Thermochimica Acta, 152 (1989) 421–425
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF 1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE (MEIC)/ALUMINUM CHLORIDE MOLTEN SALTS

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(Received 6 February 1989)

ABSTRACT

The thermal decomposition of the room temperature molten salt system 1-methyl-3-ethylimidazolium chloride/aluminum chloride has been studied. The decomposition temperatures were determined from TG curves by drawing tangents to the curve. The intersection of the two lines was taken to be the onset of decomposition. The decomposition was a two-step process. The percent weight losses, calculated activation energies and procedural decomposition temperature values obtained indicate that the first step is decomposition of the organic cation. The upper operating temperature of a battery utilizing this system as an electrolyte would be limited by decomposition of the organic fraction of the melt, and was found to be around 270 ° C under the experimental conditions given.

INTRODUCTION

The addition of $AlCl_3$ to 1-methyl-3-ethylimidazolium chloride (MEIC) results in the formation of a room temperature molten salt. The melting point of the salt obtained is dependent on the ratio of inorganic to organic compound [1,2]. The melts are described in terms of their apparent mole fraction N of $AlCl_3$. Salts with $N < 0.50$ are described as 'basic', owing to the presence of the Cl^- anion, whereas salts with $N > 0.50$ are termed 'acidic', owing to the presence of the $Al_2Cl_7^-$ anion.

Current research efforts in our laboratory have focused on the use of these molten salts as battery electrolytes, because of their wide electrochemical window, good conductance properties and potential for high specific energy. The use of this molten salt system as a battery electrolyte has been demonstrated previously [3,4]. Although these melts remain liquid at low temperatures, operation at elevated temperatures of a battery employing them as an electrolyte would be advantageous because of improved transport properties. The upper temperature limits of such melts have not been investigated previously, and are the subject of the current study. Compositions of melts over the range $N = 0.40$–0.60 were analyzed by TG.

EXPERIMENTAL

Preparation of starting materials and melts was performed as described previously [5]. The thermograms were obtained under argon (99.995%) using a Perkin–Elmer TGA 7 TG analyzer. The sample purge was adjusted to 26.4 ml min^{-1} and the balance purge set to 49.1 ml min^{-1}. The TGA 7 was controlled with a Perkin–Elmer 7500 computer. The samples were scanned from 40 to 700 °C at 10 °C min^{-1}. Sample sizes ranged from 20–30 mg. A platinum sample holder was used.

RESULTS AND DISCUSSION

Figure 1 shows a typical thermogram, with its corresponding DTG curve, for a basic melt ($N = 0.45$). The decomposition is a two-step mechanism with overlap between the two processes. Figure 2 shows a thermogram and corresponding DTG curve for an $N = 0.60$ acidic melt. The decomposition of the acidic melt is more complicated than that of the basic melt, with an increase in the overlap of the two processes seen in the basic melt.

Table 1 shows the procedural decomposition temperatures (PDT) for MEIC and the melts over the composition range studied. The onset of decomposition starts with the breakdown of the organic molecule, as shown by the similarity between the PDT values for MEIC and the melts. The percent weight loss for the first transition was determined by means of the differential thermogram. The maximum in the curve was taken to be the plateau for the end of the first transition. Table 2 lists the results of these calculations along with the theoretical percent weight losses for the loss of the organic and inorganic fractions of the melt. The actual percent weight

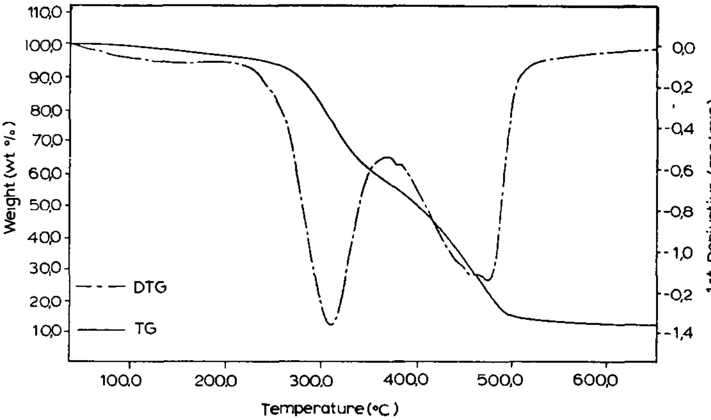

Fig. 1. TG and DTG curves for an $N = 0.45$ melt.

