Combustion Science and Technology
1973, Vol. 8, pp. 121–131

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Printed in The United Kingdom

Ignition of Polymers in a Hot Oxidizing Gas

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Abstract—Experiments were performed using a shock tube in which both pure polymer and propellant specimens, mounted on the end wall, are suddenly exposed to a hot stagnant gas at about 1800 °K and 47 atm. The test gas consists of oxygen/nitrogen mixtures in which the oxygen mole fraction is varied from 0.18 to 1.00. The resultant ignition delay is observed to increase sharply as the mole fraction of oxygen is reduced and typical ignitability limits are $0.2 \sim 0.3$ mole fraction or $10 \sim 15$ atm oxygen partial pressure. Ignition delay time is found to be sensitive to total pressure as well as partial pressure. The effect of imbedded oxidizer is found to be significant when the ambient oxygen mole fraction is below 0.5 mole fraction. The theoretical ignition delay predictions of the gas phase and heterogeneous theories are shown to be too close for the experimental data to distinguish between them. A simple flat-surface stagnant exposure (a one-dimensional model) is found to be inadequate to resolve the question as to the dominant reaction in the ignition mechanism.

INTRODUCTION

The mechanism by which a hetero-phase system consisting of a solid polymer or a composite solid propellant and an oxidizing gas is brought to ignition is of interest in many combustion applications. Such processes occur in virtually all forms of chemical rocket propulsion as well as in many industrial processes. In most applications the ignition stimulus is a source of intense heat; for example, a solid propellant can be brought to ignition by the hot products of combustion of the explosive material in an igniter. Although ignition is often an ill-defined process, we shall mean by ignition the establishment of a runaway chemical reaction accompanied by self-heating of sufficient magnitude to accelerate the reaction; this is similar to the classical concept of the thermal explosion. It is generally assumed that steady-state combustion follows shortly after ingition, but ignition research has emphasized the question of how long it takes for the runaway reaction to develop, rather than the approach to the steady-state. In fact, most theoretical and experimental configurations rule out the possibility of steady-state combustion.

An early theoretical study of solid propellant ignition by Hicks (1954) attempted to explain the ignition phenomenon in terms of solid phase reactions below the propellant surface. Although the ignition delay time for this model depends on an externally applied heat flux, it is otherwise independent of the conditions in the surrounding medium. Experimental studies have shown, however, that the ignition phenomenon is quite sensitive to the conditions in the adjacent gaseous atmosphere, notably the pressure and the oxidizer concentration. Moreover, the previously published experimental results have been used to support the notion that only the fuel component in a composite propellant plays a significant role in the course of the ignition.

In order to explain the observed phenomena, McAlevy, Cowan, and Summerfield (1960) proposed a gas-phase theory of ignition. This theory, depicted schematically in Figure 1, is based on the idea that the initial heat source serves to vaporize solid fuel thus permitting an exothermic chemical reaction in the gas phase. McAlevy, Cowan, and Summerfield constructed a simple model which contained the essential features of the gas phase reaction mechanism. Experiments confirmed the theoretical predictions, displaying a strong dependence of the ignition delay time on the total pressure and the oxidizer concentration in the gas. The experiments of McAlevy, Cowan and Summerfield were performed with a composite solid propellant sample flush-mounted at the end wall of a shock tube. The ignition stimulus is the hot stagnant gas remaining behind the reflected shock.

An improved gas-phase theory was advanced by Hermance, Shinnar, and Summerfield (1965, 1966) who solved numerically the set of coupled partial differential equations describing the ignition phenomenon for a pure fuel suddenly exposed to a hot stagnant oxidizing gas. Their model includes the effect of heat feedback; this was not included in previous gas-phase theories. The heat feedback operates in the following way: the heat released by the exothermic gas phase reaction goes back,

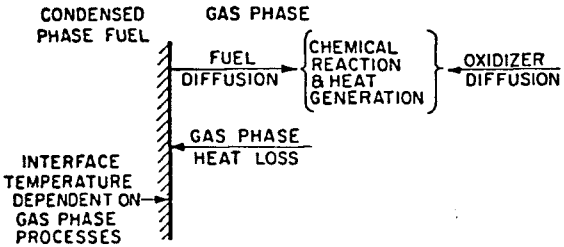

FIG. 1. Gas phase reaction ignition model.

in part, to the solid where it increases the surface temperature and vaporization rate, the increased fuel supply enhances the reaction and thus brings about the runaway reaction more rapidly. Kumar and Hermance (1969, 1970) extended the gas phase reaction model by including oxidizer in the solid phase. The model is strictly applicable for homogeneous materials such as double base propellants; it is not certain if this more sophisticated model applies to composite propellants.

