20

February 10, 1971

SOLID PROPELLANT KINETICS

I. THE AMMONIUM PERCHLORATE/COPPER CHROMITE/FUEL SYSTEM*†

S. H. Inami, Y. Rajapakse, R. Shaw, and H. Wise
Stanford Research Institute
Menlo Park, California 94025

---

* Reproduction in whole or in part is permitted for any purpose of the United States Government.

† This work was sponsored by the Office of Naval Research, Power Branch, Washington, D. C. under Contract N00014-70-C-0155, Authority NR 092-507/10-9-69.

3

Test & Evaluation

ONR, Code 473, Wash. D.C. 20360

25

February 10, 1971

SOLID PROPELLANT KINETICS

I. THE AMMONIUM PERCHLORATE/COPPER CHROMITE/FUEL SYSTEM*†

S. H. Inami, Y. Rajapakse, R. Shaw, and H. Wise
Stanford Research Institute
Menlo Park, California 94025

---

† This work was sponsored by the Office of Naval Research, Power Branch, Washington, D. C. under Contract N00014-70-C-0155, Authority NR 092-507/10-9-69.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Introduction

An extensive study of the decomposition of ammonium perchlorate (AP) with and without additives has been reported in several recent review articles[1-4], and it has been recognized that the reaction mechanism during the catalyzed decomposition of AP differs from that of the uncatalyzed reaction.[5] Moreover, in an operational solid propellant, the other ingredients (binder and metal) may alter the degradation process of AP. Thus the data obtained for pure AP have been difficult to apply to propellant ignition and deflagration.

In ~~our~~ studies of the physical and chemical parameters that control ignition and deflagration of solid propellants, ~~we~~ have concentrated on quantitative examination of the potential contribution of surface-catalyzed reactions between AP, catalyst, and gaseous organic molecules, representative of the fuel binder in an operational propellant. ( )

Experimental Details

The powder samples were prepared by ball-milling crystalline AP* and sieving into fractions. The particle size of AP used in our study was limited to 61-88 microns. Copper chromite† (CC) was added in proportions of 1, 2.9, and 4.8 wt%. The resulting mixture was pressed into 1-in. diameter pellets at 5,000 psi. The pellets were broken up, lightly ground, and sieved. Particles retained on 50-mesh but passing 20-mesh screens were used (300-800 microns). In the experimental studies, a sample mass of 2 g was used so that the quantities of reaction products so obtained were adequate for analysis. In essense the AP/CC sample was placed on a glass frit housed in a Pyrex glass cell (20 mm i.d.). In all experiments the carrier gas was helium and the total flow velocity was 200 cc/min (at NTP). The composition of the reactant gas diluted with helium was adjusted by means of suitable calibrated flowmeters. Downstream of the reaction cell, an ascarite trap was employed to remove HCl, Cl_2, and CO_2 from the stream before an aliquot was sampled by a Varian

---

* Reagent grade AP from Matheson, Coleman and Bell.

† Harshaw Cu 0202p.

variable leak valve leading to a quadrupole mass spectrometer.* With a sweeping rate of 11-1/2 sec in the m/e range of 0-50, the mass spectrometer signal output was amplified by a Keithley electrometer and recorded on an Offner type RS dynograph.** Occasionally the product stream was analyzed by infrared absorption spectroscopy in the 5 to 10μ wavelength region† and by gas chromatography (column material: Linde molecular sieve 5A at 78°C). A schematic diagram of the experimental setup is given in Figure 1, a representative mass-spectrometer record in Figure 2.

In a typical run, the gas mixture composed of fuel and carrier gas was allowed to flow through the reactor containing the AP/CC until a steady signal of the fuel component was attained on the mass spectrometer. The temperature of the furnace surrounding the reaction vessel was raised at a uniform rate, and the temperature rise of the AP/CC sample and of the furnace was followed by means of two independent 3-mil chromel-alumel thermocouples. In several experiments the temperature of the AP/CC was monitored with an infrared instrument.‡ Generally the experiment was terminated by ignition of the sample.

Since relative changes in concentration were adequate for the theoretical analysis of the experimental results, no attempt was made to calibrate the mass spectrometer signal repeatedly in terms of concentration of the individual gases. The initial gaseous fuel concentration versus signal intensity was used as a reference, except in those runs in which no fuel was added, in which cases oxygen was employed as a reference. The feed rates of the individual fuels used in our experiments were: propylene (3.0×10^{-6} mole/sec), propane (4.4×10^{-6} mole/sec), and ammonia (2.7×10^{-6}, 5.4×10^{-6}, and 10.8×10^{-6} mole/sec).

The m/e signals selected for gas analysis were 17 (NH_3), 27 (C_3H_8), 28 (N_2), 32 (O_2), 41 (C_3H_6), and 44 (N_2O). The signal intensities were

---

* Electronic Associates, Inc., Palo Alto, California, Model QUAD-200.

** Beckmen Instrument Co.

† Perkin Elmer INFRACORD 237B spectrometer.

‡ Huggins Infrascope, Huggins Laboratories, Inc., Sunnyvale, California.

corrected for the cracking pattern of the individual components.

