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SHOCK-TUBE MEASUREMENTS OF THE HOMOGENEOUS RATE OF
DECOMPOSITION OF NH_3 IN NH_3 -AR MIXTURES

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Introduction

The kinetics of the heterogeneous thermal decomposition of NH_3 has been studied in great detail and a voluminous literature is available on this subject.¹ Little information is available, however, concerning the homogeneous reaction rates. In an early paper, Hinshelwood and Burk² investigated the homogeneous decomposition and noted that no measurable reaction occurred up to temperatures of about 1500°K . More recently Sage,³ using a ballistic piston, has observed the reaction to proceed at temperatures between 1500 and 4500°K although no rate data were derived from these experiments.

The advent of the shock tube and "fast" infrared detectors has now made possible a method for the measurement of the homogeneous decomposition rate. In this paper we report the results of preliminary activation-energy measurements for the homogeneous decomposition of NH_3 .

The use of the shock tube for emission measurements has been described by several authors.⁴⁻⁶ The present investigations are probably the first published data on reaction-rate measurements using infrared emission. Many shock-tube rate measurements have, however, been made by monitoring light intensities in the visible and ultraviolet regions of the spectrum.⁷⁻¹⁰ If it is assumed that radiative equilibrium is attained in times short compared with the chemical decomposition times after passage of the shock wave and, furthermore, that the NH_3 behaves as a transparent gas, then it is possible to measure the change in NH_3 concentration directly by following the infrared emission intensity as a function of time. Radiation of intermediates may be minimized by measuring only the initial concentration changes.

Rough calculations, based on the absolute intensity data of McKean and Schatz,¹¹ indicate that the most advantageous band for a shock-tube study, considering available detectors and window materials, is the one centered near three microns. For judiciously chosen optical depths, the assumption of transparency may then be shown to be quite reasonable.

Experimental Studies

THE SHOCK TUBE AND ASSOCIATED MEASURING
EQUIPMENT

The shock tube has been constructed from commercial steel tubing. The driver section is round with an inside diameter of $4\frac{1}{2}$ inches and a length of 74 inches; the cross-section of the low-pressure end is a square, $3\frac{1}{4}$ inches on a side internally; and the square section is 142 inches in length. Accommodations for observation windows and the thin-film heat gauges which are used for shock-velocity measurement have been provided at several stations; the windows are made of synthetic sapphire and periclase.

In Figure 1 we have indicated schematically the associated electronic circuits and measuring equipment. The pressure was determined with a Wallace and Tiernan 0 to 50 mm absolute pressure gauge and a Consolidated Vacuum PHG-09 Phillips gauge. By means of a Consolidated Vacuum type MCF-60 oil-diffusion pump, backed by a Kinney KC-8 mechanical pump, the tube could be evacuated to a pressure of 0.1μ Hg, with a leak rate of 0.1μ per minute.

The detector is a Westinghouse Type 812 gold-doped Ge infrared photoconductive cell. As mounted in our experiments with a carefully constructed cathode follower and with a load resistance of $10^5 \Omega$, the measured time constant of the detector has been found to be approximately $0.7\mu\text{sec}$.

With the monochromator slits adjusted so that a spectral range from 2.7 to 3.2μ was covered, no radiation was detected in a series of control experiments with pure argon. All of our measurements were made behind the incident shock wave.

TEST GAS MIXTURES

Because of the low-specific heat ratio of NH_3 , it is impossible to achieve a sufficiently high temperature for initiation of the decomposition by shock-wave heating of the pure gas. For our rate studies, 1 per cent NH_3 -99 per cent Ar and 8 per cent NH_3 -92 per cent Ar mixtures were prepared with Matheson anhydrous grade NH_3 .

