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A SLOW REACTION RATE IN DETONATIONS DUE TO CARBON CLUSTERING*

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Theoretical calculations have been made to estimate the rate of heat release due to the carbon clustering process in detonations where elemental carbon is a reaction product. The process is assumed to be diffusion limited. Diffusion constants are determined using modified Enskog theory and the Stokes-Einstein relation. The carbon cluster energy is treated by a surface correction to the bulk. The amount of energy yet to be released has an asymptotic time dependence of $t^{-1/3}$. For some explosives, this leads to time dependent detonations where the effective CJ pressure is 10–20% above CJ for run distances of the order of centimeters.

1. INTRODUCTION

Solid carbon in detonation products is usually modeled with bulk phases such as diamond, graphite, or amorphous carbon. But, for clusters smaller than roughly 10^6 atoms, the bulk properties of carbon are significantly perturbed by the surface. In contrast to other products in a typical CHNO explosive, the formation of large clusters of C requires the gathering together of C's from a rather large volume. So, even though the carbon clustering process is very exothermic, the clusters have to diffuse to each other in order to react. It is primarily the time scale for energy release due to diffusion that we are studying here.

We picture the clustering process as carbon clusters executing Brownian motion in a hot, dense background fluid and building up through random collisions. We assume that the particles always stick if they touch. The background fluid keeps the clusters at equilibrium with respect to temperature, carrying off heat when clusters merge and causing the resulting new clusters to anneal.

2. KINETICS OF CLUSTERING

The clustering of particles undergoing Brownian motion is a straightforward diffusion problem that was first studied by Smoluchowski[1] and reviewed in English by Chandrasekhar[2].

For clusters of i carbon atoms with concentrations ν_i, where i is the number of carbon atoms in a cluster, the rate of change of concentration is

$$d\nu_k/dt = 4\pi DR\left(\sum_{i+j=k} K_{ij}\nu_i\nu_j - 2\nu_k\sum_{j=1}^{\infty}\nu_j K_{jk}\right) . \quad (1)$$

The diffusion coefficient for a cluster of i particles is $D_i, D_{ij} = D_i + D_j, D = D_1, R_i$ is the effective radius of a cluster of i particles, $R = R_1, R_{ij} = \frac{1}{2}(R_i + R_j)$, and $K_{ij} = \frac{1}{2} D_{ij}R_{ij}/DR$. The first summation in the equation is the coalescence of a cluster of i particles and a cluster of j particles. The second summation is due to a cluster of k particles combining with any other cluster. For $R_i \simeq R_j$, we have $K_{ij} \simeq 1$. The special case $K_{ij} = 1$ for all i,j leads to an analytic solution. Let $n_i = \nu_i/f_0$, and $x = 4\pi DRtf_0$ with $f_0 = \sum_{i=1}^{\infty}\nu_i$ at $t = 0$. For the initial condition $n_1 = 1$ and $n_i = 0$ for $i > 1$, the system of equations (1) has the solution

$$\eta_k = (1 + x)^{-2}\left(\frac{x}{1 + x}\right)^{k-1} . \quad (2)$$

3. DIFFUSION OF CLUSTERS

We determine D_i by combining two simple, but qualitatively accurate, methods.

First, we use the Enskog theory which can be found in McQuarrie.[3] The final result for the viscosity η is given by

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$$\eta/b_0\rho\eta^0 = Y^{-1} + 0.8 + 0.761\ Y = f(Y)\ , \qquad (3)$$

where ρ is the number density, $Y = b_0\rho g(\sigma) = (p/\rho kT) - 1$, σ is the hard sphere diameter, $b_0 = 2\pi\sigma^3/3$, and $\eta^0 = \left(\frac{5}{16}\pi\sigma^2\right)\sqrt{\pi mkT}$.

The modified Enskog theory is an ad hoc generalization to soft potentials. A real fluid is approximated by a hard sphere fluid for which the pressure is replaced by the "thermal pressure," $T(\partial p/dT)_V$.

Second, we determine D_t using the Stokes-Einstein relation, $D_t = kT/6\pi\eta R_t$. A convenient reference is Landau and Lifshitz.[4] The combined result is

$$D_t = 0.8(kT/\pi m)^{1/2}/(\pi f(Y)\rho\sigma R_t)\ . \qquad (4)$$

4. ENERGY OF CLUSTERS

At the surface of a cluster, not all bonds can be satisfied with the bulk structure because some atoms are missing. As an upper limit one could add the bond strengths of the missing bonds to get the energy difference between the cluster and the bulk, ΔE_n. The actual cluster will relax the surface atom positions in order to satisfy the bonds at the expense of strain. Alternatively, the dangling bonds might be capped off with CN (cyanide) or H.

