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Thermal Decomposition Mechanism of Silver Nitrobenzoates

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Abstract. The infra-red spectra of silver salts of 3-mono-, 3,5-di-and 2,4,6-tri-nitrobenzoic acids have been recorded at elevated temperatures in a fabricated high temperature cell. The thermogravimetry i.e. TG analysis has also been carried out. The results of this study suggest that decomposition of these salts is a two stage process i.e. decarboxylation followed by explosion.

1. Introduction

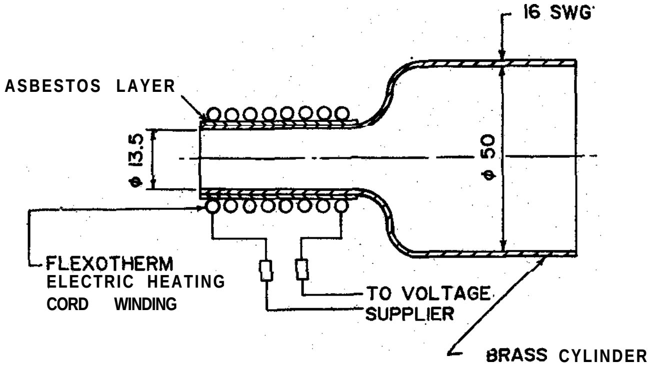
Silver salts of mono-,di-and tri-nitrobenzoic acids have been reported earlier[1-3] but a comprehensive study regarding their structural and thermal aspects has not been done. It is only recently that silver salts of mono-,di-and tri-nitrobenzoic acids have been prepared in pure forms, established their structures on the basis of elemental analysis and infra-red spectra and studied their behaviour to different stimuli like heat; impact and friction[4]. The object of the present investigation is to study mechanism of decomposition of silver nitrobenzoates on the basis of infra-red spectra at high temperatures and thermogravimetry i.e. TG analysis

2. Materials & Methods

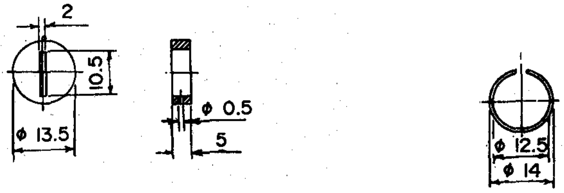
The silver salts of 3-mono-, 3,5-di-and 2,4,6 trinitrobenzoic acids were prepared by the methods mentioned in our earlier communication[4].

The infra-red spectra of these salts were recorded at room temperature in KBr matrix using Perkin-Elmer Model 547 spectrophotometer.

In order to record infra-red spectra of compounds at high temperatures, a high temperature cell was designed and fabricated as described earlier[5]. The sketch of high temperature cell is shown in Fig. 1. OS-l.0 gm of pure compound was mixed with 20 gm of pure KBr (Analar grade) and ground to very fine powder. This was sprinkled



(a) BRASS HOLDER



(b) BRASS CRYSTAL HOLDER (c) CIRCLIP (2 mm THICK)

Figure 1. High temperature cell for infrared at elevated temperatures.

in the die and a pellet (14 mm diameter and 0.5 mm thickness) was made with hydraulic press under vacuum and a pressure of 10 tons/sq. inch for a minute. The specimen pellet was held in position by the retainer rings in the high temperature cell. The, temperature of the cell was increased and IR was recorded with spectrophotometer at medium scanning speed.

TG analysis was carried out with the help of MOM Derivatograph (type-Co-102B) in the temperature range 0-500°C using the method described earlier[6].

3. Results & Discussion

The IR spectra of silver 3-nitrobenzoate at room temperature and 250°C are shown in Fig. 2. The data indicate that there is no remarkable change in their absorption bands, except fall in intensities and minor frequenc yshifts of the original absorption bands due to the effect of temperature.

