Calculation of Solid-Propellant Burning Rates from Condensed-Phase Decomposition Kinetics

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Kinetic rates of thermal decomposition reactions of three ammonium perchlorate composite propellants have been determined by the techniques of differential scanning calorimetry and thermogravimetric analysis at pressures to 500 psi (1 psi = 6894.7 Pa = 0.068 atm; 1 atm = 14.7 psi). The results of these experiments were extrapolated to give heat-evolution rates at temperatures that are believed to prevail at the surface of burning propellants. A semi-empirical condensed-phase combustion model has been used to calculate propellant burning rates from these heat-evolution rates and surface temperatures determined by equilibrium vaporization. Calculated and experimental burning rates are found to agree within an order of magnitude. The differences between these rates were attributed to a gas-phase heat-flux term in the energy balance at the propellant surface.

INTRODUCTION

A number of approaches to the description of solid-propellant combustion have been reported and have met with varying degrees of success [1, 2]. In general, investigators have attempted to explain the effect of pressure, temperature, or particle size on the steady-state burning rate or to use a steady-state burning model to describe the combustion behavior in a certain dynamic situation. However, there is currently no general agreement as to whether the individually definable processes which regulate the rate of combustion occur in the condensed phase or in the gas phase. In most models the rate of combustion of the solid has been assumed to be governed by the speed of the gas-phase flame, which has, in turn, been controlled by pressure effects on reaction rates or by diffusional effects on initially unmixed gases [3]. Such theories lead to approximately correct predictions of the pressure dependence of propellant burning rates but do not provide a means for predicting absolute values of regression rates.

Only recently have combustion-wave models been applied to ammonium perchlorate (AP) propellants which include consideration of exothermic condensed-phase or surface-coupled reactions [4].

Several Russian authors (see [5–7]) have considered models in which both condensed-phase and gas-phase effects are important. These authors used the Zel'dovich integration technique to calculate a burning rate for a material in which an exothermic reaction, described by Arrhenius kinetics, takes place prior to vaporization of the condensed phase. The vaporization temperature itself is presumed to be determined by equilibrium vaporization considerations. This model defines the regression rate in what is termed the "flameless combustion" regime [5], where there is no important heat flux to the regressing surface from the gas-phase flame. Gas-phase effects become significant in other regimes, and their effect is generally found to be additive in nature, i.e.,

$$\dot{m}c_p(T_s - T_0) = \dot{q}_g + \dot{q}_{sol}. \qquad (1)$$

where m is the mass flux per unit area, c_p is the heat capacity at constant pressure, T_s is the surface temperature, T_0 is the initial temperature, q_g is the thermal flux from the gas phase, and q_{sol} is the integrated heat release in the condensed phase; dots above the symbols denote differentiation.

In the flameless regime, the mass burning rate

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can be expressed as

$$\dot{m} = \left(\frac{2\lambda T_s^2 \rho W(T_s)}{c_p^2 E(T_s - T_0)^2} \right)^{1/2}. \tag{2}$$

Here λ is the thermal conductivity, ρ is the density, W is the rate of heat release, and E is the activation energy of the driving reaction. It is assumed that W is a function of temperature only and is governed by an expression of Arrhenius form, so that

$$W = QZ \exp(-E/RT), \tag{3}$$

where Q [cal/g] is the energy of reaction, Z is a pre-exponential factor, and R is the universal gas constant.

In using Eqs. (2) and (3) to calculate a burning rate from propellant decomposition data, the assumption is made, following the Zel'dovich model, that W is evaluated at a temperature equal to the effective surface temperature T_s. For the purposes of this study, it will be assumed that the surface temperature is a function of pressure according to the equilibrium condition suggested by the AP dissociation-pressure measurements made by Inami et al. [8] and the combustion surface-temperature measurements reported by Powling and Smith [9]. This equilibrium surface temperature, analogous to a boiling point, is determined by pressure rather than by kinetic processes. Thus, for each pressure there is a fixed surface temperature for AP and, probably, for AP propellants. The known effect of pressure on burning rate would be accounted for by changes in this surface temperature resulting from a pressure change and by resulting changes in W, which is, in turn, a function of temperature. With these surface temperatures, it is only necessary to have values for $W(T)$ to make an absolute calculation of the limiting-case flameless regression rate for AP propellants.

In an earlier paper by the present authors [10], the thermoanalytical technique of differential scanning calorimetry was used to obtain values for $W(T)$ for ammonium perchlorate. Although a slight extrapolation was necessary to obtain W, i.e., the rate of heat evolution at the surface temperature, excellent agreement with experimentally determined pyrolysis rates at atmospheric pressure was obtained.

The same approach can be applied to the consideration of propellant burning rates. In earlier studies [11], it was shown that those formulational variables which affect thermal decomposition also affect burning rates.