Mathematical Analysis

An analysis was carried out relating the disappearance of gaseous fuel due to reaction with AP/CC to the kinetic parameters of interest. The model includes convective and diffusive flow of gaseous fuel as it passes over a bed of AP/CC and reacts to form gaseous products. As shown in Figure 3, the one-dimensional analysis considers a reaction region of finite width R_2 $(0 < x < L)$, sandwiched between two regions R_1 and R_3, in which no chemical reaction occurs. The assumption is made that the gas and the solid are at the same temperature during the course of the reaction. In region R_1 the concentration of reactant fuel $n \to n_0$ as $x \to -\infty$, whereas in region R_3 $n \to n_1$ as $x \to +\infty$. To take into account the temperature changes associated with exothermic reaction, the convective flow velocity in R_2 is V_2 and, in R_1 and R_3, it is V_1. In the reactive region R_2, the fuel concentration n is governed by the differential equation

$$D \frac{dn^2}{dx^2} - V_2 \frac{dn}{dx} - K\, n^m = 0 \tag{1}$$

with n and dn/dx continuous at x = 0 and x = L. Solutions to this differential equation have been obtained for different reaction orders (m=0; 1). For m = 0, the solution reads

$$\frac{n_1}{n_0} = 1 - \frac{K}{n_0 V_2} \left[L - \frac{D(V_1 - V_2)}{V_1 V_2} \left(1 - e^{-LV_2/D} \right) \right] \tag{2}$$

where D is the diffusion coefficient, V_1 and V_2 the convective flow velocity, K the chemical rate constant, and m the reaction order. For the condition m = 1, the solution to Eq. (1) is

$$n_1/n_0 = \frac{2\lambda q e^{pL}}{[(p+q)(q-p+\lambda)e^{qL} + (q-p)(q+p-\lambda)e^{-qL}]} \tag{3}$$

with

$$\lambda = \frac{V_1}{D}\ , \quad p = \frac{V_2}{2D}\ , \quad \text{and } q = \frac{\sqrt{V_2^2 + 4KD}}{2D}\ .$$

Thus for a given set of parameters for V_1, V_2, and D, the experimentally determined n_1/n_0 permits evaluation of the rate constant and the activation energy of the process from Eq. (2) for a zero-order reaction and from Eq. (3) for a first-order reaction.

Results

A representative example of the temperature as well as the reactant and product distributions during the course of the reaction of solid AP/4.8 CC with gaseous propylene is shown in Figure 4. Since the relative change in propylene concentration due to reaction was measured, the rate constants for the disappearance of C_3H_6 could be evaluated by means of Eq. (3). Based on a first-order reaction with respect to C_3H_6, the data so obtained gave the Arrhenius plot shown in Figure 5. Similar experimental measurements carried out with AP containing varying amounts of CC-catalyst indicated that the activation energy associated with propylene oxidation varies with catalyst concentration (Table 1).

A measure of the decomposition rate of AP in the presence of catalyst and propylene can be obtained from the rate of formation of nitrogen. In Figure 6 a comparison is made of the mass rate of formation of N_2 and the mass rate of consumption of C_3H_6 in the presence of CC-catalyst assuming that the mass spectrometer sensitivity for the two species (m/e = 28 and m/e = 41) is equal. Of particular significance is the observation that the two curves, although displaced, have similar slopes, i.e., the rate of disappearance of gaseous propylene nearly parallels that of AP/CC over the temperature range studied.

A similar set of kinetic measurements was carried out with gaseous propane in the carrier stream. From the steady-state mass consumption rates of propane at various temperatures, we obtained an activation energy of $E_a = 82 \pm 5$ kcal/mole for the interaction of propane with AP/4.8 CC and AP/2.9 CC, indicative of a higher temperature coefficient of the reaction rate than was achieved with C_3H_6.

Finally a series of measurements was carried out for the system AP/CC/NH_3(g). By following the mass rate of disappearance of ammonia at different partial pressures in the gas stream and for several concentrations of CC catalyst in AP, we obtained the results shown in Table 2. By way of comparison, the activation energy for the oxidation of ammonia by the AP/CC appears to be much lower than that for propylene or propane oxidation (Table 1). In the ammonia system, the reproducibility of the experimental results was less satisfactory than that observed with the hydrocarbon systems. The Arrhenius plots (for the ammonia rate constants) tended to exhibit the existence of two straight-line portions. The values listed in Table 2 refer to the rate data obtained at $T > 545^{o}K$. Also in the presence of ammonia, nitrogen and nitrous oxide are formed from two sources, AP decomposition and the oxidation of ammonia. It makes a more detailed analysis of the kinetic data very difficult. Furthermore, the experimental results showed that the partial pressure of ammonia influences the product distribution. At a feed rate of 5.4×10^{-6} mole/sec, the nitrogen-containing product was predominantly nitrogen, whereas with 2.7×10^{-6} mole/sec, the products were nitrogen and nitrous oxide. This effect may be due to changes in the properties of the catalyst.

