Effect of Deuteration on the Diameter-Effect Curve of Liquid Nitromethane

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The detonation properties of liquid nitromethane [CH_3NO_2] are probably the most thoroughly studied of any condensed-phase explosive. Because it is homogeneous (i.e., lacks hot-spot phenomena), it provides a window into the underlying chemical processes induced by a passing shock or detonation wave—such information is submerged in the complex fluid mechanics when heterogeneous explosives are detonated. In this paper, we provide experimental data and data analysis of the effect that deuterating nitromethane's methyl group has on some aspects of the processes that occur in the detonating liquid material. In the experimental part of this study, we report diameter-effect curves (i.e., inverse charge internal radius vs steady detonation speed) for pure CH_3NO_2 and pure CD_3NO_2 confined in right-circular cylinders of C-260 brass. Large differences in the infinite-medium (i.e., plane wave) detonation speed and in the failure diameter of the two materials are observed. Interpretations of the observations based on physical and chemical theory are given. The observed large decrease in deuterated nitromethane's infinite-medium detonation speed, relative to the protonated material, is interpreted in terms of the Zeldovitch, von Neumann, and Doering theory of steady-state detonation. We also estimate the relative size of the steady plane-wave reaction-zone length of the two materials. We interpret the observed increases in NM's failure diameter and its steady one-dimensional chemical-reaction-zone length due to deuteration in terms of the quantity of NM aci ion present. The new results are placed in the context of earlier work on detonating liquid nitromethane.

I. Introduction

We report measurements of the diameter-effect curves of the liquid explosives nitromethane (= NM)···CH_3NO_2 and fully deuterated nitromethane (= DNM)···CD_3NO_2. The "diameter-effect" curve of an explosive is the relationship between the steady-state detonation speed and the reciprocal lateral charge size, in a geometry with an axis of symmetry, with all other variables being constant. A diameter-effect curve is generated experimentally by choosing a specific geometry (usually a right-circular cylinder with length much greater than its internal diameter) and then firing a set of charges of various sizes (internal diameters). A standard set of diameter-effect data, therefore, relates the steady-state detonation speed to the reciprocal of the cylinder radius over a set of cylinder internal radii. The steady detonation speed in an explosive decreases with decreasing cylinder diameter because (1) of energy losses in the lateral direction and (2) of the modifications such losses produce in the explosive's chemical-reaction zone.

The primary reasons for doing this research are 3-fold. The first two reasons are to examine the effect of deuteration on (1) the explosive sensitivity of the two types of nitromethanes as measured by their respective failure diameters and (2) the steady one-dimensional reaction-zone length of the two materials. Finally (3), we use the experimental data to make a test of the Zeldovich, von Neumann, and Doering (ZND) theory of steady one-dimensional detonation's (ref 1) prediction of the infinite-medium detonation speeds of the two materials. The observed failure diameter increase is interpreted as being due to a decreased presence of NM's aci ion due the zero-point energy changes that occur upon deuteration.

II. Experimental Section

A. Materials. Pure NM (>99 wt % CH_3NO_2) and pure (>99 wt % CD_3NO_2) DNM were obtained from Aldrich Chemical Co.; these materials were used as received.

C-260 brass was chosen as the material in which to conduct the experiments. This material was chosen because C-260 brass tubes with various internal diameters are readily obtainable and because they are relatively inexpensive. The atomic composition of C-260 brass is nominally (wt %) Cu, 68.5 to 71.1; Fe, 0.05 max; Pb, 0.07 max; Zn, the remainder.

A set of C-260 brass tubes with a variety of internal diameters was obtained from K & S Engineering, Chicago, IL. Mass density measurements were made on tubes with seven different internal diameters. These measurements gave a mean density of 8.417 g/cm^3 with one standard deviation from the mean being ±0.029 g/cm^3 at 23.4 °C. We took this as evidence that all the tubes were made from the same alloy.

Before a tube was used in an experiment, it was cleaned as follows: (1) by placing it in an ultrasonic cleaner containing the household cleaning agent Fantastik heated to ca. 50 °C and cleaned for 30 min, (2) washing with tap water, (3) placing the tube in Copper Brite for 10 min, (4) washing in hot tap water, and finally, (5) washing the tube's interior with acetone. Additionally, when a detonation speed was to be measured, the external surface onto which the pins switches (see below) were to be mounted was polished with Dupont No. 7 rubbing compound and then washed with acetone.

