研究論文

Study on Silver Nitrobenzoates

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The silver salts of 3-nitro-, 3, 5-dinitro- and 2, 4, 6-trinitro-benzoic acids have been prepared and their structures have been established on the basis of elemental analysis and infra-red spectra. Their behaviour to different stimuli like heat (on the basis of DTA), impact and friction has also been studied. The data for thermal and impact sensitivity suggest that the initiation of explosion/ignition in silver nitrobenzoates by impact is thermal in origin.

1. Introduction

Heavy metal salts of certain weak acids have found extensive applications in civil as well as in military. Lead azide has been widely used in commercial blasting caps and military ammunitions[1]. A systematic study on metal picrates and picramates has recently been carried out by Agrawal et al[2)-8)]. A literature survey reveals that silver salts of mono-, di- and tri-nitrobenzoic acids have been prepared[9)-11)] but a comprehensive study regarding their structural and thermal characterization has not been reported as yet.

The object of the present study is to prepare silver salts of 3-mono-, 3, 5-di- and 2, 4, 6-trinitrobenzoic acids in pure forms, estabilish their structures and study their behaviour to different stimuli like heat, impact and friction.

2. Materials and Methods

3-mono-, 3, 5-di- and 2, 4, 6-tri-nitrobenzoic acids were prepared by using the methods already reported in the literature[12)-14)] and all other chemicals were of BDH (AR) quality.

2.1 Preparation of silver salts of Mono-, Di- and Tri- Nitrobenzoic acids

A silver salt of 3-mononitrobenzoic acid was prepared by suspending known weight of the acid in 50% alcohol and then treating it with an equimolar quantity of silver nitrate in the aqueous solution. The resulting product was digested on a water bath to ensure complete reaction. The solution was allowed to cool. The product was then filtered and washed with water and finally with alcohol. The compound was dried in desiccator to constant weight. Similarly a silver salt of 2, 4, 6- trinitrobenzoic acid was prepared and dried to constant weight. A silver salt of 3, 5- dinitrobenzoic acid was also prepared similarly using the aqueous medium at 60-70℃.

2.2 Elemental analysis and IR spectra

The contents of carbon, hydrogen and nitrogen were determined by the standard methods. The silver content was determined by the volumetric method using an ammonium thiocyanate solution. The number of nitro groups was determined by the titanium trichloride ($TiCl_3$) reduction method. The infra-red (IR) spectra of the acids as well as their silver salts were recorded in the frequency range, 4000—250 cm^{-1}, in KBr matrix by "Perkin-Elmer Model, 457 Spectrophotometer".

2.3 Differential thermal analysis and determination of activation energy

Differential Thermal Analysis (DTA) was carried out in an apparatus fabricated in this laboratory. It consisted of a Stanton Redcraft linear rate temperature programmer giving heating rates from 2 to 20℃ per minute. The sample and a reference material (Al_2O_3) were housed in platinium cups with $Pt/Pt-Rh$ (13%) thermocouples fused to their bottoms. The temperatures and differential temperatures were recorded on a Deg-

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Table 1 Composition of Silver Salts Determined by Elemental Analysis, Silver and Nitro Group Estimation

Compound		Silver wt. %	Carbon wt. %	Hydrogen wt. %	Nitrogen wt. %	Nitro groups wt. %
Silver 3-nitrobenzoate	Found	39.25	30.62	1.85	4.95	16.69
$[C_6H_4(NO_2)COO]Ag$ (S 3-MNB)	Calc.	39.40	30.66	1.83	5.11	16.80
Silver 3, 5-dinitrobenzoate	Found	33.75	26.50	1.55	8.64	28.45
$[C_6H_3(NO_2)_2COO]Ag$ (S 3, 5-DNB)	Calc.	33.85	26.33	1.57	8.75	28.80
Silver 2, 4, 6-trinitrobenzoate	Found	29.63	23.02	0.83	11.45	37.45
$[C_6H_2(NO_2)_3COO]Ag$ (S 2, 4, 6-TNB)	Calc.	29.67	23.07	0.82	11.54	37.90

ilog Twin Channel Strip Chart Recorder with the sensitivity of 5μV. A sample (approximately 20 —30 mgs) and a reference material were taken in sample and reference cups respectively and heated at desired heating rates. The activation energy for compounds was calculated by plotting log $\frac{\phi}{(T_m)^2}$ against $\frac{1}{T_m}$ (Kissinger method[15]) and by plotting log $\frac{\phi}{T_m}$ against $\frac{1}{T_m}$ (Ozawa method[16])

