High-Temperature Decomposition of Ammonium Perchlorate—Polystyrene-Catalyst Mixtures

O. P. Korobeinichev,* G. I. Anisiforov,† and A. G. Tereschenko‡
Institute of Catalysis, Novosibirsk, USSR

The study was performed on the kinetics and mechanism of chemical reactions in the ammonium perchlorate (AP)-polystyrene (PS)-Fe_2O_3 mixtures. The experiment simulated the processes of thermal decomposition and combustion, as well as the catalysis of these processes. By means of an elaborate technique using a time-of-flight mass-spectrometer, a study was made of the influence of AP particle size (4–300μ), the ratio of AP and PS, temperature (305–390°C), pressure (15 mm Hg, 1 atm.) and concentration of the catalyst Fe_2O_3 (2.5%–12.5%) on kinetic parameters of the decomposition of rich and stoichiometric (8 : 1) AP and PS mixtures. It was concluded from analyses of the kinetic data that the thermal decomposition of these systems is a multistage process. Such stages are reactions of perchloric acid (primary product of the AP dissociation) with PS and condensed products of this interaction. The validity of this follows from direct experiments on the reaction kinetics of $HClO_4$-PS. It has been shown that in the decomposition of mixtures with AP (250–400μ), $HClO_4$ diffusion from the AP surface through a polymer film, and its simultaneous reaction with the latter are limiting stages. The developed model of the thermal decomposition of the AP-PS-catalyst system is based on the data obtained.

I. Introduction

In order to develop a model for the combustion and catalysis of condensed mixtures of AP-polymeric binder, it is necessary to determine the model for the thermal decomposition of these systems on the basis of kinetic studies of high temperature reactions.

The present data[1–3] obtained by weight and calorimetric techniques (DTA, DTG, DSC) are not enough to formulate the decomposition model for the mentioned composite systems. A recently developed technique[4] for kinetic studies of the thermal decomposition of the condensed mixtures by a time-of-flight mass-spectrometer allows us to obtain more information on the reaction kinetics and mechanism of such complicated systems as AP-PS-catalyst mixtures.

The present paper is concerned with the study of the kinetics and mechanism of high-temperature reactions which occur in the model three-component heterogenous system ammonium perchlorate-polystyrene-Fe_2O_3.

II. Experimental

In Refs. 5–8 the possibilities of the study of the kinetics and mechanism of a condensed system decomposition (including fast reactions) using dynamic mass-spectrometry under isothermal and non-isothermal conditions at pressure of 10^{-5}–10^{-6} mm Hg are shown. However, in many cases (particularly when the kinetics and mechanism of the decomposition reaction depend on pressure), it is necessary to perform the study at higher pressures (up to atmospheric.)

The kinetic apparatus with the time-of-flight mass-spectrometer and a flow reactor of a Lossing type[9] is shown in Fig. 1. This scheme involves a two-step sampling method which was used earlier for flame analyses at atmospheric pressure.[10] From the high pressure chamber 3 (1 atm) gas passes through the first orifice to the chamber with low pressure 2 (15 mm Hg), then it goes through the second orifice to the high-vacuum chamber 1 of an ion source of the time-of-flight mass-spectrometer. Both orifices (as the reactor itself) are made of glass (quartz, Pyrex glass) and are sufficiently heated to study decomposition reactions. Because of this, compounds non-volatile at room temperature and volatile at the experimental temperature can be studied. A sample (about 10–40 mg) is placed into the holder (massive aluminum block of 2 g), its temperature being measured by a thin thermo-couple copper-constantan. Due to this construction, the difference between the temperature of the substance and the sample holder measured by thermocouple is not more than 1° at a heating rate of the substance (10–20°/min) with a high decomposition thermal effect (~ 1000 cal/g). The sample holder is at 2–3 mm from the first orifice. The flow of an inert carrier gas (in this study helium with 2% of argon was used) passes from the gas-holder through the reactor with a constant rate. With known intensity ratios of mass peaks to that of argon, partial pressure of argon, and the sensitivity coefficients of reaction products with respect to argon, it is possible to calculate the partial pressure of reaction products. To obtain the differential reactor, the flow velocity of the carrier gas must be con-

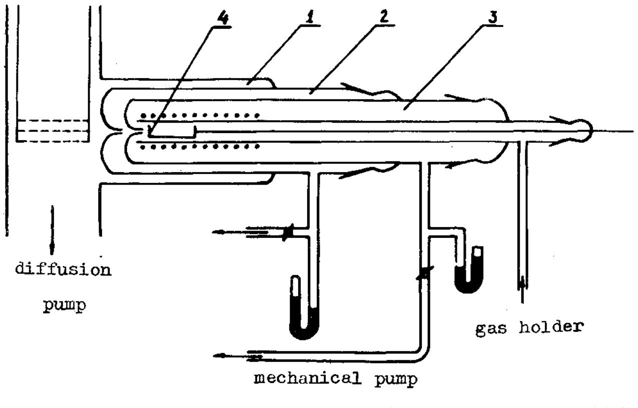

Fig. 1 Scheme of a mass-spectrometric kinetic apparatus: 1) high-vacuum chamber; 2) low-pressure chamber; 3) atmospheric pressure chamber; 4) aluminum block with a sample.

