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THERMAL BEHAVIOUR OF MILK POWDERS STUDIED BY DIFFERENTIAL THERMAL ANALYSIS AND HEAT FLOW CALORIMETRY

A. RAEMY *, R.F. HURRELL and J. LÖLIGER

Research Department, Nestlé Products Technical Assistance Co. Ltd., CH-1814 La Tour de Peilz (Switzerland)

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ABSTRACT

The technique of heat flow calorimetry was used to study the thermal behaviour of different milk powders above 20°C. Exothermic reactions of different types occurred when measurements were made with the samples in sealed cells. According to our interpretation of the calorimetric curves, these reactions correspond to: crystallization of amorphous lactose, Maillard reaction between milk proteins and lactose, oxidation of milk fat and decomposition of lactose. Their relative importance is discussed. In addition, the technique of high-pressure differential thermal analysis was used for studying spontaneous ignition and combustion of milk powders, under a large oxygen excess. The role of fat, carbohydrate and protein decomposition is underlined. Some self-ignition temperature values are given.

INTRODUCTION

Our interest in examining the thermal behaviour of milk powder by thermal analysis techniques lies especially in the detection of early exothermic phenomena. Such reactions are often related to the deterioration or decomposition of the product. A better knowledge of the reasons for their occurrence may be useful in preventing product deterioration or even in establishing safe food processing conditions.

Even weak reactions induced by heat treatments or long storage under unfavourable conditions can lead to important modifications of product properties such as reconstitutability, solubility, homogeneity, nutritional value or colour. Organoleptic deterioration can also occur due, for instance, to fat oxidation. Because of their high sensitivity, thermal analysis techniques detect even low-energy phenomena. They can help to evaluate the relative importance of these phenomena and the temperature range in which they appear. The difficulties of making such measurements are due to the

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* To whom all correspondence should be addressed.

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simultaneous appearance of different phenomena and their dependence on the surrounding atmosphere.

Another aim of these thermal behaviour studies was to understand why and how some industrial high temperature operations can present a fire risk. Thermal analysis techniques also give information about intense exothermic phenomena and even about spontaneous ignition of powder layers. The background to the problem of self-ignition of powders in the dairy industry, particularly during spray-drying, has already been outlined by Duane and Synnott [1].

Finally, we have tried to evaluate the influence of each main constituent of milk powders (protein, fat and carbohydrate) on their thermal behaviour and stability.

EXPERIMENTAL

The principles and methods of thermal analysis are described exhaustively in many books [2–5]. For the present study, heat flow calorimetry was used [6–8].

For the measurements under non-burning conditions, the instrument was a Setaram C80 heat flow calorimeter; a schematic representation of this apparatus is given elsewhere [9].

Sealed cells capable of supporting a pressure increase of up to 100 bar were used. Temperature change was programmed at 1°C $\min^{-1}$ from ambient to about 270°C. The samples were heated in an atmosphere of air and of their own volatiles. In some cases an atmosphere of argon was used. The instrument allowed the analysis of relatively large quantities, generally 1 g, of instant milk powder.

The use of sealed cells prevents endothermic phenomena such as vaporization of the water remaining in the powder. Furthermore, modification of the vapour-phase pressure above the sample, during the measurement, can maintain the sample in a condensed phase at temperatures higher than its usual boiling point. Exothermic reactions, corresponding to sample decomposition can thus be detected [10].

In addition, the technique of differential thermal analysis (DTA) was used, in an original way, for studying spontaneous ignition of milk powder and milk constituents. The measurements were performed with a special high-pressure DTA instrument from Netzsch [9].

As has been shown recently [11–13], self-ignition temperatures can be obtained by using DTA under burning conditions. In our case, the samples were generally heated under 25 bar of oxygen at a rate of 2.5°C $\min^{-1}$.

