# Mass Spectrometric Study of the Rate of Thermal Decomposition of Hydrazoic Acid

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Hydrazoic acid vapor at low pressures (0.15 mm Hg or less), has been decomposed thermally and the rate of reaction studied mass spectrometrically at 265° to 325° C. Nitrogen and ammonia are the only reaction products, and no intermediates were observed. The disappearance of HN_3 is first order and the reaction occurs on the walls of the glass reaction vessel. The experimental activation energy is 31 kilocalories per mole. The activation energy for the reaction $HN_3 \rightarrow NH + N_2$ must be at least 39 kilocalories per mole.

1. Introduction

Recent studies [1,2] [4] of hydrazoic acid have shown that the heat of the reaction

$$HN_3 \rightarrow HN + N_2 \qquad (R1)$$
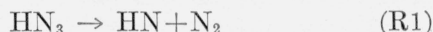
is 6 to 9 kcal/mole. However Franklin et al. [2] have pointed out, from considerations of spin-orbital correlations that this reaction cannot proceed to the $^3\Sigma^-$ ground state of NH and instead would have to go to the lowest singlet ($^1\Delta$) state of the radical. They estimated that this would be some 28 kcal/mole above the ground state, so that the activation energy for the decompositions would be about 37 kcal/mole.

For so weak a bond, one would expect the molecule to decompose readily and a measure of the activation energy for the thermal decomposition of hydrazoic acid should ordinarily correspond to the activation energy of reaction. However, Ramsperger [3] and Meyer and Schumacher [4] have shown that the decomposition of hydrazoic acid in glass occurs on the surface of the vessels and presumably is catalyzed by the glass wall. Consequently, in such a system the activation energy would at best set a lower limit to the activation energy for reaction 1. In spite of this limitation it was deemed worthwhile to study the kinetics of decomposition of HN_3 and this paper presents the results of this investigation.

2. Apparatus and Procedure

A gas analysis mass spectrometer, Consolidated Electrodynamics Corporation type 21–102, was used to observe the rate of decomposition of hydrazoic acid and the appearance of decomposition products. The all-glass sample introduction system and 2-liter sample reservoir was similar to that described by O'Neal and Wier [5] and used by them for obtaining mass spectra of high molecular weight hydrocarbons. The sample reservoir volume was enclosed in a well-insulated heating jacket and provided with thermocouples at several points. Isolation from the sample introduction manifold and the evacuating pumps was accomplished with a gallium-sealed, magnetically

operated valve. The gallium valve, connecting tube, and the tube containing the effusive leak were wrapped with individually controlled heating tapes and with thermal lagging. Chromel-alumel thermocouples were provided at the valve, the leak, and at several intermediate points for temperature measurement. The maximum operating temperature was about 350° C. At 300° C, temperatures could be read and controlled with an uncertainty of about ±4° C.

Conventional mass spectrometric techniques were used for both chemical analysis and observation of the kinetics of decomposition. The sample reservoir also served as a reaction vessel. Prior to each run, it was thoroughly outgassed, usually overnight, at temperatures somewhat above the anticipated temperature range. At the start of a run and after a stable operating temperature was attained, neon was introduced into the reservoir to a nominal pressure of about 0.05 mm of mercury as measured by gas pipet. The mass range of 16 to 46 was scanned quickly to serve as a background. Then hydrazoic acid was added to a partial pressure of about 0.1 mm of mercury and the time of introduction was noted. In order to make initial observations as frequently as possible, only selected portions of the mass scale were scanned; e. g., $m/e = 16$ to 20, 28 to 32, and 40 to 46. Each range uniformly required about 1 min to scan and the total lapsed time was noted at the start of each scan. Measurements were usually continued until the molecule ion of HN_3 ($m/e = 43$) had decreased to about 1 percent of the original abundance. The electron energy was 70 v.

