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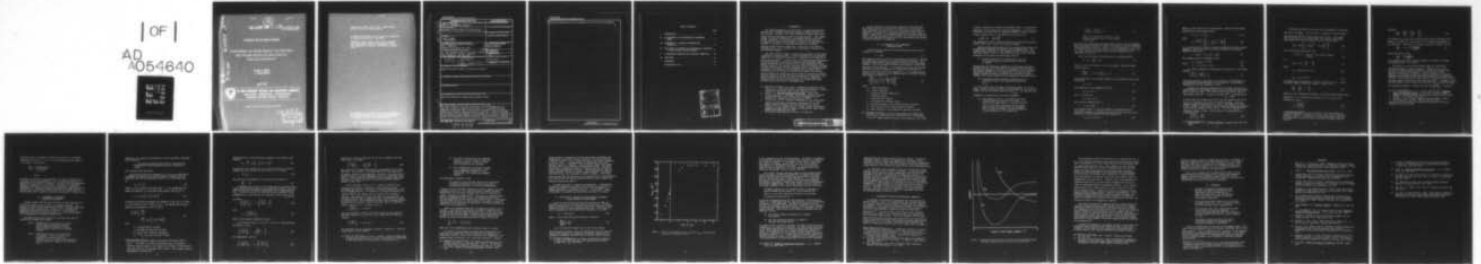
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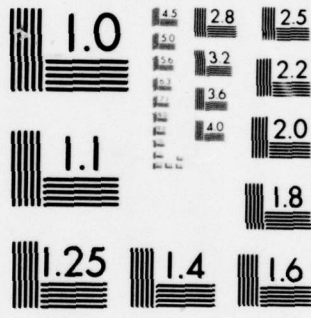
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TECHNICAL REPORT ARBRL-TR-02055

ASSESSMENTS OF RECENT MODELS FOR PRESSURE  
AND VOLUME EFFECTS ON REACTIONS OF  
BALLISTIC MATERIALS

George F. Adams  
J. Richard Ward

April 1978

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electronic excited states in the decomposition of nitrate ester compounds.



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## I. INTRODUCTION

The steady deflagration of a propellant is a complex process that involves rates of chemical reactions, changes of phase, and flow of mass and heat. Recently, Derr, Ewing and Baker reviewed several mathematical theories developed to model the burning process<sup>1</sup>. These models attempt to explain the dependence of propellant burning rate on propellant composition, initial propellant temperature, and pressure. Although all the models provide numerical values for the burning rate, the goal of the theory is to describe the physical and chemical processes occurring during combustion<sup>2</sup>. Since none of the theories reviewed by Derr, et al., provides such a description, research in the area continues unabated.

Two recent efforts attempt to provide physical models of the effect of pressure on reacting systems. A model for moderate to high-pressure combustion of a double-base propellant is suggested in work reported by Ibiricu and Williams<sup>3,4</sup>. In their model, the observed pressure dependence of the burning rate is explained by a compression enhancement model wherein the burning rate is controlled by a single unimolecular decomposition reaction. The increase in burning rate with pressure is assumed to result from change in the pre-exponential factor in an Arrhenius rate expression. This change in the pre-exponential is rationalized by consideration of the increase of vibrational frequency with pressure.

Pastine, Kamlett and Jacobs<sup>5</sup> describe the effect of pressure on chemical processes assumed to be important during detonation of explosives. This theory considers the effect of pressure on both the pre-exponential frequency factor and the activation energy for a unimolecular decomposition process occurring in a compressed solid.

1. Derr, R.L., D. Ewing and D. Baker, "Combustion Theories for Solid Propellants", report published by the Combustion Laboratory, Thermal Sciences and Propulsion Center, Purdue University, 1973.
  2. Corner, J., The Interior Ballistics of Guns, Wiley, 1956.
  3. Ibiricu, M.M. and F.A. Williams, "Influence of Externally Applied Thermal Radiation on the Burning Rates of Homogeneous Solid Propellants", *Combustion and Flame*, 24, 185 (1975).
  4. Ibiricu, M.M. and F.A. Williams, "Mechanisms for the Steady Deflagration of Double-Base Propellants", *Proceedings of the 12<sup>th</sup> JANNAF Combustion Meeting*, CPIA Publication No. 273, (1975).
  5. Pastine, D.J., M.J. Kamlett and S.J. Jacobs, "Volume and Pressure Dependence of Some Kinetic Processes on Explosives", *Naval Surface Weapons Center/WOL/TR75-149*, 1975.
- \* The pressure range modeled was 200 psi to 60,000 psi.

In the following two sections the compression enhancement model and chemical processes in solids model, respectively, are reviewed. These discussions are followed by a review of recent experimental and theoretical investigations of propellant decomposition that, taken together, cast doubt on the assumptions made in all existing combustion models. Finally, some novel research efforts that may provide descriptions of the chemical and physical processes that dominate the reactions of ballistic materials are suggested.

