

THERMAL IGNITION BEHAVIOUR OF AMMONIUM PERCHLORATE IN PRESENCE OF FUEL-RICH COMPOUNDS

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The thermal ignition behaviour of ammonium perchlorate has been investigated in the presence of fuel-rich compounds such as tetramethylammonium perchlorate, trimethylammonium nitrate, carbon and cellulose. The ignition characteristics, as studied by differential thermal analysis, have been found to be strongly influenced by self-decomposition and other physicochemical properties of the additives. For a simple system, an analytical model proposed on the basis of the coupling of two exothermic decomposition reaction kinetics and a heat-balance equation, appears to explain to some extent the observed trend in peak ignition temperature when the composition is varied. The salient features of the analysis, as regards its application to fuel-oxidizer interactions in general, have been pointed out.

The importance of thermal ignition studies on condensed fuel-oxidizer systems arises mainly because of their extensive application in the field of propellants and explosives. Of the condensed systems, the mixtures involving ammonium perchlorate (AP) are of special interest due to their wide use in solid propellants. The thermal ignition behaviour of AP is known to be modified in the presence of catalysts, impurities and additives [1]. A systematic study of the differential thermal analysis (DTA) of AP in the presence of structurally similar, fuel-rich compounds, viz. methylammonium perchlorates (MAPs), was recently carried out in our laboratory [2]. It was observed that although AP shows two exotherms due to partial and complete decomposition at around 300° and 400°, respectively [1] in DTA, it ignites in a single step at around its partial decomposition temperature in the presence of small amounts of mono-, di-, tri- or tetramethylammonium perchlorate. Interestingly, the critical concentration of a MAP needed to cause ignition in a single step corresponds to a unique composition of the mixture, expressed in terms of its elemental stoichiometric coefficient, ϕ_e [3]. However, some of the features in the DTA of the mixtures of AP and tetramethylammonium perchlorate (TMAP), such as the shift of the terminal exotherm to lower temperatures as a function of concentration, were not clearly explained.

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The decomposition characteristics of AP-TMAP mixtures may be simple because of the relatively uncomplicated decomposition behaviour of TMAP. The DTA of TMAP does not show any transition in the decomposition range of AP [4]. However, the ignition characteristics of AP are expected to be strongly dependent upon the physico-chemical properties, such as melting, decomposition characteristics, etc. of the fuel-rich additive. Besides TMAP, therefore, we report here the ignition behaviour of AP in the presence of other fuels having widely differing physicochemical properties, as revealed by their DTA in air and nitrogen. The additives used in the present study include simple fuels such as carbon and cellulose, which do not decompose exothermically in a non-oxidizing atmosphere below 400°, and also a fuel-rich compound, trimethylammonium nitrate (TMAN), which melts and decomposes below the first exotherm of AP [5].

Attempts have recently been made to analyse the ignition phenomena of two-component systems on the lines of the Semenov and the Frank–Kamenetskii models [6–10]. These methods have been applied successfully to determine, analytically [6–8] as well as numerically [9–12], the self-heating characteristics of systems involving two parallel exothermic reactions as a function of the ratio of the activation energies, the adiabatic temperature rise due to the minor component, and the ratio of the rates of the two reactions. In these analyses, which pertain mainly to static temperature conditions, i.e. where the temperature of the surroundings is kept constant, the influence of one exothermic reaction on the other in determining the ignition behaviour of the composite system has been clearly brought out. In the light of the above approach, we report an analysis of the ignition characteristics of a system of two components capable of generating heat independently, under linear heating. The emphasis in the present analysis has been placed on determining the trend in peak ignition temperature when the composition of the reactants is varied. It was envisaged that such an analysis may throw light on the mechanism of ignition of analogous simple systems, such as the AP-TMAP system in the present case.

