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The explosive, bis-trinitroethyl adipate (BTNEA), was isotopically labelled in such a manner as to provide information on how an explosive breaks up during the detonation process. The material was fired in a detonation calorimeter giving product composition and heat release that are representative of the isentropic expansion of the detonation products. Isotope ratios observed in the detonation products were compared to those in the original explosive. The observed products are compared to those calculated with a thermodynamic-hydrodynamic computer code.

An Investigation of Chapman-Jouget Detonation Theory
Using Isotopic Labelling

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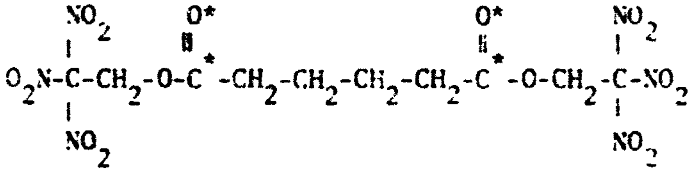
ABSTRACT

The explosive, bis-trinitroethyl adipate (BTNEA), was isotopically labelled in such a manner as to provide information on how an explosive breaks up during the detonation process. The material was fired in a detonation calorimeter giving product composition and heat release that are representative of the isentropic expansion of the detonation products. Isotope ratios observed in the detonation products were compared to those in the original explosive. The observed products are compared to those calculated with a thermodynamic-hydrodynamic computer code.

The Chapman-Jouget (C-J) theory of detonation envisions a rapid reaction (10^{-6}-10^{-8} sec) usually going from a rather complex organic molecule to a mixture simple gaseous product molecules. The question as to whether this process occurs by an almost simultaneous breaking of all of the bonds of the reactant molecule followed by a randomized recombination of atoms to form the product molecules or by a process which retains some structural features of the reactant molecule has not, to our knowledge, addressed experimentally. (The former process would require extensive atomic diffusion; the latter either a retention of certain bonds or a rapid combination of atoms in near proximity to each other). This study used an isotopically labelled explosive to distinguish between the two mechanisms.

The explosive molecule designed for the experiment was bis-trinitroethyl adipate (BTNEA), Fig. 1. This compound was chosen because it contains,



$$O_2N-\overset{\overset{NO_2}{|}}{\underset{\underset{NO_2}{|}}{C}}-CH_2-O-\overset{\overset{O^*}{\|}}{C^*}-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O^*}{\|}}{C^*}-O-CH_2-\overset{\overset{NO_2}{|}}{\underset{\underset{NO_2}{|}}{C}}-NO_2$$

BTNEA

Fig. 1

within its structure, essentially preformed molecules of CO and/or CO_2. The BTNEA was synthesized with isotopic labels (C^{13} and O^{18}) at the positions indicated by asterisks, (Fig. 1.), i.e., the ester carbonyl moiety. If all or, at least, a high percentage of the C^{13} and O^{18} appear in the CO and CO_2 products, one must conclude that where an easy mechanism to stable products is present, some structural features of the reactant explosive are retained and that atomic diffusion is minimized. A statistical scrambling of the isotopic labels into all of the C- and O- containing product species would, on the other hand, be consistent with extensive atomic diffusion and randomization of atoms.

EXPERIMENTAL

The labelled BTNEA was prepared by basic hydrolysis of labelled adiponitrile with labelled H_2O followed by esterification of the resulting adipic acid with 2,2,2-trinitro ethanol. The adiponitrile was prepared from 1,4-dibromobutane and sodium-C^{13}-cyanide (90% isotopic labelling) by standard techniques. The hydrolysis was carried out as follows:

