

Modeling of adiabatic decomposition of ammonium nitrate under pressure using BatchCAD

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Accelerating Rate Calorimeter (ARC) has been employed to study the decomposition of ammonium nitrate under 0.1 – 3 MPa helium pressure. GC and MS analysis of the gaseous products indicated that the decomposition proceeds by the same mechanistic pathway up to 3 MPa applied pressure. Kinetic fitting of the ARC data have been done using BatchCAD package. There is a good agreement between the model predicted and experimental values. For the first time, independent Arrhenius parameters for two parallel reactions for AN decomposition are reported. The reaction mechanism for decomposition, the temperature range, and the E_a and A values are given in the paper and the results are discussed. The present study is the first report on the kinetic modeling of adiabatic decomposition data using BatchCAD (BC) as well as AN adiabatic decomposition under pressure.

1. INTRODUCTION

Ammonium nitrate (abbreviated as AN, hereafter) is produced in bulk (global production capacity¹⁾ is 82.58 million tons in 1997 of which 33.45 million tons are used as fertilizer) and finds wide spread application as a fertilizer, explosive, refrigerant, energetic oxidizer, halogen free propellant, gas generating agent, despite its high hygroscopicity, solid-state phase transition characteristics, low energy, low reactivity. The explosive potential of AN is well known from its involvement in many major accidents: from the Texas city (1947) incident to the recent one at the

Toulouse²⁾ (France) during September 2001, in which 29 fatalities, more than 4500 injuries and devastation of ten thousand homes rendering 1,400 families homeless. All these incidents prove beyond a doubt that AN can be used as a detonating and explosive agent. However, such an explosive behavior during storage, processing, and transportation will lead to the devastation of plant, property, and personnel.

During the past five decades considerable effort has been made to study the decomposition of AN³⁾. Estimation of reliable kinetics is important to assess the thermal stability and design emergency relief systems. Such estimates are primarily concerned with the temperature dependence of the reaction rate. The temperature sensitivity of the reaction rate is predominantly determined by the activation energy. Therefore, reliable estimation of this parameter is essential to predict the true hazard potential. The present study is aimed towards this goal. The present investigation is the first detailed study not only on the AN adiabatic decomposition but also the kinetic modeling of the ARC data using BatchCAD (abbreviated as BC, hereafter).

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2. SALIENT FEATURES OF THE LITERATURE STUDIES

- AN thermal decomposition kinetics and reaction mechanism has been dealt^{3,14)} for more than five decades, still lot of ambiguities exist due to complex nature of the process.
- It is generally agreed that the first step prior to the exothermic decomposition is the endothermic dissociation of AN to ammonia and nitric acid.
- While the major products of decomposition is Nitrous oxide and water, there appears to be a divided opinion^{9,10)} on the pathways of the formation of these products
- The decomposition process is ionic at temperatures below 290 °C and above this temperature it shifts towards radical mechanism¹⁰⁾.
- The heat released during the decomposition process is due to the intensive exothermic reaction between ammonia and NO₂.
- Under high pressure conditions, ammonia, HNO₃ as well as the products of decomposed HNO₃ react closer to the surface, thereby the decomposition process is enhanced, yielding N₂O and H₂O as the predominant products⁹⁾.
- Fluctuations in the heat balance occurs at different times and temperatures from the onset of melting of AN to the end of gasification⁸⁾.
- The decomposition reactions are numerous and intertwined, further complicated by insidious secondary reactions¹³⁾.
- Reported activation energies vary quite significantly³⁾, most of them representing only the endothermic gasification process of AN rather than the true decomposition of AN (i.e. leading to the generation of nitrous oxide and water as the major decomposition products).

3. Experimental

3.1 ARC Experiments

The ARC (Accelerating Rate Calorimeter) used in this study was ARC 1000 supplied by CSI of Austin, USA. The working principle and diagrams of the ARC are well cited in the literature^{15,16)}. All the ARC measurements were made using hastalloy bomb. The instrument was switched to step mode

at the initial temperature of 180 °C and a wait time of 15 minutes was set prior to entering in search mode. AN (99 %) was obtained from Kishida chemicals, Japan and used without further purification. Since AN is highly hygroscopic, about 1 g of sample was loaded each time in dry box under flowing helium gas. Similarly, the sample bomb was connected to ARC under the flow of helium to avoid the absorption of moisture by AN. ARC was opened forcibly and the sample bomb was quenched with dry ice and methanol to arrest any further self-heating at 10-20 °C intervals from the onset point to collect samples for GC and MS analysis.