The aim of the present study was to extend this qualitative correlation to a quantitative determination of the rates of propellant regression as predicted by the limiting-case flameless-combustion model. The present paper describes the use of this

theory together with kinetic data obtained through application of the techniques of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to calculate burning rates for a series of propellants, thus permitting a quantitative evaluation of the magnitudes of the condensed-phase and gas-phase energy contributions to the control of the burning process.

EXPERIMENTAL TECHNIQUE

The experimental techniques used in this study included thermogravimetric analysis and differential scanning calorimetry. The DSC technique permits the direct time- and temperature-resolved measurement of the rate of heat evolution from a condensed-phase sample undergoing chemical reaction. With the differential scanning calorimeter developed by the Perkin–Elmer Corporation [12], a sample and a reference material in separate containers are together subjected to a programmed temperature rise. To accomplish this during reactions involving heat release or absorption, excess energy is fed to the sample or reference material such that their instantaneous temperatures are maintained equal. The quantity of excess energy is recorded, giving a record of power against time which is linearly related to the sample temperature. By integrating this record, the total enthalpy changes associated with the observed thermal events are obtained directly. Direct comparison of records is made possible through normalizing with respect to sample weight. (It should be noted that the calorimeter was re-calibrated with reference samples on a monthly basis and that it was not found necessary to repeat any tests as a result of these calibrations.)

For tests above one atmosphere, the calorimeter sample holder was placed in a high-pressure vessel made at United Technologies Research Center for this purpose. Pressurization and venting were accomplished through the tubes used for purge-gas flow at lower pressures. Argon was used as the pressurizing gas because of its low thermal conductivity and resultant lower heat loss from the sample holder to the surroundings. Most tests were conducted at 10°C/min; however, tests on two propellants at 5, 10, and 20°C/min gave equivalent kinetic data, and earlier tests with pure AP [10] extended this finding to isothermal conditions. The samples were prepared from shavings microtomed from a block of propellant, then punched and cut to give the appropriate mass, approximately 4 mg. The sample mass was determined with a Cahn electrobalance with a stated

TABLE 1

Propellant Compositions and Strand-Burning Rates

Propellant No.	AP, %	PBAA, %	δ, μm	r [inch/sec] for p [psi]			
				15	125	250	500
1			15	0.058	0.185	0.270	0.395
2	75	25	90	0.042	0.115	0.160	0.225
3			200	0.035	0.087	0.117	0.158

Notes. δ is the AP particle size; PBAA is a copolymer of polybutadiene and acrylic acid.

accuracy of better than 0.1%. The sample cups were usually aluminum; cups were 6 mm in diameter and 0.2 mm thick. The cup was covered with a thin cap, pierced with a 0.2-mm-diameter hole to allow gaseous products to escape. The cap was crimped to the cup to give uniform heat-transfer characteristics.

Quantitative kinetic data were obtained from DSC thermograms by a procedure, detailed in [11], which is similar to the area method of Borchardt and Daniels [13]. This procedure assumes that the rate of heat evolution from the sample is proportional to the rate of gasification or weight loss. Since the area under the curve from the beginning of a scan to any temperature is proportional to the heat evolved up to that temperature, this area divided by the total area for a reaction gives the fraction of the sample decomposed from the initial temperature up to the given temperature. The rate of heat evolution from the decomposing sample can then be related to the specific reaction rate at that temperature. As will be shown later, the assumption of first-order kinetics appeared to give excellent fits to the data with an Arrhenius expression. A minimum of three tests was conducted when kinetic data were being obtained.

The thermogravimetric analysis apparatus used consisted of a Cahn RG automatic electrobalance, a Hevi-Duty MU-3012 multiple-unit furnace, a Leeds and Northrup Model 10170 program control, and a Leeds and Northrup Speedmax G two-pen recorder. To allow tests to be made at pressures up to 250 psi, the glass vacuum bottle and hang-down tube were replaced with steel replicas.

Three PBAA propellants are discussed in this paper, which differ only in oxidizer particle size and are chosen from a large matrix set up to allow determination of the effects of several formulational variables on burning rate and decomposition. The propellants were processed at the Jet Propulsion Laboratory (Pasadena) under the direction of Mr. L. R. Feinauer. Their compositions are shown in Table 1 along with the pertinent strand-burning data obtained by JPL. As may be seen, the three propellants allow a study of particle-size effects at constant

oxidizer loading. Similar tests of the effects of catalysts and oxidizer loading were conducted, and the results of these tests are given elsewhere [14].

Sample thermograms for AP and for an AP-based composite propellant are shown in Fig. 1. The endothermic AP crystal-phase change at $T = 242°C$ is seen, as well as the exothermic low- and high-temperature decomposition stages. As follows from Fig. 1, in the propellant decomposition, the reactions occurs at lower temperatures (more rapid reaction), and the integrated energy release is four times greater than for the pure AP sample.

