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STUDIES ON BERYLLIUM SOAPS. INFRARED ABSORPTION SPECTRA AND THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

The infrared absorption spectra of beryllium soaps were compared with those of the fatty acids. The results confirm that the fatty acids exist as dimers, whereas the metal-to-oxygen bonds in beryllium soaps have some ionic character. The thermal decomposition of these soaps is kinetically a reaction of zero order and the energy of activation lies in the range 1–9 kcal $mole^{-1}$.

INTRODUCTION

The alkaline earth metal soaps have found wide application in industry as lubricants, greases, plasticizers, stabilizers, softners, candle hardners, detergents, catalysts, medicines, cosmetics, emulsifying and waterproofing agents. The physicochemical characteristics of magnesium, calcium, strontium and barium soaps have been thoroughly investigated but the references to beryllium soaps are limited [1–4]. Exact information on the nature and structure of metal soaps is of great importance for their use in industry and so it was decided to study the properties of beryllium soaps in the solid state as well as in solution. The present paper deals with the study of infrared absorption spectra and thermogravimetric analysis of the myristate, palmitate and stearate of beryllium.

EXPERIMENTAL

The soaps were prepared by the direct metathesis of the corresponding sodium soaps with a solution of beryllium nitrate in aqueous ethanol at 50–55°C under vigorous stirring. The precipitated soaps were washed with distilled water and finally with ethanol to remove the free precipitant and acid, respectively. The soaps were purified by recrystallization, dried by suction pump and stored over anhydrous calcium chloride. The absence of hydroxy groups and water in the soaps was confirmed by studying their

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TABLE 1

Analysis of the beryllium soaps used

Soap	Carbon (%)		Hydrogen (%)	
	Found	Calcd.	Found	Calcd.
Myristate	72.0	72.5	11.5	11.7
Palmitate	73.0	73.9	11.9	12.0
Stearate	74.0	75.0	12.0	12.2

infrared absorption spectra. The melting points of the purified soaps were myristate 112–116°C, palmitate 135–136°C and stearate 43–44°C.

The soaps were also analyzed for carbon, hydrogen and metal contents. The metal content was estimated as beryllium oxide [5]. The results of analysis were found to be in agreement with the theoretical calculated values as shown in Table 1. The reproducibility of the results was checked by preparing two samples of the soaps under similar conditions.

The infrared absorption spectra of the beryllium soaps and the corresponding fatty acids were produced with a Perkin Elmer Model 577 grating spectrophotometer using the potassium bromide disc method. The thermogravimetric analysis was carried out at a constant rate of heating, 10°C min^{-1}, in a thermobalance manufactured by the Fertilizer Corporation of India, Sindri.

RESULTS AND DISCUSSION

The wave numbers of the absorption maxima in the spectra of the fatty acids and the beryllium soaps were assigned and are tabulated in Table 2. The absorption maxima characteristics of the aliphatic portion of the acid molecule remained unchanged on going from the acid to the soap. The absorption maxima at 2650, 1700, 1433 and 940 cm^{-1} in the spectra of the fatty acids are associated with the carboxyl group of the acid molecule in the dimeric state and confirm the presence of hydrogen bonds between two molecules of the fatty acid. The complete disappearance of the strong absorption near 1700 cm^{-1} in the spectra of the beryllium soaps indicates that there is complete resonance in the two C–O bonds of carboxyl group of the soap molecule and the group has the structure

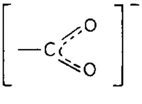

TABLE 2

Frequencies (cm^{-1}) of absorption maxima with their assignments

Assignment	Stearic acid	Myristate	Palmitate	Stearate
CH_2, C–H antisym. stretch.	2920vs	2920vs	2910vs	2915vs
CH_2, C–H sym. stretch.	2850s	2850s	2840s	2840s
OH, stretch.	2650vs			
C=O, stretch.	1700vs			
COO^-, C–O antisym. stretch.		1610vs	1615vs	1615vs
CH_2, deform.	1468m	1475m	1480m	1480w
COO^-, C–O sym. stretch.		1465s	1465s	1475s
C–O stretch., O–H in plane deform.	1433m			
CH_2 (adjacent to COOH group) deform.	1412m			
CH_3 sym. deform.	1350w	1350w	1335w	1325w
Progressive bands (CH_2 twist. and wag.)	1350–1202w	1320–1200w	1320–1185w	1320–1180w
CH_3 rocking	1110w	1115m	1110m	1110vm
OH out-of-plane deform.	940m			
Be–O bond		810s	810s	815s
CH_2 rocking	720m	725m	715m	715mw
COOH bending mode	689s			
COOH wagging mode	550s			