3.2 GAS Chromatographic and Mass Spectral Analysis

GC analysis of the gas samples of AN adiabatic decomposition collected from ARC runs at 10 – 20 °C intervals from 210 – 260 °C, were performed using Shimadzu Gas chromatographic analyzer, model GC-14 A, fitted with an SS column packed with molecular sieves. The initial column, injector, and detector temperatures were set to 60, 80 and 80 °C respectively. The column temperature was raised from 60 to 120 °C at a heating rate of 30 K/min, after a hold up period of 14 minutes at 60 °C. 1 ml of gas sample was injected using gas injection syringe. Similarly the water extract of the residue was analyzed using the quadra pole mass spectrometer supplied by Shimadzu, model GC-MS QP-1000 A by direct injection. The identities of the species were made by matching the mass spectra with that of the standard spectrum available in the MS library.

3.3 Kinetic Analysis of AN Decomposition using BatchCAD (BC)

BatchCAD is a software developed by BatchCAD Ltd., a subsidiary of GSE Systems UK Ltd. BC for windows version of 7.2 has been used for kinetic fitting of AN's ARC data. In the kinetic fitting environment, the model is the set of differential and algebraic equations (mass and energy balances) representing the process chemistry under the conditions of measurement of the data. A fourth order Runge-Kutta integrator with a fixed step size and simplex algorithm fitting method has been

Table 1 Summary of thermokinetic data of ammonium nitrate

Expt No	weight, g	He Pressure, MPa	Φ	T_0 , °C	ΔH_r kcal/mol	Reaction 1		Reaction 2	
						Ea kJ/mol	A min ⁻¹	Ea kJ/mol	A min ⁻¹
1	0.992	0.1	5.597	210.63	40.66	284.5	6.249×10^{25}	37.34	0.111
2	1.0025	0.5	5.5464	210.47	41.63	284.9	6.604×10^{25}	35.61	0.0834
3	1.0026	1.0	5.6369	210.67	44.39	284.5	6.249×10^{25}	36.93	0.1238
4*	0.999	1.5	5.6564	205.41	41.84	283.8	6.260×10^{25}	36.60	0.1217
5*	0.9975	2.0	5.6625	210.49	40.77	284.5	6.249×10^{25}	37.32	0.1200
6*	1.0015	3.0	5.6489	210.58	38.48	284.5	6.249×10^{25}	33.88	0.0827

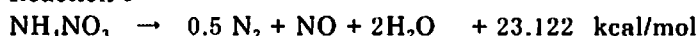
* Reaction terminated at 2500 psi pressure

Reaction 2**



$$A = 6.2 \pm 0.4 \times 10^{25} \text{ min}^{-1}, \quad E_a = 285 \text{ kJ/mol}$$

Reaction 3**



$$A = 0.12 \pm 0.04 \text{ min}^{-1}, \quad E_a = 36.28 \text{ kJ/mol}$$

**Heat of Reaction calculated using CHETAH¹⁷⁾

used to solve the model equations. Heat of reaction (ΔH_r) and thermal inertia factor (Φ) from the ARC data have been calculated using the conventional equations well cited in the literature¹⁵⁾. Kinetic fitting using BC yields a superior and reliable data over several curve-fitting methods, as the former method represents the physical phenomena and underlying chemical processes together while matching the experimental data.

4. RESULTS AND DISCUSSION

4.1 ARC Studies of AN Decomposition

The time, temperature pressure and self heat rate profiles of AN decomposition under various applied He pressures are given in Figs. 1-2 and the results are summarized in Table 1. It can be seen from Fig. 1 that the self heating decomposition process of AN onsets generally at 210 °C irrespective of the applied pressure and ends around 320 – 330 °C. Up to 1 MPa applied pressure the final temperature of the decomposition process varied between 324 – 333 °C due to slight changes in the initial weight of AN. In case of experiments above 1 MPa applied pressures, the ARC is terminated as soon as the pressure rise exceeds the set limits of maximum observable pressure rise of 2500 psi (17.0068 MPa). The maximum

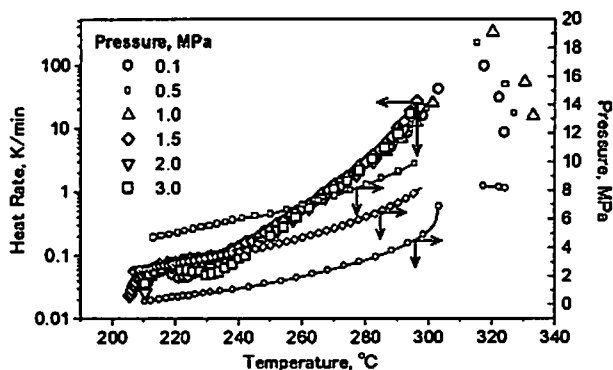


Fig. 1 Self heat rate and pressure rise plot for AN decomposition under various He pressure (1673K for 2h).

