half-order rate laws are observed.[35] Square root rate dependence has also been taken as evidence for radical intermediates in other reactions of sulfur.[36] Relative rate studies of a series of arylmethyl compounds give support to the hypothesis that the oxidation studied here involves free radicals.[26] However, it should be pointed out that sulfur–olefin reactions in hydrocarbon solvents at 140° and polysulfide oxidation in aqueous solution at 300° may differ drastically in mechanism.

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[CONTRIBUTION FROM THE IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION, RESEARCH DEPARTMENT]

The Mass Spectrum of Trimethylhydrazine

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The high resolution mass spectrum of trimethylhydrazine is given and is shown to differ in several respects from the previously published low resolution spectrum. In particular, several peaks which were considered to be singlets have now been shown to be multiplets.

The mass spectra of hydrazine and the methyl substituted hydrazines recently have been reported by Dibeler, Franklin and Reese.[1,2] The information obtained, regarding relative abundances and appearance potentials of the principal ions, has been used to estimate heats of formation and probable ionization processes. The empirical formulas of the various ion species have been suggested to be those which would be formed in the most direct processes, and it has been assumed further that only a single ion species contributed to the peak at a particular mass number.

TABLE I

MASS SPECTRUM OF TRIMETHYLHYDRAZINE

(Ions containing C^{13}, N^{15} or D are only listed when they form the major contribution to the peak)

Mass	Relative abundance (%)	Formula
14	2.2	CH_2
15	26.2	CH_3
16	0.12	NH_2
	4.4	CH_4
17	0.33	NH_3
18	14.7	NH_4
26	0.09	CN
	0.24	C_2H_2
27	1.3	CHN
	1.8	C_2H_3
28	16.4	CH_2N
29	2.2	HN_2
	1.2	CH_3N
	2.4	C_2H_5
30	51.5	CH_4N
31	6.9	CH_5N
32	11.3	CH_6N
36	3.3	$C_3H_8N_2{}^{++}$
36.5	0.89	$C_3H_9N_2{}^{++}$
38	0.18	C_3H_2
39	0.30	C_3H_3
40	0.72	C_2H_2N
41	1.3	C_2H_3N
42	0.18	CH_2N_2
	59.5	C_2H_4N
43	8.3	CH_3N_2
	8.3	C_2H_5N
44	0.24	CH_4N_2, $C^{13}H_3N_2$ $CH_3N^{14}N^{15}$
	14.3	C_2H_6N
45	1.4	C_2H_7N
46	2.9	C_2H_8N
57	11.3	$C_2H_5N_2$
58	2.2	$C_2H_6N_2$
59	100	$C_2H_7N_2$
60	3.7	$C^{12}C^{13}H_7N_2$ and $C_2H_7N^{14}N^{15}$
71	15.6	$C_3H_7N_2$
72	25.2	$C_3H_8N_2$
73	3.3	$C_3H_9N_2$
74	91.2	$C_3H_{10}N_2$
75	4.9	$C_2{}^{12}C^{13}H_{10}N_2$ and $C_3H_{10}N^{14}N^{15}$

In the course of an investigation in these laboratories we had occasion to plot the spectrum of trimethylhydrazine in a Metropolitan–Vickers M.S. 8 double-focussing mass spectrometer.[3] We took, therefore, the opportunity of measuring the empirical formulas of all ions in the spectrum under conditions of high resolution with the aid of accurate mass measurements.[4] It was found that the spectrum obtained was dependent on the temperature of the inlet line. Figure 1 shows three spectra on low resolution which were also obtained corresponding to temperatures of (a) 180°, (b) 140° and (c) 90°. At temperatures below 90° little change could be detected in the spectrum, so that spectrum of the undecomposed sample was assumed to be the one shown in Fig. 1c.