Key to abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

The appearance of two absorption bands at 1475–1465 cm^{-1} and 1615–1610 cm^{-1} corresponding to the symmetric and antisymmetric vibrations of the carboxylate ion in the spectra of beryllium soaps instead of one band at 1700 cm^{-1} confirms that these soaps are partly ionic in nature and the metal-to-oxygen bonds in beryllium soaps have some ionic character. The absorption maxima corresponding to the antisymmetric vibration of the carboxylate ion were not observed in the spectra of the fatty acids, but there appeared the C=O stretching band at 1700 cm^{-1}. The absorptions observed at 2650, 1433 and 940 cm^{-1} corresponding to the OH group in the spectra of acids disappeared in the spectra of the beryllium soaps. The absorption maxima observed at 810 cm^{-1} in the spectra of the beryllium soaps were assigned to the Be–O bond. The assigned frequencies are in agreement with the results of other workers [6–8].

The results confirm that the fatty acids in the solid state exist with a dimeric structure through hydrogen bonding between the carboxyl groups of two acid molecules, whereas the beryllium soaps are partly ionic in nature and the metal-to-oxygen bonds in these soaps have partly ionic character.

The results of the thermogravimetric analysis are recorded in Table 3. The final residue on heating the beryllium soaps was beryllium oxide and the weights of the residues were in agreement with the theoretically calculated weights of beryllium oxide from the molecular formula of the corresponding soap. A white crystalline substance was found condensed on the cold part of the sample tube surrounding the soap and it was identified as myristone (m.p. 78°C), palmitone (m.p. 82.8°C) and stearone (m.p. 88.4°C) in the cases of beryllium myristate, palmitate and stearate, respectively. The thermal decomposition of beryllium soaps can be represented as

$$(RCOO)_2Be \rightarrow RCOR + BeO + CO_2$$

where R is $C_{13}H_{27}$, $C_{15}H_{31}$ and $C_{17}H_{35}$ for myristate, palmitate and stearate, respectively.

The results of the thermal decomposition of soaps (Fig. 1) were explained in terms of Freeman and Carroll's rate expression [9]

$$\frac{\Delta \log(\mathrm{d}w/\mathrm{d}t)}{\Delta \log W_{\mathrm{r}}} = -\frac{E}{2.303\,R} \cdot \frac{\Delta(1/T)}{\Delta \log W_{\mathrm{r}}} + n$$

where E = energy of activation, n = order of reaction, W_{r} = difference between the total loss in weight and loss in weight at time t, i.e. $W_0 - W_t$, and $(\mathrm{d}w/\mathrm{d}t)$ = rate of weight loss obtained from the loss in weight vs. time curves at appropriate times.

The values of the rate of weight loss were obtained from the plots of the loss in weight of the soap, w, against time, t, by drawing tangents at appropriate times. The values of W_{r} were calculated from the total loss in weight of the soap and the loss at predetermined times and then the plots of $\Delta \log(\mathrm{d}w/\mathrm{d}t)/\Delta \log W_{\mathrm{r}}$ vs. $\Delta(1/T)/\Delta \log W_{\mathrm{r}}$ were obtained (Fig. 2). The

TABLE 3

Thermogravimetric analysis of beryllium soaps

Time (min)	Loss in weight (mg)		
	Stearate	Palmitate	Myristate
11.5			4.5
22.0			9.5
22.5	2.0	4.0	10.0
25.0	3.0	6.0	11.5
27.0	5.0	9.0	13.0
27.5	5.0		
29.0	6.0	11.0	14.0
30.0	7.0	13.0	15.0
32.0	9.0	15.0	16.5
32.5	9.0		17.5
34.0	11.0	19.0	18.5
35.0	12.0	20.0	19.5
37.5	16.0	30.0	22.0
39.5	21.0	39.0	24.5
41.0	26.0	105.5	26.5
42.5	32.0	106.0	29.0
43.5	41.0	107.0	30.0
44.5	55.0	108.0	31.5
46.0			33.5
49.0			41.0
51.0			47.0
52.5			52.0
54.0			52.7