## II. AN ASSESSMENT OF THE COMPRESSION ENHANCEMENT MODEL

The most familiar expression relating propellant burning rate to pressure is the formula

$$r = \beta p^\alpha. \quad (1)$$

The constants  $\beta$  and  $\alpha$  are fitted to experimental burning rates, measured over some range of pressures, for each propellant of interest. It is recognized that values of these parameters determined for low-pressure burning ( $\sim 70$  atm) underestimate burning rates measured at much higher pressures (2,000-6,000 atm)<sup>6</sup>. A new expression has been reported that describes the steady deflagration of a double-base propellant as a function of pressure and initial temperature<sup>3</sup>. It is assumed that the burning rate is controlled in the condensed phase. The general burning rate relation is found to be

$$m = \left[ \frac{RT_s^2 \lambda \rho A \exp \left[ -\frac{E_s}{RT_s} \right]}{E_s \left[ c(T_s - T_i) - \frac{H}{2} - H_1 \right]} \right]^{1/2} \quad (2)$$

where

$T_s$  , surface temperature

$T_i$  , initial temperature

$\lambda$  , propellant thermal conductivity

$\rho$  , propellant density

$c$  , propellant heat capacity

$A$  , pre-exponential Arrhenius factor

$E_s$  , activation energy for the surface pyrolysis reaction

$H$  , heat released by the surface pyrolysis reaction

$H_1$  , heat released by a low temperature stabilizer reaction.

6. Grollman, B.B. and C.W. Nelson, "Burning Rates of Standard Army Propellants in Strand Burner and Closed Bomb Tests," Proceedings of the 13<sup>th</sup> JANNAF Combustion Meeting, CPIA Publication 281, (1976).

In order to develop the compression enhancement model, the temperature sensitivity of the relation for  $m$  must be suppressed. By letting each  $T$ =constant, and collecting all temperature-dependent variables into a single, constant factor  $K$ , the relation for  $m$  has the form

$$m = \left[ K A \exp \left( -\frac{E_S}{RT} \right) \right]^{\frac{1}{2}} \quad (3)$$

The temperature is that in the zone where the rate-determining process occurs, while  $A$  and  $E$  retain their previous meaning.

Ibiricu and Williams assumed that the rate-determining reaction is a unimolecular decomposition reaction in the condensed phase. The obvious choice of reaction is the decomposition of the nitrate ester functional group to yield an alkoxy radical and  $\text{NO}_2$ . Thus, the first assumption of the compression enhancement model is:

- (1) The mass burning rate is proportional to the rate of the unimolecular initiation step in which  $\text{NO}_2$  is formed.

Assuming that the temperature dependence of the unimolecular decomposition reaction can be described by an Arrhenius-type expression, the pressure dependence of the rate law parameters  $A$  and  $E$  determines the pressure dependence of the burning rate. Williams and Ibiricu choose to ignore the effect of pressure on the activation energy, leading to the second assumption of the compression enhancement model:

- (2) The pressure effect operates by changing the pre-exponential term in the Arrhenius-like expression for  $m$ .

It is also stated that, on average, the pressure effect on  $E$  is not large. There is no physical basis for this assumption; the motivation seems to be that one cannot evaluate the  $\left( \frac{dE}{dp} \right)_T$ . We feel that this

assumption is contradicted by the third assumption.

- (3) The frequency factor,  $A$ , is related to the vibrational frequency of the bond to be broken. A "... characteristic bond energy...",  $E_v = h\nu$ , is defined, and it is the effect of pressure on this energy that describes the change in the pre-exponential term. In order to evaluate the rate of change of  $E_v$  with compression, it is assumed that

$$- \left( \frac{\partial E_v}{\partial V} \right)_T \approx \left( \frac{\partial E_o}{\partial V} \right)_T = P_i \quad (4)$$

where  $V$  is the specific volume,  $P_i$  is the internal pressure, and  $E_o$  is the internal energy of the solid.

We see that the compression enhancement model requires that the Arrhenius factor be frequency dependent and that the frequency be pressure dependent. These assumptions are correct. However, if one assumes that  $\nu = \nu(P)$ , then it follows that the activation energy is pressure dependent, since  $E = E_o(\nu)$ . This assumption contradicts the previous assumption that  $E$  is independent of pressure.

Given the definition of internal pressure, integration gives,

$$E_o = E_\infty + \int_V^\infty P_i dV, \quad (5)$$

where  $E_\infty$  is the zero pressure value of the energy. Using the thermodynamic identity,

$$\left( \frac{\partial E_o}{\partial V} \right)_T = P_i = T \left( \frac{\partial P}{\partial T} \right)_V - P, \quad (6)$$

and assuming that a Van der Waals equation of state describes the system, one obtains

$$P_i = a/v^2. \quad (7)$$

The integration is then completed to yield

$$E = E_\infty + a/v. \quad (8)$$

This is rewritten as

$$h\nu = h\nu_\infty + a/v, \quad (9)$$

which gives an expression for  $\nu$ ,

$$\nu = \nu_\infty + a/hv. \quad (10)$$

The frequency factor,  $A$ , has been assumed to be proportional to the vibrational frequency, so Williams and Ibiricu<sup>4</sup> deduce that the dependence of  $A$  on  $P$  can be obtained from the expression,

$$A = A_o (1 + a/hv_\infty \nu), \quad (11)$$

where  $A_0$  is the value of  $A$  for zero-pressure. Using the Van der Waals equation Ibiricu and Williams obtain

$$A = A_0 \left( 1 + \frac{P}{P_c} \right), \quad (12)$$

where

$$P_c = \frac{v_\infty h R T}{a} \left[ \left( 1 + \frac{a}{PV^2} \right)^{-1} + \frac{bP}{RT} \right], \quad (13)$$

$P_c$  is a characteristic pressure at which the compression effect becomes important. One now can write an explicit formula for the pressure-dependent burning rate

$$m = KA_0 \left( 1 + \frac{P}{P_c} \right) \exp(-E/RT). \quad (14)$$

This expression can be rearranged to give,

$$m = KA_0 \exp(-E'/RT), \quad (15)$$

where

$$E' = E - RT \ln \left( 1 + \frac{P}{P_c} \right). \quad (16)$$

The crucial assumption in developing this expression is the assumed equality,

$$\left( \frac{\partial E_v}{\partial V} \right)_T \approx \left( \frac{\partial E}{\partial V} \right)_T = P_i. \quad (17)$$

Since this equality is incorrect, we conclude that the development of the compression enhancement model is also incorrect. We now offer a demonstration that the assumption is wrong.

