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Detonation properties of ethyl diazoacetate

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Abstract

Ethyl diazoacetate is an important organic chemistry synthon, but its use as an industrial intermediate is limited due in part to the safety concerns associated with its instability and high reactivity. In a continuing effort to understand the risk of employing ethyl diazoacetate as an industrial reagent, detonation tests were completed. The results of these studies indicate that ethyl diazoacetate does not show detonation properties. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ethyl diazoacetate; Detonation; Tube test; Hazards analysis

1. Introduction

Ethyl diazoacetate (EDA) is an important two-carbon synthon for organic chemistry [1,4–15], but its use as a large-scale, industrial commodity is limited due to safety concerns. The material safety data sheet [2] indicates that this reagent is shock sensitive, flammable and toxic. Chemically, diazocarbonyl compounds are also known to be very reactive [1,4–15]. In a continuing effort to understand the risk of employing EDA as an industrial reagent [16–22], detonation tests using a standardized tube test[1] were completed. Reported are the results of these tests.

2. Results

The detonation test results for various mixtures of EDA in toluene and as a neat liquid are shown in Table 1. The EDA in experiments 1–3 was diluted with toluene to concentrations of 18.8, 35.9 and 36.0%, respectively. The damaged parts of the tubes in these experiments were 180, 175 and 185 mm, respectively. These lengths are within the typical range of a booster effect. The fragmentation pattern on the tubes showed some fissuring and strips. These results imply that the test mixtures have no detonation properties. All tube tests performed conformed to standard test procedures at ambient temperature.[2]

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[1] Detonation test were performed by Kerten and Heemskerk [3].

[2] The standardized detonation tube test (UN guidelines) employed a steel 57 tubular cylinder with an inner diameter of 50 mm, an outer diameter of 60 mm and a length of 500 mm. An electrical wire of known impedance is stretched through the cylinder over the entire length. Measured was the change in impedance across the wire upon contact with the shock wave as well as the length and the nature of the damage pattern of the tube. The bottom of the tube is closed by a booster of hexocire with a diameter of 60 mm and a height of 50 mm. A thin film of plastic in introduced between the booster and the contents of the cylinder to avoid leakage of the liquid on to the booster and/or to prevent undesired chemical reactions. The booster is initiated by a priming tube (U8) that is connected at the bottom end. The priming tube is initiated electronically. The whole system is placed in a protective outer ring and situated in a pillbox capable of withstanding the shock waves that may be due to the chemical reaction (see footnote 1).

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Table 1
Detonation test results for various EDA/toluene mixtures at ambient temperature (see footnote 1)

Experiment	EDA (%)	Detonation	Front velocity (km/s)	Tube length (500 mm)		Comments
				Undamaged, L_1 (mm)	Torn, L_2 (mm)	
Water	–	No	2.6 → 0	241	259	Potential average booster effect
1	18.8	No	2.6 → 0	320	180	Shock wave dies out
2	35.9	No	2.6 → 0	325	175	Shock wave dies out
3	36.0	No	2.6 → 0	315	185	Shock wave dies out
4	97.4	Insignificant	<0.8	190	310	Slight support at start, thereafter shock wave dies out
5	96.1	Insignificant	<0.3	220	280	Slight support at start, thereafter shock wave dies out

