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NON-ISOTHERMAL KINETICS OF HYDRAZINE DECOMPOSITION

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ABSTRACT

Accelerating rate calorimetry has been used to study the kinetics of the titanium thermal decomposition of liquid and vapor hydrazine over the temperature range 475–590 K. In a titanium reaction vessel, hydrazine decomposes exothermically to ammonia, nitrogen and trace amounts of hydrogen. While both liquid and vapor hydrazine are present the reaction has an apparent zero-order activation energy of 98.3 ± 1.7 kJ mol^{-1}. Cessation of the hydrazine liquid–vapor equilibrium is noted as a dislocation of the log (temperature rate) – inverse temperature relationship and an inflection point on the pressure rate profile.

Procedures for the analysis of chemical reaction rate data from the accelerating rate calorimeter and for modeling adiabatic reaction kinetics are presented. Comparison with the experimental results for hydrazine decomposition is made.

INTRODUCTION

The heterogeneously catalyzed decomposition of hydrazine is an exothermic, gas-producing reaction that finds wide application in propellant, gas-generating and emergency power systems [1]. Of major concern in satellite and space probe control thruster systems are the long-term storage stability of hydrazine and the possibility of pressure and thermal hazards resulting from reactions catalyzed by the materials of construction [2]. A wide variety of metals act as catalytic surfaces for hydrazine decomposition [3,4] including Pt [5], Ir [6], W [7], Mo [8], Ni [9], Cr [10] and Fe [11]. Titanium is one of the least catalytically active metals toward hydrazine decomposition. A combination of superior chemical and mechanical properties makes titanium the material of choice for the fabrication of many hydrazine fuel systems in aerospace applications [12].

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The accelerating rate calorimeter (ARC) provides for the measurement of the temperature and pressure increases in an adiabatic system as a result of an exothermic reaction [13–15]. An ARC study of the thermal decomposition of hydrazine in a titanium reaction vessel could provide data for a model of an adiabatic fuel system and allow the estimation of possible thermal and pressure hazards that may be encountered in such fuel systems [16].

In this paper we report the results of an ARC study of the thermal decomposition of hydrazine and procedures for the analysis and modeling of kinetic and thermochemical results derived from ARC data.

EXPERIMENTAL

The ARC (Columbia Scientific Industries, Austin, TX) used in these studies has been described previously [15] and utilized 2.54 cm inner diameter cp titanium reaction vessels (Midland Corrosion, Inc.) having a mass of approximately 8 g (total mass including stainless steel cap nut was approximately 30 g), a volume of 9 ml and an internal surface area of 24 cm^2. The titanium reaction vessels were cleaned with detergent and aqueous sodium hydroxide, then with a mixture of aqueous phosphoric acid and 2-butoxyethanol. A weighed reaction vessel was charged with 0.5 ml of monopropellant grade (MIL-P-26536D) hydrazine (Olin) in a nitrogen-filled glovebag, sealed, and reweighed. Note: hydrazine is acutely toxic and a suspect carcinogen. Hydrazine rapidly absorbs atmospheric moisture and carbon dioxide leading to irreproducible results in ARC experiments. A pressure transducer (0–14.5 MPa) or high pressure valve assembly could be connected to the reaction vessel through stainless steel capillary tubing. In those cases where pressure data or gas handling procedures were not required, the reaction vessel was sealed with a stainless steel nut, ferrule and plug and suspended in the calorimeter.

In a typical procedure, the temperature of the calorimeter was raised quickly to 433 K and then held isothermally for 20 min while searching for a pre-set threshold temperature increase (0.02 K min^{-1}) as evidence of an exothermic reaction. If the minimum temperature rate was not detected, the instrument raised the calorimeter temperature an additional 5 K and repeated the wait–search cycle. Once the threshold temperature rate was detected, the calorimeter heaters were microprocessor controlled to maintain zero temperature difference between the reaction vessel and the calorimeter jacket. Time, temperature and pressure data were collected at 1 K intervals until the temperature rate dropped below the threshold value. Charge masses were adjusted so that the maximum observed heat rates did not exceed 2 K min^{-1}.

