Ignition of Homogeneous Solid Propellants under Shock Tube Conditions: Further Theoretical Development

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In previous theoretical studies of gas-phase ignition of homogeneous solid propellants under shock tube conditions, the ignition criteria have been related to some specific character of the temperature distribution in the gas phase. Correspondence of these criteria to experimental criteria involving detection of light emission was uncertain. A new theoretical criterion has been developed, relating the light energy received by a photocell to the transient gas-phase distribution of reaction products and temperature. Light emission and ignition characteristics found using this criterion agree quite closely with experimental results. Investigation of ignition behavior for different relative reactivities of the ambient gaseous oxidizer and the oxidizer evolved from the solid is reported. Results indicate progressively less influence of the ambient gaseous oxidizer mole fraction on the ignition delay as the relative reactivity of the evolved oxidizer increases.

Nomenclature

A_c,A_d = cross-sectional area of emitting gas column; photocell receiver area, cm^2
A_{mn} = numerical coefficient, see Eq. 4
C = speed of light, 3×10^{10} cm/sec
$\mathfrak{D}$ = local mass diffusivity, cm^2/sec
D = $(\rho^2\mathfrak{D}/\rho_g^2)$ = constant, effective mass diffusivity, cm^2/sec
E,E_p = activation energies of gas phase reaction and pyrolysis, cal/mole
E_m = energy of excited state of molecule, erg
f = N_{mo}/N_p = ratio of molecular densities of emitting specie and combustion products
$\mathfrak{F}_e$ = emitted radiant flux from gas column, erg/sec
g_m = statistical weight of the excited state
h = Planck's constant = 6.623×10^{-27} erg sec
$\bar{J},J$ = radiation intensity, erg/str sec; relative response of photo detector
J^* = selected value of J used to define ignition
$K,\bar{K}$ = constants: $(16\pi^3\omega_{mn}{}^4C/3|R_{mn}|^2f;\ \tau_f(A_d/4\pi r_d)^2K$
k = Boltzmann constant, 1.38033×10^{-16} erg/deg
$L^*(\theta)$ = ignition criterion specification
M_t = constant = E_mR/kE
m,m_0 = total mass flux due to pyrolysis at solid-gas interface, reference flux to at 400°K, g/cm^2 sec
N = molecular density of gas phase, mole/cm^3
N_m = molecular density of excited specie under consideration, mole/cm^3
N_{m0} = total molecular density of emitting specie under consideration, mole/cm^3
n = molar stoichiometric coefficient
Q = electronic partition function
R = gas constant, 1.986 cal/mole °K
$|R_{mn}|^2$ = square of the matrix element of the transition considered
r_d = distance of photocell detector from shock tube centerline, cm
S = slit width of collimation system defining size of detected light beam, cm
T = gas phase temperature, °K
t = time, sec
t^* = ignition delay, msec
V_p = voltage output of photocell detector
x = distance, cm
Y_f,Y_{ox} = local mole fractions of fuel, oxidizer
Y_i,Y_p = mole fractions of inert and combustion products in gas phase
$Y_{ox}{}^\infty$ = initial mole fraction of oxidizer in the gas phase
Z,Z_1,Z_2 = pre-exponential factors of gas phase chemical reactions, cm^3/g sec
α = ratio of evolved fuel mass flux to total evolved mass flux
ϵ = $(\Delta\theta/\theta_{\max})(\tau/\Delta\tau)$ = constant, specified; "long time" ignition criterion is $L^*(\theta) = \epsilon$
ϵ_1,ϵ_2 = energies of excited electronic states, erg
η_i = $(\rho_g{}^3ZD/m_0{}^2)Y_i$, dimensionless inert gas mole fraction
θ,θ_0 = RT/E = dimensionless gas phase temperature; initial value of θ
ξ = $(m_0/\rho_gD)\psi$ = dimensionless coordinate in gas phase
ξ^* = ξ value corresponding to $X = S$
ρ,ρ_g,ρ_s = local and initial gas phase, and solid phase densities, g/cm^3
τ = $(m_0{}^2/\rho_g{}^2D)t$ = dimensionless time
τ_f = transmissivity of optical filter at a specified wave length
ψ = $\int_0^x [\rho(x,t)/\rho_g]dx$, Howarth length dimension, cm
ν = frequency, sec^{-1}
ω_{mn} = wave length of transition considered, cm^{-1}

