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Thermal stability of ammonium dinitramide

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Abstract

The low temperature thermal stability of ammonium dinitramide (ADN) and efforts to improve the thermal stability are presented. The decomposition rates of ADN at 60, 70, 80, and 90 °C were investigated. Several potential thermal stabilizers were investigated to suppress the low temperature decomposition (60–90 °C) of ADN. The potential stabilizers investigated were potassium fluoride, potassium dinitramide, a 6-member ring or polymeric phosphorous compound $[P(C_6H_5)]_{6,polymer}$, and perhydro-1,3,5-triazine-2,4,6-trione, commonly known as Verkade's super base (VC). Comparison of the decomposition of pure ADN and 1–2% by mass mixtures of ADN and the potential stabilizers are presented. Finally, the low temperature stabilizers are compared to hexamethylene tetramine (commonly known as urotropine or hexamine). Verkade's super base is found to be most effective.

Keywords: Ammonium dinitramide (AD); Verkade's super base (VC); Hexamethylene tetramine

1. Introduction

In the late 1960s, Hamel and Olson [1] synthesized the first dinitramide structures. These materials were covalently bonded alkyl *N*,*N*-dinitramides. The resulting dinitramides were unstable and decomposed at 75 °C or less, making them unsuitable as propellant ingredients. Recently a new class of inorganic oxidizers have been synthesized [2–10]. This class of oxidizer incorporates the newly discovered dinitramidate $[N(NO_2)_2^-]$ anion. The dinitramidic acid and its salts are thermally more stable than the original alkyl *N*,*N*-dinitramides discovered in the late 1960s.

One promising oxidizer from this class of compounds is ammonium dinitramide (ADN), $N_4O_4H_4$, which has the structural formula $NH_4N(NO_2)_2$. ADN, like ammonium nitrate (AN), undergoes residueless combustion. However, it burns more readily and predictably than AN. Therefore, it is much more attractive to use ADN as an ingredient in propellants than AN. Several solid propellant formulations of ADN in various binder systems have recently been accomplished [11,12]. Although, it is well known that dinitramides are energetic compounds, the thermal decomposition of dinitramides has not been studied extensively.

1.1. Thermal decomposition of ADN

Typical products detected during ADN decomposition are nitric acid, ammonia, nitrous oxide, nitric oxide, and water. Two distinct temperature regimes have been identified for ADN decomposition. Between 55 and 100 °C, ADN decomposes slowly, forming nitrous oxide N_2O and ammonium nitrate NH_4NO_3, AN. AN is produced from the recombination of

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ammonia, NH_3 and HNO_3, which is subsequently produced during dinitramidic acid, HN_3O_4, (HDN) decomposition. This reaction process is shown in reactions (1)–(4).

$$NH_4N(NO_2)_2 \rightarrow (NH_3 + H_3N(NO_2)_2)_{absorbed} \quad (1)$$

$$(NH_3 + H_3N(NO_2)_2)_{absorbed} \Leftrightarrow NH_{3(g)} + H_3N(NO_2)_{2(g)} \quad (2)$$

$$(HN(NO_2)_2)_{absorbed} \rightarrow N_2O_{(g)} + HNO_{3(g)} \quad (3)$$

$$HNO_{3(g)} + NH_{3(g)} \rightarrow NH_4NO_{3(s)} \quad (4)$$

ADN decomposes rapidly when $NO_{2(g)}$ is detected. During high heating rate and high temperature decomposition studies (above 110 °C), reaction (5) is the favored mechanism representing the early chemistry of the combustion of ADN.

$$HN(NO_2)_2)_{absorbed} \rightarrow NO_{2(g)} + HNNO_2 \quad (5)$$

In the combustion regime, a complex reaction scheme is suggested. In order to explain the overall approximate stoichiometry of the product gases, a 14-step reaction sequence has been proposed by Brill et al. [13] (The thermodynamic parameters of many of the steps are still unknown).

1.2. ADN stabilization studies

The stabilization of ADN has also been a recent topic of much interest. If the initial step in ADN decomposition is the transfer of a proton to form the freebase and dinitramidic acid, ADN decomposition will be stabilized with the addition of a Lewis base. Further ADN decomposition is autocatalyzed by build up of HNO_3 through the re-arrangement shown in reaction (3). Therefore, a good base stabilizer for ADN low temperature decomposition would be a strong Lewis base, which would scavenge both dinitramidic acid and nitric acid upon formation. This fundamental base stabilization has been established. Low temperature decomposition of ADN has been inhibited or decreased and a dependence of the rate of ADN decomposition on pK_b of the base has been observed. Manelis et al. [14] have reported several base stabilizing additives. The best one was urotropine (hexamethylene tetramine) at 0.1–0.6 wt.%. Russell et al. [15,16] have reported that bases like DPA, diphenylamine and NH_3 with pK_b of 9 do inhibit the ADN decomposition, while free radical scavengers like DPPH, 2,2-diphenyl-1-picryl hydrazyl, show no improvement on the decomposition of ADN. However, compounds that are both free-radical scavengers and bases like methyl nitro aniline (MNA) and 2- nitro-diphenylamine (2-NDPA), delayed the decomposition by 8 and 4 h, respectively, at 70 °C. Their pK_as are 3.5–4 and 1–2, respectively. Politzer and co-workers [17–19] and Mebel et al. [20–22] have reported theoretical study of ADN decomposition.