Kinetic Parameters

The temperatures of the peaks for the exothermic decomposition reactions give a qualitative indication of reaction rate. A change in reaction rate also implies a change in heat-release rate $k_T Q$ (k_T is reaction rate) at a given surface temperature and, therefore, a change in burning rate under the assumed model. Therefore, the comparative locations of the reaction peaks in a set of thermograms obtained for the same experimental conditions, e.g., same scan-
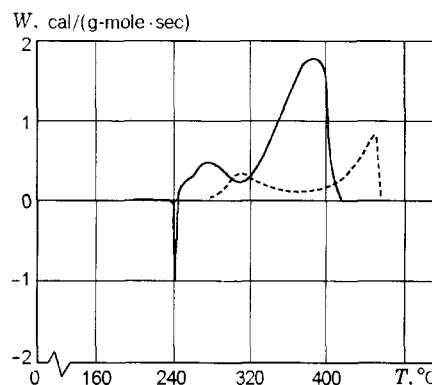

Fig. 1. Thermograms of decompositions of ammonium perchlorate (dashed curve) and propellant No. 2 (solid curve): heating rate $dT/dt = 10°C$ and $p = 1$ atm.

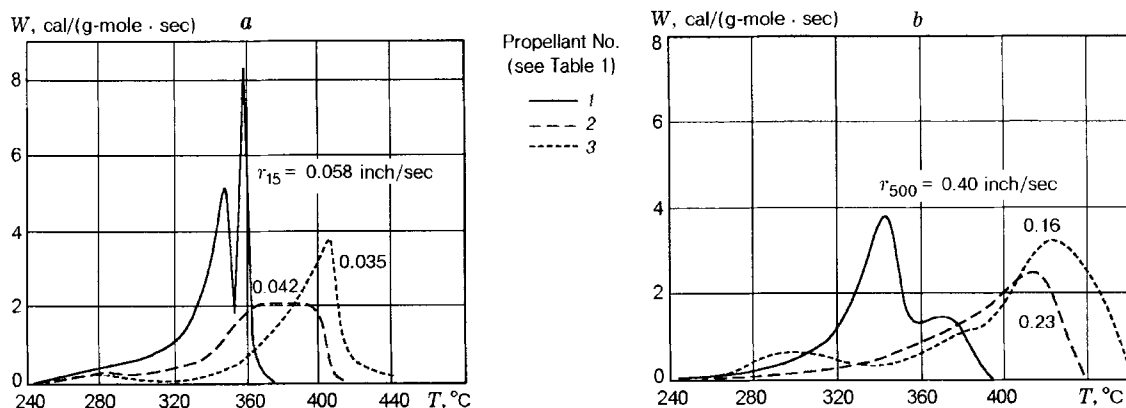**Fig. 2.** Effect of particle size on solid-propellant decomposition for $dT/dt = 10°C/min$ and $p = 1$ atm (a) and 500 psi (b).

RESULTS AND DISCUSSION

The decomposition characteristics of the three propellants were determined in the calorimeter for pressures from 14.7 to 500 psi. Figure 2a shows DSC thermograms for propellant Nos. 1–3 at atmospheric pressure. It can be seen from the relative position of the peaks that particle size has a significant effect on the decomposition rate of the propellants. The order of the temperature peaks in this series of very similar propellants corresponds with the order of the burning rates. This particle-size effect for propellants is in strong contrast to the decomposition behavior of pure AP, where the high-temperature decomposition is completely unaffected by particle size [10]. However, the propellant decomposition is far more exothermic, probably as a result of heterogeneous interaction between oxidizer and binder. Such interaction would certainly be enhanced by the greater contact permitted with finer oxidizer particles.

The effects of particle size on propellant decom-

ning rate, will give a qualitative indication of comparative burning rates if the reaction rates have a comparable temperature dependence. However, these peaks reflect only the balance between energy-release rate (rising with temperature) and undecomposed mass present (decreasing with temperature). As a result, the absolute location of a peak is strongly dependent on heating rate and can be changed by a change in heating rate. One frequently sees the position of exotherm peaks reported as a property of a given propellant. This is based on a misconception of the nature of these peaks, which are kinetic in nature and should not be confused with thermodynamically determined phase changes.

position persist at elevated pressures. Figure 2b shows comparative DSC thermograms for the three propellants at $p = 500$ psi. The ordering of the peaks is seen to agree with measured burning rates at this pressure, as at atmospheric pressure.

The thermograms for AP and AP propellants characteristically show two or more exotherms with peaks occurring at different temperatures. In AP, these exotherms represent the well-known two-stage decomposition process. In propellants, the same processes and perhaps others are operative. The treatment of these various reaction stages, which occur sequentially during slow heating, is based on an elementary chemical kinetics principle. If a given reactant can react by alternative parallel processes, the one with the lower activation energy will predominate at low temperature while the higher activation energy process will take over at high temperature.