I. Development of Light Emission Criterion for Ignition

Introduction

STUDIES of ignition of solid propellants under shock tube conditions have indicated that the ignition is very sensitive to the oxidizer present in the initial gas phase.[1,2] Several theoretical models[1,3,5] in which the runaway exothermic reactions leading to ignition were assumed to occur in the gas phase adjacent to the propellant surface resulted in similar predictions. The models became more real with the inclusion of time-dependent variation of the propellant surface temperature (called feedback[4]), and addition of an oxidizer to the fuel, which on decomposition produces an active oxidizer in a gaseous form.[5] In general, all the theoretical models indicated that the dependence of ignition behavior upon external oxidizer is strongly influenced by the choice of ignition criterion.

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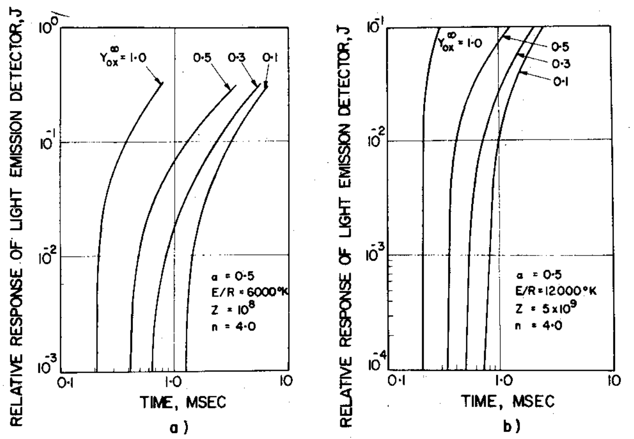


Fig. 1 Relative theoretical response *J* of a light emission detector vs time.

As is well known by now, experiments indicated that the mole fraction of oxidizer initially present in the gas phase had a strong effect on the ignition delay of the propellant and fuel samples tested. But up to this point, none of the theoretical models could unequivocally indicate the same effect of initial oxidizer mole fraction. Recently, however, further investigations have indicated a twin reaction zone structure, consisting of a primary reaction zone similar to a premixed reaction zone, and a secondary reaction zone similar to a Burke-Schumann diffusion reaction zone.[6] The existence and development of this secondary reaction zone was shown to be extremely sensitive to the amount of oxidizer present in the gas phase. A suitable ignition criterion (the "long-time" criterion of Ref. 6, applicable after this reaction zone is formed) indicates a large sensitivity of ignition delay t^* on the mole fraction Y_{ox}^∞ of the ambient oxidizer. Approximate analytical methods were developed to explain this behavior. Though these theoretical results for homogeneous propellants, and pure fuels, could indicate and explain the characteristic dependence of t^* on Y_{ox}^∞, an essential problem remained; i.e., do the theoretical ignition criteria employed have any correspondence to the criterion employed in obtaining the experimental data to which the theoretical predictions were compared?

In "end-wall" shock tube experiments on solid propellant ignition,[1,2] ignition was related to the response of a photocell to light emission from the gas phase. But the theoretical ignition criteria were based upon achievement of some specified characteristic of the transient gas-phase temperature distribution. Correspondence, or equivalence, of these criteria was assumed, but without proof. The subject of the present paper is the illustration of characteristic gas-phase ignition behavior predicted on the basis of a criterion relating light emission to the transient gas-phase distributions of species and temperature.

Model

The model considered is the same as one in Ref. 6, except for the inclusion of diffusion of inert gases. This was needed to calculate the amount of products present at any section of the gas phase.

Using the notation employed in Ref. 6, the equation for the diffusion of the inert gases can be written as

$$\partial Y_i/\partial t + (m/\rho_0)\partial Y_i/\partial \psi = D\partial^2 Y_i/\partial x^2 \qquad (1)$$

subject to the initial and boundary conditions:

$$Y_i = 1 - Y_{ox}^\infty \text{ for } t \leq 0, \quad \psi > 0$$

$$(\rho m/\rho_s)Y_i - \rho D\partial Y_i/\partial \psi = 0 \text{ at } \psi = 0, \quad t > 0 \qquad (2)$$

$$Y_i \to 1 - Y_{ox}^\infty \text{ as } \psi \to \infty, \quad t > 0$$

Defining $\eta_i = bY_i$, these equations were nondimensionalized in the same way as in Ref. 6. The mole fraction of products Y_p is calculated from the equality $Y_p = 1 - Y_f - Y_{ox} - Y_i$. The set of Eqs. (1–2), plus those of Ref. 6 were numerically integrated on an IBM 360/75 using an implicitly explicit difference method.[7] All parameter values such as initial temperature, etc., are as in Ref. 6 unless otherwise noted.