The reaction vessel and contents constituted an adiabatic reaction system if no tubing connections were made to assemblies outside the calorimeter. The connection of transducers or valve assemblies by capillary tubing provided an observable reduction in adiabaticity. Conclusions concerning reaction variables in non-adiabatic systems were made by comparison with appropriate controls and supported by modeling results.

At the completion of a test, the reaction assembly was cooled and reweighed to check for leaks. Gaseous reaction products were analyzed by venting to an aqueous HNO_3 solution. Aliquots were then back titrated with aqueous NaOH solution to determine the total base content (ammonia plus hydrazine), and titrated coulometrically [17] to measure hydrazine. Hydrogen and nitrogen products were determined gas chromatographically. The reaction vessels were used for only one ARC run.

RESULTS

The onset temperature for the thermal decomposition of hydrazine in the 9 mL titanium reaction vessels occurred at 468 ± 5 K. The adiabatic decomposition of 0.5 g of hydrazine in the 30 g vessel caused a temperature increase of 115 K and a pressure increase from ambient to 12.5 MPa (at 583 K).

Coulometric analysis of the product mixture indicated complete reaction of the hydrazine and titrimetric analysis showed that 1.28 mol of ammonia were formed for each mole of hydrazine decomposed. Analysis by GC showed the products to be 81.7%, 18.2%, and 0.13% (by volume) ammonia, nitrogen, and hydrogen respectively. For hydrazine decomposition at temperatures up to 585 K the stoichiometry is consistent with

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

This stoichiometry is typical of the low temperature decomposition of hydrazine [16]. For all practical thermochemical and stoichiometric purposes the trace of hydrogen in the product mixture is ignored.

Several distinctive features are apparent when the ARC data are presented in the usual format, a plot of log (temperature rate) against $1/T$ (Fig. 1). A typical plot for hydrazine decomposition is linear from the onset temperature, T_0 (point 0 on Fig. 1) to the start of a step (point G) in the rate near 515 K. The segment G–G′ represents a 20–25% increase in rate over a 1 or 2 K temperature range. A second linear portion from point G′ to H has the same slope as segment O–G. The rate approaches the maximum at point M and then drops sharply to a final temperature, T_f (point F) at the completion of the reaction. The step, G–G′, is an unusual feature observed in hydrazine decomposition experiments and occurs at a lower temperature if the initial charge of hydrazine is less than 0.5 g. Initial charge masses were

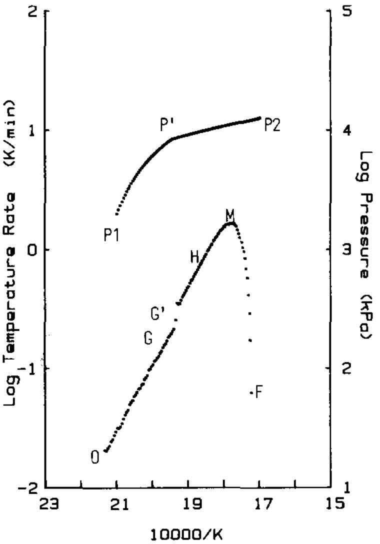

Fig. 1. Experimental ARC results for the titanium-surface-catalyzed decomposition of hydrazine. Segment O–F is the log(temperature rate), left-hand scale. Segment P1–P2 is the log(pressure), right-hand scale.

limited to 0.4–0.6 g of hydrazine since at low charge masses the overall temperature increase was small and an insufficient number of data points were obtained. At higher charge masses either the maximum temperature rate exceeded 2 K min^{-1} or the reaction vessels burst. Burst pressure for the titanium vessel is approximately 40 MPa.

