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AN ANALYSIS OF THE PRESSURE DEPENDENCE OF NITRATE ESTER THERMAL DECOMPOSITION

George F. Adams

September 1978

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An analytical study of the effect of pressure on the rate constant for the unimolecular decomposition of n-propyl nitrate is given. The Rice-Ramsperger-Kassel-Marcus theory is reviewed, and the present application is discussed in detail. Limitations on application of this model are also discussed. It is concluded that the initial decomposition reaction of nitrate esters cannot be the rate determining step for the observed variation of burning rate with pressure.

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TABLE OF CONTENTS

LIST OF SYMBOLS

h, k, N_A, R	Planck, Boltzman, Avogadro and gas constants.
p, T	pressure and absolute temperature
Q	partition function
A^*, A^+	energized molecule and activated complex
$E^* (\equiv E_{VR}^*)$	total non-fixed energy in the active degrees of freedom of a given energized molecule.
E_v^*, E_r^*	vibrational and rotational parts of E^*
E^+	total non-fixed energy in the active degrees of freedom of a given activated complex
E_v^+, E_r^+	vibrational and rotational contributions to E^+
k_1	rate-constant for energizing of reactant
k_a	rate-constant for conversion of energized molecule to products, Lindeman theory.
$k_a(E^*)$	same rate-constant with energy-dependence, as in RRKM theory
k_2	rate constant for de-energizing of energized molecule
E_o	critical energy for reaction
k_{uni}	first order rate constant, $-(1/[A])d[A]/dt$
$L^\ddagger$	statistical factor or reaction path degeneracy
$Q_1, Q_1^\ddagger$	partition functions for adiabatic rotations in A and A^+
Q_2	partition functions for active vibrational degrees of freedom in A
$\sum P(E_{VR}^+), W(E_{VR})$	number of quantum states of A^+ at all energies up to and including E^+.
$N^*(E^*)$	density of quantum states of A^* at energy E^*.
λ	collisional energy transfer efficiency
Z	second-order collision rate constant
$\Delta S^\ddagger$	entropy of activation.

I. INTRODUCTION

Several recent models have explained the effect of pressure on ballistic properties as due to an assumed change in the microscopic processes that determine the extensive properties (1,2). Each model assumes that an initial unimolecular decomposition reaction is the rate-determining step over the entire pressure regime peculiar to the macroscopic process. Both models assume that external pressure causes a major change in the rate of this decomposition reaction, thereby controlling the ballistic phenomena. This report describes an analytical study of the effect of pressure on the thermal decomposition of a nitrate ester, n-propyl nitrate. The results of the study demonstrate that the pressure-dependence of this reaction rate cannot explain the observed burning rate behavior of nitrate esters.

The second section of this report describes the chemical reaction being investigated and the methods used to perform the analytical study. This research involves the application of the Rice-Ramsperger-Kassel-Marcus (RRKM) theory to predict the rate constant for the decomposition reaction as a function of pressure. The third section describes the parameters used to describe the reacting system, and provides details of the kinetics calculations. A final section provides a comparison of the RRKM results and the observed burning-rate behavior, and contains comments on the validity of the assumptions that underly the RRKM theory. Several appendices provide information about portions of the calculation that deserve detailed explanation.

II. UNIMOLECULAR REACTION RATE THEORY

N-propyl nitrate was chosen for study because of good experimental data on the thermal decomposition reaction. The initial decomposition reaction is identified as the scission of the nitro-alkoxy bond to produce two free radicals, NO_2 and alkoxy. This unimolecular decomposition has been studied for n-propyl nitrate using the very low pressure pyrolysis (VLPP) method (3). An RRKM analysis of the temperature dependence of the high pressure rate constant has been performed but no analysis of the pressure-dependence of the unimolecular reaction rate was made (3).

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1. M.M. Ibiricu and F.A. Williams, "Mechanisms for the Steady Deflagration of Double-Base Propellants", 12th JANNAF Combustion Meeting, CPIA Publication Number 273, 1976.
2. D.J. Pastine, M.J. Kamlett and S.J. Jacobs, "Volume and Pressure Dependence of Some Kinetic Processes in Explosives", Naval Surface Weapons Center/WOL/TR75-149, 1975.
3. G.D. Mendenhall, D.M. Golden, and S.W. Benson, "The Very-Low-Pressure Pyrolysis (VLPP) of n-Propyl Nitrate, tert-Butyl Nitrate, and Methyl Nitrite. Rate Constants for Some Alkoxy Radical Reactions", Int. J. Chem. Kinetics, 7, 725 (1975).

The present research consists of an RRKM analysis of the pressure dependence of the nitrate ester bond-scission reaction. The following paragraphs outline the development of RRKM theory. More complete discussions can be found in books by Forst (4), and Robinson and Holbrook (5).

