Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Fang, Chong and Li, Shufen(2002) 'Synergistic interaction between AP and HMX', Journal of Energetic Materials, 20: 4, 329 — 344
To link to this Article: DOI: 10.1080/07370650208244827
URL: http://dx.doi.org/10.1080/07370650208244827

Synergistic Interaction between AP and HMX

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ABSTRACT: Based on the condensed-phase mechanism and thermolysis experimental results, the synergistic interactions between AP and HMX in NEPE propellants are studied from the two viewpoints of molecular structure and chemical reaction. Related to bond polarity, formal charges, chain reaction theory and the systematic comparison of solid monopropellant combustion and modeling, the "linkage–mutualism"mechanism is proposed. That implies between AP and HMX, the heat released is interlocked while the species produced are mixed and reacting with each other in the combustion wave. AP content and particle size can influence the mechanism, therefore will have significant effects on the ignition and combustion characteristics of NEPE propellants.

Introduction

Since the early 1980's, NEPE propellants have become popular because of their high energies, good mechanical properties and many other adaptable characteristics. Regarding the improvements, especially on the decrease of their relatively high pressure exponent, a variety of creative and systematical mechanisms have been proposed. From the combustion behavior of solid monopropellant, analysis on composite/modified double-base propellant to nitramine-based composite propellant,

Journal of Energetic Materials Vol. 20, 329-344 (2002)
Published in 2002 by Dowden, Brodman & Devine, Inc.

researchers have carried out a lot of instructive work [1,2]. Because AP and HMX are both important ingredients in NEPE propellants but have quite different roles, we utilize the known combustion models and experimental data, based on the synergistic interaction, to propose the "linkage-mutualism" mechanism between AP and HMX. The effects of AP content and particle size are therefore investigated and explained.

Condensed-phase Mechanism

AP's condensed-phase kinetics has great impact on combustion characteristics of propellants. AP has melted before ignition, reactions occur in the melting layer formed on AP's surface. Liquid AP can then decompose through several channels to produce gaseous products, after bubbles emerge in the foam zone; the species released entering the gas phase will react with each other. Based on this, Tanaka et al. raised AP condensed-phase mechanism [3]. See Table 1 for details.

Table 1. AP condensed-phase mechanism

No.	Reaction	Ea (kJ/mol)
1C	$AP(s) \rightarrow AP(l) \rightarrow NH_3 + HClO_4$	117
2C	$AP(l) \rightarrow H_2O + O_2 + HCl + HNO$	92
3C	$AP(l) \rightarrow 2H_2O + Cl + NO_2$	92
4C	$AP(l) \rightarrow NH_3 + OH + ClO_3$	92

Reactions 2C, 3C and 4C occur in parallel at slightly higher temperatures, and their products agree favorably with experimental results. The ensuing "bubble reaction" gives off reactive species, whose formation and release from the burning surface will have strong effects on HMX. After HMX melts, Prasad and co-workers described its

liquid-phase decomposition mechanism [4]. The three global steps give us a general idea of HMX's decomposition.

Table 2. HMX liquid-phase mechanism

No.	Reaction	Ea (kJ/mol)
1L	$HMX \rightarrow 4CH_2O + 4N_2O$	172.4
2L	$HMX \rightarrow 4NO_2 + 4H_2CN$	210.0
3L	$CH_2O + NO_2 \rightarrow CO + NO + H_2O$	57.3

The simulation study [5] reveals that this decomposition mechanism of HMX, probably the main factor to cause temperature-sensitivity differences on the burning surface, will be affected by the releasing rate of N_2O and NO_2. It's interesting that NO_2 is not only the product of HMX's bond breakage (2L in Table 2), but also can be derived from AP's condensed-phase degradation (3C in Table 1).