A 50 ml, single necked round bottom flask was charged with 10 gm of H_2O^{18} (95% isotopically pure) and cooled to ice bath temperature. 2.3 gm of Na metal (freshly cut under N_2 and kept under hexane during addition) was added in small pieces. The pieces of Na were added one at a time, allowing the reaction to come to completion between additions, through the reflux condenser. The labelled adiponitrile was then added (2.89 gm, 26.3 mmoles). A small amount of dry glyme, ethylene glycol dimethyl ether, (less than 1 ml) was used to wash out the flask that contained the adiponitrile and this was also added to the reaction flask. The reaction was then refluxed for 24 hrs. (Ammonia evolution ceased after about 16 hrs). After completion of the reaction, dry HCl gas was bubbled through the reaction mixture for 10 minutes to assure neutralization of the NaOH. About 10 ml of dry CH_3CN is used to wash out the condenser and bubbler, and the solvents, CH_3CN and H_2O^{18}, are stripped. (Approximately 50% of the H_2O^{18} can be recovered.) The solid, NaCl and the labelled adipic acid, remains in the reaction flask. To these are added 14 gm (78 mmoles) of 2,2,2-trinitroethanol and 20 ml of trifluoroacetic anhydride. The flask is fitted with a drying tube and stirred at ambient temperature for one hour. The reaction mixture is then poured into 75 ml of iced 1.5 N KH_2PO_4 solution, stirred for about 20 min. filtered and dried. The product is recrystallized from methanol-water and dried. Yield - 9.40 gm. (75% from the nitrile). mp - 87-88°C. Mass spectral analysis showed that 86.3% of the carbonyl carbon was Carbon-13 and 62.6% of the carbonyl oxygen was oxygen-18.

The detonation and product analysis were performed using procedures which have been previously described.[1,2] (These procedures yield detonation products which are characteristic of those found on the Chapman-Jouget (C-J) isentrope (Table 1).) The labelled BTNEA was detonated as cylindrical charge 6.35 mm in diameter and was heavily confined in a gold cylinder with a wall thickness equal to the charge diameter. For comparison, detonation calorimetry and product analyses of unlabelled BTNEA were performed in charge diameters of 6.35 mm and 12.70 mm (Tables 1 & 2).

The analysis of the gaseous detonation products was performed as previously described(1,2) with two exceptions: (1) All of the analyses were done by mass spectroscopy, and (2) the CO_2 was separated from the other gases in the labelled experiment only. This was done to facilitate the determination of isotope ratios. The isotopic analysis of the solid carbon was performed by combusting it to CO_2 and analyzing the CO_2 by mass spectroscopy.

The C^{13} enriched sodium cyanide was obtained from Merck and Co., Inc. The O^{18} enriched water was obtained from Mound Laboratories. These materials were used as obtained.

TABLE 1. Comparison of Calculated C-J Isentrope Products with Products Observed from Detonation of Heavily Confined Charges of BTNEA

Products	Moles per mole of BTNEA		
	Observed Heavily Confined (12.7 mm dia.)	Calculated for the C-J Isentrope[a]	
		1469°K	1863°K
$H_2O(\ell)$	4.25 ± .04	4.19	5.60
CO_2	4.07 ± .01	4.63	4.19
CO	3.58 ± .04	2.54	2.02
N_2	2.70 ± .02	2.98	2.98
CH_4	0.13 ± .01	0.81	0.15
NH_3	0.37 ± .04	0.04	0.04
H_2	0.73 ± .01	0.12	0.04
HCN	0.06 ± .006	Not Allowed	Not Allowed
C(s)	2.16 ± .04	2.01	3.64

[a] Isentrope calculated using TIGER computer code(3) and BKW equation of state.

TABLE 2. The Heat and Products of Detonation of Heavily Confined BTNEA[a],[b]

	Unlabelled		Labelled
Charge diameter (mm)	12.7	6.35	6.35
Weight (gm)	23	5	3.8
Density (gm/cc)	1.59	1.51	1.57
H Detonation[c] (Cal/gm)	1148 ± 10[d]	Not Determined	Not Determined
Products (mole/mole BTNEA)			
$H_2O(l)$	4.25 ± .04	4.32 ± .06	4.41
CO_2	4.07 ± .01	3.94 ± .04	3.80
CO	3.58 ± .04	3.98 ± .03	3.67
N_2	2.70 ± .02	2.69 ± .01	2.59
$C_{(s)}$[e]	2.16 ± .04	2.00 ± .02	2.37
H_2	0.73 ± .01	0.79 ± .05	0.72
NH_3	0.37 ± .04	0.29 ± .06	0.22
CH_4	0.13 ± .01	0.12 ± .01	0.11
HCN	0.06 ± .01	0.065 ± .0[illegible]	0.055
- H[c] (cal/gm) Calculated from Products	1170 ± 20	1171 ± 20	1169
Material Balance (Mole % Recovered)			
C[f]	78.5 ± [illegible]	80.6 ± .2	77.3
H	97.2 ± .4	97.0 ± .3	95.1
N	97.1 ± .8	95.6 ± 1.6	91.2
O	99.9 ± .4	100.3 ± .2	98.1

Footnotes - Table 2.

a. Cylindrical charges confined in gold cylinders of wall thickness equal to the charge diameter.

b. Results corrected for 0.22 gm of PETN in the initiation system.

c. H_2O (ℓ) at 298°K.

d. All errors are twice the estimated standard deviation of the mean and are based in part on the results of other explosives for which more than duplicate experiments were run.

e. Determined by difference.

f. Does not include $C_{(s)}$; see footnote e.

g. Because of complications due to separation to facilitate isotopic analysis, these values are not deemed as accurate as those on the unlabelled material.

