

Extrapolation kinetic problems solved by indiscriminating methods

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Abstract

The possibilities are compared of using kinetic information obtained by the isoconversional method (IM) and by the method of invariant kinetic parameters (IKP) for solving kinetic problems connected with predicting the behaviour of a substance in the temperature range beyond that used in the experiment. The thermolysis kinetics of individual HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctan) and HMX-based compositions doped with copper oxide and strontium carbonate have been investigated. Knowing that the combustion rate of HMX is limited by the thermolysis rate in the condensed phase, the influence of the dopes on the combustion rate has been predicted. It is shown that the software KINTOOL makes predictions on the basis of the IM more reliable and visual.

INTRODUCTION

The most widely encountered extrapolation kinetic problems are those connected with prediction of the behaviour of a substance beyond the experimental temperature range. As shown previously [1, 2], solving problems of this kind requires reliable values of the Arrhenius parameters which can only be calculated by methods using no discrimination of the formal models of the process [3, 4]. In the present paper, we consider the methodical aspects of solving the extrapolation problems on the basis of the method of invariant kinetic parameters (IKP) [5, 6] and of the isoconversional method (IM). Both methods are indiscriminating. However, effective use of the IKP method is limited [7] to simple (gross single-stage) processes. IM can be used successfully for both simple and complex processes [7] for solving extrapolation kinetic problems if

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algorithms that account for the potential complexity of a process are used [8].

The aim of this work is to formulate a convenient and reliable method for solving extrapolation problems, a particular case of which is transforming thermolysis kinetics data to the region of combustion temperatures. Obviously, such extrapolations are legitimate for substances whose combustion rate is limited by the reaction in the condensed phase. Among such substances is the widely used component of composite solid fuels (CSF), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctan) [9]. Therefore, HMX with additions of the CSF combustion regulators copper oxide [10] and strontium carbonate [11], have been chosen for this investigation. From the results of investigating the thermolysis kinetics of individual HMX and HMX-based compositions, we shall attempt to predict the possible influence of the above dopes on the combustion rate of the compositions.

EXPERIMENTAL

The thermal decomposition of HMX in the presence of combustion regulators was studied on a MOM derivatograph in a stationary air atmosphere. The heating rate was from 1 to 12 K min⁻¹. Samples weighing 30 mg were investigated. CuO and SrCO₃ dopes were introduced into HMX at levels of 5%. Aluminium powder (dilution 1:40) was used as a thermal diluent. Kinetic calculations were made using the mass-loss curve. The sensitivity of the balance of the derivatograph permitted up to 30 reliable experimental points to be obtained in the range of variation of the transformation degree w . To measure the linear combustion rate, the pressed samples of HMX doped with SrCO₃ and CuO were investigated in air under atmospheric pressure. The ratio of dope to HMX was the same as in the case of thermolysis.

Predictions on the basis of the IKP method

In essence, the solution of extrapolation problems using the IKP method is reduced to the analysis of Arrhenius dependences beyond the experimental temperature range. By comparing the relative position of the Arrhenius dependences for the thermolysis of HMX and HMX-based compositions thus obtained, we shall attempt to elucidate the possible character of the influence of the dopes on the HMX combustion rate.

It should be remembered that the character of the influence of the dopes on thermolysis and combustion rates can differ. In many cases [12] this can be explained by the substantial difference in temperatures and/or heating rates at which these processes proceed. In particular, the introduction of a dope into CSF leads, as a rule, to a change in the

TABLE 1

The Arrhenius parameters of thermolysis calculated by the IKP method for the samples under study

Sample	E (kcal mol ⁻¹)	log A (s)
HMX	32.0	8.0
HMX + SrCO ₃	31.4	7.5
HMX + CuO	23.8	4.0

thermolysis activation energy, with the result that the Arrhenius dependences corresponding to the thermolysis of CSF and doped CSF intersect. If in this case the so-called isokinetic temperature (temperature corresponding to the intersection point of the Arrhenius dependences) lies between the temperature ranges of thermolysis and combustion, the character of the influence of the dope on the thermolysis and combustion rates will be in opposition. If the isokinetic temperature lies in the temperature range of thermolysis or combustion, we can expect only an increase or a decrease in the relative efficiency of the dope action at combustion temperatures.

