

THERMOLYSIS OF POTASSIUM TETRAPEROXOCHROMATE(V). III. SELF-PROPAGATION REGIME

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ABSTRACT

The phenomenon of self-propagating high-temperature decomposition (SHD) is distinguished in the combustion of condensed substances. K_3CrO_8 is found to follow such a decomposition. The results of an experimental study of this substance are analyzed using the models of exothermal conversion wave propagation in a condensed phase. Of all the known elementary models, the second kind of model considered for high-temperature melting of the reaction product has proved to be the most suitable. This model gives a general idea of the fundamental physical and chemical processes in K_3CrO_8 SHD. Further improvement of the model requires that gas evolution should be included. The kinetic characteristics of K_3CrO_8 thermolysis agree with the SHD rate measurement results. However, the accuracy of estimating these characteristics (within conventional accuracy) is insufficient for independent discrimination of the models and quantitative calculation of the SHD rate.

INTRODUCTION

Parts I and II of this communication dealt with the kinetics and mechanism of thermal decomposition of K_3CrO_8 under isothermal conditions [1] and linear temperature rise [2], respectively. In particular, it was found that, irrespective of the thermolysis conditions, the kinetics of K_3CrO_8 decomposition are governed by the first-order equation for autocatalytic reactions.

The values obtained from non-isothermal experimental data for the activation energy (E) and pre-exponential factor (A) agree, within the errors, with the measurement results for isothermal conditions and are invariant values for the experimental conditions. In ref. 2, Arrhenius parameters with the least error were found to be E (kJ mol^{-1}) = 58.6 ± 6.7 ; $\log A$ (s^{-1}) = 5.5 ± 0.8 , and will be used in the following.

This paper concerns the study of the self-propagating high-temperature decomposition (SHD) of K_3CrO_8 that has been found to occur in the combustion of condensed substances [3].

SHD

An original version of combustion, self-propagating high-temperature synthesis, has recently been found and is now widely studied [4]. The high technological capabilities of such a synthesis make it attractive to researchers and practical workers. Studies of self-propagating high-temperature synthesis reveal the existence of so far unstudied or insufficiently studied phenomena in such an old field as combustion. These include the SHD of condensed substances characterized as follows:

- (1) SHD is a variety of combustion or deflagration;
- (2) SHD is not accompanied by reactions in the gas phase and has no flame;
- (3) there is no dispersion of the initial substance in the course of SHD that hampers complete conversion of the substance.

The first characteristic makes SHD different from ordinary exothermal decomposition, which requires a permanent heat supply from an external source and proceeds at a temperature approximately equal to that of the source. The second characteristic distinguishes combustion processes with no gas-phase reactions. Along with reactions in the condensed phase, they are known to be important in the combustion of powders, mixed solid fuels, explosives (including individual chemical compounds, e.g., ammonium perchlorate) and other compounds. For these processes, SHD may model reactions in the condensed phase and thus be of certain interest. Following the third characteristic, the process must be completed, while in many cases of flameless combustion (e.g., of mercury fulminate combustion in vacuum [5]) the initial sample is greatly dispersed and such combustion cannot be regarded as a complete decomposition. Note that characteristic (3) does not impose restrictions on the dispersion of the reaction product with the flow of generated gas.

It is difficult to solve the problem of possible individual combustion of condensed substances theoretically especially so for SHD. The stability of combustion is determined by the Zeldovich criterion [6]. The combustion theory also provides sufficient and required conditions for combustion wave propagation [7]. However, they can hardly be determined for condensed substances in practice [8]. Such simple criteria as the value of the thermal effect, Q , are groundless and inconclusive. The estimation of the adiabatic combustion temperature, T_{ad} , is more effective, yet it still does not give a unique value for a wide intermediate range of temperatures. In this case the problem can only be solved empirically [8]. Thus, there are actually no criteria that might reliably be used to determine the ability of a substance to SHD. As the theory states for combustion wave propagation, a rather high E value is required to satisfy the following condition for the Zeldovich number: $(T_b - T_0)E/RT_b^2 \gg 1$ (where T_b is the combustion temperature; and T_0 is the initial temperature). Note that, with no dispersion, the burning

of solids, with the leading reaction in the condensed phase and gas evolution, resulting in the formation of a solid porous skeleton is essentially unsteady [9].

The search for substances with SHD characteristics has revealed only a few such substances, since the majority of decomposing substances, which can burn due to their own components, evolve into the gas phase both as reactive oxidizer and reductant whose interaction can hardly be excluded a priori, if at all. Even such a priming explosive as mercury fulminate has a visible flame during steady combustion under pressure [5]. Liquid hydrazine has a decomposition flame in the gas phase [5]. The monograph of ref. 5 reports data on $\text{Ca}(\text{N}_3)_2$ and $\text{Ba}(\text{N}_3)_2$ combustion. SHD seems to take place in some azides. This property may also appear in case of some peroxide compounds. Many unstable substances prove to be incapable of SHD because they tend to detonate; i.e., explosive Ag_2C_2 -type acetylides and explosive azides (of iodine, lead, etc.).

