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THERMAL STABILITY STUDIES ON SOME METAL SOAPS OF *HURA CREPITANS* SEED OIL

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ABSTRACT

Thermal stability studies on some metal soaps of *Hura crepitans* seed oil prepared by metathesis in aqueous alcohol solution were carried out. The kinetics of the decomposition was studied thermogravimetrically in the temperature range 160 – 200^{o} C. The values of the rate constant are of the order 10^{-2}min^{-1} and temperature-dependent. The enthalpy of activation ($\Delta H^{\ddagger}$) of the initial stage of decomposition determined is in the range 9.8 – 37.8 kJmol^{-1}. The thermal stability of the metal soaps was studied in the temperature range 50 – 600^{o} C under nitrogen using thermogravimetric analyzer (TGA). The thermal stability of the soaps was assessed in terms of temperatures at which various extents of decomposition were attained and weight loss at the initial stage of decomposition. Except zinc soap, the weight loss for the metal soaps was less than 10% at temperature up to 250^{o} C. The results suggest that the metal soaps *Hura crepitans* seed oils could have some industrial applications.

KEYWORDS

Thermal stability, enthalpy of activation, decomposition, industrial applications

INTRODUCTION

The need for sustainable development has made the search for industrial raw materials from renewable sources imperative. Plant materials, particularly seed oils are at the centre of this search due to the fact that many useful products and industrial raw materials are derivable from them [1,2]. However, the characteristics of oils from different sources depend mainly on their composition and no oil from a single source can be suitable for all purposes. Seed oils are natural source of fatty acids that function as raw materials for preparation of many useful products; one of such products is soap. Soaps are generally described as sodium/potassium salts of long chain fatty acids that are soluble in water [3]. However, metallic soaps have been described as alkaline-earth or heavy-metal long-chain carboxylates which are insoluble in water but soluble in non-aqueous solvents [4]. These metal soaps have many industrial applications. Calcium and magnesium soaps are used as corrosion inhibitors in non-polar media; lead, manganese, cobalt and zinc soaps are used in paints to accelerate drying while copper soap exhibits fungicidal properties [5]. Fabrication of poly(vinyl chloride) into useful products at elevated temperature requires the use of thermal stabilizers, soaps of barium, cadmium, lead, calcium and zinc had been used for this purpose [6,7]. Silver carboxylates are used as source of silver in thermographic and photothermographic materials [8] while some other soaps have found use in greases, cosmetics and textiles [9]. Some synthesis of metal nanoparticles had incorporated some fatty acids to prevent the aggregation of the nanoparticles, some of these metal soaps can function as precursor for generating fatty acids that could be useful in the field of nanochemistry.

A number of seed oils have been characterized but the vast majority have not been explored for the preparation of metal carboxylates despite being the most abundant source of fatty acids. Many of the reports on the characterization and properties of metal soaps have been carried out on soaps prepared using pure fatty acids with little attention on the use of triglycerides, inspite of their abunbance and low cost as starting materials for the preparation of metal soaps [10]. *Hura crepitans* seed with oil content of about 51% [11] will serve as excellent source of fatty acids for the production of metal carboxylates.

Hura crepitans (Linn) is an evergreen, monoecious tropical tree of Euphorbiaceae spurge family. It is recognized by the dark, pointed spines and brown bark. These spines have caused it to be called monkey no-climb. It grows up to 100ft and the large ovate leaves grow to two feet wide as such, it is grown as shade tree. It is more wildly known as “sandbox tree” in reference to the use of its unexploded ripe fruits as dispensers of sand to assist in the drying of ink on manuscripts [12]. The fruit is a large capsule with explosive dehiscence containing seeds that are 15 -25mm in diameter.

Presently, the oil of this plant has no commercial value in Nigeria, hence the aim of this work is to prepare some metal soaps from the oil, investigate the thermal stability of the soaps so as to add commercial value to it.

MATERIALS AND METHODS

PREPARATION OF THE METAL SOAPS

The metal soaps *Hura crepitans* seed oil (HSO) were prepared as earlier described [1]. The soaps were dried in oven at 60^{o} C to constant weight. The salts used are (Analar) $BaCl_2.2H_2O$; $CaCl_2.2H_2O$; $CuSO_4.5H_2O$ and $Zn(NO_3)_2.6H_2O$.