The pressure–temperature profile, shown in Fig. 1 as curve P1–P2, displays an inflection point, P′, at the same temperature as the step G–G′.

The difference between the onset and the final temperatures is related to the amount of hydrazine decomposed and the heat capacity of the reaction system. For a typical adiabatic run with a charge mass of 0.5 g of hydrazine, a system heat capacity of 19 J K^{-1}, and a temperature increase of 115 K, the heat released is calculated to be 140 kJ mol^{-1}. This observed heat is intermediate between the heat of decomposition of gaseous and liquid hydrazine according to eqn. (1).

Using an in-house computer program (described below) the apparent zero-order activation energy for the rate of temperature increase was determined for both the pre- and post-step segments. For five runs, the Arrhenius activation energies were 98.3 ± 1.7 kJ mol^{-1} and 97.5 ± 7.9 kJ mol^{-1} respectively. The average value of the pre-exponential term was 2.4×10^9 K min^{-1} for this experimental system. The program also calculated a system-independent pre-exponential value of 1.6×10^6 mol m^{-2} s^{-1}. Zero-order activation energies calculated by commercially supplied routines [15] were not significantly different from those calculated by our program.

The effects of the reaction products on the rate of hydrazine decomposition were investigated in a series of experiments in which high pressures of nitrogen or ammonia were present in the reaction vessel at the start of the reaction. Temperature rate curves for runs containing an equimolar amount of added ammonia (0.27 g, 6.25 MPa at 475 K) or those with nitrogen pad pressures of 1.75, 2.75 or 4.25 MPa (295 K) were not significantly different from control experiments (0.08 MPa nitrogen, no ammonia).

DISCUSSION

Accelerating rate calorimeter (ARC) data analysis

The basic equation which describes the temperature rate seen in an adiabatic kinetic experiment is

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\mathrm{d}n(T, n_i)}{\mathrm{d}t}\,\frac{Q(T)}{C_\mathrm{s}(T, n_\mathrm{i})} \tag{2}$$

where $\mathrm{d}T/\mathrm{d}t$ (K min^{-1}) is the temperature rate of the system, $\mathrm{d}n/\mathrm{d}t$ (mol min^{-1}) is the rate of reactant disappearance, Q (J mol^{-1}) is the reaction heat released and C_s (J K^{-1}) is the system heat capacity. All of the terms in eqn. (2) are functions of temperature. The system heat capacity, C_s, and the instantaneous rate, $\mathrm{d}n/\mathrm{d}t$, are also functions of the chemical composition, n_i.

For a reaction in which the reactants and products are well characterized and the thermodynamic properties of the reactants and major products are known, the terms in eqn. (2) can be calculated as a function of temperature. In the case of a reactant which is not totally volatilized at the onset temperature, the heat of vaporization must be included.

ARC kinetic data for the hydrazine decomposition were analyzed by a computer program which used literature correlations to calculate the vapor pressure, heat of vaporization, vapor concentration of hydrazine, the heat of reaction and the heat capacities of the components as a function of temperature [1,18–20]. Only physicochemical relations and experimental data are employed. No adjustable parameters are included. Starting at the onset temperature, T_1, and initial charge mass, the program uses the vapor pressure and molar volume of hydrazine to determine the amounts of liquid and vapor hydrazine, and the resulting C_s. Using this heat capacity, the reaction heat necessary to raise the reaction vessel to the next observed temperature, T_2, is calculated. Assuming that the heat released is given by $-\Delta H$ at T_1 for the equation

$$N_2H_4(l) \rightarrow \tfrac{1}{3}N_2(g) + \tfrac{4}{3}NH_3(g) \tag{3}$$

$$\Delta H = -123.3\ \mathrm{kJ\ mol^{-1}}(515\ \mathrm{K})$$

or, if no liquid remains,

$$N_2H_4(g) \rightarrow \tfrac{1}{3}N_2(g) + \tfrac{4}{3}NH_3(g) \qquad (4)$$

$\Delta H = -154.8$ kJ mol^{-1}(515 K)

the incremental molar amount of hydrazine decomposed over the temperature span from T_1 to T_2 is reckoned. This amount of hydrazine divided by the time difference between T_1 and T_2 gives the average chemical reaction rate (mol s^{-1}) over the temperature interval. The reaction vessel composition is then adjusted according to the reaction stoichiometry and all terms are recalculated. This procedure is repeated at each temperature data point (generally 90–125 points for a 115 K temperature difference), and an accounting of the remaining reactant hydrazine is made.