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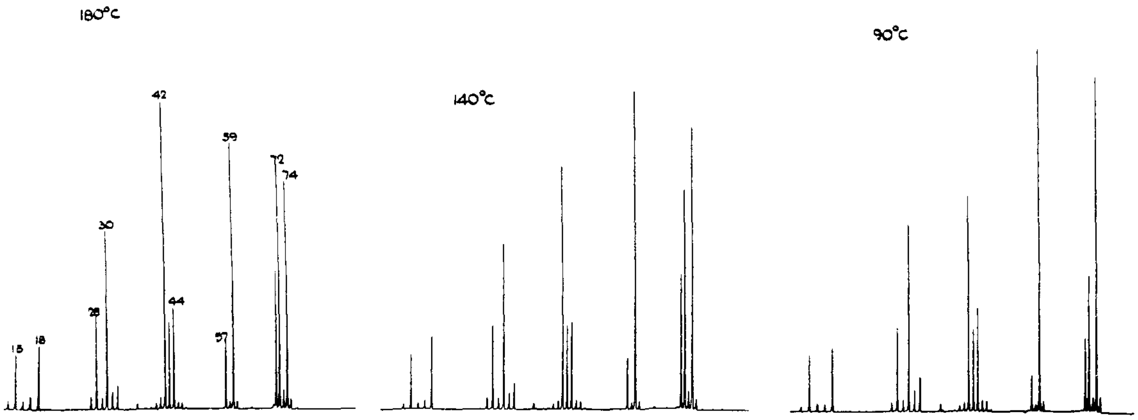

Fig. 1.

The spectrum given by Dibeler, *et al.*, would appear, in the region of the parent ion, to fall somewhere between Figs. 1b and 1c, but the high intensity of some fragment ions (*e.g.*, mass 42) would seem to suggest decomposition. The complete spectrum which we have obtained is given in Table I. There is no difficulty in assigning the ionization processes above mass 57, but below this mass number the empirical formulas of the ions produced by 70 v. electrons have now been identified directly where previously Dibeler, *et al.*, made suggestions about the ion formulas based on appearance potential measurements. Their positive identifications were limited, however, to the ions of masses 15, 42 and 44. The actual ion formulas found often differ from those suggested by Dibeler, *et al.* In some cases the peaks are actually multiplets (*e.g.*, mass 29 is a triplet and mass 43 is a doublet) and it is, therefore, not possible to explain them by a single process. In other cases (mass 32, CH_6N^+; mass 31, CH_5N^+; mass 30, CH_4N^+; mass 28, CH_2N^+) although one ion species predominates, this ion is found to differ from the composition suggested on energetic considerations alone. In the cases of masses 27, 29, 39, 40, 41, 45 and 58 it has now been possible to assign formulas which were not previously possible.

It should be noted that the abundances quoted in Table I are those which obtain for 70 e.v. electrons and it does not necessarily follow that the major species at each mass number will have the lowest ionization potential. A metastable peak 0.7% of the base peak intensity was noted on the low resolution spectrum at mass 47 which corresponds to the transition p → p-15.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A General Treatment of Equilibrium Polymerization

BY A. V. TOBOLSKY AND A. EISENBERG

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A general theory of equilibrium polymerization is presented. Three chemical categories are discussed: equilibrium polymerization in the presence of an initiator, *e.g.*, caprolactam, and two categories that do not involve an initiator, represented by sulfur and by vinyl monomers, respectively. Two mathematical approximations are considered. In certain cases the chemical facts and the experimental results allow a treatment based on a single equilibrium constant. In very many cases, however, a two constant treatment is necessary, *e.g*, caprolactam initiated by water and the polymerization of sulfur. It is suggested that a two constant treatment is also necessary for describing the equilibrium polymerization of vinyl monomers.

A General Treatment of Equilibrium Polymerization.—Three general cases of equilibrium polymerization may be distinguished: we shall classify these cases as Case I, Case II and Case III. We shall designate monomer as M, polymerization initiator (where present) as XY, concentrations (generally in moles per kilogram) will be designated as M, XY, etc.

Case I

$$XY + M \overset{K_a}{\rightleftarrows} XMY$$

$$XMY + M \overset{K_b}{\rightleftarrows} XM_2Y$$

$$XM_{n-1}Y + M \overset{K_n}{\rightleftarrows} XM_nY$$

Case II

$$M \overset{K_a}{\rightleftarrows} M^*$$

$$M^* + M \overset{K_b}{\rightleftarrows} M^*_2$$

$$M^*_{n-1} + M \overset{K_n}{\rightleftarrows} M^*_n$$

(The asterisk represents an activated state such as a diradical or a zwitterion)

Case III

$$M + M \overset{K_a}{\rightleftarrows} M_2$$

$$M_2 + M \overset{K_b}{\rightleftarrows} M_3$$

$$M_n + M \overset{K_n}{\rightleftarrows} M_n$$