This behavior is reflected in kinetic data that are obtained from thermograms. For the majority of propellant samples, the low-temperature decomposition stages result in very low slopes in the low-temperature regions of Arrhenius plots. In addition, the low-temperature decomposition is anomalous in that its kinetics is time-dependent; there is an induction period. In a combustion situation, the propellant is heated very rapidly to a high temperature. Under these conditions, the highest activation energy process available will predominate. This generally involves the high-temperature decomposition reaction. It is most important to keep this in mind when extrapolating complex reaction-rate curves to find rates representative of the combustion environment. Also, because of the induction period, it is improbable that the low-temperature reaction can come into operation rapidly enough to be influential in the combustion environment.
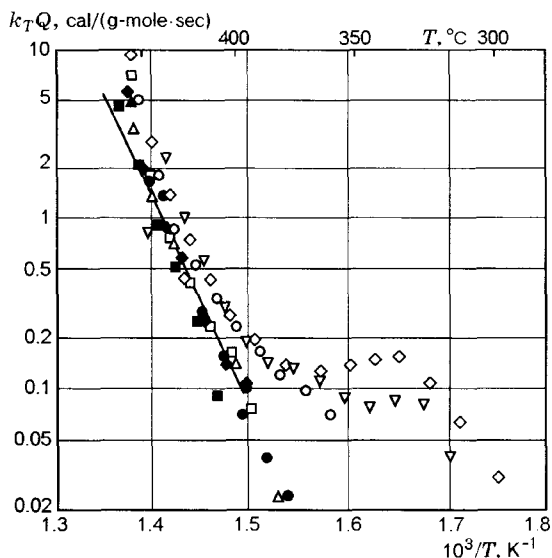
Fig. 3. Kinetics of AP decomposition: open points refer to singly recrystallized particles and filled points refer to doubly recrystallized particles.
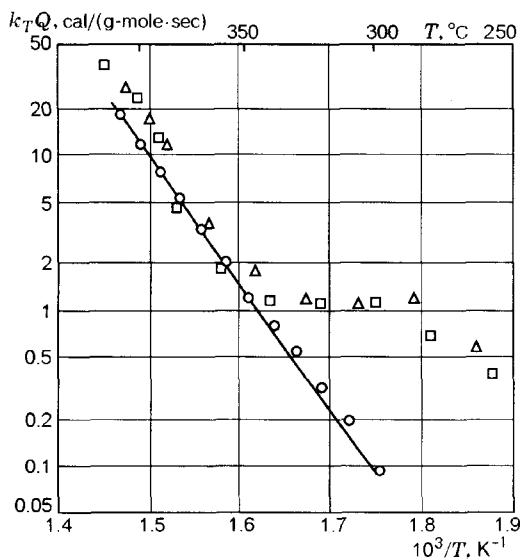

Fig. 4. Effect of predecomposition on kinetics for $dT/dt = 20°C/min$ and $p = 1$ atm; points ∘ refer to predecomposition and points ▫ and △ refer to the case with no predecomposition.

Fig. 5. Kinetics of decomposition of propellant No. 2.

The low-temperature reaction frequently tends to overlap the high-temperature decomposition stage and preclude accuracy in extrapolation procedures. To avoid complications arising from the time-dependent, low-temperature decomposition, predecomposed samples were used to obtain the kinetic data for t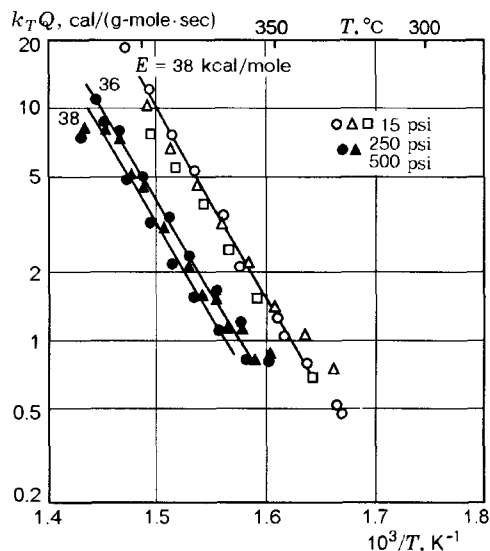he high-temperature decomposition. To achieve predecomposition, the propellant sample was heated to ≈300°C (below the temperature at which the high-temperature decomposition began) and then cooled. Thermograms were then immediately obtained using the resultant samples, and kinetic data were derived from these thermograms. At each temperature, the decomposition kinetics are unaffected by this process, and the kinetic data obtained can be interpreted with confidence since only one reaction is evidenced. Earlier tests with AP [10] showed that the low-temperature decomposition could be suppressed with doubly recrystallized particles. As shown in Fig. 3, all four samples gave reproducible kinetics in the temperature range from 400 to 450°C, with minimal scatter in the data (filled points).