The experimental data lend themselves to an interpretation of the heat release occurring at the interface of AP/CC/gaseous fuel on the basis of the following considerations. In a nonadiabatic system the rate of temperature rise of the solid dT/dt is given by the difference between the rate of heat generation by chemical reaction and the rate of heat loss between solid and gas by conduction and convection:

$$\frac{dT}{dt} = \frac{Q}{c}\left(-\frac{1}{m}\frac{dm}{dt}\right) - \frac{\alpha S}{mc}(T-T_g) \qquad (4)$$

where m is the mass, S the surface area of AP/CC sample at any time t, c the specific heat (at constant pressure), Q the exothermic heat of reaction, $-dm/dt$ the rate of mass loss due to chemical reaction, α the heat-transfer coefficient, and T_g the gas temperature passing over the sample. When the gas temperature does not differ appreciably from the sample temperature, i.e., $T \simeq T_g$, Eq. (4) reduces to

$$\frac{dT}{dt} = \frac{Q}{c}\left(-\frac{1}{m}\frac{dm}{dt}\right) \qquad (5)$$

A measure of the reaction rate of the solid and the associated mass loss is the concentration of a given product species N_j in the gas stream of velocity v

$$-\frac{dm}{dt} = N_j v \tag{6}$$

By substitution into Eq. (5) one obtains

$$\frac{dT}{dt} = \frac{Q}{c} \; N_j v/(m_o - v \int_o^t N_j dt) \tag{7}$$

For the condition that $v \int_o^t N_j dt \ll m_o$, i.e., a relatively small net mass loss of AP/CC during the course of the experiment

$$\frac{dT}{dt} \simeq Q \; N_j v/cm_o \tag{8}$$

Thus the parameter Q can be evaluated by measurement of the net rate of temperature change and the product concentration of species j in the gas stream which are related by a stoichiometric number to the mass of AP reacted. A typical plot of the experimental data is shown in Figure 7. At the higher reaction rates the curve exhibits deviations from a straight line undoubtedly due to heat loss from the sample (Eq. 4).

From a comparison of the initial slopes of the curves shown in Figure 7, we can compute the changes in the value of Q associated with the presence of CC-catalyst and gaseous fuel in the reacting system. In the absence of 1) mass-spectrometer calibration curves relating the signal intensities at various m/e to absolute gas concentrations in the stream, and 2) information on the specific stoichiometry for the decomposition of AP under the experimental conditions, we cannot compute absolute numbers for the net exothermic heat of reaction. Therefore, we have expressed the results in terms of relative changes in Q, selecting as a reference the experimental slope obtained for AP in the absence of fuel and CC-catalyst (Table 3). The marked contributions to the heat of reaction by the gaseous fuel and the catalyst are evident from these results. Also the data emphasize the important contribution of reactions occurring at the surface of the AP/CC.

Discussion

The results obtained offer some insight into the mechanism of interaction between a hydrocarbon fuel and AP in the presence of a catalyst, such as CC. As evidenced by the heat release data and the variation of activation energy with CC content (Table 1), the processes observed exhibit an important heterogeneous component involving the catalyst. It appears that the CC catalyst plays the dual function of enhancing the degradation rate of AP and promoting the oxidation of the fuel molecule. Undoubtedly, a combination of these two effects is required for a satisfactory burning-rate catalyst in solid-propellant deflagration. This observation offers an explanation for the observation why some active AP decomposition catalysts have been found to be rather poor burning-rate catalysts.

The favorable properties of CC as an oxidation catalyst for hydrocarbons are well established. Both the CuO and $CuCr_2O_4$, the ingredients of Harshaw CC (Cu 0202p) used in our work, catalyze the complete oxidation of hydrocarbons[5,6] and the oxidation of ammonia.[7] The role played by CuO and $CuCr_2O_4$ in enhancing AP decomposition is well documented.[1,2] Most likely these conclusions are applicable to a reacting system involving a solid fuel component, such as would be encountered in a typical solid propellant composed of AP/CC/binder. Surface-catalyzed reactions would be expected to play an important part in both ignition and combustion of such propellants.

An interesting application of our results may be sought in an evaluation of the surface temperature of an AP/CC propellant on the basis of the kinetic information provided by the experimental results just presented. For a specified regression rate r, the surface temperature of the solid may be estimated by examining the data obtained in this study for the mass consumption rate of solid AP/CC as a function of temperature. The sensitivity of the mass spectrometer for N_2 was assumed to be equal to that of C_3H_6. For AP/4.8CC the results of such an analysis are presented in Figure 8. Based on these data we find for the linear regression rate of 4.1×10^{-2} cm/sec (corresponding to a mass consumption rate of 1.2×10^{-3} mole/sec), a surface temperature between

640 and 660°K (depending on the stoichiometry employed). These values are in good agreement with experimental observations[8] of the surface temperature of a burning AP/4.8CC wafer ranging from 590° to 675°K at the same linear regression rate.

Finally, we would like to reemphasize the conclusion that the AP/fuel system in the presence of catalysts exhibits entirely different characteristics from those of the uncatalyzed system. In the latter case the reactions involving fuel and perchloric acid predominate in the gas phase. However, such reactions do not seem to make a significant contribution in the catalyzed system.