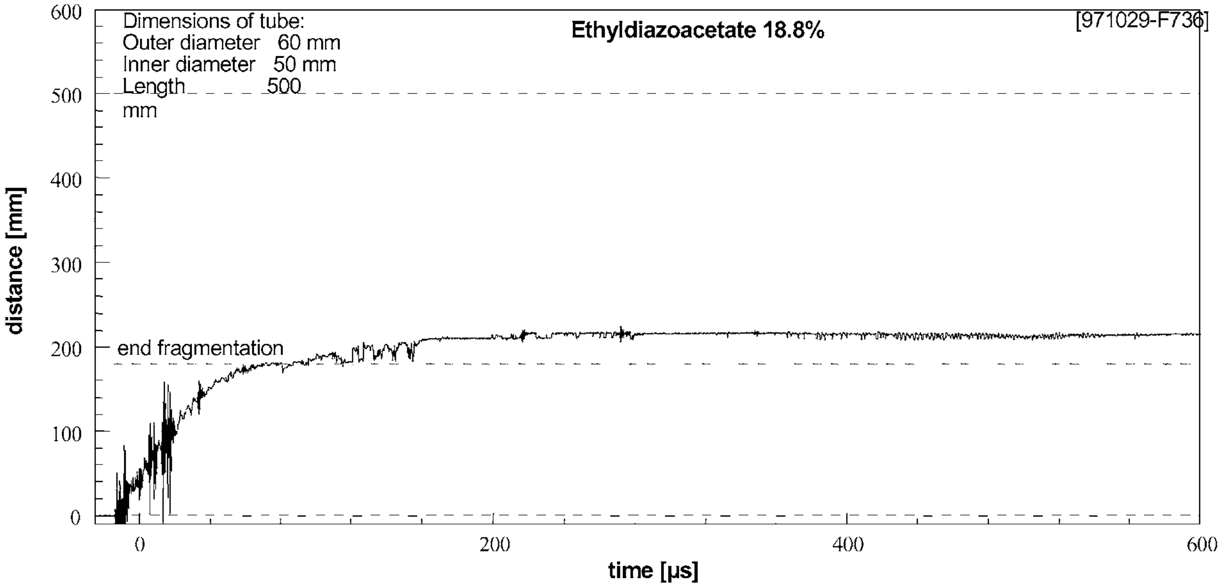

Fig. 1. Experiment 1 shock wave velocity pattern along the tube.

In experiments 1–3, the booster shock wave of about 2.6 km/s dies out to zero velocity within 100 µs. This implies that EDA at these concentrations does not substantially support the shock wave. The shock wave velocity patterns along the tube for the experiments 1–3 are shown in Figs. 1–3, respectively. The series of apparent responses in experiment 2 occurring between approximately −80 and 80 µs are noise signals and do not reflect detonation velocities.

After completing test on diluted solutions, studies were directed toward neat EDA.[3] Two experiments, 4 and 5 (Table 1), were completed. Their shock wave velocity patterns are shown in Figs. 4 and 5, respectively. The damaged parts of the tube for these experiments had lengths of 310 and 280 mm, respectively.

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[3] EDA was supplied by Sigma-Aldrich Chemie B.V., Zwijndrecht, the Netherlands. Purity was 97.4% for lot number 08891 and 96.1% for lot number 12573.

