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# BIS(2-AZIDO ETHYL)ADIPATE PLASTICIZER : SYNTHESIS AND CHARACTERISATION.

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## ABSTRACT

Bis(2-azido ethyl) adipate (BAEA) has been synthesized and characterised for solubility, moisture content, density, refractive index, impact sensitivity and thermal behaviour. Its structure has been established with the help of IR and NMR. Thermal decomposition of BAEA has been studied by DTA and its activation energy is of the order of 45 - 46 k cal/mole.

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## INTRODUCTION

Plasticizers are high boiling liquids, usually organic esters, which are added to polymers to modify their properties. The addition of plasticizers improves flexibility which, in turn, improves low temperature characteristics of a polymer. The introduction of the plasticizer between two segments of a polymer separates polar groups apart, thereby reducing the monotony of configuration and improving flexibility.

Two types of plasticizers are recognized : non-energetic and energetic.

The non-energetic plasticizers modify tensile strength, elongation, toughness and softening point , but do not contribute to the energy of a system. Some of the well known non-explosive plasticizers which are being used for the manufacture of rocket propellants are triacetin (TA), diethyl phthalate (DEP), emolein and dioctyl adipate (DOA) etc.

The energetic plasticizers improve/enhance flexibility, elasticity and spontaneous ignition properties. Moreover, they contribute to the energy of the system. In rocket propellants, they are preferred to non-energetic plasticizers because of their contribution to energy. The energetic plasticizers

invariably contain functional groups such as nitro, fluoronitro, fluoroamino, azido etc. in addition to long carbon - carbon chains.

According to literature, a number of energetic plasticizers have recently been synthesized and characterised.[1-10] However, bis(2-azido ethyl) adipate has not yet been reported. The objective of this investigation is to synthesize and characterise bis(2-azido ethyl) adipate and also to study its thermal behaviour.

## SYNTHESIS

The main chemicals required for this work are 2-chloroethanol, L.R. (b.p. – 120°C and d - 1.201), adipic acid, L.R.(m.p. 152° to 154°C) and Sodium azide, L.R., Miscellaneous chemicals and solvents required are anhydrous magnesium sulphate L.R., sodium bicarbonate L.R., solvent ether L.R., ethanol L.R., toluene L.R. and concentrated sulphuric acid. These chemicals were procured from trade and used as such, without further purification.

The synthesis of bis(2-azido ethyl) adipate was performed in two steps. Bis(2-chloro ethyl) adipate was prepared in the first step and subsequently, bis(2-azido ethyl) adipate was synthesised in the second step by reacting the dichlorodiester with sodium azide.

Bis(2-chloro ethyl) adipate in the first step was prepared by the method as used for the preparation of bis(1-chloro hexyl) adipate.[1-3]

A mixture of adipic acid (0.04 moles), 2-chloro-ethanol (0.08 moles), concentrated sulphuric acid (few drops) as a catalyst and toluene as solvent were taken in a round bottom flask and refluxed for 8 hours. The solvent was then removed under reduced pressure and the residue was poured into water. The residue was subsequently extracted with ether, treated with sodium bicarbonate, washed with water and dried over anhydrous magnesium sulphate. The ether was removed under reduced pressure and the yield of bis (2-chloro ethyl) adipate was about 90%. The intermediate product was further purified by distillation under reduced pressure.

Thin layer chromatography of the intermediate showed a single spot indicating that the compound was pure. The physico-chemical properties of the intermediate are,

| Property | Experimental | Reported[3] |
|---|---|---|
| Moisture content, % | 0.026 | -- |
| Boiling point, $^{o}$C (at 9 mm pressure) | 198 - 205 | 190 - 202 |
| Density (at 25$^{o}$C)., g/ml | 1.2 | 1.3 |

Bis(2-azido ethyl) adipate (BAEA) was prepared in the second step by taking 0.01 mole of bis(2-chloro-ethyl) adipate, 0.02 moles of sodium azide and ethanol as a solvent in a round bottom flask and refluxing the contents for 40 hours.[2,5] The ethanol was removed under reduced pressure, the product was poured in water followed by extraction with ether and drying over anhydrous magnesium sulphate. The ether was now removed under reduced pressure giving bis(2-azido ethyl) adipate. The yield was about 72% and thin layer chromatography indicated that it was a pure compound. For thin layer chromatography, a mixture of hexane and chloroform (1:1) was used as eluent.