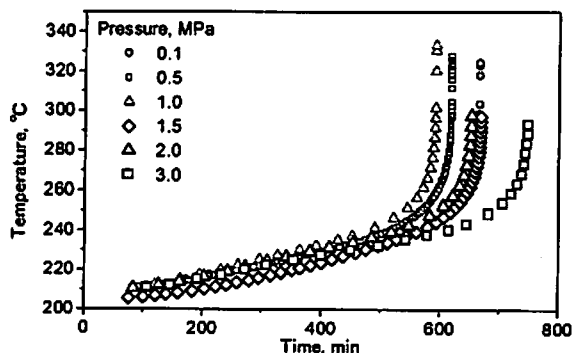


Fig. 2 Adiabatic temperature rise plot for AN under various He pressure

observable pressure limit is set to protect the equipment from rupture of the sample bomb. The

trends of heat rate, pressure, (Fig. 1) and temperature (Fig. 2) remain the same, for experiments done up to 3 MPa applied pressure. This clearly indicates that there is no change in the decomposition pattern of AN up to 3 MPa applied pressure. The discontinuity recorded in the heat rates curves beyond 300 °C indicates the explosive behavior of AN (Fig. 1). In Fig. 1, the decrease in heat rates after the onset, before its steady raise again indicates that the decomposition process proceeds via multiple pathways of simultaneous exothermic and endothermic processes. Earlier workers^{11),16)} have reported similar observation while studying the thermolysis of AN. The authors^{11),16)} also observed (as also seen in the Fig. 1 between 210 to 225 °C) that at temperatures near 200 °C the rates were capricious and fluctuations in the heat balance occurred. They have attributed to the variation of highly influential acidity to the process. The ARC data thus clearly indicates the vigor and vulnerability of AN to undergo thermal decomposition above its melting point(169.5 °C).

4.2 GC and Mass Spectral Analysis of the Decomposition Products of AN

The gas-chromatographic analysis data of the gaseous products of the decomposition of AN collected by quenching the ARC bomb at different temperatures under 0.1 and 1.0 MPa applied pressures are given in Figs. 3 and 4. At all decomposition temperatures and applied pressures the observed gaseous decomposition products were N₂, NH₃, N₂O, NO, and NO₂. Among these products, N₂ and N₂O were predominant while negligible quantities of NO and NO₂ have been observed. MS analysis of the residue extracted with water indicated the presence of ammonia and HNO₃, which may be due to the ammonium nitrate aerosol. We could not estimate the concentration of water as we extracted the residue with water. However we could achieve a mass balance greater than 90 % from the quantitative analysis of different products.

The presence of N₂O as the major decomposition gaseous products suggests that the main decomposition reaction under our conditions of

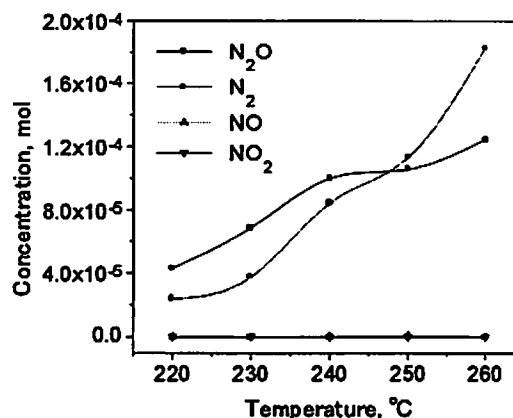


Fig. 3 Decomposition products of AN under 0.1 MPa He pressure

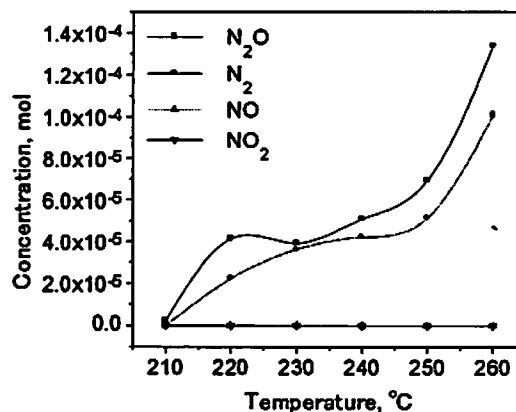


Fig. 4 Decomposition products of AN under 1.0 MPa He pressure

study is the universally accepted decomposition reaction 2. It has also been reported that N₂ is produced at all stages of AN decomposition by different pathways (reaction 3-5). Negligible quantities of NO and NO₂ recorded clearly indicates that they were further involved in oxidation of ammonia i.e., accelerating the principal decomposition reaction as noted by earlier workers from their *in-situ* studies and immediate analysis using FTIR spectroscopy¹¹⁾¹³⁾. In Figures 3 and 4, the curves going through every plotted point in each series indicates that every inflection has its inherent meaning. However discussion/reasoning for each inflection point was not possible due to complexity of the decomposition process.