Although the compression enhancement model assigns the rate-determining reaction to the condensed state, one can conclude that the authors mean a liquid-like state. The internal pressure of a polar liquid is approximately 5000 atm<sup>7</sup>. In order to evaluate  $\left( \frac{dE_v}{dV} \right)_T$  conservatively

we shall assume the largest value for  $\Delta E_v$  and the smallest value for  $\Delta V$  that can be justified on the basis of current knowledge. Since the change of volume on compression for a solid is less than for a liquid, we will estimate  $\Delta V$  for a solid. Recent infrared and Raman spectroscopic studies provide reasonable values for  $\Delta E_v$ . The rate of change of the vibrational energy is small, so the derivative is approximated by a difference ratio,

$$\left( \frac{\partial E_v}{\partial V} \right)_T = \frac{\Delta E_v}{\Delta V}. \quad (18)$$

7. Moelwyn-Hughes, E.A., Physical Chemistry, Pergamon Press, New York (1961).

The change in volume with pressure can be determined by calculating the inverse of  $\left(\frac{dP}{dV}\right)_T$ . This derivative is defined in terms of quantities associated with the binding energy of the solid. If we assume that the solid is a face-centered cubic (fcc) crystal, the Lennard-Jones energy function that describes the solid has the form\*,

$$U(R) = 2N\epsilon \left[ 12.13 \left(\frac{\sigma}{R}\right)^{12} - 14.45 \left(\frac{\sigma}{R}\right)^6 \right]. \quad (19)$$

An fcc crystal has the property that

$$V = NR^3 / \sqrt{2}, \text{ where } R \text{ is the nearest-neighbor distance,} \quad (20)$$

so

$$U(R) = U(V) = \frac{b_{12}}{V^4} - \frac{b_6}{V^2} \quad (21)$$

where

$$b_{12} = \left(\frac{1}{2}\right) (12.13) N^5 \epsilon \sigma^{12}, \quad (22)$$

$$b_6 = (14.45) N^3 \epsilon \sigma^6. \quad (23)$$

At absolute zero the entropy of a crystal is constant, so  $dU = -pdV$  is the energy change accompanying a change in volume. Thus

$$\frac{dP}{dV} = -\frac{d^2U}{dV^2} = -\frac{B_T}{V_0}, \quad (24)$$

where  $B_T$  is the isothermal bulk modulus. The Lennard-Jones potential has a minimum for  $V = V_0$ , allowing the evaluation of  $V_0$  in terms of the constants  $b_{12}$  and  $b_6$ .

$$V_0 = \left(\frac{2b_{12}}{b_6}\right)^{\frac{1}{2}}. \quad (25)$$

\* Although propellants are not fcc crystals, the volume change in a polymer is expected to be greater than that of any crystal. The choice of an fcc crystal is a convenience. To use another crystal structure will change only the value of the multiplicative constants within the brackets.

Therefore,

$$\frac{dP}{dV} = - \frac{20b_{12}}{V_0^6} + \frac{6b_6}{V_0^4} = - \frac{b_6^3}{b_{12}^2} \quad (26)$$

The constants  $b_{12}$  and  $b_6$  can be calculated for various substances using equations (22) and (23), since values of the Lennard-Jones parameters are available<sup>8</sup>. Choosing  $\text{CO}_2$  as a model, polarizable compound, we find

$$\frac{dP}{dV} = - 4.32 \times 10^8 \frac{\text{dyne/cm}^2}{\text{cc/mole}} \quad (27)$$

Taking the inverse yields

$$\frac{dV}{dP} = - \frac{2.3 \text{ cc/mole}}{\text{kbar}}$$

As an example we see that a pressure change of 1 kilobar will change the volume by about - 2.3 cc/mole.

The effect of a one kilobar pressure change on a vibrational stretching frequency is almost negligible. Murphy<sup>9</sup> points out that the effect of high pressure on polymers is to alter the secondary and tertiary structure of the materials. Cited as evidence of the stability of the primary structure is the near constancy of vibrational frequencies associated with bond stretching vibrations with variation of pressure. Recent high-pressure Raman studies by Christoe and Iqbal confirm the small effect of pressure on bond-stretching modes<sup>10</sup>. In general, if the pressure change is sixty kilobar, we expect less than a one percent change in the stretching frequency. Christoe and Iqbal found  $\left(\frac{\partial \omega_i}{\partial P}\right)_T = 1 \text{ cm}^{-1} \text{ kbar}^{-1}^*$ .

8. c.f., Hirschfelder, J.O., C.F. Curtiss, and R.B. Bird, Molecular Theory of Gases and Liquids, p. 165, Wiley, New York, (1954).

9. Murphy, R., "Effects of Very High Pressure on Organic and Biological Systems", Ph.D. Thesis, UCLA, 1975.

10. Christoe, C. and Z. Iqbal, "Raman Scattering in Alkali Azides at High Pressures", Chem. Phys. Letters, 39, 511 (1976).

\*We have used the spectroscopic convention of expressing vibrational frequency in units of energy.

