Thermochimica Acta, 175 (1991) 189–198
Elsevier Science Publishers B.V., Amsterdam

KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF MONOMETHYLHYDRAZINE BY ACCELERATING RATE CALORIMETRY

DENNIS D. DAVIS *

Department of Chemistry, New Mexico State University, Las Cruces, NM 88003 (U.S,A.)

RICHARD C. WEDLICH

Lockheed Engineering and Sciences Company, National Aeronautics and Space Administration, White Sands Test Facility, Las Cruces, NM 88004 (U.S.A.)

(Received 27 July 1990)

ABSTRACT

The thermal decomposition reaction of monomethylhydrazine was studied using an accelerating rate calorimeter. Nitrogen, ammonia, methylamine, methane and ethane were the major products. Dimethylamine, 1,2-dimethyldiazene and traces of nine other nitrogenous compounds or hydrocarbons were observed in the product mixture. The Arrhenius parameters for the decomposition reaction are compensated and linearly related by the relationship $\ln A = E_a/R\theta + \ln k_0$, with a compensation temperature θ of 478 K. The isokinetic temperature is 475 K. Activation energies were found to be in the range 71.8–114.8 kJ mol^{-1}.

A mechanism involving surface-bound amido, imido, nitrido, hydrido, methylene and methyl species is proposed to account for the major and minor products.

INTRODUCTION

Bipropellant systems of monomethylhydrazine (MMH) and nitrogen tetroxide (N_2O_4) are widely used throughout the aerospace industry. The Orbital Maneuvering System of NASA's Space Shuttle, maneuvering rockets in geosynchronous satellites, Apollo, Surveyor and Minuteman II missiles are several of the systems which utilize this bipropellant combination. The reactive nature of these compounds presents problems in the selection of materials for their handling and storage. MMH is subject to surface-catalyzed thermal decomposition reactions which are exothermic and gas-producing [1]. Possible hazards due to this decomposition require a detailed understanding of factors which characterize this reaction.

---

* Author to whom correspondence should be addressed.

Accelerating rate calorimetry [2–4] is a technique which uses the heat generated during an exothermic reaction to raise the temperature and thus accelerate the rate of the reaction. If the reaction vessel is confined in a calorimeter designed to maintain adiabatic conditions, the time–temperature history provides kinetic information and the overall temperature rise can be related to the energetics of the reaction. In this study we report the results of using the accelerating rate calorimeter (ARC) to study the products and kinetics of the thermal decomposition of MMH.

EXPERIMENTAL

A commercial ARC instrument (Columbia Scientific Industries, Austin, TX) was used in these studies. A description and schematic of the ARC has been published elsewhere [5]. The reaction vessels were 2.54 cm diameter titanium spheres having a mass of approximately 10 g. A pressure transducer with a 0–17200 kPa range was connected to the reaction vessel through stainless steel capillary tubing. A rotary high-pressure valve allowed the reaction products to be vented to an evacuated manifold for analysis. If pressure data or reaction product studies were not required, the reaction vessel was sealed with a 316L stainless steel nut, ferrule and plug weighing approximately 20 g. In a typical experiment, a cleaned and weighed reaction vessel was charged with approximately 15 mmol of propellant MMH in a nitrogen-filled glovebox, sealed and reweighed. The reaction vessel was then connected to the pressure fittings (if used), enclosed in the calorimeter and the instrument operating sequence started. Heaters in the calorimeter increased the temperature of the reaction vessel until the lower detectable limit of the temperature rate (0.02 K min^{-1}) was observed. Up to this point, heating was intermittent; between heating periods the calorimeter was isothermal for 20 min while searching for a detectable temperature rise. If no temperature rise was detected, the calorimeter repeated the heat–wait–search cycle. During an exothermic reaction, heaters were digitally controlled to maintain zero temperature difference between the reaction vessel and the calorimeter jacket. At the completion of the exotherm, the calorimeter and vessel were cooled and the vessel reweighed to check for leaks. The contents of the reaction vessel were then expanded into a pressure manifold. A known fraction of the gaseous products was trapped in a cold, standard, aqueous acid (HCl or HNO_3) solution. Aliquots of this acid solution were then back-titrated with standard NaOH to determine total base content (ammonia, amines and hydrazines) titrated coulometrically to measure hydrazines [6] or analyzed by ion chromatography for ammonia, amines and hydrazine [7]. Gas chromatography or gas chromatography–mass spectrometry was used to determine hydrogen, nitrogen, methane, ethane, 1,2-dimethyldiazene and other trace gaseous constituents in the product mixture.

