

599. *The Pyrolyses of Hydrazines and Benzylamines. C-C and N-N Bond Dissociation Energies.*

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Pyrolyses of methylhydrazines and *N*-methylbenzylamines have been studied by the toluene-carrier technique. First-order rate constants for the homogeneous decompositions have been obtained by analysis of the gaseous products. The activation energies have been equated with the strengths of the bonds broken, from which the following heats of formation of radicals have been calculated: $\Delta H_f^\circ(\text{NH}_2) = 39.8$, $\Delta H_f^\circ(\text{CH}_3\text{NH}) = 34.5$, $\Delta H_f^\circ[(\text{CH}_3)_2\text{N}] = 29.5$ kcal. mole⁻¹. Hence a pattern of bond dissociation energies has been built up from which it is concluded that alkyl-substitution has a greater weakening effect on N-H and N-N bonds than on the corresponding C-H and C-C bonds.

LITTLE is known of bond dissociation energies in nitrogen-containing compounds. Electron-impact studies on methylhydrazines¹ and amines² have been interpreted as showing that $D(\text{N-N})$ increased with increasing methyl substitution in direct contrast to the effect established for $D(\text{C-C})$ and $D(\text{O-O})$. Gowenlock, Pritchard Jones, and Majer³ have recently confirmed the electron-impact results on methylhydrazines but their interpretation leads to $D(\text{N-N})$ and $D(\text{N-H})$ values more in keeping with the trend of other isoelectronic series. The inherent inaccuracy of the electron-impact method has, however, been pointed out.³ Of the few kinetic measurements made on the thermal decompositions of nitrogen-containing compounds those of Szwarc on the pyrolyses of hydrazine⁴ and benzylamine⁵ by the toluene-carrier technique are the most extensive. The scatter of experimental results for the decomposition of hydrazine was considerable and, further, the finding that the rate constants for the homogeneous decomposition of hydrazine were substantially independent of pressure has also been questioned.^{6,7} We have, therefore, reinvestigated these systems and extended the study to related compounds.

¹ Dibeler, Franklin, and Reese, *J. Amer. Chem. Soc.*, 1959, **81**, 68.

² Collin, *Bull. Soc. chim. belges*, 1953, **62**, 411.

³ Gowenlock, Pritchard Jones, and Majer, *Trans. Faraday Soc.*, 1961, **57**, 23.

⁴ Szwarc, *Proc. Roy. Soc.*, 1949, *A*, **198**, 267.

⁵ Szwarc, *Proc. Roy. Soc.*, 1949, *A*, **198**, 285.

⁶ Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publins., London, 1955, p. 111. Gilbert, *Combustion and Flame*, 1958, **2**, 149.

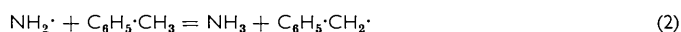
EXPERIMENTAL

Apparatus and Procedure.—The apparatus, a conventional toluene-carrier flow system, has been described previously.⁸ The 155 c.c. reaction zone was reduced to 128 c.c. when packed with quartz tubing, which gave a five-fold increase in the surface area. The hydrazines were injected directly into the toluene stream from a capillary stopcock. The less volatile benzylamines required the U-tube pick-up method. The products were separated in a train of low-temperature traps. The total fraction non-condensable in liquid air, hereinafter referred to as the non-condensable fraction, consisted of mixtures of hydrogen, nitrogen, and methane and was measured in a gas-burette. The nitrogen and methane were then condensed in a trap containing alumina at liquid-air temperature, and the hydrogen was brought back into the gas-burette and measured. The nitrogen-methane mixtures were analysed by gas chromatography on a 250 cm. column packed with 30–60-mesh molecular sieves of type 5A. The simpler hydrogen-nitrogen or hydrogen-methane mixtures were handled in the same way. The condensable second fraction, containing either ammonia or methylamine, was separated from the unchanged toluene and other involatile products by pumping it into the gas-burette from a Le Roy still maintained at -90° . These products were then measured in the gas-burette and their compositions checked from time to time by gas chromatography on a 200 cm. column packed with 40–30 mesh Celite containing 5% of potassium hydroxide and 20% of polyethylene glycol. During a pyrolysis the flow of reactant lasted 10–30 min. depending on the temperature, and with the hydrazines the toluene flowed alone for 5 min. before and after the injection. Contact times were calculated on the assumption that the ideal gas law was obeyed by all substances within the reaction zone. Rate constants were calculated from the usual first-order expression.