Ignition Criterion

Comparison of an ignition theory in combustion with the corresponding experiment is difficult at best. Such comparisons have quantitative meaning only when the assumptions made in the theory have some experimental justification, and when the theory adequately describes or approximates the ignition criterion employed in the presentation of experimental results. It is most unfortunate that detailed, quantitative descriptions of the experimental criterion are not generally given in the presentation of the experimental results. The derivation of a criterion relating light emission to the transient temperature and composition distributions, of the gas phase adjacent to the surface of igniting solid, is described below. This derivation is only intended to show the minimum order of magnitude and the appropriate dependence of light emission on temperature and the number density of a single specie producing the emission. After the experiments reported in Ref. 1, this specie is assumed to be CN, and the light emission to be due to the characteristic strong spectral line of CN in the ultraviolet region $B^2\Sigma^+ \to X^2\Sigma^+$ transitions[8] at 3590 Å (see Herzberg[9]). This transition occurs near the maximum transmissivity of the Kodak Wratten 18A filter[10] used in Ref. 1.

Consider an elementary volume dv at a distance x from the propellant surface, containing N_{m0} molecules of emitting specie/unit volume, N_m of which are in the excited state producing the violet emission. In the notation of Penner,[11] the emitted radiant flux (erg/sec) due to the transition from excited to ground state at the frequency of interest (the 3590 Å transition) from the volume dv is given by [12]:

$$d\mathfrak{F}_e = N_m(h\nu)A_{mn}dv \qquad (3)$$

where A_{mn} can be written in terms of the wave number ω_{mn} as

$$A_{mn} = (64^4\omega_{mn}^3/3h)|R_{mn}|^2 \qquad (4)$$

$|R_{mn}|^2$ is the square of the matrix element of the transition. The number of excited CN molecules N_m is given by

$$N_m = N_{m0}(g_m/Q)\exp(-E_m/kT) \qquad (5)$$

where E_m is the energy ($h\nu$) associated with the excited state, g_m is the statistical weight of the excited electronic level considered, and Q is the electronic partition function. For our purposes, $g_m/Q \simeq 1$.

Assume that at any point in the gas phase the molecular density of the emitting specie is proportional to the molecular density of combustion products N_p. Then N_{m0} is given by $N_{m0} = N_pf = N(1 - Y_f - Y_{ox} - Y_i)f$ where N is the total molecular density in the gas phase. Consequently, Eq. (3), for the emitted radiant flux of Eqs. (4) and (5), becomes

$$d\mathfrak{F}_e = (64\pi^4\omega_{mn}^4C/3)|R_{mn}|^2N(1 - Y_f - Y_{ox} - Y_i)f \times \exp(-E_m/kT)dv \qquad (6)$$

Considering the one-dimensional nature of the over-all problem, the elemental volume dv in the preceding equation can be written as A_cdx where A_c is assumed to be a unit cross-sectional area of the shock tube. The characteristic width S of the collimation slits used in the light detection system then defines the volume of gas to be considered, assuming the surface of the propellant is at one edge of the slit. The intensity of radiation issuing from this volume, in erg/str sec, is thus

$$J(S,t) = \mathfrak{F}_e(S,t)/4\pi =$$

$$K \int_0^S N(1 - Y_f - Y_{\mathrm{ox}} - Y_i) \exp\left(-\frac{E_m}{kT}\right) dx \quad (7)$$

where $K = (16\pi^3\omega_{mn}{}^4C/3)|R_{mn}|^2f$.