Where ϕ — Rate of heating

T_m — Peak temperature

2.4 Impact and friction sensitivity

The impact sensitivity was determined with Julius Peter's Impact Sensitivity Apparatus. The test consisted of dropping a hammer of definite weight from a known height on to a weighed quantity of the sample kept in between the surfaces of two stainless steel Hoffman rollers which were kept in position by the steel collors. At each height, twenty readings were taken and the percentage of explosion/ignition was calculated. The friction sensitivity was measured with the

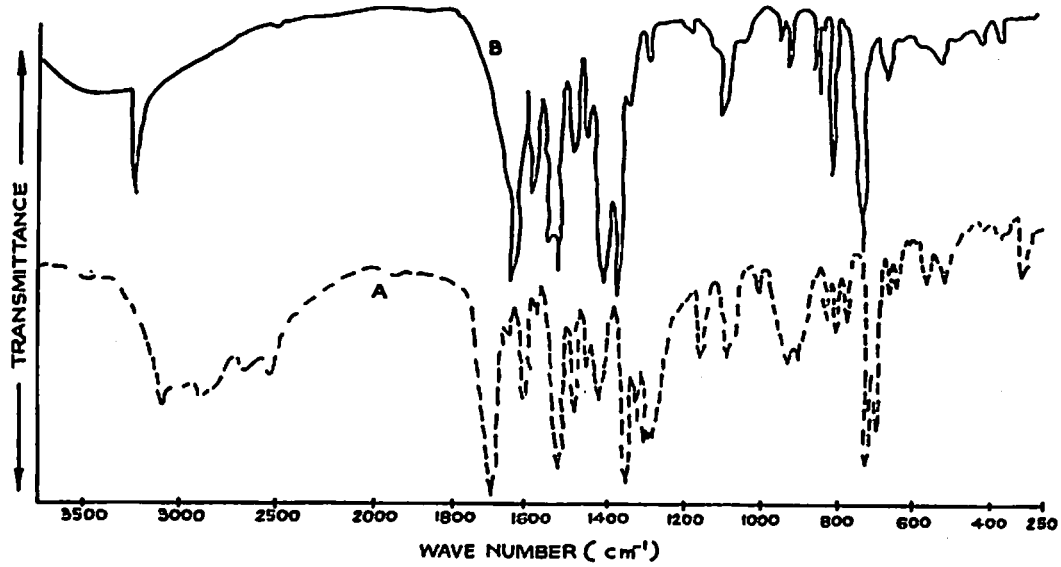


Fig. 1 I. R. spectra of 3-nitrobenzoic acid (A) and silver 3-nitrobenzoate (B)