REFERENCES

1. A. G. Keenan and Robert F. Siegmund, Quart. Rev. 23, 430 (1966).
2. P. W. M. Jacobs and H. M. Whitehead, Chem. Rev. 69, 551 (1969).
3. W. A. Rosser, S. H. Inami, and H. Wise, Combust. Flame 12, 427 (1968).
4. S. H. Inami, W. A. Rosser, and H. Wise, Combust. Flame 12, 41 (1968).
5. B. J. Wood, H. Wise, and R. S. Yolles, J. Catal. 15, 355 (1969).
6. S. H. Inami and H. Wise, J. Catal. 18, 343 (1970).
7. L. L. Holbrook, S. H. Inami, and H. Wise (to be published).
8. H. Wise, S. H. Inami, and L. McCulley, Combust. Flame 11, 483 (1967).

Table 1

ACTIVATION ENERGY AS A FUNCTION OF CATALYST CONCENTRATION FOR AP/CC/C_3H_6 SYSTEM*

Catalyst CC (wt%)	Activation Energy E_a (kcal/mole)		Activation Energy (Relative)	
	C_3H_6 Reaction	AP/CC Reaction**	C_3H_6 Reaction	AP/CC Reaction
1	45 ± 4	35†	0.80	0.76
2.9	49.5 ± 5	40	0.88	0.87
4.8	56 ± 5	46	1.00	1.00

* The initial propylene concentration was kept at 17 torr (NTP).

** Ref. 4.

† Interpolated value.

Table 2

KINETICS OF REACTION BETWEEN AMMONIA AND AP/CC*

Catalyst Conc. CC (wt %)	Initial Part. Press. NH_3 (torr)	Activation Energy E_a (kcal/mole)
2.9	15	29
	30	34
	60	30
4.8	30	25

* Volumetric flow rate of He carrier gas = 200 cc/min.

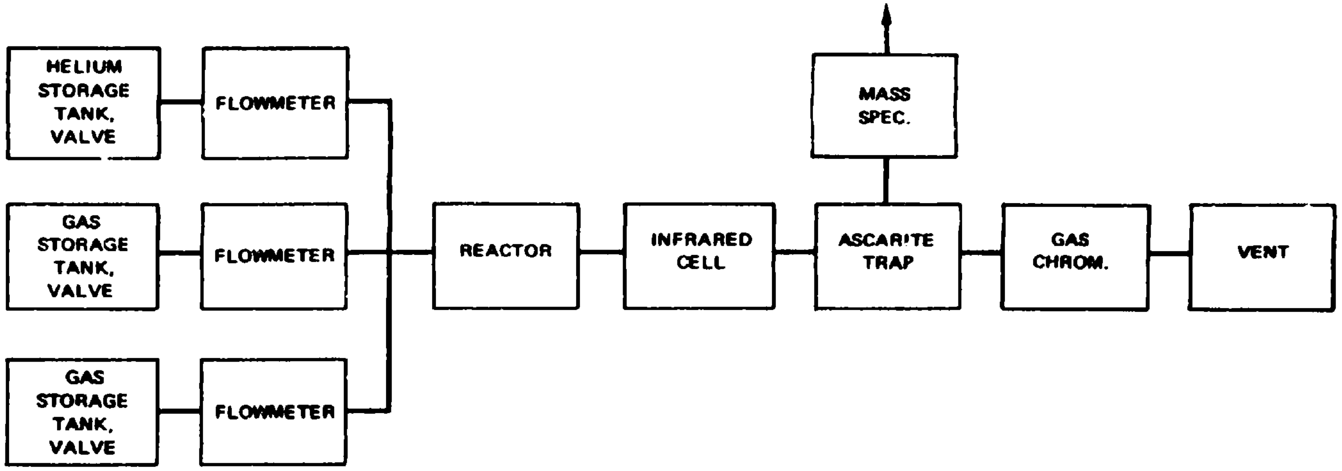
Table 3

HEAT OF REACTION OF AP/CC IN THE PRESENCE OF GASEOUS FUEL

Catalyst Concentration	Fuel Concentration Propylene (torr) NTP	Q rel.	
		S = 4*	S = 9**
0	0	1.0	1.0
0	17	1.6	1.75
4.8	0	1.8	2.0
1	17	2.8	3.0
2.9	17	4.2	4.5
4.8	17	3.8	4.25

* Stoichiometric number = 4, i.e., 1/4 mole of N_2 formed for every mole of AP reacted.