Materials.—Hydrazine was prepared by refluxing B.D.H. hydrazine hydrate over an excess of potassium hydroxide for 18 hr. under nitrogen. The fraction distilling between 110° and 111° was collected and refluxed over barium oxide for a further 24 hr.; the product distilling at 110° was then collected. 1,2-Dimethylhydrazine was prepared by Hatt's method.⁹ Tetramethylhydrazine was prepared by the pyrolysis of tetramethyltetrazen (cf. Watson¹⁰). Methylhydrazine, 1,1-dimethylhydrazine, benzylamine, *N*-methylbenzylamine, and *NN*-dimethylbenzylamine were commercial samples which were fractionated at least twice, constant-boiling fractions being collected. All the above reactants were checked by gas chromatography. Toluene was purified as before.⁸

RESULTS AND DISCUSSION

The Pyrolysis of Hydrazine.—The results are shown in Table 1. The homogeneous decomposition of hydrazine in the presence of toluene occurs by the following mechanism, established by Szwarc:⁴



The heterogeneous decomposition, reported in several previous studies, and confirmed by Szwarc,⁴ can be represented:



Whereas Szwarc calculated the rate constants for decomposition of hydrazine from the amount of bibenzyl produced, we have relied on the analysis of the hydrogen, nitrogen, and ammonia. The small amounts of methane produced at high temperatures have been neglected. The rate constants for the overall decomposition of the hydrazine, k_{total} , were calculated from the total amount of hydrazine decomposed, determined from the

⁸ Price and Trotman-Dickenson, *Trans. Faraday Soc.*, 1957, **53**, 939.

⁹ Hatt, *Org. Synth.*, Coll. Vol. II, 1943, 208.

¹⁰ Watson, *J.*, 1956, 3677.

TABLE 1.
The pyrolysis of hydrazine.

Run no.	Temp. (K)	Contact time (sec.)	Toluene pressure (mm.)	N_2H_4 NH_3 $(\text{H}_2 + \text{N}_2)$ H_2				H.F.D.*	k_{total} (sec. ⁻¹)	k_1 (sec. ⁻¹)
				(10 ⁻⁴ mole)						
175	887°	0.52	14.5	18.78	6.39	3.11	1.09	0.046	0.626	0.0288
161	900	0.45	13.1	14.59	2.76	1.19	0.419	0.119	0.285	0.0339
159	906	0.51	16.1	11.47	1.74	0.689	0.244	0.170	0.240	0.0408
172	922	0.50	14.2	23.63	8.95	4.26	1.58	0.097	0.722	0.0701
166	933	0.49	15.1	13.13	2.99	1.23	0.511	0.258	0.376	0.0969
183	943	0.48	14.8	19.78	11.00	6.50	2.75	0.083	1.83	0.109
163	952	0.49	14.9	18.69	8.91	4.31	1.78	0.171	0.940	0.161
198*	958	0.39	14.5	11.34	6.49	3.89	1.76	0.140	1.65	0.230
177	970	0.48	15.0	16.94	13.00	7.66	3.49	0.153	2.07	0.317
182	973	0.48	13.7	18.00	10.70	5.85	2.67	0.192	1.34	0.256
168	974	0.48	14.8	11.94	7.24	3.52	1.60	0.252	1.30	0.327
200*	985	0.37	14.6	16.67	10.60	5.58	2.62	0.244	1.85	0.451
167	989	0.47	14.8	9.34	7.04	3.31	1.58	0.314	1.75	0.551
199*	991	0.37	14.5	6.66	4.59	2.43	1.16	0.257	2.08	0.533
164	991	0.47	14.2	10.44	8.80	3.97	1.84	0.302	2.09	0.632
171	1001	0.46	14.2	10.03	8.48	4.43	2.22	0.314	2.24	0.704
180	1022	0.47	14.2	13.91	16.40	7.93	3.96	0.348	4.38	1.53
165	1022	0.45	14.7	11.53	12.20	6.07	2.96	0.309	3.55	1.10
170	1025	0.45	14.2	5.59	6.52	2.87	1.44	0.389	4.07	1.59
178	1029	0.46	14.3	11.78	13.50	6.45	3.28	0.352	4.06	1.43
179	1030	0.48	14.6	14.91	16.60	8.98	4.49	0.298	4.05	1.21
181	1033	0.47	13.7	7.25	8.89	3.71	1.86	0.411	4.34	1.78
169	1034	0.45	14.3	7.50	9.81	4.43	2.22	0.377	6.64	2.50

* Packed vessel. † Homogeneous fraction of decomposition.

hydrogen, nitrogen, and ammonia in accordance with the above mechanism. The rate constants for the homogeneous decomposition (k_1) were calculated from the expression:

$$k_1 = k_{\text{total}} \times (\text{Homogeneous fraction of the decomposition}),$$

where the homogeneous fraction of the decomposition is equal to [Hydrazine decomposed by reaction (1)]/[Total hydrazine decomposed]. The hydrazine decomposed by reaction (1) was calculated from the amount of ammonia, with allowance for reactions (4) and (5), made from the amounts of nitrogen and hydrogen produced. This procedure for calculating k_1 is justified from the previous results of Szwarc.