Experimental

Tetramethylammonium perchlorate [4] and trimethylammonium nitrate [5] were prepared as described earlier and the purities of the samples were checked by comparing the DTA traces with those already reported. The carbon used in the present investigation was activated charcoal supplied by Sarabhai Chemicals. The differential thermal curves were recorded using a two-channel potentiometric strip-chart recorder, as described by Jain et al. [13]. In each experiment, 200 mg of the sample was taken in the DTA platinum cup. A uniform heating rate of 12.0° min⁻¹ was employed in the case of the AP-cellulose and AP-carbon systems, whereas in the AP-TMAP and AP-TMAN systems the heating rate was 20° min⁻¹. The DTAs in nitrogen atmosphere were carried out on some typical samples under conditions identical to those in air.

Results

The DTA traces in air of AP and the fuel-rich compounds used in the present study are shown in Figure 1. The DTA of pure AP exhibits an endotherm at 240°, followed by two exotherms at 300° and 380°, which are attributed to partial and complete decomposition, respectively. Whereas carbon does not show any explicit peak up to 400°, the DTA of cellulose exhibits a complicated pattern, with a very small endotherm at 295° and two exotherms at 368° and 501°, which agrees fairly well with some of the values reported in the literature [14, 15]. The DTA trace of TMAN displays two endotherms due to phase transitions, at 90° and 126°, and a decomposition exotherm at 210°, whereas that of TMAP shows only a single exotherm at about 400°, thus agreeing with those reported [4, 5].

Figure 2 presents some selected DTA traces of AP in the presence of a higher than critical concentration [2] of TMAP. It is seen that, as the concentration of TMAP is increased, the self-ignition temperature of the mixture successively shifts to higher values.

The DTA results on the AP-carbon system are given in Figure 3. In the presence of 1% carbon by weight, the DTA of AP is slightly modified, with intensification of the peak at 295°. However, when the concentration of carbon is 1.4%, the mixture self-ignites at 295°. This concentration, incidentally, corresponds to a ϕ_e value [3] of 1.97. The stoichiometric mixture, i.e. containing 11.3% carbon by weight, also self-ignites in a single step, but at a considerably lower temperature, around 260°.

Figure 4 shows the effect of cellulose on the thermal decomposition of AP. At 3% cellulose, in addition to an endotherm at 240°, three exothermic peaks are observed, at 308°, 356° and 368°. When the concentration is increased to 5%, only two exothermic peaks appear. With 10% cellulose, the mixture starts to self-ignite, giving a single exotherm at around 290°. Beyond this concentration, the self-ignition temperature is lowered as the amount of cellulose added increases. It is interesting to note that at and above 50% cellulose, the entire mixture ignites below 240°. In all the AP-cellulose mixtures except those containing very low concentrations of cellulose, an endothermic peak occurs at around 220°, which is not observed in the DTA traces of either AP or cellulose; the intensity of this peak grows with the amount of cellulose added.

In the presence of TMAN, as shown in Figure 5, the thermal decomposition of AP is drastically modified. Between 5 and 15%, two exotherms are seen in the region 200° to 280°, whereas above 20% TMAN only one exothermic peak is observed. The peak temperature, however, appears to pass through a minimum at 40% TMAN. Interestingly, when the amount of TMAN present is 80%, two exothermic peaks are found, one at 149° and the other at 278°.

It is important to point out here that when the DTA experiments on some typical samples of AP-carbon, AP-cellulose and AP-TMAN systems are carried out in flowing nitrogen atmosphere, the results obtained are virtually unchanged as compared to those in air (Table 1).