Presented at the AIAA 12th Aerospace Sciences Meeting, Washington, D.C., January 30–February 1, 1974; submitted May 8, 1974; revision received September 10, 1974. The authors wish to thank G. K. Boreskov for supporting this work and to A. S. Shmelev for helpful discussions of the model of the process.

Index categories: Fuel and Propellants, Properties of; Thermochemistry and Chemical Kinetics; Combustion in Heterogenous Media.

* Principal Research Scientist.

† Graduate Student.

‡ Research Fellow.

siderably higher than the rate of the reaction product evolution and the rate of pumping through the orifice. In this case peak intensities in a mass-spectrum I_i/I_{40} are proportional to partial pressures of the corresponding components (P_i/P_{40}) and to the formation rates of these components (W_i):

$$W_i = A_i \times P_i/P_{40} = B_i \times I_i/I_{40}$$

A low-pressure chamber was pumped with a constant rate, the pressure being maintained constant by the valve. The sample was placed directly into the low-pressure chamber to study the reaction at 15 mm Hg. The pressure in an intermediate chamber was controlled by an oil manometer. Due to a small distance between the orifice and an ion source and to the high pumping rate of the latter, it was possible to register such compounds as Cl_2, ClO_2, HCl, NO_2, NO, $HClO_4$, while it is difficult to take them off by a general mass-spectrometric analysis.

The particle size of PS and Fe_2O_3 was 1–3μ. The size of the AP particle was 250–400μ, except for insofar as it was varied. As a rule, a composite sample was a loose mixture. Increasing the sample density via moulding at various pressures did not considerably affect the results. The specific surface area of Fe_2O_3 was 64 m^2/g (except for especially mentioned cases). The AP amount in the mixture (M_{AP}) makes up 32 mg, except as M_{AP} was varied. The plots given in this paper include the values of the relative formation rates (W_i) of the decomposition gas products. To obtain the absolute rates in cm^3/min (at NTP) it is necessary to multiply W_i by a corresponding coefficient for a given gas equal to 0.3 for CO_2, CO, N_2; 0.4 for HCl; 0.67 for Cl_2; 0.09 for styrene monomer. The system described was used to study the decomposition reactions under isothermal conditions (heating time, 1 min). For the faster processes the system[5–8] for impulse heating (heating time, 0.01 sec.) by electric current of metallic ribbons can be used.

The reaction kinetics of the perchloric acid was studied to simulate the process of the thermal decomposition of the AP-PS system. The reactor of a barbotage type was used in these experiments. The mixture of the inert gas (15 mm Hg) with the perchloric acid vapour ($P_{HClO_4} = 1$ mm Hg) passed through a porous filter and then as bubbles—through a polymer fluid layer (similarly to Ref. 11) to the mass-spectrometer chamber where it was continuously analysed.

III. Results

Decomposition Kinetics of Rich AP-PS-Fe_2O_3 Mixtures

Figure 2 gives the typical kinetic curves of the formation rates of various decomposition products of the AP-PS system as a function of time (components ratio 1:1). It is seen from Fig. 2 that the decomposition of this system is a multistage process. The first stage is PS destruction with the formation of monomer, dimer, trimer, tetramer, CO_2, and HCl. At this stage the formation rate of CO_2 and HCl is constant and is considerably lower than that of monomer formation. At the second stage the formation rate of CO_2, HCl, and $CO+N_2$ is sharply increased. The destruction rate of PS in the mixture with AP is one order of magnitude higher than that of pure PS.[4] It is seen from Table 1 that mass spectra of destruction products of pure PS and PS mixed with AP differ by the intensity ratio.

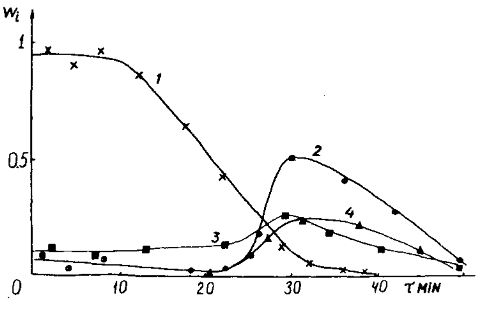

Fig. 2 AP:PS (1:1) $t = 325°C$, $P = 15$ mm Hg. 1) styrene, 2) CO_2, 3) HCl, 4) $CO + N_2$.

Table 1 Relative intensities of ion peaks (I_i/I_{104}) in mass-spectra of decomposition products of PS and its mixtures with AP at the 1st stage

		monomer					dimer	trimer	
Composition $^{m/e}$ 78		91	104	117	130	194	207	312	t°C
PS[a]	0.4	1.73	1	0.4	0.07	0.14	0.2	0.03	330
PS[b]	0.42	0.88	1	0.18	0.05	0.03	0.05	0.01	375
PS+AP	0.51	1.1	1	0.35	0.12	0.23	0.23	0.1	325
PS+AP+ 0.15 Fe_2O_3	0.7	0.92	1	0.45	0.21	0.4	0.43	0.21	325

[a] Data, Ref. 12.
[b] Data of the present study.

In the mass spectra of destruction products of PS mixed with AP the mass peaks responsible for the formation of styrene dimer, trimer, and tetramer are more intensive than peaks in the spectra of pure PS. According to the thermographic studies the first stage is a weak exothermal process. The first stage is characterized by a small rate of CO_2 and HCl formation. We have estimated that 5–10 styrene molecules are formed per HCl molecule during the first stage. Interaction of PS with $HClO_4$, which diffuses through the PS film from the AP surface, is apparently responsible for the destruction process of PS in the presence of AP. It looks likely that this interaction initiates a chain process of PS destruction.[13, 14] Obviously, the kinetic chain length is 5–10.