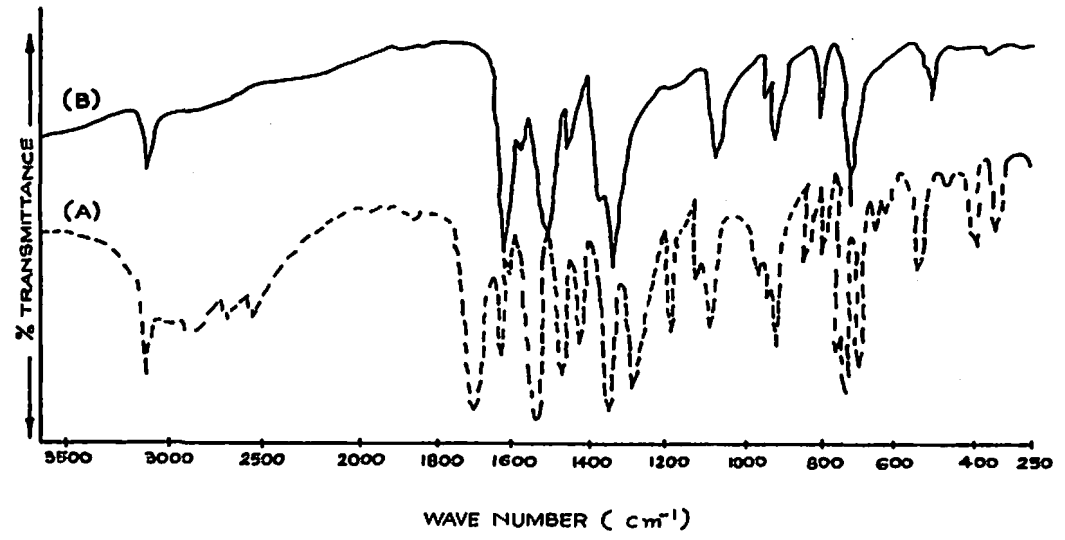


Fig. 2 I. R. spectra of 3, 5-dinitrobenzoic acid (A) & silver 3, 5-dinitrobenzoate (B)

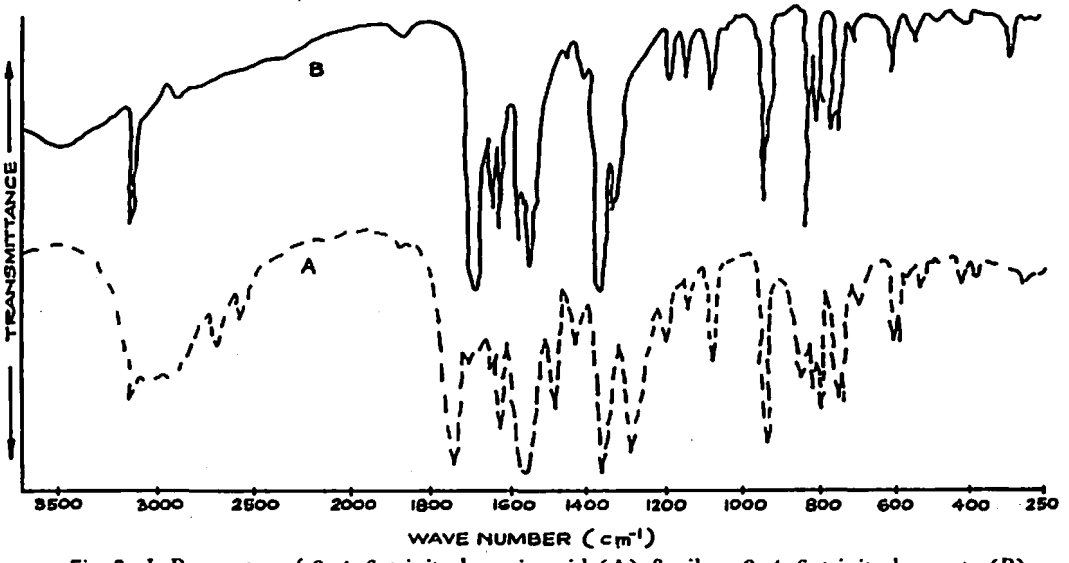


Fig. 3 I. R. spectra of 2, 4, 6-trinitrobenzoic acid (A) & silver 2, 4, 6-trinitrobenzoate (B)

help of Julius Peter's Friction Sensitivity Apparatus.

3. Results and Discussion

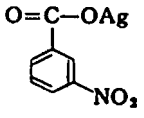
The results of silver and nitro group determinations and micro-analysis of carbon, hydrogen and nitrogen are given in Table 1.