Packing the reaction vessel or altering the partial pressure of the hydrazine did not

TABLE 2.
The effect of pressure on the decomposition of hydrazine at 989°K.

Run no.	Contact time (sec.)	Toluene pressure (mm.)	N_2H_4 NH_3 $(\text{H}_2 + \text{N}_2)$ H_2				H.F.D.*	k_{total} (sec. ⁻¹)	k_1 (sec. ⁻¹)
			(10 ⁻⁴ mole)						
190	0.60	6.7	8.31	4.75	2.23	0.920	0.181	0.978	0.177
189	0.63	6.8	8.19	4.75	2.23	0.922	0.187	0.947	0.177
187	0.64	9.7	12.19	8.45	4.60	2.10	0.196	1.26	0.246
192	0.52	10.0	11.28	7.23	4.15	1.88	0.162	1.42	0.230
191	0.54	10.1	15.50	9.74	4.81	2.18	0.241	1.22	0.295
186	0.50	11.8	18.44	10.6	5.49	2.48	0.212	1.20	0.254
184	0.46	14.4	10.13	6.75	3.57	1.170	0.252	1.59	0.400
194	0.43	17.6	18.47	13.0	6.66	3.15	0.260	1.81	0.471
193	0.43	17.8	15.59	9.48	4.69	2.15	0.248	1.46	0.363
195	0.43	23.7	18.47	14.7	7.22	3.40	0.278	2.16	0.600
196	0.41	28.5	23.34	18.5	8.77	4.11	0.292	2.21	0.646

* Homogeneous fraction of decomposition.

affect the rate constants k_1 . Since it was already established that these are independent of contact time this aspect was not investigated further. The rate constant k_1 was, however, found to be markedly dependent upon the toluene pressure, as shown in Table 2. A smaller variation of k_1 with toluene pressure was observed by Szwarc but this was

dismissed as unimportant and the pressure range covered was not as extensive as in the present work. A plot of the homogeneous rate constants, as reported in Table 2, against toluene pressure reveals that k_1 is nearly proportional to pressure. Most of the runs listed in Table 1 were done at about 14.5 mm. pressure of toluene and the corresponding rate constants have been corrected to this pressure by use of the relation determined empirically from Table 2. The pressure-dependence of k_1 supports Gilbert's conclusion¹¹ that the unimolecular reaction forming NH_2 radicals in the hydrazine flame reaction is in the second-order region. Further, it substantiates his reappraisal of Szwarc's results on the pyrolysis of hydrazine on the basis of a non-isothermal reactor, from which he finds that NH_2 radicals are formed in a second-order reaction.⁷

An Arrhenius plot of k_1 gives

$$\log k_1 \text{ (sec.}^{-1}\text{)} = 11.70 - (54,150/2.3RT),$$

and the least-mean-squares line through Szwarc's points corresponds to

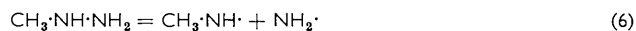
$$\log k_1 \text{ (sec.}^{-1}\text{)} = 11.39 - (54,000/2.3RT).$$

On this basis there is excellent agreement between the two studies, when it is borne in mind that the previous results were obtained at a mean toluene pressure of about 7.5 mm. and the present results at one of 14.5 mm. Szwarc favoured

$$\log k_1 \text{ (sec.}^{-1}\text{)} = 12.6 - (60,000/2.3RT).$$

The high-pressure A factor may be considerably greater than that given by the Arrhenius equation. The high-pressure activation energy (E_0) will also be slightly greater than the activation energy (E_1) determined in the fall-off region. A theoretical treatment of the variation of E with pressure has been made by Slater¹² but before a quantitative determination of E_0 from E_1 can be made a detailed study of the variation of the rate constant with pressure is required. The toluene-carrier technique is not suitable for such a study, but to allow for the effect of pressure on E we have made the arbitrary assumption that $E_0 - E_1 = 3$ kcal. mole⁻¹, which is probably an upper limit. Hence in the thermochemical calculations presented below the activation energy for the decomposition of hydrazine is taken as 57.1 kcal. mole⁻¹.

The Pyrolysis of Methylhydrazine.—As shown in Table 3 the decomposition of methylhydrazine produced hydrogen, methane, nitrogen, ammonia, and presumably bibenzyl. By analogy with hydrazine the homogeneous decomposition can be considered in terms of the following mechanism:



The reactions of $\text{CH}_3\cdot\text{NH}$ radicals are unknown but they do not appear to yield methylamine in this case. They could, however, yield other products observed in the reaction mixture. Alternatively it is possible that the methane, hydrogen, and nitrogen arise from a heterogeneous reaction represented by



Irrespective of the non-condensable fraction the homogeneous decomposition can be followed by the rate of formation of ammonia, if the above mechanism is valid. This assumes that every NH_2 radical yields ammonia, which seems likely from the hydrazine results. That the $\text{CH}_3\cdot\text{NH}$ radicals yield neither ammonia nor nitrogen was shown by the pyrolysis of *N*-methylbenzylamine, reported below, in which both gases were absent

¹¹ Gilbert, *Combustion and Flame*, 1958, 2, 137.