The results of the experimental data processing by the IKP method are given in Table 1, from which it can be seen that, unlike SrCO₃ whose introduction barely affects the Arrhenius parameters of HMX thermolysis,

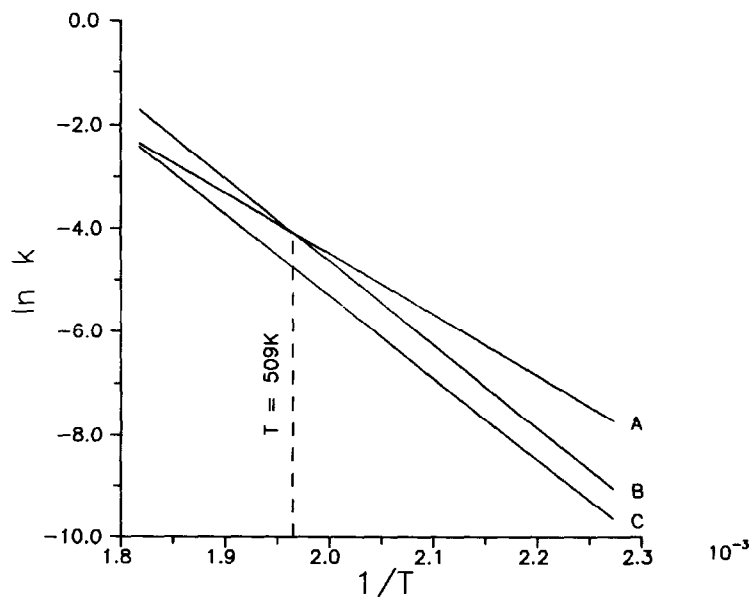


Fig. 1. Arrhenius straight lines corresponding to thermolysis of HMX (B) and HMX doped with CuO (A) and SrCO₃ (C) in the experimental temperature range (440–550 K).

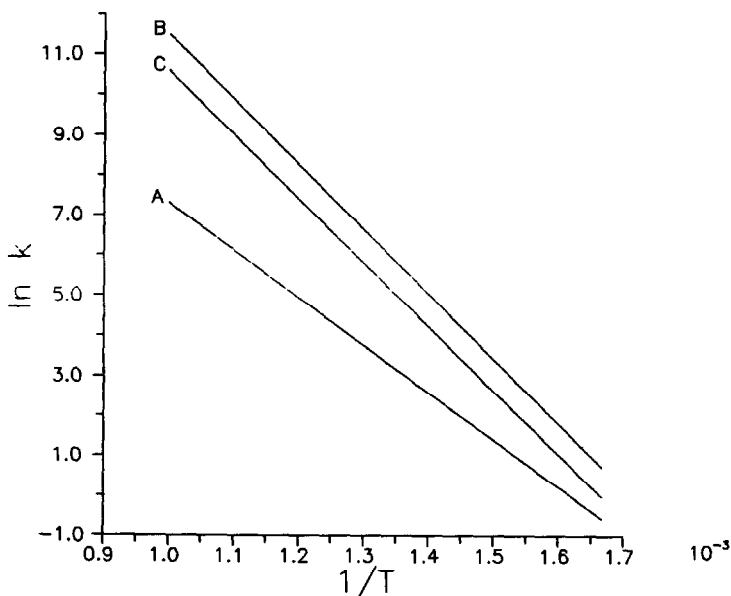


Fig. 2. Arrhenius straight lines corresponding to thermolysis of HMX (B) and HMX doped with CuO (A) and SrCO_3 (C) in the 600–1000 K temperature range.

CuO causes a marked decrease in these quantities. Figure 1 shows the corresponding Arrhenius straight lines for the temperature range from 440 to 550 K in which transformation of the compositions being investigated has been observed. Analysing the relative position of the straight lines, it may be concluded that in this temperature range, SrCO_3 is a thermolysis inhibitor. A more interesting behaviour is displayed by CuO which, in the range to 510 K, catalyses HMX decomposition, after which it becomes an inhibitor. In the range of higher temperatures from 600 to 1000 K (Fig. 2), both dopes produce an inhibiting effect on HMX thermolysis. From this, it may be assumed that both dopes will decrease the combustion rate of HMX, and that more effective inhibiting should be expected from CuO.