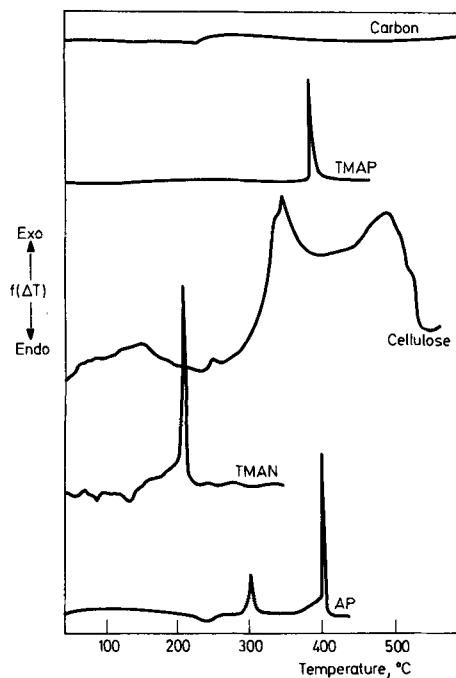


Fig. 1 DTA traces of AP, TMAN, cellulose, TMAP and carbon, in air

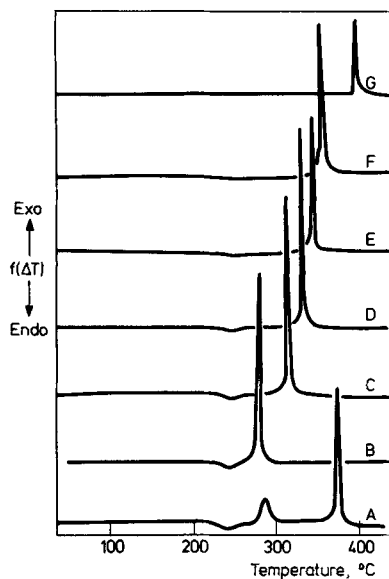


Fig. 2 DTA traces of AP-TMAP mixtures in air. TMAP concentration: A, 0%; B, 5%; C, 20%; D, 40%; E, 70%; F, 85%; and G, 100%

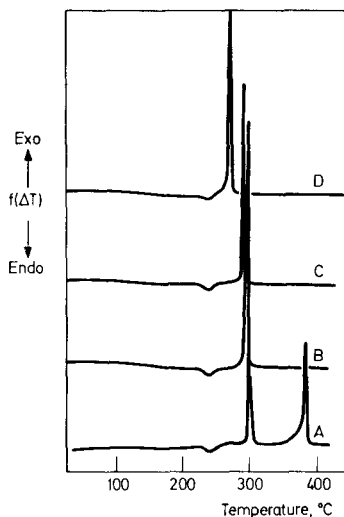


Fig. 3 DTA traces of AP-carbon mixtures in air. Carbon concentration: A, 1.0%; B, 1.4%; C, 2%; and D, 11%

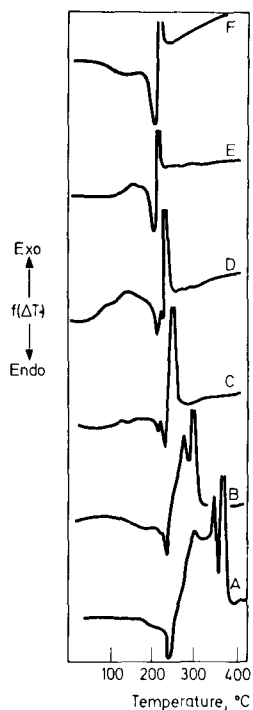


Fig. 4 DTA traces of AP-cellulose mixtures in air. Cellulose concentration: A, 3%; B, 5%; C, 10%; D, 30%; E, 50%; and F, 90%

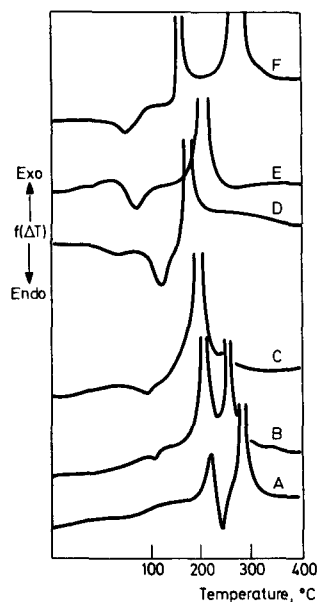


Fig. 5 DTA traces of AP-TMAN mixtures in air. TMAN concentration: A, 6%; B, 15%; C, 20%; D, 40%; E, 60%; and F, 80%

Table 1 DTA data in nitrogen atmosphere

Concentration of fuel, wt%	DTA peaks*, °C			
AP-TMAP				
5	240(-)		290(+)	
40	240(-)		322(+)	
50	240(-)		330(+)	
AP-carbon				
1.4	240(-)		265(+)	
2.0	240(-)		284(+)	
AP-cellulose				
2	240(-)	315(+)	349(+)	362(+)
8	240(-)	257(+)		
30	225(-)	240(-)	259(+)	
70	236(-)	251(+)		
100	324(-)			

