Self-propagating high-temperature synthesis in the solid-phase triphenylphosphine—chloramine system

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The macrokinetics and products of self-propagating high-temperature synthesis (SHS) in the solid-phase triphenylphosphine—chloramine system were studied by TGA-DTA, XRD, and ^{31}P NMR techniques. The temperature of SHS ignition (59 °C), the velocity of reaction waves (1.6—5.0 mm s^{-1}), and the maximum temperature (155—239 °C) in the SHS wave were measured. The chemical composition of the product obtained was established: phosphine oxide, triphenyl-*N*-(phenylsulfoyl)-phosphinimine, benzenesulfonamide, NaCl, and water. The scheme of chemical reactions occurring during SHS was proposed.

Key words: organic self-propagating high-temperature synthesis, organic solids, autowave exothermic process, macrokinetics, thermal analysis, triphenylphosphine, chloramine, triphenyl-*N*-(phenylsulfoyl)-phosphinimine.

Previously,[1,2] the principles of self-propagating high-temperature synthesis (SHS)[3—6] were used to perform autowave processes in mixtures of powders of organic substances. The formation of piperazine malonate,[1,7], quinhydrone,[2,8] hydroxyquinoline derivatives,[9,10] chrome acetylacetonate,[11] bromo-derivatives of malonic acid,[2] and *o*-carboxybenzoylferrocene (ferroceron)[12] was studied in the SHS mode. These processes are named as organic SHS.

This work is devoted to the study of regularities of the SHS process in the solid-phase triphenylphosphine (TPP)—chloramine B (CA) system.

Experimental

The procedures of organization of the autowave mode, recording of thermograms, DTA and XRD studies, and processing of experimental data have been described in detail previously.[1,7,9,10] To increase the accuracy of measurements, thermocouples were introduced into the center of the mixture through two holes arranged one above another in the lateral wall of the reaction vessel (Fig. 1).

Powders of triphenylphosphine and chloramine B (trihydrate of sodium salt of monochloramide of benzenesulfonic acid) (analytical purity grade) with a particle size of <0.2 mm were used. The content of chlorine in CA was 13.5% (*cf.* the theoretical value of 13.26%).

A mixture of the initial reagents with different molar ratios [TPP] : [CA] = *n* was carefully blended in a mortar for 0.5—1 min, then placed in a quartz glass ~17 mm in diameter, and compacted with a force of ~0.7 kg cm^{-2}. The mass of the mixture was ~4.5—5 g. SHS was ignited by touching the mixture surface by an electric Nichrome coil heated to a specified temperature (see Fig. 1).

Taking into account that the SHS process and the solid-phase mixture of products obtained are nonequilibrium, we could expect that the chemical and phase compositions of the products would change during isolation of the reaction products with the use of solvents. Therefore, analysis was carried out without separation of the solid-phase product into components.

^{31}P NMR spectra were recorded on a Brucker WP-200SY instrument at a frequency of 81 MHz in ethanol relative to

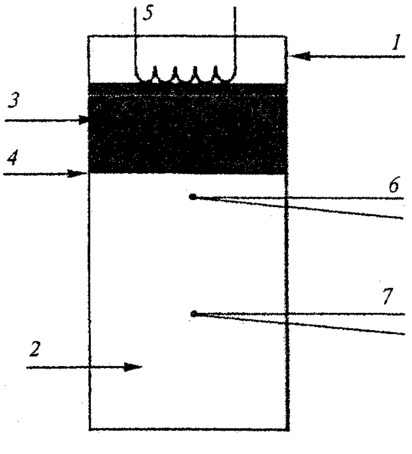

Fig. 1. Scheme of the reaction cell: *1*, quartz glass; *2*, reaction mixture; *3*, SHS product; *4*, reaction front; *5*, initiating coil; *6*, upper thermocouple; and *7*, lower thermocouple.

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35% H_3PO_4. Phosphorus-containing products were identified by the addition of authentic compounds to a solution of the reaction mixture: triphenyl-*N*-(phenylsulfoyl)-phosphinimine synthesized and characterized by the known procedure[13] and triphenylphosphine oxide (analytical purity grade).