Table 3. Isotopic Ratios in BTNEA and its Detonation Products

		C^{12}/C^{13} Ratio	O^{16}/O^{18} Ratio
Labelled BTNEA[a]		4.63	11.18
Products	H_2O	-	16.57[b]
	CO_2	4.69	11.40
	CO	4.78	11.19
	$C_{(s)}$	4.60	-
	CH_4	4.33	-

a. Isotopic ratios are based on calculated isotopic purity; see discussion.

b. The water was not analyzed for some time after the completion of the other analyses and probably was contaminated by atmospheric oxygen.

RESULTS AND DISCUSSION

The model compound for this study, bis-trinitroethyl adipate (BTNEA), was synthesized in such a way as to introduce CO and CO_2 moieties labelled with C^{13} and O^{18}. The product analysis was designed to determine if these structures, preformed in the explosive molecule, were retained in carbon monoxide and carbon dioxide of the detonation product gases. In order for the experiment to be valid, two criteria must be met. First, it must be established that the isotopic labels are introduced into the molecule at the desired positions. Secondly, it must be established that the collected product gases are representative of the isentrope through the C-J state.

The first condition was established by the mass spectral analysis of the labelled BTNEA. The explosive is not stable enough to give a parent peak. The highest mass found is the P-180 peak due to a loss of the trinitroethoxy moiety. This results in a peak at m/e of 292 for unlabelled BTNEA. This fragment (m/e = 292) then undergoes a metastable loss of CO to give a fragment, in the unlabelled material, of m/e = 264. This 264 fragment undergoes a further metastable loss of NO_2 to give a peak at m/e = 218. Statistical analysis of the isotopic peaks related to the 292 and 218 fragments in the mass spectrum of the labelled material show that between 96 and 99% of the molecules contain some isotopic label; that between 85 and 86% of the carbonyl carbons are C^{13}; that 62.3 to 62.6% of the carbonyl oxygens are O^{18} and that between 52 and 54% of the carbonyls contain both C^{13} and O^{18}. The isotopic peaks related to m/e = 264 were not used in the analysis because of complicating factor of a loss of HCO from the m/e = 292 fragment.

The second condition was established by comparing the observed detonation products with the products predicted for the C-J isentrope between about 1500°K and 1800°K (Table 1). A detailed discussion of the significance of this temperature range has been presented.(1,2) The isentrope was generated using the TIGER computer code(3) with the BKW equation of state with TNT parameters.(4) The computer calculation used thermodynamic data from the JANAF(5) tables, co-volume factors based on as LJD hard sphere model with molecular parameters from Ref 6 (6-12 potential) and a heat of formation for $C_{(s)}$ of + 8.5 Kcal/mole. The heat of formation of BTNEA was estimated as -196.5 Kcal/mole. It can be seen from Table 1 that the observed products are in good agreement with those predicted for the isentropic expansion through the C-J state.

The results of the isotopic analysis are shown in Table 3. If the structural features of the molecule are retained, one would expect values for the C^{12}/C^{13} ratio to be 3.79 for both CO and CO_2 and that no C^{13} would be found in the methane or solid carbon. Likewise one would expect no O^{18} in the water and a O^{16}/O^{18} ratio of 6.4 for the CO_2 and 5.7 for the CO. If, however, scrambling is statistical, one would expect to find that the isotopic ratios in each of the products would be the same as the ratio in the parent explosive. The observed ratios listed in Table 3 are entirely consistent with complete scrambling. Of special significance are the C^{12}/C^{13} ratios for solid carbon and methane and the O^{16}/O^{18} ratio for water.

It can therefore be concluded that the hypothesis of complete randomization of atoms during the detonation process is conclusively supported by experiment. Such a process is consistent with the dynamic chemical equilibrium assumed for the Chapman-Jouget state and for the isentropic expansion of the detonation products.

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