The infra-red spectra on nitrobenzoic acids and their silver salts are given in Fig. 1, 2 and 3. Normally carboxylic acids in liquid or solid states exist in dimeric form with very strong hydrogen bonding between the carbonyl and hydroxyl groups of the two molecules. The abnormally strong hydrogen bonding in these nitrobenzoic acids is responsible for the broad band with a series of minor peaks[17) 18)] over a range of 3000 —2500 cm^{-1} (Fig. 1A, 2A and 3A). As expected, the characteristic frequencies of the aromatic and nitro group portions of the molecules are essentially unchanged in going from acids to salts. However, the characteristic frequencies related to the carbonyl and hydroxyl groups are altered markedly. The absorption peak due to —OH of —C

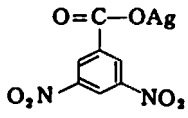
OOH group at 2700 cm^{-1} −2500 cm^{-1} completely disappears (Fig. 1B, 2B and 3B). The bands at 1730 cm^{-1} −1700 cm^{-1} for carbonyl stretching, 1440 ±10 cm^{-1} and 288 ±10cm^{-1} due to −C=O group and −OH deformation perpendicular to plane respectively either disappear or change markedly in intensity. This indicates the replacement of hydrogen of −OH group by silver (Ag). It is also supported by the work already reported in the literature[19] in case of sodium mononitrobenzoate.

On the basis of elemental analysis and infra-red spectra, the following structures may be assigned to silver salts of nitrobenzoic acids.

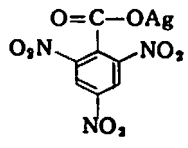
1 S 3-MNB $[C_6H_4(NO_2)COO]Ag$



2 S 3,5-DNB $[C_6H_3(NO_2)_2COO]Ag$



3 S 2,4,6-TNB $[C_6H_2(NO_2)_3COO]Ag$



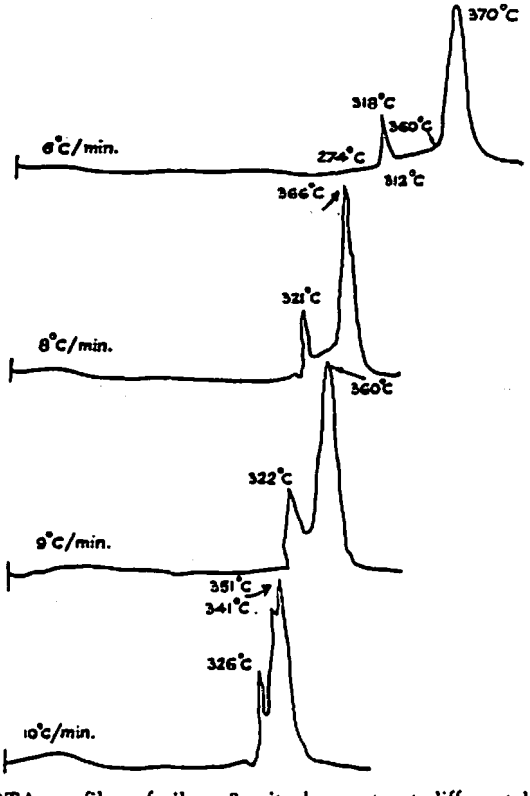


Fig. 4 DTA profiles of silver 3-nitrobenzoate at different heating rates

Fig. 4 shows DTA profiles of S 3-MNB at heating rates of 6, 8, 9 and 10℃ per min. At a heating rate of 6℃ per min, no thermal effects are seen until 274℃ where an exothermic reaction starts as shown by a rising base line. This indicates that the compound is thermally stable upto 274℃. There is a very weak endothermic dip at 312℃ which is attributed to its melting phenomenon as it is well known that several organic explosives decompose immediately after melting[20].