In the present work, we report ADN low temperature decomposition and the effect of thermal stabilizing additives such as a somewhat basic salts potassium fluoride (KF) [23] and potassium dinitramide (KDN), Lewis bases such as phenylphosphorous pentamer, hexamer and polymers, and a super base perhydro-1,3,5-triazine-2,4,6-trione [24–26] (Verkade's super base, VC) on the stabilization of ADN over this temperature regime. We would like to emphasize that a need exists for stabilization of ADN decomposition. The theme of our approach is to find a suitable stabilizer for ADN, which will promote ammonia evolution and prevent the decomposition of HDN. This may be accomplished by trapping the HDN [27], dinitramidic acid and its subsequent product, HNO_3 as a salt and reduce the photochemically favored reaction. A base stabilizer, which is a UV absorber, would be an ideal choice.

2. Experimental procedures

2.1. Materials

ADN and KDN were received from William Koppes and Al Stern of Naval Surface Warfare Center, Indian Head Division, Indian Head MD. The samples had 99% purity and no further purification was attempted. The samples were carefully stored in the dark and were not exposed to light. The moisture content of the samples was not determined. However, all samples were dried under vacuum and stored in a dry nitrogen atmosphere before analysis. Anhydrous KF and hexamethylene tetramine were purchased from J.T. Baker Chemicals, and VC was purchased from Strem Chemicals. These materials were used without further purification. Toxicity data of ADN

[28] and discussion of sensitivity of nitramines [29–32] have been reported.

The phenylphosphorous pentamer, hexamer and polymer were synthesized in our laboratory. The synthesis of cyclic phenylphosphine polymer was carried out following the procedure of Henderson and Epstein [33]. The reaction was done in a three-necked flask. Nitrogen was slowly introduced through one port, a reflux condenser connected in the middle and dropping a funnel connected at the third port. Phenylphosphine (6.1 g, 0.065 mol) in 25 ml cyclohexane was stirred at room temperature while 10.0 g (0.065 mol) of phenyl dichlorophosphine in 15 ml of cyclohexane was added slowly during the course of 1 h. The mixing was continued for an additional hour and then the temperature was raised slowly to ∼60 °C while continuing stirring. A precipitate was formed and there was gas evolution. As soon as the precipitate appeared, the heating was discontinued. The stirring was continued for an additional hour. The solution was then slowly cooled while under reflux. The precipitate formed was then filtered and the solid product was washed with hexane. The product was dried under vacuum. Finally, crystalline material was obtained in ∼95% yield. The dried crystalline product was used as made.

2.2. Data collection and analysis

All samples were loaded into an infrared gas cell, evacuated and then filled with dry nitrogen to atmospheric pressure, and finally sealed. Typical sample masses were 100 mg of material. Typical stabilization studies were accomplished with 1–2% by a mass of additive and 99–98% by mass ADN. After loading the cell, the sample was wrapped with heating tape and was placed inside the sample compartment of a Nicolet 800 FTIR spectrometer. A typical spectrum was collected with 100 scans at 1 cm^{-1} resolution using MCT-A or MCT-B detector. Spectra were taken at 1–2 h time intervals up to 7 days. Fig. 1 shows the typical experimental setup. The IR beam was focused 2–3 mm above the sample for product analysis. The cell chamber was then heated to a pre-determined temperature and kept heated for the desired length of time. An Omega temperature controller employing a thyristor controller and a silicon-controlled rectifier (SCR) controlled the power input to the heater. Automatic control of the temperature was accomplished with proportional, integral, and derivative features. This system permits routine heating of the sample in the infrared gas cell. The temperature was measured by a chromel-alumel thermocouple with its bead imbedded