A unimolecular decomposition reaction involves a single molecule that undergoes transformation to a reactive complex by some energization process. The formation of the complex is a function of intermolecular energy transfer, often via collision, and intramolecular energy transfer after the collision occurs. Thus, the process is envisioned as

$$A \xrightarrow{k_1} A^* \xrightarrow{k_a} A^+ \longrightarrow \text{products.} \qquad (1)$$

Most modern theories that describe unimolecular decomposition reactions are based on the Lindeman mechanism (6) which assumes that collisions between two reactant molecules will produce some energized molecules with enough energy to react. If conversion of reactant molecules to energized molecules is slow compared to the rate at which collisional de-energization occurs, an equilibrium population of energized molecules will exist with concentration proportional to the concentration of the reactant molecules. Thus the rate constant will be first-order with respect to reactant concentration. At low pressure, however, collisions cannot maintain an equilibrium concentration of energized intermediates, so the rate constant will depend on the rate of energization which is proportional to the square of the concentration of reactant molecules. Lindeman's mechanism predicts that at low pressure the rate constant increases with increasing pressure, but at high pressure the rate constant reaches a limit and remains constant. Although these predictions are qualitatively correct, numerical studies based on Lindeman's mechanism yield poor agreement between theory and experiment.

Hinshelwood extended Lindeman's theory and laid the basis for the development of RRKM theory by suggesting that one needs to consider the internal degrees of freedom when determining whether a molecule possesses sufficient energy to react (7). The chance for a molecule to have enough energy to react increases with the number of degrees of freedom of the reactant molecule, primarily because of the contribution of the vibrational degrees of freedom.

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4. W. Forst, Theory of Unimolecular Reactions, Academic Press, New York, (1973).
5. P.J. Robinson and K.A. Holbrook, Unimolecular Reactions, Wiley-Interscience, New York (1972).
6. F.A. Lindeman, title not available, Trans. Faraday Soc., 17, 598 (1922).
7. C.N. Hinshelwood, "The Theory of Unimolecular Reactions", Proc. Roy.Soc. (A), 113, 230 (1927).

The final important assumption, suggested simultaneously by Rice and Ramsperger (8,9) and Kassel (10), is that the rate of decomposition of the energized molecule is a function of the energy of the species. The species will not decompose unless it possesses a minimum internal energy, called the critical energy E_o, and will react at a rate that increases as a function of the energy it contains in excess of E_o. The corollary of this is that if energy is the necessary and sufficient condition for reaction, it is implied that energy is exchanged among the internal degrees of freedom. That is, there is intramolecular energy transfer. The developers of RRKM theory ignore the dynamics of such transfer, assume that the transfer is a random process, and go on to develop a statistical theory couched in the language of transition-state theory (11).

The reaction scheme for the RRKM model is

$$A + M \underset{k_2}{\overset{\delta k(E^*\to E^*+\delta E^*)}{\rightleftarrows}} A^*(E^*\to E^* + \delta E^*) \tag{2}$$

$$A^*(E^*) \xrightarrow{k_a(E^*)} A^+ \xrightarrow{k^+} \text{products.} \tag{3}$$

The notation $E^* \to E^* + \delta E^*$ means that the energized molecule has energy in the range E^* to $E^*+\delta E^*$. The second equation represents the major feature of the RRKM theory wherein Absolute Rate Theory is applied to the calculation of $k_a(E^*)$. Thus we distinguish between an energized molecule A^* and the activated complex A^+.

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8. O.K. Rice and H.C. Ramsperger, "Theories of Unimolecular Reactions at Low Pressures", J. Amer. Chem. Soc., 49, 1617 (1927).
9. O.K. Rice and H.C. Ramsperger, "Theories of Unimolecular Reactions at Low Pressures - II", J. Amer. Chem. Soc., 50, 617 (1928).
10. L.S. Kassel, *Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co., New York, 1932.
11. R.A. Marcus, "Unimolecular Dissociations and Free Radical Recombination Reactions", J. Chem. Phys., 20, 359 (1952).

The energized molecule A^* is a molecule that contains in its active degrees of freedom a non-fixed energy[#] E^* greater than the critical energy E_o. This non-fixed energy may consist of both vibrational and rotational energy.

The activated complex A^+ is a species that is recognizable as intermediate between reactants and products, and is characterized by a configuration that corresponds to a position atop a potential barrier. The total non-fixed energy of the activated complex is E^+ which is equal to E^* less the critical energy E_o.

The RRKM theory provides the following mathematical expression for the overall unimolecular rate-constant, k_{uni},

$$k_{uni} = \int_{E^* = E_o}^{\infty} \frac{k_a(E^*)dk_{1(E^* \rightarrow E^* + \delta E^*)}/k_2}{1+k_a(E^*)/k_2[M]} \qquad (4)$$

Using statistical mechanics, expressions for $\delta k_{1(E^* \rightarrow E^* + \delta E^*)}/k_2$ and $k_a(E^*)$ are obtained leading to

$$k_{uni} = \frac{L^{\ddagger} Q_1^+}{hQ_1Q_2} \int_{E^*=E_o}^{\infty} \frac{\{\sum P(E_{vR}^+)\{\ \exp(-E^*/kT)dE*}{1+k_a(E^*)/k_a[M]} \qquad (5)$$

with

$$k_a(E^*) = \frac{L^{\ddagger} Q_1^+}{hQ_1 N^*(E^*)} \sum_{E_{vR}^*=0}^{E^+} P(E_{vR}^+). \qquad (6)$$

where

Q_1^+	rotational partition function for the activated complex
Q_1	rotational partition function for the reactant
Q_2	vibrational partition function for the reactant
h	Planck's constant
$\sum P(E_{vR}^+)$	number of quantum states of A^+ at all energies up to E^+
$N^*(E^*)$	density of quantum states of A^* at energy E^*
$L^{\ddagger}$	statistical factor or reaction path degeneracy.