For a nearly spherical cluster with non-surface atoms in a bulk-like environment, $\Delta E_n/n$ is proportional to $n^{-1/3}$ to leading order. In Fig. 1, we show the available data and calculations[5] of $\Delta E_n/n$ versus n on a loglog scale. The line is

$$\Delta E_n/n = 80n^{-1/3}\ \text{kcal/mol (of carbon atoms)}\ . \qquad (5)$$

Except for the special case of C_{60}, the coefficient of 80 kcal/mole appears to give a good lower bound consistent with the available information.

5. RESULTS

We now combine the previous sections to obtain energy release as a function of time. First, we will look at the results as a function of the scaled time variable $x = 4\pi DRt/f_0$. Then we will discuss the actual time scale for reasonable choices of the constants involved.

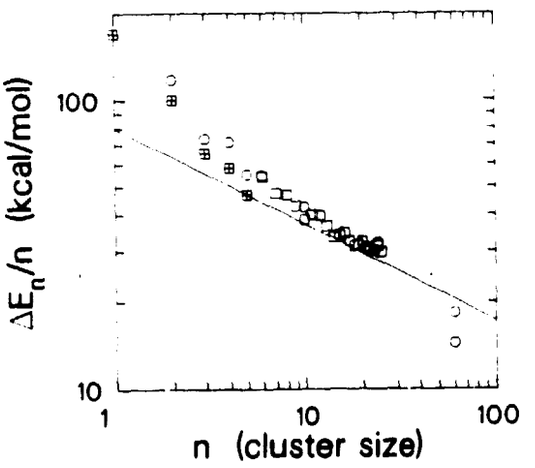

FIGURE 1
$\Delta E_n/n$ versus cluster size (n). Experiment ⊞ theory o, □ lower bound fit ——.

For the constant kernel ($K_{ij} = 1$) case Eq. (2) and Eq. (5) can be combined to give the difference in energy per carbon atom between the distribution of clusters and bulk carbon,

$$\Delta E/n = 80(1+x)^{-2}\sum_{k=1}^{\infty}\left(\frac{x}{1+x}\right)^{k-1}k^{2/3}\ . \qquad (6)$$

An accurate evaluation is easily performed on the computer.

On the other hand, the summation can be approximated by an integral for $x \gg 1$, where the resulting large x dependence is

$$\Delta E/N = 80\Gamma\left(\frac{5}{3}\right)x^{-1/3}\ . \qquad (7)$$

An ad hoc shift of the origin to agree with the true $x = 0$ energy yields

$$\Delta E/N = 80\Gamma\left(\frac{5}{3}\right)\left[x + \Gamma\left(\frac{5}{3}\right)^3\right]^{-1/3}\ . \qquad (8)$$

In Fig. 2, we compare the exact solution, Eq. (6), with the approximate expressions, Eq. (7) and Eq. (8). For large x, both Eq. (7) and Eq. (8) agree very well with Eq. (6). For all x, Eq. (8) is very close to Eq. (6) and is much more convenient to use. Note that the asymptotic time dependence of $t^{-1/3}$ is very slow indeed. For

any given time it takes 8 times as long to release the next 50% of the carbon energy.

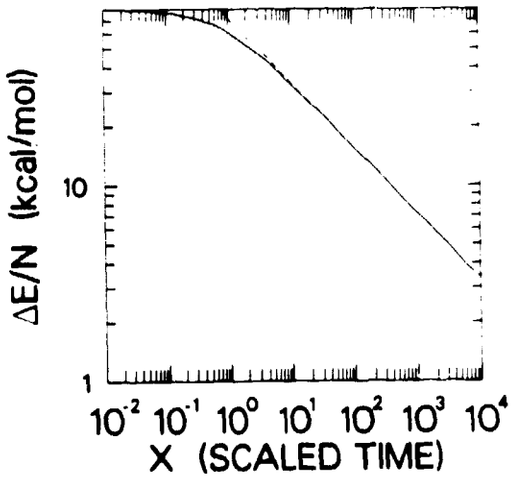

FIGURE 2
$\Delta E/N$ versus scaled time, x, for the constant kernel case. Eq. (6) ——— , Eq. (7) - - - - - , Eq. (8) ·····.

For the general K_{ij}, we then solved Eq. (1) numerically by considering only clusters less than a few thousand atoms. The numerical results for $\Delta E/N$ are nearly identical to the $K_{ij} = 1$ analytic results. More details of this result and of possible bottleneck effects may be found in a separate paper.[6]

Now we estimate the value of η for typical detonation conditions. The principal detonation products for a typical CHNO explosive are H_2O, CO_2, N_2, and solid carbon. In the fluid regime, the effective hard sphere diameter for a given species is about the radius at which the potential is equal to kT.