The preceding energy J impinges on a photocell detector over an area A_d at a distance r_d from the center of the (1.5 in. i.d.) shock tube,[1] after passing through an optical filter of transmissivity τ_f. The voltage output of the photocell V_p can be represented by

$$V_p \sim \tau_f(A_d/4\pi r_d{}^2)J(S,t) \quad (8)$$

$$V_p \sim \bar{K} \int_0^S N(1 - Y_f - Y_{\mathrm{ox}} - Y_i) \exp\left(-\frac{E_m}{kT}\right) dx \quad (9)$$

where $\bar{K} = \tau_f(A_d/4\pi r_d{}^2)K$. From the preceding equation it is clear that the integral itself is representative of the signal produced by the photocell detector and represents a relative response of the photocell output voltage. Thus the relative response J of the detector was calculated during numerical integration of the equations. In terms of dimensionless temperature and distance used in the theoretical analysis, the relative response is given by

$$J(\tau) = \int_0^\xi (1 - Y_f - Y_{\mathrm{ox}} - Y_i) \exp\left(-\frac{M_i}{\theta}\right) d\xi \quad (10)$$

In order to obtain theoretical ignition results using a light emission criterion, $J(\tau)$ values were computed during integration of the differential equations describing the process. The ignition delay t^* was defined to be the time required for the relative response J to reach some specified value J^*. Thus the ignition criterion was $J = J^* =$ specified.

To check the applicability of this criterion in terms of the RCA 935 photocell used as the ignition detector in Ref. 1, the thermally excited radiant intensity impinging on such a detector was estimated from the right-hand side of proportionality 8. The value of the integral in $J(S,t)$ was found from the numerical solution for J for $Y_{\mathrm{ox}}{}^\infty = 1$ and $J^* = 0.1$; S was 500μ. This was done for the electronic transition of CN at 3590 Å, as previously mentioned. Assuming $\tau_f = 0(1)$, $(A_d/4\pi r_d{}^2) = 0(10^{-4})$, $R_{mn}{}^2 = 0(10^{-34})$, $f = 0(10^{-10} - 10^{-12})$—or a mole fraction of CN of $10^{-9} - 10^{-11}$—and otherwise standard input parameters, the intensity incident on the detector is of the order of 10^{-2} to 10^{-4} lumens. For an RCA type 935 photocell, intensities on the order of 10^{-2} lumens are easily detectable,[13] though intensities of 10^{-4} lumens may not be. Therefore it can be concluded that thermally excited light emission must be a (major) part of the light detected in shock tube experiments. Theoretical ignition results using the previously discussed light emission criterion are discussed in the next section.

Discussion of Results

The results of the present investigation emphasize still further the conclusions of previous investigations on the characteristics of a gas-phase ignition process of solid materials. Namely, the choice of ignition criterion is decisive in determining the apparent characteristics of the ignition process. Previously, such choices were demonstrated only for the theoretical description of the ignition characteristics; the importance of the choice of ignition criterion could only be implied for experimental investigations. In fact, variation in ignition criteria may explain some of the differences in ignition data reported in Refs. 1 and 2.

On the basis of the development of the previous section, specifically using Eq. (10), it was found that the secondary reaction zone[6] contributed the greatest part of the magnitude of J. The primary reaction zone[6] generated less than some 10% of the total value of J. Consequently, it can be concluded that the secondary reaction zone would be responsible for the majority of light emission detected in a shock tube experiment of the type reported in Ref. 1 involving a homogeneous propellant igniting via a gas-phase mechanism.

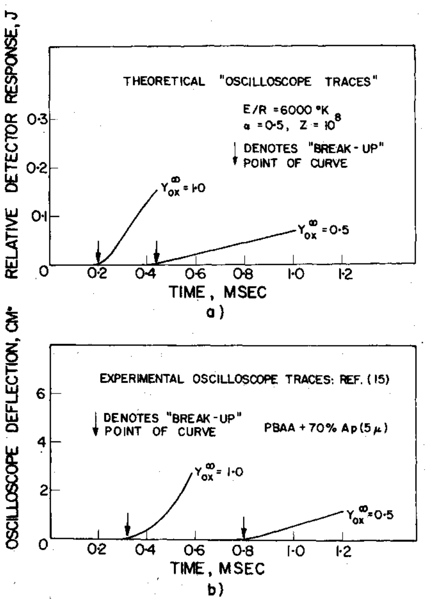
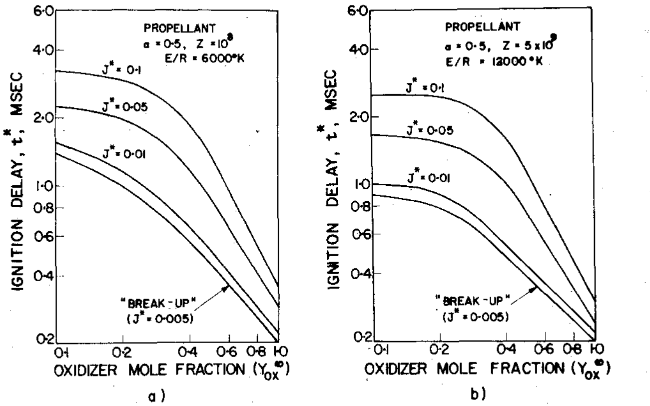


Fig. 2 Theoretical and experimental curves of the response of a light emission detector vs time in the format of experimental data.