¹² Slater, "Theory of Unimolecular Reactions," Cornell Univ. Press, New York, 1959, p. 186.

TABLE 3.
 The pyrolysis of methylhydrazine.

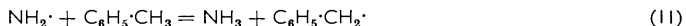
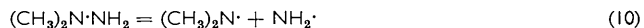
Run no.	Temp. (K)	Contact time (sec.)	Toluene pressure (mm.)	CH ₃ ·NH·NH ₂ NH ₃ (H ₂ + N ₂ + CH ₄) H ₂ N ₂					k ₆ (sec. ⁻¹)
				(10 ⁻⁴ mole)					
139	746°	1.54	15.1	6.30	0.108	0.108	0.017	0.046	0.0113
143	751	1.48	15.2	5.83	0.117	0.122	0.021	0.030	0.0137
144	756	1.50	15.7	5.13	0.111	0.126	0.023	—	0.0147
135	768	1.47	15.7	5.78	0.245	0.329	0.072	0.104	0.0308
141	783	1.43	15.1	4.89	0.304	0.440	0.117	0.151	0.0456
145	794	1.44	15.3	7.13	0.739	1.13	0.336	—	0.0778
146	796	1.23	26.7	6.37	0.561	0.790	0.264	—	0.0764
147	799	1.68	10.0	4.98	0.679	1.09	0.338	—	0.0902
156	803	0.50	15.0	7.07	0.368	0.688	0.196	—	0.108
137	806	1.39	14.9	5.11	0.751	1.05	0.326	0.322	0.119
205*	809	0.46	14.5	17.02	1.173	1.56	0.492	—	0.158
154	813	0.50	15.3	7.50	0.616	0.870	0.297	—	0.175
206*	815	0.46	13.1	10.65	0.933	1.31	0.415	—	0.203
207*	820	0.45	14.2	16.35	1.694	2.46	0.837	—	0.249
142	825	1.37	15.8	5.54	1.408	2.16	0.847	—	0.230
152	826	0.49	15.4	6.76	0.985	1.19	—	—	0.333
157	827	0.56	9.9	6.11	0.807	1.18	0.386	0.332	0.261
138	833	1.35	15.5	6.67	2.37	3.20	1.43	0.962	0.367
151	834	0.49	15.3	3.96	0.725	0.762	—	—	0.433
140	842	1.33	15.0	6.41	2.65	3.32	1.59	0.873	0.469
155	854	0.47	14.8	5.87	1.46	1.82	0.834	—	0.651
136	861	1.34	15.1	4.54	3.09	3.65	—	—	1.79
153	862	0.47	14.9	6.15	2.22	2.66	1.46	—	1.07

* Packed vessel.

from the products. Hence the rate constants for the overall decomposition were calculated from the total amount of methylhydrazine decomposed, based on the amounts of nitrogen and ammonia produced. The rate constants for the homogeneous decomposition (k_6) were obtained by multiplying the overall rate constants by the homogeneous fraction of the decomposition calculated from the amount of ammonia. The consistency of k_6 with the packed runs shows that ammonia is not formed heterogeneously. Variations of the contact time from 0.5 to 1.5 sec., the reactant pressure from 0.2 to 1.2 mm., and the toluene pressure from 10 to 30 mm. had no noticeable effect on the rate constant. The Arrhenius plot of k_6 yields

$$\log k_6 \text{ (sec.}^{-1}\text{)} = 13.19 - (51,900/2.3RT).$$

The Pyrolysis of 1,1-Dimethylhydrazine.—From Table 4 it is seen that the products of the decomposition were hydrogen, nitrogen, methane, ammonia, and, again presumably, bibenzyl. The results of the preceding decompositions suggest that the homogeneous decomposition of 1,1-dimethylhydrazine can be accounted for by the mechanism:



It is not known what happens to the dimethylamino-radicals but they do not appear to give dimethylamine in this system. It has been established from the decomposition of *NN*-dimethylbenzylamine that these radicals do not yield nitrogen or ammonia, under the present conditions. It seems probable that the nitrogen is produced in a heterogeneous reaction. The rate constants for the homogeneous decomposition (k_{10}) were calculated from the ammonia produced, as for the decomposition of methylhydrazine, and are given in Table 4. k_{10} was found to be independent of toluene pressure, contact time, reactant pressure, and surface : volume ratio. An Arrhenius plot corresponds to

$$\log k_{10} \text{ (sec.}^{-1}\text{)} = 13.22 - (49,600/2.3RT).$$

TABLE 4.
 The pyrolysis of 1,1-dimethylhydrazine.

