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Autowave Exothermic Organic Synthesis in the Mixes of Organic Solids

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SUMMARY: The autowave modes of organic exothermic synthesis in the mixes of organic solids were studied. A traveling wave of exothermic reaction of organic synthesis appeared in the mixes at local thermal ignition. Useful low-molecular organic compounds having, at least, synthetic value were found out with good yields after the reactions. Autowave modes were observed in different classes of organic reactions - red-ox, halogenation, protonation, acylation, imination etc. The possibility to organize the autowave modes is determined by the exothermic nature of the reaction (≥20 kJ/mol), phase condition and thermal stability of the reagents and products. Main peculiarities, kinetics and mechanisms of the reactions in autowave modes were investigated. The basic advantages of autowave exothermic synthesis in organic solids were analyzed.

Introduction

Recently, the stable interest to nonlinear processes in chemical reacting systems is observed. That's determined by theirs unusual properties and good scientific and industrial outlooks. As applied to polymer sciences theirs potentialities appeared in phenomenon of frontal polymerization both in liquid 1) and solid 2) phases. But the last is only particular case of organic synthesis, and the common case is considered in presented article on the base of the short review of author's results.

Since 1986 we have been studying the possibility to organize an autowave mode of organic exothermic synthesis in mixes of organic solids 3-4). This mode is very similar to those in inorganic solids where it was called self-propagating high-temperature synthesis (SHS) and was used for synthesis of wide range of different compounds 5). Therefore we classify abovementioned mode as organic SHS (OSHS). The nearest analogs of OSHS are so named furnace synthesis, exothermic decomposition 6), autowave reactions at low temperature 7),

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topochemical processes [8) etc. carrying out in organic solids. They differ from OSHS by at least one substantial criterion.

We have found out that if to mix the powders of selected organic solids, the mixture to compact as a briquette, than to feed a thermal pulse on a top of a mixture, as a result a propagating wave of exothermic reactions of organic synthesis will appear (Fig. 1). They are not the reactions of decomposition and explosion, in the result of which useless gases, gummy or coking condensed rests are formed. On the contrary, after cooling of the sample, the organic compounds with good yields (about 100 %) are found out, but not any, but having, at least, synthetic or practical value.

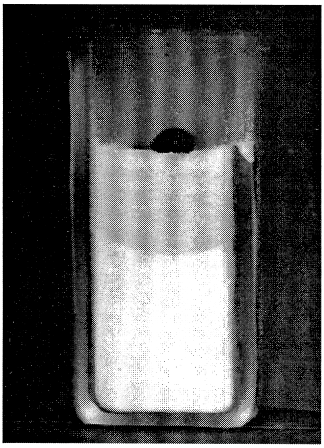

Fig. 1. Reacting sample. Malonic acid/piperazine mix; wave propagates from top to bottom (x1).

Assortment of the reactions

On the Table 1 some processes, according chemical reactions, products and kinetics parameters are presented. There are examples of oxidation [9-10)], protonation [11)], halogenation [9)], oxidation-halogenation [12)], oxidizing imination [13)] and acylation reactions [14)].

The products of OSHS are quinhydrone and quinone, piperazine malonate, organic mono- and dibromoacids, oxy- and chloroderivatives of 8-hydroxyquinoline, triphenylphosphineoxide, triphenyl-N(phenylsulfoyl)phosphinimin, benzenesulfonamide and o-carboxybenzoylferrocene.

The last product is synthesized on the basis of the prototype process developed in the Institute of Organoelemental Chemistry of Russian Academy of Sciences and protected by the patent since 1966 [15)]. Sodium derivative of o-carboxybenzoylferrocene is contained into domestic medicament – ferrocerone, used for therapy of diseases caused by iron deficit in human organism (anemia, paradontose, ozena and other).

