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Thermal Studies of Cetyltrimethyl Ammonium Tribromide for Application to Solvent-Free Brominations

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ABSTRACT

Cetyltrimethylammonium tribromide (CTMATB) has been a reagent of choice for various organic transformations, especially in the synthesis of bromoorganic compounds. The main importance of the reagent is that it acts as an alternative to the hazardous reagent bromine (Br_2). In order to assess the efficiency of the reagent as a brominating agent under solvent-free conditions at elevated temperature, the thermal properties of the reagent have been studied. The reagent was found to be quite stable even at higher temperature and therefore, considering the detrimental effects of organic solvents, an environmentally benign solvent-free method of bromination of organic compounds was developed using a hot-air oven.

Keywords: cetyltrimethylammonium tribromide (CTMATB), thermal analysis, brominations, solvent-free, environmentally benign

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INTRODUCTION

Acknowledging the importance of bromoorganic compounds, [1,2] and the need for environmentally benign brominating reagents, some development has been made through the synthesis and use of organic ammonium tribromides as alternative sources of bromine for organic brominations. [3-9,17] Among the tribromides that have been synthesized so far, cetyltrimethylammonium tribromide (CTMATB) has been found to have many important properties and has been used for a number of different type of reactions. [3,5]

In recent years, there has been increasing emphasis on avoidance of use of solvents in organic reactions. It often happens that while many reaction strategies are efficient as well as benign, use of organic solvents in these reactions, prevent them from being considered as perfectly green. Solvent-free reactions often require the reaction temperatures to be elevated. However, in order to properly utilize a reagent for solvent-free reactions at elevated temperatures, a detailed understanding of the thermal properties of the reagent becomes essential. This paper thus reports the results of the thermal studies of cetyltrimethylammonium tribromide and thereafter the study of versatility of the reagent for solvent-free bromination reactions at elevated temperature using a hot-air oven.

MATERIALS AND METHODS

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25mm). NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with tetra methyl silane as the internal standard for ^1H NMR (400 MHz) and $CDCl_3$ or DMSO-d_6 solvents as internal standard for ^{13}C NMR (100 MHz). IR spectra were recorded in KBr or neat.

Synthesis of Cetyltrimethylammonium Tribromide (CTMATB), $(C_{16}H_{33})(CH_3)_3NBr_3$

An amount of 0.34 g (0.06 mmol) vanadium pentoxide (V_2O_5) was added to 5 ml (44.15 mmol) 30% hydrogen peroxide (H_2O_2) taken in a pre-cooled 100 ml beaker (*Care should be taken to maintain ice-cold condition as the reaction between V_2O_5 and H_2O_2 is exothermic*). The reaction mixture was stirred at 0 – 5 °C temperature in an ice-water bath till all the V_2O_5 dissolved and the solution became reddish-brown. It was then diluted with 110 ml of water and poured into a 500 ml beaker that was placed in an ice-water bath. To it was added a solution of 4.89 g (41.07 mmol) of potassium bromide (KBr) and 5g (13.74 mmol) of cetyltrimethylammonium bromide (CTMAB), dissolved in 150 ml of water. An amount of 25 ml of 1M sulphuric acid (H_2SO_4) was added in small portions to the above solution. Magnetic stirring was continued for another 2 h at ice-water temperature. The product that formed was then isolated by suction filtration using Whatman 1 filter paper.

$$\mathbf{CTMAB} \xrightarrow[H^+ / \mathrm{KBr}]{\mathrm{V(V)} / H_2O_2} \mathbf{CTMATB}$$

The compound was then dried in a vacuum desiccator using anhydrous calcium chloride ($CaCl_2$) as desiccant. The product was obtained as bright yellow micro-crystals. Yield of the product was 5.52 g (96 %). M.P: 87 – 88 °C.

Thermal Studies of Cetyltrimethyammonium Tribromide

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) experiments were conducted on a Mettler-Toledo TGA/SDTA 851^e and DSC 821^e instrument. Experiments were done using either aluminium or platinum crucibles. Pure N_2 gas was used as the flow gas.