Samples

Two of the milk products were commercially available. These were a spray-dried adapted milk-based infant formula having a proximate composi-

TABLE 1

Composition and reaction enthalpies of some milk powder samples

Samples	Composition (%)			Reaction enthalpies (J g^{-1})		
	Carbo hydrate	Protein (%N × 6.38)	Lipid	Peak 1 α-Lactose cryst.	Peak 2 Maillard + oxid.	Peak 3 C.H. decomposition
Crystalline lactose	100					700
Amorphous lactose	100			85		700
Butter fat			~ 100	5	15	45
Casein		~ 100			10	
Whey protein		~ 100			1	
Casein–lactose m. 1	~ 20	~ 80		5	65	80
Casein–lactose m. 2	~ 40	~ 60		20	80	220
Casein–lactose m. 3	~ 60	~ 40		50	50	400
Casein–lactose m. 4	~ 80	~ 20		70	40	500
Infant formula	55	12	26	30	60	350
Whole milk powder	38	26	26	10	70	250
Milk powder a	48	36	2		110	320
Milk powder b	44	32	14		100	280
Milk powder c	39	29	22		90	240
Milk powder d	32	24	37		80	190

tion similar to human milk and a spray-dried whole milk powder.

Milk powders (a,b,c,d) containing variable amounts of milk fat were prepared by mixing totally skimmed liquid milk (approximately 50 kg for each run) with cream (of about 35% fat). The mixes were pasteurized (105°C, 10 s), preconcentrated to 37% DM (evaporator at 95°C, product at 21–24°C under a vacuum of 17 mm Hg during 50 min). After homogenization (60°C, 150 bar), the milks were spray-dried to a fine powder containing 2% humidity.

Fat and defatted infant formula were obtained by Soxhlet extraction of the milk-based infant formula with chloroform/methanol (2 : 1, v/v) for 3 h.

Milk constituents such as lactose or casein were purchased from chemical companies. The mixtures of casein and lactose were obtained by freeze-drying dilute solutions of both constituents in water. In such a way, intimate contact between protein and lactose was guaranteed. The casein–lactose mixture 1 (see Table 1), for example, was obtained by mixing 2 g lactose and 8 g casein with 90 g water. The solution was then freeze-dried. The composition of the other mixtures and of most samples is given in Table 1. Binary mixtures of casein and oil, or lactose and oil were prepared and analysed as such.

RESULTS AND DISCUSSION

Figure 1 shows the calorimetric curves of a milk-based infant formula and of whole milk powder. Each curve shows three poorly-resolved exothermic peaks. These peaks are thought to be caused by four main types of reactions: crystallization of amorphous lactose, Maillard reactions between protein and lactose, oxidation of milk fat and decomposition of lactose. Calorimetric curves of the main milk constituents (fat, lactose, protein) and of binary mixtures have been used to justify this interpretation. Table 1 presents the main constituents of each sample and the corresponding enthalpies for the peaks observed. As there are no comparable values available, and because of poor peak resolution, our enthalpy values must be considered as approximate.

Carbohydrate decomposition

Figure 2 shows the thermal behaviour of crystalline α-lactose, β-lactose and α-lactose monohydrate. The exothermic phenomena after fusion correspond to decomposition or pyrolysis of the lactose, the enthalpy (about 700 J g^{-1}) is similar to that of the third exothermic peak in both calorimetric curves of milk products (when related to the respective content of lactose). The most energetic peak appearing above 170°C of the calorimetric curves of milk products can therefore be attributed to lactose decomposition: it also varies in intensity with lactose content.

The thermal decomposition of different carbohydrates has already been studied in the same way [14]. Apart from sugar alcohols (e.g. xylitol,