Using this value, the change in vibrational energy for a ten kilobar compression will be,  $\Delta E_v = 10 \text{ cm}^{-1}$ ; the corresponding volume change is  $-23 \text{ cc mole}^{-1}$ . We have then

$$\frac{\Delta E_v}{\Delta V} = \frac{1.2 \cdot 10^9 \text{ erg-mole}^{-1}}{23 \text{ cc mole}^{-1}}$$

= 52 bar.

The result is, of course, an overestimate. We expect a correct result to be less than thirty atmospheres. Since the internal pressure is approximately five thousand atmospheres, we conclude that the approximate equality of assumption (3) is incorrect. Therefore, the compression enhancement model does not possess the physicochemical significance assigned to it. Although the burning rate expression obtained by Ibiricu and Williams correlates some burning rate data, we conclude that the physical model used to justify the necessary assumptions is without merit.

### III. ASSESSMENT OF A DYNAMICAL DECOMPOSITION MECHANISM

Recently another model has been derived to describe the effects of pressure and volume on the reactivity of energetic materials<sup>5</sup>. We consider the model because the predictions differ so markedly from those obtained by Ibiricu and Williams. Pastine, et al., consider both unimolecular and bimolecular kinetic processes. The treatment of bimolecular processes is completely formal, so we limit our discussion to the treatment of unimolecular decompositions.

The authors begin their discussion by specifying two types of unimolecular decomposition processes,

Type A - decomposition occurs when one or several internal modes of molecular vibration achieve amplitude sufficient to cause either internal reaction or the breaking of bonds.

Type B - decomposition that occurs via photolysis like pathways. Such a reaction is not dependent on molecular vibrations. Decomposition is envisaged as occurring when a molecule undergoes a change of its electronic state.

Pastine, et al., restrict the discussion to Type A processes, describing their approach as

"...the simplest possible model which will quantitatively describe the related decomposition rates as functions of T and V."

Let's consider their derivation.

The activation energy for decomposition to occur via normal mode  $i$  is assumed to be equal to the potential energy of vibration for the particular case that the amplitude is equal to a critical amplitude,  $\rho_i^*$ ,

$$E_a = \omega_i^2 \rho_i^{*2}, \quad (29)$$

where  $\omega_i$  is the frequency for normal mode  $i$ . It is assumed that the number of molecules,  $n_i$ , which have energy greater than  $\omega_i^2 \rho_i^{*2}$ , is

$$n_i = n \exp \left[ - \omega_i^2 \rho_i^{*2} / 2kT \right]. \quad \dagger \quad (30)$$

A molecule with sufficient energy will decompose in the time  $\tau_i/2$ , where  $\tau_i$  is the period of the  $i^{\text{th}}$  mode ( $= 2\pi/\omega_i$ ). The maximum rate at which molecules can decompose via the  $i^{\text{th}}$  mode is

$$\begin{aligned} \left( \frac{dn}{dt} \right)_i &= \frac{2bn_i}{\tau_i} \\ &= \frac{bn\omega_i}{\pi} \exp \left[ - \omega_i^2 \rho_i^{*2} / 2kT \right], \end{aligned} \quad (31)$$

with

- $b$ , a proportionality constant,
- $n$ , the number of molecules per gram,
- $\rho_i^*$ , the critical vibrational amplitude,
- $\tau_i = 2\pi/\omega_i$ , the period for the  $i^{\text{th}}$  mode.

---

 $\dagger$  This expression gives the number of molecules with energy equal to  $\omega_i^2 \rho_i^{*2}$ . The number of molecules with energy equal to or greater than this energy is equal to the integral, over energy, of this quantity with lower limit  $\omega_i^2 \rho_i^{*2}$  and upper limit infinity. This integral yields a complementary error function.

Knowing the rate at which molecules disappear, we can define a rate constant,

$$K_i = \frac{b\omega_i}{\pi} \exp \left[ - \frac{\omega_i^2 \rho_i^{*2}}{2 kT} \right] . \quad (32)$$

An effective rate constant for the overall decomposition is found by summing over rate constants for each of the (3 v - 6) modes,

$$K = \sum_i K_i . \quad (33)$$

The total rate of decomposition via unimolecular processes is,

$$-\frac{dn}{dt} = -Kn . \quad (34)$$

A treatment such as this is most interesting if one assumes that a single vibrational mode dominates the decomposition process. For this case the total rate of reactant disappearance will be approximated as  $-K_i n$ . In order to examine the volume and pressure dependence of the decomposition, one may evaluate the logarithmic derivative  $\left( \frac{\partial \ln K_i}{\partial \ln V} \right)_T$ .

One finds,

$$\left( \frac{\partial \ln K_i}{\partial \ln V} \right)_T = + \gamma_i \left[ \frac{\omega_i^2 \rho_i^{*2}}{kT} - 1 \right] \quad (35)$$

with,

$$\gamma_i = - \left( \frac{\partial \ln \omega_i}{\partial \ln V} \right)_T , \quad (36)$$

which is the Gruneisen parameter for mode i.

The activation energy is  $1/2 \omega_i^2 \rho_i^{*2}$ , and this is substituted into the brackets to give,

$$\left( \frac{\partial \ln K_i}{\partial \ln V} \right)_T = \gamma_i \left( \frac{2E_a}{kT} - 1 \right) . \quad (37)$$

The thermodynamic identity,

$$\left( \frac{\partial \ln K_i}{\partial \ln V} \right)_T = -B \left( \frac{\partial \ln K_i}{\partial P} \right)_T , \quad (38)$$

allows one to write an expression for the rate of change of the  $\ln K_i$  with respect to pressure,

$$\left( \frac{\partial \ln K_i}{\partial P} \right)_T = - \frac{\gamma_i}{\beta_T} \left( \frac{2E_a}{kT} - 1 \right). \quad (39)$$

This expression is interesting because of the signature of the right-hand term. For positive  $\gamma_i$ , the right-hand side of the equation will be negative except for high temperature conditions. The implication is that an increase in pressure decreases the rate of unimolecular decomposition. Since Gruneisen parameters for bond stretching normal modes are most often greater than zero, the predicted behavior should be observed in most cases.