THERMAL STABILITY STUDIES ON THE METAL SOAPS

The decomposition of the metal soaps in the temperature range 160 – 200° C was measured gravimetrically as a function of time using the procedure described by Egbuchunam et al.[9]. The residual weight of the sample was measured and the weight loss determined using the expression:

$$\%\text{weight loss} = \frac{w_0 - w_1}{w_0} \times 100$$

Measurement of the thermal properties of metal soaps of HSO were carried out using a Perkin-Elmer TGA 7 thermal gravimetric analyzer under N_2 at the heating rate 10^o min^{-1} in the temperature range 50 – 600° C.

RESULTS AND DISCUSSION

The thermal decomposition rate of metal soaps is generally considered to follow a first order kinetics [9,13] and may be expressed as follows:

$$\frac{dw}{dt} = k(w_0 - w_1) \qquad (1)$$

where w_0 is the initial weight of the metal soap and w_1 is the residual weight of the metal soap after heating while k is the rate constant. Rearranging and integrating (1) gave

$$\log(w_o - w_l) = \log w_o - \frac{kt}{2.303} \qquad (2)$$

The values of the rate constant for the decomposition of the metal soaps were obtained from the plots of logarithm of %weight loss against time and the result presented in Table 1.

Table 1: Rate constants for the decomposition of metal soaps of *Hura crepitans* seed oil

Metal Soap	Temperature (°C)	Rate constant ($k \times 10^2 min^{-1}$)
Zn-HSO	160	0.97
	180	1.43
	200	1.16
Cu-HSO	160	0.90
	180	1.59
	200	1.62
Ca-HSO	160	0.53
	180	0.82
	200	0.88
Ba-HSO	160	0.55
	180	0.43
	200	0.76

The rate constant are of the order $10^{-2}min^{-1}$ and are also temperature-dependent with increase of 19.6%, 66.0%, 80.0% and 38.2% within the temperature range for Zn soap, Ca soap, Cu soap and Ba soap respectively. These values are higher than values reported earlier for similar soaps of *Trichosanthes cucumerina* [1], although the trend is similar. This difference could be due to difference in experimental condition, nature of fatty acids of the oil or both. Rate constant represents the measure of energy barrier a reaction needs to overcome, the smaller the barrier, the greater the rate constant [3]. From the dependence of the values of the rate constant on the temperature, values for the activation energy (E_a) of the decomposition of the metal soaps were calculated using the relationship:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \qquad (3)$$

and the result presented in Table 2.

Table 2: Thermodynamic parameters for the decomposition of metal soaps of *Hura crepitans* seed oils

Metal Soap	E_a (kJmol^{-1})	($\Delta H^{\ddagger}$) (kJmol^{-1})
Zn-HSO	41.8	37.8
Cu-HSO	31.7	27.7
Ca-HSO	25.0	21.1
Ba-HSO	13.8	9.8

The activation energy for the decomposition of the metal soaps range from 13.8 – 41.8 kJmol^{-1}. Barium soap has the least value of 13.8 kJmol^{-1} while Zinc soap has the highest value of 41.8 kJmol^{-1}. The values for copper and calcium soaps are 31.7 and 25.0 kJmol^{-1} respectively.

These values are comparable with values reported for metal soaps of rubber seed oil [13], Snake gourd seed oil [1] and indicate potential industrial application of these metal soaps. The values of the enthalpy of activation, $\Delta H^{\ddagger}$, for the decomposition of the metal carboxylates was calculated using the expression: $\Delta H^{\ddagger} = E_a - RT$ and the result presented in Table 2. The values of the enthalpy of activation indicate that the process is endothermic.

The decomposition of metal carboxylates is a multi-stage process that involved the formation of carboxylic acids, metal oxides, carbondioxide and alkenes [8,14]. The number and nature of the phase transitions depend on the alkyl chain length of the carboxylic acids. The thermal decomposition patterns of the metal soaps are presented in Figure 1.