** Stoichiometric number = 9; i.e., 1/9 mole of N_2 formed for every mole of AP reacted.

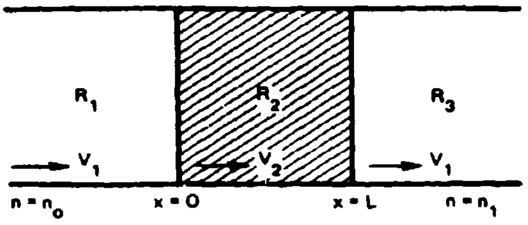


TA-3673-59R

FIGURE 1 SCHEMATIC DIAGRAM OF APPARATUS

TA-3573-60R

FIGURE 2 A TYPICAL MASS SPECTRUM OF PRODUCT STREAM



TA-8378-7

FIGURE 3 ONE-DIMENSIONAL ANALYSIS OF REACTION KINETICS WITH CONVECTIVE AND DIFFUSIVE FLOW

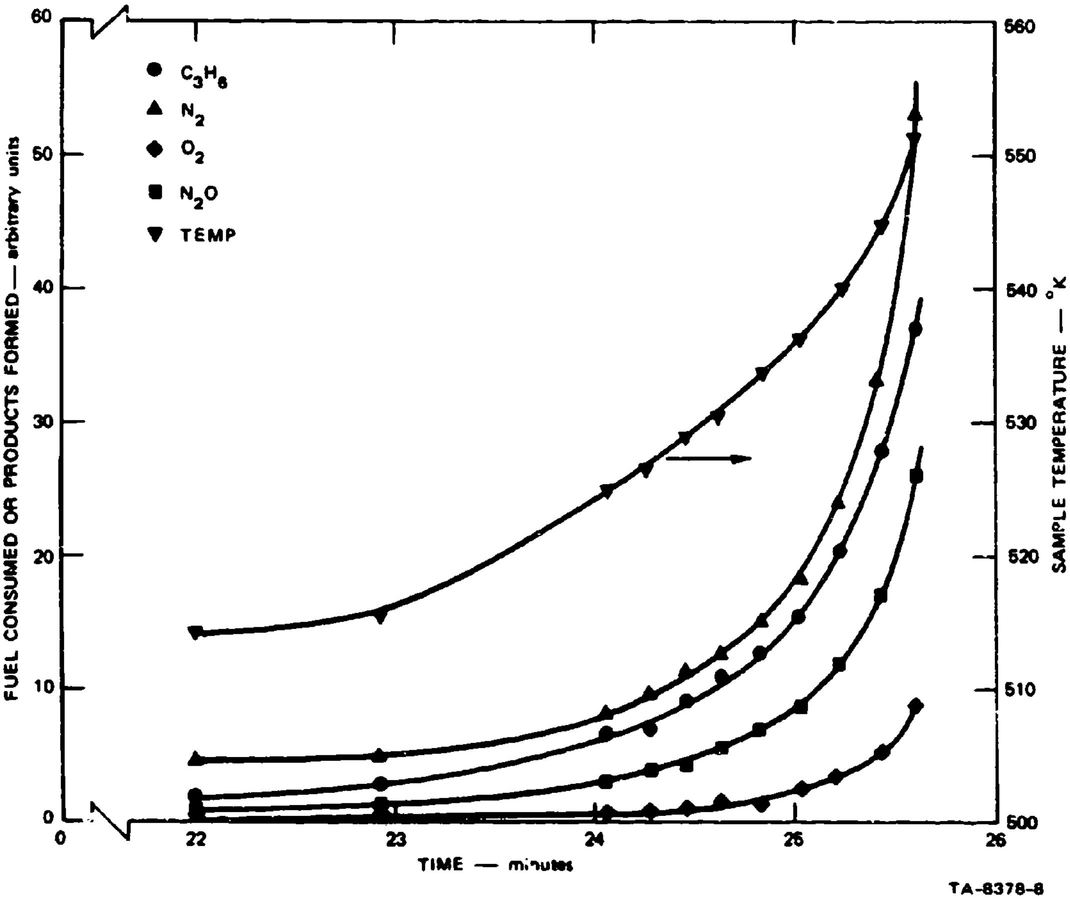


FIGURE 4 CHANGE OF CONCENTRATION OF REACTANT, PRODUCTS, AND TEMPERATURE AS A FUNCTION OF TIME (Solid: AP/4.8CC; Mass 2g. Gaseous Fuel: 17 torr NTP, Total Gas Flow = 200cc min^{-1})

