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On the Possibility of the Role of Phonon Relaxation Processes in Shock Induced Chemical Reactions in Organic Solids

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The possibility that the first step in shock breaking of intra molecular bonds of molecules in organic solids involves a transfer of lattice phonons to internal molecular vibrational modes of the molecule is examined. Rates of transfer to specific vibrations of RDX are calculated as a function of shock pressure. The results suggest the possibility of the process.

Key words: Shock induced chemical reactions – Phonon relaxation processes.

Introduction

It has been shown recently that the application of a shock pulse to organic solids can break the intra molecular bonds of the molecules of the lattice [1, 2]. For example shock pulses were shown to remove the NO_2 group from the ring of the molecules triamino trinitrobenzene (TATB) and 1,3,5 trinitro, 1,3,5 triazocyclohexane (RDX) [1, 2]. In some cases the bonds broken by shock were not the bonds broken in thermal decomposition. There is little understanding on the molecular domain of how a shock pulse can break the intra molecular bonds of the molecules making up an organic solid. The purpose of this paper is to propose a possibility and examine the feasibility of the mechanism. The possibility is considered that the rate controlling step in shock induced bond breaking is the transfer of excited lattice energy (heat) resulting from shock compression of the lattice to specific internal vibrational modes of the molecules of the lattice. The question of why different bonds are broken in shock and slow thermal decomposition is considered.

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The approach is to adapt an existing model for the transfer of three lattice phonons to a molecule of the lattice to the case where the lattice is shock compressed [3]. Once the probability for excitation of an internal vibration is obtained, it is possible using a random walk approach to estimate the rate at which a specific vibration can be excited to a state having energy equal to the dissociation energy of the bond. This is explicitly calculated as a function of peak pressure in a single crystal of RDX.

Theory

Lieberman [3] has developed a theory for the rate of transfer of three phonons to the internal vibrations of the molecules constituting a Debye lattice. It was shown, the rate of excitation of a molecular vibration of frequency ν is given by [3]:

$$W_{10} = \frac{9k^3N^4}{16\,hm(4\pi^2M)^3}\frac{A^2T^3}{\nu_\delta^7} \tag{1}$$

where M is the mass of the molecule, m is the mass of the atom vibrating in the molecule, ν_d is the Debye frequency of the lattice, ν is the internal vibrational frequency of the bond of the molecule, A is the coupling constant between the lattice mode and the molecular vibration and T is the lattice temperature in this case produced by the compression of the lattice by the shock pulse, N is Avogrado's number, k is Boltzmann's constant and h is a Planc's constant. The probability for a transition for any N to $N+1$ is given by,

$$W_{N+1,N} = (N+1)\,W_{10} \tag{2}$$

A knowledge of W_{10} allows the rate at which the molecule can be excited to an energy level equal to the dissociation energy of the bond to be estimated where the potential is assumed to be an harmonic oscillator truncated at the dissociation energy. Montroll and Shuler [4] have shown that this rate can be treated by a one dimensional random walk with an absorbing barrier with the probability that a walker will take a step from N to $N+1$ given by Eq. (1) and Eq. (2). The distribution of vibrational energies over molecules in the lattice will then be time dependent. The mean first passage time, the average time for the walker to reach $L+1$, where $D_e = (L+1)h\nu$ is given by [4]

$$\bar{t} = 1/W_{10}\sum_{j=1}^{L+1}\exp(J\theta)\left(\frac{1}{J}+\frac{1}{J+1}\cdots\frac{1}{L+1}\right) \tag{3}$$

where $\theta = h\nu/kT$. In the calculation of $\bar{t}$ it is assumed that all harmonic oscillators are in the ground state. The model is particularly appropriate to shock induced temperature rises where the short duration of the temperature rise may not permit the internal molecular vibrations to be in equilibrium with the external lattice modes. Srenzwilk [5] used this model to calculate the rate of dissociation of a diatomic molecule in a linear chain lattice when the lattice was subjected to slow heating.

To estimate the rate at which three lattice phonons can be transferred to a specific internal vibration of a molecule as complex as RDX it is necessary to make some rather severe approximations. It will be assumed that there is no coupling between the different vibrational modes of the molecule in order to require that all the energy remains in the bond it is transferred to. It also allows the molecule to be represented as a diatomic molecule with each nuclear mass equal to the mass of the separated fragments that result from the bond breaking and the force constant to be that of the bond connecting the two fragments before separation has occurred.

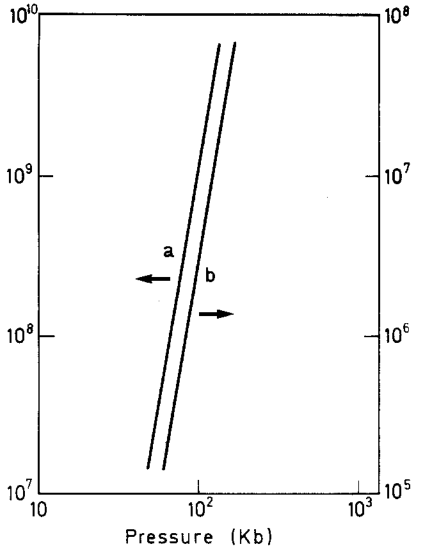
For a single crystal of RDX the temperature generated by the shock pulse can be estimated by [6],