Hydrazoic acid was prepared from sodium azide and 60 to 80 percent sulfuric acid. Preparations were carried out in a vacuum and the HN_3 was purified by simple bulb-to-bulb distillation and by pumping on the product held at liquid nitrogen temperature. A mass spectrometric analysis of the product showed no impurities of higher molecular weight or of most simple gases condensible at liquid nitrogen temperature, the exception being occasional small amounts of ammonia. For reasons of safety the quantity of stored hydrazoic acid was limited to that giving a pressure less than 50 mm of mercury at room temperature in a 2-liter bulb. As HN_3 was observed to decompose slowly in storage under these conditions, periodic analyses were necessary to assure material of suitable purity.

3. Results

Table 1 summarizes the experimental data. Hydrazoic acid and neon concentrations after various reaction times are given in all runs. The nitrogen and ammonia concentrations are given for purposes of illustration only for run 6. The only products of the decomposition of hydrazoic acid that were observed were ammonia and nitrogen. Although both hydrogen and hydrazine might have been expected none was ever found. Data from a typical experiment are plotted in figure 1. Here peak heights are corrected for differences in sensitivity and the mass 28 peak is corrected for the contribution from HN_3. The curves for ammonia and nitrogen are characteristic of those for primary products of reaction formed simultaneously from the initial reactant.

It is shown later that the decomposition of hydrazoic acid is kinetically first order. For this to occur with ammonia as the final product, at least one transient intermediate is required. This might include NH or electronically excited HN_3, as the first active species and various secondary intermediates such as N_2H_2, NH_2, etc., can be postulated. Most mechanisms for the decomposition of HN_3 have postulated NH as the initial product and we thought it worthwhile to try to establish this by identifying the products of its reaction with other materials. Specifically we made experiments in which large excesses of benzene and toluene were added to the reaction mixture and the products analyzed for postulated products of reaction. Thus, if NH were present, one might expect either biphenyl or aniline from the reaction in the presence of benzene, but none was identified, although the reaction in solution gives aniline. Similarly, in the presence of toluene one would expect bibenzyl, benzyl amine or dibenzyl amine to be produced but none was ever found. Rice and Freamo [6] report that cyanic acid was formed when CO was added to HN_3 at high temperatures but the identity of masses of HNCO and HN_3 rendered this method of identification unsuitable to our studies which depended upon mass spectra for identification and analysis of the reaction products. Similar considerations prevented our using ethylene which might have been expected to add NH giving ethylene imine.

Each mass spectrum was also examined carefully for evidence of transient intermediates but none was ever found. Of course NH would be obscured by the NH^+ peak from HN_3. However, N_2H_2 and N_2H_4 if present would have been strong evidence for the presence of NH and NH_2, respectively. In two or three runs small peaks at $m/e=30$ and 32 were found. However they always occurred together and no peak at $m/e=31$ was ever observed. Therefore it was concluded that the $m/e=32$ peak was due to O_2 introduced as an impurity and the $m/e=30$ peak was NO formed by reaction O_2 with either N_2 or HN_3. Thus it was impossible to obtain any direct evidence as to the nature of the active intermediates involved in the reaction.

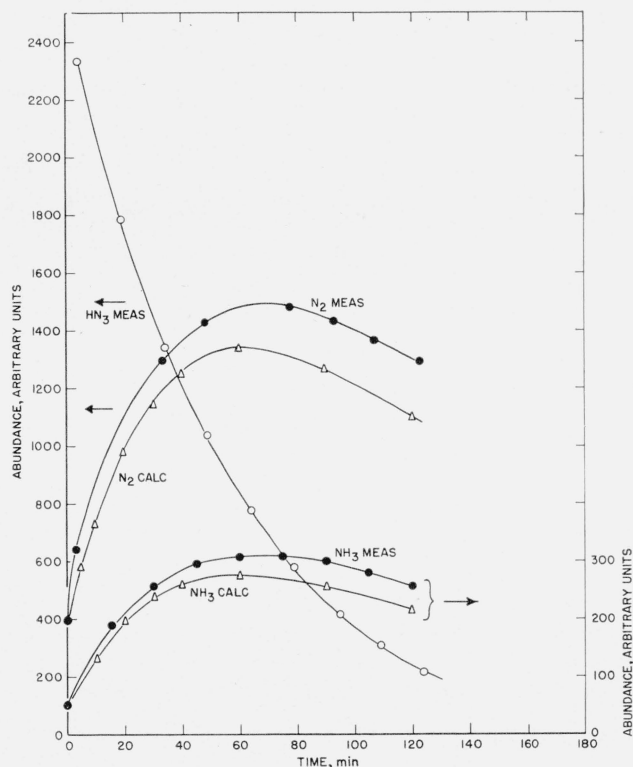Although the reaction appeared to be kinetically first order, it might conceivably have involved a