Results and Discussion

Reactions of sodium salts of chloramides of sulfonic acids with phosphines (oxidative imination) occur in solutions and lead to the formation of the corresponding imines and NaCl.[14] In the presence of water, benzenesulfamide and phosphine oxide are additionally formed.[15]

The experiments in the SHS mode were preceded by thermal analysis (TGA-DTA) of a microweighed sample of the reaction mixture upon linear heating.[7,10] The endothermic peak of melting with a minimum at 158 °C and the exothermic peak of decomposition with a maximum at 198 °C (Fig. 2, curve *1*) (*cf.* Ref. 16) are seen on the DTA curve of CA. It follows from the TGA data for CA (see Fig. 2, curve *3*) that mass losses (H_2O) begin at 104 °C, and 1.7 moles of H_2O are released gradually to 170 °C. At temperatures above 170 °C, the decomposition is explosion-like (see Fig. 2, curve *3*).

The mixtures of the reagents exothermically interact in the thermal explosion mode at linear heating (see Fig. 2, curve *2*) already at 59 °C *i.e.*, below the melting temperature of TPP (80 °C[17]) and CA. The thermal explosion is preceded by a weak solid-phase endothermic interaction with a minimum of the DTA peak at ~33 °C (see Fig. 2, curve *2*), resulting, most likely, in the nucleation of the eutectic phase.

Comparison of the curves of heat release and mass loss (see Fig. 2, curves *2* and *4*, respectively) suggests that the thermal explosion at the initial stages is accompanied by the sharp rejection of water vapor, whose formation was observed in other systems involving CA.[9,10,13–15] The calculations performed under this assumption show that the amount of released water (6.2%) in the temperature range studied is 1.8 moles per mole of TPP and CA. This is close to the value of mass loss of water measured for CA.

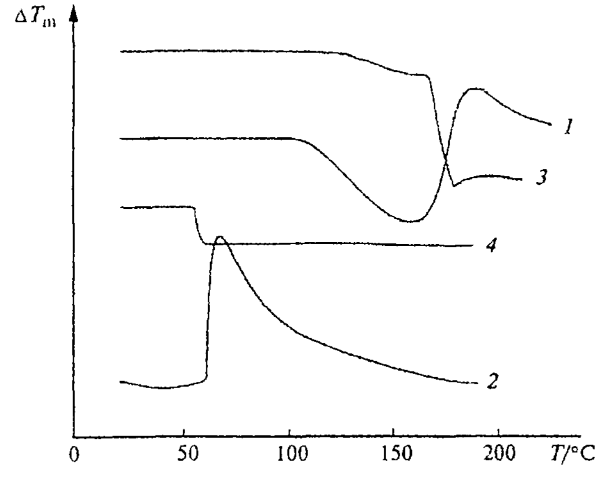

Fig. 2. Derivatogram of the TPP—CA system: *1* and *2*, DTA curves; *3* and *4*, TGA curves; *1* and *3*, CA; *2* and *4*, mixture with $n = 1$; ΔT is differential temperature, *m* is the weight of the sample.

No mass loss is observed directly during the exothermic reaction and below 200 °C (see Fig. 2, curve *4*), which indicates that the reaction occurs in the condensed phase, an excess of the reagents is absent, and the products are thermally stable.

No thermolysis of CA occurs, since the mixture contains no excess of CA, and no inflection points at the temperature of decomposition of CA are observed on the TGA and DTA curves.

The exothermic character of the reaction of TPP and CA powders indicates that the autowave exothermic mode can be performed, in principle, for macroquantities of a mixture of the reagents.[3] The studies show that the SHS process can be easily initiated by a heat pulse of ~120 J at the ignition temperature ≥60 °C established from the DTA data.

The interaction of the reagents is not accompanied by luminescence in the visible spectral region; however, the starting mixture and products have different colors in the