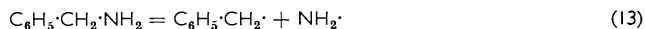
Run no.	Temp. (K)	Contact time (sec.)	Toluene pressure (mm.)	(CH ₃) ₂ N·NH ₂	NH ₃	(H ₂ + N ₂ + CH ₄)	H ₂	N ₂	<i>k</i> ₁₀ (sec. ⁻¹)
				(10 ⁻⁴ mole)					
133	709°	1.57	15.4	7.98	0.112	0.170	0.300	0.034	0.0090
115	722	0.57	15.7	7.25	0.055	0.066	—	—	0.0136
129	728	1.57	14.3	7.03	0.273	0.430	0.100	—	0.0247
131	733	1.53	15.8	8.13	0.312	0.614	0.149	0.078	0.0259
119	738	0.56	14.5	7.33	0.124	0.183	—	—	0.0305
123	740	0.56	15.2	7.53	0.180	0.205	0.061	0.049	0.0435
128	746	1.52	14.2	7.23	0.647	1.025	0.231	0.335	0.0631
113	751	0.56	13.9	7.08	0.223	0.336	0.105	—	0.0576
130	754	1.51	15.1	8.33	0.687	1.571	0.465	0.431	0.0582
118	767	0.53	14.8	9.68	0.534	0.985	0.331	—	0.109
132	770	1.48	15.0	8.07	1.24	2.857	—	—	0.117
126	771	1.57	15.3	15.07	3.98	11.0	—	—	0.211
120	772	0.54	13.7	10.35	0.675	1.30	0.438	0.388	0.127
121	778	0.53	15.9	9.15	0.899	1.60	0.596	—	0.200
209*	780	0.47	13.7	16.3	1.60	3.07	—	—	0.224
149	783	1.80	9.9	5.28	1.86	5.27	—	—	0.274
208*	787	0.46	14.7	12.0	1.42	2.51	0.987	—	0.283
111	791	0.53	14.5	7.95	1.13	1.99	0.794	0.530	0.300
148	795	1.26	28.7	7.87	2.72	5.40	2.22	—	0.379
122	804	0.51	15.2	7.78	1.61	3.04	1.52	—	0.480
117	809	0.52	15.3	6.83	1.77	3.14	1.46	—	0.625
112	822	0.50	14.4	6.05	2.26	3.83	2.05	—	1.07
124	826	0.50	15.2	5.80	2.15	3.97	1.65	—	0.891
116	831	0.51	15.3	7.42	2.94	7.16	3.39	—	1.15

* Packed vessel.

 TABLE 5.
 The pyrolysis of benzylamine.

Run no.	Temp. (K)	Contact time (sec.)	Toluene pressure (mm.)	C ₆ H ₅ ·CH ₂ ·NH ₂	NH ₃	(H ₂ + CH ₄)	H ₂	<i>k</i> ₁₃ (sec. ⁻¹)
				(10 ⁻⁴ mole)				
60	829°	2.95	15.0	7.65	0.0474	0.016	—	0.0021
77	839	1.51	13.9	11.6	0.0511	0.102	—	0.0029
76	843	1.49	13.7	11.4	0.0559	0.152	—	0.0032
215	856	1.71	16.0	26.5	0.249	0.100	0.083	0.0055
81	861	1.45	15.0	13.0	0.124	0.095	—	0.0066
59	865	2.86	15.0	8.66	0.193	0.105	—	0.0079
79	868	1.58	15.3	10.2	0.140	0.091	—	0.0087
78	883	1.58	15.2	9.82	0.244	0.260	—	0.0159
55	886	2.92	15.0	5.38	0.325	0.148	—	0.0214
90	891	1.40	15.9	11.4	0.341	0.205	—	0.0217
274	894	1.60	15.4	22.7	0.891	0.350	0.271	0.0251
210	897	1.56	15.6	8.18	0.343	0.136	0.098	0.0275
50	902	2.76	14.6	6.22	0.498	0.198	—	0.0302
80	903	1.46	15.0	11.9	0.575	0.244	—	0.0339
61	905	0.58	10.7	14.7	0.225	0.210	—	0.0269
213	907	1.51	15.3	15.7	0.876	0.344	0.263	0.0374
63	908	0.51	15.8	11.6	0.280	0.117	—	0.0479
62	917	0.5	13.1	15.5	0.341	0.317	—	0.0437
49	919	2.74	15.2	6.05	0.864	0.425	—	0.0562
212	923	1.55	15.5	12.9	1.43	0.496	0.372	0.0759
66	924	0.51	15.5	12.6	0.427	0.168	—	0.0676
68	943	0.57	17.2	8.90	0.576	0.228	—	0.118
65	943	0.49	15.4	9.85	0.736	0.380	—	0.159
53	945	2.65	14.6	7.34	2.34	1.02	—	0.145
211	951	1.50	15.5	11.2	2.85	1.06	0.817	0.195
51	960	2.57	15.3	5.05	1.32	1.10	—	0.240
67	969	0.53	15.0	10.8	1.60	0.653	—	0.302
73	985	0.49	15.8	8.50	1.97	0.645	—	0.537
72	996	0.42	14.5	7.98	2.44	0.665	—	0.871
71	1009	0.46	15.6	10.0	4.70	1.36	—	1.38
70	1026	0.44	15.7	8.68	5.29	1.85	—	2.14
69	1031	0.43	15.7	9.05	5.36	2.36	—	2.09
75	1043	0.47	15.5	6.93	5.36	2.07	—	3.16
74	1061	0.47	15.7	7.10	6.05	2.95	—	4.07