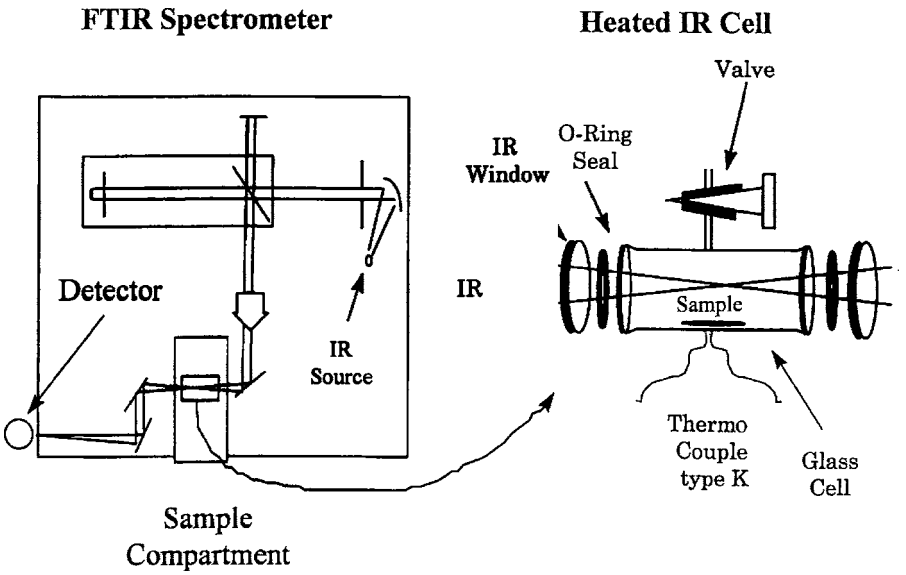

Fig. 1. Experimental setup showing FTIR and an enlarged gas IR cell

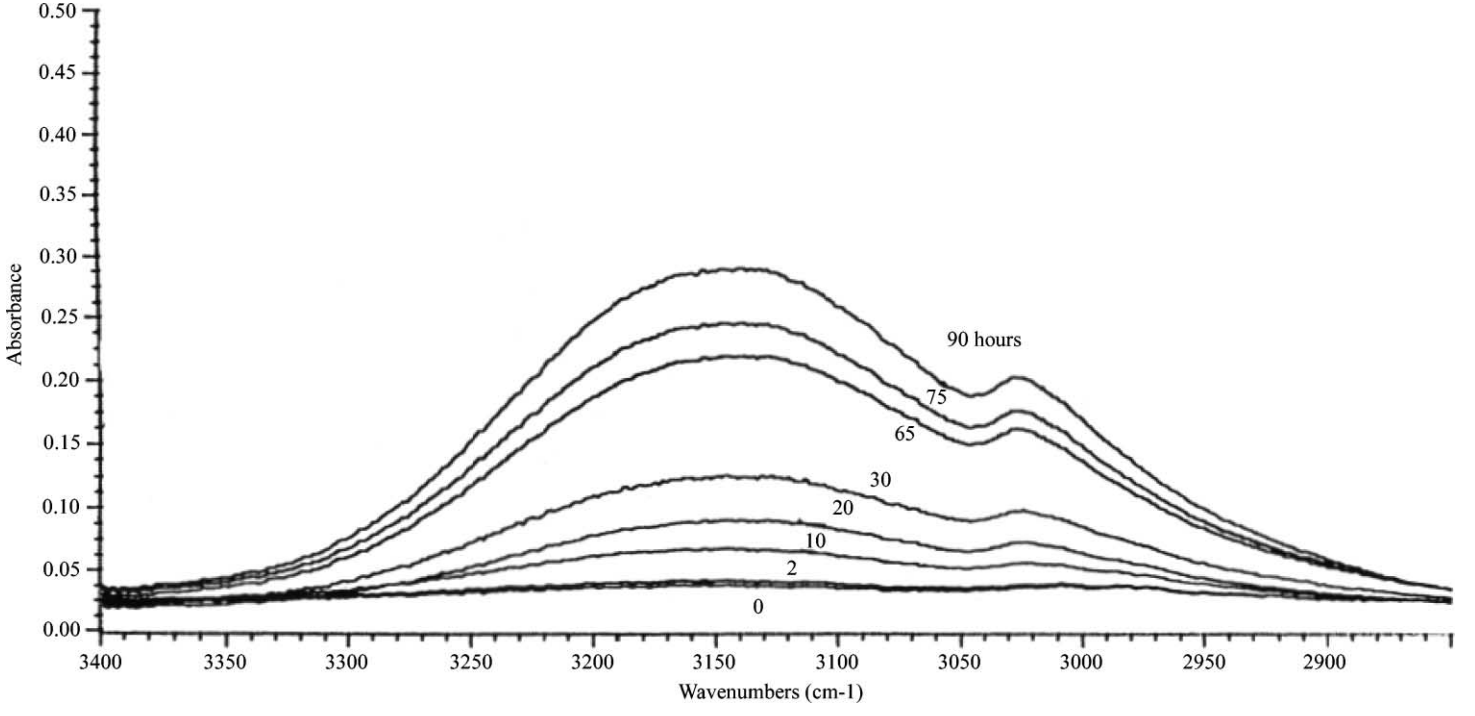

Fig. 2. Ammonium nitrate formation with time from ADN heated at 90 °C.