## CHARACTERIZATION

The infra-red spectra were recorded at room temperature by smear method using a Perkin-Elmer IR Spectrophotometer, Model 683. The $^1H$ NMR spectra were recorded with a Bruker 90 MHz FTNMR using $CDCl_3$ as a solvent with Tetramethyl Silane (TMS) as an internal standard.

The moisture content was determined using Karl - Fischer reagent (Qualigen Fine Chemicals, Bombay). The solution of sample in dry methanol was titrated with standard Karl-Fischer reagent using Mettler DL 40 RC Memotitrator and the value of moisture content was read directly from the printer.

The impact sensitivity was determined with a Julius-Peter Apparatus (West Germany). The test consists of dropping a hammer of definite weight (2 kg) from a preset height onto a weighed quantity of the sample. A number of 25 similar tests were carried out at each height and the number of ignitions were recorded. The critical height which corresponds to 50% ignitions was accordingly calculated.

Differential Thermal Analysis (DTA) was carried out from 20°C to 500°C by using a locally manufactured DTA apparatus. 10 mg of sample were taken in an open platinum cup and heated at a rate of 10°C/min in an atmosphere of static air. The reference sample (calcined alumina - 10 mg) was taken in another platinum cup. The temperature difference of the test sample and reference sample was measured as a function of temperature. In order to calculate the activation energy of thermal decomposition of BAEA, runs were recorded at a heating rate of 4°C/min, 6°C/min, 8°C/min and 10°C/min. The peak maxima obtained at various rates of heating are 216°C, 221°C, 223°C and 225°C respectively as shown in Fig. 1 . The activation energy of thermal decomposition of BAEA was determined by applying Ozawa's method as well as Kissinger's method.