The Pyrolysis of Benzylamine.—The mechanism for the homogeneous decomposition in the presence of toluene has been established by Szwarc: ⁵



The rate constants (k_{13}) given in Table 5 were calculated from the ammonia produced, and were found to be independent of contact time, toluene pressure, and reactant pressure, in agreement with Szwarc's results. The Arrhenius plot of both sets of results gives a good straight line and the least-mean-squares treatment of all the results yields

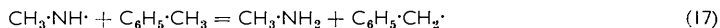
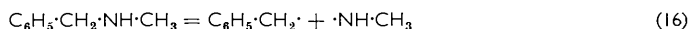
$$\log k_{13} \text{ (sec.}^{-1}\text{)} = 13.00 - (59,800/2.3RT).$$

Essentially, then, the present work confirms and extends the results obtained by Szwarc who found

$$\log k_{13} \text{ (sec.}^{-1}\text{)} = 12.80 - (59,000/2.3RT).$$

In addition, gas-chromatographic analysis showed that the non-condensable fraction did not contain nitrogen, which establishes that NH_2 radicals do not yield this product under these conditions, a further confirmation of the mechanism suggested for the hydrazine decomposition.

The Pyrolysis of N-Methylbenzylamine.—The non-condensable fraction consisted of hydrogen and methane, and the condensable fraction entirely of methylamine. The simplest mechanism to account for the homogeneous mechanism is as follows:



The hydrogen and methane are presumably formed heterogeneously. The absence of nitrogen indicates that the $\text{CH}_3\cdot\text{NH}$ radicals do not yield this product under these conditions. It is not clear, however, why the $\text{CH}_3\cdot\text{NH}$ radicals should form methylamine in

TABLE 6.

The pyrolysis of *N*-methylbenzylamine.

Run no.	Temp. (K)	Contact time (sec.)	Toluene pressure (mm.)	$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_3$ $\text{CH}_3\cdot\text{NH}_2$ ($\text{H}_2 + \text{CH}_4$) H_2				k_{16} (sec. ⁻¹)
				(10 ⁻⁴ mole)				
100	819°	1.46	15.3	11.36	0.047	0.102	0.051	0.0028
102	832	1.47	15.9	10.91	0.073	0.173	0.088	0.0045
97	832	1.45	15.2	8.22	0.077	0.137	—	0.0065
101	846	1.45	15.6	8.40	0.094	0.252	0.137	0.0078
96	851	1.43	15.9	9.20	0.134	0.305	0.182	0.0103
91	857	1.58	15.6	9.02	0.206	0.328	0.190	0.0145
92	863	1.40	15.3	8.12	0.236	0.393	0.230	0.0210
94	878	1.40	15.7	7.18	0.310	0.855	0.563	0.0315
89	891	1.44	16.7	8.90	0.575	1.47	0.948	0.0463
104	903	0.58	15.6	6.85	0.292	0.860	0.563	0.0750
98	906	1.33	15.8	9.32	1.16	2.44	1.62	0.100
99	912	1.35	15.6	8.50	1.18	2.80	1.92	0.111
93	920	1.38	15.7	8.45	1.69	3.62	2.77	0.161
103	936	0.51	13.7	7.22	0.785	2.18	—	0.226

this system and not in the pyrolysis of methylhydrazine. The experimental conditions and results are given in Table 6, where the rate constants k_{16} have been calculated from

the methylamine produced. If we assume k_{16} to be the rate constant for the homogeneous decomposition of *N*-methylbenzylamine, the Arrhenius plot yields

$$\log k_{16} \text{ (sec.}^{-1}\text{)} = 12.86 - (57,700/2.3RT).$$

The Pyrolyses of Related Compounds.—The pyrolyses of 1,2-dimethylhydrazine, tetramethylhydrazine, and *NN*-dimethylbenzylamine were investigated by the present technique. In each case the amine product expected from the homogeneous split of the C-N bond was either absent from the products or present in traces only. The products consisted of a large non-condensable fraction composed mainly of hydrogen with smaller amounts of methane. Gas-chromatographic analysis of the small condensable fraction

TABLE 7.
Summary of results and heats of formation of alkylamino radicals.

