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On thermal decomposition of sodium palmitate in restricted environment

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ABSTRACT

The possibility of using metal salts of fatty acids as carriers of metal atoms for delivery at specific sites is examined while taking sodium palmitate as an example. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Metal salts;
Fatty acids;
Thermal decomposition;
Metal atom delivery.

INTRODUCTION

The melting temperatures (T_m) of metal salts of palmitic acid (briefly metal palmitates) are spread over a wide range. The T_m of cobalt palmitate^[1] is lowest (70-75°C) and that of sodium palmitate^[2] is highest (285-290°C) T_m . It seems that metal palmitates may be used as carriers of metal ions, for delivery at any specific region of a given environment. For such requirement, it is necessary that palmitate component should be carbonizable at elevated temperatures, preferably allowing (or forcing) the metal palmitate to be in solid state. (High pressure techniques may be used for elevating T_m). Before taking up such studies, it was felt desirable to investigate the carbonization of palmitate component vis-à-vis composition of initial reaction mixture. Consequently, a constant quantity of palmitic acid and different quantities of sodium hydroxide were reacted. So that, in certain cases excess palmitic acid and in certain cases excess sodium hydroxide were present. The results of the study are presented in the present report.

MATERIALS AND METHODS

High purity sodium hydroxide (Ranbaxy made) and palmitic acid (Lobachemie) were used in the synthesis of sodium palmitate. Palmitic acid was taken in ceramic crucible and slowly heated to a temperature that was 20°C above the T_m . Powdered NaOH was added to the molten palmitic acid with stirring, which led to spontaneous formation of sodium palmitate. Non-stoichiometric of NaOH was used. The ratio of gram molecular weight of palmitic acid to NaOH = (256.43)/(40.00) = 6.41. In all the cases, 5 gms of palmitic acid was used. The required NaOH for complete neutralization of palmitic acid is = 5/(0.641) = 0.779 gms. As such, the quantities of NaOH used were either larger or smaller than 0.779 gms (TABLE 1). A factor K was defined such that,

$$K = (-) [(NaOH)_n - (NaOH)_u] / [(NaOH)_n]$$

where subscripts n and u stand for 'needed' and 'used' respectively. The value of K was estimated in each case (TABLE 1).

The sodium palmitate recovered from the crucible was a white hard lump. The powdered samples were

TABLE 1 : Composition of mixtures

S.No	(NaOH) _n gms	(NaOH) _n gms	Difference	K
1	0.779	0.61	(+)0.169	(-)0.216
2	0.779	1.22	(-)0.441	(+)0.566
3	0.779	2.44	(-)1.66	(+)2.132
4	0.779	0.220	(+)0.559	(-)0.71
5	0.779	0.430	(+)0.349	(-)0.448

slowly heated on a hot stage (fitted with a magnifier), whose temperature was measured with a Hg thermometer (up to 320°C) and a thermocouple based temperature indicator.

The temperature at which samples were becoming (i) brownish (ii) dark brownish, (iii) blakish (carbonization), (iv) melting and (v) softening (detected via changes in the shape of the grains due to minute flattening) were recorded. The data is shown as a function of K (Figure 1). In order to use a reference (amorphous organic material), maize powder was also heat treated in the same way, as that of the sodium palmitate mixtures and the related data is shown in Figure 1.

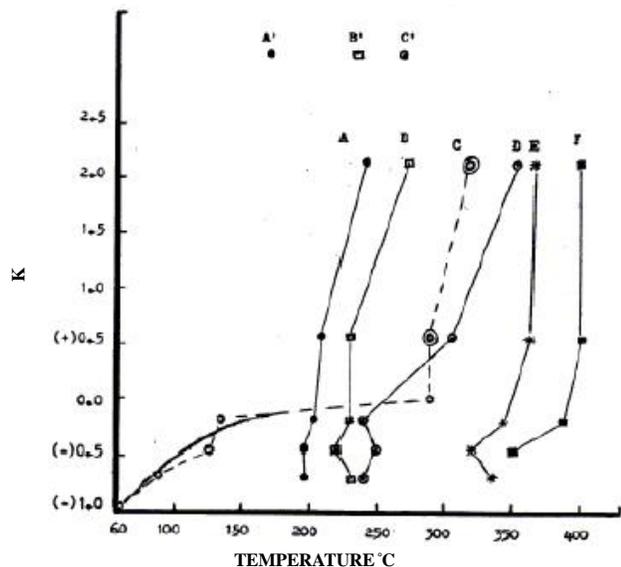


Figure 1 : Temperature vs K in case of sodium palmitate. (A) turning to brownish. (B) turning to dark brownish. (C) melting (the double circles stand for softening). (D) carbonization (E&F) oxidation. Case of maize powder (points are at the top): (A') turning to brownish, (B') Turning to dark brownish. (C') Carbonization

OBSERVATION AND DISCUSSION

The melting behaviour of the mixture in the range of

K = -1 to 0 is due to the presence of free fatty acid. Extrapolation of the curve to the T_m of pure sodium palmitate^[2] gives almost an exponential curve, where the T_m and K can be connected by

$$T_m = Ce^{\zeta(1+K)}$$

where C = 62 and $\zeta = 0.677$. Above K = 0, the mixture did not melt, but showed symptoms of softening. The temperature where fatty acid component was converted into carbon was almost constant below K = 0 and matched with the value of maize powder. However, above K = 0, the carbonization temperature increased sharply and touched 350°C for K = +2.1. Also, above K = 0, the oxidation temperature was fairly constant (maize carbon remained stable at 400°C), with out any signs of oxidation).

It may be noted that carbonization temperature increased from +0.5 to 2.21. It may be an indication that modification of the (packing) environment of palmitate component leads to a shift in carbonization temperature. In the present case, it seems that excess NaOH may be shielding the metal palmitate molecules, such that the carbonization temperature is pushed towards higher side (curve D in Figure 1). In the actual case, NaOH shall be replaced by the proper matrix material, into which a special metal atom has to be delivered.

It is shown^[2-4] that sodium carboxylates (in the range of $(C_2 - C_{12})$) decomposes to sodium carbonate at 350-360°C and also to sodium oxide at about 760°C, and that carbonate and oxide decomposes very rapidly in vacuum^[5,6]. Further, decomposition of metal carbonate into carbon dioxide and metal oxide depends on the electro-positivity of the metal^[2]; consequently, thermal stability decreases^[2] as Na>Ca>Fe>Mn etc. Therefore, if decomposition of palmitate component into CO₂ is restricted (in an oxygen-less environment), then the two oxygen atoms, associated with the palmitate component are the only oxygens available for formation of metal oxide, which however can be decomposed^[2]. Therefore, it seems plausible that palmitates (and perhaps also stearates) may be useful as carriers of metal atoms for delivery at specific sites.

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