[#] Non-fixed energy is internal energy available for redistribution.

In practice the product $k_2[M]$ is replaced by the collisional deactivation rate,

$$k_2[M] = \lambda Z p \tag{7}$$

where

λ, collisional efficiency
Z, collision number
p, pressure.

The RRKM integral is rewritten as a sum, resulting in the following working equation for the evaluation of k_{uni}.

$$k_{uni} = \frac{L^{\ddagger} Q_1^{+}}{h Q_1 Q_2} \exp(-E_o/RT)\, \Delta E^{+} \sum_{L=1}^{i_{max}} \left[\frac{\{\sum P(E_{VR}^{+})\} \exp(-E^{+}/RT)}{1 + k_a(E^{*})/\lambda Z p} \right]_i \tag{8}$$

where the energy relations,

$$E^{*} = E_o + E^{+}, \quad E^{+} = (i + \tfrac{1}{2}) \Delta E_i \tag{9}$$

have been used. The rate constant will have units sec^{-1} if the energies are expressed in kcal mol^{-1} and the constants h and R have the values

$$h = 9.537 * 10^{-14} \text{ kcal mol}^{-1} \text{ sec} \tag{10}$$

$$R = .0019872 \text{ kcal mol}^{-1} K^{-1}. \tag{11}$$

The expressions given in equations 6 and 8 are the expressions used in our study of the decomposition of n-propyl nitrate. In the following section the methods used to evaluate variables in these expressions are reviewed and the model used for the n-propyl nitrate calculations is specified.

III. RRKM PARAMETERS FOR N-PROPYL NITRATE

There are a number of variables that must be determined before a prediction of k_{uni} can be made. The computation of these variables requires input information about the structure and properties of the reactant molecule and the activated complex. In general, information about the reactant is available, whereas information about the complex is unknown. Important data that are required include:

1. Vibrational frequencies
2. Moments of inertia
3. Collision number
4. Critical energy, E_o.

Vibrational frequencies for the reactant are needed for calculation of the vibrational partition function, Q_2, and the density of quantum states, $N^*(E^*)$. Vibrational frequencies for the activated complex are needed in order to calculate the sum of quantum states of A^+.

The vibrational frequencies for N-propyl nitrate are known, but those for a transition state are neither known nor measurable. Often, vibrational frequencies for the transition state can be assigned by transfer of data from molecules with analogous structures. In the case of bond stretching frequencies, bond force constants are predicted on the basis of bond-order correlations (12). However, there is no well-established method for estimating the force constants for bending and torsional modes.

Benson and O'Neal have tabulated frequencies for stretching and bending modes and used these values for predicting the high-pressure A-factors of unimolecular reactions (13,14).

Any attempt to deduce the properties of the activated complex leaves some of the variables undetermined. Generally, these variables are used as adjustable parameters to make the model predict the correct value for the experimental high-pressure frequency factor. Mendenhall, Golden and Benson (3) have made no effort to deduce the properties of the complex since it is known that the calculated fall-off behavior is insensitive to the model used provided that it predicts the correct value of A_∞. The high-pressure rate constant, k_∞, is given in RRKM theory by the expression,

$$k_\infty(\text{RRKM}) = L^\ddagger \frac{kT}{h} \frac{Q_1^\ddagger Q_2^\ddagger}{Q_1 Q_2} \exp(-E_o/kT) \qquad (12)$$

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12. H.S. Johnston, Gas-Phase Reaction Rate Theory, Ronald, New York, 1966.
13. S.W. Benson, Thermochemical Kinetics, Wiley, New York, 1968.
14. H.E. O'Neal and S.W. Benson, "The Biradical Mechanism in Small Ring Compounds", J. Phys. Chem., 72, 1866, 1968.

This implies that the logarithm of the high-pressure frequency factor is given by

$$\ell n\ A_\infty(\mathrm{RRKM}) = \ell n\ (L^{\ddagger}\ e\ kT/h) + d\ \left(T\ \ell n\ \frac{Q_1^+ Q_2^+}{Q_1 Q_2} \right) /dT \tag{13}$$

$$= \ell n(L^{\ddagger} ekT/h) + {}^{\Delta S^{\ddagger}}/_{R}\ . \tag{14}$$

A convenient numerical value of this expression is

$$\log_{10} A_\infty = 10.753 + \log_{10}(L^{\ddagger} T) + {}^{\Delta S^{\ddagger}}/_{4.756}. \tag{15}$$