Experiments on the decomposition of sandwich systems were performed to reveal the role of perchloric acid in the oxidative destruction of PS. This system consists of the pelleted mixture AP+ 2.5% Fe_2O_3 (32 mg) and of the PS (32 mg) layers separated by a layer of pelleted pyrex glass particles of 200μ (20 mg), so as Cl_2 and NO_2 (products of the AP catalytic decomposition) pass through a PS layer reacting with it. It follows from these experiments that the main products of AP catalytic decomposition, Cl_2 and NO_2, react completely with a polystyrene layer as they pass through it and form mainly HCl, N_2+CO, CO_2, and a small amount of styrene monomer. The formation rate of styrene during decomposition of a sandwich system is considerably lower than that of the decomposition of a composite system. These experiments prove that $HClO_4$

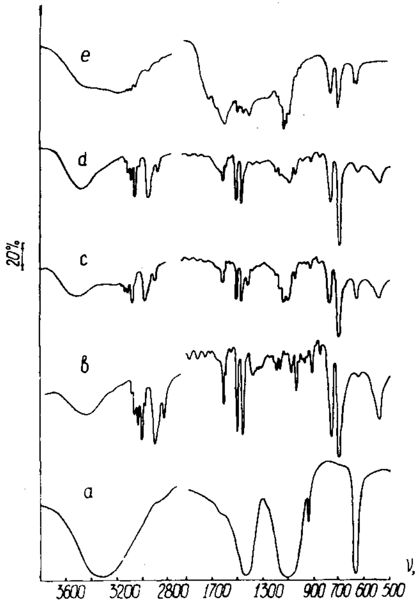

Fig. 3 IR-spectra: a) AP; b) PS; c) mixture of AP+10 PS; d) AP+PS decomposed into 15%; e) 50% mixture washed with water.

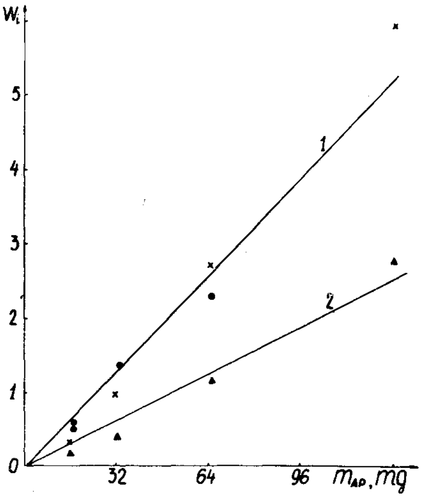

Fig. 4 Plot of maximum rates of thermal decomposition vs components ratio at 325°C, 15 mm Hg; vs M_{AP} at $M_{PS} = 16$ mg. 1) x styrene, ● CO_2, 2) Δ HCl.

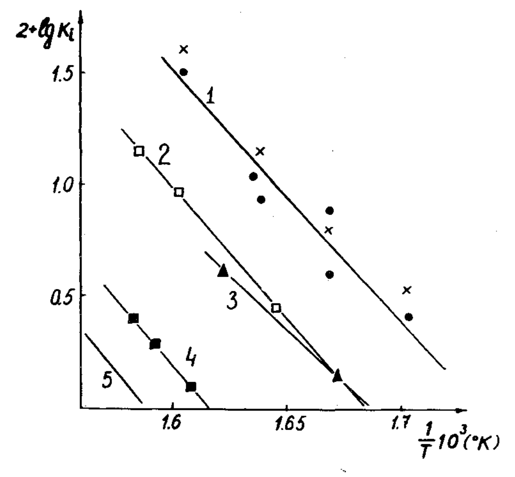

Fig. 6 Plot of the maximum decomposition rate constants vs temperature $K(\text{min}^{-1})$: 1) mixture of AP and PS (1:1) at 15 mm Hg ● styrene, x CO_2; 2) the same mixtures at 1 atm, □ CO_2; 3) oxidative destruction of PS in $HClO_4$ vapour-Δ styrene; 4) ■ destruction of PS according to Ref. 13; 5) PS according to Ref. 1.

induces oxidative destruction of PS in the composite system. At the same time such oxidizers as Cl_2 and NO_2 are very active in the interaction with PS, their activity being considerably higher than that observed by Hansel and McAlevy.[15] It was observed with a tenfold magnifying lens that during the decomposition process gas bubbles (about 1 mm) were formed resulting in an intensive mixing of the AP particles and liquid PS. At the end of an induction period a fluid polymer film disappeared and a boiling porous product ("residue") was formed; gas bubbles were not observed. The coefficient of $HClO_4$ diffusion through this product sharply increases. This leads to a sharp increase in the AP decomposition at the second exothermal stage. Obviously, stages observed during the experiment are caused by the formation of an intermediate product in a condensed phase (*K* phase). IR-spectrum of *K* phase at the second stage differs from that of the AP and PS mixture (Fig. 3). In particular, an intensive band at 540 cm^{-1} in polystyrene spectrum disappears, while a band of a carbonyl group appears at 1720 cm^{-1} which is observed in Ref. 16 at PS oxidation with oxygen. This supports the idea which follows experimental data, that intermediate products are formed in a condensed phase of AP reaction with PS. Similar stages are observed during decomposition of AP and polymethylmethacrylate (PMMA) and they are not observed during decomposition of AP-polyethylene mixtures.