In addition to the gas-phase ignition theory another model has been proposed by Anderson and co-workers (1963, 1964) which is equally successful in predicting the experimental trends. Anderson's model is based on the assumption that the exothermic runaway reaction is a heterogeneous one, occurring at the surface between gaseous oxidizer and solid fuel. The heterogeneous ignition theory is illustrated schematically in Figure 2. As the reaction proceeds, the surface temperature increases and thereby increases the reaction rate, leading ultimately to a runaway reaction and ignition. Unfortunately, the heterogeneous theory, as developed by Anderson and co-workers, is a qualitative one and hence no quantitative proof of its validity is possible. Experiments performed by Shannon (1966) suggest that dependence of the ignition delay time on the oxidizer concentration (or partial pressure of oxidizer) is independent of the total pressure, in agreement with the heterogeneous theory of Anderson, *et al.* However, these results are in contrast with both the gas-phase theory and more recent versions of the heterogeneous theory as well as with the current experimental data; this fact will be discussed in greater detail later.

Williams (1966) presented a theory of propellant ignition by heterogeneous reaction in which the solid propellant and the oxidizing gas are taken at the same initial temperature. This is the so-called hypergolic ignition case, which would occur, for example, when cold gaseous fluorine is brought suddenly in contact with a hydrocarbon solid fuel. But when oxygen is the ignition gas, an initial high temperature is necessary to cause ignition (this combination is not hypergolic). Waldman and Summerfield (1969) have extended Williams' work to the case corresponding to the heterogeneous theory (different initial temperatures for the solid and gas phases). The treatment of Williams and Waldman constitutes a more formal heterogeneous theory than is presented by Anderson and co-workers.

It was stated previously that both the gas-phase and heterogeneous models are built on the assumption that only the fuel component of a composite solid propellant plays a significant role in the ignition phenomenon. One of the difficulties of including the effect of the imbedded oxidizer in a theoretical analysis is that the problem is no longer one-dimensional. Other effects related to the role of the imbedded oxidizer have also received scant attention in the past. In addition, the question arises as to what effect, if any, the surface nature of the solid fuel has upon the ignition. It is well known that some solid fuels exhibit a dry surface during decomposition while others exhibit a wet surface (i.e. they melt prior to decomposing). No attempt has been made to clarify these questions theoretically nor have any systematic experiments been performed previously.

This paper presents the results of an experimental program conducted at Princeton University which was designed to examine the theoretical questions at issue. The theoretical questions examined here are:

1) The location of the initial exothermic reaction (homogeneous gas phase or heterogeneous surface oxidation).

2) The dependence of the ignition delay time on the partial pressure of oxidizer.

3) The role of imbedded oxidizer.

4) The effect of binder characteristics on ignition delay.

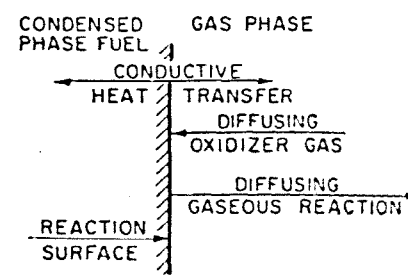

FIG. 2. Heterogeneous reaction ignition model.

THEORETICAL PREDICTIONS

Theoretical solutions of the gas-phase and heterogeneous models are available and can be readily extracted from the existing literature. No attempt will be made here to review this material but rather only the pertinent results will be presented. An extensive review of the theoretical work done prior to 1966 has been presented by Price *et al.* (1966). Shown in Figure 3 is a comparison of the gas-phase and heterogeneous theories in a plot of the ignition delay time versus the partial pressure of oxygen after shock reflection from the solid. These theoretical curves were constructed from the solutions presented by Hermance, Shinnar, and Summerfield (1966) for the gas-phase theory and by Williams (1966) and Waldman and Summerfield (1969) for the heterogeneous theory. The computations are based on the numerical constants shown in Table I.

Aside from the obvious fact that the two models suppose different locations for the exothermic reaction the solutions shown in Figure 3 do have additional differences which warrant consideration. There are two significant differences between these

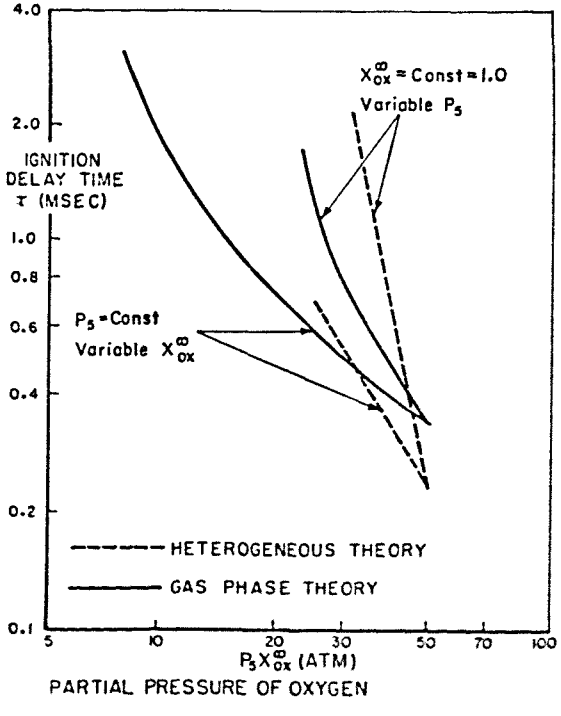

FIG. 3. Comparison of theoretical predictions of the effect of partial pressure of oxygen on the ignition delay.