We know that in the condensed-phase reaction layer of nitramine particles such as RDX and HMX, two competitive processes exist: evaporation and exothermic decomposition. The former is the controlling step at low pressures, while the latter dominates at high pressures. Compared with RDX, HMX has the higher melting temperature, whereas its volatility and vapor pressure are relatively low. That results in its significant self-catalysis involving NO_2 and CH_2O. The effective activation energy for HMX's gasification is 192.5 kJ/mol, which is much larger than the AP value 117.2 kJ/mol, so it's easier for AP to decompose first during the heating process. AP can therefore influence HMX by heat and species transferred within the heterogeneous melting layer.

From the chemical reaction angle, HMX's initial decomposition won't be affected by environmental atmosphere, such as H_2, Ar, O_2, CO and NO. Experiments conducted by Palopoli et al. [6] show that NH_3 and NO_2 experience the different reaction mechanism; they can readily participate in reactions that are normally kinetic or thermodynamic dominant, and can influence the original decomposition channel of HMX as well. Due to the N atom's electronic configuration ns^2np^3 (n=2), its oxidation number ranges from –3 (np subshell is full), +3 (np subshell is empty) to +5 (n shell is empty), so NH_3 and NO_2 are reactive and can produce various species.

Experimental Results

Through many experiments carried out on the new series of NEPE propellants, the effects of AP content and particle size on samples' combustion characteristics have been studied systematically [7]. The interaction between AP and HMX plays an important role, which corresponds to different parameters. The basic formula of propellant samples is (AP+HMX)/Al/(PEG+NE), among which the oxide content is 57% and aluminum content is 18%. Based on the formula of sample H–b, the variance of AP content and particle size will account for changes listed in Table 3.

Table 3. Combustion characteristics of propellants with different AP content and particle size

Sample No.	AP Content (%)	AP Particle size	HMX content (%)	Pressure exponent *n*	Deflagration heat Q **(J/g)
H–a	8	<90um	49	0.67	6637.3
H–b	13	<90um	44	0.60	7584.9
H–c	20	<90um	37	0.56	8030.6
H–d	13	Grading*	44	0.64	8284.9
H–e	13	Superfine	44	0.72	7780.3

* "Grading" stands for that the proportion of the amount of <90um AP particle to the amount of superfine AP particle is 1 to 1. "Superfine" means the average AP particle size is 1~2um.

** The propellants' deflagration heat was measured by the thermostatic oxygen bomb calorimeter, at 1.96MPa in N2 atmosphere.

We can conclude safely that the increase of AP content results in the decrease of n and the increase of deflagration heat of samples. Though the effect of AP particle size is less manifest, it also indicates some meaningful differences.

Table 4.* Condensed-phase degradation of propellants with different AP content and particle size

Sample No.	Peak shape	Peak initiating temperature (°C)	Peak temperature (°C)	Heat release Q_c (J/g)
H-a	Three peaks	164.25 181.31 216.27	188.64 197.55 241.91	527.40 337.46 146.37
H-b	Single	157.62	194.65	427.02
H-c	Single	156.54	178.77	177.58
H-d	Single	159.08	194.11	488.92
H-e	Single	159.72	191.93	438.74

* The DSC heating rate is 10°C /min, the atmosphere around the sample is N_2 with its flow rate set to be zero. The sample pan is sealed.

The DSC data in Table 4 reveal that H-b and H-c with the relatively high AP content release less heat in the condensed phase, while they effectively lower the peak temperature. As a consequence, the deflagration heat represented in Table 3 shall be divided into two parts: heat from the condensed phase and heat from the gas phase.

"Linkage-mutualism"

In order to explain the experimental phenomena, we consider the interactions between AP and HMX from both the macroscopic and microcosmic view. Beckstead et al. [8] published the combustion characteristics of RDX, HMX and AP as typical solid monopropellants, which can sublime or decompose in the solid phase. Comparisons between HMX and AP elucidate that HMX can form a visible, definite liquid layer

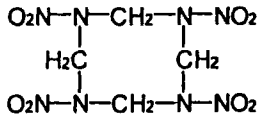
where effective exothermic reactions won't occur below HMX's melting point; while AP's melting layer cannot be observed directly, but AP can decompose quickly below its anticipated melting point and breed a kind of reactive atmosphere.