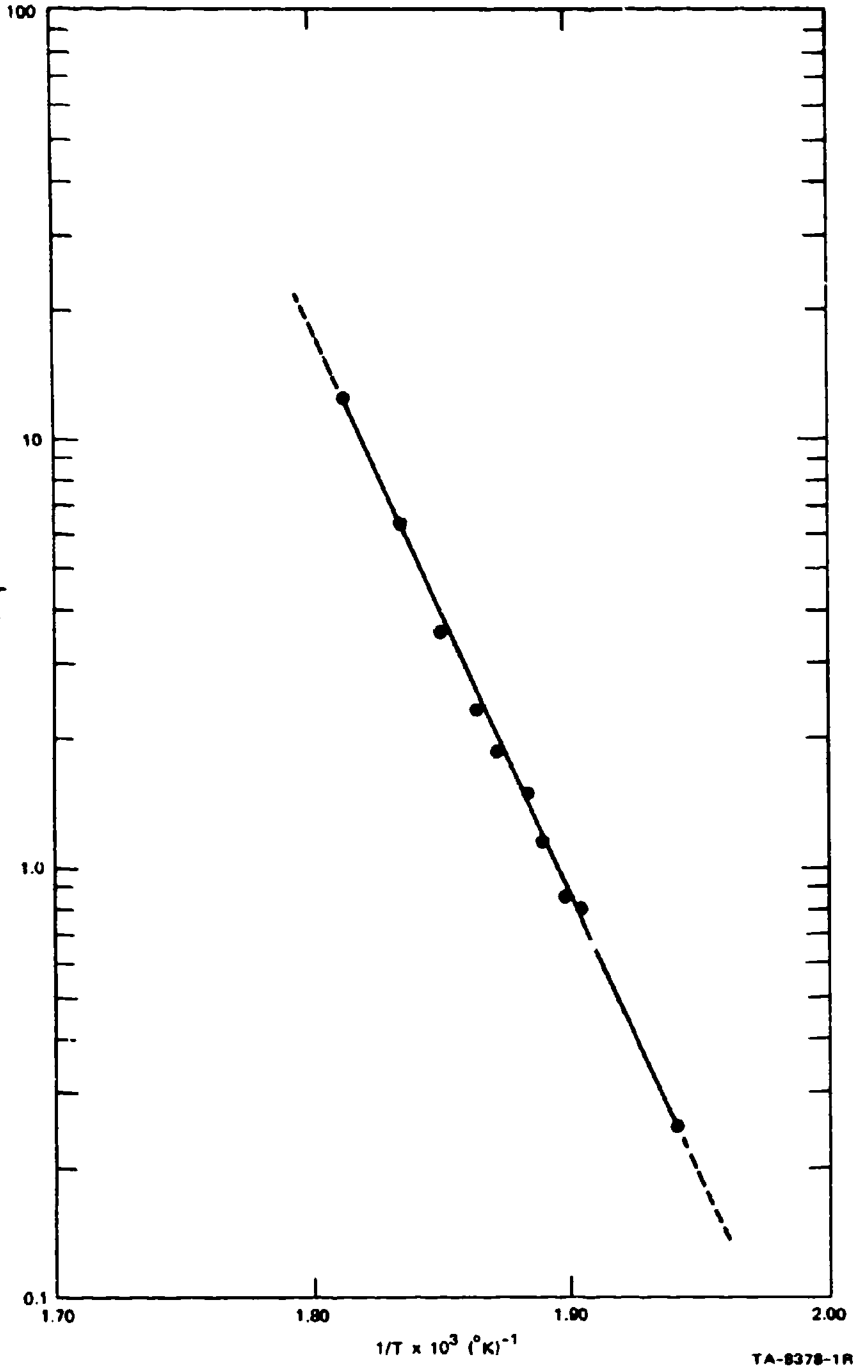


FIGURE 5 KINETICS OF SOLID PROPELLANT REACTIONS (Solid: AP/4.8CC; Mass 2g. Gaseous Fuel: 17 torr NTP, Total Gas Flow = 200cc min^{-1})