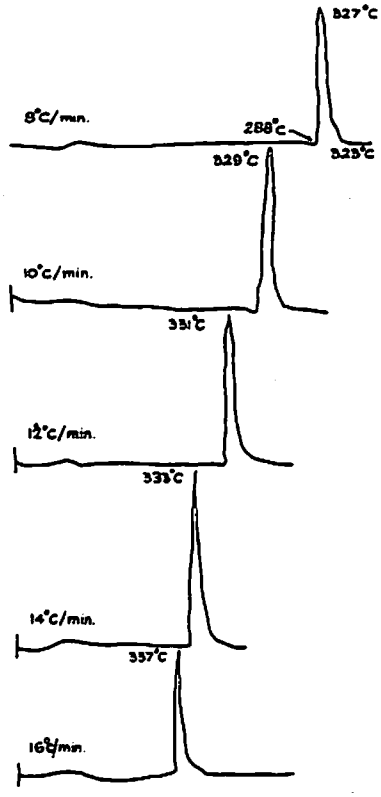


Fig. 5 DTA profiles of silver 3, 5-dinitrobenzoate at different heating rates

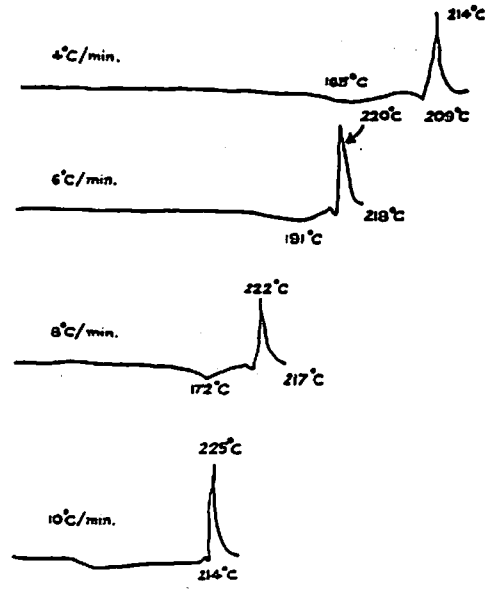


Fig. 6 DTA profiles of silver 2, 4, 6-trinitrobenzoate at different heating rates

This is followed by two exothermic peaks at 312 ℃ and 360℃. First exotherm shows a moderate heat effect with a peak temperature of 318℃ and this reaction almost over-laps on the earlier endothermic effect. The exothermic reaction represented by the first peak does not seem to reach completion before the on-set of the second prominent exothermic reaction. The second exotherm has a very large heat effect with the inception at 360℃ and a peak temperature of 370℃. The reaction seems to continue over a fairly wide range of temperature until the curve reaches the base line at around 600℃.

The DTA profiles of S 3, 5-DNB at 8, 10, 12, 14 and 16℃/min heating rates are shown in Fig. 5. At a heating rate of 8℃ per min, no thermal effects are seen until 288℃ where an exothermic reaction starts as shown by a rising base line. This is followed by a sharp but weak endothermic dip at 323℃ which appears to be due to the melting of the silver salt. This is followed by a strong exothermic peak at 327℃ where the salt decomposes violently and the product is blown off.

The DTA profiles of S 2, 4, 6-TNB at heating rates of 4, 6, 8 and 10℃/min are shown in Fig. 6. The first endotherm appears at 165℃ which is probably due to its phase transformation, while the second weak endotherm at 209℃ shows a melting phenomenon. This is followed by a prominent exotherm at 210℃ where the salt decomposes violently and the product is blown off.

The plots for the purpose of calculation of activation energy by Kissinger method and Ozawa method are given in Fig. 7 and 8 respectively. The data of activation energy derived from both the methods are given in Table 2. The values of activation energy for different salts suggest that the thermal sensitivity increases as the number of nitro groups increases.

The data showing the percentages of explosion /ignition at various heights are given in Fig. 9. The critical heights which bring about 50% explosion/ignition by impact are shown in Table 3 and the results of the friction sensitivity are also given in Table 3. It is seen from the friction sensitivity data that S 3-MNB, S 3, 5-DNB and