Figures 1a and 1b are plots of the calculated relative response of a light emission detector J vs time for two values of the gas-phase activation energy, assuming equal reaction rates for both activation energy values at a temperature of 1800°K. "J" values of 0.1 indicate an emission intensity received at a hypothetical photocell detector of $0(10^{-2})$ lumens as detailed in the previous section [or Lumens received $= 0(10^{-1}J)$]. These figures can be used in two ways. The data may be used by replotting the results in Cartesian coordinates to produce theoretical "oscilloscope" traces of oscilloscope deflection vs time for any desired vertical sensitivity of the detector display. Such plots have a form similar to experimental traces of photocell output vs time. Or, achievement of a particular value of J, J^*, can be chosen to denote ignition, and thus generate t^* vs $Y_{\mathrm{ox}}{}^\infty$ plots for a particular light emission criterion defined as the time required to reach a particular J^* value.

Thus, Fig. 2a, a Cartesian plot of relative detector response J vs time, was derived from Fig. 1a. Figure 2a contains plots of J vs t for $Y_{\mathrm{ox}}{}^\infty = 1.0$ and 0.5, and illustrates the present theoretical prediction of the way similar experimental curves should look for a solid undergoing a gas-phase ignition process. It also indicates that $J = 0.005$ corresponds to the first readily discernible upward deflection of the curve, or "break-up." Figure 2a may be compared to Fig. 2b, which is a replot of experimental photocell response[15] vs time during the ignition of a composite propellant, for $Y_{\mathrm{ox}}{}^\infty = 1.0$ and 0.5, exposed to a reflected shock wave. Note the high degree of correspondence between Figs. 2a and 2b, particularly the marked change in character of the curves between $Y_{\mathrm{ox}}{}^\infty = 1$ and $Y_{\mathrm{ox}}{}^\infty = 0.5$. A factor of three decrease in "sensitivity" of Fig. 2a (i.e., a replot with a vertical scale contracted by a factor of three) would produce curves looking very much like those of Fig. 2b, at least in the initial stages near break-up.

The effect of the sensitivity of the experimental readout device is clearly important. In fact, it appears that at least two sensitivities of the experimental readout device ought to be used in shock tube ignition experiments if real information on the ignition mechanism is to be obtained.



a) b)

Fig. 3 Effect of initial oxidizer mole fraction upon ignition delay with different light emission ignition criteria.

Figures 3a and 3b are plots of t^* vs Y_{ox}^∞ with the ignition criteria of $J^* = 0.01$, 0.05, and 0.1. It can be seen from the figures that the dependence of t_{ign} upon Y_{ox}^∞ becomes increasingly strong as the value of J^* is increased from 0.01 to 0.1. Beyond 0.1, any further increase in J^* does not cause the dependence of t^* on Y_{ox}^∞ to become much stronger, though the magnitude of the ignition delay changes. Values of $J^* >$ 0.1 correspond to the long-time conditions discussed in Ref. 6, and the asymptotic analysis outlined therein can be employed to predict the ignition behavior. A value of $J^* = 0.005$ corresponds very closely to the break-up point on a theoretical oscilloscope trace such as that shown in Fig. 1a. Comparison between Figs. 3a and 3b indicates there is not much difference between the ignition behavior for $E/R = 6000°K$ and 12,000°K. This might be expected since the chemical time for both activation energies was chosen to be the same at 1800°K.