Previous work has indicated that the reaction rate, but not product composition, is proportional to the surface area of the vessel or added materials [8]. In this study, the surface area of the titanium reaction vessel was constant (24 cm^2) and no other materials were added. Monomethylhydrazine was propellant grade (MIL-P-27404B). Data analysis was performed as described in an earlier work [4] using the thermochemical balance and stoichiometry determined in this work.

RESULTS

The decomposition of MMH, as noted by a minimum detectable temperature rate of 0.02 K min^{-1} began at 490 ± 5 K. A plot of log (temperature rate) vs. $10000/T$ (K^{-1}) for a typical reaction is shown in Fig. 1. For 15 mmol of MMH in a 30 g reaction vessel, the adiabatic temperature increase was 145 K and the pressure increased to a maximum of 12500 kPa at 635 K. A step corresponding to a 20% increase in reaction rate occurred at 510 ± 5 K. This feature, along with other aspects of the kinetics, is detailed in the Discussion.

The products of MMH decomposition are shown in Table 1. The stoichiometry can be described by eqn. 1 with $x = 0.07$:

$$\begin{aligned} \mathrm{MMH} \rightarrow & (1/2 + x)\mathrm{NH_3} + (1/2 - x)\mathrm{CH_3NH_2} + 1/2\mathrm{N_2} \\ & + (1/2 - x)\mathrm{CH_4} + 2x(\mathrm{CH_3}) \end{aligned} \quad (1)$$

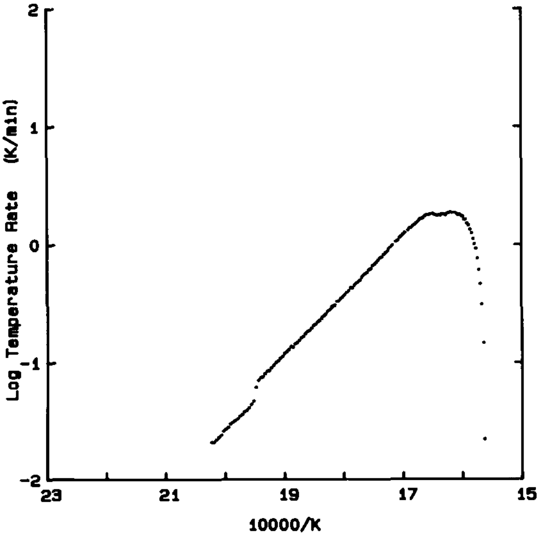

Fig. 1. Monomethylhydrazine (MMH) decomposition reaction kinetics in the ARC presented as log (temperature rate, K min^{-1}) vs. 10000/T (K^{-1}). The ~ 30 g titanium reaction vessel contained ~ 0.7 g of MMH.

TABLE 1

Major products of the titanium-surface-catalyzed decomposition of MMH (485–625 K) [a]

Product	N_2	NH_3	CH_4	CH_3NH_2	CH_3	Base [b]
Observed:	0.51	0.56	0.41	0.41	0.12	0.99
Calculated [c]:	0.50	0.57	0.43	0.43	0.14	1.0

[a] Moles of product per mole of MMH.

[b] Total basic products in moles of base per mole of MMH.