Ignition threshold

HMX can greatly improve the propellant's energetic properties, because it has high deflagration heat and deflagration rate, etc. Though AP doesn't have these properties, it can offer many other advantages, such as the improvement of the propellant's ignition characteristics. Since AP has the rather low ignition threshold, it can initiate the proceeding, and produce chemically reactive gases such as NH_3, NO_2 and O_2 because of its high oxygen content. Hence, AP can be considered as "activated stimulation point" in the propellant, when absorbing heat, it will be excited first and experience some physical/chemical changes, i.e. produce NH_3 and NO_2 (Table 1). Due to the high solubility and reactivity of NH_3 and NO_2 in heterogeneous melting layer, AP will then impress on HMX with its product species and heat release.

Bond conversion

HMX can be written in the structural formula as:



Up till now, two major mechanisms have been proposed: one takes the breaking of HMX's covalent chain as its first chemical change, while the other thinks that the

elimination of strong intermolecular electrostatic forces between HMX molecules or HMX and its decomposition products is the rate-controlling step. The same basis of both theories lies in that N and O are small atoms with very high electronegativity. As for the molecular accumulation structure, the polar covalent bonds already existing within HMX such as N–C, N–O and C–H will be strong, so is the lattice energy of HMX crystal. This explains the high melting point and decomposition temperature of HMX, at about 280 °C.

Formal charge

By assuming that two atoms share each bond equally, we can rely on the reasonable approximation to count atom formal charges in HMX molecule.

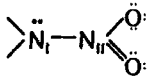
$$\text{Atom formal charge} = \text{group number} - \text{number of lone pair electrons} - \tfrac{1}{2}(\text{number of bonding electrons}) \quad (1)$$

For the 8-electron-structure molecule, another equation is also valid:

$$\text{Atom formal charge} = \text{bond number} - \text{character number} \quad (2)$$

$$\text{While character number} = 8 - \text{valence electron number} \quad (3)$$

To be a focus of attention, $N–NO_2$ structure can be analyzed by counting the atom



formal charges. We mark N_I, N_{II} here for reference.

Since N atom has the valence electron number of 5, its character number is 3. In the

formula, four bonds surround N_{II}. So (1) and (2) can be written respectively as,

$$N_{II} \text{ formal charge} = 5 - 0 - \tfrac{1}{2}(2 \times 4) = +1 \quad (4)$$

$$N_{II} \text{ formal charge} = 4 - 3 = +1 \quad (5)$$

Then we may find out that N_{II} is somewhat active, because a molecule or ion won't be stable if any positive formal charge resides on a very high electronegative atom. N_I atom formal charge can also be calculated and the result is zero, since this atom has two lone-pair electrons.

Hydrogen bonding

When AP's decomposition product NH_3 moves to the melting surface of HMX, hydrogen bonds such as $N-H\cdots N-$ and $N-H\cdots O-$ can be formed easily. Because of the considerably high electronegativity of N (3.0) and O (3.5) atoms, interactions between them and the H (2.1) atom belonging to NH_3 (high polarity) will generate unusually strong dipole-dipole forces. So it's probable that N_I with lone pair electrons will be involved in this type of hydrogen bonds and the bonding electrons between N_I and N_{II} will be greatly attracted to N_I. Together with the activity of N_{II}, the N_I–N_{II} bond can be easily broken. Additionally from some logical inference, C–N bond is much more polar than N–N bond, so the breakage of C–N bond costs more energy, while C atom doesn't readily interact with H atom in NH_3. Above analyses point out the great possibilities for N–N bond to be broken earlier.

Certain experiment [9] has proved that in nitramine composite propellants, $N–NO_2$ bond within HMX would break at the beginning of HMX's decomposition in its

condensed-phase reaction zone, and the initial products included NO_2, N_2O.