A comparison between the present theoretical results, using several different ignition criteria, and experimental shock take data is shown in Fig. 4; descriptions of the numbered curves are given in Table 1. The long-time criterion curve 5* and the light emission curve 4* with $J^* = 0.1$, exhibit the same slope for high initial oxidizer mole fractions, Y_{ox}^∞. Curve 1 is from data obtained at ONERA—and reported by Kurylko[2]—and curves 2 and 3 are from data obtained by McAlevy.[1,14] The slopes of curves 1–3 are in good agreement with those of curves 4 and 5. Magnitudes of the ignition delays are of the same order for the theoretical and experimental curves, except for curve 5*, which is an order of magnitude higher and probably corresponds to the ONERA data curve. Curve 6 is the result of employing $J^* = 0.005$ as the ignition criterion, corresponding to the break-up criterion mentioned previously. It should be compared to curve 7 from Kurylko[2] in which a break-up criterion was reported to have been used. Although details of the experimental ignition criteria used in obtaining the data shown in curves 1–3 have not been reported, the marked differences between ignition data for ostensibly the same propellant, curves 1 and 7, may be attributable to differences in the ignition criterion employed. Theoretical curves 4* and 6* illustrate the change in results obtained when different ignition criteria are used.

The difference between pure fuel and homogeneous propellant ignition characteristics is illustrated in Fig. 5, when a light emission criterion is used for indicating ignition in a gas-phase ignition process. The calculations, as plotted, indicate that fuel ignition is far more sensitive to the quantity of oxidizer, or Y_{ox}^∞, present in the initial gas phase than is a homogeneous propellant constructed from the same fuel. At large values of Y_{ox}^∞, $t_{fuel}^* \leq t_{propellant}^*$, for equal J^* values; the situation reverses as Y_{ox}^∞ decreases. The behavior is at variance with the previous result, using a long-time criterion, which indicated that t_{fuel}^* was always greater than $t_{propellant}^*$ though the dependence of t^* on Y_{ox}^∞ was the same.[6] These differences have not yet been resolved. It may be significant in terms of deciding upon the ignition mechanism of polymeric fuels from shock tube studies, however, that a theoretical break-up criterion ($J^* = 0.001$) applied to the pure fuel ignition indicates a (−1) slope in Fig. 5, as do some experimental shock tube data on polymeric fuel ignition,[2] which also used a break-up criterion.

Conclusions

New theoretical results were found using a light emission criterion for ignition. This criterion was derived by determining the time required for a quantity (J), proportional to the output signal of a hypothetical photocell detector, to reach some selected value J^*. This photocell sensed the calculated intensity of thermally stimulated light emission incident on it. The emitted light was generated by high-temperature chemical reactions occurring in the gas phase adjacent to a solid exposed to tailored interface reflection of a shockwave which stimulated decomposition of the solid. This criterion is a reasonable theoretical equivalent to that used in shock tube experiments having a configuration similar to that assumed theoretically and a photocell system.

For the most part, there is significant agreement of the theoretical and experimental results in terms of the characteristic behavior of light emission vs time, and t^* as a function of Y_{ox}^∞. The theoretical results illustrate the behavior to be expected of gas-phase ignition process of pure fuels and homogeneous propellants if photocell detection systems are used experimentally. They thereby indicate a means of interpreting experimental data on the ignition of such materials, using reflected shock techniques. This requires the use of at least two sensitivities of the device used to record the photocell output, careful definition of the ignition criterion used for each sensitivity, and the reporting of ignition results using each sensitivity and criterion.

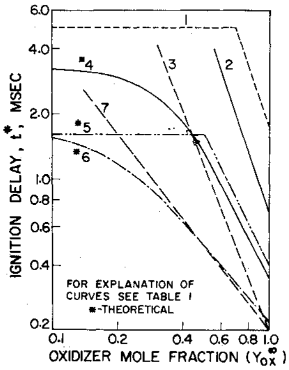


Fig. 4. Comparison of theoretical ignition behavior, using various ignition criteria, with experimental results.

Table 1 Curve descriptions for Fig. 4

Curve	Reference		
1	Kurylko, L. (20% PBAA + 80% NH_4ClO_4, ONERA data)	2	Fig. 16
2	McAlevy (Double base)	2	
3	McAlevy (22.5% polyester + 77.5% NH_4ClO_4)	2	
4	Light emission criterion $J^* = 0.1$		
5	Long-time criterion ($\epsilon = 0.01$; note that time values for the curve have to be multiplied by 10)	6	
6	Light emission criterion $J^* = 0.01$		
7	Kurylko, L. (20% PBAA + 80% NH_4ClO_4)	2	

It was also found that the secondary reaction zone,[6] or the reaction zone involving the oxidizer initially in the gas phase, was responsible for the majority of the light intensity detected. This quite substantiates the importance of the presence of such reactions in determining the long-time characteristic behavior of gas-phase ignition processes of solid materials as first discussed in Ref. 6. However, there exist some unresolved differences between ignition characteristics of pure fuels derived from using the light emission and long-time ignition criteria that require further investigation.