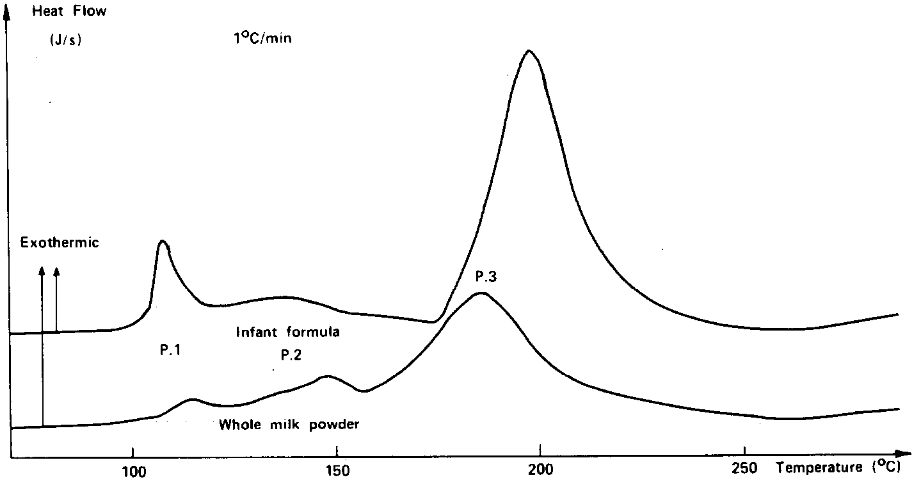

Fig. 1. Calorimetric curves of a milk-based infant formula and whole milk powder (both heated in sealed cells).

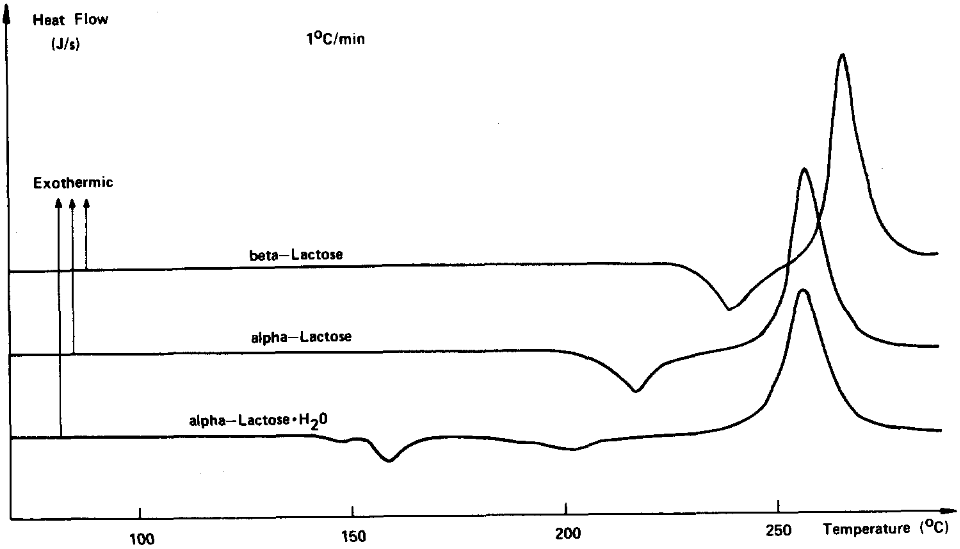

Fig. 2. Calorimetric curves of crystalline lactose (heated in sealed cells).

sorbitol) and cyclitols (myo-inositol) which exhibited only an endothermic peak, corresponding to their melting, all carbohydrates showed an exothermic decomposition. Such intense exothermic phenomena have also been observed with other foods containing a large proportion of carbohydrate such as chicory, coffee [15] and cereals [16].