Bond	Dissociation energy		log <i>A</i>		<i>k</i> (874°K)		Radical	ΔH_f° (radical)	ΔH_f° (parent compound)
	This work	Szwarc ^{4, 5}	This work	Szwarc ^{4, 5}	This work	Szwarc ^{4, 5}			
NH ₂ -NH ₂	57.1	60	12.2 *†	12.6 *	0.0079	0.0040	NH ₂	39.8	22.5 ‡
NH ₂ -NH·CH ₃	51.9	—	13.2	—	1.6	—	CH ₃ NH	34.5	22.4 §
NH ₂ -N(CH ₃) ₂	49.6	—	13.2	—	6.3	—	(CH ₃) ₂ N	29.5	19.7 §
C ₆ H ₅ ·CH ₂ -NH ₂ ...	59.8	59	13.0	12.8	0.010	0.010	NH ₂	30	14.7 ¶
C ₆ H ₅ ·CH ₂ -NH·CH ₃	57.7	—	12.9	—	0.032	—	CH ₃ NH	—	?

D and ΔH values in kcal. mole⁻¹; *A* and *k* in units of sec.⁻¹.

* Measured in fall-off region; high-pressure *A* may be considerably greater. † Experimental value corrected to allow for estimated high-pressure *E*. ‡ Hughes, Corruccini, and Gilbert, *J. Amer. Chem. Soc.*, 1939, **61**, 2639; Heiber and Woerner, *Z. Elektrochem.*, 1934, **40**, 252. § Aston, Rock, and Isserow, *J. Amer. Chem. Soc.*, 1952, **74**, 2484. ¶ Petit, *Ann. Chim. Phys.*, 1889, **18**, 149.

showed the presence of C₂ and C₃ hydrocarbons. Obviously, then, the toluene-carrier technique is not suitable for a study of the pyrolyses of these compounds.

Bond Strengths and Heats of Formation of Radicals.—The preceding activation energies can be equated to the strengths of the bonds which are broken by making the usual assumption that the reverse radical-recombination reactions have zero activation energy. This leads to an upper limit for the bond strength which should not be in error from this assumption by more than 1–2 kcal. mole⁻¹. Hence the heats of formation of the radicals produced can be calculated when the heat of formation of the parent compound is known. Table 7 contains the heats of formation of the NH₂, CH₃·NH, and (CH₃)₂N radicals obtained in this way, and also a summary of other relevant results.

The slight difference in the heat of formation of the NH₂ radical calculated from the pyrolysis of hydrazine from this work and the previous results of Szwarc arises mainly from the difference of 3 kcal. mole⁻¹ in the activation energies. The difference found here between the heat of formation of the NH₂ radical from the hydrazine results and from the benzylamine results is much greater than that reported by Szwarc.⁵ This is because we have used in the calculation from the benzylamine pyrolysis a more recently determined^{13,14} value for the heat of formation of the benzyl radical, *i.e.*, $\Delta H_f^\circ(\text{C}_6\text{H}_5\cdot\text{CH}_2) = 44.5$ kcal. mole⁻¹. The difference of about 10 kcal. mole⁻¹ between the two determinations of $\Delta H_f^\circ(\text{NH}_2)$ is well outside experimental error. However, it has already been pointed out that the heat of formation of benzylamine used in these calculations may be considerably in error.^{5,15} Obviously, then, a proper comparison of the two values of $\Delta H_f^\circ(\text{NH}_2)$ cannot be made until a reliable value of the heat of formation of benzylamine is available and in the meantime the value from the hydrazine experiments, *i.e.*, $\Delta H_f^\circ(\text{NH}_2) = 39.8$ kcal. mole⁻¹, is more acceptable. The values $\Delta H_f^\circ(\text{CH}_3\cdot\text{NH}) = 34.5$ and

¹³ Price, *Canad. J. Chem.*, 1962, **40**, 1310.

¹⁴ Esteban, Kerr, and Trotman-Dickenson, unpublished results.

¹⁵ Benson and Buss, *J. Phys. Chem.*, 1957, **61**, 104.

TABLE 8.

Comparison of $D(\text{C-H})$, $D(\text{N-H})$, and $D(\text{O-H})$ values (kcal. mole⁻¹).

		ΔH_f° (parent compound)	
HO-H	118 *	CH ₃ -H	103.9 †; NH ₃ -H 102.9; NH ₃ = -11.0 ‡
CH ₃ O-H	100 *	CH ₃ ·CH ₂ -H	98.3 †; CH ₃ ·NH-H 91.1; CH ₃ ·NH ₂ = -5.1 §
		(CH ₃) ₂ CH-H	94.5 †; (CH ₃) ₂ N-H 86.7; (CH ₃) ₂ NH = -4.5 §

* Ref. 3. † Fettis and Trotman-Dickenson, *J.*, 1961, 3037. ‡ "Selected Values of Thermodynamic Properties," Nat. Bur. Stand., U.S.A., Circular 500, Washington, 1952. § Johnson, Prosen, and Jaffé, *J. Res. Nat. Bur. Stand.*, 1961, **65**, A, 71; Jaffé, Thesis, Univ. of Maryland.