TABLE I

Physical properties selected for ignition calculation

	Heterogeneous theory	Gas phase theory
Activation Energy (kcal/mole)	15	12
Reaction Order	0.75	2
Heat of Combustion (cal/gm)	2700	12,000
Gas Temperature after reflected shock wave (°K)	1800	1800

models which can affect the solutions. First, the gas-phase model has included all convective effects, while the heterogeneous model has neglected all convective effects. Although it has been shown by Hermance, Shinnar, and Summerfield that the convective effects are of minor consequence in the gas-phase model, no such study has been performed with the heterogeneous model.

Second, and more important, is the nature of the ignition in the solutions shown in criteria used in each of the models. It is generally recognized that hydrocarbon fuels burning with oxygen exhibit gas phase flames in the steady state. The heterogeneous theory merely says that the initiating exothermic reaction is at the surface, it does not attempt to take into account the mechanism of transfer from heterogeneous to homogeneous reaction. For this reason the heterogeneous model should only be examined under weak ignition criteria.† The gas-phase model exhibits no such difficulties and can be subjected to stronger ignition criteria. The criterion employed for the gas-phase theory in Figure 3 is that the temperature in the gas phase reaches a value of 50 per cent higher than the ambient gas temperature.

The major difference in the two theories depicted in Figure 3 is that the gas-phase solutions exhibit curvature. This can be attributed, in part, to the strong ignition criterion. It is well known that as the partial pressure is decreased the runaway reaction slows down and the ignition interval itself becomes distended. In this regime the gas-phase model is quite sensitive to the choice of ignition criterion and shorter ignition delays would result with weaker criteria. Another possibility, mentioned previously, is the effect of convection on the heterogeneous model, this is not as yet understood.

† The weak ignition criterion is typically the occurrence of rapid increase in surface temperature. While on strong ignition, criterion may require that steady state combustion be obtained following removal of ignition source.

The linearity of the heterogeneous solutions can be attributed to the choice of a weak ignition criterion. While it would be desirable to examine the heterogeneous model under a strong criterion this is not feasible under the assumed model. The difficulty here is due to the nature of the heterogeneous solution. These solutions exhibit, in the latter stages, a very rapid surface temperature increase with time which is suddenly terminated at some maximum temperature whose value is determined by the ambient conditions. Thus one can visualize that the ignition delay time is critically sensitive to the choice of the ignition temperature. If the ignition temperature is lower than the maximum surface temperature then the ignition delay is relatively insensitive to the ignition criterion (or ignition temperature). If, however, the ignition temperature exceeds the maximum surface temperature then ignition cannot occur. The important point is that the transition from ignition to non-ignition is a very sharp one, a small change in the ignition temperature can mean the difference between achieving and not achieving ignition. For this reason a strong ignition criterion can lead to difficulties in the heterogeneous model.

An important aspect of the theoretical predictions shown in Figure 3 is that both theories predict a dependence on the total pressure at a given partial pressure of oxidizer. This can be attributed to the sensitivity of the initial surface temperature on the ambient pressure. As the pressure is decreased with the oxidizer mole fraction held constant the initial surface temperature decreases and therefore the initial vaporization rate (gas-phase theory) or the initial reaction rate (heterogeneous theory) decreases and the ignition delay time increases.

Previous experimental studies of McAlevy, Cowan, and Summerfield (1960) and Shannon (1966) failed to distinguish this phenomenon, as did the early heterogeneous theory. It will be seen below that the current experimental data do verify these theoretical predictions.

EXPERIMENTAL IGNITION DELAYS

All the data in this experimental program were obtained using a 1.6 inch I.D., 19 foot long stainless steel shock tube. The driver section of the shock tube was 10 feet long, the driven section was 9 feet long. The fuel or propellant sample was flush mounted at the end wall. A quartz window mounted near the sample allowed the observation of the ignition event during a test. Through a system of mirrors and beam splitters, which sent the light beams in a path parallel to the shock tube, it was possible to eliminate effects of the slight recoil movement of the shock tube on the measurements or photographs. The combination of a Kodak Wratten 18-A filter with the type 935 photo cell (yielding peak sensitivity at ~3800 Å) detects the ignition event. It was possible to photograph the fuel or propellant surface and at the same time record the intensity of the radiation emitted during the ignition event. A schematic drawing of the experimental apparatus is presented in Figure 4. The use of a double diaphragm in the shock tube triggering section made it possible to trigger the shock tube at exactly the desired pressure level and at the desired moment. Exposure conditions after shock reflection were typically 47 atm and about 1800 °K, and oxygen mole fraction ranged from 0.18 to 1.00.