FIGURE 1. *Variation of concentrations with time for run 6.*

self-regenerating chain process. Accordingly a few percent of NO was added in one of the runs to ascertain whether the rate of reaction was markedly reduced thereby. It is evident from table 1 that NO caused only a small reduction in rate. This reduction may be enough to indicate that free radicals are involved in the reaction and are partly removed by the NO. This very small reduction in rate, however, clearly implies that a chain reaction is not being interrupted.

4. Kinetics

The gases in the reaction vessel passed into the mass spectrometer by molecular flow, the rate for various components of the gas mixture being inversely proportional to the square root of the mass. In all runs except one, neon was mixed with the hydrazoic acid in the reactor and the rate of disappearance of the neon, as indicated by the peak at $m/e=20$, was employed to calibrate the rate of flow of other components into the mass spectrometer. The rate of flow of neon from the reactor should be proportional to the neon concentration so that

$$\ln \frac{[\mathrm{Ne_0}]}{[\mathrm{Ne}]} = k_1 t \qquad (1)$$

where k_1 is the rate constant in reciprocal seconds. Data from a typical run plotted in figure 2 bear this out.

TABLE 1. *Summary of experimental data*

(Peak heights (PH) are given in arbitrary units.)

Run 2 — Temperature 325 °C; Initial presence: HN$_3$ 0.025 mm Hg, Ne 0.063 mm Hg
Run 3 — Temperature 300 °C; Initial presence: HN$_3$ 0.047 mm Hg, Ne 0.150 mm Hg
Run 4 — Temperature 275 °C; Initial presence: HN$_3$ 0.085 mm Hg, Ne 0.060 mm Hg
Run 5 — Temperature 275 °C; Initial presence: HN$_3$ 0.150 mm Hg, Ne 0.140 mm Hg

Run 2 HN$_3$ t (min)	PH	Run 2 Ne t (min)	PH	Run 3 HN$_3$ t (min)	PH	Run 3 Ne t (min)	PH	Run 4 HN$_3$ t (min)	PH	Run 4 Ne t (min)	PH	Run 5 HN$_3$ t (min)	PH	Run 5 Ne t (min)	PH
0	----	3	390	0	1740	2	2085	0	2700	----	750	0	5800	0	----
7	87	18	285	4	1140	17	1800	3	1954	1	725	4	5440	2	1884
23	6	33	249	18.5	645	31.5	1545	19	1593	17	637	19	3934	17	1524
37	1	48	240	34	365	47	1320	34	1290	32	505	34	2980	32	1254
52	0.3	73	210	49	189	62	1110	49	993	47	476	49	2301	47	1047
----	----	----	----	64	90	78	940	64	729	62	411	64	1773	62	882
----	----	----	----	80	41	92	790	79	531	77	353	79	1353	77	713
----	----	----	----	94	21.5	113	620	94	386	92	298	94	1017	92	589
----	----	----	----	116	8.5	143	430	108	281	106	253	109	755	107	449
----	----	----	----	146	3.5			124	138	121	183	141	409	139	336

	Run 2	Run 3	Run 4	Run 5
k_e(Ne) sec^{-1}	1.5×10^{-4}	1.82×10^{-4}	1.67×10^{-4}	2.17×10^{-4}
$k_r + k_e$(HN$_3$) sec^{-1}	28.0×10^{-4}	7.7×10^{-4}	3.41×10^{-4}	3.11×10^{-4}
k_r sec^{-1}	27.0×10^{-4}	6.44×10^{-4}	2.27×10^{-4}	1.65×10^{-4}

