tetramethylhydrazines will form an ion of mass 44 most simply by rupture of the N–N bond. Here no rearrange-

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(10) G. G. Hall, *Trans. Faraday Soc.*, **49**, 113 (1953); **50**, 319 (1954).

(11) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).

ment is involved and the appearance potentials of these three are grouped rather closely and are somewhat removed from those of the mass 44 ion from the other two hydrazines. If we assume this mechanism and employ Collin's[12] value of 227 kcal./mole for $\Delta H_f[(CH_3)_2N^+]$ obtained by electron impact studies of $(CH_3)_3N$, we can calculate the heats of formation of the radicals NH_2, CH_3NH and $(CH_3)_2N$. We obtain in this way 44, 48 and 51 kcal./mole, respectively. The value of 44 for NH_2 agrees within experimental accuracy with the accepted value of 41 kcal./mole given by Szwarc.[13] The other values are concordant with this and thus we consider the proposed mechanism to be the most probable for the formation of the mass 44 ion from these three hydrazines.

m/e = **43**.—The only process for the formation of ions of this mass that can be identified with confidence is that leading to the formation of $CH_3N_2^+$ from monomethylhydrazine. In view of the rather low appearance potential and the high degree of unsaturation of the ion it is probable that H_2 and H are the neutral species formed.

m/e = **42**.—Ions of this mass are observed in all of the methylhydrazines and again the abundance pattern divides them into two classes. The mono-methyl and 1,2-dimethyl compounds have small peaks at mass 42 whereas the other methylhydrazines give this ion in great abundance. However, appearance potentials group all of the higher methylhydrazines together with only the methylhydrazine showing a marked difference from the others. This ion from methylhydrazine is $CH_2N_2^+$, and we are inclined to think that the mass 43 ion from the tetra-, tri- and 1,1-dimethylhydrazines is $(CH_2)_2N^+$. The composition of the ion from the 1,2-dimethyl compound is more doubtful.

m/e = **31**.—The ion of mass 31 from N_2H_4 is $N_2H_3^+$ and its heat of formation is 230 kcal./mole. The corresponding ion from methylhydrazine might be either $N_2H_3^+$ or $CH_3NH_2^+$. The heat of formation calculated on the assumption that the ion is $N_2H_3^+$ is 237 kcal./mole in reasonable agreement with that from hydrazine. If the ion were $CH_3NH_2^+$, we would calculate a heat of formation of of 188 kcal./mole which is in poor agreement with the value of 210 kcal./mole[3] for this ion as calculated from the ionization potential of methylamine. We conclude, then, that this ion is $N_2H_3^+$.

Peaks of modest abundance were also obtained at this mass with both 1,2-dimethyl- and trimethylhydrazine. The appearance potentials of these ions were similar to those obtained with N_2H_4 and $CH_3N_2H_3$. It is possible to devise mechanisms for the formation of either $N_2H_3^+$ or $CH_3NH_2^+$ in reasonable agreement with the measured appearance potentials. These would necessarily be highly speculative and no unique interpretation of the results seems possible at present.

m/e = **30**.—Ions of this mass are formed in considerable abundance from all of the hydrazines. That from N_2H_4 has two appearance potentials corresponding to the formation of H_2 and of 2H along with $N_2H_2^+$. Foner and Hudson also observe two appearance potentials for the $N_2H_2^+$ ion[14] in hydrazine. We are in agreement (see Table I) with their value (~16.4 e.v.) for the higher energy process but not with their value (11.0 e.v.) for the lower energy process. Their voltage interval (approx 5.4 ev.) is 0.9 e.v. greater than the energy required for $D(H_2)$.

If the ion from methylhydrazine is $N_2H_2^+$ and methane is formed concurrently, the heat of formation is found to be 298 kcal./mole. in excellent agreement with the value of 297 from hydrazine. This ion, however, could also be CH_3NH^+ and, if so, the corresponding neutral fragment would be NH_2. Collin[12] gives appearance potentials of CH_4N^+ from several amines and these lead to rather widely divergent values of $\Delta H_f(CH_4N^+)$. If we take the value of 226 kcal./mole as determined from $(CH_3)_2NH$, we calculate $\Delta H_f(NH_2)$ of 54 kcal./mole from our appearance potential of CH_3NH^+ from methylhydrazine. This is 13 kcal./mole greater than the accepted value, but the discrepancy is not sufficient to permit us to reject this mechanism with complete assurance.

In the case of 1,2-dimethylhydrazine, two appearance potentials are found for the ion of mass 30. If, by analogy to hydrazine, we assume the ion to be $N_2H_2^+$ we find

	$A(N_2H_2^+)$	ΔH ion
$CH_3NHNHCH_3 \rightarrow N_2H_2^+ + C_2H_6$	11.0 ± 0.2	295
$\rightarrow N_2H_2^+ + C_2H_4 + H_2$	13.0 ± 0.2	309

in good agreement with the value from hydrazine. However, if the ion is CH_3NH^+ it is reasonable to assume the neutral fragment to be the CH_3NH radical for which we calculate a heat of formation of 49 kcal./mole. The higher appearance potential could well correspond to further decomposition of the radical to CH_3 and NH (or other fragments), the calculated and measured values being in reasonable agreement.