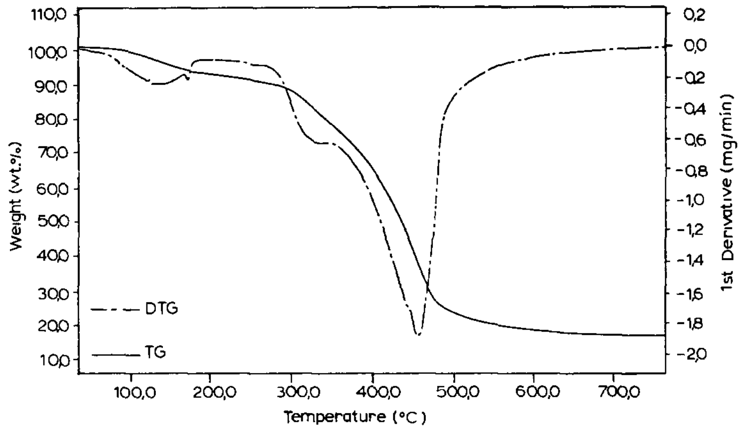

Fig. 2. TG and DTG curves for an $N = 0.60$ melt.

loss shows a similar trend to that for the percent weight loss for the organic fraction of the melt. For the basic melts the percent loss is within 1.5% of the theoretical value for loss of the organic fraction. As the melts become more acidic, the calculated percent loss deviates further from the theoretical value. This is because of a decreased ability to determine a maximum in the DTG curve, caused by an increase in the overlap of the two decomposition

TABLE 1

Procedural decomposition temperature (PDT) values ± standard deviation (SD) for 3 runs

N	PDT ± SD (°C)
0.40	277.9 ± 2.14
0.45	271.3 ± 1.19
0.50	275.2 ± 1.45
0.55	281.3 ± 3.60
0.60	311.8 ± 16.7
MEIC	273.2 ± 2.52

TABLE 2

Percent weight losses: actual (± SD) and theoretical

N	% lost in first step ± SD	% lost if MEIC	% lost if $AlCl_3$
0.40	48.9 ± 0.2	47.2	35.1
0.45	42.3 ± 1.2	43.5	39.3
0.50	35.5 ± 2.3	39.7	43.5
0.55	26.3 ± 0.1	35.4	47.6
0.60	20.6 ± 0.6	32.1	51.7

TABLE 3

Activation energy data ±SD

N	E_a (kcal mol^{-1})±SD	
	Coats and Redfern	Freeman and Carroll
0.40	32.9±0.06	23.0±1.6
0.45	33.6±2.8	26.4±0.23
0.50	21.7±1.5	20.7±1.6
0.55	24.4±2.0	23.1±2.5
0.60	35.0±4.4	28.0±4.7
MEIC	38.3±2.2	36.6±2.5

processes. This overlap also accounts for the increase in the error of the $N = 0.60$ PDT value. Also, the PDT values show that the acidic melts are slightly more stable than the basic melts.

The TG data were subjected to two general methods for the calculation of the activation energy for the first transition of the decomposition: the methods of Freeman and Carroll [6] and Coats and Redfern [7]. The results are shown in Table 3. The results obtained by the two methods are comparable, and are indicative of simple bond breaking in organic molecules. This supports the hypothesis that the first step in the decomposition is breakdown of the organic fraction of the melt. The apparent minimum at $N = 0.5$ may be due to changes in interaction of the organic cation with anions in the melt. At this composition, the melt is described as 'neutral'. The ions present are the organic cation and the $AlCl_4^-$ anion. The calculated activation energy for MEIC is slightly higher than that for the first transition of the melts. The percent weight loss showed stoichiometric loss of MEIC less the chloride ion, which may account for this difference.

CONCLUSIONS

The similarities between the PDT values, the percent weight losses and the activation energies of the melts and MEIC indicate that the first step in the decomposition of the room temperature molten salt MEIC/$AlCl_3$ is decomposition of the organic fraction of the melt. The acidic melts show a more complicated decomposition pattern and are more stable under the experimental conditions given. The upper operating temperature of this molten salt system as an electrolyte in a battery is set by the decomposition of the organic molecule, and is around 270 ° C.

ACKNOWLEDGMENT

The author would like to acknowledge the assistance of Mr. Jeffrey A. Boon, who wrote the computer programs for calculation of the activation energy by the two methods used.

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