To test the model, Pastine, et al., compare estimates of the derivative with respect to pressure to time-to-explosion data<sup>11</sup>. It is assumed that the time to explosion is inversely proportional to the rate of decomposition,  $K_i$ . For several of a series of explosives, the time-to-explosion data suggest that  $K_i$  decreases with increasing pressure. These materials include PETN, HMX, and dinitropropane. On the other hand, the time to explosion of TNT is insensitive to changes in pressure, while  $\tau$  for nitromethane decreases with increasing pressure, implying that  $K_i$  increases. Based on the first series of explosives, however, Pastine, et al., estimate a value of

$$\left( \frac{\partial \ln K_i}{\partial P} \right)_T \approx - 0.06 \text{ kbar}^{-1}.$$

They then attempt to estimate a theoretical value by using order of magnitude values for  $\gamma_i$ ,  $\beta_T$  and  $E_a$ . For a temperature of 550 $\frac{1}{2}$ K they estimate

$$\left( \frac{\partial \ln K_i}{\partial P} \right)_T = - 0.074 \text{ kbar}^{-1}. \quad (40)$$

This agreement with the experimental estimate is impressive. There are several points to note, however.

11. Lee, E.L., R.H. Sanborn, and H.D. Stromberg, "Thermal Decomposition of High Explosives at Static Pressures, 10-50 Kilobars", Proceedings of the Fifth Symposium (International) on Detonation, 1970.

- (1) The times to explosion for the compounds studied (11) did not always increase with increasing pressure, so there is doubt about the generality of the model.
- (2) The interpretation of the data by Pastine, et al., implicitly assumes that a solid-state decomposition reaction is rate-controlling. Lee, Sanborn and Stromberg disagree.

The experimental researchers state,

"The behavior of PETN and HMX indicates the suppression of gaseous intermediates by the high pressure and a corresponding reduction in the rate of decomposition."

It seems to us that available experimental evidence supports the interpretation of Lee, et al. In a series of papers, Cosgrove and Owen demonstrated that the thermal decomposition of RDX is initiated by a thermal, vapor phase, decomposition<sup>12</sup>. One should be especially aware that it was demonstrated that the rate of decomposition of RDX was directly proportional to the volume of the reaction vessel. This suggests that the effect of pressure on the explosive is to reduce the rate of sublimation of the solid into the vapor phase, effectively reducing the overall rate of decomposition.

Finally, the assumption made about the meaning of equation (30) is incorrect. This expression represents the number of molecules with a specific energy, not the number of molecules with at least that energy. In order to calculate the number of molecules with energy greater than or equal to this critical energy, one must integrate equation (30) between the limits  $E^*$  and infinity giving an integral of the form

$$\int_a^{\infty} e^{-t^2} dt = \frac{\sqrt{\pi}}{2} \operatorname{erfc}(a)$$

where  $\operatorname{erfc}$  is the complementary error function, equal to  $1 - \operatorname{erf}(a)$ .

The results of the treatment of unimolecular decompositions outlined here are incompatible with the results of other theories of unimolecular kinetics. This is best illustrated by a comparison of the dynamical theory of Pastine, et al., with that of Slater<sup>13</sup>. Slater's

12. Cosgrove, J.D. and A.J. Owen, "The Thermal Decomposition of 1,3,5-Trinitro Hexahydro 1,3,5 Triazine (RDX) - Part I: The Products and the Physical Parameters", *Combustion and Flame*, **22**, 13 (1974).

13. N.B. Slater, *Theory of Unimolecular Reactions*, Methuen, London, 1959.

theory assumes an energization step for the molecule and assumes that decomposition occurs when a chosen coordinate in the molecule attains a critical extension. This is almost the same as the initial assumption of Pastine, et al. The difference in the predictions of the two theories, however, is complete. Slater's analysis leads to the characteristic result of all unimolecular decomposition models. The effect of pressure on decomposition rate is to increase the rate of reaction until a limiting pressure is attained. For pressures greater than the limiting pressure the rate of reaction remains constant. A characteristic plot of  $k_{uni}$  versus pressure is shown in Figure 1. More recent work has shown that the unimolecular rate theories fail for high pressures; the reaction rate will begin to increase beyond the limit found by the idealized unimolecular models<sup>14</sup>.

It seems clear that "...simplest possible model..." treatments do not provide reasonable explanations of the effects of pressure on the chemistry and physics of reactive materials. The two examples considered here lead to contradictory results. At this point, a review of the effects of pressure on decomposition reactions is in order.

#### IV. THE EFFECTS OF PRESSURE ON PHYSICOCHEMICAL PROCESSES. A BRIEF REVIEW OF EXISTING MODELS.

There are two well-known theories that describe the effect of pressure on the rate of gas-phase unimolecular reactions. The Slater theory, mentioned above, is a dynamical model that considers the intramolecular transfer of energy among molecular bonds. This theory predicts a high-pressure limit rate constant expression of the form

$$k_{\infty} = \nu \exp(-E_0/kT) \quad (41)$$

where  $\nu$  is an average vibrational frequency, defined by

$$\nu = \sum_{k=1}^n \left( \mu_k^2 \nu_k^2 \right)^{1/2} \quad (42)$$

$E_0$  is an activation energy equal to the critical energy.