The above control tests have demonstrated that combustion at atmospheric pressure is atypical of pressed KClO_4 , NaN_3 and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, although under certain conditions ammonia salts of chromic acids are capable of burning [10]. K_3CrO_8 as a pressed pellet is capable of independent SHD-type burning. No self-propagating decomposition has been observed for the loose compound, the decomposition area concentrated only adjacent to the igniter. It is interesting that K_3TaO_8 and K_3NbO_8 , close analogs of K_3CrO_8 , did not show an ability to SHD.

THEORETICAL SHD MODELS

It is very difficult to develop and mathematically describe a physical SHD model that would be completely consistent with reality. Elementary models are well known in the combustion theory assuming that the burning rate is determined by one stage which takes place in the leading zone. Models exist for the combustion of volatile substances, for those turning into gas upon decomposition, for gasless combustion, for combustion taking into account dispersion, etc. [11]. The most practically important condensed systems are characterized by multi-region combustion [12], which generally requires a combination of the elementary combustion models, allowing for their interaction and changing combustion regimes. Hence, problems concerning the role of processes in the gas and condensed phase, as well as of diffusion and kinetic regimes, are still debatable. In practice, it is difficult to estimate their contribution to combustion. Some ideas concerning these contributions can be understood from an analysis of the time parameters of reaction and diffusion in the granular-diffusion model [13], and of the parameters of the burning rate power law [14,15].

The difficulties of a qualitative description of combustion are due to a

paradox that alternative combustion models with the leading reaction in the gas and condensed phases can be applied to one and the same combustible condensed system. The ambiguous description of condensed substance combustion in this case is similar to the formal kinetics of solid-phase reactions when different kinetic equations are applied to one and the same reaction.

In the case of K_3CrO_8 SHD, the problem is more simple because gas-phase reactions are excluded a priori from the main process. It is therefore natural when describing SHD to rely upon models with the leading reaction in the condensed phase.

Models for exothermal reaction front propagation in condensed medium, including reaction kinetics, were obtained in ref. 16. The autocatalytic first-order reaction, including a monomolecular stage (1) and a catalytic stage (2), is of the form

$$u^2 = \left[\lambda RT_b^2 A_2 \exp(-E_2/RT_b) \right] / \left\{ \rho Q E_2 \ln \left[1 + (A_2/A_1) \exp[-(E_2 - E_1)/RT_b] \right] \right\} \left\{ \ln \left[1 + (A_2/A_1) \exp[-(E_2 - E_1)/RT_b] \right] \right\}^{(E_1/E_2)-1} \quad (1)$$

where u is the linear burning rate; λ is the thermal conductivity; and ρ is the density.

Model (2) of flameless combustion [17], which was also used in more complex mixed fuels [18], is expressed as

$$u^2 = \frac{2\lambda T_s^2 R Q A \exp(-E/RT_s)}{\rho c_p^2 (T_s - T_0)^2 E} \quad (2)$$

where T_s is the surface combustion temperature and c_p is the heat capacity. In the model, u vs. external pressure (P) is determined by T_s vs. P following the condition of dissociation equilibrium of subliming substances, e.g., ammonium perchlorate. The thermal decomposition of KO_2 (at atmospheric pressure between 773 and 823 K [19], including melting) is the stage that may be affected by the ambient pressure in the total K_3CrO_8 SHD process.

The difference between models (1) and (2) is not only in the kinetic function $f(\alpha)$, but of most importance is the difference in T_b and T_s , and in the degree of transformation; $\alpha = 1$ (1) and $\alpha = \alpha_s$ (2), $c_p(T_s - T_0)/Q = \alpha_s$. The differences in T and α underline the division of the combustion models as first- and second-kind models. In general, the second-kind models are expressed as [20]

$$u^2 = \frac{\lambda RT_s^2 A \exp(-E/RT_s)}{\rho Q E \psi(\alpha_s)} \quad (3)$$

where α_s is the degree of transformation on the combustion surface, and

$$\psi(\alpha_s) = \int_0^{\alpha_s} \frac{\alpha_s - \alpha}{f(\alpha)} d\alpha$$

In eqn. (2), $f(\alpha) = 1$ (zero-order reaction). At $T_s \rightarrow T_b$ and $\alpha_s \rightarrow 1$, they become the first-kind models.

Models intermediate between the first- and second-kind models can be developed. These describe combustion with wide reaction regions due to decelerated heat release. In these cases, the combustion rate is determined by the values of T and α achieved on the boundary of rapid and slow heat release sub-regions rather than by the maximum combustion temperature [21].

Proceeding from general considerations, these models may be used to describe SHD. For their further selection and specification, experimental study is needed.