It was shown that purely thermal excitation of certain (CN) reaction products was of sufficient magnitude to produce light intensities detectable by an ordinary photocell, i.e., RCA type 935. It is possible that some of the light emission detected experimentally may be due to chemiluminescence. Since chemiluminescence is normally attributed to radical-radical interactions, its dependence on gas-phase properties is difficult to predict. One could argue that such interactions will not be frequent until relatively large radical concentrations exist, such as after establishment of an intense, thick reaction zone involving the external gas-phase oxidizer. Such a condition would correspond to the long-time behavior of a gas-phase ignition process. Thus it could be argued that the thermally excited light emission used in the present investigation is an adequate representation of reality.

In the foregoing analysis it has been assumed that a major portion of the light emitted by CN in the uv region is of thermal origin. There is some argument as to the nature of the radiation produced by the radicals like C_2, CH, OH and CN during exothermal chemical reactions. It is known that the radiation from C_2, CH and OH are of nonthermal origin for premixed flames.[16,17] However, for diffusion flames, such as are dealt with in the secondary reaction zone in the present paper, radiation from OH may be of thermal origin, as may be the emission from C_2 and CH.[16–18] In addition, shock tube studies of CN formation in CO_2/N_2 atmospheres[19,20] indicate that, at the flame temperatures of 2500–3000°K used to estimate the magnitude of thermally excited CN emission in this paper, strong thermal excitation of CN radicals is quite possible, particularly at the high pressures considered herein.[19] This is especially true if the CN radicals persist in the high-temperature diffusion reaction zone. That CN does persist in the high-temperature region in, and following, the reaction zone of a composite propellant has been shown by Povinelli.[20] Thus, until experiments conclusively show that the rotational/vibrational temperatures of CN radicals in composite propellant flames are greatly in excess of the flame temperature, it may be assumed that any CN emission is thermally generated (see p. 152 of Ref. 16).

In case it becomes clear that the emission from CN in composite propellant flames is entirely of nonthermal origin, some other radical which is known to emit due to thermal excitation can be considered and our results for CN emission, discussed previously, are applicable. For example, for diffusion flames, it is known that OH radiation in the uv region is of thermal origin.[21,22] Since OH has a strong emission band at 3064 Å and the energy per quanta of this emission is within 15% of that of the assumed CN emission at 3590 Å, there is a negligible difference between our results when OH emission is assumed instead of CN. Consequently, the ignition characteristics that have been found using our emission criterion are not limited by the assumption of thermal excitation of CN alone.

Therefore, it is concluded that the ignition criteria based on some specified behavior of the temperature in the gas phase give essentially the same ignition behavior as the experimental, and theoretical, light emission criteria. The "short-time" behavior[6] $[L^*(\theta) = 1.5\theta_0]$ corresponds to first detection of light by a very sensitive detector. The long-time criterion[6] $[L^*(\theta) = (\Delta\theta_{\max}/\theta_{\max})\cdot(\tau/\Delta\tau)]$ corresponds to intense light emission, or a certain specified deflection of a signal generated by a detector having low sensitivity.

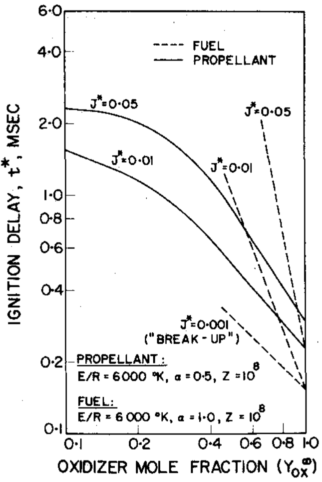


Fig. 5 Effect of initial oxidizer mole fraction on the theoretical ignition delay for propellants and pure fuels, using various light emission criteria.