Four polymers were tested to examine the effect of the partial pressure of oxygen on the ignition delay. The polymers tested were P-13 (polyester resin), Butarez (polybutadiene, carboxyterminated), PBAA (polybutadiene acrylic acid), and PU (polyurethane). The results of these tests are shown in Figures 5–8. These figures show the variation of the ignition delay time with the partial pressure of oxygen in region 5 (i.e. the conditions existing after shock reflection). In each test the partial pressure of oxygen was varied in two ways, first with the total pressure held constant and the oxidizer mole fraction varied and then with the oxidizer mole fraction held constant and the total pressure varied. Notice that for each specimen the results are qualitatively similar; the ignition delay time at a given partial pressure of oxygen is pressure dependent being shorter at the higher pressure. These results also exhibit a rapid increase in the ignition delay time as the partial pressure is lowered, indicating that the experimental ignition criterion (measured in terms of light intensity) is a fairly strong one. Furthermore, each polymer exhibited definite ignition limits in each of the experimental tests.

Another set of experiments was conducted to determine the role of the imbedded oxidizer on the ignition phenomenon. The propellant tested was a 30% PBAA/70%, 5 μ AP sample. The small particle size (5 μ) was selected so as to have as homogeneous a solid phase as possible for the purpose of comparing with the one-dimensional

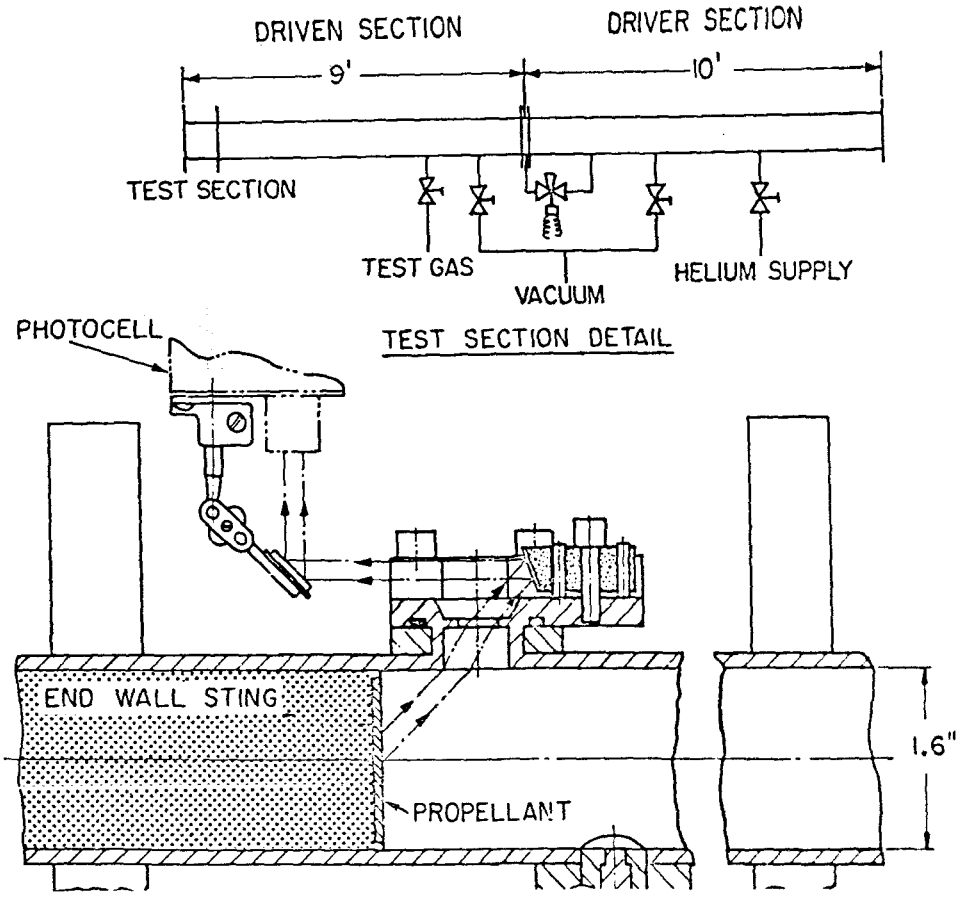

FIG. 4. Experimental apparatus and test section detail.

configuration achieved with the pure polymer. The results of these experiments are shown in Figure 9, where they are compared with the results for the pure PBAA. It can be seen in Figure 9 that the effect of the imbedded oxidizer is quite small when the ambient oxidizer is sufficiently abundant. This is particularly noticeable in the case of fixed ambient oxidizer mole fraction where the imbedded oxidizer is seen to have little or no effect over the entire ignition range. In the case of constant total pressure, however, the imbedded oxidizer has little or no effect above 50 per cent mole fraction but significantly lowers the ignition delay time below this value of oxygen mole fraction. This indicates that, in the higher oxygen mole fraction regime, the ignition delay time is so short that most of AP does not have time to decompose. As a result, the addition of AP in the region of the higher oxygen mole fraction has no effect on the ignition delay time. With decreasing ambient oxygen mole fraction, however, the ignition delay time becomes longer, and below a certain percentage of oxygen, the delay time becomes long enough for AP to start to decompose. Thus it appears that the effects of the imbedded oxidizer are dwarfed when sufficient quantities of ambient oxidizer are available but do become important when the oxidizer mole fraction is below 50 per cent. Similar behavior was observed in experiments by Beyer and Fishman (1960) with radiative heating.