EXPERIMENTAL

Fine-crystal powdered K_3CrO_8 , with a crystal size of $\leq 50 \mu\text{m}$, was used in the experiments. The powder was pressed to obtain cylindrical charges (10, 15 and 20 mm in diameter and 15–20 mm high) at a pressure of $3 \times 10^8 \text{ N m}^{-2}$, which ensured a substance density of 1.12 g cm^{-3} . The samples 10 mm in diameter burnt at atmospheric pressure at a somewhat higher rate than the other samples. Therefore, to allow butt-end combustion of the samples, the side surfaces of the samples were covered with several layers of glue containing a water/ CaCO_3 suspension. SHD was initiated by an incandescent Ni–Cr alloy filament. The SHD rate was measured in 3-l nitrogen bomb at 0.1–10 MPa. The SHD time was recorded tensometrically by a relatively small pressure increase in the bomb and then measured by the tensor probe signal registered on a light-beam oscillograph to within 0.01 s. To record the temperature profile in the SHD wave, a chromel–alumel thermocouple with $30 \mu\text{m}$ diameter wire was pressed into the charge. To protect the thermocouple against oxidation, it was covered with a thin layer of silicon varnish stable up to 1500 K. The thermocouple provided a high accuracy and reproducibility in control graduation experiments. The thermocouple signal was recorded on the light-beam oscillograph. Six experiments showed a $\pm 30 \text{ K}$ accuracy in the temperature measurements.

The heat of K_3CrO_8 decomposition was measured on a DSC-1B (Perkin-Elmer) differential scanning calorimeter in argon atmosphere. Indium was used as a reference substance. X-ray diffraction was performed as in ref. 1.

RESULTS

Figure 1 includes a photograph of the starting dark-brown pressed K_3CrO_8 sample (Fig. 1a) and of the sample photographed during SHD reaction (Fig.

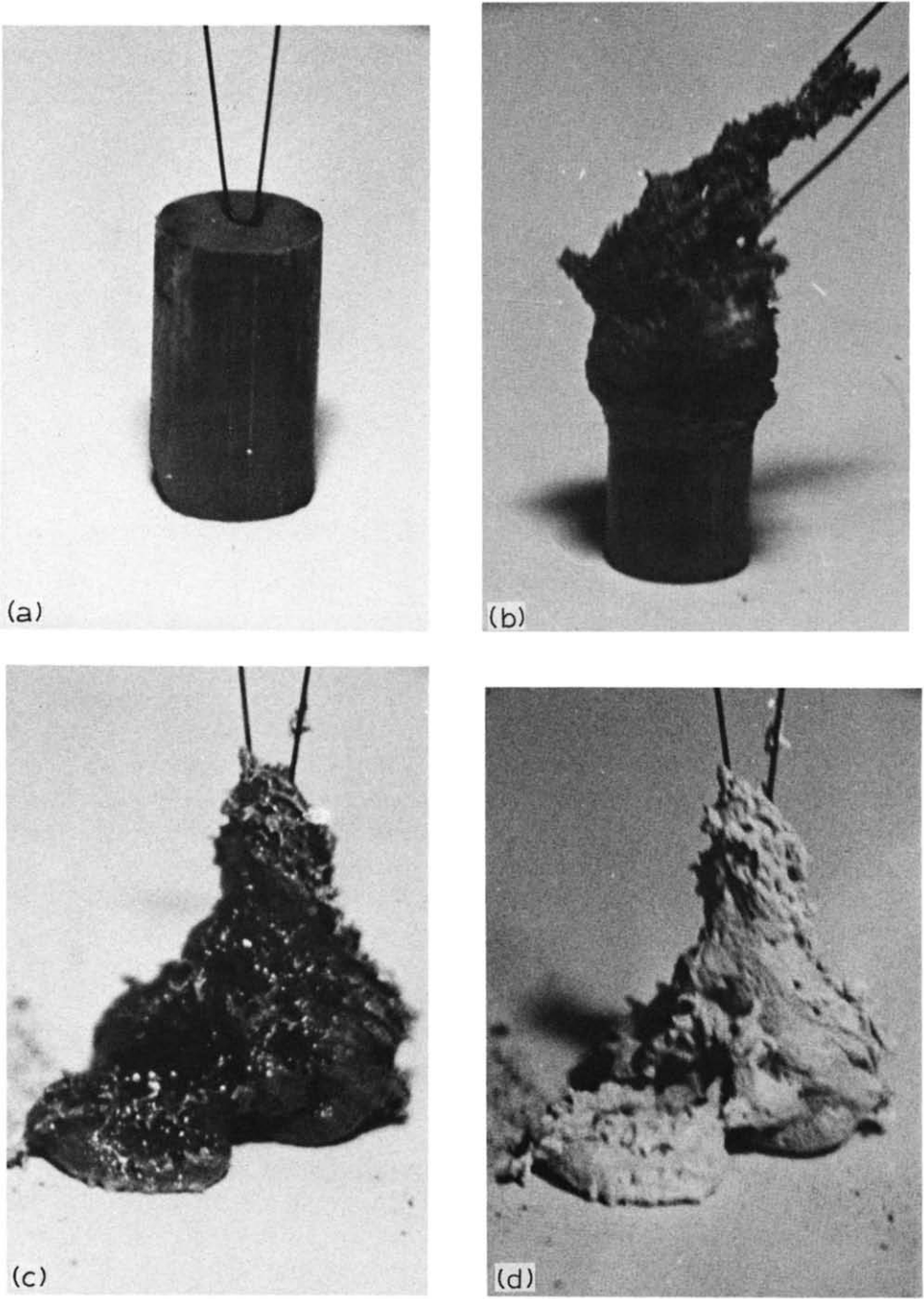


Fig. 1. K_3CrO_8 sample (without glue coating): (a) initial sample with ignition filament; (b) at SHD stage (elongated portion by the ignition filament formed in the course of SHD initiation); (c) SHD product with melt characteristics; (d) SHD product after cooling.