Figure 4 shows kinetic data obtained in runs on predecomposed and as-received samples of propellant No. 2. This figure illustrates the advantages gained from the predecomposition process. The results obtained from predecomposed samples of propellant No. 2 over a range of pressures are illustrated in Fig. 5. In this figure, all experimental points from 10- to 90-percent decomposition are shown.

In the case of propellant No. 1, a somewhat variant behavior is noted. In this case, the high-temperature exotherm is characterized by double peaks for reasons as yet unknown (see Fig. 2b). This occurs whether or not the sample has been predecomposed. When kinetic data are taken from such thermograms, results similar to those illustrated in Fig. 6 are obtained. In such cases, the highest tem-
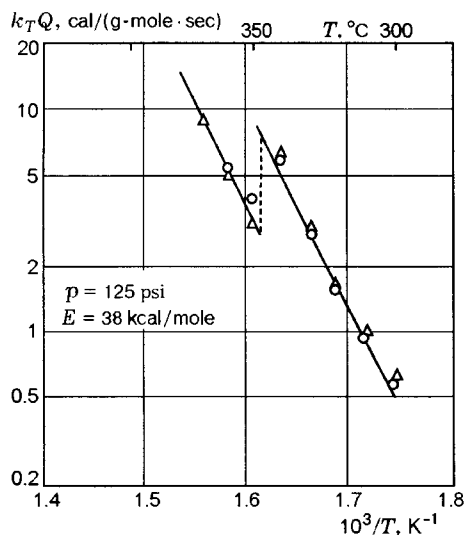
Fig. 6. Kinetics of decomposition of propellant
No. 1.

TABLE 2

Reaction Kinetic Data for Propellant Nos. 1–3

Propellant number	p, psi	E, kcal/mole	QZ, cal/(g · sec)
1	15	39	$3.7 \cdot 10^{14}$
	125	39	$3.7 \cdot 10^{14}$
	250	39	$3.7 \cdot 10^{14}$
	500	39	$3.7 \cdot 10^{14}$
2	15	38	$3.0 \cdot 10^{13}$
	125	36	$4.1 \cdot 10^{12}$
	250	36	$3.3 \cdot 10^{12}$
	500	38	$7.4 \cdot 10^{12}$
3	15	36	$4.8 \cdot 10^{12}$
	125	40	$2.6 \cdot 10^{13}$
	250	40	$2.6 \cdot 10^{13}$
	500	40	$2.2 \cdot 10^{13}$

perature portion of the kinetic curve drops and then
begins to rise again. Since the kinetic rate of inter-
est in combustion is the one which is highest at the
propellant surface temperature, the first rise, which
predicts the highest heat-release rate at high temper-
ature, was used in the present study for purposes of
extrapolation.

Particle-size effects on decomposition kinetics
are illustrated in Table 2, which gives best-fit curves
for the decomposition of the three propellants at
$p = 15$-500 psi. Particle size is seen to affect only the
pre-exponential factor, as the activation energies are
all between 36 and 40 kcal/mole for all pressures. The
highest pre-exponential factor is observed for the pro-
pellant with the smallest oxidizer particle size. Such
behavior is consistent with the greater surface area
for the finer oxidizer and the resultant increase in
contact sites for possible heterogeneous reactions.

The decomposition kinetic data illustrated by
these figures are given in more detail in Table 2,
which gives values of the pre-exponential factors QZ
and the apparent activation energy E for each for-
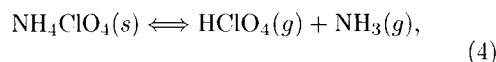mulation at each pressure.

Combustion Surface Temperature

Before the results of these kinetic studies can
be used in connection with the theoretical ap-
proach described above, it is necessary to know the
vaporization-limited surface temperature which pre-

vails at a given pressure. Under vacuum conditions,
the reaction

$$NH_4ClO_4(s) \Longleftrightarrow HClO_4(g) + NH_3(g),$$
(4)

$$\Delta H \approx 58 \text{ kcal/mole}$$

is certainly important. The temperature at which the
pressure of the gas in equilibrium with the solid be-
comes equal to the ambient pressure would define the
vaporization-limited surface temperature, analogous
to a sublimation temperature for a solid composed
of molecules stable in the gas phase. The measure-
ment of equilibrium pressures and their temperature
dependence is difficult in the case of ammonium per-
chlorate because thermal decomposition becomes ap-
preciable in the same temperature range where mean-
ingful pressure measurements are convenient. How-
ever, Inami et al. [8] have effected useful equilibrium
pressure measurements for AP by means of a novel
flow technique. The result was an expression for the
equilibrium pressure of the form

$$\log (p, \text{ mm of Hg}) = 10.56 - 6283.7/T.$$
(5)

The limiting surface temperatures that would prevail
at the experimental pressures used in this study can
be calculated using this equation and are given in
Table 3.

