Thermal Decomposition of Hydrazine

HAROLD W. LUCIEN
Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio

THE THERMAL STABILITY of hydrazine has been studied in the temperature and pressure intervals of 175° to 250° C. and 300 to 430 p.s.i., respectively. Previous studies of the decomposition of hydrazine indicated that several factors affect its stability (*2, 5, 7*). The rate of decomposition is increased by the presence of certain surfaces (especially metals and salts), pH, oxygen, and carbon dioxide. Further explosive decomposition is attributable to the uncontrolled heterogeneous, gas-phase decomposition. These factors were considered in selecting the following experimental conditions: Highly purified hydrazine was prepared in a nitrogen atmosphere, and this product was decomposed over triply distilled mercury in outgassed borosilicate glass tubes at ullages that were initially zero. This study also included the effects of added quantities of ammonia on the rate of decomposition and an investigation of the products of the decomposition.

EXPERIMENTAL

Apparatus and Materials. The apparatus for preparing hydrazine and that for charging reaction tubes were located in a dry box with a nitrogen atmosphere. Oil-pumped nitrogen was purified by flowing through the following train: CuO at 575° C. to destroy organic matter, Drierite-Ascarite (removal of carbon dioxide and partial removal of water), P_2O_5 to remove water, Cu on silica gel at 300° C. to remove oxygen, and P_2O_5 to remove water.

Hydrazine was obtained by the ammonolysis of hydrazine sulfate by adapting a procedure described by Brown and coworkers (*3*). Upon distillation, a fraction of hydrazine 99.9 ± 0.1% pure was obtained. The acidimetric and iodate method of Penneman and Audrieth (*6*) was used to determine hydrazine analytically. The other fractions contained ammonia, and were used to obtain the various hydrazine-ammonia compositions that were studied.

Procedure. Decomposition studies were conducted in borosilicate glass tubes with inner diameters of 3.00, 5.00, 5.56, and 7.00 mm. These tubes were "J" shaped, closed at both ends with a hole located near the end of the long leg. The tubes were cleaned with chromic-sulfuric acid solution and rinsed with tap and distilled water. Each tube was evacuated to 10^{-4} mm. of mercury and periodically heated for the purpose of outgassing. While evacuated, the tube was filled with triply distilled mercury that was redistilled in a nitrogen atmosphere prior to use. A weighing buret was used with a flexible 0.015-in., stainless-steel tubing to place hydrazine above the mercury in the shorter leg of the tube without a gas space above the sample. Reactions were conducted in an oil bath in a heavy steel enclosure with a plastic window. The charged reaction tube was attached to the positioning swivel, pressurized, and placed in the oil bath, which was maintained within ±1° C. of a preset temperature. The bath temperature was measured with a copper constantan thermocouple and recording potentiometer. The decomposition was followed by observing with a cathetometer the change of the mercury column height with time. Decompositions were allowed to progress for periods varying from a few hours to 20 days. The pressure and temperature ranges studied were 300 to 430 p.s.i. and 175° to 250° C., respectively.

Duplicate samples of the hydrazine used for the decompositions were dissolved in dilute HCl and analyzed by iodometry and potentiometric acid-base titration. At the conclusion of the experiment, the soluble components were washed from tube with dilute hydrochloric acid and distilled water. This solution was analyzed for hydrazine and ammonia. The residual insoluble gas was washed several times with concentrated sulfuric acid and transferred to the gas sampling tube. The nitrogen and hydrogen that composed the mixture were chromatographically determined. Molecular nitrogen and hydrogen among the products were analyzed by a vapor fractometer with a 1-meter Molecular Sieve column at 35° C., and a thermal conductivity type detector was used. Argon was used as the carrier gas. Two expressions represent the decrease of the original mass of hydrazine: the change of volume of products, and the mass fraction of hydrazine that was decomposed. Each decomposition curve consisted of two linear parts. The rates of decomposition refer to the second rates unless otherwise indicated.

RESULTS AND DISCUSSION

The rates of decomposition of hydrazine varied from 10^{-4} to 2% per hour, depending on reaction conditions. These decompositions were characterized by an initial linear rate followed by an increased constant rate (Figures 1 and 2). Both rates varied with the initial concentration of ammonia, with pressure, and with temperature (Figure 2 to 5). It was not possible to assign any significance to the initial rate or to the ratio of the second and initial rates. This ratio varied with experimental conditions and was 1.0 to 2.5 for pure hydrazine. Both slopes showed similar dependencies on all reaction parameters. The rates of decomposition, all slightly less than 2% original hydrazine per hour, were independent of the tube diameter over the range of diameters studied.