5. KINETIC MODELING USING BC

5.1 Scenario of AN Thermal Decomposition under Adiabatic Conditions

The scenario of thermal decomposition of AN

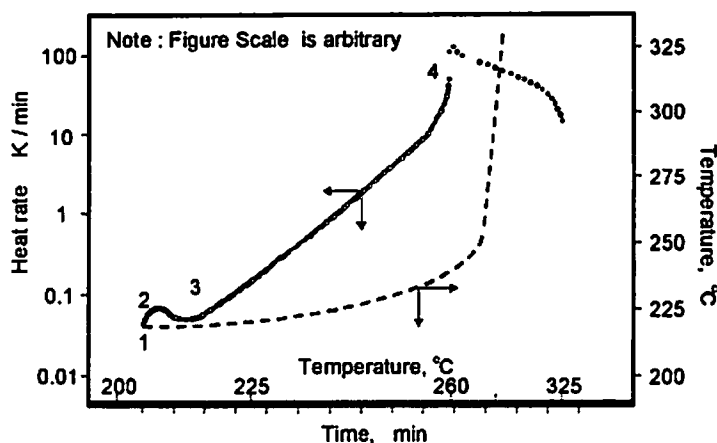
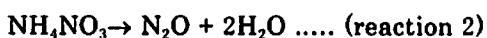


Fig. 5 Scenario of thermal decomposition of AN under adiabatic conditions

under adiabatic condition is given in Fig. 5. From the GC and MS data, as well as from the reported information, the decomposition of AN under our experimental conditions is thought to proceed via four distinct zones, the first zone is the endothermic dissociation into ammonia and nitric acid i.e. gasification reaction zone.

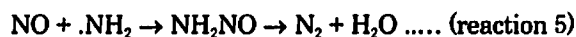
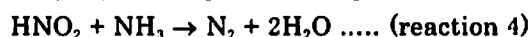
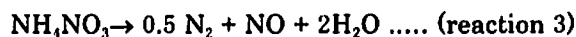


It is assumed that further reactions take place both in the gas phase and in the melt. Initiation Reaction Zone 2: Under this reaction zone 2, the acid in the melt initiates the principle exothermic decomposition of AN (Reaction 2). However, the fall in the initial heat rates are due to simultaneous occurrence of exothermic and endothermic reaction, at one point of time i.e., around 215 °C, the endothermicity dominates and pulls down the rate of the ongoing principle exothermic reaction. The endothermic reaction could be any one of the following a). Gasification of AN, b). Decomposition of nitric acid to produce NO_2 ($\text{HNO}_3 \rightarrow 2\text{NO}_2 + \text{H}_2\text{O} + 0.5 \text{O}_2$). As the temperature rises, the principle exothermic decomposition reaction is accelerated (exothermic acceleration reaction zone), by the generation of NO_2 from the decomposition of HNO_3 . NO_2 reacts with NH_3 to produce the decomposition products N_2O and water, and this dominates up to the reaction zone 3.



At and above reaction zone 3, the reaction occurs predominantly in the gas phase, as all ammonium

nitrate would have gasified. During the reaction zone 4, thermal explosion occurs (explosive reaction zone) as is evidenced from the sudden and sharp rise in heat rate, pressure and temperature. During the reaction zone 2 – 4 nitrogen is produced continuously from reaction 3 and other side reactions, which may be either ionic or radical as observed by earlier workers^{10,11}.



The heat liberation during AN decomposition is predominantly due to the occurrence of reaction 2 and 3. This is further confirmed as can be seen from the Table 1, that there is an excellent agreement between the heat of reaction values calculated using CHETAH¹⁷ and ARC data.