B. Failure Diameter Experiments. From earlier work, it was thought that the failure diameter (≅ d_f, the smallest internal-diameter (i.d.) tube in which it is possible to propagate a steady detonation wave) of pure NM was ca. 2.6 mm in C-260 brass at ambient temperature.[2] To obtain an improved value of d_f under the conditions at which we were to fire the remaining

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experiments, we constructed a rack of six C-260 brass tubes. The length of all of the tubes was ca. 110 mm, and their internal diameter varied between 1.55 and 4.04 mm. The explosive within the tubes was strongly boosted with an RP-1 detonator and a high-density 12.5-mm diameter by 12.5-mm long PBX-9407 pellet. Evidence of the presence of detonation was obtained from a ca. 50-mm long copper dent plate glued to the tube at the end away from the booster. The temperature of the tubes in this assembly was controlled and was measured to be 23.5 ± 0.5 °C when the shot was fired. The tube with an i.d. of 2.44 mm propagated detonation, while the one with an i.d. of 1.55 mm failed. This implies a failure diameter of 1.99 ± 0.44 mm for pure NM confined in C-260 brass and fired at 23.5 ± 0.5 °C. This value was used to choose the array of tubes to be constructed for the detonation speed measurements.

In further work, to be described below (see the Rate-Stick Experiments section), we found that a detonation wave will propagate under these circumstances in a C-260 brass tube with an i.d. of 2.16 mm and will fail in one with an i.d. of 2.07 mm. Thus, the failure diameter of 99+ wt % NM fired in C-260 brass tubes at 23.5 ± 0.5 °C is

$$d_f = 2.12 \pm 0.05 \text{ mm}$$

where the error bar is a range.

A similar rack of tubes was constructed to define the d_f of the deuterated NM (DNM). In this experiment, we found that a detonation wave will propagate in a C-260 brass tube with an i.d. of 4.80 mm and will not do so in a tube with an i.d. of 4.04 mm. This gives a d_f of 4.42 ± 0.38 mm at a temperature of 23.5 ± 0.5 °C. This value was used to help choose the array of tubes to be used to measure the detonation speed of DNM as a function of tube i.d.

In later experiments (see the Rate-Stick Experiments section below), we found that a tube with an i.d. of 4.80 mm, but fired at slightly lower temperature than that in the d_f experiment (i.e., ca. 0.3 °C lower), failed. Thus, the d_f of DNM, under these conditions, is very close to 4.80 mm. The next larger tube in the six-tube rack that propagated detonation had an i.d. of 5.08 mm. Therefore, our estimated d_f of DNM fired under these conditions is

$$d_f = 4.94 \pm 0.14 \text{ mm}$$

with the actual value being close to 4.80 mm. This value is an improvement over and supersedes the analogous value given in ref 2.

Thus, deuteration of NM when fired in C-260 brass at a temperature of 23.5 ± 0.5 °C produces an increase in failure diameter of over a factor of 2, with the actual ratio being 2.33. This fact implies that the protons on NM play an important role in the detonation chemistry of NM.

It is pertinent to recognize the earlier results of French workers concerning the failure diameter of DNM. They showed that a DNM rate stick failed in a 27-mm i.d. Pyrex tube but detonated in a 25-mm i.d. Cu tube.[3]

C. Rate-Stick Experiments. Next, using the d_f results described above, we chose a set of tube i.d.'s in which to measure the steady speeds at which the detonation waves propagated down the tube lengths.

The type of experimental assembly used to make such measurements is called a "rate stick" (see Figure 1). As can be seen from the figure, a detonation in the explosive loaded tube is initiated by a detonator and booster at the lower end. The resultant detonation wave propagates up the tube. At intervals on the outside wall of the tube, 0.051-mm diameter enamel-coated copper "pin" wires have been fixed to the tube using Mylar tape. Typically, seven or eight pins were mounted on a rate stick. The detonation wave in the explosive produces a shock wave in the tube wall that crushes the pin's enamel coating and shorts the electrically charged pins to ground. The pins are connected to a pulse-forming circuit, and the resultant "pin" signals are fed into fast Textronic TDS 684C and LeCroy 9310M oscilloscopes. A set of such signals are a time history of the detonation wave's progress up the tube. An early description of this method is given in ref 4.