According to the combustion model being con-
sidered in this paper, the surface temperature of
burning propellants should show a similar variation
with pressure. There have been a number of attempts
to measure the surface temperature of deflagrating
AP propellants. The methods used have included
the microscopic analysis of the thermal history of ex-
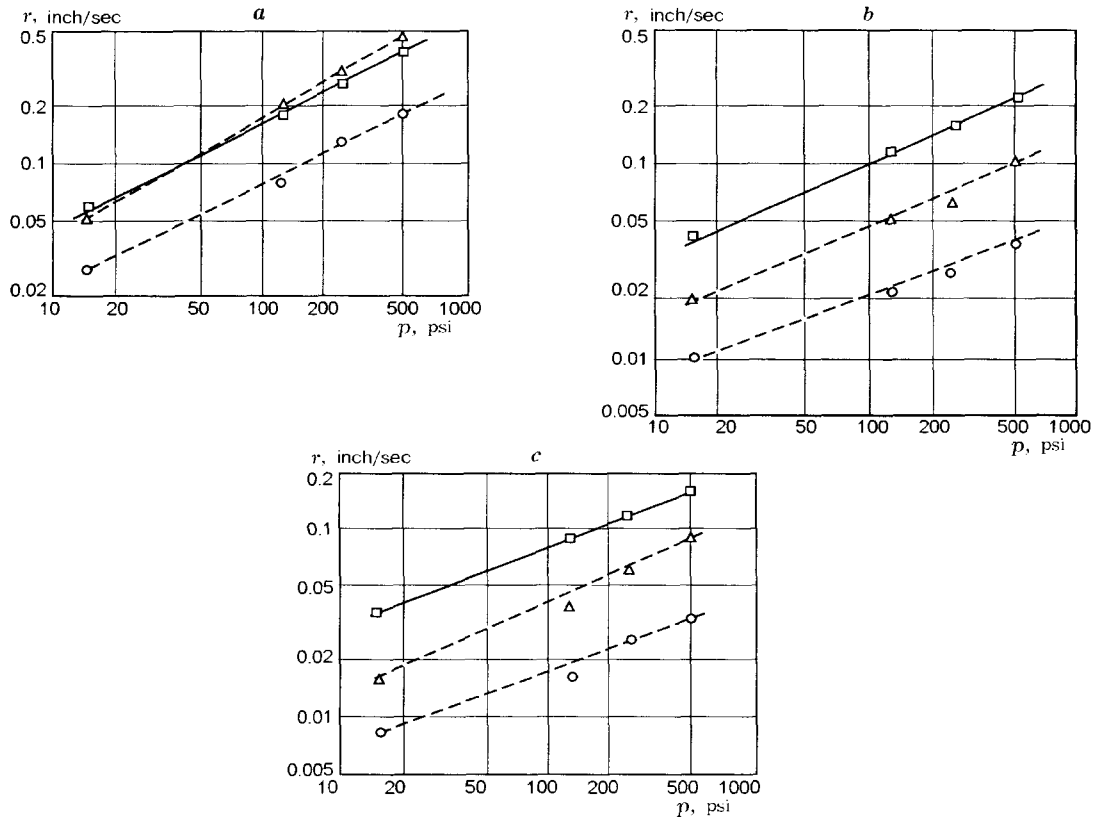tinguished samples [15], the use of flame traverses by

Fig. 7. Calculated and measured burning rates for propellant Nos. 1 (a), 2 (b), and 3 (c): points □ refer to measurements and points ○ and △ refer to calculations from the data of [9] and [8], respectively.

ultra-fine thermocouples [16], and the use of radiometric techniques [9]. All the methods have fundamental limitations that preclude general applicability over wide pressure ranges. However, the infrared radiometric technique of Powling and Smith [9] has been applied at pressures from subatmospheric to 300 psi. One interpretation of their results indicates that the surface temperature of burning ammonium perchlorate and propellant samples follows a law very similar to Eq. (5). The surface temperatures calculated from the data of Powling and Smith [9] are also given in Table 3. The temperatures are close to but somewhat lower than those calculated from the data of Inami et al. [8].

At the present time, there is no way to select between these two sets of surface-temperature data. Therefore, all burning rates are calculated on the basis of both, and two sets of results are given. While the magnitudes of the temperatures used seem consistent and reconcilable with each other, they are certainly not absolutely correct and represent a major element of uncertainty in the results. The heat-

release rates resulting from extrapolations to the surface temperatures are shown in Table 4: two values are given for each pressure, corresponding to the two sets of surface temperatures given in Table 3. The extrapolated heat-evolution rate ranges from about 10^3 to 10^6 cal/(g·sec). While these rates seem very high, it should be remembered that they are a product of a heat of reaction Q and a first-order, temperature-dependent reaction rate. The value of Q for these propellants is $\approx 10^3$ cal/g. Thus, the first-order reaction rate would be less than 10^3 sec^{-1} in all cases, a reasonable reduction rate for an exothermic material of the type considered.