Run 6 — Temperature 275 °C; Initial presence: HN$_3$ 0.075 mm Hg, Ne 0.160 mm Hg
Run 7 — Temperature 300 °C; Initial presence: HN$_3$ 0.080 mm Hg, Ne 0.100 mm Hg
Run 9[a] — Temperature 300 °C; Initial presence: HN$_3$ 0.090 mm Hg, Ne 0.040 mm Hg

Run 6 HN$_3$ t	PH	Ne t	PH	N$_2$ t	PH	NH$_3$ t	PH	Run 7 HN$_3$ t	PH	Ne t	PH	Run 9 HN$_3$ t	PH	Ne t	PH
0	2650	0	----	0	400	0	50	0	2230	0	1900	0	2300	0	----
4	2334	2	2067	3	640	----	----	4	1461	2	1674	5	1875	1	640
19	1785	17	1809	18	1040	15	190	19	768	17	1440	20	1176	16	623
34	1371	32	1557	33	1300	30	259	34	401	32	1215	35	702	31	585
49	1041	47	1347	48	1430	45	295	49	190	47	990	50	445	46	563
64	777	62	1149	63	1500	60	307	64	91	62	800	65	277	61	525
79	581	77	952	78	1480	75	310	79	41	77	663	80	163	76	498
94	419	92	805	93	1430	90	301	94	19	92	530	95	93	91	471
109	308	107	699	108	1370	105	286	110	9	108	419	110	56	106	451
124	221	122	593	123	1295	120	269	----	----	----	----	125	31.5	121	419

	Run 6	Run 7	Run 9
k_e(Ne)	1.80×10^{-4}	2.32×10^{-4}	0.58×10^{-4}
$k_r + k_e$(HN$_3$)	3.29×10^{-4}	8.48×10^{-4}	5.73×10^{-4}
k_r	2.04×10^{-4}	6.89×10^{-4}	5.33×10^{-4}

Run 12 — Temperature 265 °C; Initial presence: HN$_3$ 0.010 mm Hg, NE 0.010 mm Hg
Run 14 — Temperature 290 °C; Initial presence: HN$_3$ 0.015 mm Hg, Ne 0.015 mm Hg
Run 15[b] — Temperature 278 °C; Initial presence: HN$_3$ 0.020 mm Hg, Ne 0.051 mm Hg

Run 12 HN$_3$ t	PH	Ne t	PH	Run 14 HN$_3$ t	PH	Ne t	PH	Run 15 HN$_3$ t	PH
0	340	0	123	0	340	----	----	0	----
5	340	----	----	4	315	0	129	4	735
16	282	10	97	12	270	8	111	15	633
29	240	25	81	17	240	12	103	25	495
39	210	35	74	22	215	18	98	35	343
55	177	50	69	31	185	27	89	50	184
69	153	65	64	41	155	37	81	65	101
79	140	75	60	51	134	47	76	----	----
89	124	85	55	64	113	57	71	----	----
104	108	100	51	76	78	72	63		
114	96	110	47	91	64	87	57		
152	63	148	40	106	50	102	53		

	Run 12	Run 14	Run 15
k_e(Ne)	1.05×10^{-4}	1.2×10^{-4}	----
$k_r + k_e$(HN$_3$)	1.84×10^{-4}	3.06×10^{-4}	----
k_r	1.12×10^{-4}	2.25×10^{-4}	----