Since ullages are initially zero, the initial vapor space must be produced by the decomposition of pure liquid hydrazine. The vapor space resulting from hydrazine-ammonia mixtures could result from the decomposition of liquid hydrazine and/or volatilization of ammonia from the liquid. After the vapor space is produced, decomposition could occur in either or both phases. It has been suggested (*7*) that, depending on conditions, the gas-phase decomposition of hydrazine can be homogenous or heterogeneous. Over the range of surface areas investigated, it does not appear that gas- or liquid-phase decomposition could be heterogeneous. The rate of decomposition became and remained constant after a constant initiation period, while the surface to which the vapor was exposed was changing constantly.

The Effect of Ammonia on the Rate of Decomposition. Ammonia retarded the rate of decomposition (Figure 3). The rate was most affected by initial ammonia concen-

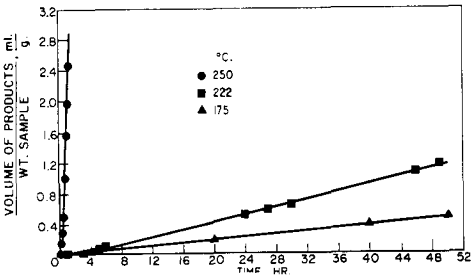

Figure 1. Thermal decomposition of anhydrous hydrazine at 430 p.s.i. pressure

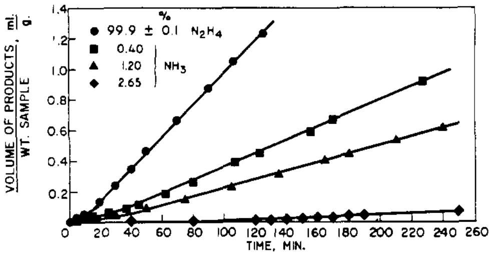

Figure 2. Thermal decomposition of anhydrous hydrazine at 250° C., and 430 p.s.i.

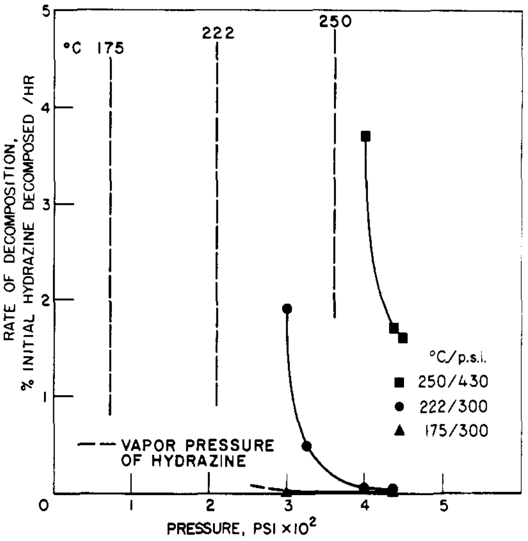

Figure 4. Rate of decomposition of hydrazine as affected by pressure

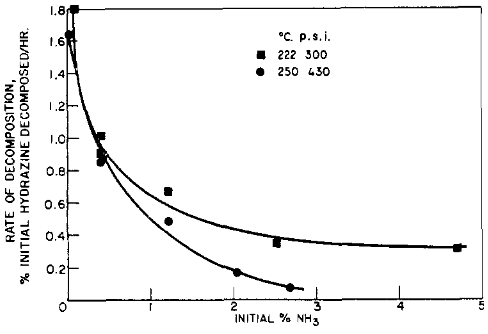

Figure 3. Effect of ammonia concentration on the rate of decomposition of hydrazine

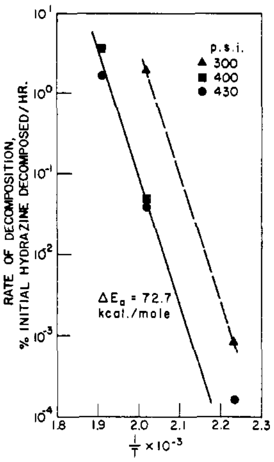

Figure 5. Dependence of the rate of decomposition of hydrazine on temperature

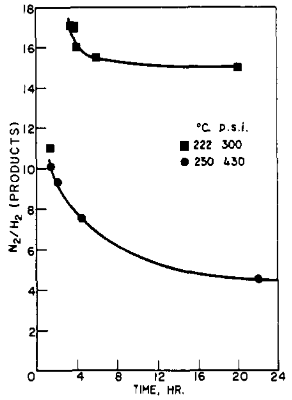

Figure 6. Relation between time and N_2 to H_2 among the products from the thermal decomposition of hydrazine

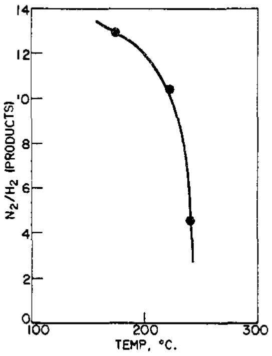

Figure 7. Relation between the N_2 to H_2 ratio and temperature during thermal decomposition of hydrazine at 430 p.s.i.