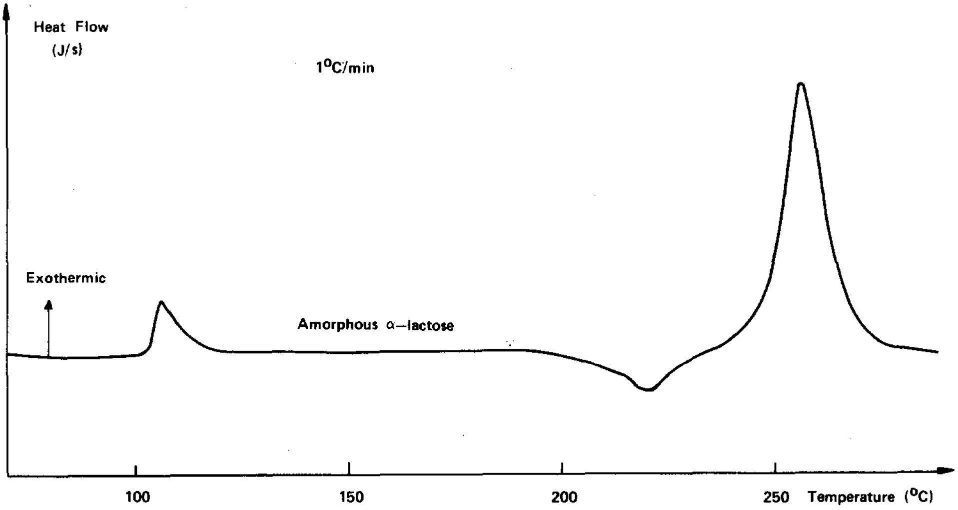

Fig. 3. Calorimetric curves of amorphous α-lactose (heated in sealed cells).

Crystallization of amorphous lactose

In milk products, lactose can be found either in two amorphous states (α or β) or in three crystalline states (anhydrous α or β, hydrated α). Depending on the processing or storage conditions, the presence of crystalline lactose can be a result of a carefully designed process or, most often, be unintentional or even unwanted. Lactose crystals can affect the homogeneity and solubility of dry dairy products.

Figure 3 shows the calorimetric curve of amorphous lactose. The exothermic peak appearing at temperatures around 70 to 120°C is due to the crystallization of amorphous lactose into anhydrous α-lactose. The first exothermic peak present in each calorimetric curve of Fig. 1 can therefore be attributed mainly to lactose crystallization.

To and Flink [17] have already shown that calorimetric techniques can give information on carbohydrate (e.g. sucrose) crystallization. Methods based on thermal analysis were also proposed [18–20] for the determination of crystalline lactose in milk products; they were founded on endothermic phenomena like fusion and water vaporization. Further experiments have shown that the calorimetric curves change, depending on whether lactose is in the α or β anomeric forms, amorphous, or crystalline [21].

Fat oxidation

The second peak in Fig. 1 is flat and broad; it certainly cannot be attributed to one effect only. Other workers have shown [22] that the

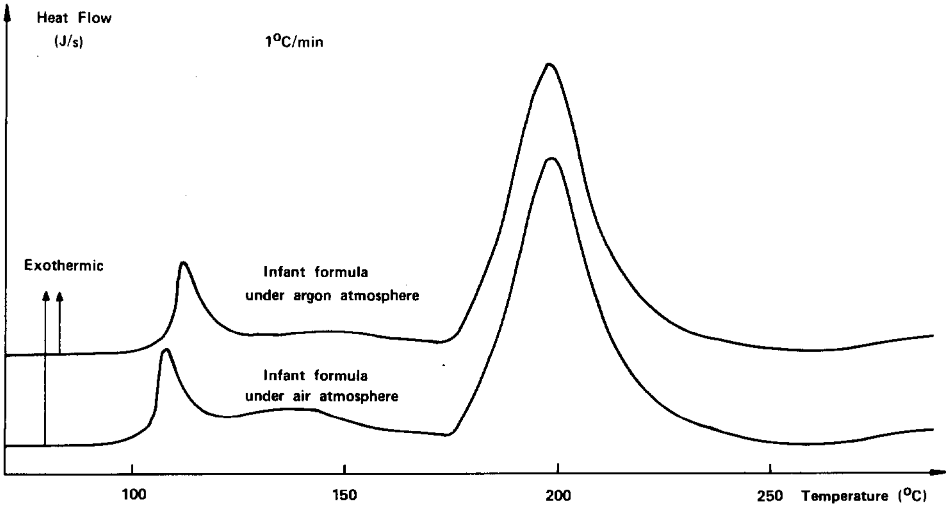

Fig. 4. Calorimetric curves of a milk-based infant formula under air and argon atmospheres (heated in sealed cells).