1b). The SHD product is a viscous brown liquid (Fig. 1c) that becomes bright yellow upon solidification and cooling to room temperature (Fig. 1d). When dark, red glowing can be seen in the portion of the sample where SHD took place. When the SHD product layer adjacent to the combustion surface is stripped by a gas flow, multiple small "sparks" can be seen against a luminous background in the dark.

The photographs do not show a significant scatter (typical dispersion) of the starting sample during K_3CrO_8 SHD. Only some splashes of the SHD product are observed. This may be attributed to the high viscosity of the melt formed during SHD, and to the comparatively low gas evolution. In Fig. 2 the X-ray results for K_3CrO_8 SHD products are given. A comparison with the X-ray diagram of ordinary K_3CrO_8 thermolysis products [1] shows that the main decomposition products are identical in both processes. Hence, the SHD process for K_3CrO_8 proceeds mainly as



However, the lines of non-identified phases indicate that the main reaction involves further transformations of the products, perhaps of KO_2 . According to ref. 22, on heating KO_2 even to about 400 K, brownish-orange products of the disproportionation $4 KO_2 \rightleftharpoons K_2O_3 + K_2O_5$ appear, which are stable above 870 K. This disproportionation is evidenced by the change of SHD products on cooling from brown to bright yellow. Also, as noted above, at temperatures of ~ 800 K, KO_2 starts to decompose and generate O_2 . The formation of these reaction products, and solid solutions with high-temperature modifications of K_2CrO_4 and KO_2 (rapid enantiomorphous transition $\alpha-KO_2 \rightleftharpoons \beta-KO_2$ proceeds at 350–415 K [23]) resulting in extra lines on the X-ray diagram changes their intensity ratios and causes a shift in some lines.

The DSC measurements give a Q value for K_3CrO_8 thermolysis of ~ 1322 $J g^{-1}$. The K_3CrO_8 heat capacity is estimated by the number of atoms in the compound [24] and assumed to be $1.13 J g^{-1} K^{-1}$. These data yield the adiabatic temperature of SHD for K_3CrO_8 to be $T_{ad} \approx 1465$ K.

The K_3CrO_8 combustion rate at atmospheric pressure (samples 15 and 20 mm in diameter) is 21 ± 2.5 $mm s^{-1}$. In nitrogen at 2–10 MPa it is approximately governed by the power law $u = BP^{\nu} = 1.46 P^{0.18}$ (Fig. 3).

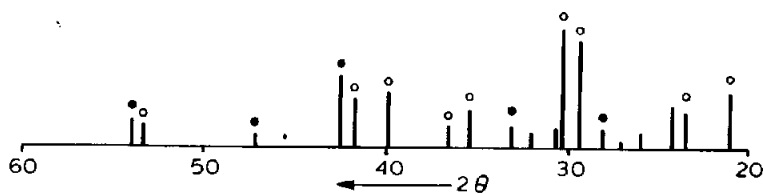


Fig. 2. Dashed roentgenograms of the K_3CrO_8 product of SHD: (●) KO_2 ; (○) K_2CrO_4 .

Figure 4 presents the temperature profile of the SHD wave in K_3CrO_8 . It is characterized by a plateau at 900 K, where the temperature again increases to ~ 1000 K resulting in a thermocouple failure, perhaps due to mechanical stresses. The heating zone before the reaction is established is relatively small. The plateau may be attributed to KO_2 melting, the exact temperature of which is unknown, because of its simultaneous decomposition. Extrapolation yielded $T_{melt} \approx 820$ K [19]. Using this T_{melt} value, its heat of melting has been approximated to 404 J g^{-1} . One more endothermic process, namely the polymorphous conversion of K_2CrO_4 (938 K, $\Delta H_{trans} = 52.7 \text{ J g}^{-1}$ [25]), is possible within the plateau. The heat consumption for the above processes and KO_2 decomposition results in the maximum combustion temperature being slightly different from the T_{melt} of K_2CrO_4 (1253 K, $\Delta H_{melt} = 150 \text{ J g}^{-1}$ [25]).