In practice, the value of $\Delta S^{\ddagger}$ is adjusted so that the high-pressure frequency factor agrees with the experimental value. The change in entropy is divided into vibrational and rotational contributions;

$$\Delta S_v^{\ddagger} = S_v(A^+) - S_v(A) \tag{16}$$

$$\Delta S_r^{\ddagger} = S_r(A^+) - S_r(A)\ . \tag{17}$$

To solve for these contributions it is assumed that the vibrations are quantum harmonic oscillators and the rotations are classical. The statistical mechanical expression for the entropy is

$$S = R\ \ \ell nQ + RT\ \frac{d\ \ell n\ Q}{dT}\ . \tag{18}$$

The appropriate expressions to calculate the vibrational and rotational entropy are

$$Q_{v_i} = \left[1 - \exp(-\ h\ \nu_i/kT)\right]^{-1} \tag{19}$$

$$T\ \frac{\ell n\ Qv_i}{dT} = \frac{(h\nu_i/kT)}{\left[\exp(h\nu_i/kT)-1\right]} \tag{20}$$

$$Q_r = \pi^{\frac{1}{2}}(8\pi^2 kT/h)^{3/2}(I_a I_b I_c)^{\frac{1}{2}} \tag{21}$$

$$T\ \frac{d\ell n\ Q_r}{dT} = 3/2\ \ . \tag{22}$$

Given these expressions, the use of the RRKM method to study unimolecular decomposition kinetics is straightforward. The molecular parameters chosen by Mendenhall, et al, are given in Table I with one exception. In this study, the RO-NO_2 distance was reduced by .06 Å in both the reactant and the complex. This change has almost no effect on the overall calculation. The parameters listed yield a value for the logarithm of the high-pressure A-factor of 16.5. This relatively high-value is expected because the nitro-moiety becomes a free-rotor in the transition state.

In order to complete the RRKM integration as a function of pressure, one must specify the collision number, Z, and the collisional efficiency, λ. The experimental apparatus used by Mendenhall, et al, (3), is claimed to have a collisional efficiency near one. The collision number, Z, is given by the expression

$$Z = (\sigma_d^2 \, N_A/R) \, (8\pi \, N_A \, k/\mu)^{\frac{1}{2}} (1/T)^{\frac{1}{2}}, \tag{23}$$

with Z in units $\text{Torr}^{-1} \text{ sec}^{-1}$ when:

σ_d = collision diameter (cm)

μ = reduced molar mass (g mol^{-1})

T = temperature (K)

$N_A = 6.0225 * 10^{23} \text{ mol}^{-1}$

$R = 6.2362 * 10^4 \text{ cm}^3 \text{ Torr K}^{-1} \text{ mol}^{-1}$

$k = 1.3805 * 10^{-16} \text{ erg K}^{-1}$.

The temperature used in this study was 600°K, a temperature assumed to be the surface temperature of a burning double-base propellant. The collision diameter, σ_d, was chosen to be 10^{-7} cm, slightly greater than the distance between the most separated atoms in the equilibrium structure of n-propyl nitrate.

IV. RESULTS OF THE RRKM INTEGRATION AND COMPARISON WITH BURNING-RATE DATA

The data given in Table I have been used to estimate values for $k_a(E^*)$ and $\sum P(E^+_{vR})$ using the Hase-Bunker computer code (15). These results and the collision number have been used to evaluate k_{uni} as a function of pressure - using a desk-top computer (Tektronix 4051) to calculate the rate constant. Table II lists the value for k_{uni} as a function of pressure, and the results are shown in Figure 1. It is apparent from the figure that the unimolecular rate constant is a constant for pressures above ~ 400 Torr, or slightly more than one-half atmosphere. Thus, this research predicts that the rate constant for the initial scission reaction of this medium-size nitrate ester is independent of external pressure for pressures above one atmosphere, for temperatures comparable to those at the surface of a burning propellant. What does this imply in regard to the burning of nitrocellulose?

Nitrocellulose, a polymeric material, possesses an indeterminately large number of vibrational frequencies. It is a characteristic of unimolecular reactions that as molecules become large, the effect of pressure on the rate constant disappears; that is, the fall-off region moves to lower pressure. Consequently, we expect that the effect of pressure on k_{uni} for nitrocellulose decomposition is negligible. Note, however, that we mean only the initial scission of the nitrate ester; our results cannot be extended to the decomposition reactions of secondary radicals formed in the overall chemical kinetic scheme of nitrocellulose combustion. The next report in this series will demonstrate the crucial role played by pressure-variation for the decomposition of small radicals.

Given this demonstration of the virtual pressure-independence of the nitrate-ester bond-scission reaction, it can be concluded that the pressure-dependence of propellant burning-rate cannot be explained on the basis of this reaction. This conclusion, however, must be tempered by a consideration of the assumptions made in developing RRKM theory, assumptions that limit the applicability of the theory. There are two assumptions made in the statistical development of RRKM theory.

The first assumption is a corollary of the assumption that energy is the necessary and sufficient condition for reactions, it is that the internal energy of the energized molecule is randomly distributed. If the energy is not randomly distributed, then the high

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15. W.L. Hase and D. Bunker, RRKM, Program No. 234, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana.