A final series of tests were conducted to determine the effects of the binder characteristics. It is known that PU decomposes with a wet surface and the question arises as to whether the wet surface can affect the ignition delay. For example, the liquid polymer may cover the solid oxidizer crystals and impede solid oxidizer gasification. The test sample was a 30% PU/70%, 5 μ AP propellant. The test results are shown in Figure 10

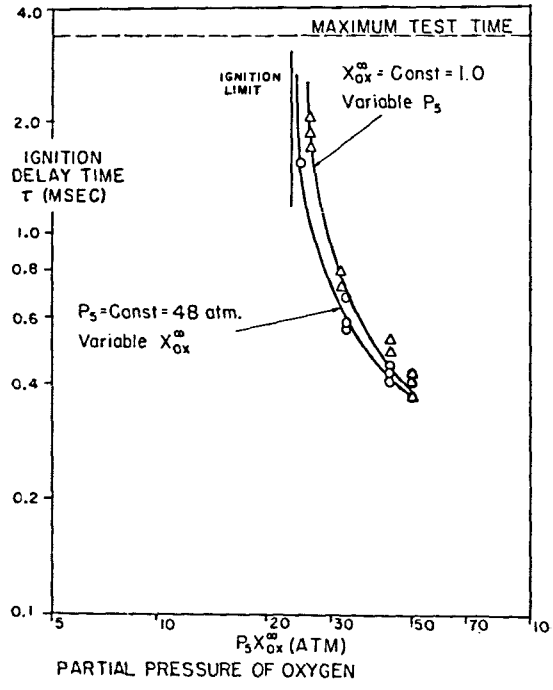

FIG. 5. The effect of partial pressure of oxygen on the ignition delay with P-13 (Polyester resin).

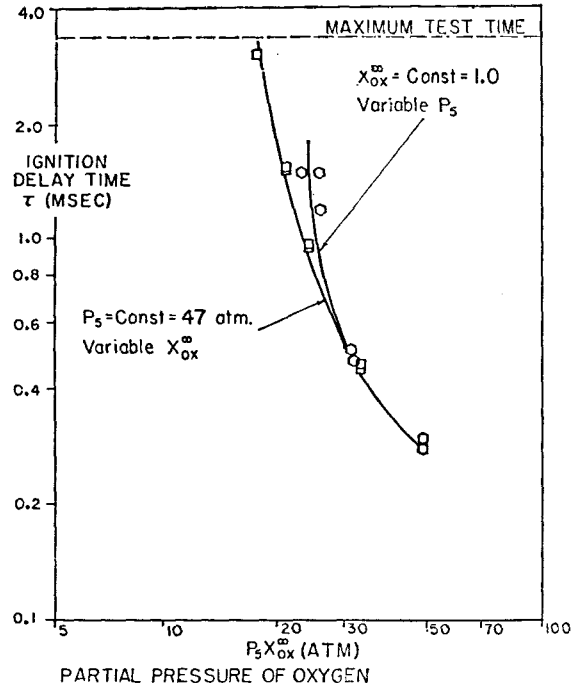

FIG. 7. The effect of partial pressure of oxygen on the ignition delay with PBAA (Polybutadiene acrylic acid).

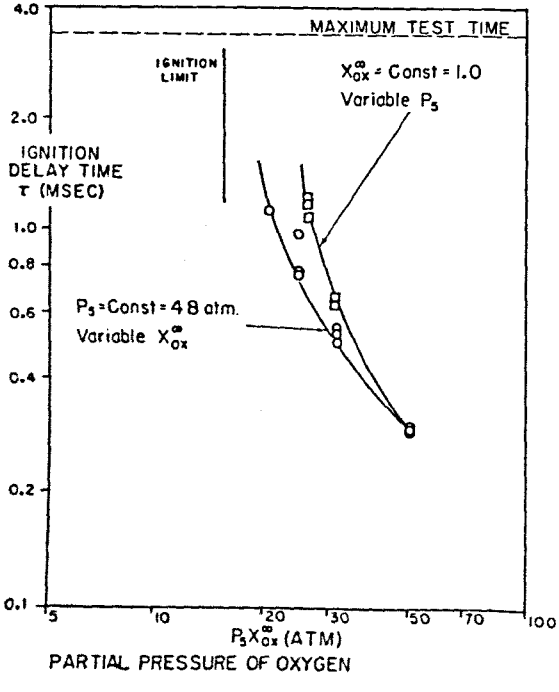

FIG 6. The effect of partial pressure of oxygen on the ignition delay with Butarez (Polybutadiene carboxy terminated).