Analysis of more than 40 experiments shows that this stepwise procedure accounts for $100 \pm 5\%$ of the initially charged hydrazine as judged by comparison of the calculated and observed temperatures at 100% reaction. The step in the temperature rate curve corresponds to the temperature at which the total volume of all the remaining hydrazine, as vapor at that pressure and temperature, just equals the volume of the reaction vessel in use. At this point the vapor–liquid equilibrium can no longer be maintained and a change in the heat of reaction occurs as the heat of vaporization of liquid hydrazine (31.5 kJ mol^{-1} at 515 K) no longer makes an endothermic contribution to the overall heat (Eqns. (3) and (4)).

Similarly, the inflection point p′ in the pressure profile occurs at the temperature at which the pressure rate decelerates as hydrazine vapor is not replenished from the liquid phase. The observed step temperature and the calculated temperature of liquid disappearance generally agree within ±2 K.

The net result of these calculations is to convert the experimentally observed temperature rates, $\mathrm{d}T/\mathrm{d}t$, to system-independent chemical reaction rates, $\mathrm{d}n/\mathrm{d}t$, as a function of temperature.

The general rate law for the reaction using the Arrhenius relationship to represent the temperature dependence for the rate constant can be written

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = A\exp(-E_a/RT)[C_a^{\alpha}C_b^{\beta}\ldots]^m \qquad (5)$$

where $[C_a^{\alpha}C_b^{\beta}\ldots]$ is the composition dependence of the reaction, m is the order, A is the Arrhenius pre-exponential term and E_a is the activation energy. The composition term is mechanism dependent and not known a priori. The computerized computational method can calculate a number of different composition functions involving terms which it tracks, such as reactant and product pressures, concentrations and the fraction of reactant remaining. Using eqn. (5), activation parameters can be derived for assumed composition functions as shown in Table 1.

The standard deviations of the E_a values for all the calculations shown in Table 1 are 0.5–0.8 kJ mol^{-1}. Goodness of fit is not a viable criterion for selecting a most probable rate law.

TABLE 1

Activation parameters for the decomposition of hydrazine with assumed composition functions and orders

Order m	Function	E_a (kJ mol^{-1})	A
Temperature range 470–507 K (pre-step, run 249)			
0	–	103	6.11×10^9 K min^{-1}
0	–	101	3.84×10^6 mol s^{-1} m^{-2}
1	Pressure [a]	60	7.44×10 mol s^{-1} m^{-2} atm^{-1}
1	Fraction [b]	125	1.93×10^9 mol s^{-1} m^{-2}
1	Θ [c]	101	3.84×10^6 mol s^{-1} m^{-2}
Temperature range 523–548 K (post-step, run 249)			
0	–	103	7.52×10^9 K min^{-1}
0	–	103	7.04×10^6 mol s^{-1} m^{-2}
1	Pressure [a]	134	2.36×10^8 mol s^{-1} m^{-2} atm^{-1}
1	Fraction [b]	149	5.28×10^{11} mol s^{-1} m^{-2}
1	Θ [c]	105	1.08×10^7 mol s^{-1} m^{-2}

[a] Pressure (atm) of hydrazine.

[b] Fraction of hydrazine remaining.

[c] Fractional surface coverage (Langmuir function, eqn. (7)).