* (+) and (-) indicate exotherm and endotherm, respectively

Discussion

The results of the present investigation bring into focus two aspects of the ignition of AP in the presence of a fuel. The first is the single-step ignition of AP. At lower concentration of fuel, it is observed that AP ignites in a single step. The elemental stoichiometric coefficient, ϕ_e , corresponding to these mixtures with a critical concentration of a fuel, has been found to be approximately the same (about 1.96), at least for AP-carbon and AP-MAP [2] mixtures. It is significant to note here that whereas carbon is considered as a pure fuel, MAPs are only fuel-rich compounds, and that the decomposition characteristics of these compounds are widely different. These results conform to our earlier observations [2].

The other aspect is the observed shift in ignition temperature, which appears to be dependent upon both the nature and the concentration of the fuel, when the amount of fuel present is more than that needed for the single-step ignition of AP. For instance, let us take the case of AP-TMAP mixtures, which is the simplest combination considered, as pointed out earlier. The single exotherm observed shifts to higher temperatures as the concentration of TMAP is successively increased above 3.5%. Such a shift in ignition temperature cannot easily be explained.

In order to account for this behaviour, it may be envisaged that once AP starts igniting in a single step, any further increase in concentration of TMAP might influence the kinetics of the overall ignition process, which may lead to shifts in ignition temperatures. Further, assuming heterogeneous reactions to be of minor importance, the overall behaviour of such a system may be looked upon as due to the coupling of the kinetics of two decomposition reactions, viz. the complete decomposition of AP at 300° and the decomposition of TMAP at around 400°. An analysis of such a system for a set of hypothetical reactions is presented in the Appendix. It is shown that in order for one chemical reaction to influence the other, without chemically affecting it, the temperature rise produced by the first decomposition reaction must be sufficient to initiate and also to sustain the second reaction. In this case the kinetics of the reactions may be said to couple with each other. The extent of coupling then depends on the decomposition characteristics and heats of reaction of the individual reactions. It is apparent that the greater the gap in temperature between the two peaks, the less will be the coupling. The analysis shows that when the two reactions are coupled to a sufficient degree to produce a single peak, there is a progressive shift in peak temperature with changes in composition.

In comparing the above results with those obtained on the AP-TMAP system, it is important to point out that an exact reproduction of the experimental results in such a system is neither feasible nor desirable, because of the limitations of the approach and the lack of the necessary kinetic parameters. However, a comparison (given in Figure 6) of the observed shift in the ignition temperature with the composition of the AP-TMAP system, with that predicted by the hypothetical system described by the second data set in the Appendix, reveals that the trends in the shift in the two cases are almost identical. It appears, therefore, that the shift observed in

the ignition temperature of the AP-TMAP system may be a consequence, at least in part, of the coupling of the kinetics of two exothermic reactions.

The AP-carbon system was investigated only up to the stoichiometric concentration of carbon, mainly to find out if the ignition of AP occurs in a single step when the composition of the mixture is around a ϕ_e value of 1.96. However, it is pertinent to note that at higher than the critical concentration of carbon, the ignition temperature shifts to lower values. These results may not really be surprising, if proper account is taken of the facts that AP starts decomposing, though slowly, in the range 150–200° and that the products formed react immediately with carbon. That is to say, the heterogeneous reaction rate, which may be appreciable at low temperature, influence the decomposition at 300° to such an extent that the overall reaction rate is significantly increased at lower temperatures and the ignition occurs at around 260°. Similar results obtained in the case of potassium perchlorate-carbon mixtures [16] were explained by postulating the solid-state oxidation of carbon. However, to explain the decomposition of an AP-carbon mixture under vacuum at as low a temperature as 240°, a catalytic effect of carbon on the thermal decomposition of AP was proposed by Galwey and Jacobs [17].