Table 1. Investigated systems

No		$\mathbf{u}^*$ mm/s	$\mathbf{T_m}^*$ °C	Ref.
	OXIDATION			
1	$C_6H_6O_2$ + $KBrO_3$ hydroquinone $\rightarrow C_6H_4O_2 \bullet C_6H_6O_2 + KBr + H_2O$ quinhydrone $\rightarrow C_6H_4O_2 + KBr + H_2O$ quinone	0,1	160	9,10
	PROTONATION			
2	$C_4N_2H_{10} + C_3H_4O_4 \longrightarrow C_4N_2H_{10} \bullet C_3H_4O_4$ piperazine malonic acid piperazine malonate	1,4	130	11
	HALOGENATION			
3	$C_3H_4O_4$ + $C_4H_4O_2NBr$ malonic acid N-bromsuccinimide $\rightarrow C_3H_3O_4Br + C_4H_4O_2NH$ brommalonic acid $\rightarrow BrC_2H_3O_2 + CO_2$ bromacetic acid $\rightarrow C_3H_2O_4Br_2 + C_4H_4O_2NH$ dibrommalonic acid $\rightarrow Br_2C_2H_2O_2 + CO_2$ dibromacetic acid	1,0	90	9
	OXIDATION-HALOGENATION			
4	C_9H_7NO + $C_6H_5SO_2NNaCl \bullet 3H_2O$ 8-oxyquinoline chloramine B $\rightarrow C_9H_6NOCl + C_6H_5SO_2NH_2 + NaOH + 2H_2O$ Cl-substituted 8-oxyquinoline $\rightarrow C_9H_7NO_2 \bullet H_2O + C_6H_5SO_2NH_2 + NaCl + H_2O$ 8-oxyquinoline N-oxide hydrate	0,5	110	12
	OXIDATIVE IMINATION			
5	$(C_6H_5)_3P + C_6H_5SO_2NNaCl \bullet 3H_2O$ $\rightarrow (C_6H_5)_3PO + C_6H_5SO_2NH_2 + NaCl + 2H_2O$ triphenylphosphineoxide $\rightarrow (C_6H_5)_3P{=}NSO_2C_6H_5 + NaCl + 3H_2O$ triphenyl-N-(phenylsulfoyl)-phosphinimine	4,9	240	13
	ACYLATION			
6	$(C_5H_5)_2Fe + C_8H_4O_3 \xrightarrow{\text{AlCl3}} C_5H_5FeC_5H_4COC_6H4COOH$ ferrocene phtalic anhydride o-carboxybenzoylferrocene	0,5	185	14

*) **u** is wave velocity, $\mathbf{T_m}$ - maximum temperature in chemical wave

Important is the question - are the OSHS modes widely distributed or not? We answer affirmatively on this question. Indeed, on the Table 1 are presented not all examples of OSHS, and at nowadays we have found out more than thirty such kind of reactions. Moreover, it is necessary to bethink that total number of organic compounds is from 10 to 20 times more than inorganic one, and it permanently increased. Therefore, it should be expected, from the simple probability reasons, that absolute number of useful reactions of OSHS should be quiet large than those in inorganic systems 5).

Undermentioned approach allows us to found and investigate the modes of OSHS.

Basic peculiarities

Differential Thermal Analysis (DTA). As it is known, the main condition of auto-wave mode realization is exothermic nature of the powders mixes. This property of mixes was checked with the help of a Differential Thermal Analysis (DTA). The DTA-curves for powder micromixes (about 100 mg) are shown on Fig.2 in coordinates heat-up-temperature-contents for oxidation reaction No 1 (Table 1).

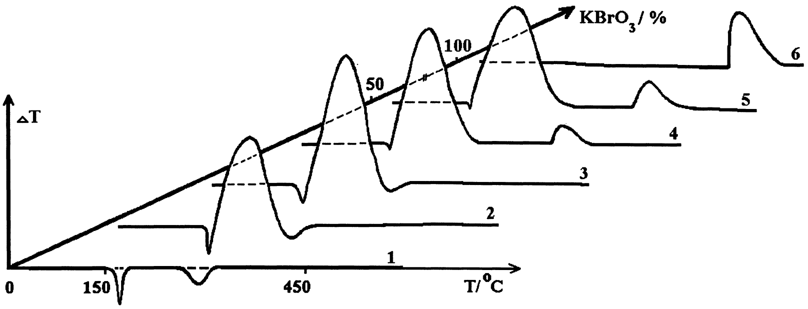

Fig. 2. DTA-curves of hydroquinone and $KBrO_3$ mixes; molar ratio **n**=[hydroquinone] / [$KBrO_3$]=12 for curve 2; **n**=6 for 3; **n**=3 for 4; **n**=1,5 for 5.

One can see that the mix, unlike individual substances, react exothermically. That determines an opportunity to realize an interaction in auto-wave mode. Besides that, the data allow to estimate ignition temperature (about 160 °C) and the vicissitude of the process.