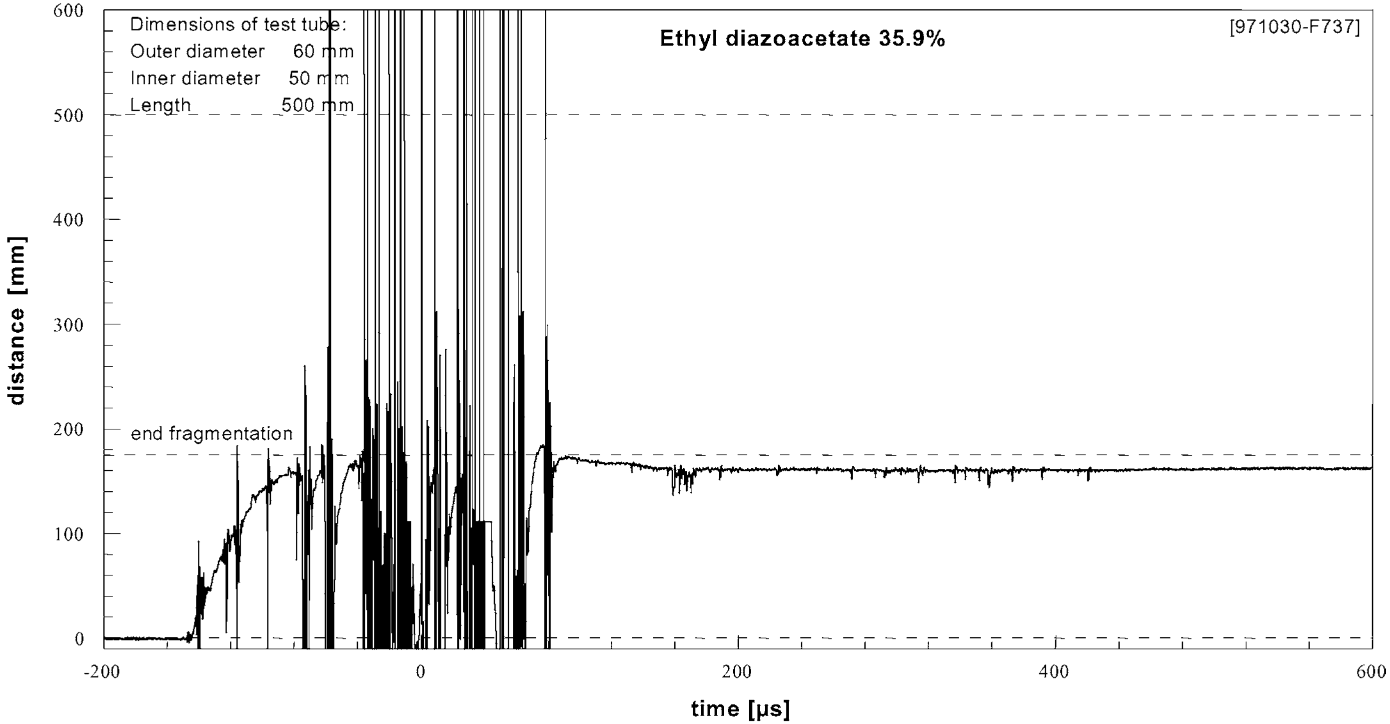

Fig. 2. Experiment 2 shock wave velocity pattern along the tube.

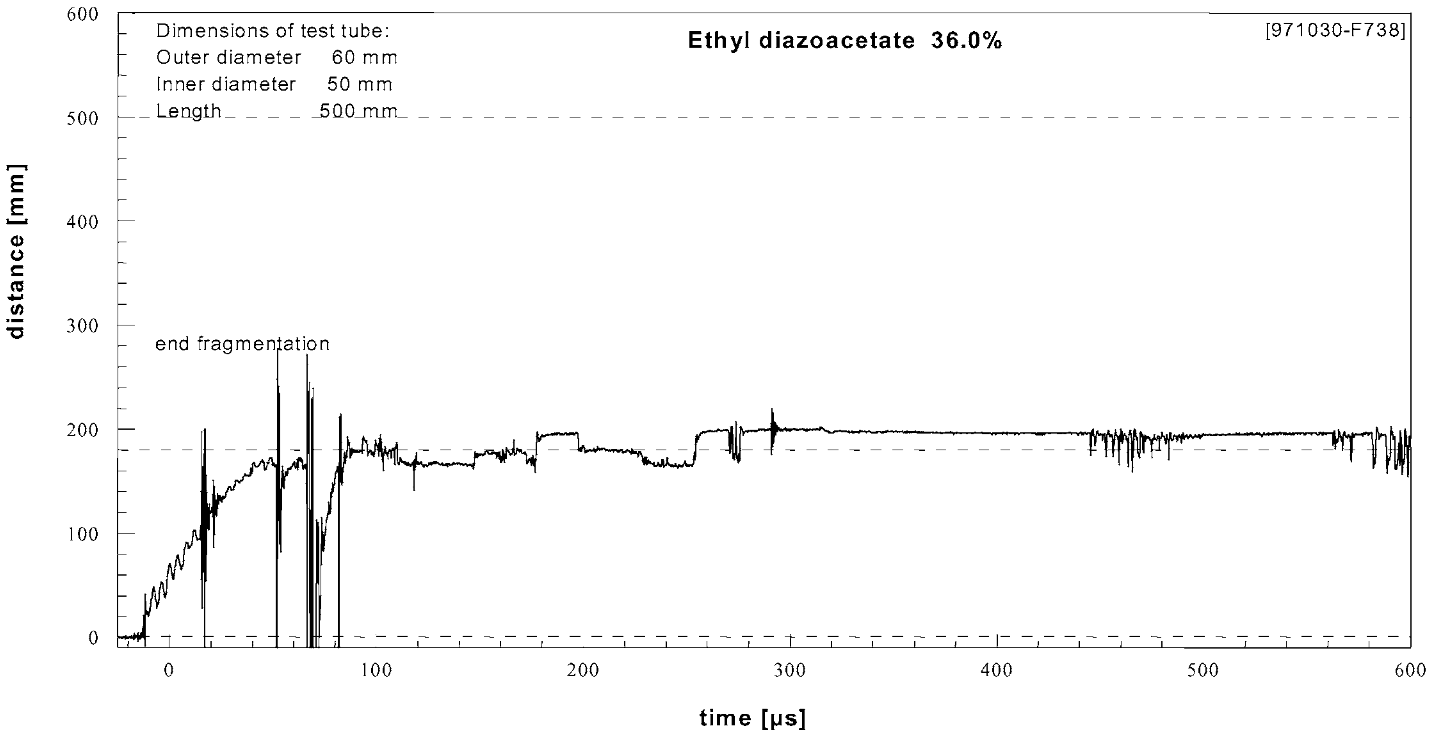

Fig. 3. Experiment 3 shock wave velocity pattern along the tube.