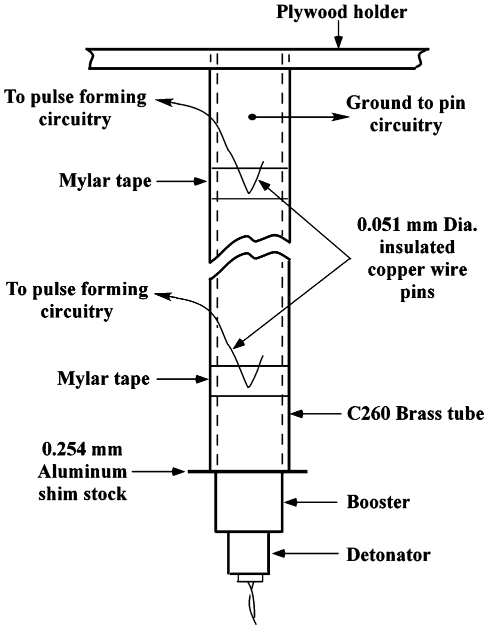

Figure 1. Schema of a rate-stick assembly.

TABLE 1: Pure Nitromethane Diameter-Effect Data Fired at 23.5 ± 0.5 °C in C-260 Brass Confinement

shot no.	i.d. (mm)	o.d. (mm)	$^1/_R$ (mm^{-1})	D (mm/μs)	T (°C)
8-788	22.377	23.800	0.0894	6.286 ± 0.001	23.3 ± 0.5
8-786	6.401	7.112	0.3124	6.261 ± 0.001	23.4 ± 0.5
8-787	4.039	4.750	0.4952	6.244 ± 0.002	23.4 ± 0.5
8-790	2.870	3.937	0.6969	6.213 ± 0.002	23.4 ± 0.5
8-791	2.464	3.175	0.8117	6.199 ± 0.002	23.4 ± 0.5
8-793	2.159	3.200	0.9263	6.160 ± 0.002	23.5 ± 0.5
8-795	2.070	2.375	0.9662	FAILED	23.5 ± 0.5

The pin spatial positions were measured using a Newport 2-axis positioning system typically used for precision movement of optics in optical systems (Newport Motion Controller Model ESP 300 controlling an x-stage Model ILS 200PP and a y-stage Model ILS150PP, reading resolution was ca. 0.5 μm). Each pin position on a rate stick was measured two or three times. Given the reproducibility of these measurements, we think the pin positions are determined to within 2 to 3 μm, while the separation of two pins was typically 35 000 μm.

With the space and time measurements, one has a space–time history of the detonation wave's trajectory from which the detonation speed can be determined by least-squares fitting.

Seven rate-stick experiments were fired using the protonated NM. The results of these experiments are given in Table 1 and in Figure 2. Six of the rate sticks propagated detonation, and the smallest i.d. stick failed (see Table 1). Portions of the smallest tube (shot 8-795) were recovered—guaranteeing that failure occurred. The i.d. of this tube was used to improve the d_f measurement of pure NM as described above.