[c] Based on $x = 0.07$ in eqn. 1.

where (CH_3) represents the minor alkyl-group containing constituents. Ethane, propane, ethylene, acetylene, ethylamine, 1,2-dimethyldiazene, 1-ethyl-2-methyldiazene, dimethylamine, trimethylhydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, and other nitrogen compounds were detected in small amounts ($< 0.5\%$ each). There was only a trace of MMH remaining at the end of the reaction. The hydrogen content of the reaction mixture was less than 0.1%, typical of the low temperature decompositions of hydrazines [9]. The overall mass balance is excellent and in good agreement with a previous isothermal study at 448 K [10]. The heat of reaction ΔH_{rxn} calculated from the heats of formation of MMH vapor and the major products shown in eqn. 1 is -172 kJ mol^{-1}. The initial portion of the reaction during which liquid MMH was present has a ΔH_{rxn} value of -131 kJ mol^{-1}. The "CH_3" constituents were treated as ethane for thermochemical and material balance purposes.

Based on this stoichiometry, the observed temperature rate (K min^{-1}) was converted to a reaction rate (mol m^{-2} sec^{-1}) using the system heat capacity, enthalpy of reaction and surface area of reaction vessel. The calculated heat balance of the reaction was $90 \pm 10\%$ based on the observed stoichiometry and published thermodynamic properties. Arrhenius activation parameters were determined for the linear post-step portion of the reaction using an assumed zero order rate law.

TABLE 2

Activation parameters for the titanium-surface-catalyzed decomposition of monomethylhydrazine

A [a] (mol m^{-2} s^{-1})	E_a (kJ mol^{-1})
7.7×10^2	71.8
4.3×10^5	97.3
2.9×10^6	104.9
3.8×10^7	114.8

[a] Activation parameters derived from the final portion of reaction with only vapor present.

For this series of experiments in titanium vessels, the standard deviations of the slopes of the Arrhenius plots are in the range 0.8–1.0 kJ mol^{-1}. The wide variation of the observed activation parameters is apparently not a random phenomenon since a larger A-value is always accompanied by a larger activation energy. The variation is apparently not a random experimental error. This interdependence of the E_a and A-values (enthalpy/entropy relationship) in the Arhennius expression, eqn. 2, is commonly observed in heterogeneous kinetics [11–13],

$$k = A \exp(-E_a/RT) \tag{2}$$

where k is the rate constant, E_a is the Arrhenius activation energy, A is the Arrhenius pre-exponential factor, R is the gas constant and T is the absolute temperature (K).

DISCUSSION

Adiabatic decomposition kinetics

The adiabatic temperature rate measured in an ARC experiment is described by eqn. 3:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\mathrm{d}n}{\mathrm{d}t}\frac{\Delta H_{\mathrm{rxn}}}{C_s} \tag{3}$$

where $\mathrm{d}T/\mathrm{d}t$ is the observed temperature rate (deg min^{-1}), $\mathrm{d}n/\mathrm{d}t$ is the chemical reaction rate (mol min^{-1}) and is a function of both the temperature T and composition n_T; ΔH_{rxn} is the enthalpy of the reaction at T, and C_s is the system heat capacity at T and composition n_T.

The general rate law for a surface-catalyzed reaction can be written:

$$\mathrm{d}n/\mathrm{d}t = k[\text{conc}]^m[\text{surface area}] \tag{4}$$

where k is the observed rate constant and $[\text{conc}]^m$ is a generalized concentration dependence with order m. The concentration function is usually such that it determines the fraction of the total surface area covered by reactant. The rate constant k can be expressed by the Arrhenius expression, eqn. 2. Conversion of the observed temperature rates to reaction rates was accomplished by a digital computer algorithm which takes into account C_s and ΔH_{rxn} as functions of temperature and composition [4,8]. Regression analysis of the rates suggests that the rates are best characterized with $m = 0$ up to at least 90% reaction. Under the high reactant pressure ARC conditions it is probable that the catalytic surface is saturated and the fraction of the surface covered is unity. Earlier studies have shown that the decomposition rates for hydrazine are linearly related to the catalytic surface area

