

EFFECTS OF SOME ORGANIC DILUENTS ON DETONATION PROPAGATION IN TETRANITROMETHANE

M.I. TRTANJ, Z.B. MAKSIMOVIĆ, A.A. VLAHOV, and V.N. DJAKOVIĆ

Chemical Dynamics Laboratory, The Boris Kidrič Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade (Yugoslavia)

(Received July 21, 1987; accepted in revised form April 25, 1988)

Summary

The influence of hexane (C_6H_{14}), propylene oxide (C_3H_6O), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) on detonation characteristics of tetranitromethane (TNM, $C(NO_2)_4$) was investigated, and the dependence of detonation velocity on various glass tube diameters was measured. Experimental data on detonation velocity were compared with those calculated using the BKW equation of state. The measurements were performed using pure TNM solutions and mixtures of TNM with diluents at stoichiometric and critical concentrations (the concentration without detonation wave propagation).

On the basis of the experimental measurements performed, the critical diameters, d_{cr} , were determined for each solution investigated. The results obtained were discussed and compared with the physicochemical properties of the diluents.

Introduction

This work is a continuation of our previous investigations of the influence of different additives on detonation characteristics of TNM. A detailed explanation regarding selection of additives and TNM was reported in our earlier paper [1]. Critical diameters, given here, provided a clearer picture of the influence of additives on detonation characteristics of TNM, than the ones obtained by the detonation velocities. In addition to this, a more sophisticated Mader [3] computer program, based on the BKW equation of state, was used instead of the Avakain method [2] which we used previously for calculation of the detonation velocities of mixtures. We employed here the same set of co-volume values for detonation products as Mader [4]. The parameters of the BKW equation of state are also taken from Mader. The Cowan equation of state for solid carbon is used. The detonation products were included: H_2O , H_2 , O_2 , CO_2 , CO , NH_3 , H , NO , N_2 , OH , CH_4 , and solid carbon for hexane and propylene oxide. For chloroform and carbon tetrachloride we also used Cl , Cl_2 , ClO , and CCl_4 . Only the detonation products which genuinely appear were assigned a value in Table 2.

Experimental

Tetranitromethane was prepared and purified as described previously [1]. Other chemicals used were purified by distillation, a standard procedure for these reagents.

To determine the dependence of detonation velocity on the tube diameter, glass tubes 2–26 mm in diameter wall thickness below 1 mm, and 150 mm long were used. This dependence was determined for stoichiometric and critical concentrations of TNM with each additive. Since the critical concentrations in CCL_4 and CHCl_3 are very close (25% and 35% of TNM), the measurements were performed for stoichiometric concentrations only. Initiation and detonation velocity measurements were performed as given previously [1].

Results and discussion

Detonation parameters (velocity and products) of the investigated solutions were calculated using Mader's computer program with the Becker–Kistia-kowsky–Wilson (BKW) equation of state. Dependence of the detonation velocity, D , on TNM concentration is graphically presented in Fig. 1. The curves represent the calculated values. Experimental values of the diluent investigated are denoted by the various marks. As can be seen, the detonation velocity of the TNM–propylene oxide and TNM–hexane liquid mixtures increases with additive concentration, reaching a maximum at 0.47 mole fraction for propylene oxide and 0.27 for hexane, and then decreases. For these two diluents, the curve has an inflexion point. It should be noted that this part of the curve corresponds to the critical concentrations of these two additives, determined experimentally and expressed in mole fractions of 0.86 and 0.52 for propylene oxide and hexane, respectively.

For chloroform and carbon tetrachloride (see Fig. 1), the detonation velocity decreases with increasing diluent concentration, so that the change of slope takes place in the critical concentration range, 0.79 for CCl_4 and 0.85 for CHCl_3 .

The maximum detonation velocity values of the liquid mixtures of TNM with propylene oxide and hexane were very close to their stoichiometric concentrations of 0.42 and 0.24, respectively.