Figure 4 gives dependences of the maximum formation rates of styrene (1st stage) and CO_2 (2nd stage) on the component ratio in the mixture, on AP quantity (M_{AP}) at the fixed PS quantity (M_{PS}). It is seen from Fig. 4 that the rates of the first and the second stages are proportional to M_{AP}. If the rate of both processes is proportional to the contact surface between AP and PS the same dependence is observed.

It is seen in Fig. 5 that the rate of both stages decreases as the AP particle size is increased from 100–300 μ. This dependence must be observed when interaction of the perchloric acid with PS (1st stage) or with the "residue" (2nd stage) proceeds in the diffusion or intradiffusion regions. The conclusion about the influence of diffusion on the rates of both processes is in agreement with the decrease of process rates when pressure is increased from 15 mm Hg to 1 atm.

Figure 6 gives temperature dependences of the maximum rate constants of both stages in Arrenius coordinates within 305–350°C temperature range. An activation energy is 51 kcal/mole for rate constants of these stages. The maximum rate constants were determined via equation

$$K_{i^*} = W_i^* \Big/ \int_0^{t^*} W_i \, dt \qquad (1)$$

where W_i^* is a maximum rate, t^* is the time of experiment. Integration of the denominator determines the yield of a given product. The yield of styrene and CO_2 at 15 mm Hg was approximately constant. Therefore, activation energies for K_{i^*} ($i^* = 1.2$) and W_i ($i = 44.104$) were approximately equal.

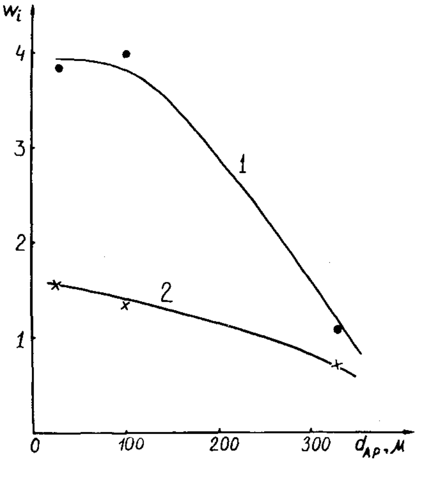

Fig. 5 Plot of maximum rates of thermal decomposition of the AP mixture with PS 1:1 [1) styrene, 2) CO_2] vs diameter of the AP particles at 325°C; 15 mm Hg.

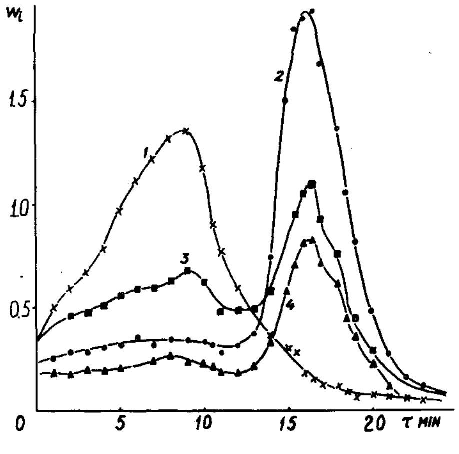

Fig. 7 AP:PS (1:1)+ 2.5% Fe_2O_3 (26 m^2/g) $t = 325$°C, 15 mm Hg. 1) styrene; 2) CO_2; 3) HCl; 4) $CO+N_2$.

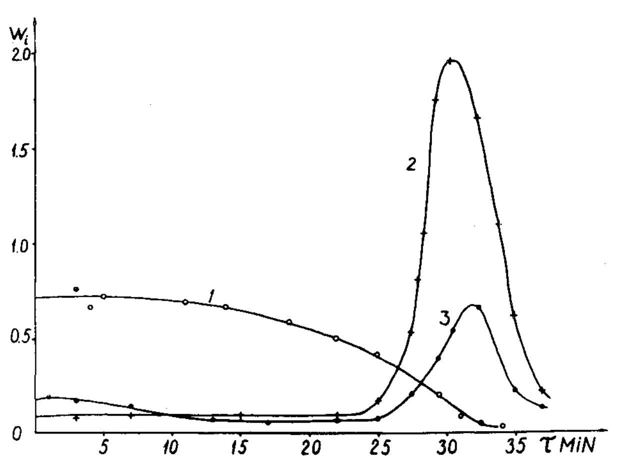

Fig. 8 $t = 326°C$, 15 mm Hg, AP:PS (1:1)+ 4.7% SiO_2 ($S_{sp} = 200\ m^2/g$). 1) styrene; 2) CO_2; 3) HCl.

The yield of CO_2 increases to 2–2.5 times as pressure is increased to 1 atm. It is seen in Fig. 6 that the maximum rate constants of both stages at 15 mm Hg are approximately the same. They are determined via expression:

$$K_{1,2} = 2.3\,10^{17}\exp(-51000/RT)\,\text{min}^{-1} \qquad (2)$$

Figure 6 gives a comparison of data in Refs. 1 and 13 on the maximum rate constants of PS destruction (our data are close to those in Ref. 13).