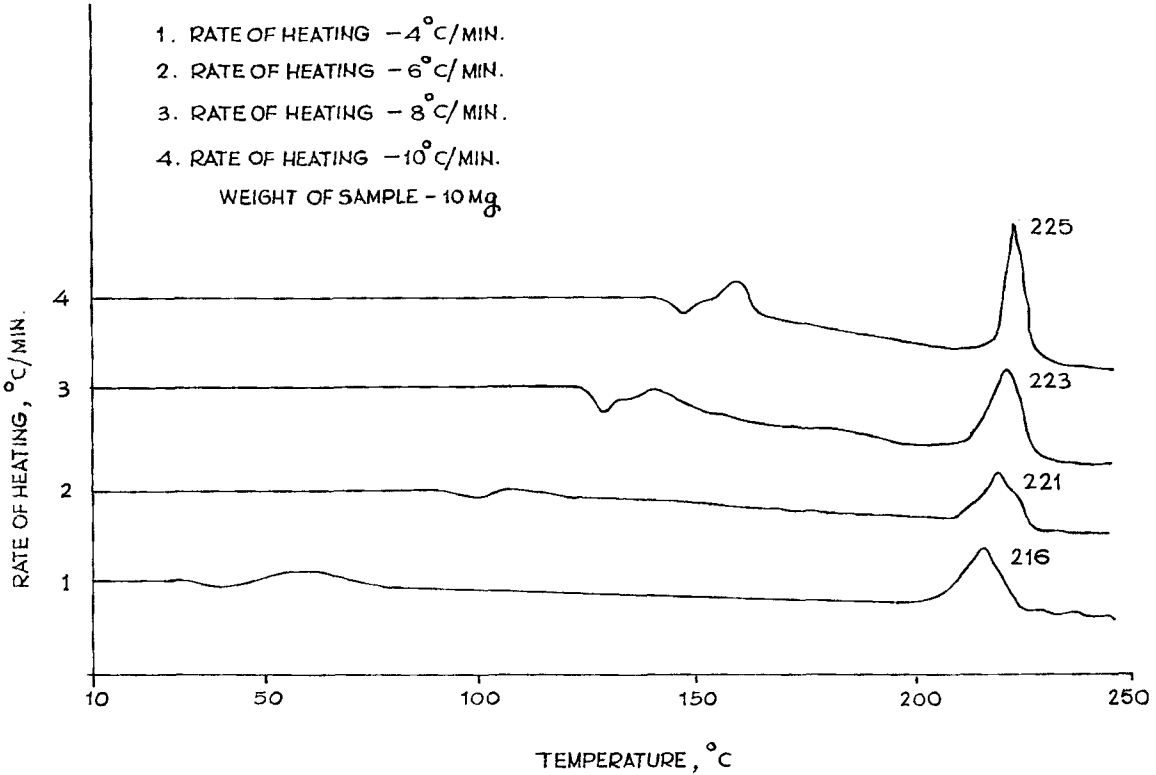



FIG.1 : RATE OF HEATING VERSUS TEMPERATURE FOR BIS(2-AZIDO ETHYL) ADIPATE

In Ozawa's method, a curve was plotted between the logarithmic rate of heating and the reciprocal of peak maximum temperature i.e. log $\beta$ Vs $(1/T_m)$ where $\beta$ is rate of heating and $(1/T_m)$ is the reciprocal of peak maximum temperature. It gives a straight line as shown in Fig. 2 and E was calculated from its slope.

$$\text{Slope} = \frac{0.4567}{1.987} E$$

The activation energy was calculated by Kissinger's method by plotting curve between $\ln \frac{\beta}{(T_m)^2}$ Vs $\frac{1}{T_m}$ which is also straight line (Fig. 2) and its slope gives E

$$\text{Slope} = \frac{E}{1.987}$$

The calorimetric value was determined using a Bomb Calorimeter (Toshniwal Instruments and Engineering Company, Bombay, India). Nicrome wire is used as fuze wire. The heat liberated during combustion increased the temperature of the water inside the jacket. The temperature rise was monitered with the help of a Beckmann Thermometer and the calorimetric value was calculated as described in the manual.

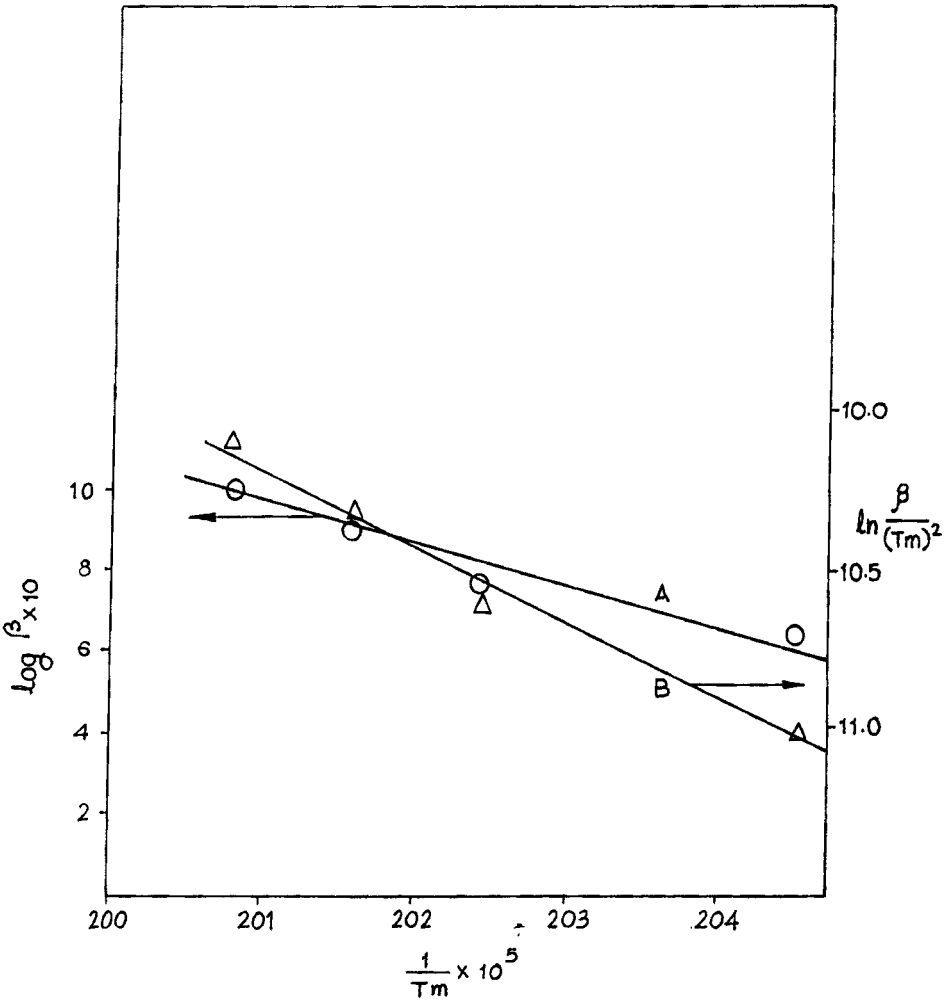
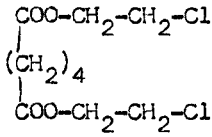