In order to understand the thermal decomposition mechanism, 10 mg. of sample (in sealed quartz tube 100 mm. long and 3 mm. diameter) was heated at a rate of 10°C/min. in differential thermal analysis furnace. The sealed quartz tube containing the salt was subsequently cooled to room temperature by lifting the furnace when

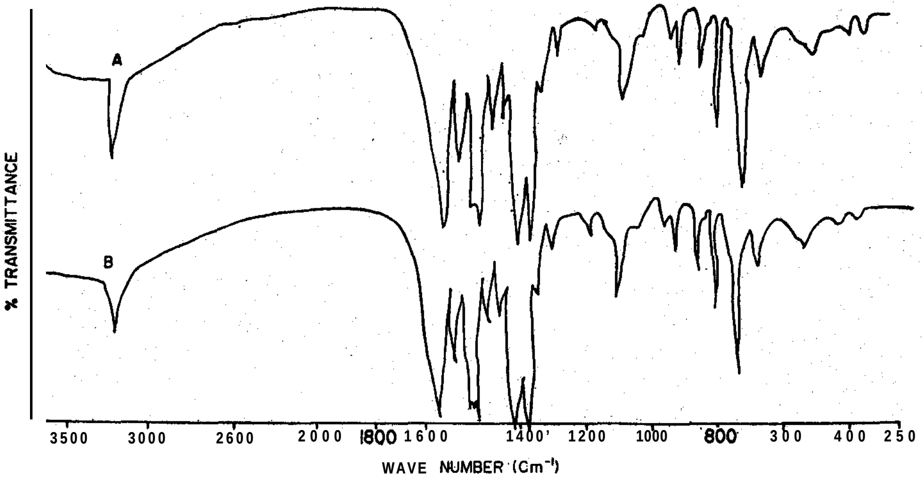


Figure 2. IR spectra of silver 3-nitrobenzoate at (A) room temperature (30°C) and (B) 250°C.

first stage decomposition of the sample was over i.e. at 327°C. The IR spectra of the liquid condensed at the top. residue at the bottom of the sealed tube and nitrobenzene were recorded at room temperature and are shown in Fig. 3.

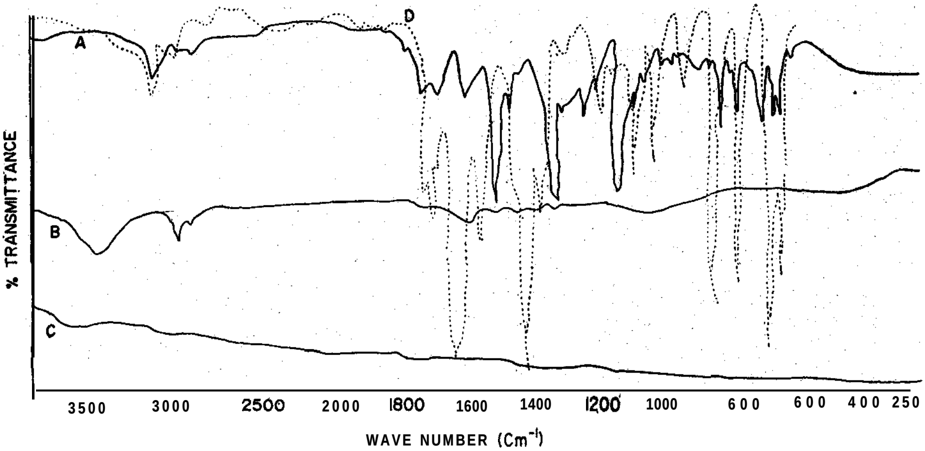


Figure 3. IR spectra of (A) liquid phase, (B) solid phase residue left at 327°C, (C) solid phase residue left at 370°C obtained as a result of decomposition of silver 3-mononitrobenzoate and (D) Nitrobenzene.

A comparison of JR spectra of liquid phase (Fig. 3A) and that of nitrobenzene (Fig. 3D) suggests that liquid obtained as a result of decomposition of silver

3-mono-nitrobenzoate is nitrobenzene due to its decarboxylation. Therefore, the first stage of decomposition of silver 3-mononitrobenzoate is decarboxylation.

