



Non-thermal solvate ignition of solid-state combustion at organic self-propagating high-temperature synthesis

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ABSTRACT

The original mechanism of the solid-state combustion, ignited by local addition of microquantities of water to mixture of disperse piperazine and malonic acid (hydroignition), was proposed. It consists eliminating the diffusion barrier at dissolving the product crust previously formed on the reagent particles at them mixing and jumping mechanism of proton transfer (Grotthuss mechanism).

The data obtained and their explanations seems unusual from the point of view of ignition theory which did not consider ignition as a non-thermal process at the expense of intrinsic resources of reacting solids.

New method of ignition (hydroignition) can be successfully applied for effective one-pot click-synthesis of both organic and inorganic products in the self-propagating high temperature synthesis (SHS) mode and for designing of autonomous ignition systems of mixes.

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1. Introduction

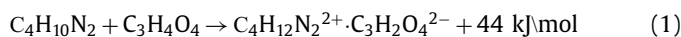
Organic self-propagating high-temperature synthesis (OSHS) is an effective method for obtaining organic compounds because it is carried out by simple operations in the absence of solvents [1–3]. Similar processes are named as solvent-free, click- or one-pot synthesis [4,5]. The essence of OSHS lies in organization of a stationary wave of chemical exothermic reaction in a mixed stoichiometric composition of disperse reagents (solid-state combustion) by means of local ignition, i.e. delivering small (≈ 120 J) external impulse of heat on the mixture top. After finishing the process and cooling the reacted mixture, a target organic product, material or an item is obtained.

As a rule, igniting device includes an electric spiral, forming an external local thermal impulse at SHS [6]. It strongly accelerates the exothermic reaction, initially slowly flowing in the initial mixture of powders, so that a combustion wave appears. It is the similar model that is taken as a principle and developed in the thermal theory of ignition [7].

However, in the present communication, possibility of OSHS by means of non-thermal local ignition of the process via addition of solvents microquantities to the top of initial mixture (solvent initiation, hydroignition) is demonstrated. This fact seems unusual from the point of view of ignition theory [7], because zero

value of thermal impulse turns the ignition equations into trivial. This means that the reaction is practically stopped and combustion is impossible except systems with $E_{act} \sim 0$ which must explode at mixing. These considerations are in contradiction with the observed facts, which is investigated and discussed in this article.

For the experiments, piperazine/malonic acid system was selected for sake of convenience as far as a simple addition reaction occurs as a result of H-bonds formation. It proceeds with 100% yield of the only product (organic salt–piperazine malonate), displaying antiparasite activity [1,2]:



As it has been shown [3,8,9], a continuum crust (a capsule) of the end product, growing with time, is formed on the surface of particles of the reagents at their mixing (Fig. 1). It inhibits the further reaction (Eq. (1)) (which is practically stopped), though in the dissolved state the reagents quickly and fully interact with activation energy $E_{act} \sim 0$. The crust formation leads to the strong diffusive retardation of the reaction and essential increasing of effective E_{act} . Respectively, it is possible to subsequently organize usual OSHS process in this admixture by means of local thermal ignition [1–3], in agreement with the thermal theory of combustion [7].

2. Experimental methodology

The OSHS technique in the chosen system and its basic peculiarities were described [3]. Piperazine (CAS 110-85-0), 99% extra

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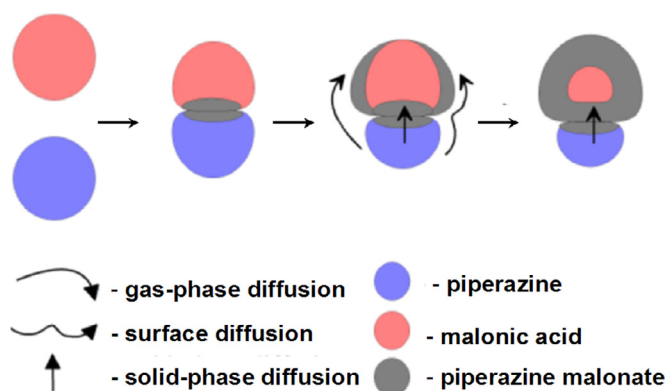


Fig. 1. The mechanism of the crust formation on the surface of reagent particles.

pure, “Acros”; malonic acid (CAS 141-82-2), pure, “Reachem”; water for hydroignition—mono-distillate. Two Chromel–Alumel thermocouples (0.16 mm), located on a porcelain tube (3 mm) at a distance of ~ 13 mm, were introduced into a pot centre together with the initial mixture. Melting points were measured on derivatograph Q-1500 (Hungary).