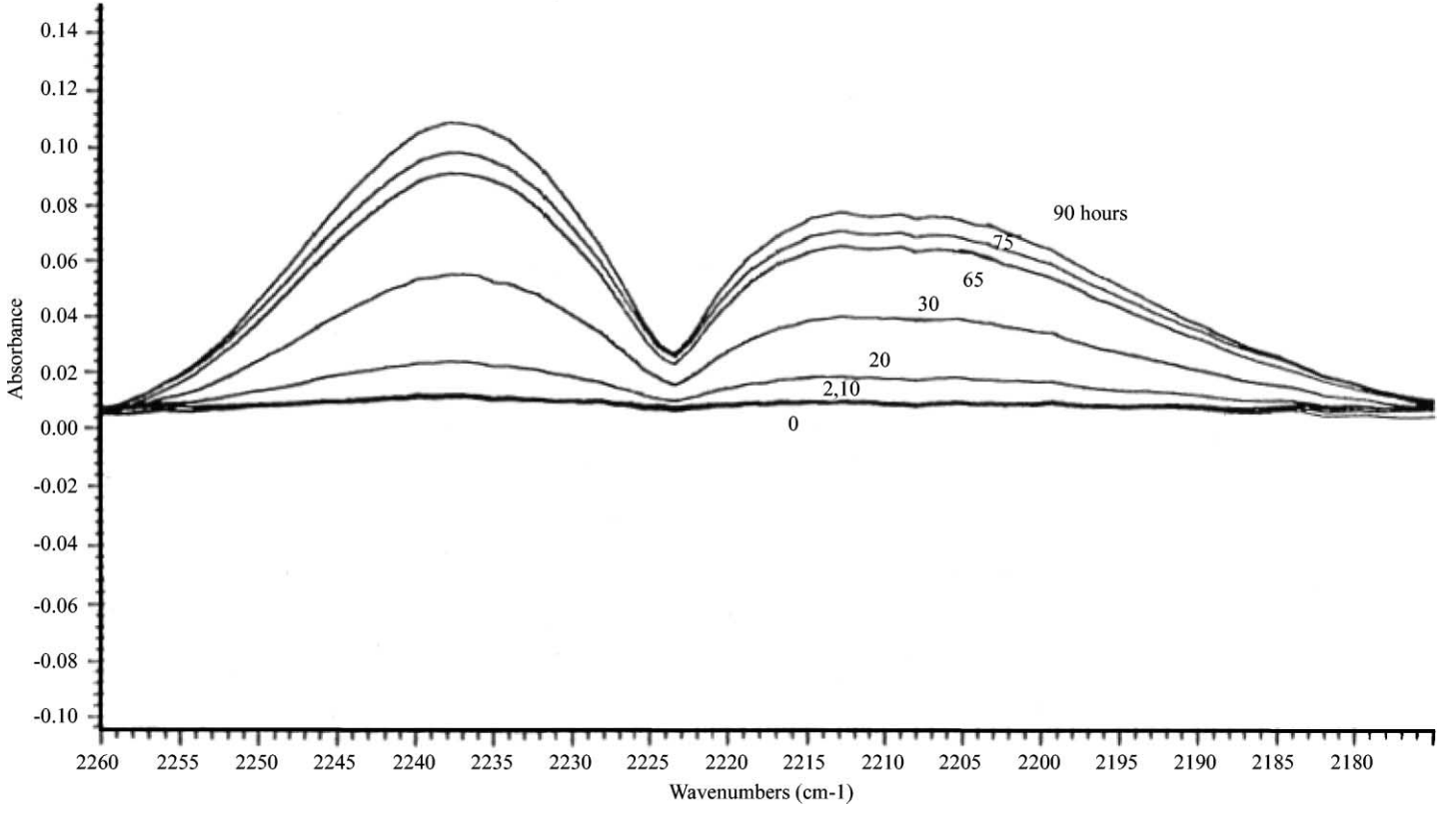

Fig. 3. Nitrous oxide formation with time from ADN heated at 90 °C

into the glass below the sample. The sample temperature can be set and automatically maintained to ±1 °C with an estimated accuracy of ±1 °C. The sample temperature was calibrated using a fixed-point temperature calibration method on the melting point of pure materials.

The spectra of the gaseous decomposition products N_2O and NH_3 and the condensed ammonium nitrate on the cold part of the cell window were monitored every 1, 2, or 4 h. The data collected was stored in the computer and later analyzed using the 680-DSP spectral workstation for N_2O, NH_3 and NH_4NO_3 evolution. A typical sequence for N_2O and AN is shown in Figs. 2 and 3. Each spectra was collected in situ during isothermal heating at a constant temperature of 90 °C. Over the duration of the experiment the only products detected were N_2O and AN. As can be seen in Figs. 2 and 3 an increase in the concentration of N_2O and AN is observed during the experiments. Determining the relative concentration of N_2O and AN produced during decomposition was accomplished by integrating over the infrared absorption of the ammonium ion of AN (3350–2850 cm^{-1}) while the concentration of N_2O was accomplished by integrating over the wavelength region 2260–2180 cm^{-1}. The changes in concentration of these two products in time at a constant temperature were employed to evaluate the decomposition and stabilization of ADN in the low temperature decomposition regime.