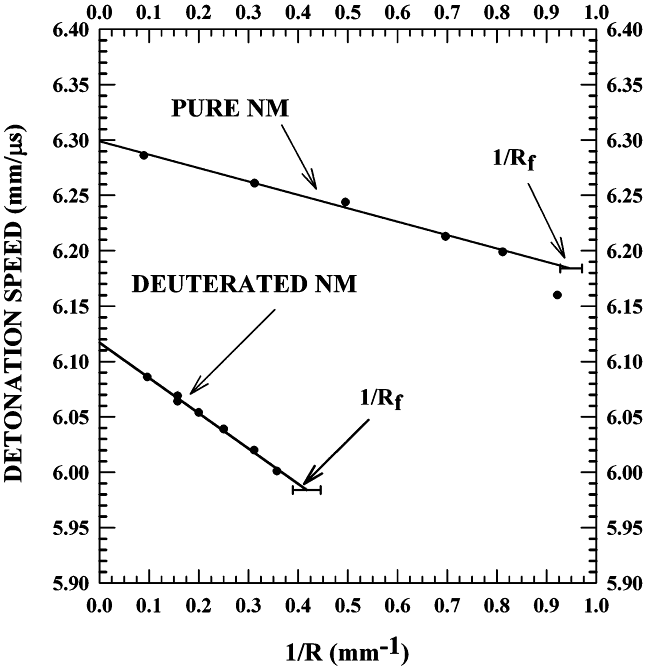

Figure 2. Measured and fitted diameter-effect results for NM and DNM fired in C-260 brass at 23.5 ± 0.5 °C. The least-squares line fit to the NM points is $D(R) = (6.299 \pm 0.003)[1 - (1.921 \pm 0.094) \times 10^{-2}/R(\mathrm{mm})](\mathrm{mm}/\mu\mathrm{s})$ and to the DNM points $D(R) = (6.117 \pm 0.002) \times [1 - (5.20 \pm 0.02) \times 10^{-2}/R(\mathrm{mm})](\mathrm{mm}/\mu\mathrm{s})$. The horizontal error bars at the ends of the line fits are the experimental estimates of the inverse failure radii, that is, for NM $1/R_f = (0.946 \pm 0.022)$ mm^{-1} and for DNM $1/R_f = (0.405 \pm 0.028)$ mm^{-1}.

TABLE 2: Pure Deuterated Nitromethane Diameter-Effect Data Fired at 23.5 ± 0.5 °C in C-260 Brass Confinement

shot no.	i.d. (mm)	o.d. (mm)	$^1/_R$ (mm^{-1})	D (mm/μs)	T (°C)
8-782	20.75	22.25	0.096	6.086 ± ≤0.001	23.7 ± 0.5
8-765	12.77	13.44	0.157	6.069 ± 0.002	23.6 ± 0.5
8-766	12.77	13.44	0.157	6.064 ± 0.002	23.6 ± 0.5
8-771	10.01	11.13	0.200	6.054 ± 0.002	23.2 ± 0.5
8-783	8.00	8.74	0.250	6.039 ± 0.002	23.5 ± 0.5
8-772	6.43	7.14	0.311	6.020 ± 0.001	23.7 ± 0.5
8-773	5.61	6.35	0.357	6.001 ± 0.002	23.8 ± 0.5
8-769	4.80	5.54	0.417	FAILED	23.7 ± 0.5

Eight rate sticks were fired using the deuterated NM. The tube with the smallest i.d. failed to propagate a detonation wave. The results of these experiments are given in Table 2 and Figure 2.

As can be seen from Figure 2, the diameter-effect curves of pure NM and pure DNM are strikingly different.

III. Interpretation of the Data

A. Data Analysis. From earlier work,[5] it is known that the diameter-effect curves of liquid explosives can be accurately fit by a line in the detonation speed vs reciprocal internal-cylinder-radius plane, that is

$$D(R) = D(\infty)[1 - A/R] \tag{1}$$

From the results shown in Figure 2, one can see the validity of this fact.

Our linear least-squares fit to the pure NM data obtained from the five largest i.d. tubes is

$$D(R) = (6.299 \pm 0.003)[1 - (1.921 \pm 0.094) \times 10^{-2}/R\ (\mathrm{mm})]\ \mathrm{mm}/\mu\mathrm{s}$$

where the error bars are one standard deviation. The tube with the smallest i.d. that propagated detonation (shot 8-793) was deleted from the data fit, since it was known from earlier work that the diameter-effect data for points near failure tend to be less reproducible than those obtained at larger i.d.'s.[6] This is also visible in Figure 2.

A similar treatment of the DNM data using all seven points gives

$$D(R) = (6.117 \pm 0.002)[1 - (5.20 \pm 0.02) \times 10^{-2}/R\ (\mathrm{mm})]\ \mathrm{mm}/\mu\mathrm{s}$$

where the error bars are one standard deviation.