Accelerating rate calorimeter kinetic modeling

The data analysis algorithm can also be used to model an ARC kinetic run. With the input of an activation energy, pre-exponential term, assumed composition function and a reactant charge mass, model temperature rate vs. $1/T$ plot (Figs. 2–5) can be generated for comparison with the experimental profile shown in Fig. 1.

A reasonable test of proposed models for the hydrazine decomposition is the ability to reproduce the overall shape of the ARC temperature rate profiles as shown in Figs. 2–5. The maximum in rate near the end of the reaction arises because the rate effect of decreasing reactant concentration becomes more important than the rate increase due to the increased temperature. The composition dependence for hydrazine decomposition cannot be zero order over the entire range since no local maximum rate is observed for a zero-order reaction (Fig. 2). For a composition function which is first order in reactant pressure (Fig. 3), the deceleration in rate begins immediately after the step temperature and is a slowly changing function. Assumption of rate law which is first order in the fraction of remaining reactant, including that present in both the liquid and the vapor phases, gives a rate profile similar to the experimental if activation parameters derived from the pre-step portion of the reaction are used (Fig. 4). These and more extensive modeling results suggest that a composition function which is relatively unchanging for most of the reaction and then decreases

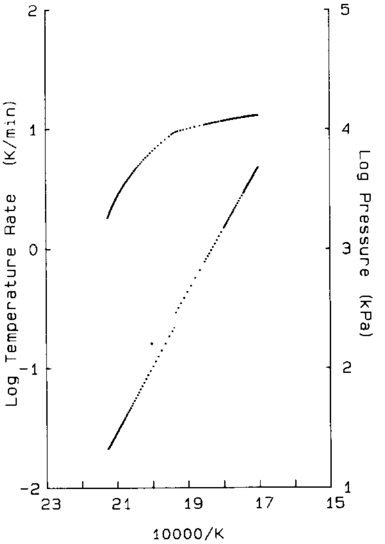

Fig. 2. Modeled ARC results for the titanium-surface-catalyzed decomposition of hydrazine. Rate law is assumed zero order with pre-step activation parameters taken from Table 1.

rapidly as the reactant pressure drops is required to describe the rapid deceleration near the end of the reaction. It has been found that reaction rates (at a fixed temperature) are linearly dependent on the surface areas of

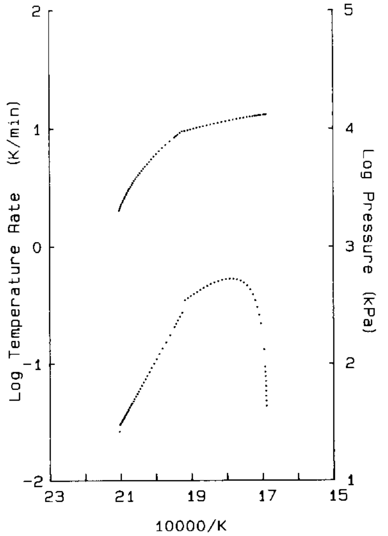

Fig. 3. Modeled ARC results for the titanium-surface-catalyzed decomposition of hydrazine. Rate law is assumed first order in hydrazine pressure with pre-step activation parameters taken from Table 1.

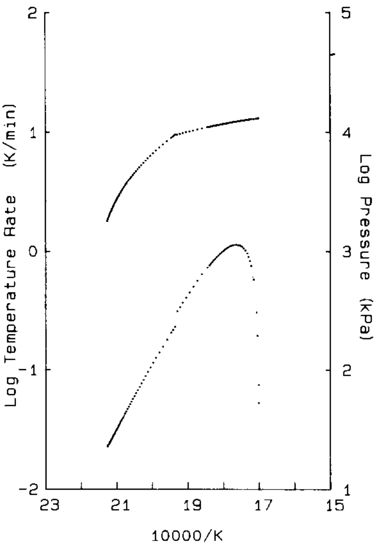

Fig. 4. Modeled ARC results for the titanium-surface-catalyzed decomposition of hydrazine. Rate law is assumed first-order in fraction remaining hydrazine with pre-step activation parameters taken from Table 1.