Predictions on the basis of IM

All the kinetic information presented in this section has been obtained using the KINTOOL software developed by Vyazovkin and Goryachko. KINTOOL is based on the isoconversional calculation of Arrhenius parameters and on special algorithms [8] designed for solving applied kinetic problems with consideration for the potential complexity of the process being investigated. The description of some potentialities of KINTOOL, as well as the results of comparative calculations performed with its aid and by means of the methods on which the kinetic software of Mettler and DuPont thermoanalysers are based, can be found in ref. 13.

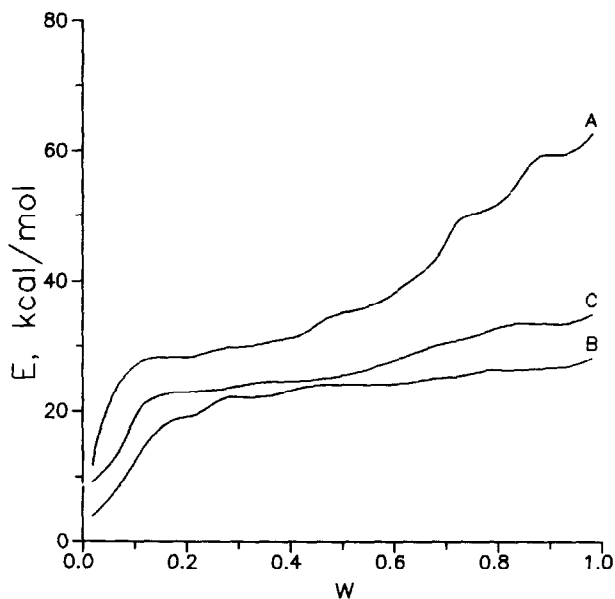


Fig. 3. Transformation-degree dependences of effective activation energy corresponding to thermolysis of HMX (A) and HMX doped with CuO (C) and SrCO₃ (B).

Figure 3 shows the transformation-degree dependences of the effective activation energy which indicate unambiguously [7] a complex thermolysis mechanism for both pure HMX and HMX in mixtures with SrCO₃ and CuO dopes. From a comparison of the dependences, it can be seen that the action of the dopes on the thermolysis kinetics of HMX manifests itself as a marked decrease in the activation energy of the process, especially at high transformation degrees. The similarity between the transformation-degree dependences of activation energy for the doped HMX leads to the assumption that the dopes have an analogous influence on the thermolysis rate of the mixtures.

To elucidate the influence of the dopes on the thermolysis kinetics of the HMX mixtures to be investigated using KINTOOL, we plotted the times of attaining a given transformation degree as a function of temperature. Figure 4 gives this dependence for a transformation degree of 0.3 in the range of experimental temperatures; similar dependences are obtained at other transformation degrees.

The dependences obtained indicate that SrCO₃ slightly catalyses the HMX thermolysis at temperatures up to about 470 K, after which it becomes an inhibitor of this process. The catalytic effect of CuO on the HMX thermolysis is more pronounced and lasts to the higher temperature of 480 K, after which the action of this dope also reverses.

The temperature dependences of the time of attaining a given transformation degree shown in Fig. 5 characterize the behaviour of the dopes

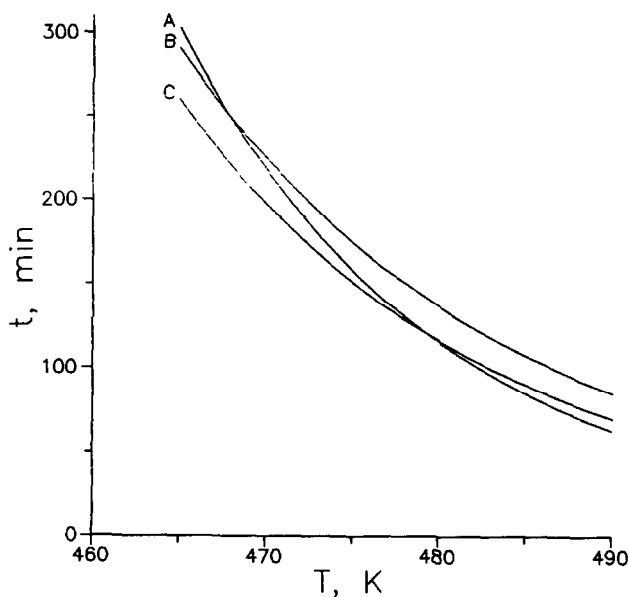


Fig. 4. Temperature dependences of the time of attaining a transformation degree of 0.3 for thermolysis of HMX (A) and HMX doped with CuO (C) and SrCO_3 (B) in the experimental temperature range.