Burning-rate calculations were made for the three propellants based on the limiting case of the flameless-regression model and using the decomposition data of Table 4. The burning rates calculated as a function of pressure for the two sets of surface temperatures are shown in Fig. 7 and tabulated in Table 4, together with the strand data supplied by JPL (Pasadena). These calculations assume a thermal conductivity of $5 \cdot 10^{-4}$ cal/(cm^3·sec·K), a density

TABLE 3

Surface Temperatures
Used in Calculations

p, psi	T, °C	
	data of [9]	data of [8]
15	500	550
125	580	650
250	620	680
500	650	750

Fig. 8. Comparison of decomposition kinetics obtained by DSC (curve) and TGA (points) for propellant No. 2 at $p = 1$ atm.

of 1.6 g/cm^3, and a heat capacity of 0.3 cal/(g·K) for all propellants. In addition, it was assumed that the heat absorbed in the condensed-phase transformation could be ignored as being small relative to the overall heat release. The results shown in Fig. 7 reveal that the present model is capable of predicting an approximately correct pressure dependence of burning rate. The ability of the model to predict the absolute value of burning rate depends on the choice of vaporization-limited surface temperatures. However, in the worst cases the agreement is within a factor of five and in most cases a factor of 2–3 of the measured value of the burning rate. In addition, the procedure results in the correct prediction of the effect of the oxidizer particle size.

These results are noteworthy in that correct predictions of combustion properties have been achieved well within an order of magnitude on the basis of a semi-empirical model and experimental data obtained independently. All factors used in Eq. (2) are based on experimental results. No previous model has been able to effect a priori predictions of burning rates with the present degree of accuracy.

Despite the excellence of the predictions, it is well to examine the nature of the disagreement to see if any of the techniques used in obtaining and applying the experimental data or the assumptions of the model is invalid. The technique of TGA was used to test the validity of the assumption made in obtaining kinetic parameters from DSC traces that the fraction reacted at a given temperature is proportional to the fractional area traced out at that time. The TGA kinetic data for propellant No. 2 are shown in Fig. 8, together with comparable DSC kinetic data represented by a best-fit line through the points in Fig. 4. The DSC data have been modified for presentation in this manner using the assumption that the proportionality factor Q in the heat-release rate $k_T Q$ is equal to 1000 cal/g, approximately the integrated heat release for this propellant at $p = 15$ psi. It is seen that the two sets of experimental results have about the same activation energy, although there is
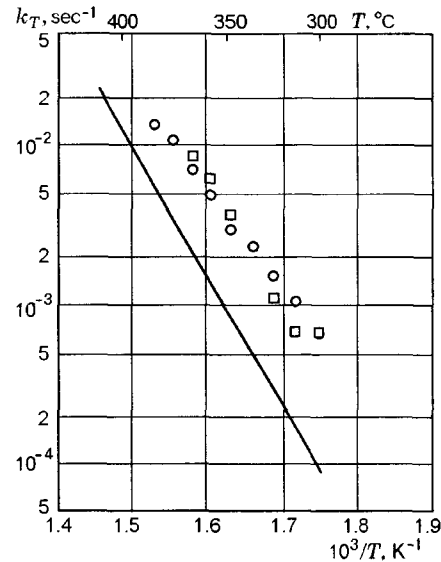
more scatter in the TGA data, and the TGA experiments yield higher specific reaction rates than the DSC experiments. Similar results were obtained at elevated pressures. Possible causes for such systematic discrepancy were discussed in detail in [14], and include differences in temperature-measurement techniques and sample environments.

Another essential assumption, that of normal time-independent Arrhenius kinetics, was also tested by varying heating rates. It was found that the kinetic data which resulted from the thermograms were not affected by scan rate over the range tested (isothermal to 20°C/min), even though the shape of the thermograms were.