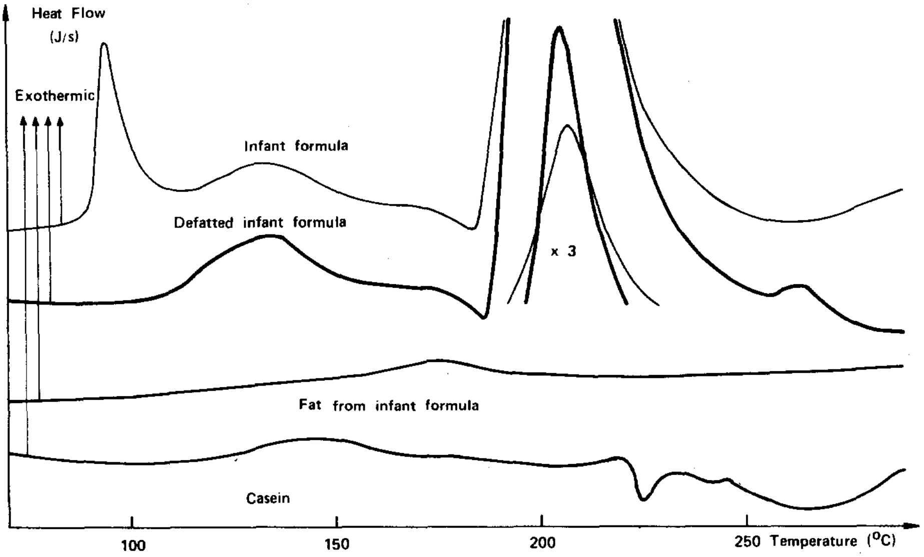

Fig. 5. Calorimetric curves of an infant formula, defatted infant formula, casein and fat extracted from an infant formula. The samples were heated in sealed cells.

oxidation reaction of lipids is associated with an exothermic phenomenon between 100 and 170°C. Figure 4 shows the calorimetric curves of the same milk product under air atmosphere and under argon atmosphere. It can be seen that the second peak (between 110 and 170°C) varies with oxygen concentration. It seems, therefore, that at least part of this second peak can be attributed to fat oxidation. Figure 5 shows the calorimetric curves of the milk-based infant formula before and after Soxhlet defatting (the lactose crystallization peak having disappeared because of the heat treatments), of the extracted fat and casein. It confirms that fat oxidation contributes to the high-temperature part of the peak but that another important phenomenon also takes place in this temperature range.

The rate of reaction, particularly during the initiation phase [23] is very low, so only very sensitive detection systems will be able to detect the thermal release. At the same time, during thermal treatment of multicomponent mixes of carbohydrates, fats and proteins, the formation of browning products can be observed [24]. These browning products are inhibitors of oxidation reactions and therefore counteract the oxidative degradation of the lipids. Pro-oxidant catalysts which accelerate the oxidation reaction may also be present and the net reaction due to the oxidation of lipids during the propagation phase of the autoxidation reaction [23] is normally sufficiently exothermic to be detected.

Maillard reactions

Maillard reactions [25,26] between proteins and reducing sugars are the major cause of browning and nutritional damage during the heating or

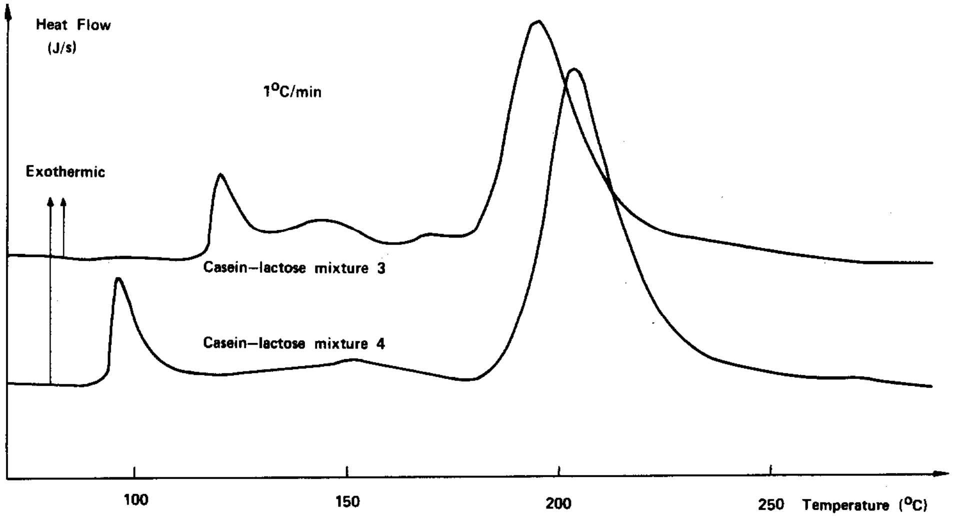

Fig. 6. Calorimetric curves of casein–lactose mixtures (heated in sealed cells). For composition, see Table 1.