B. Change in $D(\infty)$ Due to Deuteration. As can be seen from Figure 2 and the numerical values produced by the least-squares fits, deuteration of NM decreases the infinite-medium detonation speed by 0.182 mm/μs (i.e., 182 m/s). It is of interest to attempt to explain this difference using physical theory. The major part of the difference can be understood in terms of the reduction in the heat of detonation per unit mass (q) when NM is deuterated. If q is the heat of detonation per unit mass of NM, then the same quantity for DNM is given by $(61/64)q = 0.9531q$, because of the higher molecular weight of DNM (it being assumed that the quantity of product species is unchanged by deuteration). In the ZND theory of steady detonation,[1] $D(\infty)$ is given by the expression $[D(\infty)]^2 = 2q(\gamma^2 - 1)$, where q is the energy per unit mass released in the chemical-reaction zone of the detonating material and γ is the polytropic exponent of the γ-law equation-of-state that is assumed to govern both the reactants and products. A small change in q will result in a small fractional change in $D(\infty)$ given by

$$\frac{\Delta D(\infty)}{D(\infty)} = \frac{1}{2}\frac{\Delta q}{q} \tag{2}$$

In the present case, the small change in q is given by $(0.9531 - 1.0000)q = -0.0469q$. By the use of this value of Δq, along with the value of $D(\infty)$ for NM of 6299 m/s in the above equation, gives a predicted change in $D(\infty)$ of −148 m/s, upon deuteration. (Perhaps, it is worth noting that this effect would be −283 m/s if the hydrogens were replaced with tritium atoms.) Thus, the predicted value of $D(\infty)$ for DNM based on these considerations is 6299 − 148 = 6151 m/s, whereas the experimental value is 6117 m/s. The difference between the two values (34 m/s) is well outside of experimental error (i.e., ca. ±2 m/s). Therefore, it is appropriate to seek other sources of reduction in the value of q for DNM.

Another effect of deuteration is to alter the zero-point oscillation energy (ZPE) of a molecular species and, in this case, also of the product species produced by the detonation chemical reactions. The equilibrium products have been modeled by Mader;[7] he found that in a detonation of liquid NM

$$\mathrm{CH_3NO_2} \rightarrow (1.48)\mathrm{H_2O} + (0.166)\mathrm{CO_2} + (0.190)\mathrm{CO} + (0.498)\mathrm{N_2} + (0.64)\mathrm{GRAPHITE}$$

Upon deuteration, $CH_3NO_2 \rightarrow CD_3NO_2$ and $H_2O \rightarrow D_2O$. Since NM and H_2O are the only reactant or product species altered by deuteration, the alteration of their ZPEs are the only ones we need to consider.

Ab initio quantum-chemical calculations were performed with the Gaussian 03W computer code[8] to estimate the ZPEs. The quantum-mechanical model used in all of the calculations was the density functional B3LYP with a 6-311+G(d,3p) basis set.[9] The results of these calculations are presented in Table 3. The

TABLE 3: Zero-point Energy Corrections

molecule	gas phase (kcal/mol)	solution ($\epsilon = 38.2$) (kcal/mol)
H_2O	12.91	13.31
D_2O	9.43	9.72
CH_3NO_2	31.11	31.11
CD_3NO_2	25.09	25.08

change in ZPE due to the detonation reaction chemistry can be obtained from Table 3 via, for example

$$\Delta E(\mathrm{NM}) = \mathrm{ZPE}(\mathrm{NM}) - (1.48)\mathrm{ZPE}(\mathrm{H_2O}) \qquad (3)$$

and similarly for ΔE(DNM).

For the system assumed to be in the gas phase, ΔE(NM) and ΔE(DNM) are, respectively, 12.00 and 11.13 kcal/mol. That is, the heat of detonation (q) values for NM and DNM are larger by these energies than those for classically oscillating systems. These results indicate that deuteration of NM results in a decrease in q given by $\Delta q = 11.13 - 12.00 = -0.87$ kcal/mol. This energy change can be converted to the detonation speed change using eq 2, provided we have a value of q for NM. Literature values of this quantity are given by Dobratz and Crawford[10] ($q = 1.23$ kcal/g $= 75.03$ kcal/mol) and by Meyer[11] ($q = 1.19$ kcal/g $= 72.59$ kcal/mol); we use the average of the two values ($q = 1.21$ kcal/g $= 73.81$ kcal/mol) in our calculations. Substituting $D(\infty) = 6299$ m/s, $q = 73.81$ kcal/mol, and $\Delta q = -0.87$ kcal/mol into eq 2 yields $\Delta D(\infty) = -37$ m/s.

Combining the speed changes due to the mass-change effect with the ZPE effect produces a predicted change of $(-148 - 37) = -185$ m/s, which is very close to the measured value of -182 m/s.