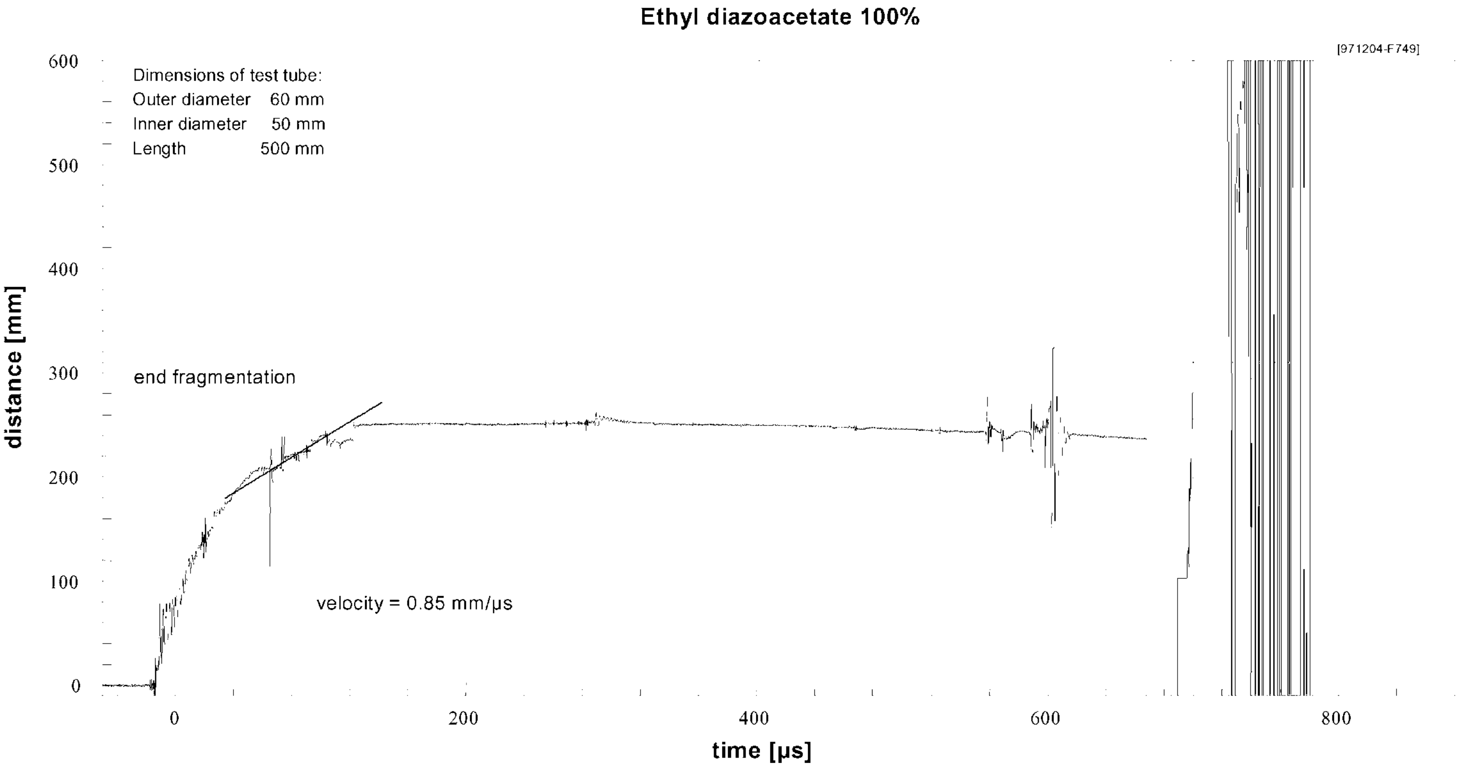

Fig. 4. Experiment 4 shock wave velocity pattern along the tube.