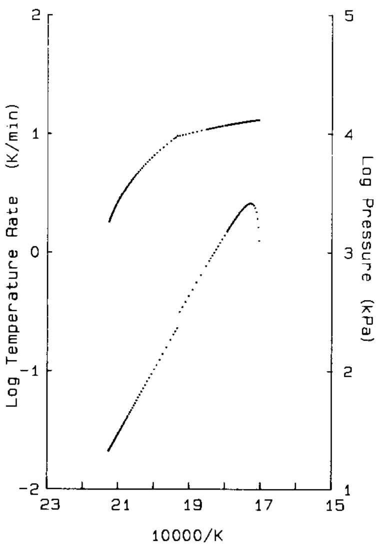

Fig. 5. Modeled ARC results for the titanium-surface-catalyzed decomposition of hydrazine. Rate law is assumed first order in hydrazine surface coverage as calculated by eqn. (7). Pre-step activation parameters are taken from Table 1.

added catalysts [21]. If the rate is related to surface area then the following equation applies:

$$-\frac{dn}{dt} = k\Theta\, SA \qquad (6)$$

where Θ is the fraction of surface area covered by reactant and SA is the total surface area of the catalyst.

At the high pressures of hydrazine involved for most of the reaction, either complete monolayer ($\Theta = 1$) or multilayer surface coverage is expected [9] and the observed rate would show zero-order characteristics. During the last few per cent of the reaction, depletion of the reactant becomes important and the surface coverage by hydrazine decreases. The combined effects of an increasing k (with temperature) and a decreasing surface coverage (with reactant pressure) result in a local maximum in rate.

A Langmuir adsorption term with a temperature-dependent K has been used to model the rate maximum [22]

$$\Theta = bP/(1 + bP) \tag{7}$$

where Θ is the fraction of surface covered by hydrazine, b the hydrazine adsorption factor and P the hydrazine pressure, and b has the general form

$$b = B_0 \exp(Q_a/RT) \tag{8}$$

where Q_a is the heat of adsorption and B_0 is the adsorption pre-exponential.

Modeling runs have shown that this approach accounts for the rate maximum and gives a good fit to the observed curve (Fig. 5). The introduction of two additional parameters should improve the fit. Further work toward an exact fit has not been attempted.

A more stringent test of an assumed model is a linear Arrhenius plot for the rate constants calculated from the experimental data (with the assumed rate law and thermochemical parameters) over the entire experimental temperature range. If the bivalued nature of the reaction heat, Q, and the composition function are appropriately modeled then the Arrhenius plot of the rate constants derived from the experimental temperature rate profile should show no effect of the cessation of liquid–vapor equilibrium or the deceleration of rate near the end of the reaction. As Fig. 6 shows, a zero-order model satisfactorily accounts for the step temperature and shows collinearity over the pre-step and post-step parts of the reaction. Since the rate maximum and final temperature are strongly dependent on an exact match between the computed and actual composition, near the end of the reaction a discrepancy of 1–5% in composition, which is acceptable for a reasonable thermochemical balance, is too large an error to allow the assumed model in its current form to reproduce accurately the reactant pressures or concentrations.