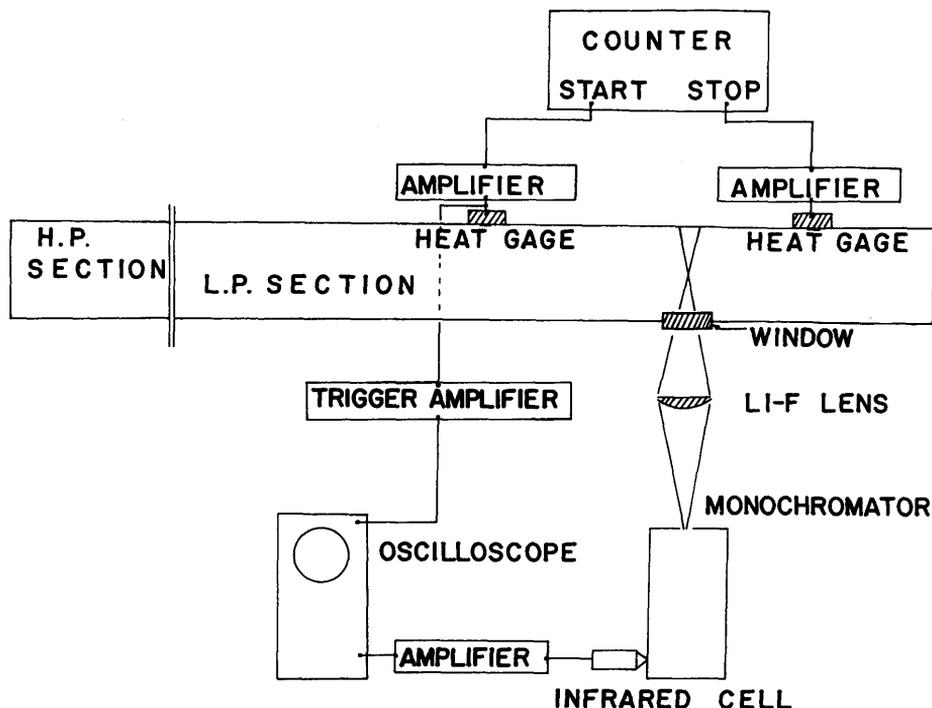


FIG. 1. Schematic drawing of shock tube electronic circuits and measuring equipment

(99.99 per cent) and Matheson standard grade Ar (99.998 per cent). Before each run, a gas sample was taken directly from the low-pressure end of the tube for chemical analysis. For data reduction, only those runs which fell within about 3 per cent of the desired composition were used.

CALCULATION OF THERMODYNAMIC PROPERTIES BEHIND THE SHOCK

From measured initial conditions and shock velocity, the thermodynamic parameters after the passage of the shock may be calculated by the use of the well-known conservation relations. Because the kinetic measurements were to be restricted to initial rates, only properties immediately behind the shock front were required. For the mixture containing 1 per cent NH_3 , the calculations were performed neglecting the presence of the NH_3 . Calculations for the 8 per cent mixture were carried out by assuming equilibrium before and after the shock wave with respect to the internal degrees of freedom but not with respect to chemical composition. Enthalpies for NH_3 were computed in the 2000 to 3000°K range with standard methods.¹²

Experimental Results

The initial rate of decomposition of NH_3 in Ar has been measured between 2000 and 3000°K by following the rate of decrease of emission intensity in the 2.7 to 3.2 μ wavelength region. A typical experimental record is shown in Figure 2. As was pointed out earlier, the intensity of the emission is assumed proportional to the concentration of NH_3 . From the record it may be seen that the emission intensity jumps very rapidly to a maximum value after passage of the shock wave and then decays, approaching the zero level asymptotically.

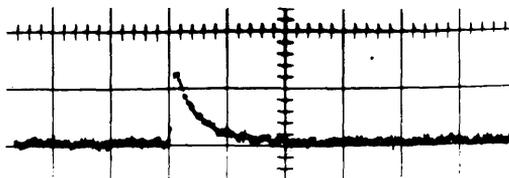


FIG. 2. Typical experimental record. Vertical lines are at 20 μsec intervals. $X_{\text{NH}_3} = 0.08$, $T = 2720^\circ\text{K}$.

For reduction of the data it was assumed that

$$-\frac{d(\text{NH}_3)}{dt} = k(\text{NH}_3)(M) \quad (1)$$

where (M) represents either Ar or NH_3 .

In terms of the NH_3 partial pressure, p_{NH_3} , and the mole fractions X_M and X_{NH_3} , Equation (1) may be written as

$$\frac{-RT}{X_{\text{NH}_3} p_T^2} \frac{dp_{\text{NH}_3}}{dt} = kX_M. \quad (2)$$

Here p_T is the total pressure and T the temperature after the passage of the shock; t represents the actual time for the decomposition reaction and may be obtained from the "oscilloscope time" by multiplying by an appropriate density ratio. For transparent gases, p_{NH_3} is directly proportional to the emission intensity and, with properly designed electronic circuits, directly proportional to the oscilloscope voltage V registered by the detector. Hence

$$V = \text{const } p_{\text{NH}_3} \quad (3)$$

or

$$\frac{dV}{dt} = \text{const } \frac{dp_{\text{NH}_3}}{dt}.$$

The constant of proportionality may be evaluated at $t = 0$ from the oscilloscope trace and the known partial pressure of NH_3 immediately behind the shock front. Thus, in terms of the initial voltage V^0 and mole fraction $X_{\text{NH}_3}^0$, and with an assumed Arrhenius temperature dependence, Equation (2) becomes

$$\frac{-RT}{X_{\text{NH}_3} p_T^2} \frac{dp_{\text{NH}_3}}{dt} = \frac{-X_{\text{NH}_3}^0}{X_{\text{NH}_3}} \frac{RT}{p_T} \frac{dV}{dt} = Be^{-E/RT}. \quad (4)$$