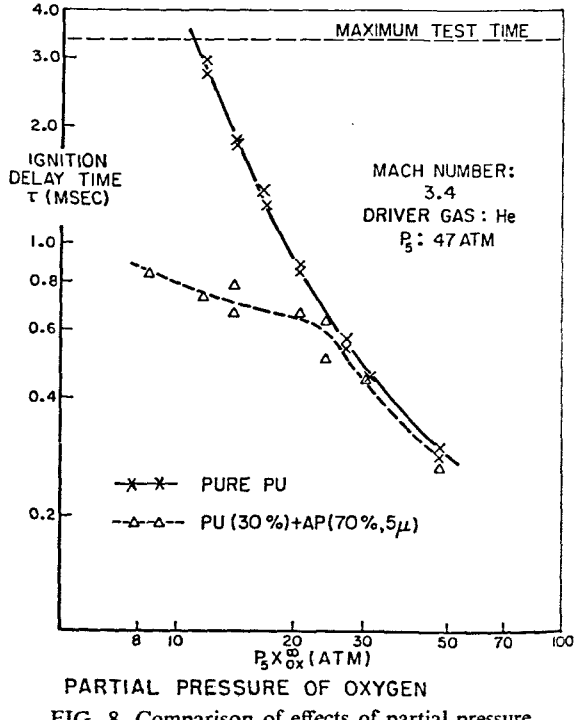

FIG. 8. Comparison of effects of partial pressure of oxygen on the ignition delay with Polyurethane and Polyurethane with Ammonium Perchlorate.

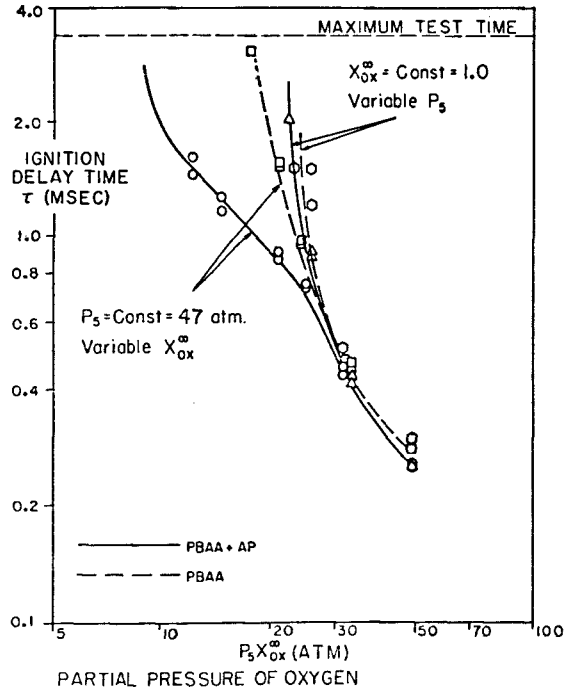

FIG. 9. Comparison of effects of partial pressure of oxygen on the ignition delay with PBAA and PBAA with AP.

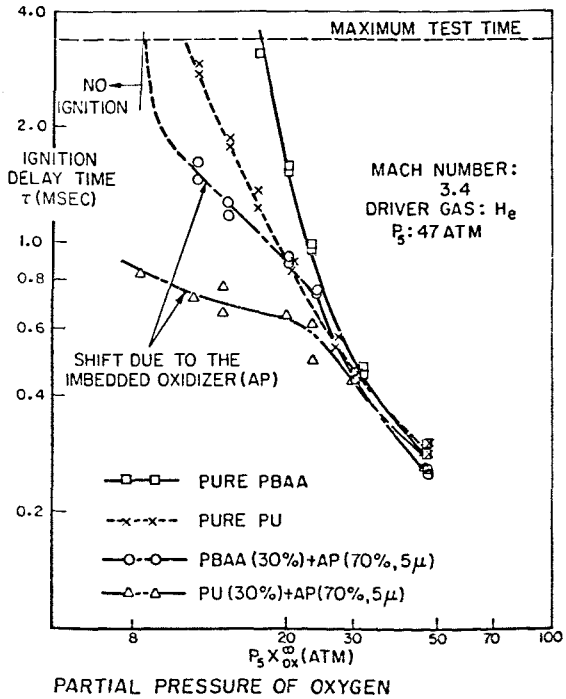

FIG. 10. Comparison of effects of partial pressure of oxygen on the ignition delay with addition of AP between PBAA and PU.

where they are compared with the results of the PBAA-AP propellant. These results are seen to be qualitatively similar even though the PU-AP propellant exhibits a weaker sensitivity to the oxygen mole fraction. The observed behavior tends to disqualify any speculation about surface coverage due to a wet surface binder. A more satisfactory explanation of this observation is simply in terms of a lower activation energy of pyrolysis or reaction for PU than for PBAA. The pure fuel data exhibit this as well. This question is by no means closed, however.

COMPARISONS WITH PREVIOUS EXPERIMENTAL AND THEORETICAL STUDIES

It was mentioned previously that experimental studies conducted by Shannon (1966) at United Technology Center are in contrast with theoretical predictions as well as with the current experimental results presented in the previous section. Typical results reported in his work have been reproduced here in Figure 11. These experiments were conducted in a shock tube and the oxidizer concentration (or partial pressure) was varied in the same ways as described in the present study.