FIG. 2: PLOTS FOR CALCULATION OF ACTIVATION ENERGY
A - OZAWA'S METHOD
B - KISSINGER'S METHOD

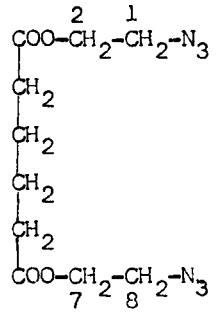
## RESULTS AND DISCUSSION

The preparation of bis(2-azido ethyl) adipate consists of 2 steps i.e. synthesis of bis(2-chloro ethyl) adipate followed by its reaction with sodium azide.

The IR spectra of bis(2-chloro ethyl) adipate show major bands at 1750 $cm^{-1}$, 680 $cm^{-1}$ and 2960 $cm^{-1}$ which correspond to the ester, C-Cl and C-H stretching vibrations respectively. This implies that the structure of bis(2-chloro ethyl) adipate may be shown as



In the second step, bis(2-chloro ethyl) adipate was reacted with sodium azide to give bis(2-azido ethyl) adipate (BAEA) by replacing Cl by $N_3$. The IR spectra of (BAEA) show major bands at 1740 $cm^{-1}$, 2980 $cm^{-1}$, 2110 $cm^{-1}$ which correspond to ester, C-H and azide stretching vibrations, respectively. Thus, both the method of synthesis and the IR data suggest the following structure for bis(2-azido ethyl) adipate (BAEA).



The structure is supported[10] by NMR spectra (Fig. 3) which suggests the presence of

$H^1$ and $H^8$ -- 3.9 ppm

$H^2$ and $H^7$ -- 4.1 ppm

$H^3$ and $H^6$ -- 2.7 ppm

$H^4$ and $H^5$ -- 1.9 ppm

The various properties such as density, moisture content, refractive index, calorimetric value, impact sensitivity and solubility were determined and are shown in Table 1.

The solubility data show that BAEA is soluble in most of the organic solvents including nitroglycerine (NG). Therefore, it may easily replace triacetin (TA) or diethyl phthalate (DEP) which are used in casting liquid for double-base (DB) and composite modified double-base (CMDB) propellants.