$$\Delta T_s = \frac{2p^3}{\rho^3 C_p V_s^4} \tag{4}$$

where C_p is the specific heat, V_s is the velocity of sound and ρ is the density. The coupling constant A has been calculated for a number of different organic solids and is typically in the order of 10^{20} g/cm^2 sec^2 [7, 8, 9]. Rather than attempt an a priori calculation of A in a crystal as complex as RDX a representative value will be employed to calculate W_{10} for the C—N and N—N bond in RDX as a function of shock pressure. In the estimate the pressure dependence of the Debye frequency was taken into account by assuming it increased linearly with pressure at a rate of 0.6 cm^{-1}/Kb obtained from hydrostatic pressure measurements of the Raman frequencies of the lattice modes of RDX [10]. The results are plotted in Fig. 1. The estimated relaxation times are shorter than the typical pulse widths used to cause the bond breaking indicating that there is time for the lattice energy to be transferred to the internal modes of the molecules during the duration of the shock pulse. Taking the dissociation energy of the N—N bond as 3.0 eV, a value calculated from molecular orbital theory, the mean time for the N—N stretch vibration to be excited to $N = 20$ where $D_e = (N+1)h\nu$ can be calculated [11]. A similar calculation can be made for the C—N bond using 2.0 eV as the activation energy, measured from thermal decomposition studies [12]. The reciprocal of the mean time for excitation of the CN vibration and the NN vibration to a state having energy equal to the dissociation energy is plotted in Fig. 2 as a function of peak shock pressure.

Discussion

The possibility has been considered that the initial step in shock induced intra molecular bond breaking is a transfer of lattice phonons to internal vibrational levels of the molecules of the solid. The rate of transfer of three phonons to the CN and the NN vibration of the RDX molecule has been estimated, and the estimated relaxation time for the process is at high shock pressures smaller than the pulse width of the shocks used to break the bonds suggesting that there is time in the duration of the pulse for transfer to occur.



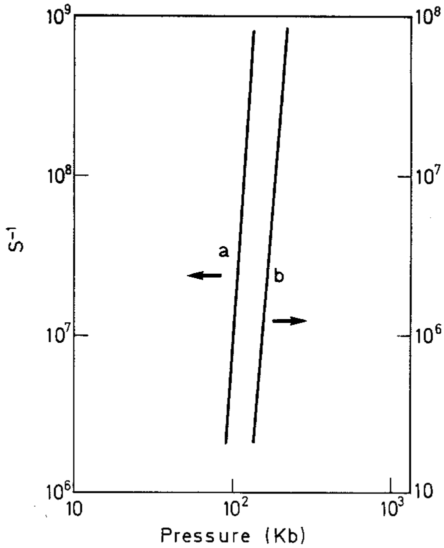


Fig. 1. The rate of excitation of the $N = 0$ to $N = 1$ vibrational levels of the CN stretch vibration (a) and the N—N symmetric stretch vibration (b) as a function of peak shock pressure in a single crystal of RDX. This data is for a Debye frequency of $8.7 \times 10^{12}\ s^{-1}$. A is taken as $10^{20}\ g/cm^2\ sec^2$

Fig. 2. The reciprocal of the mean passage time for the C—N bond to be excited to a vibrational level having energy equal to the dissosciation energy of the bond, as a function of peak shock pressure. Data (b) is the same calculation for the N—N bond

The inverse of the mean time for excitation of a vibration to a dissociative state is in the order of magnitude of the reaction rates deduced from experiments [13]. However, it is not clear whether $1/\bar{t}$ can be associated with a rate of unimolecular bond breaking because coupling between internal vibrational modes which would provide a channel for dissipation of excited energy has not been taken into account. The reaction rate may be $1/\bar{t}$ if the time to excitation to the dissociative state were short compared to the internal mode relaxation time which is typically of the order of picoseconds. The data of Fig. 2 suggests that the t could be shorter than picoseconds at high shock pressures greater than about 200 Kb.

The analysis also allows an explanation for why different bonds may be broken in shock heating than in slow thermal heating. The W_{10} relaxation process cannot occur unless $\nu < 3\nu_d$. Bonds which do not meet the condition at one bar may at high shock pressures because ν_d increases more strongly with pressure than does an internal mode frequency. Also in slow thermal decomposition there may be time for excitation energy to be transferred to another mode of vibration of the molecule whereas in the pulse heating of shock $\bar{t}$ may be shorter than internal mode relaxation time.

The model can also account for the decrease in the rate of thermal decomposition with increasing hydrostatic pressure at constant temperature that has been observed in a number of organic solids [14, 15]. At constant temperature increasing the pressure on the material will increase the Debye frequency, ν_d. Since the reaction rate at constant temperature in the model depends on $1/\nu_d^7$ a decrease in the reaction rate is predicted.

This analysis using Eq. (4) to estimate shock temperature does indicate that transfer of lattice phonons to internal vibrations of the molecules of the solid could be involved in shock induced bond breaking in solids. On the other hand another approach to estimating shock temperature in RDX leads to lower temperatures than predicted by Eq. (4) ruling out relaxational processes [16]. A definitive conclusion regarding the possibility of such processes in shock induced bond breaking will require more accurate theoretical as well as experimental determinations of shock temperatures.

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