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An assessment of the solid state reactivity of sodium bicarbonate in the presence of solid dental excipients using thermal analysis

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Abstract

Sodium bicarbonate ($NaHCO_3$) is used as an anti-plaque agent in a variety of dental formulations. The aim of this study was to understand the active ingredient–excipient type of interactions in the solid state using thermal analysis. A simple formulation such as a the dental formulation was chosen as an example. Equivalent-ratio w/w binary, tertiary and quaternary mixtures of commercially obtained $NaHCO_3$ were prepared with solid excipients used in dental formulations. The thermal decomposition of $NaHCO_3$ was studied in the presence of these excipients, using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Apart from kinetic analysis, two other methods were developed during the course of this project to assess the solid state reactivity of $NaHCO_3$. The reactivity of $NaHCO_3$ changed in the presence of other solid excipients. The methods developed during this project were successfully used in assessing the solid state reactivity of $NaHCO_3$ in the presence of other substances. It was concluded that these thermal analysis methods could also be applied to other substances for similar solid state studies. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal analysis; Sodium bicarbonate; Dental formulations

1. Introduction

The decomposition reaction for sodium bicarbonate is represented by the equation

$$2NaHCO_3 \rightarrow Na_2CO_{2(S)} + CO_{2(g)}\uparrow + H_2O_{(l)} \qquad (1)$$

in the range of 100–180°C (373–453 K). The decomposition is both time and temperature dependent [1]. The decomposition process has been investigated from time to time because of its numerous uses in different types of industries [2–9]. A typical example would be its use as a dentifrice (a substance used with a toothbrush for the cleaning and polishing of teeth). The published information discusses the decomposition temperature and the enthalpy of the reaction.

The thermal decomposition of sodium bicarbonate was studied under different environments with various heating rates [10] during the first phase of this project. In order to study the effect of the presence of other solids used in the formulation of a dentifrice on the reactivity of sodium bicarbonate, a simple model formulation such as a dental formulation was chosen. Sodium bicarbonate is used as a dentifrice, and contributes about 40–60% of the total solid content of dental formulations.

Dental formulas are usually based on one or more of the following polishing materials: sodium bicarbonate; calcium carbonate; anhydrous dicalcium phos-

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phate [11]. Sodium monoflurophosphate is a commonly used tartar control agent in dental formulations. The detergent, usually a synthetic surfactant like sodium lauryl sulfate, is selected for good foaming action in a dental formulation. It aids in dislodging foreign material from the tooth surfaces and facilitates removal of the polishing agent from the mouth. It also assists in dispersing lipophilic products, such as flavor oils. Polyol such as sorbitol is included in the liquid portion of the paste to enhance its consistency and to preserve the texture of the paste. They provide good mouthfeel and aid in retaining paste gloss. A binder such as sodium carboxymethylcellulose is used for holding all the solids together in a toothpaste base, and titanium dioxide is a commonly used pigment in dental formulations.

2. Experimental

2.1. Materials

The following materials were used in this project:

1. Sodium bicarbonate (Lot # 926222 and Lot # 920139), Fisher Chemical, Fair Lawn, NJ;
2. Precipitated calcium carbonate (Lot # 923690), Fisher Chemical, Fair Lawn, NJ;
3. Anhydrous calcium phosphate dibasic (Lot # 5340948), Sigma Inc, St. Louis, MO;
4. Sodium monofluorophosphate, 95% (Lot # 00805JW), Aldrich Chemical Company, Inc., Milwaukee, WI;
5. Sodium carboxymethycellulose, USP, high viscosity grade, City Chemical Corp.;
6. Sodium lauryl sulphate (Lot # 914995), Fisher Chemical, Fair Lawn, NJ;
7. Titanium dioxide (Lot # 9105), TRI-K industries, Inc., Emerson, NJ;
8. Sorbitol, USP (Lot # 3219214), E Merck, Germany.

2.2. Methods

The thermogravimetric and differential thermal analysis experiments were performed on a model SDT 2960, simultaneous TGA/DTA unit from TA Instruments. The experiments were carried out with a heating rate of 8°C/min under an atmosphere of dry nitrogen. The sample size was 15 mg ± 10%. The raw data from the TA instrument was converted to DOS modality and then analyzed in the temperature range of the decomposition process.

The identification of a set of compatible excipients for a formulation is the primary aim in studying active ingredient–excipient interactions in the solid state. The degradation in the solid state is affected by several factors such as the method of mixing, the homogeneity of the powder mixture, the hygroscopicity of the substances involved, the humidity of the surroundings, temperature, particle size distribution, particle surface area and powder packing. There may be other factors depending on particular ingredients and excipients chosen. The proportions of the active substances to the excipients are also important [12].

In solid state studies, the behavior of the mixture of powders needs to be assessed when first exposed to accelerated stability conditions. This can be done by initially assessing the behavior of each component of the mixture under the prescribed conditions. This is followed by the assessment of combinations of the individual components in all possible permutations under the same conditions. When all these results are correlated, a good behavioral profile can be attributed to the system [12].