TABLE 9.

Comparison of $D(\text{C-C})$ and $D(\text{N-N})$ values (kcal. mole⁻¹).

		ΔH_f° (parent compound)	
CH ₃ -CH ₃	85.7 *	NH ₂ -NH ₂	57.1.
CH ₃ ·CH ₂ -CH ₃	84.7 *	CH ₃ ·NH-NH ₂	51.9.
(CH ₃) ₂ CH-CH ₃	83.7 *	(CH ₃) ₂ N-NH ₂	49.6.
CH ₃ ·CH ₂ -CH ₂ ·CH ₃	82.2 *	CH ₃ ·NH-NH·CH ₃	47.4; CH ₃ ·NH·NH·CH ₃ = 21.6 †
(CH ₃) ₂ CH-CH ₂ ·CH ₃	80.5 *	(CH ₃) ₂ N-NH·CH ₃	44.8; (CH ₃) ₂ N·NH·CH ₃ = 19.2 ‡
(CH ₃) ₂ CH-CH(CH ₃) ₂	77.7 *	(CH ₃) ₂ N-N(CH ₃) ₂	42 (CH ₃) ₂ N·N(CH ₃) ₂ = 16.6 ‡

* Based on results of Fettis and Trotman-Dickenson, *J.*, 1961, 3037. † Aston, Rock, and Isserow, *J. Amer. Chem. Soc.*, 1952, **74**, 2484. ‡ Ref. 1.

TABLE 10.

Comparison of $D(\text{C-C})$ and $D(\text{C-N})$ values (kcal. mole⁻¹).

		ΔH_f° (parent compound)	
CH ₃ -CH ₃	85.7 *	CH ₃ -NH ₂	78.8.
CH ₃ ·CH ₂ ·CH ₃	84.7 *	CH ₃ ·NH·CH ₃	72.9.
CH ₃ -CH(CH ₃) ₂	83.7 *	CH ₃ -N(CH ₃) ₂	68.9; (CH ₃) ₃ N = -5.5 **
C ₆ H ₅ -CH ₃	91.7 †;	C ₆ H ₅ -NH ₂	89.9 †;
C ₆ H ₅ -3N ₂ ·CH ₃	88.6 †;	C ₆ H ₅ -NH·CH ₃	81.6 †;
C ₆ H ₅ -CH(CH ₃) ₂	86.4 †;	C ₆ H ₅ -N(CH ₃) ₂	76.4 †;
		C ₆ H ₅ ·NH·CH ₃	21.6 ¶
		C ₆ H ₅ ·N(CH ₃) ₂	22.8 ‡

* See Table 9. † Based on $D(\text{C}_6\text{H}_5\text{-H}) = 102$ kcal. mole⁻¹ (Duncan and Trotman-Dickenson, *J.*, 1962, 4672). ‡ Calc. from data in "Handbook of Chemistry and Physics," Chem. Rubber Publ. Co., Cleveland, 43rd edn., 1961. § Anderson and Gilbert, *J. Amer. Chem. Soc.*, 1942, **64**, 2369. ¶ Klages, *Chem. Ber.*, 1949, **82**, 358. ** Jaffé, Thesis, Univ. of Maryland.

$\Delta H_f^\circ[(\text{CH}_3)_2\text{N}] = 29.5$ kcal. mole⁻¹ compare reasonably with the values of 32.5 and 32.2 kcal. mole⁻¹, respectively, obtained by Gowenlock, Pritchard Jones, and Majer³ by the electron-impact method. Unfortunately it is not possible to compare $\Delta H_f^\circ(\text{CH}_3\cdot\text{NH})$ from the pyrolysis of methylhydrazine with that from *N*-methylbenzylamine since thermochemical data for *N*-methylbenzylamine are not available.

With the heats of formation of the radicals thus established, the bond dissociation energies of many nitrogen-containing compounds are available. Tables 8—10 list some of these values where they are compared with the corresponding hydrocarbons and other related compounds. The results for the isoelectronic series C-H, N-H, and O-H (Table 8) are necessarily scanty owing to structural limitations in the compounds studied. It might be concluded from Table 8 that the series runs $D(\text{O-H}) > D(\text{C-H}) > D(\text{N-H})$ would disagree with the predictions of Gowenlock, Pritchard Jones, and Majer.³ In both cases, however, the conclusions are based on energy differences of about 1—2 kcal. mole⁻¹, with error limits of about the same or larger size. The most striking feature of Tables 8—10 is that increased alkyl substitution has a much greater weakening effect on a N-H, N-C, or a N-N bond than on the corresponding C-H or C-C bond.

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