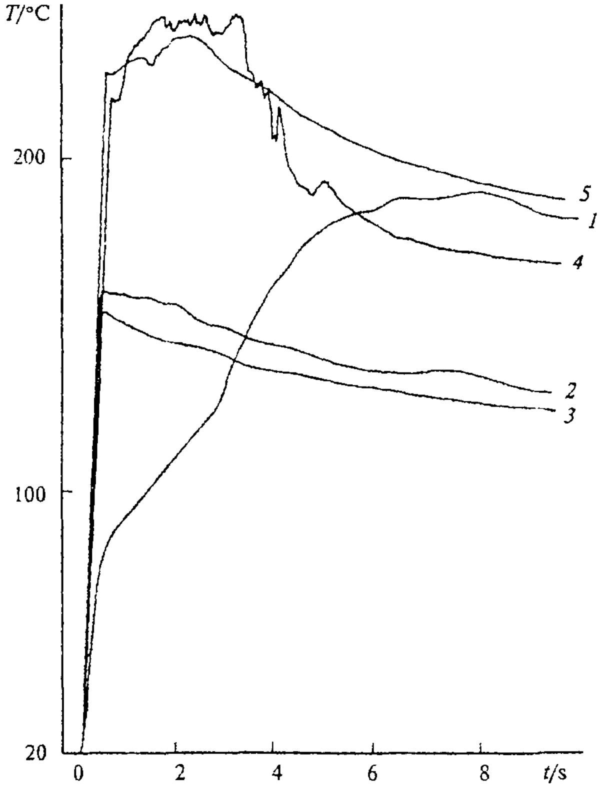

Fig. 3. Temperature profiles of the reaction wave for TPP and CA detected by the upper ($n = 2$ (*1*), 0.5 (*2*), 0.67 (*3*), and 1.0 (*4*)) and lower ($n = 1$ (*5*)) thermocouples.

reflected light (white and orange, respectively). Therefore, the starting blend and final product separated by the reaction front are visually discernible in the sample during SHS. Frothing of the mixture due to water vapor release and insignificant smoke formation are observed during the reaction. The reaction results in caking and shrinkage of the mixture to a uniform resin-like mass.

After the wave passed through the sample, the formation of crystals of the product elongated in the radial direction was observed in several cases. Often no crystallization occurs, probably, due to the formation of supercooled melts.

The temperature profiles of the synthesis wave detected in samples with different molar ratios TPP : CA = n are presented in Fig. 3. When the oxidant is deficient ($n = 2$), the process of heat release occurs in two stages. This is seen from the inflection at 120 °C in the complex temperature profile (see Fig. 3, curve *1*). Frothing of the reaction mass, which occurs at temperatures >100 °C due to water vapor release, appears as temperature fluctuations, which results in a poor detailed reproducibility of the profiles.

At $n < 1$ (excess CA), the ascending lines of the profiles are virtually straight (see Fig. 3, curves *2* and *3*), without discernible isothermic plateau and inflection points. The maximum temperature in the wave (T_m) differs substantially from the initiation temperature, as usually observed in autowave processes, and is achieved within a short time.

Excess CA does not result in the development of side oxidation processes, as observed previously.[9-10] This is seen from the coincidence of the profiles with $n \le 0.67$ (see Fig. 3, curves *2* and *3*). The maximum SHS temperature (155—165 °C) is probably restricted by melting of an excess of CA at 158 °C (see Fig. 2, curve *1*) and, as shown below, of one of the reaction products, triphenylphosphine oxide (153 °C, *cf.* Ref. 16, p. 595).

The highest values of temperature and, hence, heat effect are observed near $n = 1$. The temperature fluctuations caused by frothing of the mixture are seen in the profile detected by the upper thermocouple (see Fig. 3, curve *4*). These fluctuations are less pronounced in the profile of the lower thermocouple (see Fig. 3, curve *5*) due to shrinkage of the mixture. The high rate of temperature increase in the sample (>1000 deg s^{-1}) explains jumpwise mass losses upon thermal explosion (see Fig. 2, curve *4*) when the rate of temperature increase is higher.

The observed values of T_m (Fig. 4, curve *1*) and velocity of the SHS wave (u) (Fig. 4, curve *2*) have the maximum values among the organic systems studied[1,2,7-10] and approach to those in the "low-temperature" inorganic systems (Al—I$_2$ [18]). The maximum values of u and T_m are achieved near $n = 1$, which corresponds to stoichiometry of the reaction when the conversion is maximum.[3]