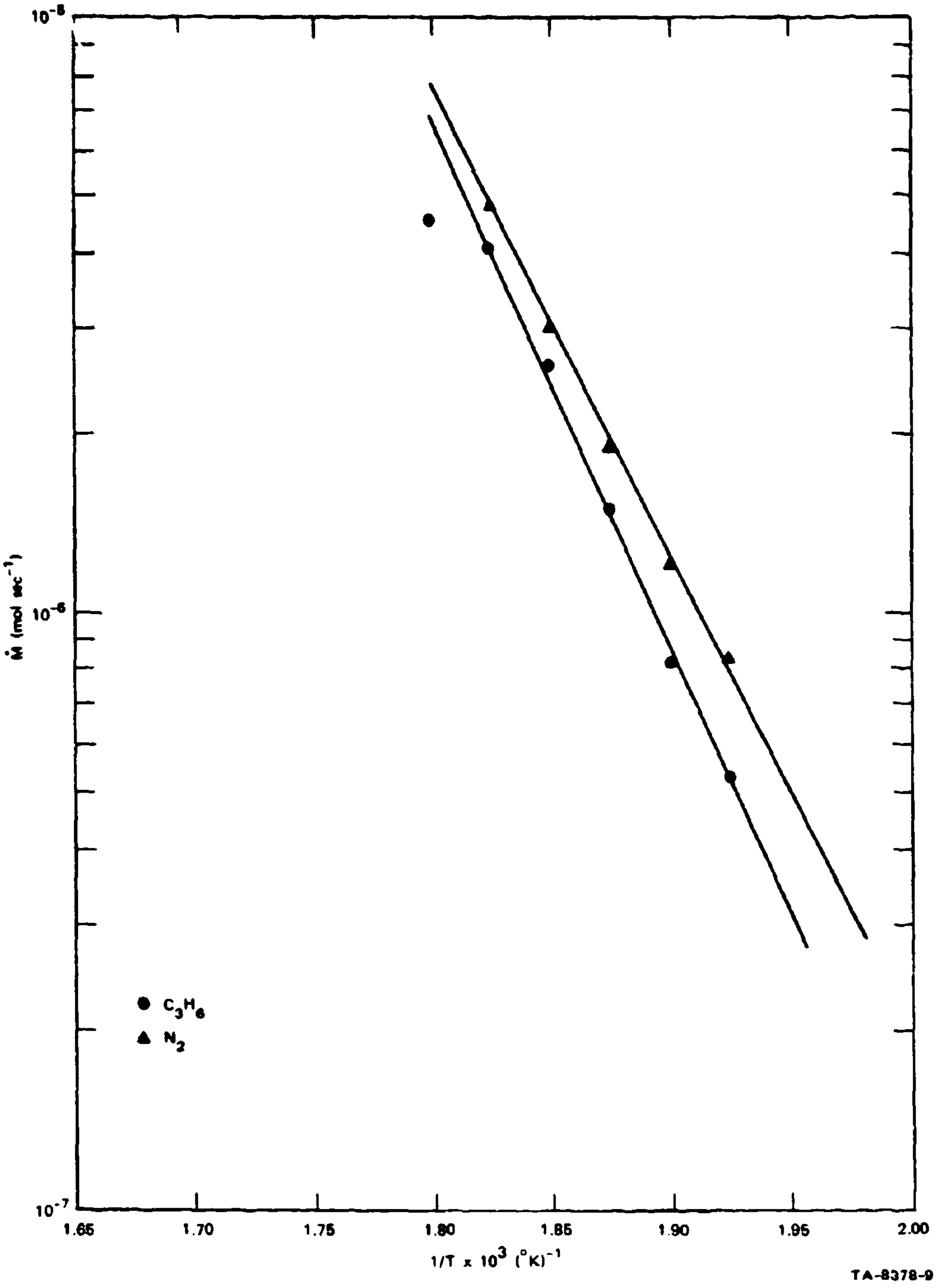


FIGURE 6 EFFECT OF CATALYST ON AP DECOMPOSITION AND FUEL OXIDATION (Solid: AP/4.8CC; Mass 2g. Gaseous Fuel: 17 torr NTP, Total Gas Flow = 200cc min^{-1})