[a] Contains about 0.5 percent of NO.   [b] Reactor packed with glass wool.
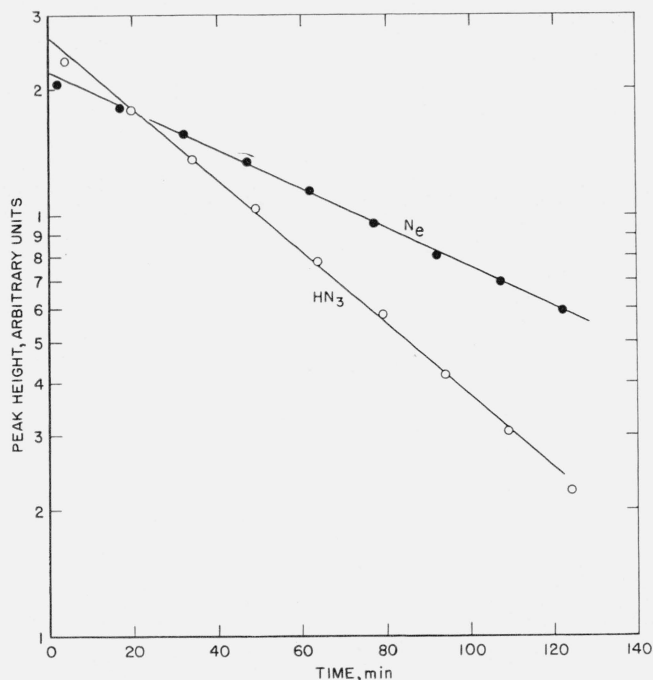
FIGURE 2. *Semi-log plot of concentration versus time for run 6. Observed rate constants are $k_{N_e} = 1.8 \times 10^{-4}$ sec^{-1}, and $k_{HN_3} = 3.29 \times 10^{-4}$ sec^{-1}.*

Hydrazoic acid will disappear from the reaction vessel by reaction and by flow into the ionization chamber. The rate of disappearance is

$$\frac{-d[\mathrm{HN_3}]}{dt} = k_r[\mathrm{HN_3}]^n + k_2[\mathrm{HN_3}], \qquad (2)$$

where k_r and k_2 are respectively, the rate constant for reaction and for flow out of the reactor and n is the order of the reaction. From figure 2 it appears that $[\mathrm{HN_3}]$ is an exponential function of time and that the reaction is first order i. e., $n = 1$. However, since the over-all disappearance is influenced by the flow rate, which is first order, it seemed desirable to apply a more sensitive test of reaction order. For this the differential rate equation is more suitable than the integrated expression. Equation (2) can be rewritten

$$\frac{-d \ln [\mathrm{HN_3}]}{dt} = k_r[\mathrm{HN_3}]^{n-1} + k_2. \qquad (3)$$

By calculating the slopes of tangents to the curve of $[\mathrm{HN_3}]$ versus time, such as that in figure 1, $d\ln[\mathrm{HN_3}]/dt$ is readily calculated for various points along the curve. If this parameter varies with the concentration of $\mathrm{HN_3}$ the order can be obtained graphically since k_2 is known. If $d\ln[\mathrm{HN_3}]/dt$ is independent of the $\mathrm{HN_3}$ concentration the reaction is first order. A typical set of results is given in table 2 and shows that within experimental accuracy $d\ln [\mathrm{HN_3}]$ is independent of the $\mathrm{HN_3}$ concentration and thus the reaction is indeed first order. Since $n=1$,

(2) becomes $-d[\mathrm{HN_3}]/dt = (k_r + k_2)[\mathrm{HN_3}]$ and $(k_r + k_2)$ can be determined from the slope of a plot of $\ln[\mathrm{HN_3}]$ against t. Also $k_2 = k_1\sqrt{M_2/M_1}$, where M is molecular weight, so k_r is determined. The rate constants for all runs were determined in this way and the results are given in table 1.

Ammonia and nitrogen are formed simultaneously by reaction and are withdrawn by effusion into the mass spectrometer. Since the total reaction is $3\mathrm{HN_3} \rightarrow \mathrm{NH_3} + 4\mathrm{N_2}$ we may write

$$\frac{d[\mathrm{NH_3}]}{dt} = \frac{k_r}{3}[\mathrm{HN_3}] - k_3[\mathrm{NH_3}] \qquad (4)$$

$$\frac{d[\mathrm{N_2}]}{dt} = \frac{4k_r}{3}[\mathrm{HN_3}] - k_4[\mathrm{N_2}] \qquad (5)$$

where k_3 and k_4 are, respectively, the rate constants for effusion of ammonia and nitrogen from the reactor. Integration leads to the following relations between concentrations and time:

$$[\mathrm{NH_3}] = \frac{k_r[\mathrm{HN_3^\circ}]}{3(k_r + k_2 - k_3)}\{\exp(-k_3 t) - \exp(-k_r - k_2)t\} + [\mathrm{NH_3^\circ}]\exp(-k_3 t) \qquad (6)$$

$$[\mathrm{N_2}] = \frac{1.33k_r[\mathrm{HN_3^\circ}]}{k_r + k_2 - k_4}\{\exp(-k_4 t) - \exp(-k_r - k_2)t\} + [\mathrm{N_2^\circ}]\exp(-k_4 t). \qquad (7)$$