3. Results and discussion

3.1. Thermal decomposition of ADN

Figs. 4 and 5 show the detected amount of AN and N_2O produced during the decomposition of ADN at 60, 70, 80, and 90 °C. The evolution of the products as a function of time was described in the experimental section. AN is determined by the measured infrared spectrum of gaseous N_2O. These two products provide an in situ analysis of early reaction proposed for the decomposition of ADN. Nitrogen dioxide is a direct measurement of HDN decomposition (reaction (3)) while AN is a measurement of the recombination of HNO_3 and NH_3 produced during this reaction process (reaction (4)). ADN decomposition is observed to be first order for the production of N_2O and AN over the temperature regime 60–90 °C. As the temperature is increased, the rate of formation of N_2O and AN is also increased. At a temperature of 80 °C and above, a steady increase in vapor phase ammonium nitrate is detected. Below 80 °C, AN formation increases steadily until it reaches an asymptotic limit (first order in

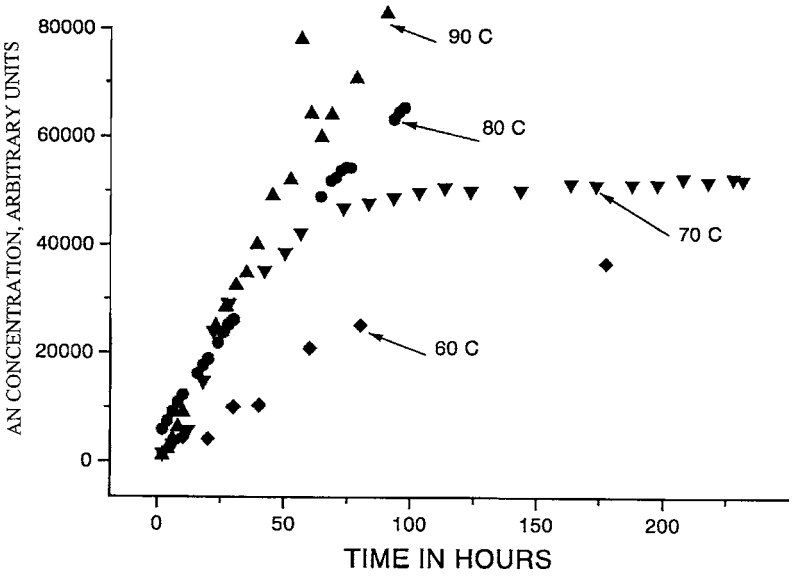

Fig. 4. Ammonium nitrate concentration with time for ADN heated at 60, 70, 80 and 90 °C.

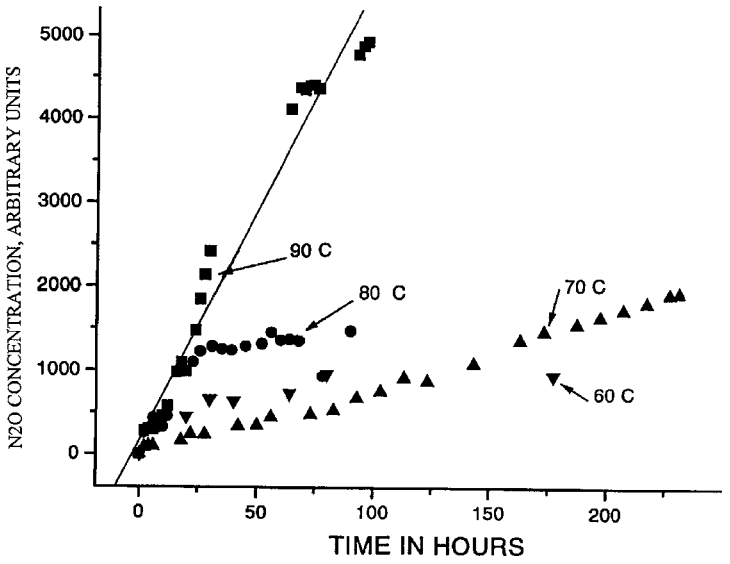

Fig. 5. Nitrous oxide concentration with time for ADN heated at 60, 70, 80 and 90 °C.

reactant; it indeed tapers off asymptotically). N_2O production (Fig. 5) shows a similar temperature dependence as AN. However, an asymptotic limit is also achieved at 80 °C. A steady production of N_2O is only observed at 90 °C. Again, this represents a first order decomposition process over the temperature regime studied. It is interesting to note that a rate change in the decomposition of ADN is observed between 60 and 70 °C. The early N_2O production at 60 °C is higher than what is observed at 70 °C. However, after ≈100 h, the N_2O production rate at 60 °C falls below the production rate at 70 °C. This appears to be reproducible within the limited number of experiments performed rather than an experimental error. This interesting rate change is still under investigation. Therefore, no explanation for this observation will be discussed at this time.