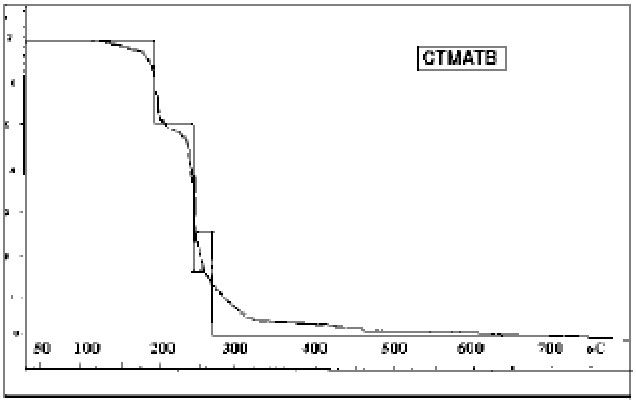


Fig. 1: Thermogram of CTMATB

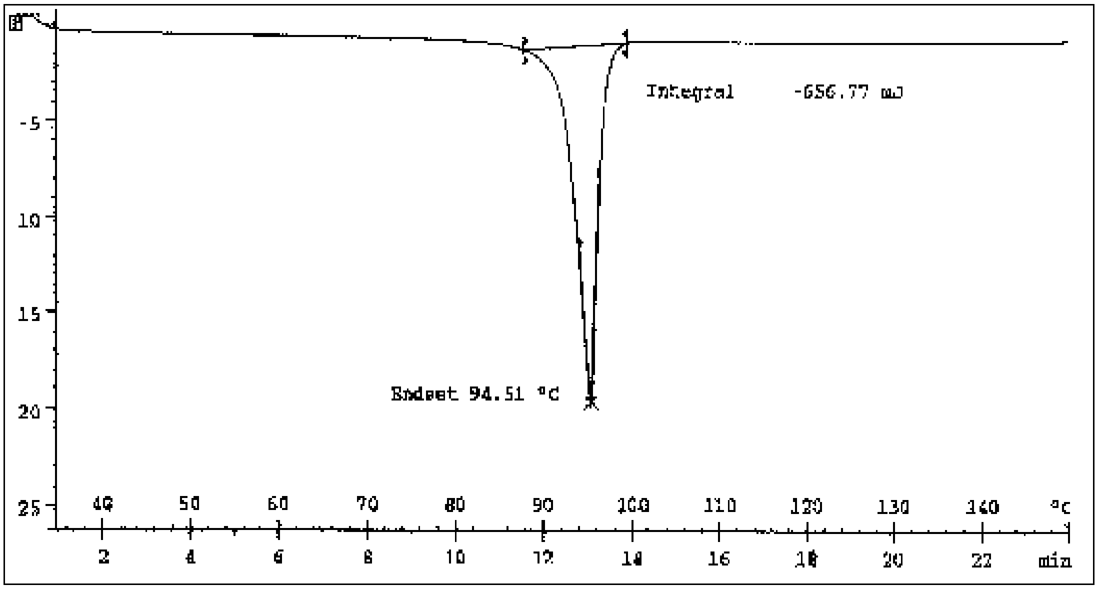


Fig. 2: DSC curve of CTMATB

Typical procedure for bromination reactions in hot air oven using CTMATB

A homogeneous mixture of substrate (2mmol) and reagent (2 mmol) in the ratio 1:1 was taken on Petri dish. The reaction mixture was mixed thoroughly. The reaction mixture was then inserted in hot air oven in a pre-controlled temperature 60±5°C (a higher temperature of 70±5°C was required for reaction of anthracene only). The progress of reaction was monitored by thin layer chromatography on silica gel by using ethyl acetate-hexane solvent system (volume ratio varied for different substrate). After completion of reaction the reaction mixture was diluted with 30 ml ethyl acetate and filtered through a short column of silica gel to remove the spent reagent. The crude product thus obtained was subjected to column chromatography over a pad of silica gel using ethyl acetate-hexane (volume ratio varied for different substrate) solvent system as an eluent to afford the product. The products were identified by comparison of their melting points, IR and NMR spectra with those of authentic samples.

RESULTS AND DISCUSSION

Cetyltrimethylammonium tribromide (CTMATB) has been prepared by using the strategy of bromide oxidation. Accordingly, the strategy is based on preparing quaternary salt of tribromide wherein, the bulky cationic moiety is the cetyltrimethylammonium unit and the anionic portion is the tribromide portion. The reaction proceeds without the involvement of bromine or HBr and the quaternary bromide salt is used as a source of primary bromide.

The bromide oxidation is conducted under mild conditions and the oxidant used is hydrogen peroxide. Vanadium (V) has been used as catalyst for activation of hydrogen peroxide; however, other similar higher valent transition metal catalyst which is capable of activating hydrogen peroxide can also be used. An acidic medium is required as promoter for bromide oxidation.

In the reaction, monobromide is converted to tribromide and 1/3 of the bromide is obtained from the quaternary bromide salt and remaining 2/3 of the bromide is obtained from an additional secondary source, which is KBr in the present case. The reaction does not require the use of organic solvent.