Figure 1 gives typical curves of $[\mathrm{NH_3}]$ and $[\mathrm{N_2}]$ against time obtained experimentally and by calculation from eq (6) and (7). The agreement leaves something to be desired but is close enough to be considered as confirmation of the method.

TABLE 2. *Test of reaction order by differential rate equation for run 5*

t	$[\mathrm{HN_3}]$	$-d\dfrac{[\mathrm{HN_3}]}{dt}$	$-1000d\dfrac{[\ln \mathrm{HN_3}]}{dt}$
Min			
20	3,800	70.0	18.43
30	3,200	60.0	18.73
40	2,600	52.5	20.2
50	2,150	40.0	18.6
60	1,800	32.5	18.1
70	1,500	26.3	17.6
80	1,275	21.3	16.7
90	1,075	18.7	17.4
100	900	15.0	16.7
110	750	13.8	18.4
120	625	11.2	17.9
130	525	10.0	19.1

5. Activation Energy

An Arrhenius-type plot of reaction rate constant versus temperature is given in figure 3. The data, although somewhat scattered, define a reasonably good straight line from which the activation energy E‡, is found to be 31 kcal/mole. The rate constant is thus

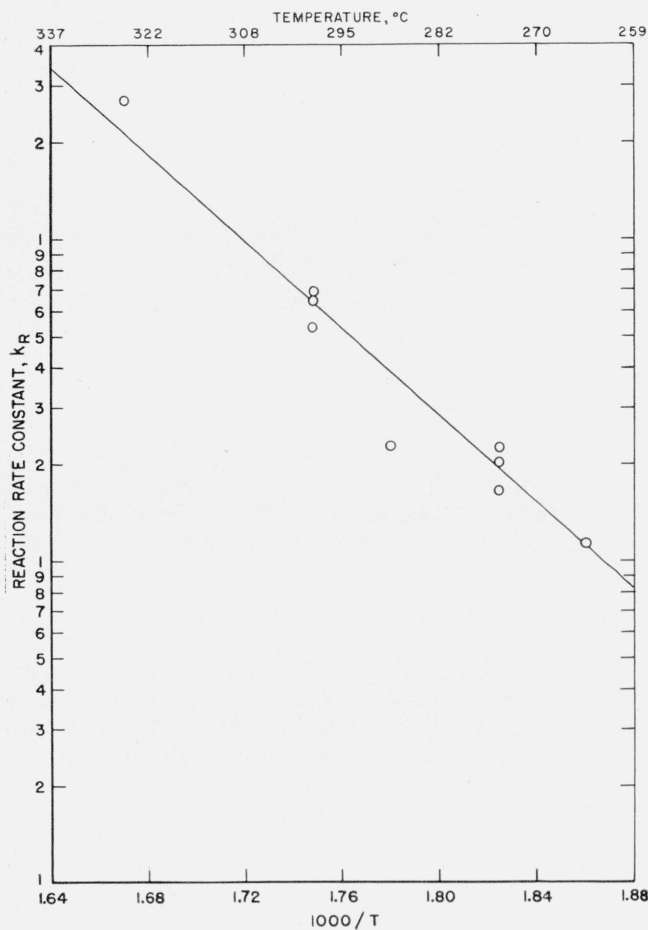$$k = 4.5 \times 10^8 \exp(-31000/RT) \text{ sec}^{-1}. \qquad (8)$$