3.2. Thermal stabilization of ADN

Figs. 6 and 7 show the detected amount of AN and N_2O produced during decomposition of ADN at a constant temperature of 90 °C, when potential stabilizers are added. The stabilizers studied were KDN, KF, VC, and PP. The amount of N_2O and AN produced during stabilization is compared to the decomposition of pure ADN. Only VC and KF reduced the amount of AN produced during decomposition (Fig. 6). PP and KDN actually enhanced the formation of AN during decomposition at 90 °C. VC suppressed the production of AN for 65 h. However, an initial NH_3(g) evolution is observed in ADN decomposition when VC is added as a stabilizer to ADN. However, no more ammonia evolution was detected. This indicated that VC is a good base stabilizer and probably reacts with the HNO_3 thereby consuming it. We do observe some N_2O evolution and do not observe any NH_4NO_3, which leads us to conclude that perhaps it reduces the production of HNO_3 during decomposition. The rate of N_2O production in Verkade's super base (labeled VC2 in Fig. 7) is similar to that observed in pure ADN, although it is markedly lower. All other materials studied enhance the rate of N_2O production during decomposition at 90 °C. In a second experiment, ADN was mixed with Verkade's super base (labeled VC in Fig. 7) and the decomposition was performed with exposure to room light in an effort. Because VC absorbs in the ultra violet, VC was used to determine whether small mass percent additions of an ultra violet absorber could be a protection against ADN photochemistry. At a 1% by mass addition of VC, no stabilization of ADN is observed in the presence of room light (labeled VC in Fig. 7). Therefore, if a stabilizer for photolytic effects is to be discovered a higher mass percent addition will most likely be necessary.

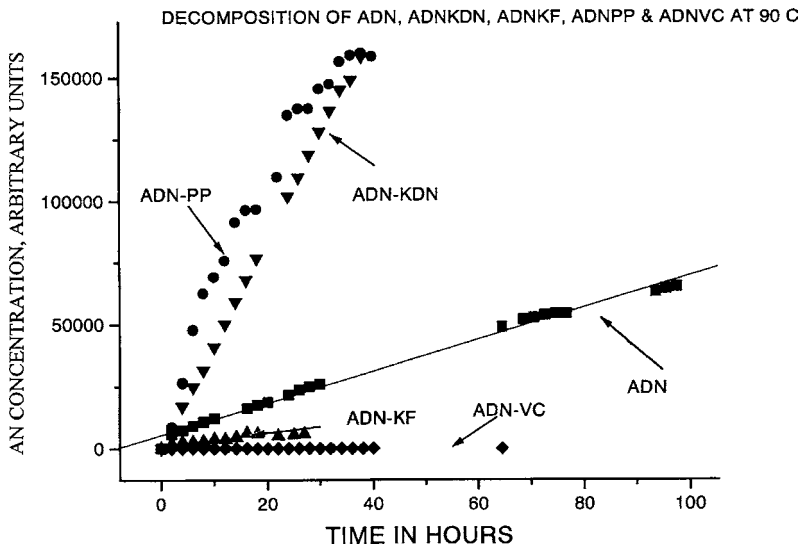

Fig. 6. Ammonium nitrate concentration with time for ADN, ADN-KDN, ADN-KF, ADN-PP, and ADN-VC at 90 °C