Results of the study on the influence of the Fe_2O_3 catalyst on the rate of both stages are presented in Fig. 7. As a comparison of Figs. 2 and 7 shows, the rate dependence of oxidative destruction on the reaction time is of the autocatalytic character in the presence of the catalyst (2.5%); the maximum rate of the oxidative destruction increases by 30%. The rate increase of the second stage in the presence of 2.5% Fe_2O_3 is much greater (in 2.5–3 times), the formation rate of CO_2 and HCl increases at the 1st stage. The maximum rates of both stages were slightly changed as the catalyst concentration was increased to 12.5%. Increasing the specific surface area of Fe_2O_3 by 2 fold (2.5% of the catalyst) did not appreciably affect the decomposition rate.

It has been found that the decomposition rate of AP and PS mixtures at the 2nd stage considerably increases (Figs. 2 and 8) as SiO_2 (which is a bad catalyst for the $HClO_4$ and AP decomposition) is added.[17] This effect is apparently caused by a strong increase in the specific surface area of the "residue" (an intermediate product of the first stage which is, obviously, deposited on SiO_2) in the presence of SiO_2 and, therefore, by its reactivity in reaction with $HClO_4$. Probably, a high efficiency of SiO_2 as a catalyst of combustion of composite systems with AP[18] can be also explained by the cited above reasons.

The comparison of Figs. 2 and 9 proves the idea that the reaction of perchloric acid with PS is responsible for the described regularities of thermal decomposition of the AP-PS system. The similar kinetic dependences are observed for the AP-PS and $HClO_4$-PS systems (the consecutive formation of styrene, CO_2 and HCl).

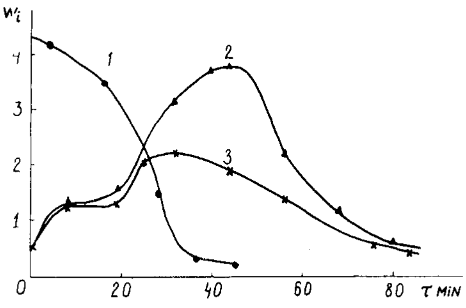

Fig. 9 Plot of the evolution rate of gas products of the PS oxidative destruction (0.5 g) in $HClO_4$ vapours vs time (P_{HClO_4} 1 mm Hg) at 340°C, 15 mm Hg. 1) styrene; 2) CO_2; 3) HCl.

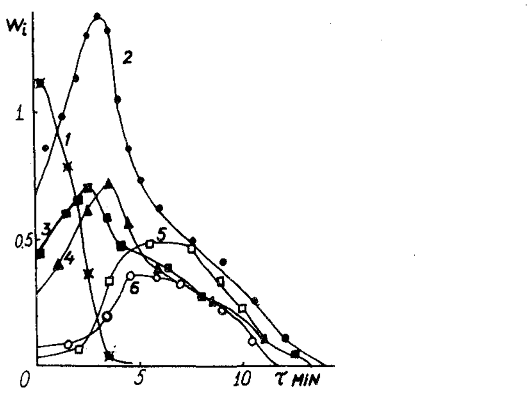

Fig. 10 AP:PS (4:1). 1) styrene; 2) CO_2+N_2O; 3) HCl; 4) $CO+N_2$; 5) Cl_2; 6) $NO+NO_2+N_2O$, $t = 325°C$.

Kinetics of Thermal Decomposition of Stoichiometric PS and AP Mixtures

Kinetic curves of the AP (250–400 μ) and PS mixtures with 4:1 ratio at 15 mm Hg are given in Fig. 10. It is seen in Fig. 10 that the rate maxima of styrene, CO_2+N_2O, and Cl_2 formation are separated with time. Hence thermal decomposition has at least three stages. The similar regularities are observed during decomposition of stoichiometric AP (250–400 μ)-PS mixtures at 1 atm. (Fig. 11). As the pressure is increased from 15 mm Hg to 1 atm., the decomposition rate decreases over 10 fold, HCl yield increases, while Cl_2 yield decreases. The peculiar character of the rate dependence of the 44th peak formation at 1 atm is due to the fact that $NO+NO_2$ yield decreases and N_2O yield increases when pressure is increased to 1 atm. At the initial reaction stages CO_2 makes the main contribution to the 44th peak, while at the maximum W_{30} (3rd stage) N_2O makes a substantial contribution to the same peak. It is seen in Fig. 11 that at the third stage a fast formation of the molecular oxygen takes place. We propose that the third stage starts as the fuel has completely reacted (its appreciable portion being liberated into a gas phase as products of oxidative destruction: monomer, dimer, etc.) and involves destruction of oxidizers.

In the presence of Fe_2O_3 the first stage disappears, the yield of gas products of the PS oxidative destruction (monomer, styrene, etc.) sharply decreases. At the same time at 15 mm Hg the yield of final decomposition products is increased to 1.5–2 fold. As the pressure is increased to 1 atm (Fig. 12), the decomposition degree considerably increases—composition of the decomposition products (CO_2, $CO+N_2$, HCl, H_2O) becomes equal to equilibrious. At 1 atm the dependence of the decomposition rate on time is of the autocatalytic character. The

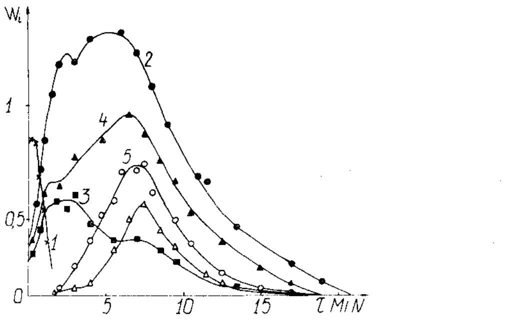

Fig. 11 AP:PS (8:1), $t = 375°C$. 1) styrene; 2) CO_2+N_2O; 3) HCl; 4) $CO+N_2$; 5) $NO+NO_2+N_2O$; 6) O_2.