FIGURE 3. *Arrhenius plot of activation energy.*

Rice and Freamo [7] decomposed HN_3 thermally at $1,000°$ C and allowed the gases to impinge on a cold surface, thereby obtaining a characteristic blue solid. By varying the distance from the furnace to the cold surface they obtained a half-life of about 10^{-3} seconds for the active species which formed the blue solid and which they concluded was NH. Their results might also be explained as giving the half-life of HN_3 which decomposes to an active intermediate (such as NH) of very short life. If we calculate the half-life of HN_3 at $1,000°$ C from eq (8) we obtain a value of 3×10^{-4} sec which, in view of the fact that the two sets of measurements were made under very widely differing conditions, is a reasonable check on the results of Rice and Freamo [7].

Glasstone, Laidler, and Eyring [8] show that the rate constant may be expressed in terms of the experimental activation energy

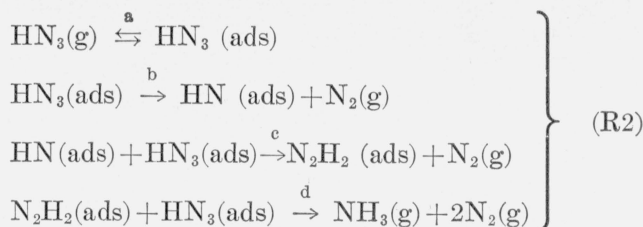$$k = \frac{kT}{h} \exp \left(2 + \frac{S\ddagger}{R} - \frac{E\ddagger}{RT}\right). \qquad (9)$$

For reasons that will be given later (see eq 10, 11, and 12) the right-hand side of eq (9) must be multiplied by 3 to give the over-all rate constant. Taking

$E\ddagger = 31$ kcal/mole and employing eq (8) and (9) we calculate $\Delta S\ddagger$ to be -26 e. u. This is much too large a negative entropy for a gas phase, first order reaction. The value is best explained as resulting from a reaction occurring on a solid surface. Indeed, such an entropy value corresponds approximately to the entropy of condensation of a gas.

In order to corroborate this conclusion a run was made using a reactor packed loosely with glass wool. The results are not as satisfactory as those obtained with an unpacked reactor, probably because diffusion was impeded by the packing. However, they do show that the added surface greatly increased the reaction rate. We may conclude, therefore, that the reaction occurs predominately on the glass surface of the reaction vessel.

Since the reaction is kinetically first order and the surface is involved, two kinds of mechanism can be adduced which would be in accord with our observations.

1. HN_3 is adsorbed reversibly and the surface is sparsely covered. The adsorbed material undergoes a series of reactions resulting eventually in the production of nitrogen and ammonia which are desorbed. The following mechanism is one of several possibilities of this kind

$$
\left.
\begin{aligned}
&HN_3(g) \overset{a}{\leftrightarrows} HN_3 \text{ (ads)} \\
&HN_3(ads) \overset{b}{\to} HN \text{ (ads)} + N_2(g) \\
&HN(ads) + HN_3(ads) \overset{c}{\to} N_2H_2 \text{ (ads)} + N_2(g) \\
&N_2H_2(ads) + HN_3(ads) \overset{d}{\to} NH_3(g) + 2N_2(g)
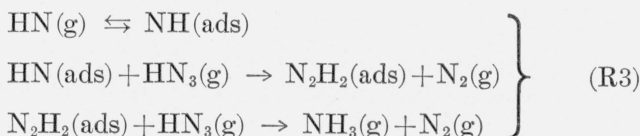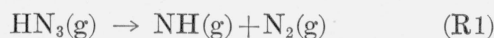\end{aligned}
\right\} \quad (R2)
$$

If one assumes that reaction b is the slow, rate-controlling step and employs a steady-state treatment for all transient species the following rate expression is obtained:

$$\frac{-d[HN_3(g)]}{dt} = 3k_b \, K_{ads} \, [HN_3(g)] \qquad (10)$$

where K is the equilibrium constant for the adsorption of hydrazoic acid on glass.