The predictions of Slater's theory of unimolecular reactions have not been in good agreement with experiment, principally because of the assumption of harmonic vibrations and the need for careful selection

14. I. Oref, "Nonrandomization of Energy in Unimolecular Reactions. The Effects of High Pressures on the Apparent Rate Constant", J. Chem. Phys., 63, 3168 (1975).

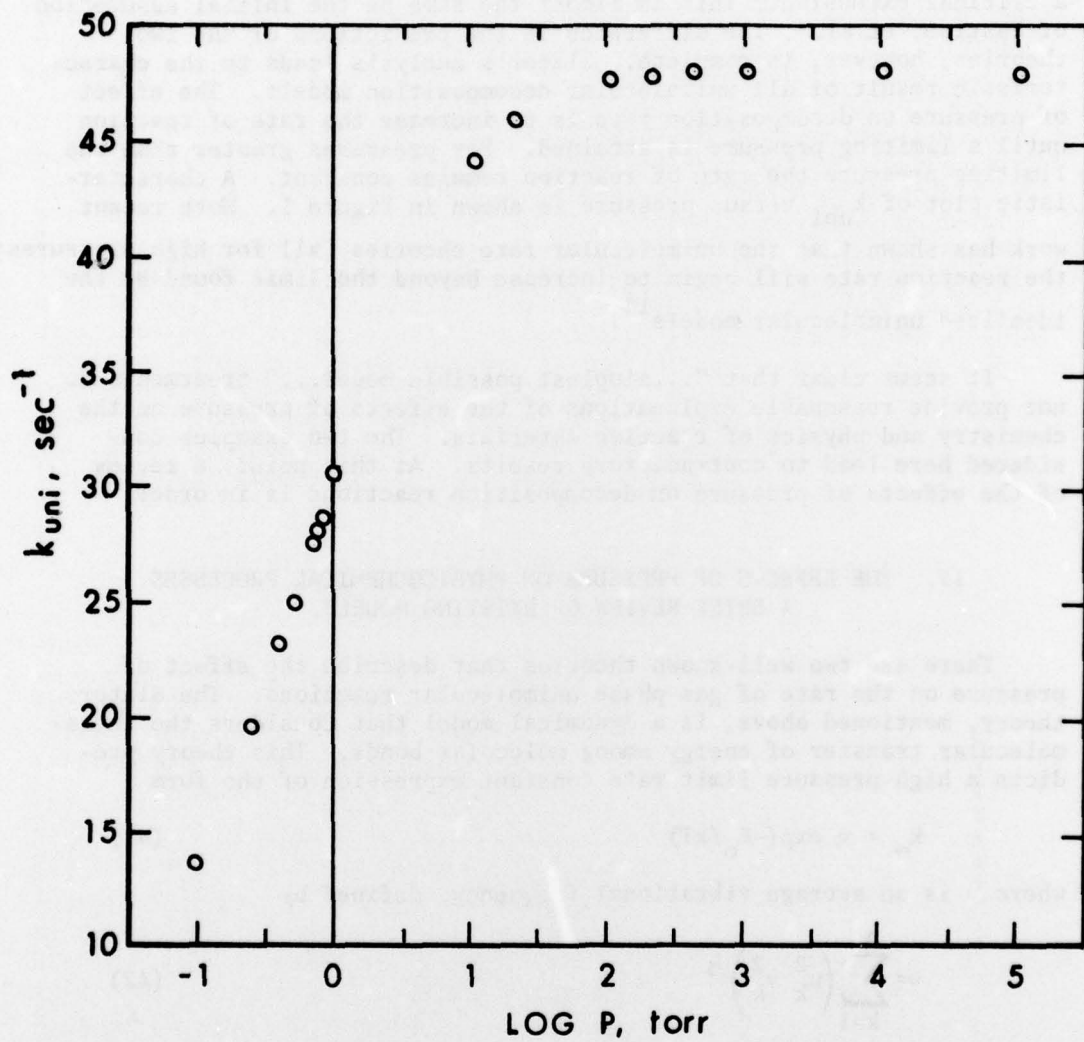


Figure 1. Plot of the unimolecular rate constant,  $k_{uni}$ , versus log of pressure for N-propyl nitrate.

of the configuration of the activated complex. The factor  $n$  in equation (42) represents the number of oscillators that contribute to changes in the critical coordinate. In the harmonic Slater theory, normal modes that belong to a symmetry species other than that of the reaction coordinate do not contribute to the model. It is this restrictive condition that is responsible for the poor agreement between Slater theory and experimental results for small molecules.

Let us recall the basic physical premise of the preceding models. Each of the models reviewed has assumed that the unimolecular decomposition reaction under investigation has been thermally activated; that is, the molecule exists at some temperature,  $T$ , in a heat bath, the molecule is vibrationally excited, and the molecule decomposes. The classic theory used to describe such systems is the Rice-Ramsperger-Kassel-Marcus (RRKM) Theory. This theory differs from the others in its crucial assumption, first stated independently by Rice and Kassel:

"A chemical species will not decompose unless it possesses a certain minimum internal energy,  $E_0$ , and the molecule will react at a rate that increases as a function of the energy it possesses in excess of  $E_0$ ."<sup>15</sup>

If the rate-determining process for the burning of a double-base propellant is a unimolecular reaction, then the theory to use in describing the process is the RRKM method. The RRKM theory predicts that the reaction rate increases with pressure until a limiting rate is attained. At pressures above that where this limiting rate is attained, the rate remains constant. These results of the theory are dependent upon two important criteria:

- (1) The internal energy of the molecule is randomly distributed.
- (2) Only one vibrational potential is needed to describe the nuclear motion.