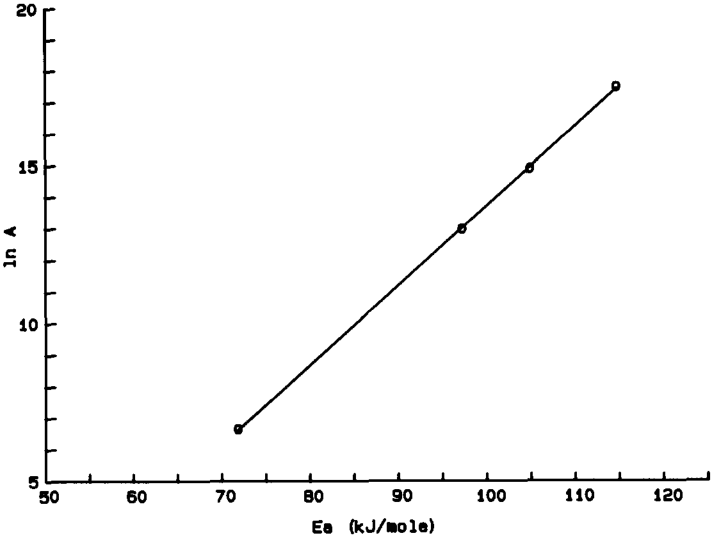

Fig. 2. Compensation relationship for the titanium-surface-catalyzed MMH decomposition. Data from Table 2, slope $=1/R\theta$, $\theta=478$ K.

available [8]. Equation 4 then simplifies to a zero order rate law, except at the very late stages of the reaction [4].

The step observed in the decomposition plot for MMH and hydrazine has been explained as being due to the disappearance of the liquid phase hydrazine and a change in the heat of reaction as the endothermic component due to the heat of vaporization of 41 kJ mol^{-1} is no longer involved [4]. The observed temperature rate increases abruptly as the reaction becomes more exothermic. The calculated reaction rate (mol s^{-1}) exhibits no such abrupt change, however.

For a series of different experiments in different reaction vessels it was found that the values of the pre-exponential term and the activation energies are correlated according to the relation:

$$\ln A = E_a/R\theta + \ln k_0 \tag{5}$$

where θ, with units of temperature, is referred to as the compensation temperature [11–13]. The compensation temperature determined from eqn. 5 is 478 K, Fig. 2. A true compensation effect implies an isokinetic effect, i.e., that there exists a temperature T_{iso} at which the rates for the various experiments will coincide. A test of this isokinetic relationship is shown in Fig. 3. A coincidence of the Arrhenius curves for all experiments occurs at 475 K, the isokinetic temperature. The compensation effect expressed in eqn. 5 can be combined with the Arrhenius relationship, eqn. 2, into a single relationship, eqn. 6.

$$\ln\left(\frac{k}{k_0}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{\theta} - \frac{1}{T}\right) \tag{6}$$

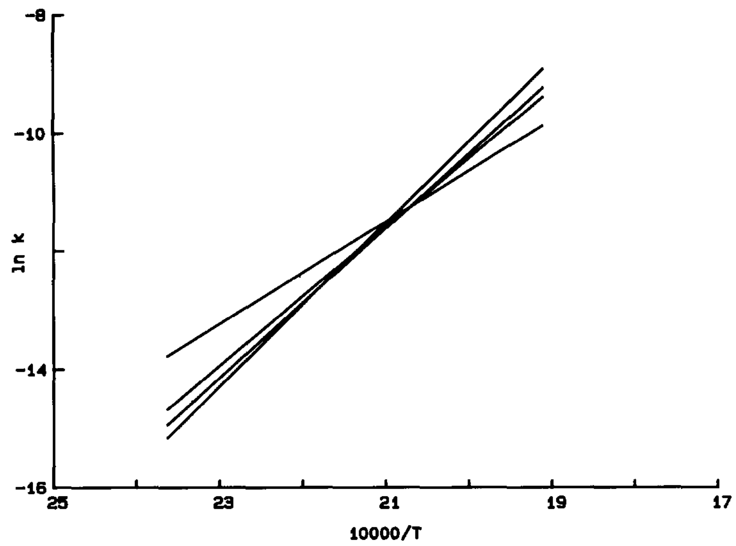

Fig. 3. Isokinetic relationship for the MMH decomposition. Arrhenius lines calculated from the activation parameters in Table 2. $T_{iso} = 475$ K.

where k is the zero order rate (constant) at T, k_0 is the zero order rate (constant) at θ, θ is the compensation temperature (K) and E_a is the activation energy.