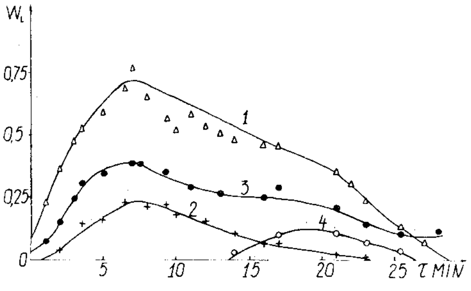

Fig. 12 AP:PS (8:1) + 2.5% Fe_2O_3, 328°C, 1 atm. 1) $CO_2 + N_2O$; 2) HCl; 3) $CO + N_2$; 4) $N_2O + NO$.

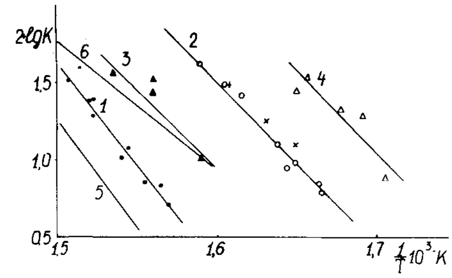

Fig. 14 Plot of decomposition rate constants vs temperature at 1 atm. 1) AP:PS (8:1); 2) AP:PS (8:1) + 2.5% Fe_2O_3; and AP + 2.5% Fe_2O_3; 3) AP (4 μ):PS (8:1); 4) AP (4 μ):PS (8:1) + 2.5% Fe_2O_3; 5) data of Ref. 1 for AP-PS; 6) data of Ref. 3.

Table 2 Kinetic parameters of the decomposition of AP mixtures with PS (8 : 1) and Fe_2O_3 at 1 atm

% catalyst	0		2.5%	
dispersity AP μ	250–400	4	250–400	4
activation energy kcal/mole	60	46	49	49
Log of pre-exponential factor 1/min	19.35	15.0	16.65	17.3

dependence of the maximum decomposition rates of AP and PS stoichiometric mixtures at 15 mm Hg and at 1 atm is given in Fig. 13 in Arrenius coordinates. Dependences of the maximum decomposition rates of PS and AP stoichiometric mixtures with and without the catalyst, Fe_2O_3, and of pure AP at 1 atm on temperature are plotted in Fig. 14 in Arrenius coordinates. For comparison, in Fig. 14 the data of Ref. 1 for AP and PS (4:1) and of Ref. 3 for the fuel on the basis of AP (90 μ) and polybutadiene acrylic acid (PBAA) are given.

Though the data on the decomposition kinetic curves of the stoichiometric AP and PS mixtures at 1 atm in the present paper and in Ref. 1 differ, the kinetic parameters of the constants of the maximum formation rate of CO_2 and the maximum heat release rate of the second stage in Ref. 1 are close by value (Fig. 14). It follows from data in Figs. 13 and 14 that the catalyst efficiency Z (ratio of reaction rate with catalyst to that without the catalyst) increases with pressure from $Z = 2$ at 15 mm Hg to $Z = 10$ at 1 atm (at 2.5% Fe_2O_3). Figure 15 gives kinetic curves of the final product yield of the AP decomposition (250–400μ) with 2.5% Fe_2O_3 at 1 atm. The constants of the maximum decomposition rates of AP-Fe_2O_3 and AP-PS-Fe_2O_3 mixtures are practically equal (Fig. 14). Therefore, the AP catalytic decomposition (its mechanism is studied in some detail in Refs. 4, 8, 19 is a limiting stage in the region of the maximum decomposition rate of AP-PS-Fe_2O_3 mixtures.

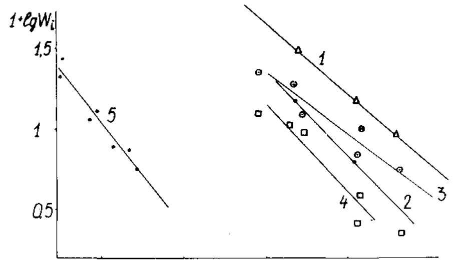

Fig. 13 Plot of maximum decomposition rates of mixtures AP:PS (8:1) with the catalyst 2.5% Fe_2O_3 at 15 mm Hg. 1) △ $CO_2 + N_2O$; 2) ● $Cl_2 + \frac{1}{2}$-HCl; and without the catalyst at 15 mm Hg. 3) ⊙ $CO_2 + N_2O$; 4) □ $Cl_2 + \frac{1}{2}$-HCl; at 1 atm; 5) $CO_2 + N_2O$.