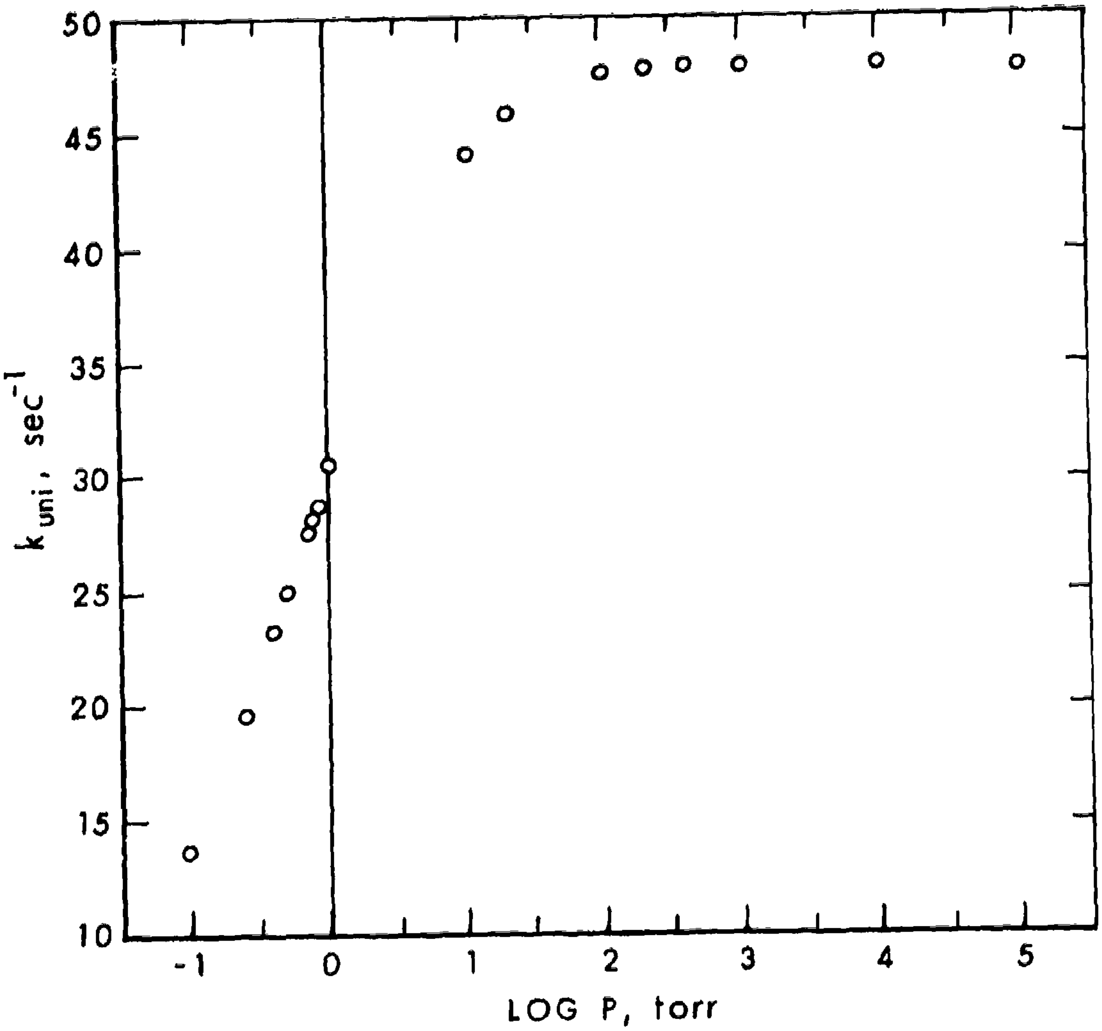

Figure 1. Plot of the unimolecular rate constant, k_{uni}, versus log of pressure for N-propyl nitrate.

Table I. Molecular Parameters for N-Propyl Nitrate.

Vibrational frequencies, cm^{-1}, with degeneracy in parentheses		Molecule	Complex
		3000 (7)	3000 (7)
		1600	1600
		1450 (4)	1450 (4)
		1350 (4)	1350 (4)
		1200	1150 (5)
		1000	1000 (2)
		1150 (4)	720 (2)
		750 (3)	
		350 (4)	
		250 (3)	125 (6)
		100	50 (3)
		50 (2)	
$RO\text{-}NO_2$, bond length,A°		1.407	2.407
Moments of Inertia, amu $A^{\circ 2}$	I_a	58.1	68.5
	I_b	412.3	542.8
	I_c	460.8	601.7
	I_{red}		39.1

Table II. Rate Constant versus Pressure Data for 600°K Decomposition of N-Propyl Nitrate.

Pressure (torr)	k_{uni}
0.5	24.858
1.	30.559
10.	44.088
20.	45.902
100.	47.615
200.	47.849
400.	47.969
1000.	48.04
10000.	48.08
100000.	48.09

pressure rate constant will not be constant, but will show an increase over a finite range of pressure above the limit for the decomposition of molecules with randomly distributed internal energy. The effect of non-random distribution of energy has been discussed by Oref (16) and commented on by Adams and Ward (17). It is unlikely that such an effect will be observed in molecules such as n-propyl nitrate or nitrocellulose, since the temperature remains relatively low during the decomposition process.