From our previous studies of the EOS of dense molecular fluids,[7] σ's are about 3Å. The value for Y will be taken from the EOS itself through the modified Enskog prescription, $\rho kT(Y+1) = T(dp/dT)_V$ to give a value of 4 or higher. Now for an average molecular weight of about 30 and a typical CJ density of about 2.4 g/cm³, we use Eqs. (3) and (4) to obtain $\eta = 0.010\ g/cm - s$ and $kT/6\pi\eta = 2.2 \times 10^{-12} cm^3/s = DR$.

The initial carbon concentration f_0 is estimated assuming only H_2O, CO_2, N_2, and C are present. Let ΔH_x denote the heat of explosion in kcal/mol of the explosive, M_w the molecular weight, N_C the number of free carbon atoms in the products per explosive molecule, and ρ_{CJ} the CJ density. Then we have $f_0 = N_C \rho_{CJ} N_A / M_w$, where N_A is Avogadro's number. Writing x as $x = t/t_0$, we have $t_0 = (4\pi DRf_0)^{-1}$. The fraction of energy remaining to be released due to carbon clustering at time t, $F(t)$, is approximately $F(t) = (\Delta E/N)/(\Delta H_x/N_C) = 80 N_C \Gamma\left(\frac{5}{3}\right)(t/t_0)^{-1/3}/\Delta H_x$ which is proportional to $N_C^{2/3}$ if other values are constant. At $t = 10^{-7}$s, $F(t)$ is about 1% for HMX and 3% for TNT, using conservative values. If instead we take average values and assume there is some bottleneck effect, then the energy available for slow release is more like 2–4% for HMX and 5–10% for TNT. This energy seems small until we take into account the hydrodynamic effects of a slow energy release process interacting with a fast reaction zone.

Bdzil[8] has demonstrated that a slow release of energy of $O(\delta^2)$ produces changes in the shock state $O(\delta)$ for times long compared to the slow reaction. This effect comes primarily from the fact that the Rayleigh line is tangent to the fully reacted Hugoniot at the CJ point. (Refer to Fig. 3 for an illustrative example using a polytropic gas with $\gamma = 3$, $P_0 = 0$, $\delta^2 = 0.04$, and $\delta = 0.2$.) The intersection of the partially reacted Hugoniot with the Rayleigh line is shifted by $O(\delta)$. When the fast reaction zone is relatively small, the intersection, denoted A, looks like the von Neumann spike in the usual ZND theory. For times comparable to the slow reaction zone and longer, the detonation runs at the CJ velocity for the fully reacted Hugoniot rather than for the partially reacted Hugoniot. Until times much larger than the slow reaction zone, the states from A to CJ along the Rayleigh line appear to be part of the Taylor wave instead of a separate negligible reaction zone. So, we are looking at potential changes in the shock state of 10–20% for time scales of microseconds and distance scales of centimeters. Tang[9] has made hydrodynamic calculations that demonstrate this type of effect for a two rate model of TATB.

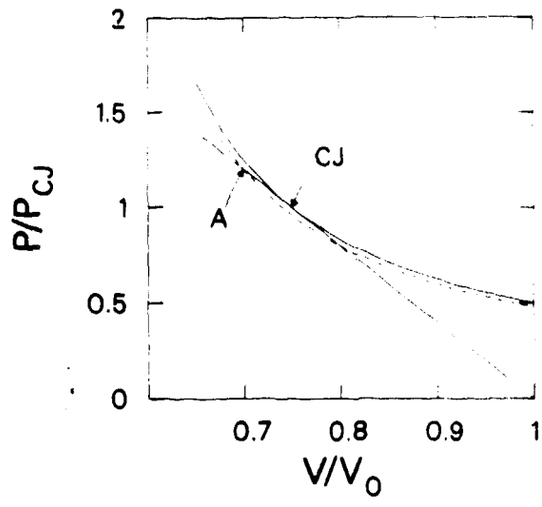

FIGURE 3
The fully reacted Hugoniot and the Rayleigh line through the CJ point ——— , the 96% reacted Hugoniot - - - - - , and the state A at the end of the fast reaction zone for a polytropic gas with $P_0 = 0$ and $\gamma = 3$.

6. CONCLUSION

We have demonstrated that diffusion limited carbon clustering is inherently a slow reaction mechanism in the detonation regime. The amount of energy released after the fast reactions are complete is sufficient to perturb the flow significantly when coupled with the hydrodynamics.

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