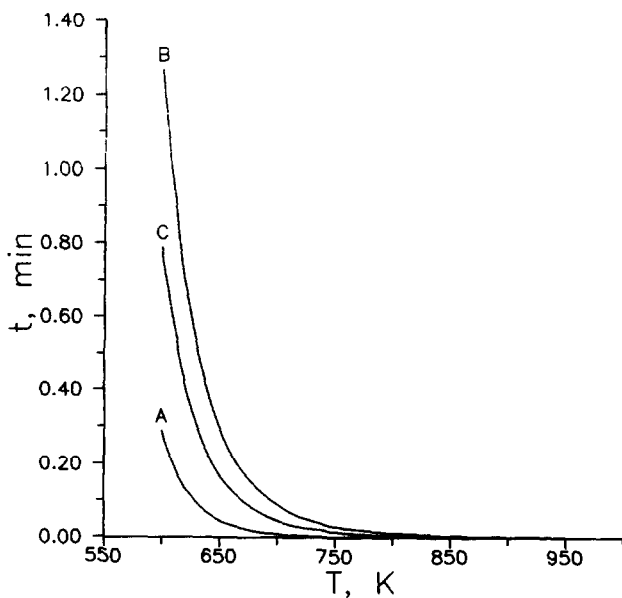


Fig. 5. Temperature dependences of the time of attaining a transformation degree of 0.3 for thermolysis processes of HMX (A) and HMX doped with CuO (C) and SrCO_3 (B) in the 600–1000 K temperature range.

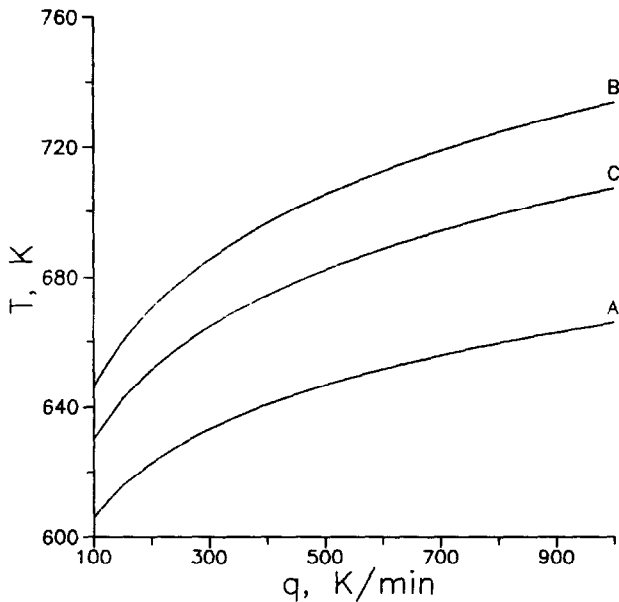


Fig. 6. The dependences of the temperature at which a transformation degree of 0.3 is attained for thermolysis of HMX (A) and HMX doped with CuO (C) and SrCO₃ (B) at heating rates of 100–1000 K min⁻¹.

under investigation in the region of higher temperatures. It can be seen from Fig. 5 that both dopes produce an inhibiting effect on HMX thermolysis. Thus, it can be assumed that both CuO and SrCO₃ will decrease the combustion rate of HMX, with SrCO₃ being the more effective inhibitor.

The trends in the action of the dopes being investigated on HMX thermolysis are followed not only on extrapolation to higher temperatures, but also to the higher heating rates characteristic of combustion. This is demonstrated by the heating rate dependences of the temperature of attaining a given transformation degree (Fig. 6).

DISCUSSION

Let us compare the results of predicting the potential action of CuO and SrCO₃ on the combustion rate of HMX. First of all, it should be noted that the kinetic data-processing methods employed indicate the inhibiting action of the dopes on HMX thermolysis at temperatures exceeding 510 K. Consequently, both methods predict that the dopes under investigation will be combustion inhibitors. However, IM and IKP differ in predictions of the relative efficiency of the dopes: from the results obtained by the IKP method, CuO must be a more effective combustion inhibitor, whereas the IM-based calculations favour SrCO₃. We shall try

to resolve this contradiction which originates from the nature of the extrapolation itself.