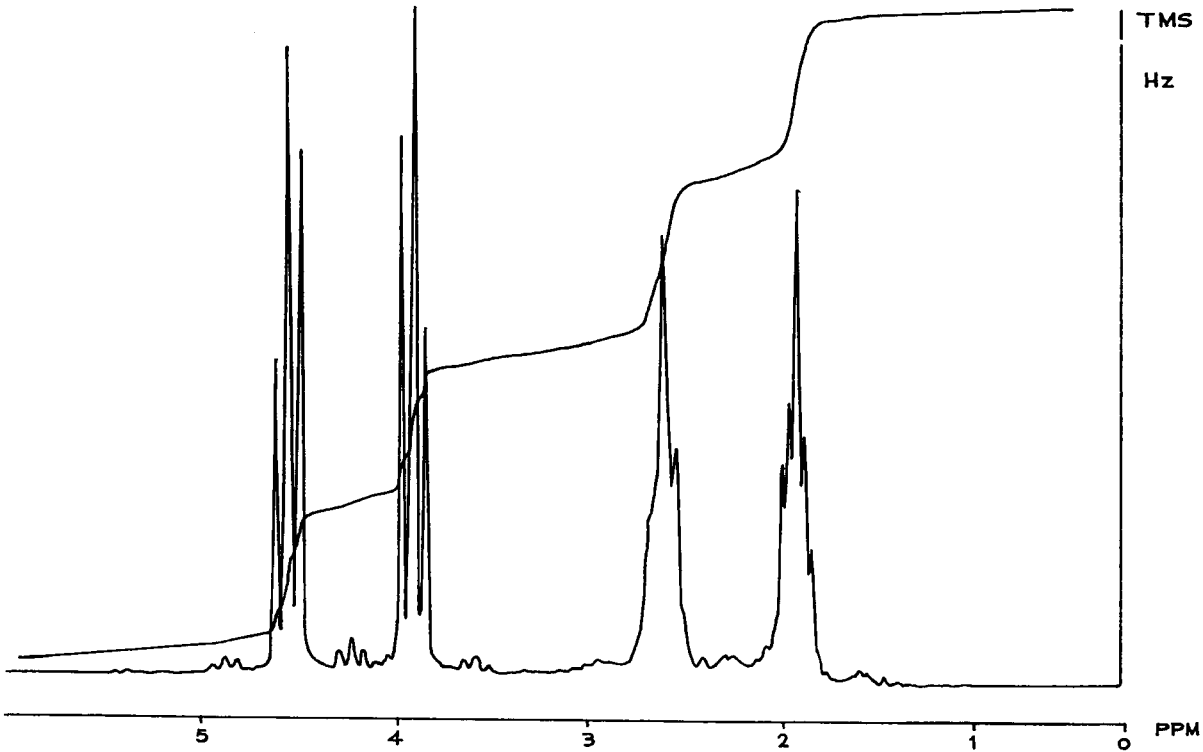



FIG.3 : NMR SPECTRA OF BIS(2-AZIDO ETHYL) ADIPATE

TABLE 1

Various Properties of Bis(2-azido ethyl) adipate (BAEA)

Moisture content, % - 0.9340

Density (at 25°C), g/ml - 1.1543

Refractive Index (at 25°C)- 1.463

Cal value, cal/gm - 1530

| Figure of Insensitiveness | (F of I) |
|---|---|
| Composition (% of mass) | Height (cms) |
| i) NG + DEP<br>80 20 | 175 |
| ii) NG + BAEA<br>80 20 | 58 |
| iii) NG + DEP + BAEA<br>80 10 10 | 61 |
| iv) NG + DEP+BAEA<br>80 15 5 | 72 |

Solubility

i) Soluble in ethanol, acetone, chloroform, dimethyl formamide, methanol, diethyl phthalate, triacetin and nitroglycerine

ii) Partially soluble in benzene and toluene

iii) Insoluble in hexane and water

The "Figure of Insensitiveness" (F of I) of BAEA in combination with NG/DEP is also shown in Table 1. The reference explosive is tetryl. The "F of I" for a conventional casting liquid like NG:DEP (80:20) is 175. The "F of I" for BAEA (80:20) comes down to 58. This indicates that the casting liquid based on BAEA is more sensitive as compared to conventional casting liquid based on NG and DEP. Therefore, DEP cannot be completely replaced by BAEA in view of safety considerations. By replacing a part of the DEP by BAEA, the "F of I" increases and becomes 72 with the (80:15:5) composition.

The DTA curves at different heating rates are shown in Fig. 1 . The DTA curve (heating rate 10°C/min) indicates that the exothermic decomposition of BAEA starts at 197°C and is completed at 223°C with the peak maxima at 213°C. The evolution of smoke is also observed during this exothermic reaction.

The activation energy of BAEA, by Ozawa's method and Kissinger's method are calculated to be 46.28 K cal/mole and 45.03 K cal/mole respectively. This indicates that BAEA is quite thermally stable as compared to DB propellant Block; where activation energy has been reported[11] as 31 k cal/mole.

The solubility, calorimetric value, impact sensitivity data suggest that a part of non-energetic plasticizer i.e. DEP/TA can be replaced by BAEA and as a result, the specific impulse of the propellant will increase.

The experiments for detailed study of thermal behaviour and mechanism of decomposition of BAEA are in progress and will be reported shortly.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