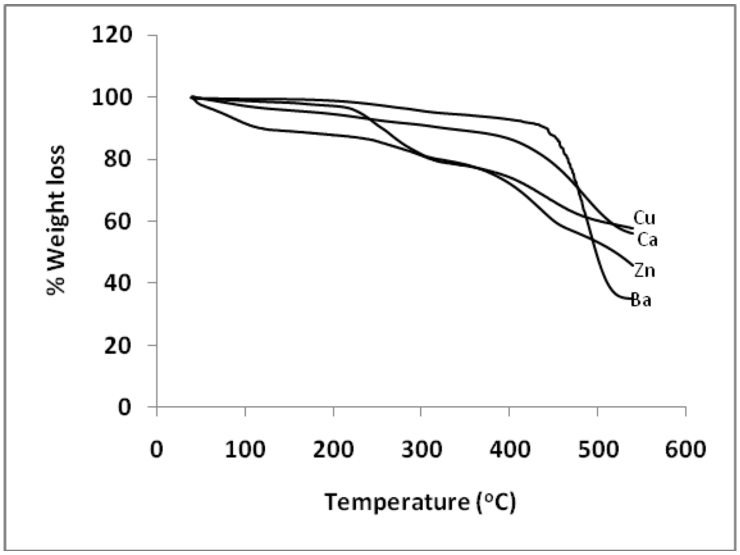

Figure 1: Thermogram of some metal soaps of *Hura crepitans* seed oil

These patterns are similar to previous reports for metal soaps of rubber seed oil [13]; metal soaps of *Ximenia americana* and *Balanites aegyptiaca* seed oils [2]. The thermal stability of the metal soaps was evaluated from the temperatures at which various extents of decomposition occurred and the residual weight of the soaps at 500° C (Table 3) and percentage weight loss at temperature up 250° C (Table 4). Weight loss of up to 2% is frequently attributed to loss of moisture associated with the soaps. At 5%-10% conversion, the result in Table 3 shows that the stability of the soaps is in the order Ba-HSO>Ca-HSO>Cu-HSO>Zn-HSO. At 30% conversion, the thermal stability order is Ca-HSO>Ba-HSO>Zn-HSO>Cu-HSO.

Table 3: Evaluation of thermal stability of the metal soaps: Temperatures at which various extents of decomposition were attained and %Residual weight at the end of decomposition.

Metal soap	Temperature at which decomposition was attained (°C)					RW (%) at 500° C
	1%	2%	5%	10%	30%	
Zn-HSO	52.9	61.6	91.3	131.6	460.2	63.8
Cu-HSO	90.8	150.2	210.4	250.4	402.6	68.9
Ca-HSO	80.0	100.3	203.6	353.2	514.8	74.2
Ba-HSO	160.1	205.6	300.9	411.3	476.4	46.2

RW = Residual Weight

The weight loss occurring at temperatures up to 250° C is less than 10% for the soaps except Zn-HSO (Table 4). Thus, the results show that the thermal stability of metal soaps of HSO are comparable with the stability of soaps of *Ximenia americana* and *Balanites aegyptiaca* seed oils [2] and those of metal soaps of stearic acids within the temperature range (170 – 220° C) frequently used in processing of PVC [13]. The residual weights of the metal soaps at 500° C which could be oxides or carbonates of the respective metals [15] was highest for Ca-HSO (74%) and least for Ba-HSO (46%).

Table 4: % Weight loss of metal soaps at temperature up to 250° C

Metal Soap	%Weight loss
Zn-HSO	13.1
Cu-HSO	9.2
Ca-HSO	6.5
Ba-HSO	2.5

CONCLUSION

Thermal stability studies on barium, calcium, copper and zinc soaps of *Hura crepitans* seed oil prepared by metathesis in alcohol solution was carried out. The results show that metal soaps of the seed oil are fairly stable with Ba-HSO being the most stable followed by Ca-HSO and Cu-HSO while Zn-HSO is the least stable. Based on these results, these metal soaps could be useful as PVC thermal stabilizers and other applications requiring the use of metal soaps even at relatively high temperatures.

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