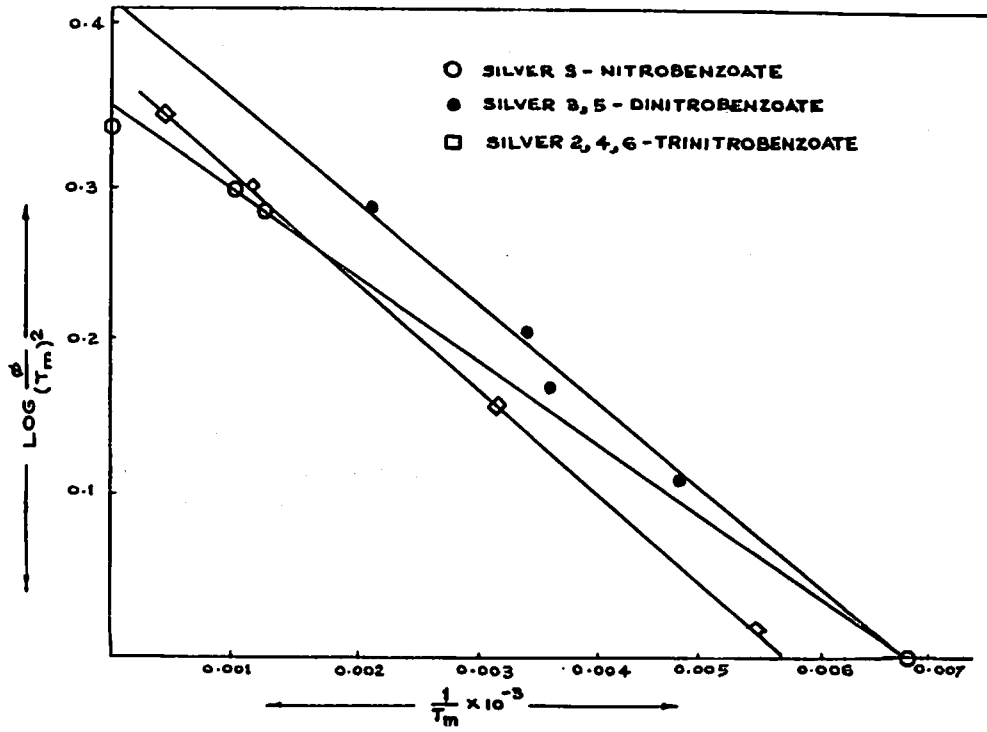


Fig. 7 Plots for activation energy of silver nitrobenzoates (by Kissinger method[15])

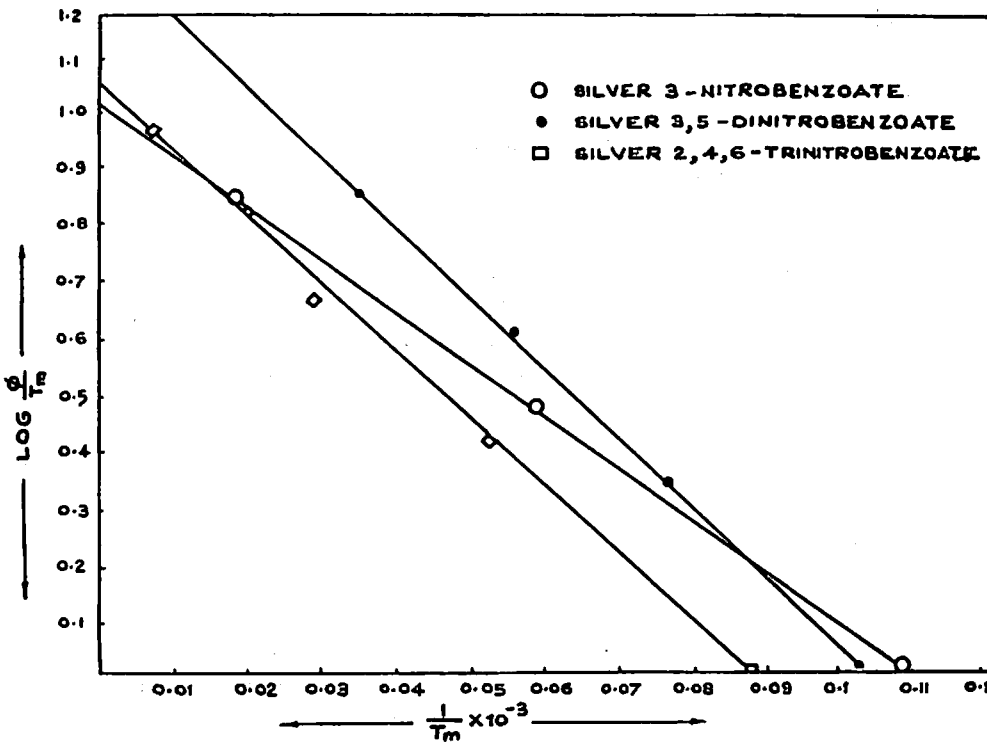


Fig. 8 Plots for activation energy of silver nitrobenzoates (by Ozawa method[16])