The AP dispersity affects the decomposition rates of its mixtures with PS, as well as the shape of kinetic curves. More complete decomposition takes place and the maximum decomposition rate of AP mixtures with PS at 1 atm is a 3 fold increase when the AP particle size is decreased from 250–400 μ to 4 μ. The maximum rate of catalytic decomposition of PS mixtures with AP particle size equal to 4 μ is about 4 times greater than that with AP particle size equal to 250–400 μ (Fig. 14). Table 2 gives kinetic parameters of the maximum rates of CO_2 evolution during decomposition of stoichiometric mixtures of AP with PS at 1 atm with Fe_2O_3 catalyst and without it for AP of various dispersity.

IV. Discussion

Model of Thermal Decomposition of the AP-PS-Fe_2O_3 System

In order to explain the mentioned experimental facts the following reaction scheme was proposed which includes the stages:

1) AP equilibrium dissociation at the surface of the AP particle $NH_4ClO_4 \rightleftarrows NH_3 + HClO_4$.
2) Diffusion of $HClO_4$ from the AP particle surface through the PS film and simultaneous two-stage reaction of $HClO_4$ with PS. At the first macro-stage the PS oxidative destruc-

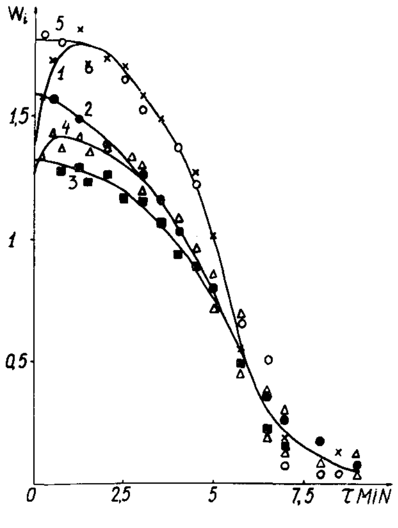

Fig. 15 AP + 2.5% Fe_2O_3, $t = 341$°C, 1 atm. 1) Cl_2; 2) N_2O; 3) HCl; 4) N_2; 5) $NO + N_2O$.

tion takes place, which is accompanied by the formation of an intermediate condensed product A_k

$$HClO_4+(C_8H_8)n \rightarrow A_k+\nu C_8H_8+2CO_2+HCl+\cdots \qquad (3)$$

Obviously, this macro-stage is a chain process, as with thermal destruction of PS. This process is initiated by the reaction of perchloric acid with PS which results in the formation of radicals. These radicals are decomposed forming new radicals and splitting monomers, dimers, trimers, and tetramers. Recombination of these radicals results in a chain termination and in the formation of a slightly volatile solid product A_k which accounts for a small fraction of the initial PS ($\varepsilon = 0.05$–0.1).

At the second stage the interaction of perchloric acid with A_k takes place.

$$HClO_4+A_k \rightarrow 2CO_2+HCl+\cdots \qquad (4)$$

Obviously, the diffusion coefficient of the perchloric acid in pores of $A_k(D_2)$ is considerably greater than that of $HClO_4$ diffusion in a liquid film of the initial polymer (D_1). The effective diffusion coefficient, D_{ef}, of the perchloric acid in the film which consists of the PS and A_k mixture is expressed via formula

$$D_{ef} = D_2\gamma\frac{1-\alpha-\varepsilon\alpha}{1-\alpha+\varepsilon\alpha\gamma} \qquad (5)$$

where α is a degree of the PS conversion via reaction 1, $\gamma = D_1/D_2 \ll 1$. We propose that $A_k(n_2)$ and $PS(n_1)$ concentrations which are proportional to reaction rates, Eqs. (3) and (4), are constant in the film. It follows from Eq. (5) that at $\gamma \ll 1$, $D_{ef} \simeq D_1$ when d changes from 0 to $1-\varepsilon$. This fact explains an unusual shape of kinetic curves, in particular, the appearance of the pronounced induction period for the formation rate of CO_2, HCl.

Using the results of Ref. 4 we can write the following equation for the rates of PS destruction—$d\alpha/dt$ and AP decomposition $d\beta/dt$

$$d\alpha/dt = A' \times K_1 \times n_1 \times n_p \times \psi_1 \qquad \Delta = R_o - R \qquad (6)$$

$$\frac{d\beta}{dt} = C\frac{d\alpha}{dt} + B' \times \frac{K_2 \times n_2 \times n_p \times \psi_2}{1+\dfrac{D_{ef}R_o}{3D_g\Delta}\theta_2{}^2\psi_i}$$

$$\psi_i = 1/\theta_i\, th\theta_i \qquad \theta_i = \delta(K_i n_i/D_{ef})^{1/2} \qquad (7)$$

where R_o, R are initial and current radiuses of the AP particles, D_g—coefficient of $HClO_4$ diffusion in gas gap between AP and PS; K_1, K_2 are rate constants of reactions in Eqs. (3) and (4), respectively; δ_0, δ—initial and current film thickness. The experimental data for rich mixtures are in agreement with the results calculated via Eqs. (6) and (7) at $\gamma = 0.01$.

Similar equations can be also written for the AP-PS-Fe_2O_3 system. The perchloric acid is decomposed more quickly on Fe_2O_3 (forming the decomposition products, Cl_2, NO_2, etc., which are less active than $HClO_4$ during initiation of the PS destruction) than it reacts with PS. As a result, the decrease of the destruction rate of PS in the presence of Fe_2O_3 at small α is observed. The initiation rate of the PS destruction by products of catalytic decomposition of $HClO_4$ (1st stage) and the AP decomposition rate (2nd stage) increase as α is increased. This is a result of the increase in the catalyst concentration in the film as the film thickness decreases.