An important feature of compensated reactions, as clearly shown in eqn. 6, is that reactivities of the related reactions depend not only on the activation energy, but also on the difference between the temperature of comparison and the compensation (or isokinetic) temperature.

There have been a number of explanations for the isokinetic effect in heterogeneous catalysis [13]. Although no explanation is widely accepted, a physical description which has the virtue of simplicity is based on the premise that greater binding energies of reactive species to surfaces result in more restriction of the vibrational, rotational and translational modes accessible to the adsorbate. In a process where desorption of products may be the rate limiting step, a more strongly bound surface species must surmount a higher desorption energy barrier (E_a), but gains more in freedom in doing so (A-term). Galwey has suggested [11a] surface heterogeneity or multiple concurrent processes as possible causes of variation in binding energies. A similar effect is noted in ARC studies of the surface-catalyzed decomposition of hydrazine where the isokinetic temperature for a series of different metal catalysts was found to be 430 K. The similarity of the compensation temperatures for hydrazine and MMH suggests a possible commonality in the rate controlling steps for both these reactions.

Mechanism of the surface catalyzed decomposition

The mechanism of the surface-catalyzed decomposition of the propellant hydrazines must be closely related to the reactions involved in ammonia synthesis and decomposition [14–15]. Based on the products of decomposition and the overall kinetic behavior, the reaction sequence shown below accounts for the general and detailed features of this reaction.

Dissociation steps

$$CH_3NH{-}NH_2 \rightarrow CH_3NH + NH_2 \tag{7}$$

$$NH_2 \rightarrow NH + H \tag{8}$$

$$NH \rightarrow N + H \tag{9}$$

$$CH_3NH \rightarrow CH_3 + NH \tag{10}$$

$$CH_3NH{-}NH_2 \rightarrow CH_3N{-}NH_2 + H \tag{11}$$

$$CH_3N{-}NH_2 \rightarrow CH_3N{=}NH + H \tag{12}$$

$$CH_3N{=}NH \rightarrow CH_3 + N_2(g) + H \tag{13}$$

Surface recombination–desorption reactions

$$NH_2 + H \rightarrow NH_3(g) \tag{14}$$

$$CH_3NH + H \rightarrow CH_3NH_2(g) \tag{15}$$

$$N + N \rightarrow N_2(g) \tag{16}$$

$$CH_3 + H \rightarrow CH_4(g) \tag{17}$$

$$CH_3 + CH_3 \rightarrow CH_3{-}CH_3(g) \tag{18}$$

$$CH_3N + CH_3N \rightarrow CH_3N{=}NCH_3(g) \tag{19}$$

Vapor phase induced decomposition

$$CH_3 + CH_3N{=}NCH_3 \rightarrow CH_2N{=}NCH_3 + CH_4 \tag{20}$$

$$CH_2N{=}NCH_3 \rightarrow CH_2{=}N_2 + CH_3 \tag{21}$$

$$CH_2{=}N_2 \rightarrow CH_2 + N_2 \tag{22}$$

Alkylation

$$CH_2 + N{-}H \rightarrow N{-}CH_3 \tag{23}$$

$$CH_2 + CH_3 \rightarrow CH_3CH_2 \tag{24}$$

$$CH_2N{=}NCH_3 + CH_3 \rightarrow CH_3CH_2N{=}NCH_3 \tag{25}$$

The initial sequence of the above steps involves the dissociation of MMH and dehydrogenation or dealkylation of the fragments on the surface, eqns. 7–13. Recombination of these fragments, eqns. 14–19, provides the major products. The formation of dinitrogen by the surface recombination of adsorbed nitrogen atoms, eqn. 16, is suggested as the overall rate limiting step, in accord with the ammonia decomposition reaction mechanism [14]. A feature of eqn. 19 is the formation of 1,2-dimethyldiazene (azomethane), the only reasonably stable non-hydrazine intermediate formed in the reaction. The induced decomposition of 1,2-dimethyldiazene, eqns. 20–22, yields not only methane, but an alkylating agent formulated here as methylene, CH_2 or its precursor, CH_2N_2 (diazomethane). This active alkylating agent can convert N–H bonds into $N-CH_3$ groups which would account for the minor homolog products such as dimethylamine, dialkyl and ethyl hydrazines.