If either of these criteria is violated, the effects of pressure on the decomposition rate must be re-evaluated. The complications introduced by non-random distributions of vibrational energy have been mentioned above. The assumption that only a single vibrational potential is operative is equivalent to the rejection of Type B unimolecular decomposition by Pastine, et al. If more than one vibrational potential is operative during the course of the decomposition, the reaction is said to be non-adiabatic, and some account must be taken of the "forbidden"

15. Forst, W., Theory of Unimolecular Reactions, p. 14, Academic Press, New York, 1973.

transition from one potential energy surface to another. Though most researchers choose to ignore the complications introduced by such processes, there is evidence that suggests that the initial decomposition reaction of a nitrate ester occurs by a change in vibrational potential energy function.\* We consider this point of view in the following section.

An assessment of the available literature of unimolecular decomposition reactions leads to several conclusions. The body of research performed in the past half-century demonstrates that the effect of pressure on the rate of a unimolecular decomposition reaction is to increase the rate to a limiting value,  $k_p$ . Research at high pressures indicates that the hypotheses needed to justify the statistical treatment of decomposition kinetics, the RRKM method, fail; the non-random distribution of energy leads to an increase in the rate of unimolecular decomposition. Most important is the recognition that the rate of reaction is dependent on the total internal energy of the activated molecule. The effect of these conclusions is to further discredit the basic hypotheses of both the compression enhancement model and the dynamical theory of Pastine, et al.

#### V. A MICROSCOPIC MECHANISM FOR PROPELLANT COMBUSTION

We consider now decomposition mechanisms that involve photolytic reaction channels. There is no demonstration that justifies ignoring such reaction channels; in fact, there is evidence that such channels are important. In the recent past several researchers have invoked the participation of low-energy electronic states in nitrate esters to rationalize the phenomenon of super-rate burning in double-base propellants<sup>16,17</sup>. We shall outline the essence of these hypotheses with the aid of Figure 2. The illustration shows cuts through three multi-dimensional hypersurfaces. The curves represent the electronic energies of the ground electronic state and the  $a^3A'$  excited electronic state as functions of the bond length between the bridge oxygen and the nitrogen atom in the nitro group. (The spectroscopic notation used refers to a simple alkyl nitrate ester with a single plane of symmetry.)

\*We have used Forst's expression "...vibrational potential..." because it is descriptive of the classic point of view as to the role of electronic potential energy surfaces, i.e., defining the force field in which molecular vibrations occur. An equivalent expression is "...potential energy (hyper) surface...".

16. L.E. Harris in, "The Annual Review of the Ignition and Combustion Program", BRL Report No. 1708, 1974; L.E. Harris, J. Chem. Phys., 58, 5615 (1973).
17. G.F. Adams and J.R. Ward, Proc. Thirteenth JANNAF Combustion Meeting, CPIA Publication No. 281 (1976).