prolonged storage of foods. They are also important in flavour production. The Maillard reactions occur during the baking of bread, the production of breakfast cereals, the heating of meats and, most importantly, during the processing of milk products since milk is the major naturally-occurring protein food that has a high content of reducing sugar.

To identify their influence on the calorimetric curves of milk powders, we have analysed some freeze-dried aqueous mixtures of casein and lactose. Figures 6 and 7 show calorimetric curves of such mixtures; the first ex-

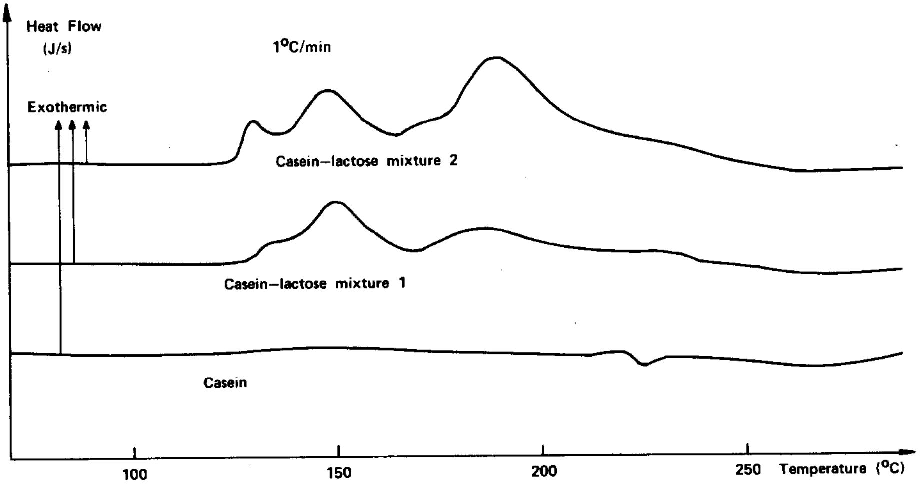

Fig. 7. Calorimetric curves of casein–lactose mixtures and casein (heated in sealed cells). For composition, see Table 1.

othermic peak can again be attributed to lactose crystallization, but the second peak (between about 100 and 160°C) can be attributed to Maillard reactions. Other binary mixtures (oil–lactose; oil–casein) gave no real exothermic effect. It seems therefore, that the second peak in the calorimetric curves of milk powders can also be attributed in part to Maillard reactions between milk proteins and lactose. Under a restricted air atmosphere, the contribution of these reactions to the low temperature part of the second peak is more important than that of fat oxidation.

Spontaneous ignition and combustion

Further investigations were made to evaluate the role of oxygen in the spontaneous ignition of milk powders. Self-ignition or spontaneous ignition means sudden inflammation of a uniformly heated mass of material. Milk fat, casein, lactose and milk powders were analysed with high-pressure DTA, generally under 25 bar of oxygen (i.e. under burning conditions). Figure 8 shows the combustion of the infant formula under 25 bar of oxygen; the lower curve is the furnace response: the beginning of the peak indicates self-ignition of the product. It can also be seen on the ΔT curve that lactose crystallization does not participate in the thermal runaway leading to self-ignition. Indeed, crystallization phenomena are virtually unaffected by the amount of surrounding oxygen. The role of oxygen during Maillard reactions