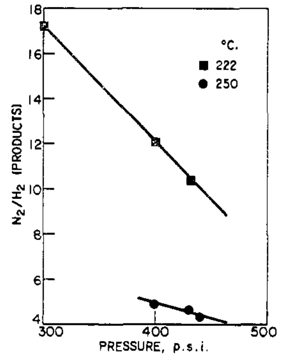

Figure 8. Relation between pressure and N_2 to H_2 ratio during thermal decomposition of hydrazine

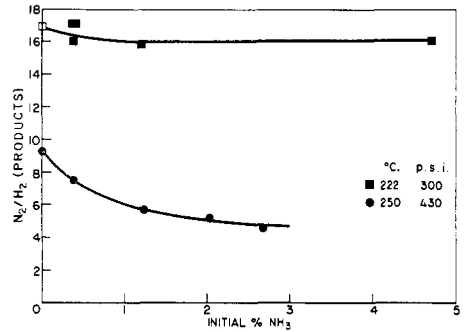

Figure 9. Relation between the N_2 to H_2 ratio and the concentration of NH_3

trations below 2%; above this amount the additional effect was small. At 222° C. and 300 p.s.i., the rate of decomposition decreased from 1.8% per hour at 0.1% ammonia to 0.4% per hour at 2.5% ammonia. When the initial concentration of ammonia increased from 2.5% to 4.7%, the rate decreased to 0.3% per hour. A similar effect was observed at 250° C. and 430 p.s.i. The two observed rates for each decomposition were inversely related to the initial ammonia concentration, whereas the duration of the initiation period was directly related (Figure 2).

The Effect of Pressure. The inverse effect of pressure on the rate of decomposition of hydrazine is shown in Figure 4. At 250° C., the rate was decreased from 3.7% per hour at 400 p.s.i. to 1.7% per hour at 440 p.s.i. pressure. The most rapid changes in rate were observed at those conditions where the difference between the confining pressure and the vapor pressure of hydrazine was small. The order of magnitude of this pressure-difference dependence of the rate is shown in Figure 4. The minimum pressure differences for the decompositions in this study were 230, 90, and 40 p.s.i. at 175°, 222°, and 250° C., respectively. All attempts to decompose hydrazine at pressure differences less than 10 p.s.i. resulted in extremely rapid reactions that ended in explosions. At 250° C., the rate was decreased from 3.7% per hour at 400 p.s.i. to 1.3% per hour at 440 p.s.i. At 222° C., a change in pressure from 300 to 430 p.s.i. caused a change in rate from 1.3 to 0.04% per hour.

The Effect of Temperature. The temperature dependence of the decomposition is shown in Figure 5. The rate increased from 10^{-4} to 1% per hour over the temperature range of 175° to 250° C. This represents a 3.4-fold change in the rate per 10° C. An activation energy 72.7 kcal. per mole was calculated from Figure 5. Similar effects were observed at 300 and 400 p.s.i.

The N_2 to H_2 Ratio. The ratio of molecular nitrogen and hydrogen among the products was inversely related to all of the reaction parameters (Figures 6 to 9). This ratio decreased to what appeared to be a limiting value for each set of experimental conditions. The N_2 to H_2 ratio decreased with time (Figure 6) from 17 toward a constant value of 15 at 222° C. and 300 p.s.i., and from approximately 10 to 5 at 250° C. and 430 p.s.i. The ratio decreased by 5 per 100 p.s.i. increase of pressure at 222° C. and by 1.4 per 100 p.s.i. at 250° C.

The N_2 to H_2 values indicated that a substantial part of the decomposition proceeded by Equation 1:

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad (1)$$

The small quantities of hydrogen that formed are due in about equal amounts to the dissociation of ammonia (Equation 2) and probably hydrazine (Equation 3):

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (2)$$

$$N_2H_4 \rightarrow N_2 + 2H_2 \qquad (3)$$

For the purpose of establishing the extent to which Equation 2 contributes to the N_2 to H_2 ratio, an upper limit was obtained by calculating the amounts of N_2 and H_2 that should have resulted from the dissociation of ammonia under experimental conditions. In this way, it was possible to account for about one-half of the hydrogen found among the products. If the analytical N_2 and H_2 data are used in the general Equation 4,

$$3N_2H_4 \rightarrow 4(1-x)NH_3 + (1+2x)N_2 + 6xH_2 \qquad (4)$$

for the decomposition of hydrazine into ammonia, nitrogen, and hydrogen, the value of x when N_2 to H_2 tends to become constant (Figure 6) was 0.017 at 222° C. and 300 p.s.i. pressure. This value at 250° C. and 430 p.s.i. pressure was 0.034.