One could argue that the calculations discussed above are deficient since they are representative of gas-phase materials, while the experiments were done with materials in the liquid phase or with very dense product gases. To try to include the fact that the experiments involve dense-phase materials, the quantum-chemical calculations were redone using the most advanced solvent model present in the Gaussian 03 code, that is, the self-consistent isodensity-polarized-continuum model.[12] A dielectric constant characteristic of NM ($= 38.2$) was used in all the calculations. The results are given in Table 3. Computations similar to those described above for the gas-phase situation give for the solvent-model case $D(\infty) = 6299$ m/s, $q = 73.81$ kcal/mol, and $\Delta q = -0.71$ kcal/mol. The detonation speed change predicted by eq 2 is, therefore, $\Delta D(\infty) = -30$ m/s. Combining the speed changes due to the mass-change effect and the solvent model ZPEs gives a predicted speed change of $(-148 - 30) = -178$ m/s with the measured value being -182 m/s.

Thus, the gas-phase and solvent values of $\Delta D(\infty)$ bracket the measured value and are within a few meters per second of it. The close agreement should be viewed as somewhat fortuitous, given the simplicity of the theoretical models used in the calculations (e.g., the equation-of-state properties of the reactant and product species are assumed to be identical). However, it seems safe to say that the types of calculations outlined above include all the effects that produce large changes in $D(\infty)$ when NM is deuterated.

C. Relative Chemical-Reaction-Zone Length. We have shown elsewhere[13] that the "A" parameter (see eq 1) for two explosives with closely related chemical structures fired in the same confinement and at the same temperature can be used to give an estimate of their relative one-dimensional steady detonation chemical-reaction-zone lengths. That is, under such conditions, the ratio of the "A" values is such a measure. Ratioing the "A" value of DNM to that of NM gives

$$A^{\mathrm{DNM}}/A^{\mathrm{NM}} = 2.71$$

This indicates that replacing protons by deuterons on NM increases the steady one-dimensional chemical-reaction-zone length (i.e., the distance from the shock wave to the sonic locus[1]) by nearly three times, which is noteworthy. We will propose a chemical explanation of this in the next subsection.

D. Chemical-Reaction-Rate Effects on Failure Diameter. Within the ZND model, the quantity $D(\infty)$ discussed above is independent of the chemical kinetics occurring within the chemical-reaction zone.

The failure diameter of an explosive *is* dependent on the way heat is released within the reaction zone. The energy divergence along the radial direction of a detonating rate stick and the accompanying shift in the sonic locus toward the detonation shock can be thought of as an endothermic process in competition with the exothermic chemical processes that drive a detonation wave. Reducing the radial dimension of a rate stick increases this effective endothermicity. This view of a mechanically induced endothermic term in the flow energetics is obtained from theoretical treatments of steady-state two-dimensional detonation. This theory is based on solutions of the Euler equations of compressible fluid mechanics and, therefore, rests on a firm dynamical foundation. The early theoretical work was done by Wood and Kirkwood,[14a] and their work was refined and extended by Bdzil.[14b] At failure, this mechanical endothermicity becomes dominant and the exothermic processes are catastrophically suppressed via an induced hydrodynamic instability in the flow.

Thus, the large observed increase in d_f caused by deuteration of NM provides a clue concerning the critical chemical-kinetic steps that drive a detonation wave in NM.

Since the failure diameter increases by ca. 2.7 times upon deuteration, one suspects that some controlling kinetic step has been subdued by the replacement of protons by deuterons. This points to some process involving NM's methyl group being a controlling factor in the reaction-zone kinetics of NM.

It is know from previous work that additions of extremely small amounts of organic base (e.g., diethylenetriamine) to NM radically reduces NM's d_f value.[15,16] Since NM is a weak acid, a base [B] addition drives the reaction

$$[\mathrm{NM}] + [\mathrm{B}] \rightleftarrows [\mathrm{CH_2NO_2}]^- + [\mathrm{BH}]^+ \qquad (4)$$