Comparison with the approach of Townsend and Tou [13]

If the physical and thermochemical properties of the reactants and products are well characterized, the rate of temperature increase can be interpreted in terms of chemical reaction rates. Many systems, however, are

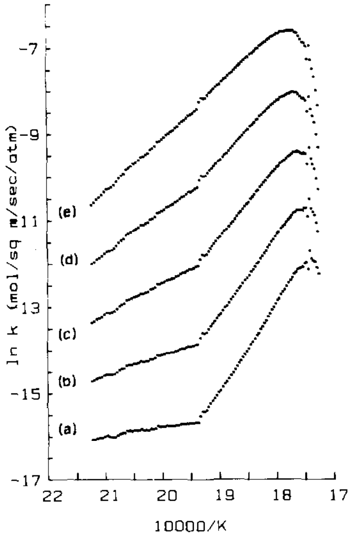

Fig. 6. Arrhenius relationships for rate constants calculated with assumed orders in hydrazine pressure: (a) second order; (b) three-halves order; (c) first order; (d) half order; (e) zero order.

not fully characterized and the approximate kinetic analysis of Townsend and Tou [13] is convenient. In this approach both the system heat capacity and heat of reaction are assumed to be constant over the temperature range of the experiment. Eliminating time as a variable from eqn. (2) gives

$$n_1 - n_2 = (C_s/Q)\,|_{T_2} T_2 - (C_s/Q)\,|_{T_1} T_1 \tag{9}$$

where n_1 is the number of moles of reactant at T_1, n_2 is the number of moles of reactant at T_2 and $(C_s/Q)\,|_T$ is C_s/Q evaluated at T. Expressed in terms of the average value of C_s/Q

$$(C_s/Q)\,|_{T_1} = (C_s/Q)_{\text{ave}} - \delta \tag{10}$$

and

$$(C_s/Q)\,|_{T_2} = (C_s/Q)_{\text{ave}} + \delta \tag{11}$$

where δ is the absolute value of the deviation of $(C_s/Q)\,|_T$ from the mean value $(C_s/Q)_{\text{ave}}$ over the temperature span T_1, T_2. Then

$$n_1 - n_2 = (C_s/Q)_{\text{ave}}(T_2 - T_1) + \delta(T_2 + T_1) \tag{12}$$

If C_s/Q is constant then $\delta = 0$ and the Townsend and Tou approximation is valid. However, in a system which involves phase changes for polar liquids such as hydrazine, the heat capacities of the liquid and vapor reactant and gaseous products can be appreciably different. In our system, over the temperature range 478–513 K with liquid hydrazine present, $(C_s/Q)_{\text{ave}}$ has the value 1.52×10^{-4} mol K^{-1} and $\delta = 4 \times 10^{-6}$ mol K^{-1}. Ignoring the second term in eqn. (12) then leads to a 75% error in the amount of hydrazine decomposed. Over the range 533–573 K with only vapor present, the value of δ is 1×10^{-6} mol K^{-1} and the error caused by assuming a constant C_s/Q ratio is 15%. This error appears as a discrepancy between the observed temperature change, $T_f - T_o$, and the expected adiabatic temperature change.

The C_s/Q ratio is also temperature dependent and the apparent activation energy derived from an Arrhenius plot of the temperature rate (dT/dt) includes this dependence. For the hydrazine decomposition this correction is on the order of 5 kJ mol^{-1}. This is of the same magnitude as the deviations between duplicate runs.

The assumption of a constant C_s/Q ratio over a range of temperatures is expected to present the greatest error in those reactions involving a neat liquid or solid converting to gaseous products. In solution reactions, the solvent heat capacity may effectively dampen changes in C_s/Q.

CONCLUSIONS

The results of an ARC study of the titanium-surface-catalyzed decomposition of liquid hydrazine have been treated by a computerized procedure for analysis and modeling of ARC data. For most of the reaction, the decomposition of hydrazine to nitrogen and ammonia can be described by zero-order kinetics. A step increase in the temperature rate curve is caused by an increase in the exothermicity at the cessation of the liquid–vapor equilibrium. A local maximum in the rate is suggested to be the result of decreased surface coverage due to decreased hydrazine reactant pressure and a change in the apparent zero-order kinetics.

Computer modeling experiments support these conclusions and provide a convenient means of investigating the effects of reaction variables.

The analysis and modeling techniques are general and can be extended to other reactions provided that the stoichiometry and thermodynamic properties of the reaction system are well characterized.

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