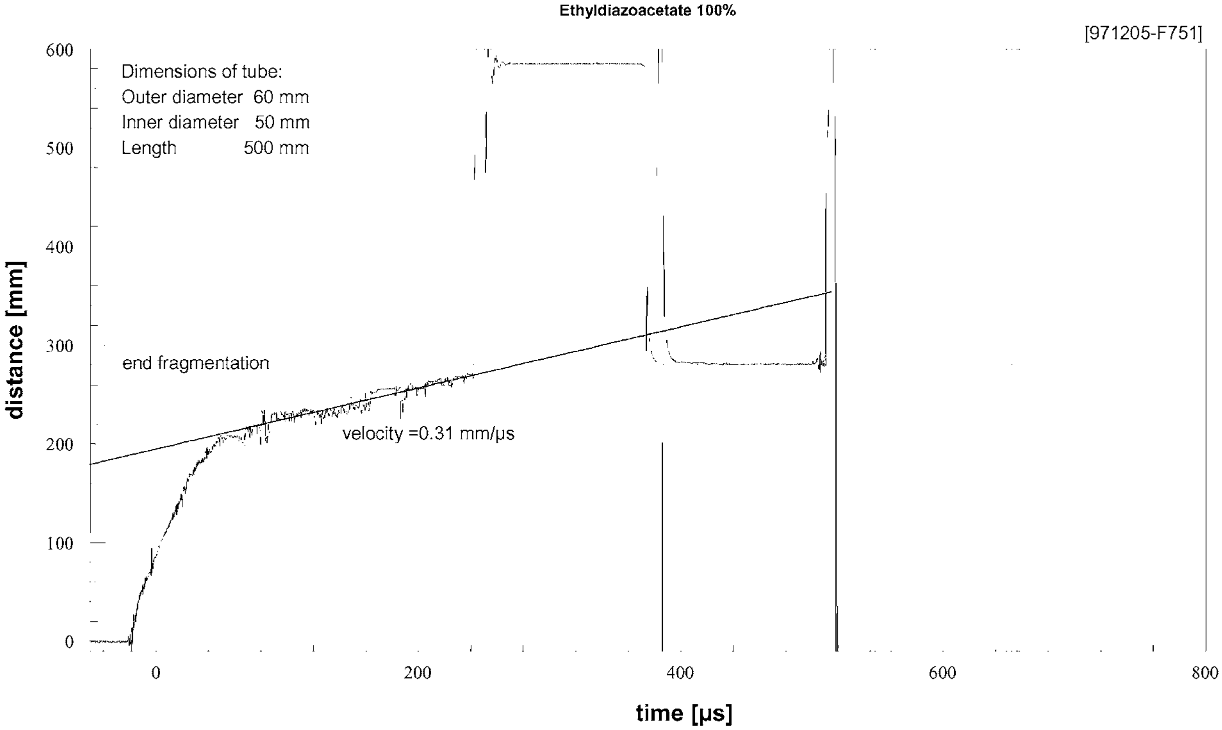

Fig. 5. Experiment 5 shock wave velocity pattern along the tube.

These lengths slightly exceed the range typical of the booster effect. These results suggest that these mixtures do slightly respond to the booster-initiated shock wave. The fragmentation patterns of the tubes again showed some fissuring and strips. This type of fragmentation pattern implies that no detonations occurred. The velocity of the booster initiated shock wave decreased from its initial velocity of 2.6 km/s to less than 0.8 km/s in approximately 50 µs. Thereafter, a slow decrease to 0.3 km/s over approximately a 50 µs period was observed. This 0.3 km/s velocity is then maintained for about 150 µs. The observed front velocities were 0.8 km/s for approximately 50 µs and about 0.3 km/s for about 150 µs in experiments 4 and 5, respectively. These tests suggest that the compound slightly responds to the shock wave, but does not support the wave.

3. Discussion

EDA belongs to a functional group class that is known to be reactive [1,4–15]. Taking this into account as well as the energy available in the EDA molecule,[4] it could not be ruled out that EDA may show detonative properties. Chemical compounds and mixtures of chemicals in the condensed phase are defined to have detonative properties if they can propagate a chemical reaction by means of a reaction front and that front proceeds with a velocity greater than the velocity of sound in the chemicals (see footnote 1). Tests that show whether a detonation wave can proceed throughout a material are the so-called gap[5] or tube tests. This test has an advantage over impact, friction, or thermal stability tests because these studies show only that a detonation may be initiated. They do not give detail as to how the chemical medium may support or accentuate the wave front.

The standard tube test results for EDA solutions and neat liquid described herein indicate that no detonation was observed. Concentrations approaching 100%

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[4] Theoretical value for EDA is $\Delta H_r = 2500\,\mathrm{kJ/kg}$.

[5] USA: GAP test 8.

by weight shows signs of responding to the shock wave, but at velocities well below that of the speed of sound. The test results further imply that any EDA mixture can be used at a production scale without significant hazard of a condensed phase detonation. This does not imply, however, that no explosion can occur. Such an explosion would rather be a consequence of a pressure increase above the design pressure of the reactor resulting in vessel rupture. The potential for pressure increase and increase rate in a closed or semi-closed vessel is determined by investigating the runaway and venting properties of the mixture. This study shall be the topic of another report.

4. Conclusion

Detonation test for various concentrations of EDA were completed. The results indicate that EDA does not show a propensity for detonation.

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