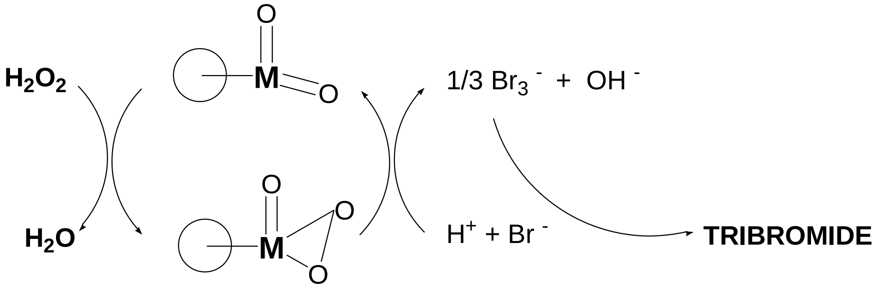
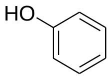
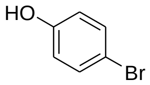
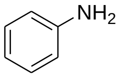
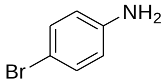
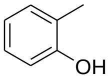
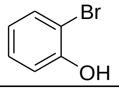
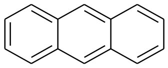
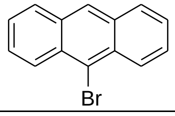
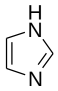
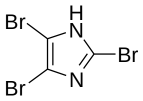
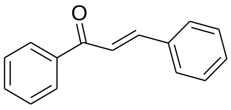
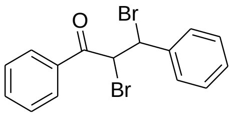
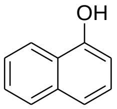
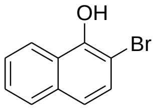


Fig. 3: Mechanism for CTMATB Formation

Cetyltrimethylammonium tribromide (CTMATB) is a crystalline solid with sharp melting point at 87-88°C. However, from thermo gravimetric analysis it is revealed that the compound is stable even up to *ca.* 200°C. One of the major implications of this property is that the tribromides may be very useful for the appropriate solvent-free organic transformations at relatively higher temperatures as well. Thermal studies have another important implication. It is obviously feared that tribromides, upon heating, release bromine, which is an environmentally hazardous chemical. However, while investigating their thermal stability by thermo gravimetric (TG) experiments, it was observed that CTMATB loses Br_2 as the tail fragment at the temperature of 265–267°C, which is a temperature much higher than the temperature at which solvent-free brominations take place. While this is important from environment point of view, there is another implication of this information. In bromination reactions involving CTMATB it was so far assumed that during the reactions, the tribromide does not react as such, but as bromine (Br_2). However, from thermal studies it is understood that at the temperature at which the reaction is taking place, the tribromide moiety does not release the bromine molecule. The bromine molecule is released at a much higher temperature, therefore it can be assumed with a certain amount of confidence that the reactive species is not bromine, but the tribromide entity itself.

The results of the bromination reactions have been presented below in Table 1. Different classes of organic compounds were selected for bromination to determine the versatility of CTMATB under solvent free reaction condition. Reaction of activated benzene derivatives resulted in the formation of para brominated products. The effect of the cationic part of the tribromide reagent on the regioselectivity of bromination of phenol, aniline and o-cresol resulting in para brominated and ortho substituted as a by-product in trace amount. The direct bromination of anilines and phenols with molecular bromine in solution often results in polybromination, and when brominated in the presence of oxidants, they also get oxidized rather than undergoing substitution and, in some cases, require protection of the amino ($-NH_2$) group.

Table 1: Brominations using CTMATB[a]

Entry	Substrate	Time (min)	Product [b]	Yield [c]
1.		10		72
2.		8		70
3.		15		60
4.		125		80
5.		10		62
6.		60		72
7.		15		74

[a] Reactions were monitored by TLC. [b] Products were characterized by IR, ^{1}H NMR and ^{13}C NMR. [c] Isolated Yields are reported.

APPLICATIONS

Hot-air oven can provide a good option for conducting reactions under solvent-free conditions. [18] However, it is important to also know the thermal stability of the reagent that is involved in these reactions, because the reagent may not be stable at the temperature at which the reaction is conducted, or it might decompose to liberate certain toxic chemicals. This first-ever report of thermal analysis of an organic ammonium tribromide, prior to its use as brominating agent will provide a methodology for thermal analysis of a reagent prior to its use, especially at higher temperature.

CONCLUSION

Cetyltrimethylammonium tribromide (CTMATB) has been synthesized by environmentally friendly method. The thermal stability of the synthesized reagent has then been studied in order to understand the decomposition pattern of the compound, and in consequence of this study, this paper reports solvent-free organic bromination reactions in hot-air oven involving CTMATB.

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