II. Effect upon the Ignition Behavior of a Highly Reactive Oxidizer Evolved at the Propellant Surface

Introduction

All the previous gas-phase ignition theories under shock tube conditions considered that either the propellant is a pure fuel or it contains an oxidizer having the same physical and kinetic properties as the ambient oxidizer on decomposition. Thus it was found that the dependence of ignition times upon the ambient oxidizer becomes weaker as the amount of oxidizer contained in the propellant increases. On the other hand, it is not known how the ignition behavior is affected if the evolved oxidizer were more reactive or less reactive than the ambient oxidizer. If the evolved oxidizer is very much less reactive compared to the ambient oxidizer, then the ignition behavior can be predicted both by analytical and numerical means. The results applicable to pure fuel may be used in this case. However, if the evolved oxidizer is more reactive than the ambient oxidizer, it is not clear if the ignition behavior—shortly after the secondary, diffusion reaction, zone is established—is affected. This is discussed in the following sections.

Description of the Model

The equations for this case are essentially the same as those in Ref. 6, but the combination of diffusion equations for the oxidizing species can no longer be combined into one equation and must be written separately; the boundary conditions for

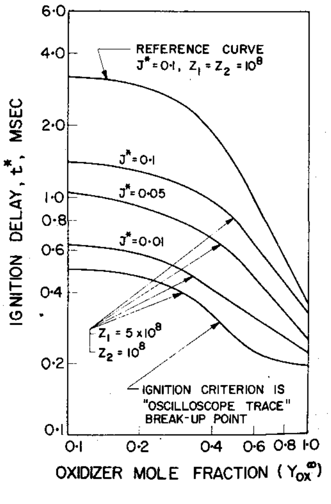


Fig. 6. Behavior of the ignition delay when the oxidizer supplied by the solid is much more reactive than that initially in the gas phase (α = 0.5, E/R = 6000°K for all curves).

oxidizer species were altered appropriately. Secondly, the chemical reaction terms in the equations must be altered to account for which oxidizer species—that evolved from the solid and/or the ambient gas-phase oxidizer—is taking part in the reaction. In general, the chemical reaction of the evolved fuel gases and each oxidizer species will involve differing pre-exponential factors, activation energies, and heats of combustion. But in order to separate the effects of reactivity alone, it was assumed that only the pre-exponential factors were different. Therefore, the temperature dependence and adiabatic flame temperature of the two reactions were kept the same as the equal reactivity situation of Part I. The pre-exponential factors of the evolved and ambient oxidizer are designated as Z_1 and Z_2, respectively.

Results and Conclusions

As previously mentioned, only the case of the less reactive ambient oxidizer is considered herein. Figure 6 is a plot of t^* vs Y_{ox}^{∞} for $Z_1 = 5Z_2$, or an evolved oxidizer five times more reactive than the ambient oxidizer, at the same temperature. For any selected ignition criterion, it was found that the dependence of the ignition delay upon Y_{ox}^{∞} decreases as the reactivity of the evolved oxidizer increases. To illustrate this effect, Fig. 6 contains two curves (for $\alpha = 0.5$ and $E/R = 6000°K$) for the cases $Z_1 = Z_2$, and $Z_1 = 5Z_2$. It is evident that for $J^* = 0.1$, the slope of the curve for $Z_1 = 5Z_2$ is less than that for $Z_1 = Z_2$. If $Z_1 \gg Z_2$, then the ambient oxidizer essentially acts as a neutral gas compared to the evolved oxidizer, and asymptotic methods may again be used to deduce the t^* vs Y_{ox}^{∞} behavior for both light emission and temperature distribution ignition criteria. This is because the results presented in Part I, Fig. 4, show that insofar as characteristic ignition behavior is concerned, weak ($J^* < 0.01$) emission criteria and the short-time temperature criteria described in Ref. 6 give equivalent results. Similarly, a strong ($J^* = 0.1$) emission criterion and the long-time temperature criterion of Ref. 6 are also equivalent.

Note the snake-like character of the lowest curve in Fig. 6. It resulted from making a theoretical oscilloscope trace similar to Fig. 2a, and applying a break-up criterion for the case where $Z_1 = 5Z_2$. It is interesting that it bears a marked resemblance to homogeneous propellant ignition data recently presented by Summerfield et al.[23] Such ignition characteristics can be interpreted as indicating a gas-phase ignition process in which the evolved oxidizer is considerably more reactive than initially present in the gas phase.

Since shock tube experiments on composite propellant ignition[1] indicate a large effect of Y_{ox}^{∞} on the ignition delay, the gas-phase theory presently formulated leads to the conclusion that either little or no oxidizer was produced by propellant decomposition during the primary ignition process, or that the evolved oxidizing species have kinetic properties similar to oxygen.

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