In the cases of the remaining hydrazines, mechanisms can be devised to produce either $N_2H_2^+$ or CH_4N^+ in reasonable agreement with the measured appearance potentials.

m/e = **29**.—Although this ion is formed in moderate abundance in four of the hydrazines studied, no very satisfactory values for ionic heats of formation could be calculated and hence in most cases the composition of the ion and the mechanism of its formation are uncertain. With hydrazine it can only be N_2H^+ and for this we calculate a heat of formation of 311 kcal./mole, which is considerably greater than the value of 278 kcal./mole obtained by Franklin, Dibeler, Reese and Krauss[4] from hydrazoic acid. In the case of methyl hydrazine the value calculated on the assumption that the ion is N_2H^+ is 296 kcal./mole, which also agrees rather poorly with the value from hydrazoic acid. If the ion is assumed to be CH_3N^+, the result is in no better agreement with Kandel's[15] value obtained from nitromethane. The higher hydrazines give values even more difficult to interpret and so we are unable to make reasonable assignments as to the nature of these ions.

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[12] J. Collin, *Bull. soc. chim. Belges*, **62**, 411 (1953).

[13] M. Szwarc, *Chem. Revs.*, **47**, 75 (1956).

[14] Private communication, Dr. S. N. Foner.

[15] R. J. Kandel, *J. Chem. Phys.*, **23**, 84 (1955).

m/e = **28.**—This ion is relatively abundant in all of the methylhydrazines but the peak is quite small (2.7%) in hydrazine. If it is assumed that the ion is N_2^+ and that the neutral fragments are released in a double, four-center decomposition across the N–N bond, quite good agreement is obtained in most cases with the known $\Delta H_f(N_2^+)$. The exception is hydrazine and this is not unexpected as the abundance was too small to permit reliable appearance potential measurements.

m/e = **15.**—The spectra of all of the methylhydrazines exhibited peaks at mass 15, the abundance increasing with the molecular weight of the parent. The appearance potential in all cases was in the neighborhood of 14 volts, the greatest departure from this being 14.5 v. for 1,1-dimethylhydrazine. The ion abundance curves for the compounds of lower molecular weight were quite well behaved, but the trimethyl and especially the tetramethylhydrazine gave curves that approached the axis very slowly, resulting in a considerable increase in the uncertainty of measuring the onset potential. Such behavior could result from formation of the *m/e* = 15 ion by two or more processes with appearance potentials differing by amounts less than the energy spread in the electron beam.

The mass 15 ion could, of course, be either CH_3^+ or NH^+. If we assume it to be the latter and calculate its heat of formation, we obtain values 50–70 kcal./mole lower than the known heat of formation of NH^+. We conclude then that in all cases this ion is methyl. Since the ionization potential of methyl is known to be 9.96 v.[3] we can calculate the strength of the C–N bond and the heat of formation of N_2H_3 and various methyl-substituted hydrazyl radicals. For these calculations to be valid, correction must be made for any excess energy involved in the fragmentation process. However, Foner and Hudson[14] have recently obtained a direct measure of the ionization potential of the hydrazyl radical of 7.88 ± 0.2 e.v. This combined with either their or our measurement of the appearance potential of the $N_2H_3^+$ ion in hydrazine results in a quite reasonable N–H bond strength of about 76 kcal./mole. This leads to a heat of formation of N_2H_3 which is considerably lower than would be obtained from our indirect measurements, and we are forced to conclude that our determinations of the $A(CH_3^+)$ ion must include some excess energy.

Secondary Ions.—With all of the hydrazines a surprisingly large peak always was observed at one mass unit above that of the parent ions. The relative abundance of these peaks varied with pressure indicating that the ions are formed by a secondary process. We made approximate measurements of the appearance potentials of these ions and found that they agreed fairly well with the ionization potential of the hydrazine under investigation. From this we conclude that these ions probably are formed by the process

$$RH^+ + RH \longrightarrow RH_2^+ + R$$

The present instrument provides no suitable means to determine accurately the pressure in the ionization chamber. Thus a study of the rates of these reactions is not presently feasible. We hope to undertake such a study in the near future.

Bond Strengths.—In these studies we have determined the heat of formation of various hydrazyl radicals and of the CH_3NH and $(CH_3)_2N$ radicals. From these and appropriate heats of formation, the strength of various bonds involving these radicals can be computed. Table VIII gives the strength of C–N and N–H bonds in the methylamines and of the N–N bond in the various hydrazines. It is interesting that the C–N and N–H bonds in the amines increase in strength with increasing methyl substitution. This behavior is in marked contrast to that of the paraffin hydrocarbons where bond strengths tend to decrease as molecular weight and substitution of methyls for hydrogens increase.

TABLE VIII

BOND STRENGTHS IN CERTAIN NITROGEN COMPOUNDS, KCAL./MOLE

	CH_3	NH_2	CH_3NH	$(CH_3)_2N$
H	102	104	107	110
CH_3	84	80	87	94
NH_2		60	67	72
CH_3NH			74	80
$(CH_3)_2N$				85

Bond Strengths in Ions.—The strength of a given bond in an ion can be computed from the heats of formation of the parent ion and appropriate fragments. If one makes these calculations, one finds, in common with the paraffin hydrocarbons, that the $D(R^+\text{–}H)$ and $D(R^+\text{–}CH_3)$ are much smaller than the corresponding bond strengths in the neutral molecule. On the other hand, the strengths of the N–N bond in the hydrazine ions are about twice as great as those in the neutral compounds.

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