Possibility of the autowave process. After establishing of exothermic nature of the micromixes we tried to organize an auto-wave mode in macromixes of powders (3-10 g), using the known technique. It was shown, that OSHS process is easily initiated by a little pulse of heat. For a mix of piperazine with malonic acid it is about 200 J [11] (Fig. 1). As an initial mix and products have different color (nuances of gray) so reaction product and green mixture are separated each from other by distinct front line.

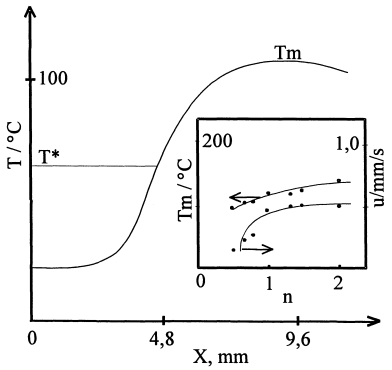

Fig. 3. Temperature profile of chloramine B/8-oxyquinoline reaction; $\mathbf{T_m}$ and **u** dependence on reactants molar ratio (**n**); X – distance along direction of the wave propagation.

Temperature profiles. A thermocouple entered in a reacting sample write a temperature profiles of the auto-wave processes. It is possible to distinguish three zones on the profiles of oxidation-halogenation reaction No 4 (Table 1) - preheating, reaction and cooling zones in which according processes occurs (Fig. 3). The two first zones are separated by the ignition point (**T***), third lie after $\mathbf{T_m}$. Attention should be paid on the $\mathbf{T_m}$ (Table 1) which are much lower then those in inorganic systems [5].

Fig. 4. Microstructure of piperazine malonate synthesized by OSHS

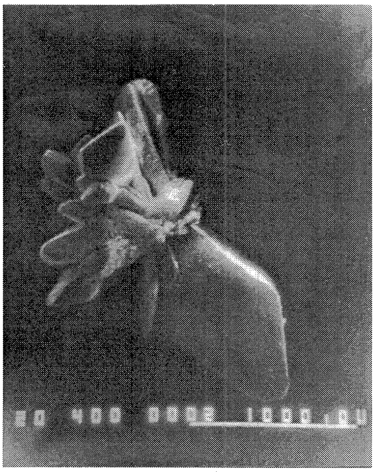

Fig. 5. Microstructure of piperazine malonate synthesized in solvent

Chemical analysis and reactions schemes. For the chemical analysis of reaction products formed all possible methods were used: elemental analysis, the X-ray analysis, NMR, IR-spectroscopy, ESR and so on. With their help the schemes of investigated autowave reactions (Table 1) were established.

Fig. 6. Microstructure of the quenched samples; on the top is end product, on the bottom - green mixture

For the improvement of the mechanisms of autowave reactions there was investigated microstructure of the end product of reaction No 2 (Table 1) (Fig. 4 and 5) and the sample, in which the front of reaction No 4 (Table 1) was arrested by fast cooling in liquid nitrogen (Fig. 6). It is clear that the differences in the form and size of piperazine malonat crystals (Fig. 4 and 5) indicates the conditions of their formation: equilibrium (in solvent) and nonequilibrum (at OSHS) accordingly.

In the quenched samples (Fig. 6) were found out three areas - initial mix, final product and intermediate area, where the particles had partially melted and had spread in mix. The structure of final product is not similar to those for green mixture. It is clear that known mechanism of a capillary spreading [5)] is realized in this case: the low-melting component melts first forming reaction melts, which diffuses in sample pores, formed by a refractory component.

Mechanism of the interaction

On the base of the data obtained it was possible to suppose common mechanism of the interaction at autowave mode. The chemical reaction proceeds insignificantly by the mechanism of surface and gas-phase diffusion in an initial mix at staying it at room temperature, and also in a warming-up zone of the wave, where the reagents have not melted. With this, a crust of a reaction product is formed on a particle's surface. After heating, depending on a ratio of the melting and OSHS temperatures, homogeneous melt or suspension are formed, from which crystals of reaction products appears after cooling.

Advantages of autowave modes in organic solids

The basic advantages of autowave exothermic synthesis in organic solids, in comparison with the traditional methods of organic technologies comes from theirs peculiarities (Table 2).