In Table 1 the K_3CrO_8 SHD rates calculated using the elementary models for conditions corresponding to the processes in air are given. The kinetic parameters are taken from earlier works [1,2]. The autocatalytic behaviour of K_3CrO_8 decomposition was taken into account, following model (1) [26], by the first-order autocatalytic equation $d\alpha/dt = A_1 \exp(-E_1/RT)(1 - \alpha) +$

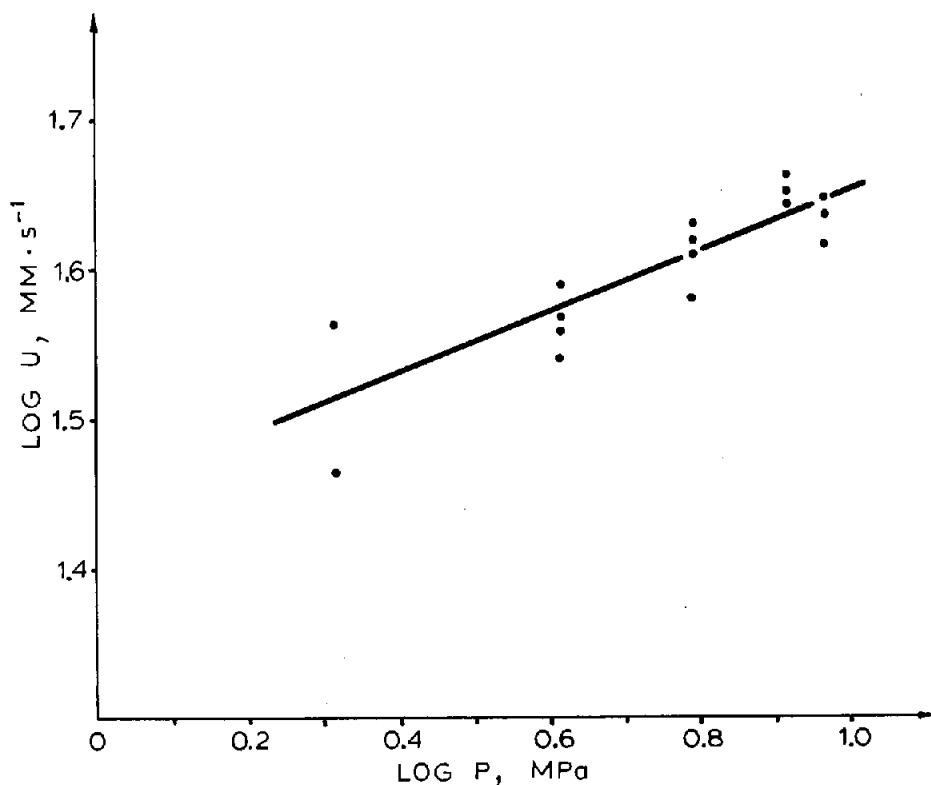


Fig. 3. Log u vs. log P for SHD of K_3CrO_8 .

$A_2 \exp(-E_2/RT)\alpha(1-\alpha)$ which for $E_1 = E_2$ reduces to $d\alpha/dt = k_2(1-\alpha)(A_1/A_2 + \alpha)$ and at $A_1 = A_2$ reduces to $d\alpha/dt = k(1-\alpha^2)$. The kinetic functions $f(\alpha) = 1$, $1-\alpha^2$, $(1-\alpha)^n$ and α^{-1} , which, although they do not describe the autocatalytic acceleration of K_3CrO_8 decomposition, were used to define how the change in $f(\alpha)$ under combustion or the error in choosing $f(\alpha)$ affects the combustion rate.

The first-kind models used $T = T_{ad}$ and $T = T_s$. It was assumed in the latter case that K_2CrO_4 gave fusible eutectics and Q was equal to the experimental thermal effect of K_3CrO_8 thermolysis, minus the heats of KO_2 melting, of polymorphous transformation and K_2CrO_4 melting, i.e., $Q \approx 715 \text{ J g}^{-1}$. This value of Q and a T value of $\sim 900 \text{ K}$, correspond to $\alpha \approx 1$, which is required in first-kind models. Finally, there is a third possibility for these models implying that neither eutectics are formed, nor the T_{melt} of K_2CrO_4 is achieved. Then $Q \approx 1322 - 404 - 52.7 = 865.3 \text{ J g}^{-1}$ and $T_b = 1060 \text{ K}$.

The values of E and $\log A$ cited in Table 1 correspond to the centre and limits of the confidence interval found in ref. 2. By using these values we have considered that the confidence interval for the factors $\log A$ and E has an extended elliptical shape (the compensation effect, CE [27]) and, there-