At any extrapolation, it is usual to assume that the laws of the phenomenon observed under these conditions also hold under the conditions to which the extrapolation is made. For this reason, the reliability of the extrapolation is determined by the reliability of the F description of the phenomenon in the experimental region. Thus, as applied to our problem, the prediction made by the method that best describes the process kinetics in the experimental temperature range, should be more reliable.

Figure 7 shows the experimental thermogravimetric curves in the form of temperature dependences of the transformation degree in the range of temperatures at which the transition from catalyst to inhibitor occurs. It should be noted that the transition temperatures remain practically unchanged in the range of the heating rates used. From comparison of the curves, it can be seen that for CuO the temperature of the catalyst–inhibitor transition is about 490 K. This temperature estimated by the IKP method is 510 K, whereas IM gives a closer value, 480 K. For SrCO₃, the experimental value for the transition temperature is 480 K. The calculated values of this temperature are about 210 K (IKP method) and 470 K (IM). Consequently, the IKP method gives a less reliable description of the kinetics of the processes under study than the IM. It should therefore be

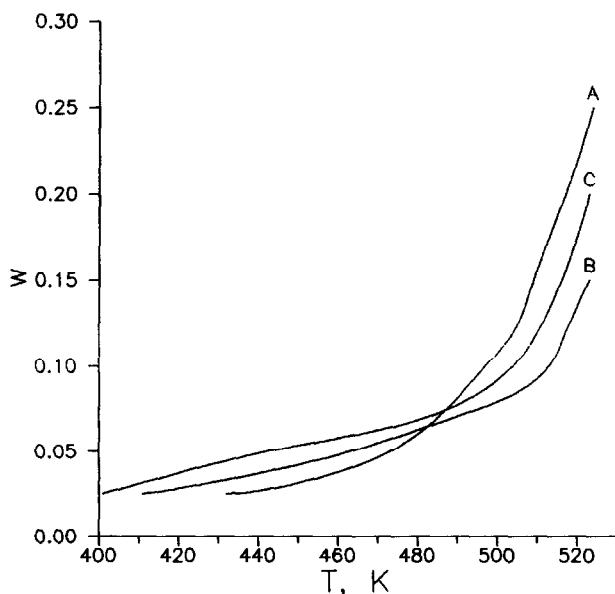


Fig. 7. Experimental TG curves (A, HMX; B, HMX + SrCO₃; C, HMX + CuO) expressed as transformation degree plotted against temperature at a heating rate of 2 K min⁻¹.

expected that the prediction made on the basis of the IM will be more plausible.

Now let us compare the predicted and experimental results. It was found that the combustion rate of HMX is about 0.05 cm s^{-1} . The employed dopes decrease the combustion rate by approximately twice. Because the efficiencies of the dopes are almost equal, we cannot conclude which prediction was better. We can only conclude that the inhibiting influence of the employed dopes was predicted correctly.

In conclusion, we shall make a few remarks on the solution of extrapolation problems by the above methods. For instance, when using the IKP method we deal with the rate constants which characterize the contribution of temperature to the change in the process rate. However, as follows from the common equation

$$dw/dt = k(T)f(w)$$

the rate of a process also depends on the mechanism of the process which it is customary to describe by formal models $f(w)$. In calculating the Arrhenius parameters by the IKP method, the model of the process remains unknown. For this reason the transition from the rate constant to the transformation degree of the process rate, i.e. quantities which can be estimated experimentally, turns out to be impossible. As a result, we can determine whether a certain dope produces a catalytic or an inhibiting effect, but we cannot determine how perceptible this effect will be.

For IM, this problem is easily solved by means of special algorithms [8] underlying the KINTOOL software which can be used to plot the complete set of dependences between the values of the heating rate, transformation degree, temperature and time. Because all these dependences contain the transformation degree as a parameter or a variable, it becomes possible to evaluate the effect of the dopes not only qualitatively, but also quantitatively. Thus, because of KINTOOL, the solution of extrapolation kinetic problems on the basis of IM becomes not only reliable, but also more visual.

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