Table 2 Activation Energies for Silver Nitrobenzoates

Compound	Activation energy, Kcal/mole	
	Kissinger Method	Ozawa Method
$[C_6H_4(NO_2)COO]Ag$ (S 3-MNB)	89.00	87.00
$[C_6H_3(NO_2)_2COO]Ag$ (S 3, 5-DNB)	53.00	53.00
$[C_6H_2(NO_2)_3COO]Ag$ (S 2, 4, 6-TNB)	36.00	38.00

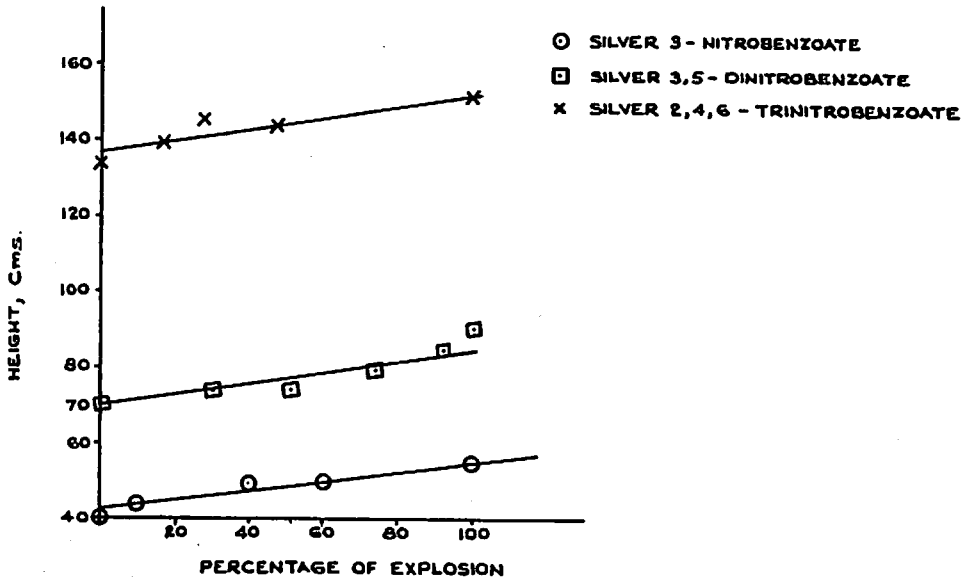


Fig. 9 Impact sensitivity of silver nitrobenzoates

Table 3 Impact and Friction Sensitivities of Silver Nitrobenzoates

Compound	Impact Height for 50% Explosion/Ignition, cm Weight—2kg	Friction Sensitivity upto 36 kg weight
S 3-MNB	144	Insensitive
S 3, 5-DNB	77	Insensitive
S 2, 4, 6-TNB	50	Insensitive

S 2, 4, 6-TNB do not explode/ignite upto 36 kg weight whereas the critical height for 50% explosion/ignition decreases as the number of nitro groups increases in case of the impact sensitivity i. e. the impact sensitivity increases as the number of nitro groups increases.

It has already been established that the thermal sensitivity is also in the same order. It means that the initiation of explosion/ignition by impact in silver salts of nitrobenzoic acids is thermal in origin[21] similar to metal picramates[7]. That is to say, the mechanical energy of impact is first changed into heat and concentrated in a small localized region to form hot spots of suitable size and temperature within the material. A thermal decomposition takes place at the hot spots and

because of the exothermic nature of the decomposition, the rate of decomposition rapidly increases and a thermal explosion results[22]. The way in which explosion/ignition grows from the hot spot may be accounted in terms of the thermal theory of explosion[21]

Acknowledgements

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ニトロ基を含有する安息香酸銀塩に関する研究

3-ニトロ，3，5-ジニトロ，および 2，4，6-トリニトロ安息香酸の銀塩を合成し，その構造を元素分析と赤外吸収スペクトルから確認した。熱(DTAによる)，衝撃および摩擦に対する感度についても調べた。熱および衝撃感度のデータはニトロ安息香酸銀塩類の衝撃による爆発・発火の開始が本来熱に起因することを示唆している。