For the initial stages of the reaction, T and p_T are approximately constant and $X_{\text{NH}_3}^0 \simeq X_{\text{NH}_3}$. On this basis, an activation energy has been determined from Equation (4). The logarithm of the left-hand side of Equation (4) has been plotted against $1/T$ for our measurements and the resulting graph is shown in Figure 3. Least-square straight-line fits of these data yield apparent activation energies of 51 kcal/mole for the mixture containing 1 per cent NH_3 and 53 kcal/mole for the mixture containing 8 per cent NH_3 .

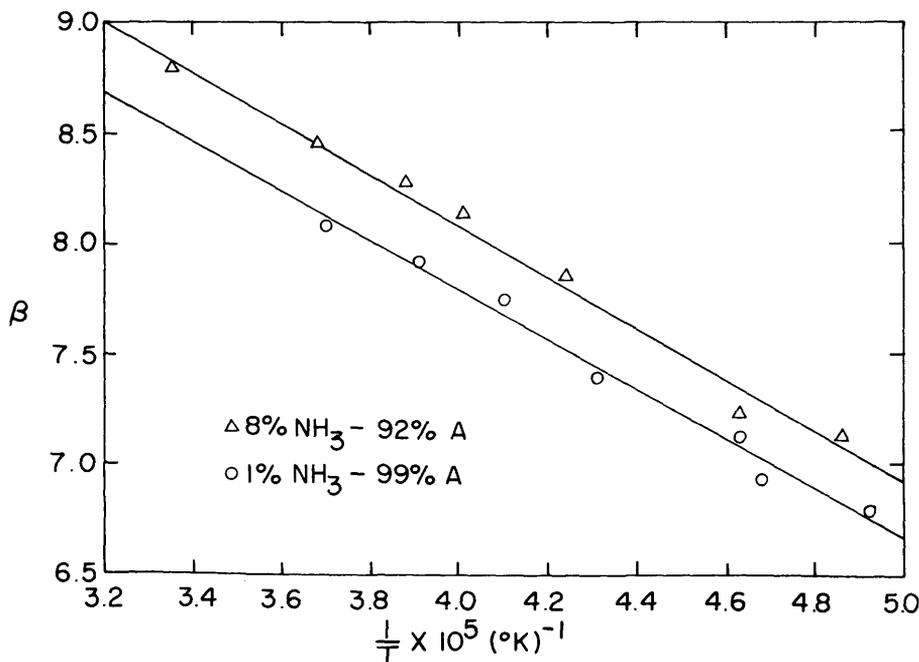


FIG. 3. The quantity $\beta = \log_{10}[(RT/X_{\text{NH}_3} p_T^2)(dp_{\text{NH}_3}/dt)]$ versus $(1/T)$. The term dp_{NH_3}/dt has been evaluated for the initial decrease in NH_3 emission.

Conclusions

It is natural to assume that the initial step in the homogeneous decomposition of NH_3 is



where M is either Ar or NH_3 . Comparing our measured activation energy of about 52 kcal with the experimental value of about 105 kcal for the $\text{NH}_2\text{-H}$ bond strength,¹³ it is clear that our data do not represent the initial decomposition rate. No doubt we are measuring the early rate and a chain mechanism is a reasonable explanation of our low-activation energy.^a We shall not attempt to guess the details of the actual mechanism but shall simply note that a chain with bimolecular termination would involve the square root of the initial rate constant, indicating an initial activation energy of about twice our measured value. This result follows, at least qualitatively, from the assumption that the reaction rate may be written¹⁴

$$\text{rate of reaction} \propto r_p \left(\frac{r_i}{r_b} \right)^{1/2}, \quad (6)$$

where r_p , r_i and r_b are the rates of chain propagation, initiation and breaking, respectively. For simple Arrhenius temperature dependence the apparent activation energy of Equation (6) would be

$$E = E_p + \frac{1}{2}(E_i - E_b), \quad (7)$$

where the subscripts have the same meaning as for the rates in Equation (6). For E_p and E_b small, we have $E_i \simeq 2E$ in accord with our experimental findings.

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^a The author is indebted to Dr. Norman Davidson for a discussion of this point.

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