BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume X, No. 6, 1962

Thermal Analysis of Tetranitromethane Mixtures with Benzene and Nitroaromatic Compounds

by

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Presented by T. URBAŃSKI on April 4, 1962

It is known that tetranitromethane by itself does not possess explosive properties. It forms, however, explosive mixtures with combustible substances.

This property was utilized during World War II in Germany when mixtures of tetranitromethane with hydrocarbons were used for rocket propulsion [1]. Experiments on this application of tetranitromethane are, as it appears being continued in different countries [2].

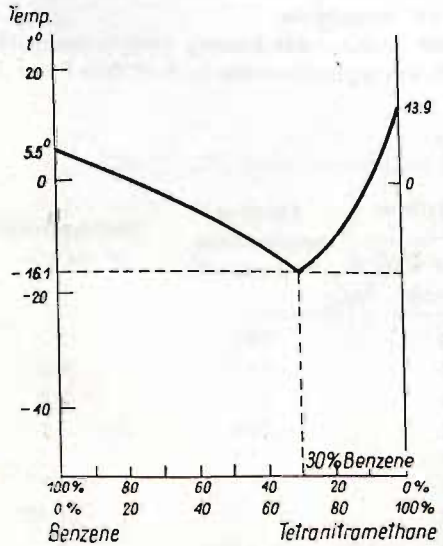

Fig. 1

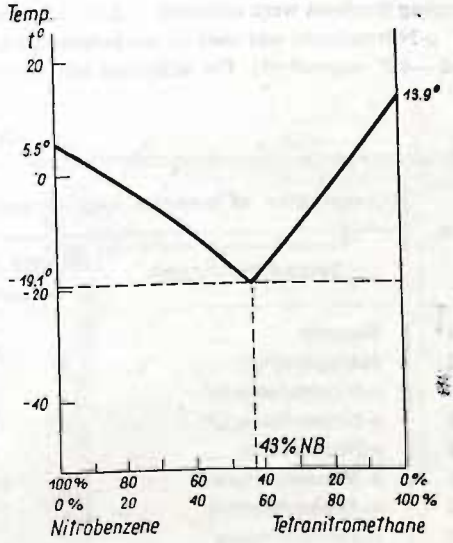

Fig. 2

Experimental

Tetranitromethane was prepared by the method of McKie and Orton [3], [4] by nitrating acetylene with conc. nitric acid in presence of mercuric nitrate. The product was shaken with sulphuric acid, washed with water, dried over sodium sulphate and distilled under reduced pressure.

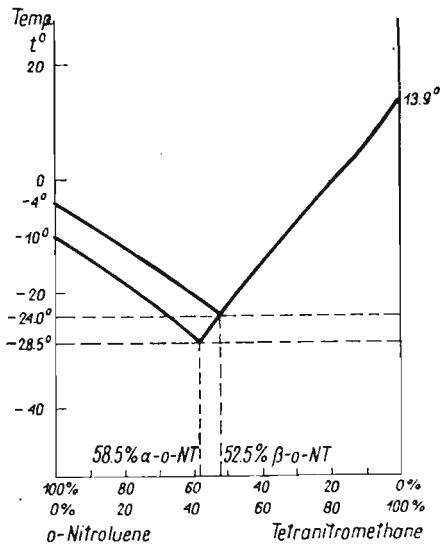

Fig. 3

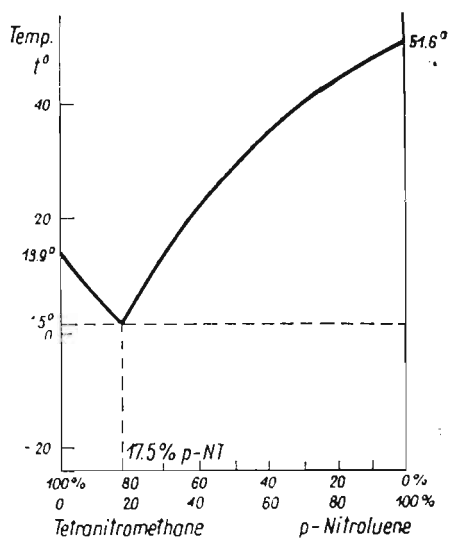

Fig. 4

The product was then purified by freezing. The fraction which froze above 13.9° was collected and used for thermal analysis.

The other — commercial grade substances — were purified in various ways.

Benzene, nitrobenzene and *o*-nitrotoluene were purified by distillation and freezing. High freezing fractions were collected at 5.4°, 5.5° and —4.0°, respectively.

o-Nitrotoluene was used in two polymorphic forms: α and β with freezing temperatures —10.0 and —4.0°, respectively. The technique used previously was applied to obtain each of these forms [5]

TABLE

No.	Composition of eutectics with tetranitromethane		Freezing temperatures of eutectics °C	Melting points of eutectics
	Second component	Weight % of second component		
1	Benzene	30.0	—16.1	—16.1
2	Nitronbczene	43.0	—19.1	—19.4
3	*o*-Nitrotoluene (α)	58.5	—28.5	—28.5
4	*o*-Nitrotoluene (β)	52.5	—24.0	—24.0
4	*p*-Nitrotoluene	17.5	+ 1.5	+ 1.5
5	α-Nitronaphthalene	10.0	+ 9.25	+ 9.5
6	*m*-Dinitrobenzene	3.0	+11.35	+11.65
7	α-Trinitrotoluene	3.0	+12.36	+12.36

p-Nitrotoluene, α-nitronaphthalene, *m*-dinitrobenzene, α-trinitrotoluene and 2,4,6,N-tetranitro-N-methylaniline (tetryl) were purified by crystallization, according to standard methods.