On the basis of bond dissociation energies[7,8] of different linkages present in nitrobenzene obtained as a result of decarboxylation i.e. first stage, it may be suggested that the decomposition of nitrobenzene starts by the rupture of N-O linkages[9,10]. This then enables oxygen, which was wholly linked to nitrogen to be consumed for the oxidation of carbon & hydrogen obtained from the ring rupture. This is in agreement with the decomposition mechanism suggested by Agrawal et al[11] in case of metal picramates.

The residue left after first stage decomposition was further heated upto 370°C and infra-red spectrum of residue was recorded and is shown in Fig. 3. This indicates the presence of Ag or Ag_2O as no absorption bands are seen in the region 3500-250 cm^{-1} (the bands corresponding to metal-oxygen bonds appear in the far infra-red region i.e. below 200cm^{-1} because M-O bonds are highly ionic[12]). Therefore, the second stage involves breaking of N-O linkages in nitrobenzene followed by benzene ring rupture and oxidation of carbon and hydrogen with the available oxygen.

This is supported by TG studies also. TG curve (Fig. 4) of silver 3-mononitrobenzoate (S3-MNB) suggests that its decomposition is 2-stage process. The 'loss in weight' as a result of first stage comes out to about 50 per cent which compares well with the theoretically calculated 'Loss in weight' ($\approx$ 5 1.9 per cent) considering decarboxylation as first stage as shown Fig. 5.

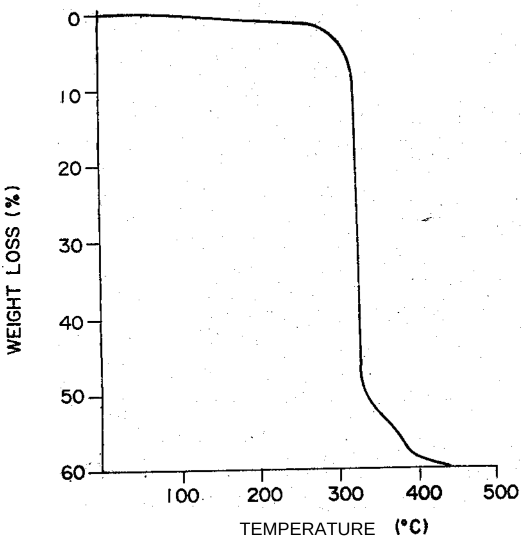


Figure 4. TG curve of S 3-MNB.

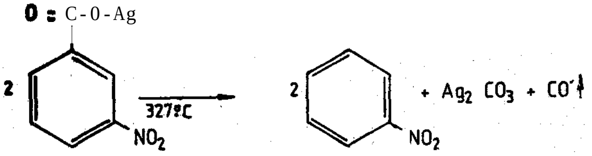


Figure 5,

TG curve further shows a loss of about 9 per cent where reaction is completed. This 'loss in weight' matches with the theoretically calculated 'loss in weight' i.e. 7.0 per cent on the basis of following equations.

$$Ag_2CO_3 \xrightarrow[\text{Heat}]{} Ag_2O + CO, \uparrow \qquad \text{[Intermediate]}$$

370°C

$$2Ag_2O \rightarrow 4Ag + O_2 \uparrow$$

The IR spectra of silver 3, **5-dinitrobenzoate** (S **3,5-DNB)** at room temperature, **225°C, 302°C,** 330°C and 380°C are shown in Fig. 6. It is noticed that the IR spectra upto 302°C are comparable to the spectrum at room temperature except some changes in the intensities of some absorption bands. But when sample mixed **KBr** disc was heated to 330°C and IR spectrum recorded, there was a remarkable change particularly in the absorption band corresponding to – OC = 0 -group which completely vanishes suggesting decomposition by decarboxylation process. When it