The stoichiometric concentrations of the TNM–chloroform and TNM–carbon tetrachloride mixtures are close to their critical concentrations of 0.75. The stoichiometric concentrations refer to available oxygen in the liquid mixture. The dependence of detonation velocity on the tube diameter was experimentally determined for pure TNM, diluent concentrations close to stoichiometric, and for concentrations of propylene oxide and hexane close to their critical concentrations. All the measurements are illustrated in Fig. 2.

Critical diameters of the solutions of TNM with given diluents were determined on the basis of the data presented in Fig. 2. The observed and the cal-

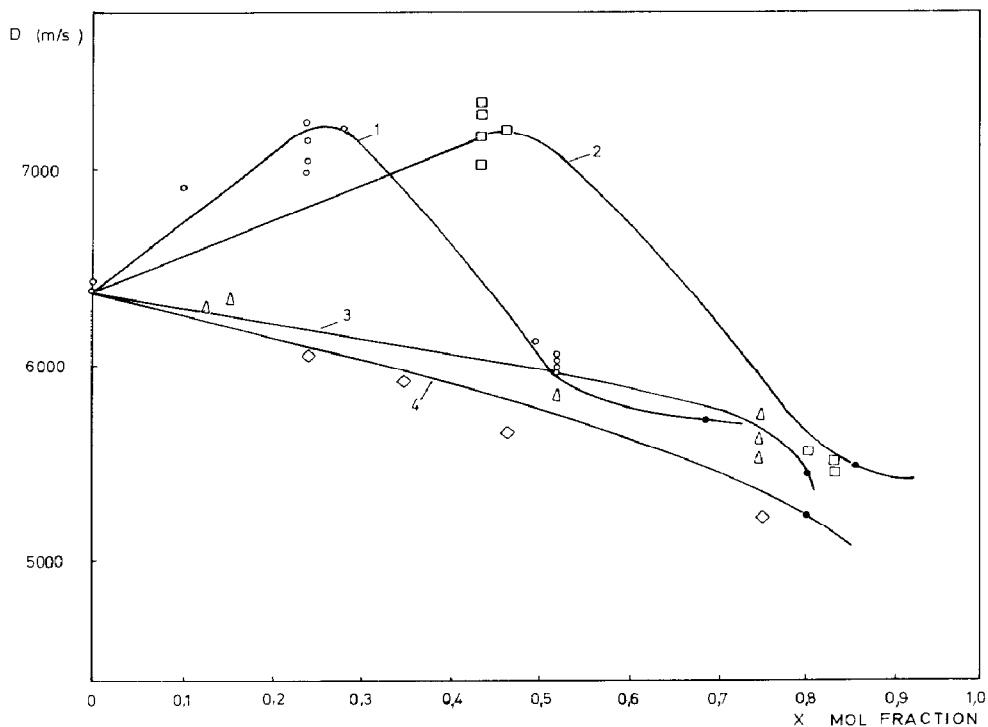


Fig. 1. Dependence of detonation velocity on additive concentration. 1. TNM-hexane \circ , 2. TNM-propylenoxide \square , 3. TNM-chloroform \triangle , and 4. TNM-carbontetrachloride \diamond . Symbols denote experimental values, solid lines calculated values. \bullet not detonated.

culated detonation velocities, together with the critical diameters, are collected in Table 1. As can be seen, the stoichiometric concentrations of the solutions of TNM with propylene oxide, hexane and chloroform show a very strong tendency towards detonation. The tube diameter, on the other hand, has the least influence on these solutions, and the critical diameter is under 2 mm. The 11 mm critical diameter of TNM explains the rather low sensitivity of this explosive to initiation. The three diluents mentioned, within their stoichiometric concentrations, improve the sensitivity of TNM, while carbon tetrachloride, with $d_{cr} = 16$ mm, lowers it even further. The critical concentration of TNM in solution in hexane is relatively high (1 mole of TNM/1 mole of hexane), so that this solution, with $d_{cr} = 7$ mm, is more sensitive by comparison with pure TNM. The critical concentration of pure TNM in propylene oxide is relatively small (1 mole of TNM/2 moles of propylene oxide), $d_{cr} = 18$ mm, which means that this solution is less sensitive than pure TNM, due to the existence of a quenching effect.