The second assumption made in developing RRKM theory is that a single vibrational potential defines the reaction hypersurface. This means, in dynamic terms, that the entire reaction proceeds along a pathway corresponding to a single potential energy surface. The problem can be understood with the aid of Figure 3, a schematic that shows the electronic energy for the first three electronic states of a nitrate ester plotted as a function of the alkoxy-nitro bond length. The curve labeled W_1 corresponds to the energy of the electronic ground state, while W_2 and W_3 label the first two triplet excited states. (This figure is based on assignments first discussed by L.E. Harris (18)). Curves W_1 and W_2 are everywhere separated by an energy difference, so the state represented by W_2 cannot influence the decomposition of a nitrate ester in state W_1. (It is expected that all the nitrate ester molecules are initially in the state represented by W_1). If only states W_1 and W_2 occur, then the nitrate esters meet the second criterion for the applicability of RRKM theory. However, if the state W_3 intersects the state W_1, as indicated in the figure, then the molecule has a curve-crossing in the reaction channel. In this case, the intersection involves states of different spins, and coupling between such states is said to be "spin forbidden". To the cogniscenti forbidden is a hollow expletive, since many examples of "spin-forbidden" reactions proceeding at measurable rates exist. The curve-crossing shown, if it is real, will have the effect of accelerating the rate of reaction at high-temperature and pressure. In this case, the pressure dependence of the nitrate ester decomposition cannot be determined by RRKM theory.

The question remains, however, does the curve crossing exist? Harris (18) postulated the crossing on the basis of the diffuse nature of the electronic spectra of nitrate esters, an interpretation then

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16. I. Oref, "Nonrandomization of Energy in Unimolecular Reaction. The Effects of High Pressures on the Apparent Rate Constant", J. Chem. Phys., 63, 3138 (1975).
17. G.F. Adams and J.R. Ward, "Assessments of Recent Models for Pressure and Volume Effects on REactions of Ballistic Materials", Tech. Rpt. ARBRL-TR-02055, April 1978. (AD #A054640)
18. L.E. Harris, "The Lower Electronic States of Nitrite and Nitrate Ion, Nitromethane, Nitramide, Nitric Acid, and Nitrate Esters", J. Chem. Phys., 58, 5615 (1973).