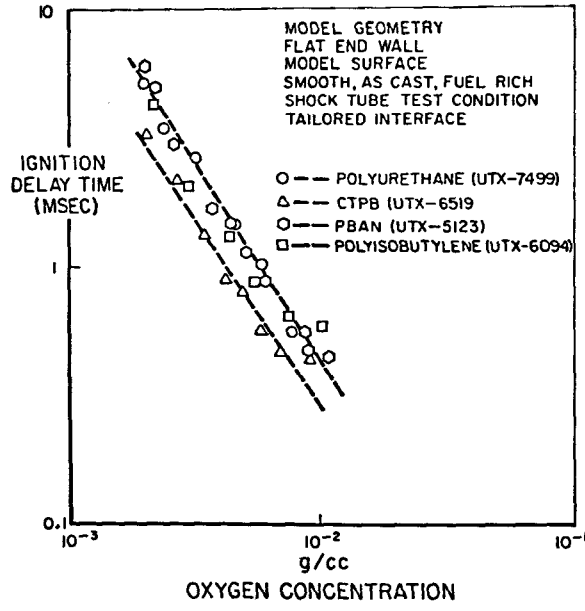

FIG. 11. Effects of oxygen concentration on the ignition delay reported by UTC [Shannon (1966)].

On the basis of his experimental data, Shannon concluded the following:

1) Ignition time dependence on oxygen concentration can be correlated by a linear behavior on a log-log plot.

2) The ignition delay time at a given oxygen concentration is independent of the total pressure. Alternatively, variations in the initial surface temperature do not alter ignition times.

These conclusions are contested on the basis of the present results shown in Figures 5–10. Closer examination of Figure 11 indicates a more subtle dependence on the oxidizer concentration than is indicated by the linear fit; however, it is difficult to be more precise, because no distinction of total pressure is made in Figure 11.

The observed effects of the addition of imbedded AP illustrate clearly the role of AP in the ignition mechanism of AP-based composite propellants. To the best of the authors' knowledge, all previously published experimental studies for AP-based composite propellants using shock tubes deduced the linear relation between the ignition delay and oxygen concentration on a log-log plot. These conclusions missed the key point of the role of AP in the ignition mechanism, i.e. no AP effect in the range of higher oxygen concentration and strong AP effect for lower oxygen levels. It is believed that decomposition of AP proceeds by continued surface diffusion of free perchloric acid ($HClO_4$) [Jacobs and Whitehead (1968)]. In a recent study of $HClO_4$-hydrocarbon flames, it is observed that such reactions are typically three times faster than hydrocarbon–oxygen–nitrogen flames of the same equivalence ratio and flame temperature. Another interesting result by Pearson (1968) is that premixed CH_4—$HClO_4$—O_2 flames have a two-stage character in which some CH_4 is oxidized by $HClO_4$ in the first stage, and the remaining CH_4 reacts with O_2 in the second stage. Therefore, in the region where AP decomposes, the ambient oxygen is of secondary importance compared to $HClO_4$ so that the oxygen concentration dependency on the ignition delay time becomes weaker. These trends are experimentally observed as two different slopes of ignition delay time with partial pressure of oxygen under constant total pressure on a log-log plot. Kumar and Hermance (1970) successfully predict similar behavior even with a homogeneous solid propellant. However, the predicted result differs considerably from the present experimental data in the high initial oxygen region. In the experiment, there is very little difference in ignition delay time between a pure fuel and a propellant based on the same fuel. On the contrary, in the theoretical prediction, a fuel binder ignites much earlier than a propellant due to more available fuel surface area. Therefore, the model predicts

correctly one of the roles of imbedded oxidizer, higher reactivity of decomposed oxidizer than oxygen, but it does not include the other mechanism which is the previously discussed differing pyrolysis processes between a fuel and an oxidizer. All previous experimental results of AP-based composite propellants with shock tube ignition misinterpreted the above-discussed physical meaning of the ignition mechanism, even though it looks linear.

It was stated in the Introduction that one of the purposes of this paper is to distinguish the location of the initial exothermic reaction. Comparisons of the experimental data for Butarez with the gas phase and heterogeneous theory predictions are shown in Figures 12 and 13 respectively. As can be seen from these figures, the experimental data agree qualitatively with both theories; this fact is true also of the other polymers tested. While it is true that the gas phase theory is in closer agreement with the experimental data in that the solutions exhibit curvature, this must be interpreted in light of the discussion concerning the ignition criterion. Recall that the experimental criterion is in terms of light emission while the theoretical criterion is in terms of temperature; the relationship between these phenomena is unknown. Until precise numerical values of the physical and chemical parameters are known it will not be possible, on the basis of these experimental results, to determine the controlling mechanism of the initial exothermic reaction.