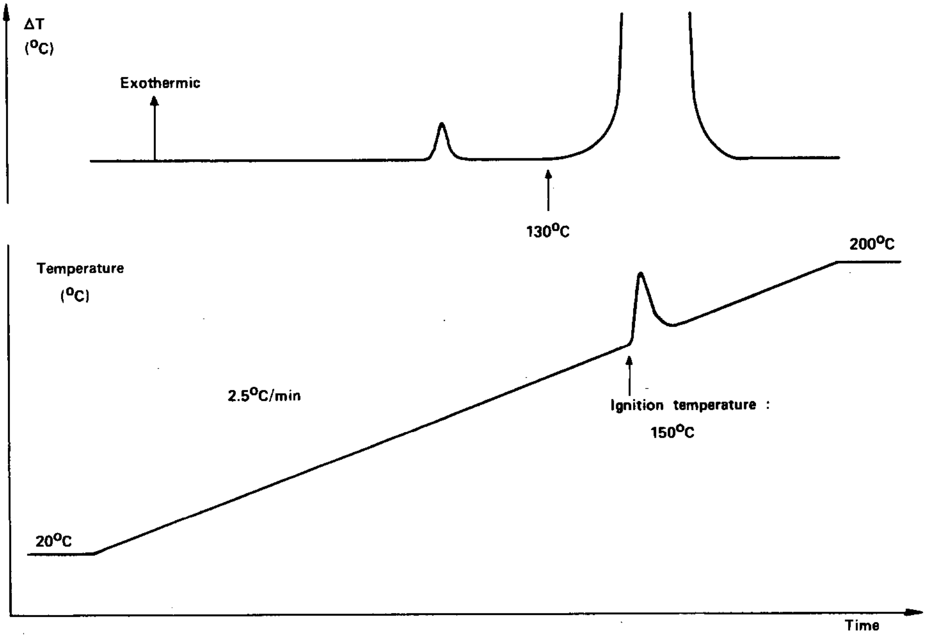

Fig. 8. DTA curves of a milk-based infant formula heated and burned under 25 bar oxygen.

TABLE 2

Self-ignition temperatures of foods determined by DTA
Atmosphere, 25 bar oxygen.

Samples	Self-ignition temperatures (°C)
Crystalline lactose	
Amorphous lactose	260
Butter fat	225
Casein	185
Whey protein	195
Casein–lactose mixture 1	175
Casein–lactose mixture 2	170
Casein–lactose mixture 3	185
Casein–lactose mixture 4	200
Infant formula	150
Whole milk powder	150
Milk powder a	140
Milk powder b	140
Milk powder c	145
Milk powder d	150

Literature data relating to more usual industrial situations are given elsewhere [27–29].

is unclear. Table 2 gives the measured self-ignition temperatures; such data are generally compiled as the minimum ignition temperature for dust layers. It can be seen that carbohydrates which melt, like crystalline lactose, do not ignite spontaneously. But under this large excess of oxygen, even protein can self-ignite. As was expected, the thermal runaway due to oxidation and decomposition phenomena increases very rapidly if oxygen is readily available.

The self-ignition temperatures given in Table 2 depend on many different parameters such as sample size, particle size, oxygen to solid interface, instrument type, etc. As one would expect, they vary widely with oxygen concentration or, as in our case, with oxygen pressure. For instance, whole milk powder ignites at 150°C under 25 bar oxygen and at 170°C under 5 bar. These extreme conditions rarely, if ever, correspond to industrial situations. Values obtained under normal industrial conditions have been reported elsewhere [27–29].

CONCLUSION

Our results indicate that four main types of reactions are involved in the thermal degradation of milk powders. These are, in order of increasing temperature, crystallization of amorphous lactose, Maillard reactions, fat oxidation and lactose decomposition. They were observed when the samples were heated in the presence of a fixed amount of oxygen. Maillard reactions and lactose crystallization do not participate in the thermal runaway when oxygen is readily available. On the contrary, oxidation and decomposition phenomena are strongly dependent on oxygen. If materials are heated under a large excess of oxygen, as in our DTA measurements, fat oxidation, carbohydrate and protein decomposition become so fast that they can bring milk powders to spontaneous ignition even at relatively low temperatures.

From our results, it is clear that fat oxidation, as was often thought [1], is not the only phenomenon that can lead to self-ignition of a milk product.

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