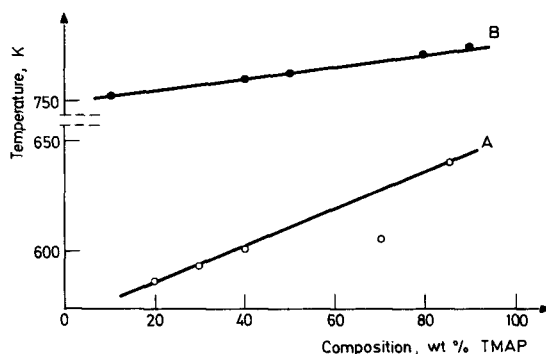


Fig. 6 Variation of ignition temperature with composition: A, experimental (AP-TMAP system); B, theoretical (Set II data given in Appendix)

The behaviour as regards the shift in the ignition temperature can be explained only qualitatively on the basis of the simple model presented in the Appendix. This is because the model is based on essentially a two-reaction system whereas in fact a minimum of three reactions, viz. low and high-temperature decompositions of AP and the heterogeneous reactions should be considered. The observed behaviour may therefore be due to a complex interplay of these reactions. Carbon being susceptible to oxidation, the onset of the heterogeneous reactions occurs at around the partial decomposition temperature of AP, i.e. at 300°. Thus when the rate of heat release due to the heterogeneous reaction, which depends on the amount of carbon, and

the decomposition of AP is high enough to start the third reaction, single-step ignition is observed. Otherwise, depending upon the heat effects, two peaks with differing gaps are observed.

In the AP-cellulose mixtures, depending on the concentration of cellulose, three different patterns in the thermal curves are evident. Though, at first glance, these results appear complicated, on close scrutiny it is revealed that if a heterogeneous reaction is assumed to occur between AP and fuel-rich species emerging from cellulose depolymerization and decomposition, the results fit into an explanation similar to that offered for AP-TMAP mixtures.

In all AP-cellulose mixtures (above 5% of cellulose) an endotherm is observed at around 220°. Based on analogous results obtained in the decomposition of cellulose containing a low concentration of ammonium hydrogen phosphate [18], where an endotherm is observed at 240°, the endotherm at 220° may be attributed to acid-catalysed depolymerization and decomposition. The acid in this case may result from the decomposition of AP. This is supported by the evidence that the DTA of cellulose in the presence of a very small amount of HClO₄ does indeed show an endotherm at 220° followed immediately by an exotherm. Furthermore, no such endotherm appears in the DTA of potassium perchlorate-cellulose mixtures [19]. The depolymerized cellulose thus formed may be highly susceptible to oxidation and may catalyse the decomposition of AP, by participating in heterogeneous reactions at significantly lower temperatures. Thus, in the mixture containing 3% cellulose, the first of the three peaks may be due to the low-temperature decomposition of AP sensitized by the heterogeneous reaction between depolymerized species and AP. The sensitization is clearly seen as an enhancement in the peak intensity as compared to that for pure AP. The second peak, at around 360°, which is actually a shoulder beside the other peak, may result because the small amount of cellulose which has not depolymerized at around 220° undergoes combustion in air (as observed in the DTA curve of pure cellulose in air) or with oxidizing species arising from AP decomposition. Finally, the third peak may be the result of the high-temperature AP decomposition, slightly sensitized by other reactions. As the concentration of cellulose is increased beyond 3%, the influence of the composite heat effect due to heterogeneous reactions and the low-temperature decomposition of AP, seen as the first exotherm at around 270° in the other reactions, is also increased. Hence, for mixtures containing 3 to 6% cellulose, only two peaks are observed. Above 6% cellulose a single peak occurs at a temperature determined presumably by the extent of coupling between the two reactions, viz. the heterogeneous reaction above 220° and the decomposition of AP. The rate contribution from the heterogeneous reaction being the larger, the peak temperature is expected to be lowered as the amount of cellulose is increased.

The AP-TMAN system is rather complicated, although here again at 6% TMAN no terminal peak of AP decomposition is seen. The complication probably arises due to the formation of melt. Although melts are known to have peculiar decomposition characteristics [2], they have not been investigated in detail. The decomposition

characteristics of the AP-TMAN system appear to depend strongly upon the composition of the mixture, which cannot be accounted for on the basis of a simple model.