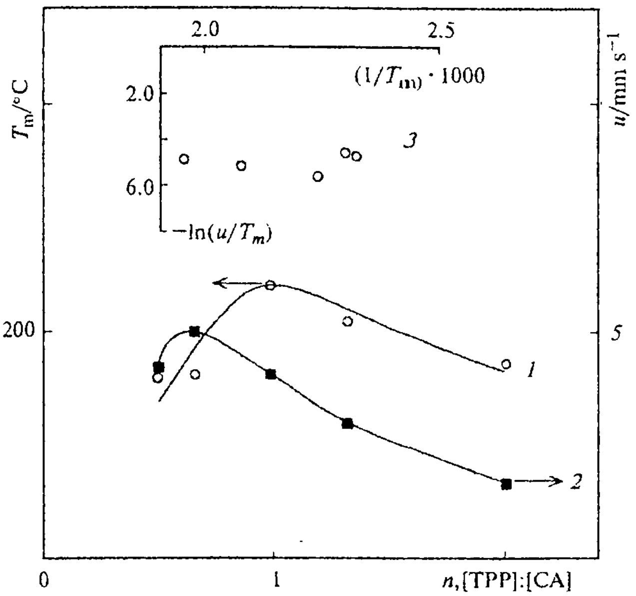

Fig. 4. Dependences of T_m (*1*) and u (*2*) on the composition of the mixture; the dependence of $\ln(u/T_m)$ on T_m (*3*) is shown in the insert.

Distinctions in the shape and amplitudes of the profiles detected by the lower and upper thermocouples are observed in some cases and are not within the error of temperature measurement (±6 °C). The difference between the highest and lowest detected values of T_m can achieve 50—65 °C at $n \ge 1$. At the same time, the error of determination of the u value does not exceed the experimental error (±0.08 mm s^{-1}). The reaction product formed has a laminated structure: the plastic and crystalline parts of the sample have an interface. The change in the SHS mode (nonuniqueness of steady combuction mode[3,19]) is a possible reason for the distinction observed in the profiles.

Presentation of the T_m—u dependence in the $\ln(u/T_m)$—$(1/T_m)$ coordinates makes it possible to estimate the activation energy (E_a) of SHS processes corresponding to the elementary model of combustion of the first kind.[20,21] In the case considered, the E_a value has a conventional character, because deviations from this model are observed. It is seen in Fig. 4 (curve *3*) that the process is activation-free. This agrees with the explosion-like development of the reaction according to the DTA data and with the fact that the mixture begins to vigorously react spontaneously upon careless stirring.

Autowave processes with an activation energy close to zero are a nontypical phenomenon in the theory of explosion and need theoretical consideration. Their possibility may be due to the strong diffusion retardation by reaction products formed on the particle surface during stirring of the powders rather than to the formation of radical species (their existence is highly probable if are takes into account the affinity of CA, triphenylphosphine, and its derivatives to radical formation[9,10,22]) and the liquid phase during SHS. The activation-free regime has been observed previously for SHS in the 8-hydroxyquinoline—CA mixtures with a high content of the latter.[10]

The cast product obtained by SHS is plastic, since it contains some amount of water observed as droplets of the condensate on the cold walls of the glass. Mass losses due to water evaporation during SHS do not exceed several wt.%.

The SHS product after cessation of the reaction is brightly orange and gains a whitish shade after dehydration above $CaCl_2$, probably due to the formation of fine NaCl crystals on the surface. It is water-insoluble, but is soluble in alcohol and acetone and precipitated from solutions with water as a white plastic mass. The color of the solid-phase SHS product is probably related to the formation of unstable complexes that decompose upon exposure to air and water.

The diffraction patterns of the SHS product exhibit reflexes of NaCl and benzenesulfamide, whose formation has been described previously,[13—15] and in the mixtures with $n \neq 1$, an excess of CA or TPP is also observed. The amplitude of reflexes of the latter decreases as n approaches 1, *i.e.*, when the stoichiometric ratio is achieved similarly to that observed previously.[10] The amplitude of reflexes of NaCl increases in the diffraction patterns during the water loss upon dehydration of the SHS product due to crystallization of NaCl.

The ^{31}P NMR method was used to identify phosphorus-containing SHS products. The possibility of changing the composition of the SHS product during its dissolution in ethanol due to solvolysis is virtually absent, since water is one of the products of SHS at temperatures >200 °C.