Another source of doubt is the nature of the extrapolation necessary to go from the kinetics measured in the DSC temperature range to those effective at combustion surface temperatures, since the maximum temperature of the range in which the reactions of interest occur in the DSC (i.e., 450°C) is lower than the minimum surface temperature estimated for propellant combustion (i.e., 500°C). The validity of this extrapolation depends on the quality of the initial measurements and on the appropriateness of treating the high-temperature peak on the thermograms as a single reaction subject to the simple kinetics assumed. These assumptions are justified on the basis of the observations that decomposition kinetics are independent of heating rate and the correspondence of DSC and TGA data, and the fact that no compet-

TABLE 4

Calculated Heat-Release Rates and Burning Rates

Propellant number	p, psi	W, cal/(g-mole·sec)	r_{calc}, inch/sec	W, cal/(g-mole·sec)	r_{calc}, inch/sec	r_{exp} inch/sec
		data of [9]		data of [8]		
1	15	$3.5 \cdot 10^3$	0.025	$1.4 \cdot 10^4$	0.050	0.058
	125	$3.8 \cdot 10^4$	0.079	$2.6 \cdot 10^5$	0.20	0.185
	250	$1.1 \cdot 10^5$	0.13	$6.5 \cdot 10^5$	0.31	0.270
	500	$2.1 \cdot 10^5$	0.18	$1.7 \cdot 10^6$	0.49	0.395
2	15	$5.0 \cdot 10^2$	0.010	$2.0 \cdot 10^3$	0.019	0.042
	125	$2.6 \cdot 10^3$	0.022	$1.6 \cdot 10^4$	0.051	0.115
	250	$4.5 \cdot 10^3$	0.028	$2.5 \cdot 10^4$	0.062	0.160
	500	$9.6 \cdot 10^3$	0.039	$6.9 \cdot 10^4$	0.10	0.225
3	15	$3.4 \cdot 10^2$	0.008	$1.3 \cdot 10^3$	0.016	0.035
	125	$1.3 \cdot 10^3$	0.016	$9.4 \cdot 10^3$	0.038	0.087
	250	$3.8 \cdot 10^3$	0.025	$2.5 \cdot 10^4$	0.060	0.117
	500	$7.2 \cdot 10^3$	0.033	$5.7 \cdot 10^4$	0.090	0.158

TABLE 5

Calculated Gas-Phase Heat Flux

Propellant number	p, psi	$\dot{q}_g$, cal/(cm^2·sec) data of [9]	data of [8]
1	15	20	10
	125	80	—
	250	120	—
	500	180	—
2	15	20	30
	125	80	90
	250	130	140
	500	190	200
3	15	20	20
	125	50	40
	250	90	90
	500	130	130

ing reactions which might become dominant at higher temperatures are known.

A major source of error that is difficult to weigh is the surface-temperature estimate. The burning rates are quite sensitive to changes in the assumed surface temperature. However, if new data become available, they can be incorporated into this approach quite readily.

Another assumption inherent in the application of the limiting-case model is that there is no important heat fed back to the surface from the gas-phase flame. In most cases (Fig. 7 and Table 4), the calculated burning rates are lower than those observed. This would be the case if there were an additional gas-phase flux that contributed to the regression-rate process. To evaluate the magnitude of this effect, the additional energy flux required to explain the measured strand-burning rate was cal-

culated using the assumption of Eq. (1), with the gas-phase contribution to the energy required to heat the propellant to the surface temperature given by $r_{meas} - r_{calc}\rho c_p(T_s - T_0)$. The results of these calculations are given in Table 5.

The calculated magnitudes of heat flux appear reasonable in view of published measurements of heat fluxes in burning propellants of the order of 100 cal/(cm^2·sec) [16]. It is also quite reasonable that in most cases the quantity of heat fed back from the gas-phase flame increases with pressure. It is more difficult to discern the effect of particle size on the additional heat flux, such as might be predicted on the basis of diffusional effects.

The limiting-case, flameless-regression approach has been found to be a promising basis for accounting for many observed characteristics of solid-propellant flames and for making predictions of propellant burning-rates, remembering that all these results are based on a series of assumptions concerning the nature of the burning process, the value of the surface temperature, and the validity of kinetic measurements and extrapolation procedures.

SUMMARY

The condensed-phase, thermal-decomposition reactions of AP composite propellants have been investigated using the technique of differential scanning calorimetry, and characteristic kinetic data have been obtained for these reactions. The effects of oxidizer particle size were determined as a function of pressure, and it was found that particle size affects the pre-exponential factor of the reaction-rate expression while leaving the activation energy unchanged and

that this general behavior persists at pressures as high as 500 psi. This conclusion was reinforced by the finding that TGA tests gave kinetics comparable to those derived from DSC thermograms.

Burning rates were calculated from these decomposition kinetic data using a limiting-case flameless-regression model where the regression rate is that of a thermal flame propagating through a reacting solid with the surface condition regulated by equilibrium vaporization. It was found that burning rates could be predicted within a factor of two or three by this prediction technique over most of the pressure range of atmospheric pressure to 500 psi. The pressure exponent and particle-size effect were also accounted for quite satisfactorily. The heat fluxes from the gas phase that would be necessary to explain the small differences between observed and predicted rates were also calculated and found to be consistent with those reported earlier. In general, the limiting-case flameless-regression model, together with the measured kinetic data, accounted for a number of features of the solid-propellant combustion process and gave predicted burning rates in good agreement with measured rates.

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