to the right.[17] This fact points to the moiety $[CH_2NO_2]^-$ (the "aci ion") being important in the detonation kinetics. This observation suggests the question: Does deuteration of NM decrease the quantity of aci ion present in the material? The ZPE calculations discussed above indicate the answer to this question is "yes". Suppose we consider removing a proton or deuteron from an NM or DNM molecule. The quantum-chemical calculations show that the CH and CD vibrational stretches in NM and DNM have energies of ca. 3100 and 2300 cm^{-1}, respectively; these energies (in kcal/mol) are 8.86 and 6.57, respectively. Thus, for a dissociation path along a CH/CD stretch, it would take ca. $(2.3)/2 = 1.15$ kcal/mol more energy to produce a deuteron than a proton (where it is assumed that dissociation is occurring from the lowest vibrational state). This energy difference will result in fewer $[CD_2NO_2]^-$ molecules being present than $[CH_2NO_2]^-$ molecules under a given set of conditions. An alternate simpler way of saying this is that deuteration reduces the acidity of NM.

We suggest that this is the reason for the decrease in detonation sensitivity when NM is deuterated and that this is evidence of the importance of the aci ion in the detonation chemistry of NM.

IV. Conclusions

Figure 2 shows the effect of deuteration on the diameter-effect curve of NM. One notes a large decrease in the steady infinite-medium detonation speed (i.e., −182 m/s). Furthermore, the slope of the lines representing the NM and DNM data are substantially different, with the DNM line being much steeper. A steeper slope line implies a longer chemical-reaction-zone length.

The calculations discussed in section IIIB demonstrate that the classical ZND theory is capable of accounting for the change in $D(\infty)$ of NM, when it is deuterated. Most of the speed change results from the diminution of the explosive's detonation energy release per unit mass due to the increase in mass per mole of explosive. However, the calculations also indicate that it is necessary to include energy corrections resulting from zero-point energy effects to fully account for the observed speed change.

The observed failure diameter change and the inferred chemical-reaction-zone length change indicate that chemical-kinetic processes involving NM's methyl group play an important role in the chemistry of detonating NM. Using a ZPE argument, we have related the observed changes to a decreased presence of NM's aci ion.

To the best of our knowledge, the first suggestion that the *aci ion* of NM plays an important role in NM's detonation chemistry was made in 1980.[15] One should note that it had been suggested earlier that the aci form of NM (CH_2NO_2H) is a controlling species (cf. Chaiken et al.[18] and references therein).

It seems worthwhile to point out that there is a significant amount of experimental and theoretical evidence that is consistent with the hypothesis that NM's aci ion plays an important part in the detonation kinetics of NM. Some of the earlier experimental evidence is summarized in refs 19 and 20.

As noted above, the addition of an organic base to NM sensitizes it to detonation. Earl and co-workers[21] showed via ^{13}C NMR experiments that such additions increase the amount of aci ion present in liquid NM.

Russian workers showed that exposure of NM to broad-band UV light increases its sensitivity to detonation; for example, by decreasing its failure diameter.[16] In ref 22, it was shown by ^{13}C NMR experiments that UV light exposure increases the quantity of aci ion present, thus, cross correlating with the detonation experiments.

Piermarini et al.[23] showed, using diamond-cell techniques (in the pressure range 20−50 kbar), that high pressure speeds up the NM decomposition process over the entire pressure range. In ref 24, it was shown via isotope-exchange experiments (employing diamond-cell techniques) that aci ion concentration is increased by high static pressure. This connects Piermarini's decomposition experiments with increased aci ion presence.

In recent theoretical and experimental work, done by various workers, a consensus is developing that the aci ion hypothesis is correct. Politzer et al.[25] using quantum-chemical calculations produced evidence that aci ion presence is the favored hypothesis over other possibilities that have been advanced. Gruzdkov and Gupta[26] using time-resolved visible-light absorption spectroscopy found evidence that the initial important species involved in the chemical kinetics of shocked liquid NM is the aci ion. Additionally, they found that the quantity of the species present has square-root dependence on the concentration of base present. Such dependence is implicit in eq 4, since that equation requires [aci ion] vs [base concentration]$^{1/2}$ dependence—as noted much earlier in ref 15. Recent density-functional molecular-dynamics simulations[27,28] of hot, dense NM found that the first new chemical species produced by high pressure and temperature is the aci ion (along with the cation $CH_3NO_2H^+$).

What would be most desirable concerning this question would be an observation of the appearance and disappearance of a molecular signature (e.g., a UV absorption spectrum) of the aci ion of NM in a system shocked to the pressure and temperature conditions characteristic of the detonating system. Such an observation would do much to finally settle this question.

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