Only two singlets are observed in the spectra of the samples with $n \leq 1$: triphenylphosphine oxide (TPO) with δ 31.7 and triphenyl-*N*-(phenylsulfoyl)-phosphinimine (TPS) with δ 15.7. At $n > 1$, a singlet (δ 5.3) of the starting TPP appears. When the reference TPS compound is added to solutions of the SHS products in NMR-tubes, only an increase in the amplitude of the signal is observed, which proves the identity of the substances and the absence of solvolysis upon dissolution of the reaction products in ethanol.

When n increases from 0.5 to 1, the relative content of TPO and TPS (in percentage of the total content of phosphorus derivatives) at first remains approximately unchanged and then decreases due to the appearance of an excess of the initial TPP (Fig. 5, curves *1* and *2*). Herewith the TPO : TPS ratio (normalized to the maximum value) remains approximately unchanged at all n, whereas the content of TPO is always higher than the content of TPS.

Thus, the complete conversion of the reagents occurs at their equimolar ratio, and an excess of the reagents at $n \neq 1$ remains chemically inert at the temperature of the reaction and does not result in the development of secondary exothermic processes. These facts allows the absolute content of reaction products to be calculated.

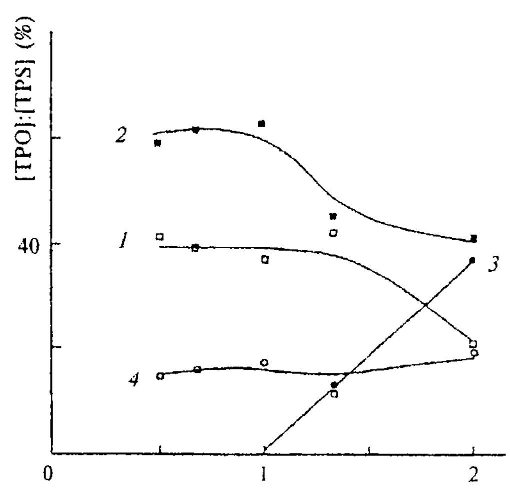

Fig. 5. Dependence of the content of phosphorus-containing products on n: *1*, TPS (%), *2*, TPO (%), *3*, TPP (%), and *4*, TPO : TPS (rel. units).

Taking into account the data obtained and using an analogy with the known works,[13—15] we can suggest the scheme of formation of phosphorus-containing products upon SHS:

$$Ph_3P + PhSO_2NNaCl \cdot 3\ H_2O \longrightarrow$$

$$\begin{cases} \to Ph_3P{=}NSO_2Ph + NaCl + 3\ H_2O \\ \to Ph_3P{=}O + PhSO_2NH_2 + 2\ H_2O + NaCl \end{cases} \quad (1)$$

Two mechanisms of TPS formation are possible for oxidative imination in solvents.[23] One of them assumes the direct reaction of reagent molecules. In this case, TPO appears upon the subsequent hydrolysis of TPS

$$Ph_3P{=}NSO_2Ph + H_2O \longrightarrow Ph_3P{=}O + PhSO_2NH_2 \quad (2)$$

or direct oxidation of TPP by chloramine, which reacts according to the formal scheme:[24]

$$PhSO_2NNaCl \cdot 3\ H_2O \longrightarrow PhSO_2NH_2 + NaOCl + 2\ H_2O, \quad (3)$$

$$NaOCl + Ph_3P \longrightarrow Ph_3P{=}O + NaCl.$$

The second mechanism suggests the reaction of benzenesulfamide with the TPO formed *via* the reaction inverse to reaction (2).

The mechanisms offered for oxidative imination in solutions do not contradict the experimental data obtained by us and can be used for their interpretation. However, it should be taken into account that there is no correlation, in the general case, between processes of organic SHS and reactions in solutions, since different products can be obtained from the same reagents in different solvents. For example, hydrate of piperazine malonate is the product of the reaction of piperazine and malonic acid in aqueous solutions,[25] whereas the anhydrous salt is formed in SHS;[7] quinhydrone is the product of the oxidation of hydroquinone by potassium bromate,[2] but it is benzoquinone in an aqueous medium.[26]

Thus, this study shows that it is possible, in principle, to produce organophosphorus compounds by the SHS method. This process, as well as those studied previously,[1,2,7–10] occurs with high conversion. The difference is in the relatively high maximum temperature (to 250 °C) and velocity of the wave of organic SHS.

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