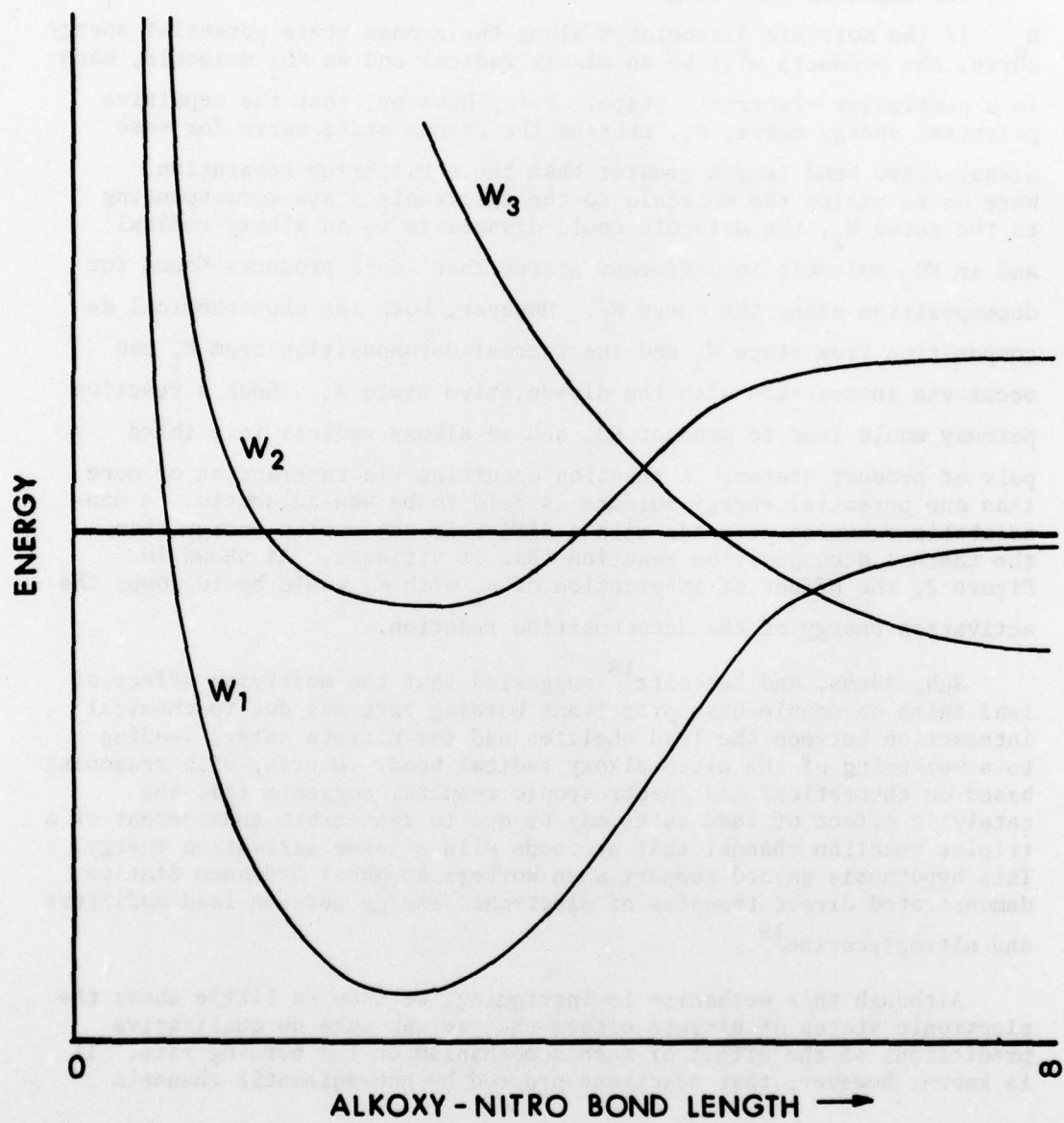


Figure 2. Schematic Representation of the Variation of Electronic Energy With Bond Length for Several States of a Nitrate Ester.

The dissociation energy of the molecule in its ground state,  $W_1$ , is  $D_0$ . If the molecule dissociates along the ground state potential energy curve, the products will be an alkoxy radical and an  $\text{NO}_2$  molecule, each in a particular electronic state. Note, however, that the repulsive potential energy curve,  $W_3$ , crosses the ground state curve for some alkoxy-nitro bond length greater than the equilibrium separation. Were we to excite the molecule to the electronic state corresponding to the curve  $W_2$ , the molecule could dissociate to an alkoxy radical and an  $\text{NO}_2$  molecule in different states than those products found for decomposition along the curve  $W_1$ . However, both the photochemical decomposition from state  $W_2$  and the thermal decomposition from  $W_1$  can occur via interaction with the dissociative state  $W_3$ . Such a reaction pathway would lead to product  $\text{NO}_2$  and an alkoxy radical in a third pair of product states. A reaction occurring via interaction of more than one potential energy surface is said to be non-adiabatic. A non-adiabatic reaction proceeds with a different activation energy than the thermal decomposition reaction that it vitiates. As shown in Figure 2, the effect of interaction of  $W_1$  with  $W_3$  would be to lower the activation energy of the decomposition reaction.

Suh, Adams, and Lenchitz<sup>18</sup> suggested that the modifying effect of lead salts on double-base propellant burning rate was due to chemical interaction between the lead chelates and the nitrate ester, leading to a weakening of the nitro-alkoxy radical bond. Harris, with reasoning based on theoretical and spectroscopic results, suggests that the catalytic effect of lead salts may be due to spin-orbit enhancement of a triplet reaction channel that proceeds with a lower activation energy. This hypothesis gained support when workers at Naval Ordnance Station demonstrated direct transfer of electronic energy between lead modifiers and nitroglycerine<sup>19</sup>.

Although this mechanism is intriguing, we know so little about the electronic states of nitrate esters that we can make no qualitative predictions of the effect of such a mechanism on the burning rate. It is known, however, that reactions proceed by non-adiabatic channels

18. Suh, N.P., G.F. Adams, and C. Lenchitz, *Combustion and Flame*, 22, 289 (1974).

19. L.A. Lee, T.D. Austin and A.T. Camp, "A Photochemical Combustion Mechanism for Mesa and Plateau Burning Double-Base Propellants in Proceedings of Eleventh JANNAF Combustion Meeting (1975).

which are strongly pressure and temperature sensitive. Furthermore, it should be remembered that as pressure increases, there is no longer a need for a metal salt to catalyze the non-adiabatic reaction, since the effect of external pressure will be to enhance the interaction between the electronic states. Thus, one can understand the loss of catalytic effect by the modifier at high pressure.

This is not to suggest that we understand the reasons for the effect of pressure on the burning rate of a double-base propellant. Hopefully the microscopic mechanism outlined here will disturb, enrage, interest, and stimulate the reader, leading to new initiatives and outlooks in the study of propellant combustion.

## VI. CONCLUSION

1. Although the compression enhancement model provides a reasonable correlation for some experimental data on burning rates of double-base propellants, since the physical model is incorrect, we regard the burning-rate formula as empirical.
2. The decomposition models employed by Ibiricu and Williams, and Pastine, et al., are based on assumptions that are not valid at high pressure.
3. The activation energy for a unimolecular decomposition reaction is pressure dependent. It follows that phenomena that occur over a range of pressures cannot be described by a simple Arrhenius rate law.
4. Consideration should be given to the rate of non-thermal decomposition mechanisms when modeling the dynamics of propellants.

Finally, we should point out that most of the comments made in this report, and the assumptions used by the authors referenced, refer to vapor phase molecules\*. This is unfortunate, but the reality is that chemistry and kinetics in condensed phases are poorly understood. At our current state of knowledge, however, the understanding of gas-phase reactions will be of great assistance in our attempts to understand condensed phase reactions.

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\*Although it is true that Pastine, et al., developed their model using solid-state concepts, the crucial hypothesis is the definition of activation energy. This definition was in no way dependent upon the phase of the material.

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