When carbon tetrachloride is used as a diluent it does not appear as a product of detonation in the calculation. This may be explained in the following

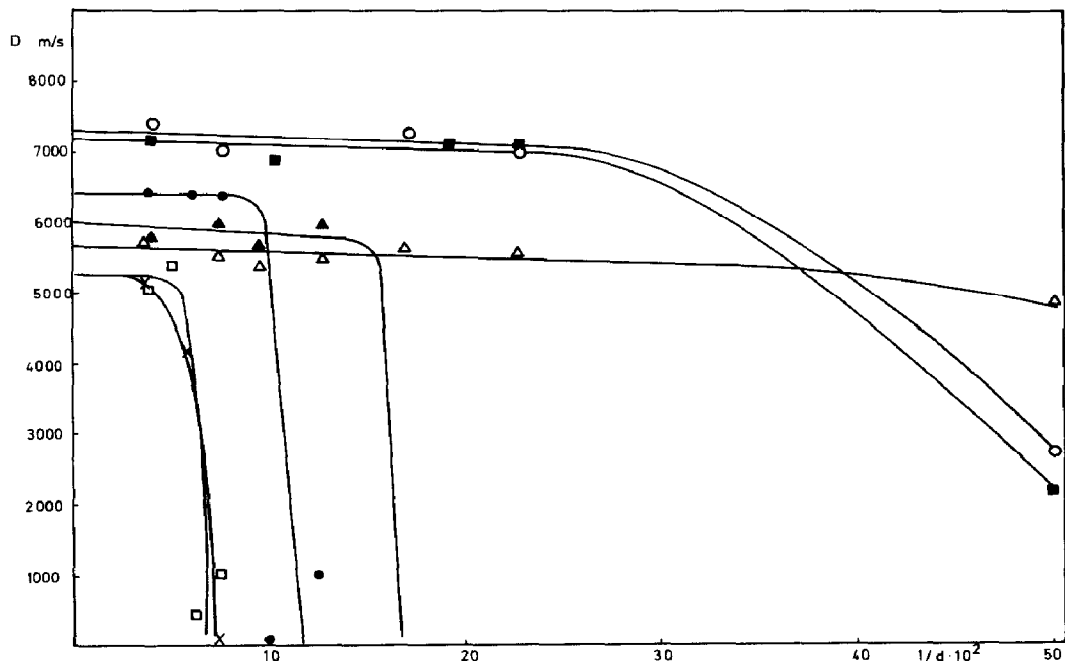


Fig. 2. Dependence of detonation velocity on reciprocal value of tube diameter. \circ PO $X=0.4256$, \square PO $X=0.6451$, \blacksquare C_6H_{14} $X=0.2371$, \blacktriangle C_6H_{14} $X=0.5175$, \triangle $CHCl_3$ $X=0.7530$, \times CCl_4 $X=0.7483$, and, \bullet TNM $X=1.000$.

TABLE 1

Detonation velocity and critical diameter of the solutions TNM-investigated diluents, determined experimentally and by calculation

No.	Solution		D_C (m/s)	D_E (m/s)	d_{cr} (mm)	
	X_{TNM}	$X_{diluents}$				
1	0.57	0.43	PO	7160	7350	<2
2	0.35	0.65	PO	5560	5250	18
3	0.76	0.24	Hexane	7200	7150	<2
4	0.48	0.52	Hexane	6030	5970	7
5	0.25	0.75	$CHCl_3$	5720	5750	<2
6	0.25	0.75	CCl_4	5380	5200	16
7	1.00	-	-	6360	6420	11

manner: Mader's BKW program treats the mixture of tetranitromethane and carbon tetrachloride as an explosive which is completely destroyed in the explosion. An essential assumption of the program is that the explosion actually occurs, which means that, for the program, no carbon tetrachloride exits after