All these facts result in a pronounced autocatalytic character of the W_i dependence on time in the presence of Fe_2O_3. A strong influence of pressure on decomposition rates at all stages can be explained by the pressure effect on the diffusion coefficient (D_{ef}).

References

[1] Merzhanov, A. G., Shteinberg, A. S., and Goncharov, E. P., "Peculiarities of High-Temperature Decomposition of Ammonium Perchlorate and Heterogenous Systems on its Basis," *Fizika Gorenia i Vzryva*, Vol. 9, No. 2, 1973, pp. 185–191.

[2] Sammons, G. D., "Study of Solid Propellant Combustion by Method of Dynamic Calorimetry," AIAA Paper 69–504, U.S. Air Force Academy, Colo., 1969.

[3] Waesche, R. H. W. and Wenograd, G., "Estimation of Combustion Rates of Solid Propellant Fuel with respect to Kinetics of the Condensed Phase Decomposition," AIAA Paper 69–145, New York, 1969.

[4] Korobeinichev, O. P., Anisiforov, G. I., and Shkarin, A. V., "Kinetics of Catalytic Decomposition of Ammonium Perchlorate and its Mixtures with Polystyrene," *Fizika Gorenia i Vzryva*, Vol. 9, No. 1, 1973, pp. 67–75.

[5] Korobeinichev, O. P., "Application of Mass-spectrometry for Study of Kinetics and Mechanism of Decomposition of Solids," *Uspekhi Khimii*, Vol. 38, No. 12, 1969, pp. 2113–2128.

[6] Korobeinichev, O. P., Boldyrev, V. V., and Karpenko, Y. Y., "Pulse Mass-spectrometric Study of Fast Processes of High-temperature decomposition of Ammonium Perchlorate," *Fizika Gorenia i Vzryva*, Vol. 4, No. 1, 1968, pp. 33–38.

[7] Korobeinichev, O. P., Aleksandrov, V. V., and Lyakhov, N. Z., "Study of Kinetics and Mechanism of High-temperature Decomposition of Nitrocellulose by the Time-of-flight Spectrometer," *Izvestiya Akademii Nauk SSSR*, seriya khim., No. 3, 1970, pp. 612–616.

[8] Korobeinichev, O. P. and Karpenko, Y. Y., "Study of Kinetics and Mechanism of Ammonium Perchlorate Sublimation by the Mass-spectrometric thermal Analysis," *Izvestiya Akademii Nauk SSSR*, seriya khim., No. 7, 1971, pp. 1557–1559.

[9] Lossing, F. P., "Mass-spectrometry of Free Radicals," Mass-spectrometry, Ed. C. A. McDowell, New York, N.Y., McGraw-Hill, 1963, pp. 442–505.

[10] Milne, T. A. and Green, F. T., "Mass-spectrometric Sampling of 1 atm. Flames," 10th International Combustion Symposium, The Combustion Institute, Pittsburgh, Pa., 1965, pp. 153–159.

[11] Emanuel, N. M., Denisov, E. T., and Meizus, E. K., *Tsepnye Reaktsii Okislenia Uglevodorodov v Zhidkoi Fase*, Nauka, Moscow, 1965, pp. 26–28.

[12] Bradt, P., Dibeller, V. H., and Mohler, F. L., "A New Technique for the Mass-spectrometric Study of the Pyrolysis Products of Polystyrene," *Journal of Research of the National Bureau of Standards*, Vol. 50, No. 4, April 1953, pp. 201–202.

[13] Madorsky, S. L., *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964.

[14] Lengell, G., "Thermal Degradation Kinetics and Surface Pyrolysis of Vinyl Polymers," *AIAA Journal*, Vol. 8, No. 11, Nov. 1970, pp. 1989–1996.

[15] Hansel, J. G. and McAlevy, R. F., "Energetics and Chemical Kinetics of Polystyrene Surface Degradation in Inert and Chemically Reactive Environments," *AIAA Journal*, Vol. 4, No. 5, May 1966, pp. 841–848.

[16] Beachell, H. C. and Smiley, L. H., "Oxidative Degradation of Polystyrene," *Journal of Polymer Science*, Vol. 5, No. 7, 1967, pp. 1635–1643.

[17] Korobeinichev, O. P., Anisiforov, G. I., Polyakov, N. N., and Shkarin, A. V., "Kinetics of Catalytic Decomposition of Perchloric Acid and Ammonium Perchlorate," *Fizika Gorenia i Vzryva*, Vol. 9, No. 2, 1973, pp. 199–204.

[18] Bakhman, N. N., Lobanov, I. N., Margolis, L. Y., Nikiforov, V. S., and Sakharov, M. M., "Heterogenous-homogenous Catalysis at Combustion of Composite Systems," *Doklady Akademii Nauk SSSR*, Vol. 202, 1972, pp. 1107–1110.

[19] Korobeinichev, O. P., Shkarin, A. V., and Shmelev, A. S., "Catalytic Mechanism for Decomposition and Combustion of Ammonium Perchlorate," *Proceedings of the 3rd All-Union Symposium on Combustion and Vzryv*, Nauka, Moscow, 1972, pp. 752–755.