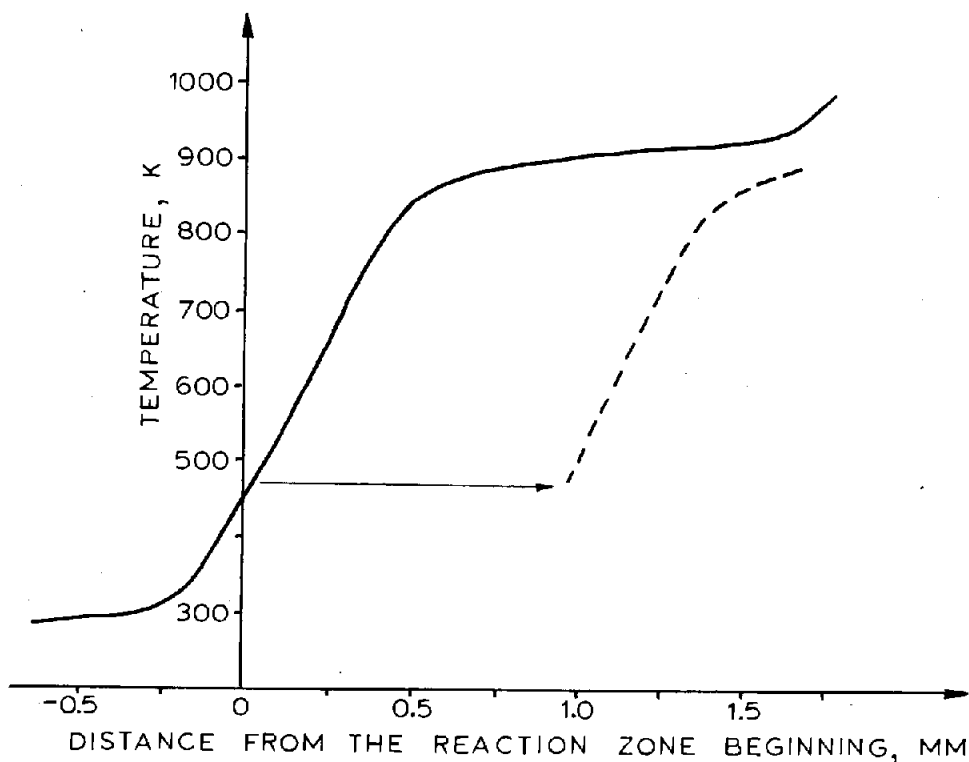


Fig. 4. Temperature variation with SHD wave in K_3CrO_8 . (→) Particle evolution into melt; (- - - -) further temperature change during decomposition of these particles.

fore, the combinations of maximum E with minimum A or vice versa are groundless. As Table 1 shows (lines 4 and 5), such combinations result in up to a 20-fold change in u , i.e., the calculation of u becomes meaningless. The inclusions of the compensation effect gives a 10-fold reduction of the scatter in u values, i.e., on the limits of the confidence interval for $\log A$ and E gives a u value of ~ 2 ($T = T_s$) and ~ 3 ($T = T_{ad}$) times different. Due to the above errors, however, this uncertainty range for u also overlaps the range of u values caused by changes in the theoretical model of combustion or kinetic function. Thus, the experimental value of the rate $u = 21 \pm 2.5$ is satisfied by first-kind autocatalytic model, $f(\alpha) = 1 - \alpha$ and $1 - \alpha^2$ and second-kind autocatalytic model, $f(\alpha) = 1$, $1 - \alpha$, $1 - \alpha^2$, and α^{-1} . Hence, even if the calculation of u by the elementary models is assumed to be in good agreement with experiment, the errors in the estimates of A , E and T eliminate the differences between models for K_3CrO_8 SHD. Only the experimental data, especially temperature measurements in the SHD wave, pointing to the existence of a horizontal section that ends with T growth, have permitted a conclusion about the realization of second-kind model with the high-temperature melting of an SHD product.

The difference in the effect on u of some kinetic functions is small even if A and E are constant (Table 1, second-kind model). However, three groups of functions, $f(\alpha)$, may be distinguished. The first group, $f(\alpha) = 1$, $1 - \alpha$, $(1 - \alpha)^2$, and $1 - \alpha^2$ at the upper limit of A , E and T_s gives u values close to experimental ones. The second group, represented by $f(\alpha) = \alpha^{-1}$, is at the lower limit. The third group includes autocatalytic functions with $A_1/A_2 \approx 0.01$ and gives u values close to experimental ones at mean values of the kinetic parameters. The first and third group of functions are most suitable for SHD of K_3CrO_8 . The second group (and those similar to it) reflect the hyperbolic law of metal oxidation [28] and does not agree with the mechanism of K_3CrO_8 thermolysis. It should be noted that the implementation of second-kind model with high-temperature melting makes it possible to define $f(\alpha)$ from combustion data [8]. To do so, it is necessary to analyse the dependence of u on α_s , varying α_s by changing T_0 or diluting the initial substance with the reaction products. We have analysed such a possibility for K_3CrO_8 . In Fig. 5, the dependence of the ratio $1/\sqrt{[\psi_1(\alpha_s)]}$ (proportional to u) to $1/\sqrt{[\psi_1(\alpha_s)]}$ on α_s for the first-order reaction is presented. It is seen from Fig. 5 that for $\alpha_s = 0.4-0.7$ the form of curves for different $f(\alpha)$ differs only slightly. Incidentally, this range of α_s requires that T_0 be changed from approximately 430 (i.e., from the temperature at which K_3CrO_8 decomposes intensively) to 80 K. It is also very difficult to dilute K_3CrO_8 with SHD products containing components that interact with CO_2 and H_2O . Figure 5 proves that for α_s values near 0.5 it is advisable to discriminate $f(\alpha)$ by the quantitative value of $1/\sqrt{[\psi_1(\alpha_s)]}$ or u , which is discussed below.