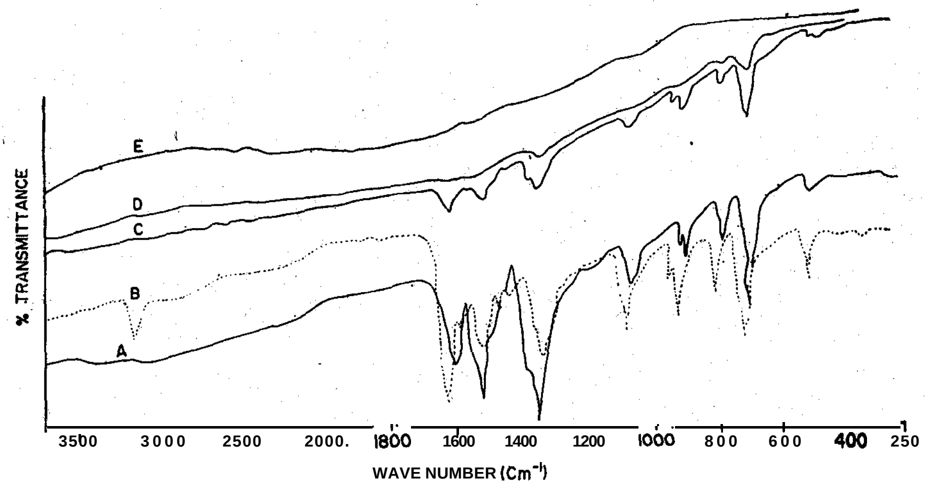


Figure 6. **IR** spectra of silver **3,5-dinitrobenzoate** at (A) room temperature, (B) **225°C,** (C) **302°C, (D)** 330°C and **(E)** 380°C.

was further heated to 380°C and IR spectrum recorded, it was seen that all absorption bands disappeared. This indicates that the decomposition starts by decarboxylation process at a temperature of 330°C and is completed. at 380°C, where all absorption bands disappear. The decarboxylation is followed by explosion.

The IR spectra of S 2,4,6-TNB in KBr matrix at room temperature, 108, 140, 150, 190 and 200°C are shown in Fig. 7. A comparison of IR spectra shows that S 2,4,6-TNB is thermaly stable upto 150°C as there is no change in absorption bands except some change in their intensity. The absorption. band corresponding to-O=C - O-group vanish at 190°C, which indicates that the decomposition reaction starts at 190°C by decarboxylation process followed by explosion at 200°C where all absorption bands disappear.

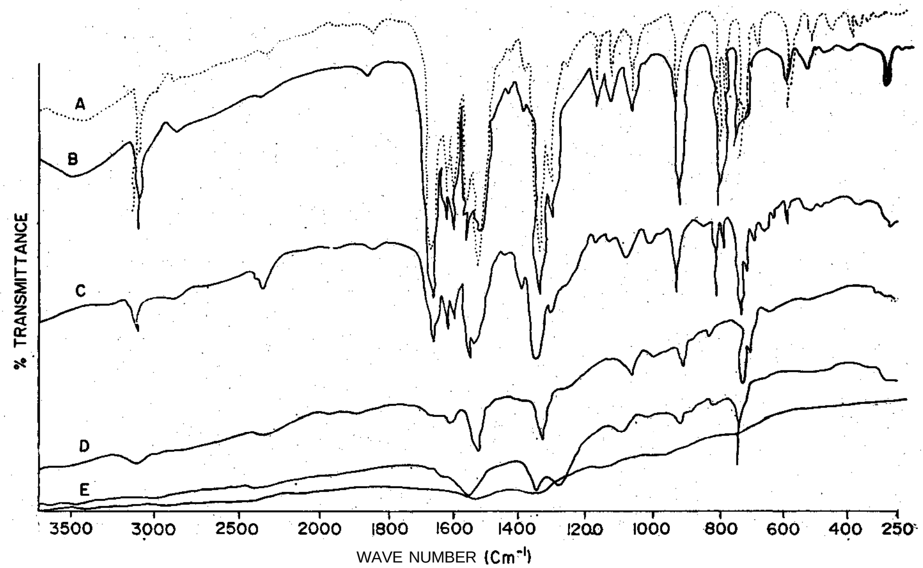


Figure 7. IR spectra of silver 2,4,6-trintrobenzoate at (A) room temperature, (B) 100°C, (C) 140°C, (D) 150°C, (E) 190°C and (F) 200°C.

The second stage reactions involved in the decomposition of S 3,5-DNB and S2,4,6-TNB are similar to those of S3-MNB.

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