In conclusion, it seems that the ignition characteristics of AP-fuel mixtures are strongly dependent upon various physical parameters, such as the decomposition and melting points of the fuel additive, the nature of the fuel and the composition of the mixture. For systems exhibiting very low chemical interaction, these factors may be analysed to some extent by means of a model based on the heat-balance equation. However, the influence of other parameters must not be ignored in such an analysis.

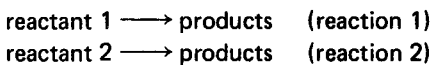
Appendix

Thermal ignition of two-component systems under non-isothermal conditions

The ignition phenomenon in a system comprised of two components capable of undergoing independent exothermic reactions at different temperatures may be viewed as follows. When a two-component system is subjected to a uniform rate of heat input, the exothermic reaction of the component decomposing at lower temperature occurs first. When the temperature rise in the system due to the first exothermic reaction is so high that the rate of the second exothermic reaction becomes appreciable, the kinetics of the two reactions may couple with each other. The overall behaviour of the reaction will then be determined by the extent of coupling and the combined rate of heat build-up of the reactions.

The mathematical analysis of the description of a DTA curve has been carried out on the basis of an idealistic model [21], i.e. assuming that the temperature distribution within the sample is uniform and that the heat loss term is linear in temperature.

Let us consider two independent exothermic reactions whose kinetics may possibly couple, as represented by the following scheme:



The equations employed could be written as:

Heat balance:

$$\begin{aligned} m \cdot C \cdot \frac{dT}{dt} = & m_1 \cdot Q_1 \cdot A_2 \cdot \exp(-E_1/RT) \cdot f(\lambda_1) + \\ & + m_2 \cdot Q_2 \cdot A_2 \cdot \exp(-E_2/RT) \cdot f(\lambda_2) - \frac{\alpha S}{V} (T - T_0). \end{aligned}$$

Reactant consumption:

$$\frac{d\lambda_1}{dt} = A_1 \cdot \exp(-E_1/RT) \cdot f(\lambda_1),$$

$$\frac{d\lambda_2}{dt} = A_2 \cdot \exp(-E_2/RT) \cdot f(\lambda_2).$$

Temperature variation of the medium:

$$T_0 = T_i + Wt.$$

Initial conditions:

$T = T_0 = T_i$ and $\lambda_1 = 0 = \lambda_2$ at $t = 0$ where C is the heat capacity of the mixture; Q_i is the heat effect of the i th reaction; m_i is the mass of the i th component; $m = \sum m_i$, the total mass of the mixture; E_i is the activation energy of the i th reaction; A_i is the Arrhenius parameter for the i th reaction; λ_i is the fraction of the i th component reacted at any time t ; α is the heat transfer coefficient; V is the volume; T_0 is the temperature of the medium; T_i is the initial temperature; and W is the heating rate. It has been assumed that $f(\lambda) = 1 - \lambda$.

The values of the parameters with subscripts i refer to those of reactions 1 and 2.

The equations were solved by the Runge-Kutta [22] method. Typical sets of parameters used in the analysis are as follows:

	$E_1, \text{kJ mol}^{-1}$	$E_2, \text{kJ mol}^{-1}$	A_1, sec^{-1}	A_2, sec^{-1}	$Q_1, \text{J g}^{-1}$	$Q_2, \text{J g}^{-1}$	$W, \text{°C/min}$	m, g
Set I	125.4	198.5	10^9	10^{13}	1672	1254	20	0.2
Set II	125.4	182.1	10^9	10^{13}	1254	940	20	0.15

The results obtained are presented in Figures 7 and 8 as temperature rise, ΔT , vs temperature plots for various compositions. With the first set of data, depending upon the relative concentrations, either a single peak or two peaks with a differing gap is seen. The results show moderate coupling of the kinetics where the composition range within which a single peak is observed is limited; nevertheless, the peak shifts with change in composition. The results obtained from the second data set (Figure 8) represent a case of strong coupling of the kinetics over a wide range of composition. There is a clear-cut shift in peak temperatures as the relative concentration is varied. In other words, it is clearly seen that when the compositions and kinetic parameters are appropriate, a two-reaction system will behave as if consisting of one reaction only.