Because of the comparatively low sensitivity of the combustion rate of the form of $f(\alpha)$ within the first group of these functions, the invariant \hat{A} and \hat{E}

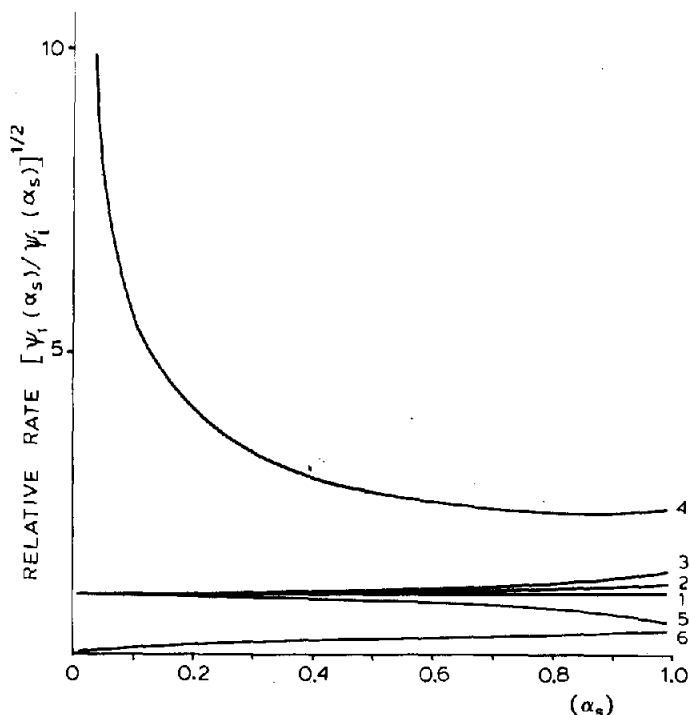


Fig. 5. Predicted relative SHD rate vs. decomposition degree α_s : (1) $f(\alpha) = 1 - \alpha$; (2) $f(\alpha) = 1 - \alpha^2$; (3) $f(\alpha) = 1$; (4) $f(\alpha) = \alpha^{-1}$; (5) $f(\alpha) = (1 - \alpha)^2$; (6) autocatalysis $A_1/A_2 = 0.003$; $E_1 = E_2$.

values [2] found in thermolysis experiments may be used in the appropriate SHD model for any probable $f(\alpha)$ of this group, provided this group includes $\hat{f}(\alpha)$, i.e., the kinetic function consistent with \hat{A} and \hat{E} [2]. In other words, insignificant changes in the decomposition kinetics of SHD (as compared with ordinary thermolysis) may be neglected in calculations of u .

In the following [1,2], K_3CrO_8 thermolysis is described by the first-order autocatalytic equation. SHD autocatalytic functions also give u values close to experimental ones: $f(\alpha) = 1 - \alpha^2$ corresponding to the degenerate autocatalysis yields a u value close to the measured one provided $\log A = 6.3$ and $E = 65.3$, and with different values of the pre-exponential factor for monomolecular ($\log A_1 = 5$) and catalytic ($\log A_2 = 7$) reactions provided $E_1 = E_2 = 58.6$.

DISCUSSION

The experimental data show that at SHD of K_3CrO_8 the condition required for the propagation of the exothermal reaction front, $(T_s - T_0)E/RT_s^2 \approx 5 \gg 1$, is fulfilled. The values of Q and E for K_3CrO_8 make the SHD possible. With decreasing Q value, the value of T_s , other conditions

being equal, decreases and for more stable K_3TaO_8 and K_3NbO_8 the required condition is probably not satisfied although the value of E is high [29].

A noticeable scatter of the predicted rates of SHD for K_3CrO_8 due to the errors in the estimation of E and A allows neither discrimination of SHD models nor the use of the data on the variation of kinetic characteristics (when introducing additives, changing pressure, etc.) when estimating the effect of this change on the SHD rate. In the case of SHD for K_3CrO_8 , the situation is unfavourable, as with the ordinary absolute values of the errors in $\log A$ and E the relative errors due to the low values of $\log A$ and E prove to be rather high. However, at large A and E values, the errors in their estimation together with the errors in T and u lead to the estimation of the order of magnitude alone. Note that the exact values of A and E often reported in the literature for solid-phase reactions should not delude us, since they only characterize the reproducibility of the results within the chosen method and do not give the systematic error of the method. However, the problem of high sensitivity of the characteristics to the errors in A and E values undoubtedly does not only concern u [30]. Since there are no grounds that the accuracy of estimation of kinetic characteristics can be essentially increased without appreciable changes in the form of the temperature dependence of the reaction rate, then the SHD models, like other combustion situations, must be found by analysing the set of experimental events. Upon choosing the model, the kinetic characteristics of the leading SHD reaction would be specified by matching. However, the elementary models do not completely represent the complicated process, and such matching will not, therefore, permit the statement that the kinetic characteristics change due to the SHD regime rather than to the model's inadequacy. In the case of K_3CrO_8 , such matching allows the assumption that SHD is characterized by degenerate autocatalysis and somewhat higher values of A and E than the ordinary thermolysis of the salt. These values, however, are not the upper limit of the confidence interval, obtained for K_3CrO_8 thermolysis, and the assumption that the catalysis is degenerate is consistent with close values A_1 and A_2 , E_1 and E_2 [1]. Such degeneration may favour practical elimination of the diffusion effect on nucleation [1] in the SHD regime (due to high SHD rate).