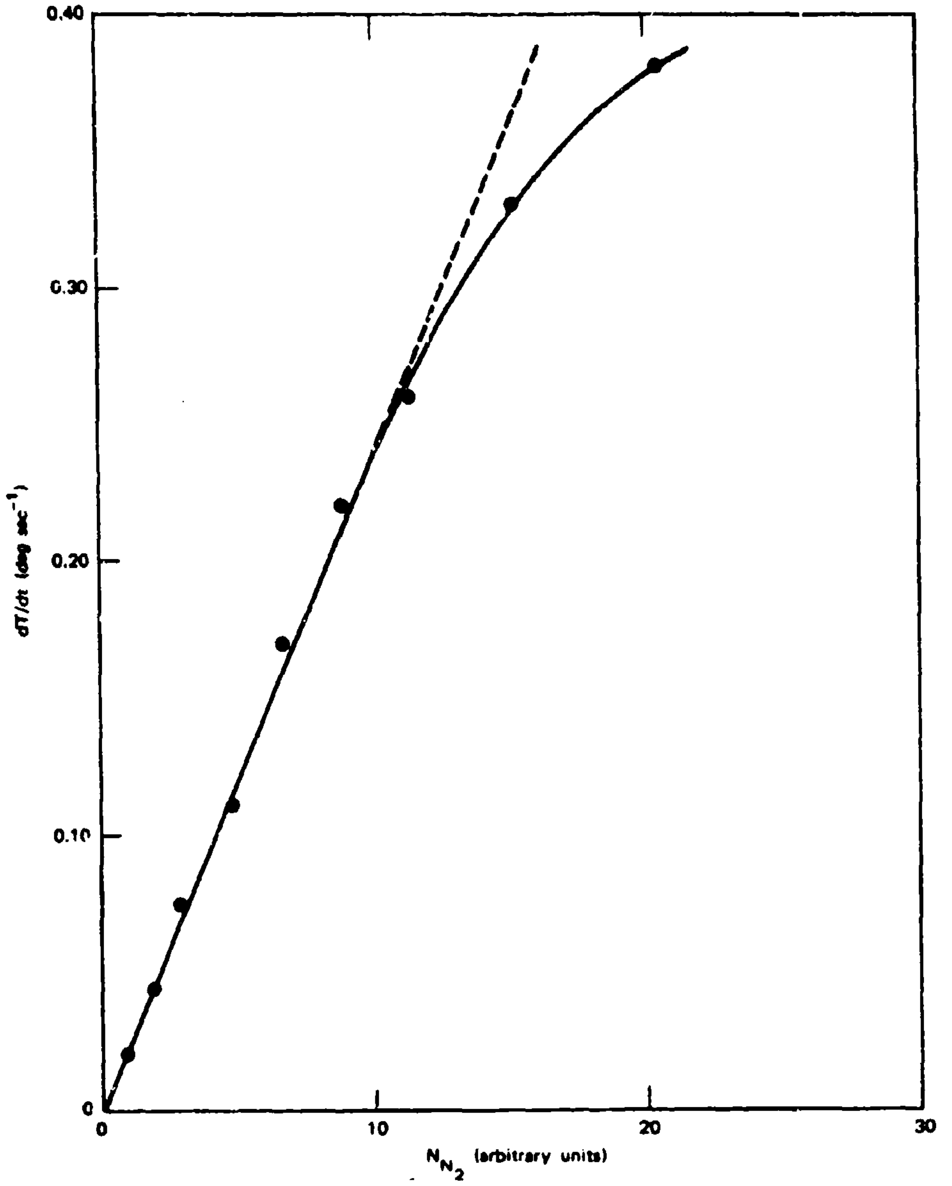


FIGURE 7 HEAT RELEASE DUE TO INTERACTION OF PROPYLENE (Solid: AP/4.8CC; Mass 2g. Gaseous Fuel: 17 torr NTP, Total Gas Flow = 200cc min^{-1})

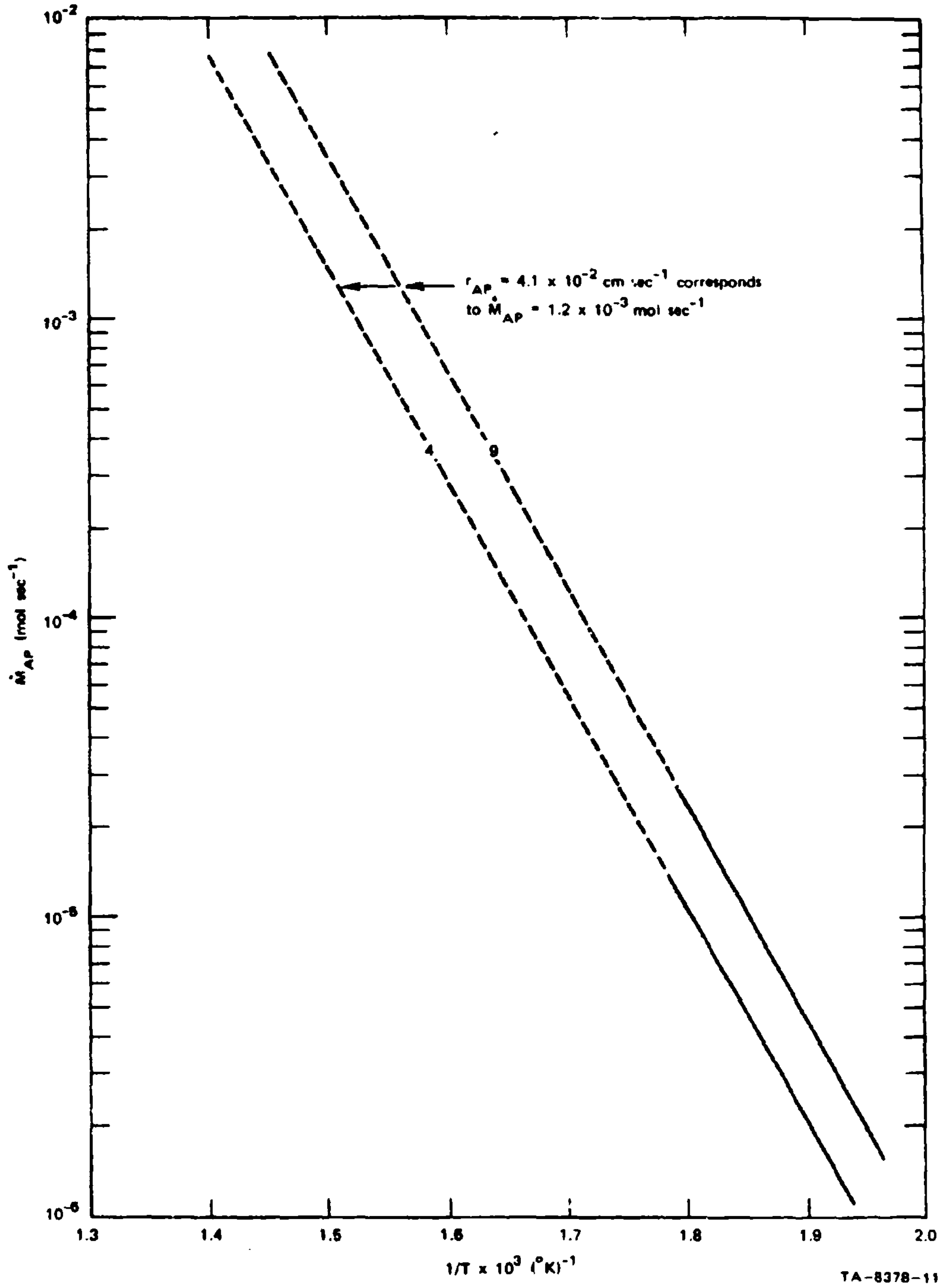


FIGURE 8 VARIATION OF THE SURFACE TEMPERATURE WITH THE CONSUMPTION RATE OF AP/4.8CC; FOR TWO STOICHIOMETRIES: $\Delta N_2/\Delta AP = 4$ AND 9