Chain reaction

After all, NO_2 emerges in the condensed phase either from the degradation of AP, the abruption of N–NO_2 bond or the evaporation of HMX, and it tends to react with HMX. The movability of gases released in the condensed phase is limited to some extent, so NO_2 will be bounded to the remaining ring compound to form nitramine again. With the heat flux added to the propellant, NO_2 will have more chances to escape from the cage and due to its special chemical structure:

It can therefore abstract the skeletal methylene proton of HMX to form 8-electron-structure stable molecule HONO. Symmetrical molecular construction of HMX is related to its "cage effect", then NO_2's abstraction and the further fragmentation of those covalent chains will eliminate the "cage effect" and enhance the decomposition of HMX. Some representative probable reactions are listed below.

$$C_4H_8N_8O_8 \rightarrow NO_2 + CH_2{=}N\cdot + 3N_2O + 3CH_2O \quad (6)$$

(at characteristic pressure, see Table 2 for comparison)

$$H_2CN + NO_2 \rightarrow HCN + HONO \quad (7)$$

$$HONO \rightarrow OH + NO \quad (8)$$

$$NH_3 + OH \rightarrow NH_2 + H_2O \quad (9)$$

$$CH_2O + OH \rightarrow CHO + H_2O \quad (10)$$

$$NH_2 + NO \rightarrow N_2 + H + OH \quad (11)$$

$$NO_2 + H \rightarrow OH + NO \quad (12)$$

$$CHO + H \rightarrow CO + H_2 \quad (13)$$

$$OH + H_2 \rightarrow H_2O + H + 63.2kJ \quad (14)$$

Both H and OH are intermediate resources of great importance to maintain the chain reaction. The NH_x, NO_x species are also reactive, which reflects the various oxidation numbers of N atom discussed in section 2. Compared with the inert Ar, NH_3 or NO_2 atmosphere can make the pyrolysis products of HMX emerge about 200ms in advance [6], which affirms their high reactivity.

This kind of "linkage-mutualism" between species can greatly increase the heat release, transfer and feedback. And the mechanism has been demonstrated here from varied aspects to indicate that the condensed-phase reaction zone really plays an important role in determining the decomposition features of AP and HMX.

Deflagration Heat Analysis

The basic concept of deflagration experiments is to use heat effect to account for inner changes taking place in propellants. The data in Table 3 and 4 correspond to the overall heat release (Q) and the condensed-phase heat release (Q_c), respectively.

AP content effect

The increase of AP content will significantly improve Q due to the fact that,

(1) AP can decrease the ignition threshold and ignition delay time of propellants, as "activated stimulation point";

(2) The increase of AP content (with the same particle size) will enlarge AP surface area, which can strengthen the "linkage-mutualism" between AP and HMX, the main solid ingredients in propellants;

(3) AP's pyrolysis will release more active gases abundant in oxygen or nitrogen to participate in the chain reaction, and then to enter the gas phase, which can make the dark zone thinner, enhance gas-phase reactions, increase the heat feedback to the combustion surface and raise the burning rate;

(4) Large amounts of oxidative gases can be produced to effectively oxidize aluminum powders and C–H class of compounds, so they will improve the propellants' combustion efficiency.

That's why sample H–c (with the highest AP content) has the largest heat of deflagration, Q (Table 3). However, from Table 4, H–c releases, by far, the least amount of heat in its thermal decomposition (177.58 J/g) compared to the other formulations (over 400 J/g), possibly because there is a decrease in the peak decomposition temperature which, in turn, will cause a decrease in the fraction of condensed-phase decomposition of HMX. This implies that the major contribution to the deflagration heat Q comes from the gas phase.

In Al-based compositions with (AP+HMX)/Al/(PEG+NE) formulations, Al will react with Cl_2, gaseous product of AP's decomposition, and generate so much heat that Al melts and continues to burn [10],

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 1408.4kJ \qquad (15)$$

If the micro carbon structure can exist on the burning surface for some time, another reaction containing the coating Al_2O_3 can also occur to release much heat,

$$Al_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 3CO(g) \qquad (16)$$

When the burning surface retires to make aluminum particles expose to the gas phase, these kinds of chemical reactions can benefit the combustion efficiency of many species and increase the intensity of the flame.