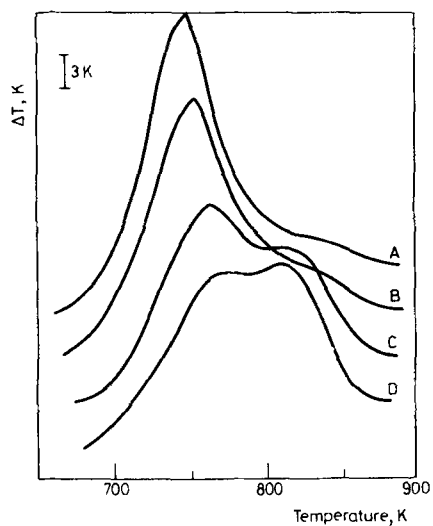


Fig. 7 Variation of peak temperature with composition, for Set I. Component 2 concentration: A, 20%; B, 30%; C, 50%; and D, 60%

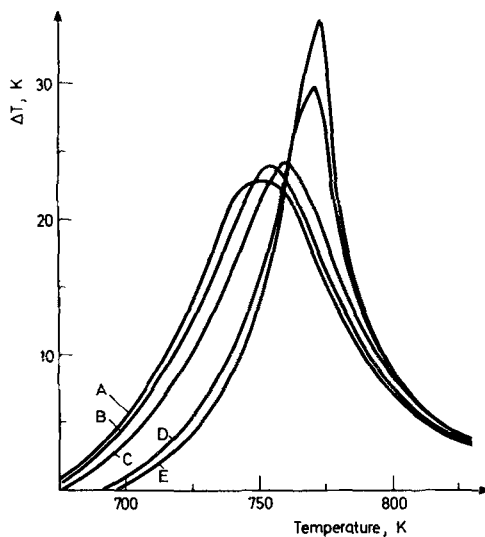


Fig. 8 Variation of peak temperature with composition, for Set II. Component 2 concentration: A, 10%; B, 20%; C, 40%; D, 70%; and E, 80%

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Zusammenfassung – Das sich auf die thermische Entzündung beziehende Verhalten von Ammoniumperchlorat in Gegenwart von an brennbaren Komponenten reichen Verbindungen wie Tetramethylammoniumperchlorat, Trimethylammoniumnitrat, Kohlenstoff und Cellulose wurde untersucht. Die durch DTA untersuchten Entzündungskennwerte werden stark durch die Selbstzersetzung und andere physikalisch-chemische Eigenschaften der Zusatzstoffe beeinflusst. Im Falle eines einfachen Systems scheint ein auf der Kombination von zwei kinetischen Fällen der exothermen Zersetzungsreaktion und der Wärmebilanzgleichung beruhendes Modell den beobachteten Trend der Entzündungstemperatur in Anhängigkeit von der Zusammensetzung bis zu einem gewissen Grade zu erklären. Die wesentliche Züge der Analyse hinsichtlich ihrer Verwendbarkeit zur Untersuchung von Brennstoff-Oxydationsmittel-Wechselwirkungen im allgemeinen wurden hervorgehoben.

Резюме – Исследована термическая воспламеняемость перхлората аммония в присутствии таких высоко теплотворных соединений, как тетраметиламмоний перхлорат, триметил-аммоний нитрат, углерод и целлюлоза. Характеристики воспламеняемости, изученные методом ДТА, сильно зависят от саморазложения и других физикохимических свойств добавок. В случае простой системы, как аналитической модели, предложенной на основании соединения двух экзотермических реакций разложения и уравнения теплового баланса, представлялась возможность объяснить наблюдаемую тенденцию некоторого протяжения пика температуры воспламенения с изменением состава. Были отмечены характерные черты такого анализа для применения его в реакции взаимодействия топливо-окислитель.