TABLE 2

Calculated detonation products of the solutions investigated

System	Detonation products (mol)												
	H ₂ O	CO ₂	CO	N ₂	O ₂	H ₂	Cl ₂	HCl	NO	OH	C	NH ₂	CH ₄
TNM-CCl ₄	-	1.0	-	0.59	0.19	-	1.4	-	-	-	-	-	-
TNM-CHCl ₃	0.25	0.86	0.0023	0.49	-	-	1.0	0.25	-	-	0.14	-	-
TNM-PO	1.174	1.764	0.0196	1.171	0.228	-	-	-	0.0908	-	-	-	-
Stoichiometric conc.													
TNM-PO critical conc.	1.915	0.554	0.459	0.707	-	0.0117	-	-	-	-	1.276	0.0036	0.0018
TNM-Hexane stoichiometric conc.	1.7	2.1	0.095	1.5	-	-	-	-	0.061	0.0011	-	-	-
TNM-Hexane critical conc.	3.5	0.02	0.09	0.87	-	0.14	-	-	-	-	3.6	0.06	0.084

detonation. After detonation there is a recombination of elements to form the products of detonation. The only species that are in competition for the interaction with carbon are oxygen and chlorine. There is an excess of oxygen at all concentrations. The heat of formation of carbon tetrachloride is greater than the heat of formation of carbon dioxide. Under these conditions it is clear that only carbon dioxide can appear in the calculation.

A different influence of inert diluents on detonation characteristics of TNM can be seen in the case of CHCl_3 and CCl_4 . At the same concentration of TNM, the solution with CHCl_3 is extremely sensitive to detonation, while the solution of CCl_4 is just the opposite. An explanation for this kind of behaviour can be perhaps found in the different detonation products obtained. In the first case the product is HCl whose exothermic heat of formation (92 kJ/mol) contributes actively to the heat of detonation, enabling the detonation to propagate over a wide range of concentrations.

A similar situation is observed for critical concentrations of TNM in solutions with hexane and propylene oxide. In the former case, the critical diameter is 7 mm and in the latter 18 mm. According to Table 2, the detonation products in the hexane solution are hydrogen (H_2) and methane (CH_4) with concentrations much higher than in propylene oxide solutions. Additional burning of these products causes an increase of the heat of reaction, and contributes to the detonation sensitivity of the solution.

Conclusion

1. Experimental measurements were performed to determine the dependence of detonation velocity on tube diameter for the mixtures: TNM- CHCl_3 , TNM- $\text{C}_3\text{H}_6\text{O}$, TNM- C_6H_{14} , and TNM- CCl_4 .
2. A good agreement, with an error up to $\pm 2\%$, was observed between the calculated values, using the BKW equation of state, and the experimental ones.
3. Maximum detonation velocities were obtained at mole fractions of 0.47 for propylene oxide and 0.27 for hexane, while the critical concentrations were 0.86 and 0.52 for propylene oxide and hexane, respectively.

References

- 1 Z.B. Maksimovič, M.I. Trtanj and V.N. Djakovič, Influence of Some Additives on Detonation Characteristics of Tetranitromethane, Progress in Aeronautics and Astronautics, 106 (1986) 649.
- 2 B.N. Kondrikov, G.D. Kozak, and V.N. Sopoal, Zbornik zadač i upražnjenii po teorii gorenija i vzriva Ministarstvo viššego i srednego specialnogo obrazovanija SSSR, Moskva, 1981, pp. 17-20.

- 3 C.L. Mader, Fortran BKW: A Code for Computing the Detonation Properties of Explosives. LA-3704 (1967), Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico.
- 4 C.L. Mader, Detonation Properties of Condensed Explosives Computed Using the Becker-Kistiakowsky-Wilson Equation of State. LA-2900 (1963), Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico.
- 5 M. Kuskabe and Shuzo Fujiwara, Effects of Liquid Diluents on Detonation Propagation in Nitromethane, 6th. Symp. on Detonation, 1976, p. 133.