2. HN_3 reacts in the gas phase to give an active species which adsorbs rapidly and then undergoes a series of reactions with gaseous HN_3. It is assumed that the surface is almost completely covered by the active species. As an example

$$HN_3(g) \to NH(g) + N_2(g) \qquad (R1)$$

$$
\left.
\begin{aligned}
&HN(g) \leftrightarrows NH(ads) \\
&HN(ads) + HN_3(g) \to N_2H_2(ads) + N_2(g) \\
&N_2H_2(ads) + HN_3(g) \to NH_3(g) + N_2(g)
\end{aligned}
\right\} \quad (R3)
$$

Again, if one assumes the first reaction to be the slow, rate controlling step and applies a steady-state treatment, the reaction rate is found to be

$$\frac{-d[HN_3(g)]}{dt} = 3k_1[HN_3(g)] \qquad (11)$$

Both kinds of mechanisms give first order kinetics for the decomposition of HN_3, but the over-all rate constant for mechanisms of type 1 includes the adsorption equilibrium constant whereas those of type 2 do not.

Mechanisms of type 2 usually prevail for the recombination of atoms or simple radicals where a third body is required to remove the energy of reaction. It seems unlikely that this should be the case here since various reactions of the probable intermediates other than simple recombination can readily be visualized and these would provide a means of removing excess energy without the need of a third body or wall. Further, the rate of disappearance of HN_3 by this mechanism is given simply by $3k_1$ and so is independent of surface effects. This would not account for the negative entropy of activation and so mechanisms of this kind can be discarded.

Since the rate constant for mechanism 1 includes the equilibrium constant for adsorption of HN_3 on glass, we may write

$$k_{expt} = 3k_bK = \frac{3kT}{h}\exp\left(\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R}\right)$$
$$= \frac{3kT}{h}\exp\left(\frac{\Delta S^{\ddagger} + \Delta S_{ads}}{R}\right)\exp\left(\frac{-\Delta H^{\ddagger} - \Delta H_{ads}}{RT}\right).$$
$$(12)$$

$\Delta S^{\ddagger}$ for a unimolecular reaction is usually small and, as a first approximation may be taken as zero. The entropy of adsorption is negative and is often comparable in magnitude to that obtained for $\Delta S^{\ddagger}$ in these studies.

In deriving eq (10) and (12) we assumed that the adsorption of HN_3 was reversible and that equilibrium existed at all times between HN_3 in the gas and on the surface. At equilibrium, $\Delta F = 0$ and so

$$\Delta H_{ads} = T\Delta S_{ads}$$

The heat of adsorption then, at temperatures near $300°$ C would be about 8 kcal/mole. Since

$$E^{\ddagger}_{expt} = \Delta H^{\ddagger}_b + \Delta H_{ads}$$

$$\Delta H^{\ddagger}_b = 39 \text{ kcal/mole.}$$

The activation energy, $\Delta H^{\ddagger}_b$ is, of course, the activation energy of reaction b, the slow step in the process. In the example given this is shown as a bond breaking reaction but it might also be a simple elevation of the molecule to a higher electronic state. Since reaction b occurs on the surface, $\Delta H^{\ddagger}$ is not necessarily the same as it would be for the gas phase reaction. Further, it is probably somewhat smaller that it would be for the gas phase process, since otherwise, in view of the small entropy of activation of a first order reaction in the gas phase, the reaction would occur in the gas and not on the surface. Also, if the rate controlling step is some reaction other than the simple bond breaking process shown in the example then it follows that the activation energy for the gas phase reaction

$$HN_3 \rightarrow NH + N_2 \qquad (R1)$$

is greater than $\Delta H^{\ddagger}$ since otherwise the latter reaction would occur at a greater rate and would be the process observed. It follows therefore that the measured $\Delta H^{\ddagger}$ is equal to or less than the heat of activation of reaction R1; i. e., $\Delta H^{\ddagger}$ for R1 is at least 39 kcal/mole. This is surprisingly close to the value of 37 kcal/mole estimated by Franklin et al.[2] It would appear from these data that the true value of the activation energy of R1 is somewhat greater than this, but the amount would be difficult to estimate.

6. References

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WASHINGTON, January 22, 1958.