AP particle size effect

To decrease the particle size of AP at the constant content will expand its surface area, and tend to merge its high-temperature-decomposition peak into the lower one. As a result, the apparent activation energy will be reduced and the decomposition rate of AP will be raised. Attributing to the high diffusion mixing rate between AP's and surrounding binder's decomposition products, chemical reaction kinetics will be more important to determine the burning rate of propellants, while such control is obviously influenced by pressure because of the involvement of many gaseous species. Hence, the pressure exponent will increase with the decrease of AP particle size (Table 3).

Kumar [11] pointed out that in the condensed phase, the first step for AP crystal grains to decompose to produce NH_3 and $HClO_4$, was the degradation of those AP grains to form smaller NH_4ClO_4 groups. As the molecule with stable electron structure, NH_4ClO_4 relies on van der Waals interactions to form the whole crystal.

First, the grain boundary is a kind of two-dimensional defect, while the dislocation

defect is one-dimensional. When solid AP macrograins absorb heat, empty spaces or interstitial atoms inside the grains will become more active with the increase of temperature, and they tend to move along the grain boundary while the degeneration of their variation energy levels has been removed. Such effects can also be regarded as the diffusion of those defects within the crystal. Hence, the inner localized stress concentration will accelerate the intercrystalline fracture of AP.

Second, considering the concept of "entropy" S as a macroscopic measure of the disorder of a system, we can easily conclude that AP crystal's degradation represents the increase of the disorder, which means the entropy change ΔS relating to free energy change for system is positive. Taking this as isothermal transformation, in accordance with second law of thermodynamics, we can find the expression,

$$Q = T\Delta S \qquad (17)$$

Here, a positive entropy effect implies that the system shall absorb heat. Since the amount of reaction heat released in the gas phase is mainly determined by AP content, the deflagration heat won't exhibit significant difference for propellants with varied AP particle size (but the same AP content). On the other hand, because the condensed-phase heat releases between II-b, II-d and II-e (Table 4) are not very different (427 to 489 J/g), it can be inferred that the differences possibly arise from AP intercrystalline fracture.

Further discussions can be focused on the combustion surface, dark zone thickness, heat transfer, species moving trace, fluid field temperature distribution and sensitivity,

and premixed-diffusion flame, etc. This paper emphasizes the initial stage of the burning process, but "linkage–mutualism" can also be applied to each part of the combustion wave, since complex interactions among various species will go on and play their particular roles. For instance, AP's addition can lower the pyrolysis temperature of the binder partly because of the easily established diffusion flame between them; and aluminum can act as an energy pump to release some heat in the primary flame zone in advance. The reduction of ClO_x species can also be considered. But the limitations of the present experimental data preclude drawing a firm conclusion, so further precise and systematical investigations shall be carried out on the combustion wave, especially on the condensed-phase reaction zone of propellants.

Concluding Remarks

The embodiment of "linkage–mutualism" stands for the strong interactions between AP and HMX within the different time period, in the various regions of the combustion wave and among the manifold species. That can influence the overall combustion behavior of NEPE propellants significantly. Discussions on molecular level imply the formation of hydrogen bond and the breakage of the N–N bond, while pyrolysis experimental analyses on chemical reactions explain the range of various species concentrations. Results show that the increase of AP content can enhance the condensed-phase degradation, weak the dark zone, foster the establishment of diffusion flame and improve the combustion efficiency of aluminum powder; the grading AP can also benefit the combustion characteristics of propellants. In the near future, the systemization and abundance of experiments, together with the gradually being

perfected combustion model, are sure to aid us understand and probe into the "linkage-mutualism" between AP and HMX, and expand this mechanism to other ingredients in NEPE propellants.

Acknowledgement

This research was supported by the National Natural Science Foundation of China (No. 59786005).

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