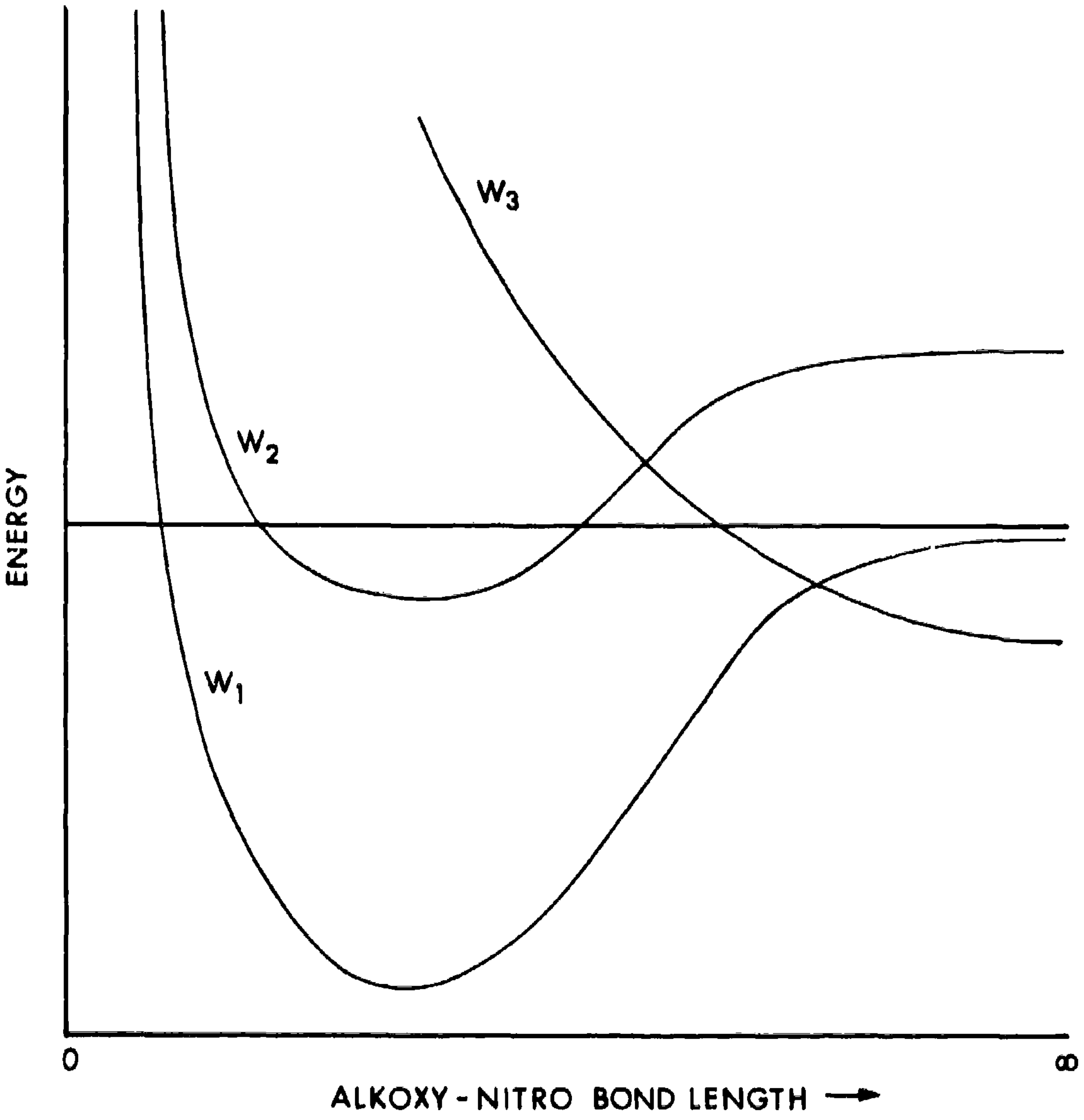

Figure 2. Schematic Representation of the Variation of Electronic Energy With Bond Length for Several States of a Nitrate Ester.

considered quite reasonable. Recently, however, a theoretical analysis by Pack (19) demonstrated that there are alternative explanations of diffuse structure in electronic spectra. This being the case, it is not clear that such a crossing occurs in the electronic structure of nitrate esters. Experimental (20) and theoretical (21) investigations of this problem are underway in this laboratory, and a resolution of the problem is anticipated.

In any event, such an esoteric perturbation on the decomposition rate is outside the ranges of validity of the published models for the effects of pressure on ballistic properties, since both models were limited to consideration of the effects of pressure on vibrational frequencies. It is concluded, on the basis of the analysis described in this report, that the initial decomposition reaction of the nitrate esters contained in double-base propellants cannot be the rate-determining step for the observed variation of burning-rate with pressure.

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19. R.T. Pack, "Simple Theory of Diffuse Vibrational Structure in Continuous UV Spectra of Polyatomic Molecules. I.", J. Chem. Phys., 65, 4765 (1976).
20. R. Beyer, private communication.
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APPENDIX A. COMMENTS ON DETAILS OF THE RRKM CALCULATION

The working expressions for k_{uni} and $k_a(E^*)$ are repeated here for convenience.

$$k_{uni} = \frac{L^{\ddagger} Q_1^{+}}{h Q_1 Q_2} \exp(-E_0/RT)\, \Delta E^{+} \sum_{i=1}^{i_{max}} \left\{ \frac{\{\Sigma P(E^{+}_{vR})\} \exp(-E^{+}/RT)}{1 + k_a(E^*)/\lambda ZP} \right\}_i \qquad (A.1)$$

$$k_a(E^*) = \frac{L^{\ddagger} Q_1^{+}}{h Q_1 N^*(E^*)} \sum_{E^{+}_{vR}=0}^{E^{+}_{vR}} P(E^{+}_{vR}) \quad . \qquad (A.2)$$

For the sake of completeness, the methods used to evaluate the sums and densities of molecular quantum states should be outlined. Application of the RRKM method is critically dependent in the methods used to evaluate the density of quantum states $N^*(E^*_{vR})$ for the reactant A and the sum of quantum states $\Sigma P(E^{+}_{vR})$ for the postulated activated complex A^{+}. The computation of N^* and ΣP[#] for n-propyl nitrate was performed using the semiclassical method developed by Whitten and Rabinovitch (1), and this method will be described briefly.

The density of quantum states N(E) can be obtained from the sum of quantum states $W(E) = \Sigma P(E)$ by differentiation with respect to energy. That is

$$N(E) = \frac{dW(E)}{dE} = \frac{d(\Sigma P(E))}{dE} \ , \qquad (A.3)$$

so we need only find a differentiable form for W(E). For a set of s oscillators, each set of quantum numbers v_i gives rise to one quantum state. The total number of states at all energies up to and including E_v is given by,

---

[#] We shall hereafter adapt the notation $W(E) = \Sigma P(E)$, and omit superscripts.

1. G.Z. Whitten and B.S. Rabinovitch, "Accurate and Facile Approximation for Vibrational Energy-Level Sums", J.Chem. Phys. 38, 2466 (1963).

$$\sum_{E_v=0}^{E_v} P(E_v) = \sum_{v_s=0} \sum_{v_{s-1}=0} \cdots \sum_{v_1=0} 1 \qquad (A.4)$$

where the summation is taken over all v_i such that the total vibrational energy is less than or equal to E_v. In the classical approximation, this sum is replaced by an integral over the occupation number, v_i. The evaluation of the integral is given by Robinson and Holbrook (2), in Appendix 6, and the result is

$$W(E_v) = P(E_v) \approx \frac{E_v^s}{s!\Pi h\nu_i} \ . \qquad (A.6)$$

Marcus and Rice (3) extended the classical treatment by suggesting that an oscillator with non-fixed energy E_v has a total vibrational energy above the ground state of E_v+E_z, where E_z is the zero-point vibrational energy. Modification of the classical expressions (A.5) and (2a) yields

$$W(E_v) = \frac{(E_v+E_z)^s}{s!\ \Pi h\nu_i} \qquad (A.7)$$

$$N(E_v) = \frac{(E_v+E_z)^{s-1}}{(s-1)!\ \Pi h\nu_i} \ . \qquad (A.8)$$

These expressions, though more accurate than the classical approximations, always overestimate the number of states at any level. An improved version of the semiclassical expressions has been developed by Rabinovitch and co-workers.