The results relating to the stoichiometry of decomposition suggested a changing reaction mechanism at the higher temperatures. This observation is based on the variation of the N_2 to H_2 ratio with reaction parameters and the inability to account for all of the hydrogen by the dissociation of ammonia. It was not possible to obtain indications of competing processes from the rate-temperature relation (Figure 5) because of the incomplete nature of these data. If the decomposition process involves competing reactions, a calculated activation energy from Figure 5 would have doubtful meaning. The calculated activation energy was ≈ 73 kcal. per mole, which is greater by a factor of 2 than the reported values (*1, 4*). Hydrazine is relatively stable under the conditions described. Results such as those found in Figures 4 and 5 suggest that there are pressure and temperature conditions which determine the reaction mechanism and hence control the rate of decomposition. The 222° C.–300 p.s.i. and 250° C.–430 p.s.i. conditions apparently are in the regime of changing mechanisms. It appears that up to 250° C. the total pressure should exceed the vapor pressure of hydrazine by at least 200 p.s.i. if the rate of decomposition is to be confined to relatively low values.

LITERATURE CITED

(1) Adams, G.K., Stocks, G.W., "Fourth Symposium (Intern.) on Combustion," p. 239, Williams & Wilkins Co., Baltimore, Md., 1953.
(2) Audrieth, L.F., Ogg, B.A., "The Chemistry of Hydrazine," Wiley, New York, 1951.
(3) Browne, W., *J. Am. Chem. Soc.* **33**, 1728 (1911).
(4) Gilbert, M., "The Hydrazine Flame," Progr. Rept. No. **20-318**, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., 1957.
(5) Kilpatrick, M.L., Pertel, R., Gunning, H.E., "Thermal Decomposition of Hydrazine on Various Surfaces," ONR Project **NR 096162**, Studies on Hydrazine, Tech. Rept. No. 2, 1953.
(6) Penneman, R.A., Audrieth, L.F., *Anal. Chem.* **20**, 1058 (1948).
(7) Thomas, D.D., "The Thermal Decomposition of Hydrazine," Progr. Rept. No. **9-14**, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., 1947.

RECEIVED for review September 16, 1960. Accepted May 12, 1961.

Prediction of Boiling Points of Liquid Mixtures

ISAMU NAGATA[1] Department of Chemical Engineering, Kyoto University, Kyoto, Japan

KNOWLEDGE of vapor-liquid equilibrium of a mixture is necessary in distillation calculations. It is practical to predict multicomponent vapor-liquid equilibria only from the data for pure components and their binary combinations to save further experimentation. There are generally two types of methods to correlate vapor-liquid equilibrium data. One involves the vapor phase imperfections and the liquid phase activity coefficients as a thermodynamically consistent function of liquid composition in various empirical forms of representation. In this case the effect of temperature on the activity coefficient also should be taken into consideration. This method is exacting, but is laborious even for the prediction of isobaric ternary vapor-liquid equilibria, since this involves the above effects and the correlation of vapor pressure *vs.* temperature. The other method uses several different empirical algebraic equations, which correlate compositions of vapor phase directly with those of liquid phase without the use of the composition–boiling point relationship. Thus, one can avoid the complexities in dealing with the activity coefficient and the temperature dependence of the vapor pressures of pure components (*32*). The main advantage of those algebraic equations which have been proposed so far consists in simplicity of their expressed forms. However, the fact that those equations do not have temperature terms seems to be unreasonable.

This article presents an empirical method to correlate boiling temperatures of a binary liquid mixture with its equilibrium compositions by such an algebraic equation. The method is applied for the prediction of boiling points of ternary systems.

PROPOSED METHOD

Most empirical algebraic equations treat only binary systems. An essential requirement is that the method can treat not only binaries, but also multicomponent mixtures. The most useful is the equation developed by Prahl (*31*). This equation is flexible because it covers the whole range of concentrations of many binary systems by using three constants, and because it can be extended to multicomponent systems (*23*). For binary systems, the equation is expressed as follows:

$$\frac{y_i}{y_j} = \frac{x_i}{x_j}\left(\frac{x_i + x_i a_{ij}}{x_j b_{ij} + x_i c_{ij}}\right) \qquad (1)$$

---

[1] Present address, Kanazawa University, Kanazawa, Japan