5.2 BatchCAD Fitting

The ARC data of AN decomposition under 0.1 – 3 MPa applied He pressure have been subjected to kinetic modeling using BC. Reaction 2 and 3 have been considered as the major reactions contributing to the heat liberation during adiabatic decomposition of AN according to the scenario presented above. Kinetic fitting have been done using the heat of reaction values obtained from ARC data. Since the reactions 3 and 4 proceed simultaneously, it is difficult to determine the ratio of their heat contribution. Therefore, we adopted trial and error method and found that a 60:40 ratio

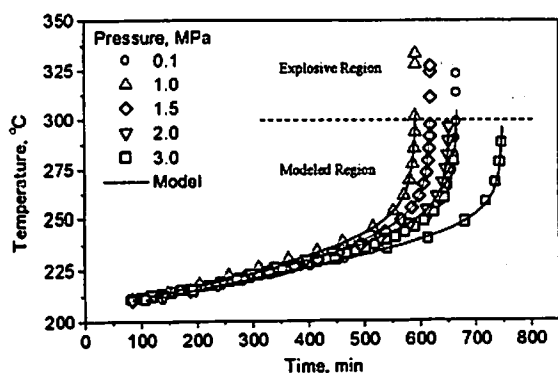


Fig. 6 Kinetic modeling of AN decomposition: comparison of modeled and experimental adiabatic temperature rise

of the total heat for the reactions 2 and 3 gave the best fit. A first order rate expression with respect to AN was necessary to obtain an acceptable match over the entire region of the adiabatic temperature rise curve. The results are presented in Fig. 6. The data could be fitted nicely up to 300 °C, i.e. up to the discontinuity explosive region of adiabatic temperature rise with a consistent Arrhenius parameters for both the reactions. The Arrhenius parameters are listed in Table 1. Thus it is for the first time, Arrhenius parameters involving two parallel reactions for AN decomposition have been reported rather than a lumped-up value.

Validation of the AN kinetic fitting have been done by calculating heat rates (i.e., the first order derivative of the adiabatic temperature rise) from the fitted data of adiabatic temperature rise and matching with the experimentally determined heat rate curve. The results are presented in Fig. 7.

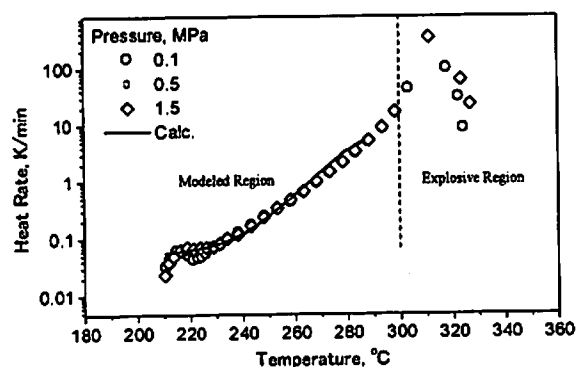
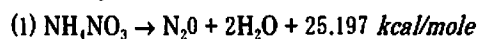


Fig. 7 Kinetic modeling of AN decomposition: comparison of calculated and experimental heat rates

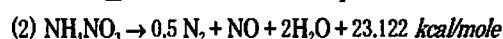
The deviation in the initial portion of the heat rate curve in the temperature range of 210-225 °C, though not very clear, could be attributed to the complex competitive behavior i.e., to the occurrence of competitive exothermic and endothermic processes. The falling rate is due to the dominance of the endothermic processes over the exothermic process (listed in the previous section) during this temperature range. The fitting in Fig. 6 is better than that in Fig. 7, as the curves in Fig. 7 are the first order derivative curves of Fig. 6, in which the small variations are enhanced and seen clearly, and so in this case the fitting appears poor but approximately equivalent. Kinetic fitting using BC thus adequately explains the adiabatic AN decomposition scenario presented in this investigation.

6. Conclusions

AN undergoes self-heating decomposition under adiabatic conditions. The studies have led to the conclusion that during the initial stages i.e. around 210-225 °C, endothermic and exothermic reactions occur simultaneously. The adiabatic temperature rise during AN decomposition is due to the two predominant parallel reactions yielding N_2O , H_2O and N_2 as the major decomposition products. The process becomes explosive nature beyond 300 °C, which accompanies large heat rates and pressure rise. Up to 3 MPa applied He pressure, the decomposition proceeds by the same mechanistic pathway. With the built-up reaction scenario, kinetic modeling could be done to a reasonable accuracy of consistent values. Thus for the first time, independent values of Arrhenius parameters involving two parallel reactions for AN has been reported, rather than a lumped up value. The heat liberated during AN adiabatic decomposition can be described by the following reaction schemes and kinetic expressions.



$$K = 6.2 \pm 0.4 \times 10^{25} \text{ min}^{-1} \exp(-285 \text{ kJ/mol})/RT$$



$$K = 0.12 \pm 0.04 \text{ min}^{-1} \exp(-36.28 \text{ kJ/mol})/RT$$

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