The freezing temperatures of the liquid phase were determined in test tubes with thermometers calibrated to 0.1°. Slow cooling was accompanied by vigorous stirring and the temperature of appearance of the "first crystal" was taken as freezing temperature. The cooling temperature was also plotted against time.

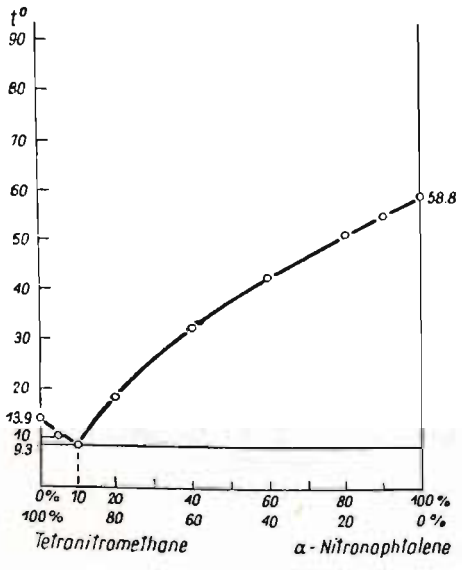

Fig. 5

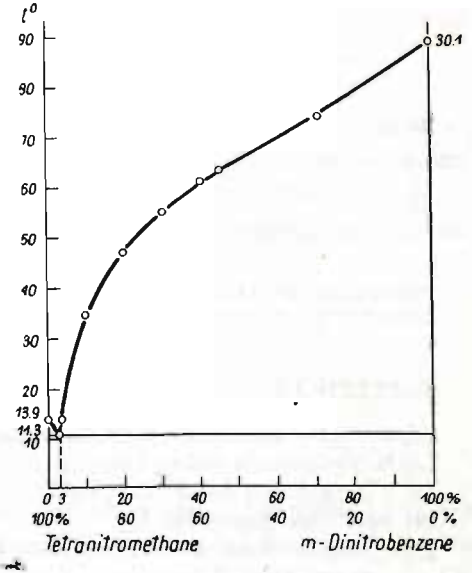

Fig. 6

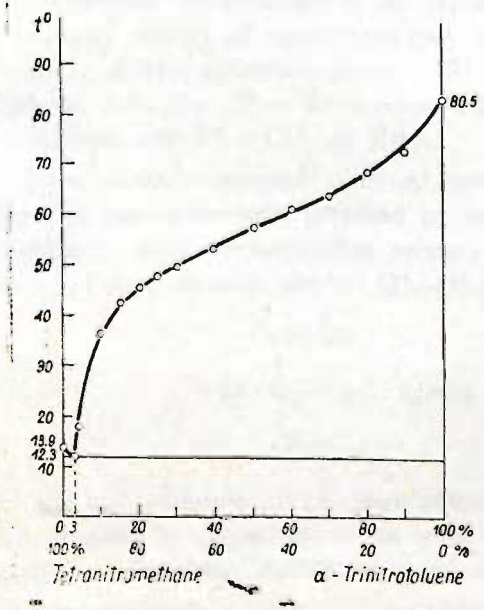

Fig. 7

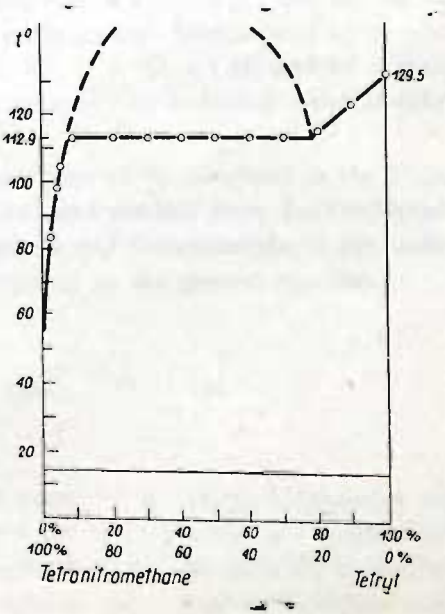

Fig. 8

If a strong supercooling was noticed, the freezing temperature was corrected by extrapolation. The freezing temperature of the eutectic was checked by determining the melting point.

The results are presented in Figs. 1—8. The composition, freezing temperatures and melting points of the eutectics are also summarized in the Table.

Conclusions

It can be seen that in all investigated systems with the exception of tetranitromethane—tetryl, simple eutectics were found.

In the system: tetranitromethane—tetryl, the mutual sulubility of both compounds is very limited.

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