It was suggested that only a fraction of the zero-point energy should be added to the vibrational energy E_v. An empirical factor a was introduced to multiply E_z in equations (A.7) and (A.8). Whitten and Rabinovitch discovered a relation between the parameter, a, and a modified frequency dispersion parameter, β, defined by

$$\beta = \frac{s-1}{s} \ \frac{\langle\nu^2\rangle}{\langle\nu\rangle^2} \ . \qquad (A.9)$$

The relation is

$$a = 1 - \beta \cdot \omega(E') \qquad (A.10)$$

---

2. P.J. Robinson and K.A. Holbrook, Unimolecular Reactions, Wiley-Interscience, New York (1972).
3. R.A. Marcus and O.K. Rice, "The Kinetics of the Recombination of Methyl Radicals and Iodine Atoms", J. Phys. and Colloid. Chem., 55, 894 (1951).

where $E' = {}^{E_v}/_{E_z}$, and $\omega(E')$ is a function of E' defined by

$$(0.1 < E' < 1.0) \qquad \omega = (5.E' + 2.73\,E'^{0.5} + 3.51)^{-1} \qquad \text{(A.11a)}$$

$$(1.0 < E' < 8.0) \qquad \omega = \exp(-2.4191E'^{\,0.25}) \qquad \text{(A.11b)}$$

The molecular frequencies are used to calculate β and E_z, and then for a non-fixed energy E_v, the reduced energy E' is calculated and used to obtain $\omega(E')$. Given this data, the parameter a and the sum of states can be computed. The density of states can then be computed using the expression

$$N(E_v) = \frac{(E_v + aE_z)^{s-1}}{(s-1)!\,\Pi h\nu_i}\left[1 - \beta\left(\frac{d\omega}{dE'}\right)\right]$$

where $\left(\frac{d\omega}{dE'}\right)$ is obtained by differentiating (A.11a) and (A.11b).

The Whitten Rabinovitch method has been thoroughly tested, and the results are in good agreement with the direct-count for non-fixed energies E_v greater than E_z, and often for lower energies. Whitten and Rabinovitch have extended the treatment to include the case where active rotations need to be taken into account. Again, the equations suggested have been widely tested and the results appear to be good approximations to $W(E_{vr})$ and $N(E_{vr})$.

APPENDIX B: DATA FORMAT FOR RRKM

The computer code RRKM is stored as an UPDATE file on the BRL Cyber 173. This code can be used by submitting the following deck of cards.

```
 1.   JOBCARD
 2.   ACCOUNTING CARD
 3.   ATTACH (ØLDPL,RRKM,ID-GEOFADAMS)
 4.   UPDATE(F)
 5.   FTN,I.
 6.   LGO.
 7.   *EOR
 8.   * ID,(MARY) ← arbitrary choice of ID
 9.   *EOR
      DATA
10.   *EOI.
```

This job will produce values for $N(E^*)$, $W(E^+)$ and $k_a(E^*)$. These data can be used to calculate k_{uni} as a function of pressure by solving equation (A.1). Unless one has substantial experience with such computations, it is recommended that the computation of k_{uni} be carried out on a desk-top computer or as an interactive exercise on a terminal. By following this procedure, one need not compute k_{uni} for an excessive pressure range. Users are, however, invited to disagree with this philosophy.

The data required to perform a standard RRKM calculation is as follows:

1. Format 3F 10.0, I5, F10.0. A card with E_o (threshold energy), E^* (lowest molecular energy used in the calculati· ıs), ΔE^+ (upward increment of same), n, the number of successive molecular energies for which the calculation will be made, and σ_p, the statistical factor.

2. Two title cards. Say anything you like.

3. Format 2I10. n_f, the number of reactant frequencies and n_r, the number of free internal rotors.

4. Format 7F10.0. The n_f molecular frequencies, seven per card. Units, cm^{-1}.

5. Reduced moments of inertia for the internal rotors of the reactant. Units amu $A°^2$. Format 7F10.0. Omit this card if $N_r = 0$.

6. Symmetry numbers corresponding to item 5. Same format. Omit if $n_\sigma=0$.

7. Format, I10. KROT=0.

8. FORMAT, 3F.10. Three overall moments of inertia for the reactant; units amu-A^2.

9. FORMAT, I10. NANH=0.

10. FORMAT, 2I10. JDEN=0, JSUM=0.

11. FORMAT, I10. NCRIT=0.

12. FORMAT, 2I10. n_f^+ and n_r^+ , same as item 3 but for the critical configuration. $n_f^+ + n_r^+ = N_f + N_r - 1$.

13. Frequencies, like item 4 except for critical configuration.

14. Reduced moments, like item 5, except for critical configuration.

15. Symmetry numbers, like item 6, except for critical configuration.

16. The overall moments of inertia for the critical configuration as in item 8. I_x, I_y, and I_z sequence must be the same as for the molecule.

17. Format F10.0. Rotational temperature for adiabatic rotations, °K.

18. Format I10. NTRAN = 0.

Input may be stacked. To stop the program add a blank card after item 18.

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