The elementary SHD model for K_3CrO_8 as a second-kind model with high-temperature product melting does not represent the process quantitatively but makes it possible to understand its physicochemical essence. KO_2 melting and K_2CrO_4 polymorphous transformation start at the degree of K_3CrO_8 decomposition $\alpha_s = (T_s - T_0)c/Q \approx 0.52$. Within the temperature profile plateau (Fig. 4), the accumulated and forming KO_2 and K_2CrO_4 are transformed. By the time of repeated temperature growth, the accumulated KO_2 and K_2CrO_4 seem to have completely undergone the above transformations. The newly formed KO_2 and K_2CrO_4 are generated as high-temper-

ature phases. The heat of KO_2 melting (and K_2CrO_4 phase transition) is below the Q value of K_3CrO_8 decomposition; therefore, the repeated temperature growth in the SHD wave (SHD of K_3CrO_8 must actually be described within the stage combustion theory [31]). The screening of the high-temperature region with an isothermal area makes it possible to consider that the respective phase transitions proceed under conditions of chemical K_3CrO_8 transformation. In this case, the SHD rate is controlled by K_3CrO_8 decomposition preceding these phase changes. Using the results of ref. 31, the length, x_{melt} , of the plateau on the temperature profile can be estimated. Assuming simply that the physical and kinetic characteristics are constant up to the end of the decomposition, we arrive at

$$x_{\text{melt}} = u(\alpha_{s,2}^2 - \alpha_{s,1}^2)/2A \exp(-E/RT_s) \quad (4)$$

where

$$\alpha_{s,2} = 1 - [2(T_b - T_s)\lambda A \exp(-E/RT_s)/(Q - L)u^2\rho]^{1/2}$$

$$\alpha_{s,1} \approx 0.52$$

$$L = \Delta H_{\text{melt KO}_2} + \Delta H_{\text{phase trans K}_2\text{CrO}_4} = 456.7 \text{ J g}^{-1}$$

The value of x_{melt} is calculated to be 200 times less than the plateau in Fig. 4. It may be seen from eqn. (4) that the error in the estimation of $\alpha_{s,2}$ cannot have given such a great discrepancy in x_{melt} values. Therefore, this discrepancy may be attributed to the overestimated denominator in eqn. (4), i.e., the rate constant. A and E being constants, the value of the rate constant is only decreased by the temperature. A satisfactory agreement between x_{melt} and experiment may be obtained at about 530 K, i.e., assuming that within the plateau K_3CrO_8 decomposes at 530 K. This difference is probably explained by the fact that eqn. (4) has been obtained for gasless combustion systems. The oxygen generated on SHD of K_3CrO_8 may entrain unreacted or partially reacted K_3CrO_8 particles to the zone of molten KO_2 (a peculiar variant of dispersion) where they decompose under self-heating due to the heat-insulating effect of the oxygen being released around these particles. The temperature variation in the K_3CrO_8 portion evolved into the melt is schematically shown in Fig. 4. It is easily seen that K_3CrO_8 particles in the melt region may have $T < T_s$ for the time corresponding to the plateau length. It is these particles decomposing with delay that probably give off the "sparks" described earlier. A quantitative description of the SHD for K_3CrO_8 with allowance for dispersion into the melt seems to be very complicated mainly because of the difficulties in calculating the distance of evolution of the particles into the melt.

It is now clear that the SHD of K_3CrO_8 is essentially affected by the absence of any ordinary dispersion of the sample, resulting in the formation of the above SHD wave structure and complete transformation of K_3CrO_8 .

The effect of the ambient pressure on SHD may be associated, to a certain

The effect of the ambient pressure on SHD may be associated, to a certain degree, with the shift of the equilibrium of reversible KO_2 dissociation and the resultant formation of O_2 . The dissociation of KO_2 involves the formation of K_2O_2 and K_2O which, when mixed with KO_2 , have different melting temperatures and, consequently, different α_s and T_s values. The effect of pressure on the evolution of the substance into the melt may also have certain consequences. On the whole, the low value of ν indicates that the dominating part of the processes proceeds without participation by the generated O_2 . This conclusion agrees with the situation when the SHD of K_3CrO_8 is described in a first approximation by the elementary second-kind model, including the reaction product melting. Note that, in accordance with ref. 32, the ambient pressure may change u due to the effect exerted by the defects found in crystals on the generation energy. In Part I of this communication [1], the importance of the role of defects in K_3CrO_8 thermolysis was emphasized.

The difficulties due to large errors in the calculation of u may be avoided by using experimental and statistical methods for the description of multiparametric relationships. The version of such an approach [33], as applied to the SHD of K_3CrO_8 with admixtures of other substances, will be considered separately.

The problems of K_3CrO_8 thermolysis dwelt upon in the present work (Parts I–III) are far from being comprehensively studied, and require further examination and, perhaps specification. In the series under consideration we have only generally interpreted many of the unstudied properties of K_3CrO_8 which is of great interest in elucidating various aspects of thermal chemistry.

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