The dehydrogenation of the NH group and subsequent recombination of N-adatoms suggests that the dinitrogen product should be formed with scrambling of the nitrogen atoms. Several isotope-scrambling studies have suggested this not to be the case for hydrazine decomposition [16]. The sequence shown in eqns. 11–13 provides for the formation of dinitrogen without scrambling of the N-atoms. The full implications of these isotope-scrambling experiments on the mechanistic overlap between hydrazine decomposition and ammonia synthesis remains to be unraveled.

CONCLUSIONS

Accelerating rate calorimetry has been used to study the adiabatic kinetics of the titanium-surface-catalyzed decomposition reaction of monomethylhydrazine. Extension of the principles and procedures developed earlier for the study of hydrazine shows that the technique can be applied to other reaction systems, including those with complex product mixtures.

The isokinetic effect has now been observed in the decomposition of both hydrazine and its methyl derivative and with a large number of catalytic surfaces. This effect appears to be a general phenomenon which is readily studied by the ARC experiment.

REFERENCES

1 E.W. Schmidt, Hydrazine and Its Derivatives: Preparation, Properties, Applications, Wiley-Interscience, New York, 1984.
2 D.F. Townsend and J.C. Tou, Thermochim. Acta, 37 (1980) 1.
J.C. Tou and L.F. Whiting, Thermochim. Acta, 48 (1981) 21.
3 W.W. Wendlandt, Thermal Analysis, 3rd. edn., Wiley-Interscience, 1986, pp. 747–755.
4 R.C. Wedlich and D.D. Davis, Thermochim. Acta, 171 (1990) 1.
5 D.W. Smith, M.C. Taylor, R. Young and T. Stephens, Am. Lab., 12 (1980) 51.

6 E.C. Olson, Anal. Chem., 32 (1960) 1545.

7 N.E. Fraley, Jr. and E.L. Miller, unpublished results.

8 D. Davis and R.C. Wedlich and N.B. Martin, Thermochim. Acta, 175 (1991) 175.

9 C.R. Bennett, D.R.B. Shaw and D. Sutton, J. Hazard, Mater., 4 (1980) 23.

10 D.S. Ross, D.G. Hendry and N.A. Kirshen, Study of the Basic Kinetics of Decomposition of MMH and MHF and the Effects of Impurities on Their Stability, AFRPL-TR-71-114, Stanford Research Institute, Menlo Park, CA, September, 1971.

11 (a) A.K. Galwey, Adv. Catal., 26 (1977) 247.
  (b) A.K. Galwey and M.E. Brown, J. Catal., 60 (1979) 335.
  (c) W.C. Conner, Jr., J. Catal., 78 (1982) 238.
  (d) Z. Adonyi and G. Korosi, Thermochim. Acta, 60 (1983) 23.
  (e) P.K. Gallagher and D.W. Johnson, Jr., Thermochim. Acta, 14 (1976) 255.

12 (a) R.K. Agrawal, J. Thermal Anal., 31 (1986) 73.
  (b) R.R. King, W.G. Hunter and R.A. Grieger, J. Phys. Chem., 80 (1976) 2335, 2341.

13 W. Linert and R.F. Jameson, Chem. Soc. Rev., 18 (1989) 477.

14 M. Grunze, Synthesis and Decomposition of Ammonia in D.A. King and D.P. Woodruff, Eds., The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Elsevier, Amsterdam, 1982, Chapter 5.

15 K. Tamaru, Acc. Chem. Res., 21 (1988) 88.

16 R. Maurel and J.C. Menezo, J. Catal., 51 (1978) 293.