energies of activation for the decomposition of beryllium myristate, palmitate and stearate were found to be 2.2, 7.1 and 8.8 kcal mole^{-1}, respectively, and the order of the decomposition reaction is zero. The energies of activation were also calculated using the Coats and Redfern equation for a zero-order reaction [10]

$$\log\frac{\alpha}{T^2} = \log\frac{AR}{aE}\left[1-\frac{2\dot{R}T}{E}\right] - \frac{E}{2.303\,RT}$$

where α, a, A and E are the fraction of the soap decomposed, the rate of heating (°C min^{-1}), the frequency factor and the energy of activation, respectively.

The values of the energy of activation were also calculated from the plots of $\log(\alpha/T^2)$ vs. $1/T$ and were found 1.4, 6.9 and 7.0 kcal mole^{-1} for beryllium myristate, palmitate and stearate, respectively. The results are in agreement with the values obtained by using the Freeman and Carroll equation. The activation energies for the decomposition of other metal soaps

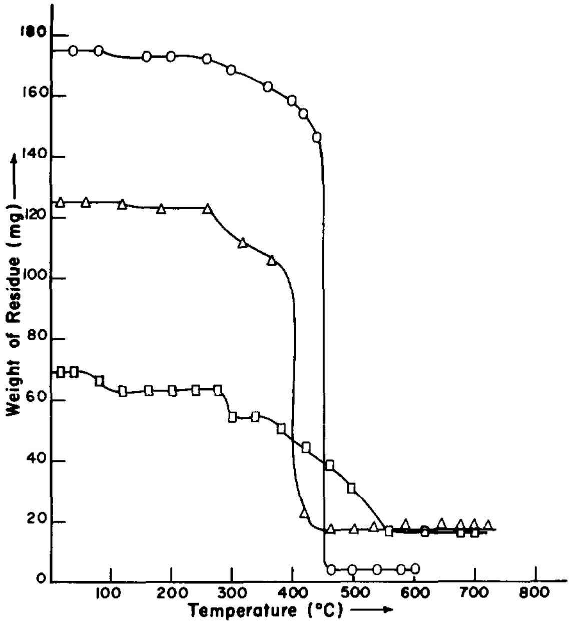

Fig. 1. Thermogravimetric analysis of beryllium soaps. □, Myristate; △, palmitate; ○, stearate.

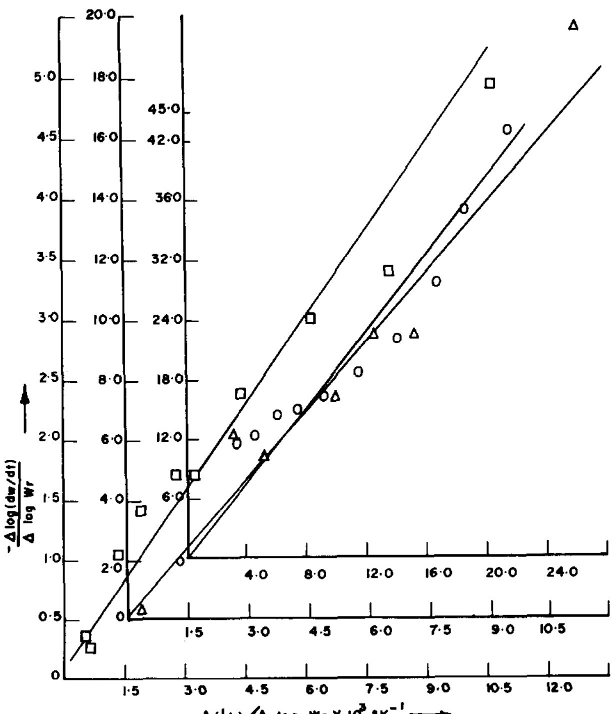

Fig. 2. Freeman and Carroll plots. □, Myristate; △ palmitate; ○, stearate.

were also found to lie in the range 3–9 kcal $mole^{-1}$ and were almost independent of the nature of the cation and anion in the soap molecule [11]. It is concluded that the decomposition reaction of these soaps is kinetically of zero order and the energy of activation for the process lies in the range 1–9 kcal $mole^{-1}$.

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