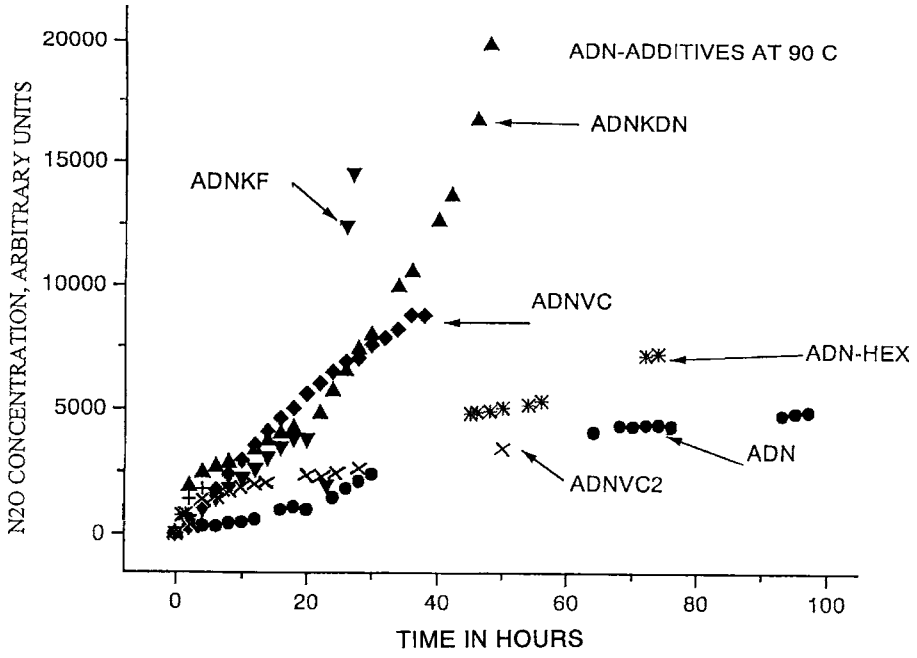

Fig. 7. Nitrous oxide concentration with time for ADN, ADN-KDN, ADN-KF, ADN-HEX, and ADN-VC at 90 °C.

4. Conclusions

The thermal decomposition of ADN in the solid state has been examined at 60, 70, 80, and 90 °C by monitoring the evolution of N_2O and AN produced during decomposition. The reaction is observed to be first order in reactant over the temperature regime investigated. In order to slow the decomposition of ADN in this temperature regime, several additives were examined. While monitoring AN production,

KF and VC show reductions in AN formation. However, AN is still produced (detected) when KF is added to ADN. No AN is observed with the addition of VC. While monitoring N_2O(g) production, all additives enhanced the rate of production. Only Verkade's super base appeared to have a slowing effect on N_2O formation. On the basis of AN and N_2O formation, VC was the only suitable additive studied. VC kept AN under control; however, there was very small N_2O evolution. Although the evidence is less compelling to say that VC controlled the decomposition, it appears to be the best of all additives studied. It is safe to conclude that VC scavenged the HNO_3 more effectively than NH_3.

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References

[1] E.E. Hamel, R.E. Olsen, US Patent 3,428,667 (18 February 1969).
[2] J.C. Bottaro, R.J. Schmidt, P.E. Penwell, D.S. Ross, US Patent 5,198,204.
[3] J.C. Bottaro, R.J. Schmidt, P.E. Penwell, D.S. Ross, US Patent 5,254,324.
[4] R.J. Schmidt, J.C. Bottaro, P.E. Penwell, D.C. Bomberger, US Patent 5,316,749.
[5] J.C. Bottaro, P.E. Penwell, R.J. Schmidt, A new synthesis of alkyl-*N*,*N*-dinitramines by direct nitration of isocyanates, Synth. Commun. 21 (7) (1991) 945–949.
[6] M.J. Rossi, D.F. McMillen, M. Golden, Low pressure thermal decomposition of new energetic material ammonium dinitramine $NH_4N(NO_2)_2$ and NH_4NO_3, Int. J. Chem. Kinet. 25 (1993) 549.
[7] M.J. Rossi, D.F. McMillen, M. Golden, Low pressure thermal decomposition studies of selected nitramine and dinitramine energetic materials (available from NTIA) AD-A247972 SRI Project 8999, March 1992.
[8] O.A. Luk'yanov, O.V. Anikin, V.P. Gorelik, V.A. Tartakovsky, Dinitramide and its salts. Part 3. Metallic salts of dinitramide, Russ. Chem. Bull. 43 (9) (1994) 1457–1994.
[9] O.A. Luk'yanov, A.R. Agevnin, A.A. Leichenko, N.M. Seregina, V.A. Tertakovsky; N.D. Zelinsky Inst. Org. Chem., Moscow, 1117913, Russia; Izv. Akad. Nauk. Ser. Khim. (1) (1995) 113–117 (in Russian).
[10] V.A. Shlyapochnikov, N.O. Cherskya, O.A. Lukyanov, V.P. Gorelik, V.A. Tartakovsky, Dinatramide and its salts. Part 4. Molecular structure of dinitramide, Izv. Akad. Nauk. Ser. Khim. 43 (9) (1994) 1522–1525.
[11] C. Hinshaw, R.B. Wardle, T.K. Higshmith, Propellant formulations based on dinitramide salts and energetic binders, Thiokol Corporations, US Patent 5,498,303.
[12] Z. Pak, Some ways to higher environmental safety of solid rocket propellant application, AIAA-93-1755, American Institute of Aeronautics and Astronautics, 1993.
[13] T. Brill, P.J. Brush, D.G. Patil, Thermal decomposition of energetic materials. Part 58. Chemistry of ammonium nitrate and ammonium dinitramide near the burning surface temperature, Combust. Flame 92 (1993) 1787–1886.
[14] G.B. Manelis, et al., Thermal Decomposition of ADN, in: Proceedings of the 26th International Annual Conference on ICT (Pyrotechnics) 15-1-15-17, 1995.
[15] T.P. Russell, G.J. Piermarini, S. Block, P.J. Miller, Pressure temperature reaction phase diagram for ammonium dinimtramide, J. Phys. Chem. 100 (8) (1996) 3248–3251.
[16] T.P. Russell, A.G. Stern, W.M. Koppes, C.D. Bedford, Thermal decomposition and stabilization of ammonium dinitramide, CPIA Publication # 593 (11) (1992) 339–345.
[17] P. Politzer, J.M. Seminario, Computational study of the structure of dinitraminic acid, $HN(NO_2)_2$, and the energetics of some possible decomposition steps, Chem. Phys. Lett. 216 (1993) 348–352.
[18] P.C. Redfern, P. Politzer, Computational analysis of structural properties of the dinitramide ion, $N(NO)_2$, and some related molecules, $HN(NO_2)_2$ and $N(NO_2)_3$, Office of Naval Research Contract N00014-85-K-0217, available from NTIS, AD A228-139 September 1990.
[19] P. Politzer, J.M. Seminario, M.C. Concha, P. Redfern, Density functional study of structure and some decomposition reactions of the dinitramine anion, $N(NO_2)_2$, J. Mol. Str. Theochem. 287 (1993) 235–240.
[20] A.M. Mebel, M.C. Lin, M. Morokuma, Theoretical study of the gas phase structure, thermochemistry, and decomposition mechanism of NH_4NO_2 and $NH_4N(NO_2)_2$, J. Phys. Chem. 99 (1995) 6842–6848.
[21] A.M. Mebel, M.C. Lin, M. Morokuma, Theoretical study of the gas phase structure, thermochemistry, and decomposition mechanism of NH_4NO_2 and $NH_4N(NO_2)_2$, Chem. Phys. Process. Combust. (1994) 282–85.
[22] A.M. Mebel, K. Morokuma, M.C. Lin, Ab Initio molecular orbital study of potential energy serface for the NH + NO_2 reaction, J. Chem. Phys. 101 (5) (1994) 3916–3922.
[23] I.B. Mishra, Phase stabilization of ammonium nitrate with potassium fluoride, US Patent 4,552,736 (November 1986).
[24] J. Tang, T. Mohan, J.G. Verkade, Selective and effective synthesis of perhydro-1,3,5-triazine-2,4,6-triones and carbodimides from isocyanates using $ZP(MeNCH_2CH_2)_3N$ catalysts, J. Org. Chem. 59 (1994) 4931–4938; US Patent 5,051,533.
[25] J. Tang, J.G. Verkade, $[P(MeNCH_2CH_2)_3N]$ as a superior catalyst for the conversion of isocyanates to isocyanurates, Angew. Chem. Int. Ed. Engl. 32 (6) (1993) 896–898.