SUMMARY OF CONCLUSIONS

A number of important conclusions can be drawn on the basis of the work presented herein, some of which have already been indicated. It has been shown that ignition by stationary hot oxidizing gas with the fuel or propellant in the end-wall mode depends separately on the mole fraction of oxygen and on the total pressure, and not simply on the partial pressure of oxygen. In particular, at a fixed partial pressure of oxygen the ignition delay time decreases when the pressure is increased. These results have been observed for both pure fuels and composite solid propellants and are in agreement with both the heterogeneous and gas phase theories of ignition. It must be borne in mind, however, that this result is a consequence of the shock tube testing configuration. As related in the text, the effect of increasing the pressure is to increase the surface temperature and hence the

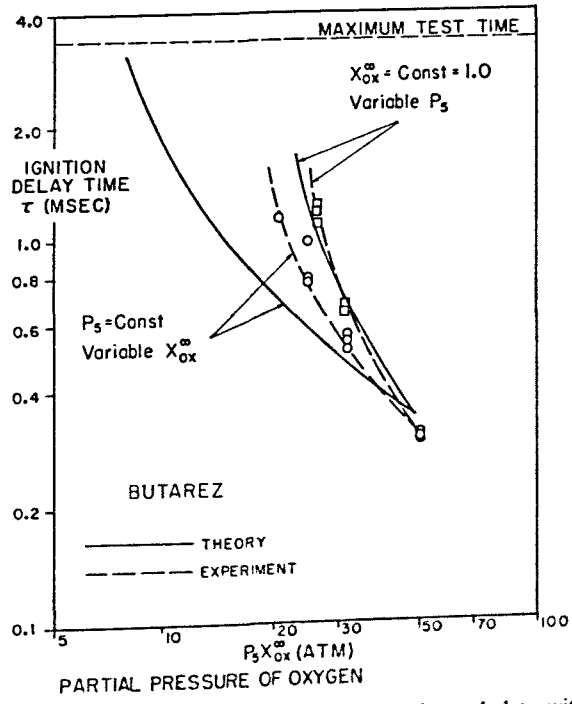

FIG. 12. Comparison of gas phase theory with experimental data with Butarez.

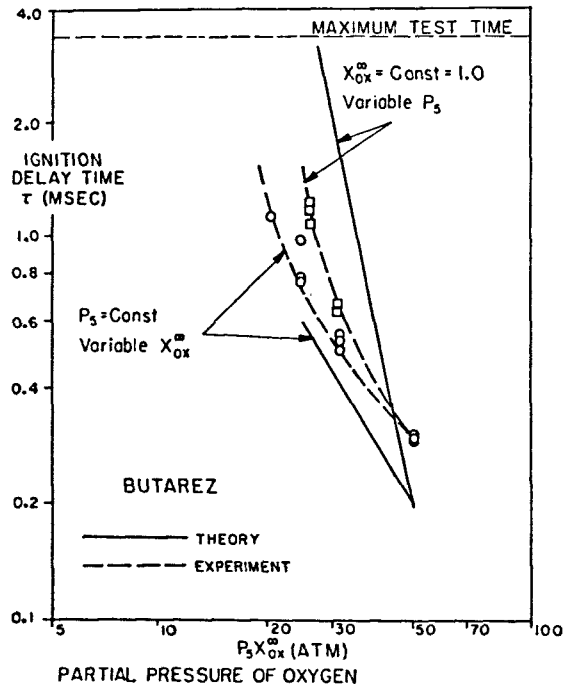

FIG. 13. Comparison of heterogeneous theory with experimental data with Butarez.

vaporization rate of the surface reaction rate. But in realistic solid rocket motors the grain is never shocked but rather experiences a more gentle convective heating from the flow of igniter gases. It is not possible on the basis of the present experiments to predict the effect of partial pressure of oxygen in the case of convective heating, although it is reasonable to assume that such effects would not be as pronounced as in the case of shock tube operation.

The experimental curves for several pure polymers (no AP) resemble qualitatively the predictions of both the gas phase and heterogeneous theories and resemble each other, approximately. In general it was found that the ignition delay increased sharply as the partial pressure of oxygen was reduced. In each sequence of tests a definite limit in the partial pressure of oxygen was found, below which the polymer did not ignite. Although these experimental data show trends that look more like gas phase predictions, it is not possible to draw any firm conclusions as to the dominant mechanism.

It was found that, under high oxygen level, the effect of imbedded AP is negligible on the ignition delay time and, under low oxygen level, imbedded AP shortens the ignition delay time considerably. Considering the two step mechanisms of the fast $HClO_4$-hydrocarbon reactions during the ignition period, there exist two different slopes of ignition delay time with oxygen mole fraction on a log-log plot, instead of the previous linear relation. Therefore, theoretical predictions of the one-dimensional model for a pure fuel as the condensed phase cannot be used to interpret the experimental data for AP-based composite propellants over the whole experimental range of external oxygen level. The results for the two propellants tested [PBAA(30%) + AP(70%, 5 μ) and PU(30% + AP(70%, 5 μ)] are qualitatively similar, despite the fact that the two polymers have different decomposition characteristics. Specifically, PBAA exhibits a dry surface decomposition while PU decomposes with a wet surface, that is, it melts prior to vaporizing.

We wish to acknowledge the support provided by the Energetics Division of the Air Force Office of Scientific Research, under Contract AF69-1651. The mechanical operation of the equipment by Mr. E. R. Crosby and the skillful production of fuel and propellant samples by Mr. C. R. Felsheim are gratefully acknowledged. T. Kashiwagi is now with National Bureau of Standards: C. H. Waldman is now with Utrasystems, Inc., Irvine, Calif.

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Received July 3, 1973