3. Results and discussion

3.1. Solid-state reaction: the crust formation

A strong nodulizing of the mixture happens at the initial moments of the reagents mixing, because particles adhere to each other in contact points, where the surface reaction (1) occurs due to $E_{act} \sim 0$ (Fig. 1). The reaction was reported to finish after some

months [8,9] even carried out in vacuum 10^{-3} torr. As it was revealed with the use of DTA, under these conditions the mixture temperature raises, so heat release reaches $\sim 5\%$ from the maximal values [3]. Upon subsequent accurate mixing, bridges connecting the particles are broken, and the admixture becomes again free-flowing, because all particles are covered by continuous crust of the product, preventing the particles adhering.

Thermocouples introduced in the sample, made for carrying out of OSHS (mass $m = 13.4$ g; atmospheric pressure $p = 1$ atm; molar ratio of the reagents $n = 1:1$; sample diameter $d = 27.5$ mm; height $h = 35.5$ mm; compaction pressure $P = 95$ g/cm²) (Fig. 2), show slow warming up of the admixture to ~ 28 °C that is then replaced by temperature decreasing back to room temperature $T = 22$ °C (Fig. 3(a)). This fact is proved by the DTA data [3].

Evidently, the time, during that crust of sufficient depth is formed (capsulation) to produce diffusive difficulties (i.e. $E_{act} \gg 0$) for the subsequent wave ignition [8], is ~ 20 min. It can be obtained from the location of the curve maximum (Fig. 3(a)). Future results of thermal measurements become reproducible after just that time interval. Otherwise, a sample loses uncontrolled quantity of heat, which is reflected on scatter of the measured combustion macrokinetic parameters.

To ensure the reagents continue to react after their mixing, it is necessary to remove the crust or to make its permeable for reagents. Earlier, it was reached by a thermal impulse melting encapsulated low-melted piperazine, which pass through the product crust and exothermically react with malonic acid crystals. Afterwards, this reaction was self-organized in the wave mode of OSHS [1,3].

Another possible method of ignition studied in the present work is the crust dissolution with a suitable solvent. In this case, for this purpose water was chosen because it well dissolves the both reagents and reaction product.

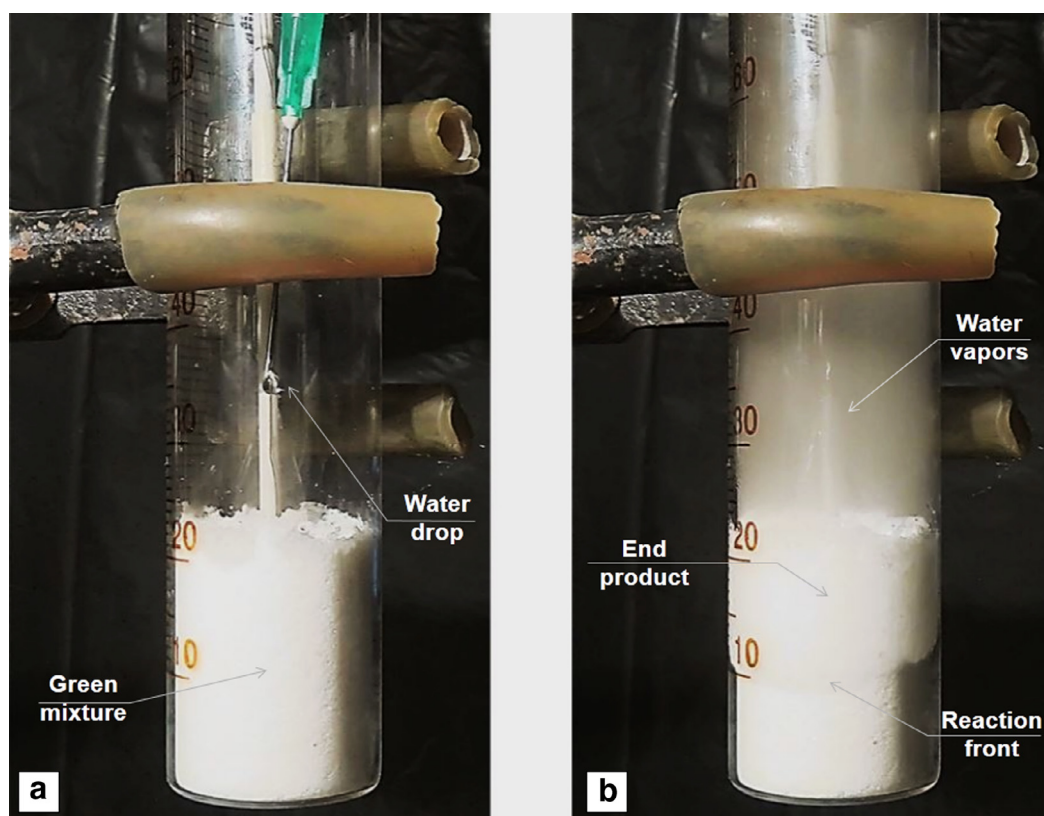


Fig. 2. Photos of the reacting samples. (a) Initiation of OSHS by a water drop; (b) propagation of the OSHS front.

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