[26] C. Lensink, S.K. Xi, L.M. Daniels, J.G. Verkade, The unusually robust P–H bond in the novel cation, $HP(NMeNCH_2CH_2)_3N$, J. Am. Chem. Soc. 111 (1989) 3478–3479.

[27] A.Snelson, A.J.Tulis, D.C.Heberlein, D.L.Patel, Vaporization of ADN and tentative isolation of HDN by matrix isolation spectroscopy, in: Proceedings of the 19th International Pyrotechnical Seminar, 1994, pp. 531–534.

[28] D.R. Tocco, S.A. Salins, R.E. Wolfe, E.R. Kinhead, in: Proceedings of the Meeting on Acute and subacute toxicity of ADN, JANNAF Safety and Environmental Protection, CPIA 614, Vol. 1, San Diego, August 1994, pp.331–334.

[29] T. Mukundan, C.P. Constantinou, M.M. Chaudhri, Mass spectrometric and spectroscopic investigation of the chemical sensitization of nitrocompounds by an amine, in: S.S. Schmidt, R.D. Dick, J.W. Forbes, D.G. Tasker (Eds.), Proceedings of the Meeting on Shock Compression of Condensed Matter (1991), Elsevier, North-Holland, Amsterdam, 1992, pp. 659–662.

[30] M.D. Cook, P.J. Haskins, Decomposition mechanisms and chemical sensitization in nitro, nitramine and nitrate explosives, in: Proceedings of the 9th International Symposium on Detonation, Vol. 1, 1988, pp. 427–433.

[31] W.L. Engelke, 43% increase of failure diameter of nitromethane by adding 0.03% of diethylene triamine (DETA), Phys. Fluids, 23 (1980) 875.

[32] W.L. Engelke, C.M. Earl, J. Rohlfing, Amine leads to enhancement in concentration of the aci-ion(CH_2NO_2-) ion, Chem. Phys. 84 (1) (1986) 142.

[33] Wm.A. Henderson, H. Epstein Jr., F.S. Seichter, Some aspects of the chemistry of cyclopolyphosphines, J. Am. Chem. Soc. 85 (1963) 2462–2466.