They are the follows - the possibility of nonequilibrum products and materials synthesis, power and resource saving, intensification and simplicity, caused by an opportunity to avoid usage of heating and mixing devices at the synthesis stage. Cardinal advantage is possibility to avoid usage of organic solvents which are characterized by high volatility, toxicity and ignitability. That determine a possibility to synthesize pure, as well as solvolised substances.

Table 2. Peculiarities of the OSHS

	TECHNOLOGICAL	POWER	OTHER
DVANTAGES	ABSENCE		intensification
	solvents	Exothermic nature	efficiency
	heating		purity
	mixing		ecologisity
LIMITATION	PRESENCE		
	grinding	⇐ spending on	relatively high temperature
	burdening		
	ignition		

Thus, so called "dry" technologies on base of the OSHS should have such qualities as high safety, economical and ecological effectiveness. The scientific interest to organic SHS is caused by the possibility to discover new basic laws in the field of chemistry and physics of nonequilibrum processes in solids. In application to polymer sciences, the mixes reacting in auto-wave modes can appear as good experimental models for frontal polymerization both in solid or liquid phases.

References:

1. N. M. Chechilo, R. J. Khvilivitskii, N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR* (Rus), **204**, 1180, (1972)
2. J. A. Pojman, I. P. Nagy, C. Salter, *J. Am. Chem. Soc.*, **115**, 11044, (1993)
3. E.G. Klimchuk, G.M. Avetisyan, "Method of organic substances producing", application for Author's Certificate No 4360401/04/155339, 16 Oct 1987, (Rus)
4. E.G. Klimchuk, G.M. Avetisyan, "Synthesis of organic substances in mode of self-propagating reaction". Report on VI All-Union school-workshop "Theory and practice of SHS-processes" 21-30 June 1988, Chernogolovka. Program, p.5. Information proceeding 1989, p.50, (Rus)
5. A.G. Merzhanov, *Int.J. of SHS*, **6**, No 2, 119, (1997)
6. A.I. Lesnikovich, S.V. Levchik, A.I. Balabanovich, O.A. Ivashkevich, P.N. Gaponik, *Thermochim. Acta*, **200**, 427, (1992)

7. Barelko V.V. at al., *Adv.Chem. Phys.*, **74**, 339, (1988)
8. J.M. Thomas, S.E. Morsi, J.P. Desvergne, *Adv. Phys. Org. Chem.*, **15**, 64, (1977)
9. E.G. Klimchuk, G.M. Avetisyan, A.G. Merzhanov, *Zhurnal prikladnoi khimii* (Rus), **6**, 1436, (1990)
10. E.G. Klimchuk, G.M. Avetisyan, A.G. Merzhanov, *Doklady Akademii nauk SSSR* (Rus), **311**, No 5, 1161, (1990). (*Doklady Physical chemistry* (Engl.), Apr 01, **311**, No 4/6, 360, (1990)
11. E.G. Klimchuk, A.G. Merzhanov, *Fizika gorenya i vzryva* (Rus), **6**, 104, (1990). (*Combustion, explosion, and shock waves* (Engl), Nov 01, **26**, No 6, 722, 1990)
12. E.G. Klimchuk, G.M. Avetisyan, V.T. Minasyan, A.A. Khodak, K.G. Gazaryan, A.S. Mukasyan, A.G. Merzhanov, *Russ.Chem.Bull.* (Engl), **48**, No 12, 2245, (1999). (*Izvestiya Akademii Nauk. Seriya khimicheskaya* (Rus), No 12, 2271, 1999)
13. E.G. Klimchuk, A.A. Khodak, A.G. Merzhanov, *Russ.Chem.Bull.* (Engl), **48**, No 2, 300, (1999). (*Izvestiya Akademii Nauk. Seriya khimicheskaya* (Rus), No 2, 301, 1999)
14. A.G. Merzhanov, E.G. Klimchuk, V.Kh. Sjundjukuva, V.D. Vilchevskaya, Ju.Ju. Gorelikova, Russian patent No 2080324, 21 Jan 1993. Granted 27 May 1997.
15. A.N. Nesmeyanov, L.G. Bogomolova, N.S. Kochetkova, V.D. Vilchevskaya., N.P. Palitsyn, I.G. Andrianova, O.P. Belozerova, USSR Author's Certificate No 263807, 29 Dec (1966)