Once this is established, a kinetic analysis of the degradation of the active ingredient (usually the pharmacologically active drug in the dosage of form) in question can be carried out. In a mixture, where temperature (T) and fraction decomposed (α) are changing simultaneously, a number of complimentary $f(\alpha)\ k(T)$'s can be devised to fit the data as seen in the following Eqn:

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)k(T), \tag{2}$$

where α is the fraction reacted or decomposed, T the absolute temperature;t the time; and $f(\alpha)$ and $k(T)$ are separable functions of (α) and (T).

The function $f(\alpha)$ can be chosen by using the "recognition procedure" which has been outlined by Doillimore et al. [13–16].

Owing to the complexity of many powder mixtures, a word of caution should be added if the system contains a number of components, since there would be a number of chemical and physical processes taking part in the thermal degradation of the mixture. The degradation products can be determined using appropriate analytical techniques. In this study X-ray diffraction was used to establish the presence of a degradant. The problem with applying the Arrhenius equation Eq. (3) to this complex case would be that none of the degradative processes would be dominant, except in the case of rate limiting process, in such a way that its specific Arrhenius parameters would be the most significant. The Arrhenius equation takes the form

$$k(T) = A\ \exp^{-(E/RT)}, \tag{3}$$

where R is the gas constant; E the energy of activation; and A the pre-exponential factor.

One must note here that there is no definitive method to describe the temperature kinetics and hence the Arrhenius equation, which is used to describe isothermal kinetics, and is also almost universally used for rising temperature studies.

Sodium bicarbonate is considered the active ingredient in the dental formulation. The mixtures were prepared in a glass mortar. The density and the particle size of the materials were taken into consideration before arriving at the order of mixing for the solids in the mortar. The denser materials were mixed last and the materials with larger particle size were placed first in the mortar. This was done in order to prepare homogeneous mixtures, as far as possible, and avoid the settling of the denser solids to the bottom and prevent further grinding of the smaller particles. Table 1 shows the list of all the solid materials used in the analysis of the mixtures with an alpha numeric notation ascribed to each one of them for the sake of simplicity.

The following mixtures were prepared by incorporating the above mentioned substances.

Table 1
Materials used to prepare the binary, ternary and quaternary mixtures with their alpha numeric label

Name of the substance	Alpha numeric label
Sodium bicarbonate ($NaHCO_3$)	A
Precipitated calcium carbonate ($CaCO_3$)	B
Anhydrous calcium phosphate dibasic ($CaHPO_4$)	C
Sodium monofluorophosphate (SMFP)	D
Sodium carboxymethylcellulose (Na CMC)	E
Sodium lauryl sulfate (SLS)	F
Titanium dioxide (TiO_2)	G
Sorbitol	H

Binary mixtures: AB, AC, AD, AE, AF, AG, AH.

Tertiary mixtures: ABC, ABD, ABE, ABF, ACD, ACE, ACF, ADE, ADF, AEF.

Quarternary mixtures: ABCD, ABCE, ABCF, ABDE, ABEF, ACDE, ACDF, ACEF, ADEF.

All the excipients except calcium carbonate and anhydrous dibasic calcium phosphate and the mixtures were subjected to a heating rate of 8°C/min up to a maximum of 225°C under an atmosphere of dry nitrogen. The obvious reason for choosing this temperature range is that the decomposition reaction of sodium bicarbonate, which is the reaction of interest in this study, is complete in that range with the above mentioned heating rate. The TGA/DTG plots for sodium bicarbonate and for each of the excipients mentioned above are shown in Fig. 1. The TGA/DTA plots for sodium lauryl sulfate and sorbitol are shown in Figs. 2 and 3, respectively.

3. Results and discussion

The following observations were determined by the thermographs obtained for the substance in question:

1. Sodium bicarbonate decomposes to sodium carbonate liberating carbon dioxide and water vapour (Fig. 1).
2. Calcium carbonate decomposes to calcium oxide liberating carbon dioxide.
3. Dibasic calcium phosphate (anhydrous) is stable up to 300°C. Around 5% weight loss in the range 300–400°C is possibly due to the loss of a water molecule from its internal structure as seen by the following equation:

$$Ca(HPO_4)_2 \rightarrow CaP_2O_2 + H_2O \tag{4}$$

4. Sodium monofluorophosphate is thermally stable up to 225°C.
5. Sodium carboxymethylcellulose loses weight on heating.
6. A transition occurs around 100°C on heating sodium lauryl sulfate (SLS) and its starts melting around 190°C (Fig. 3).
7. Titanium dioxide is stable up to 225°C.
8. Sorbitol melts around 100°C and is then stable up to 220°C on further heating (Fig. 4). In addition, whenever possible, solid stage decomposition products were identified by X-ray powder diffraction.

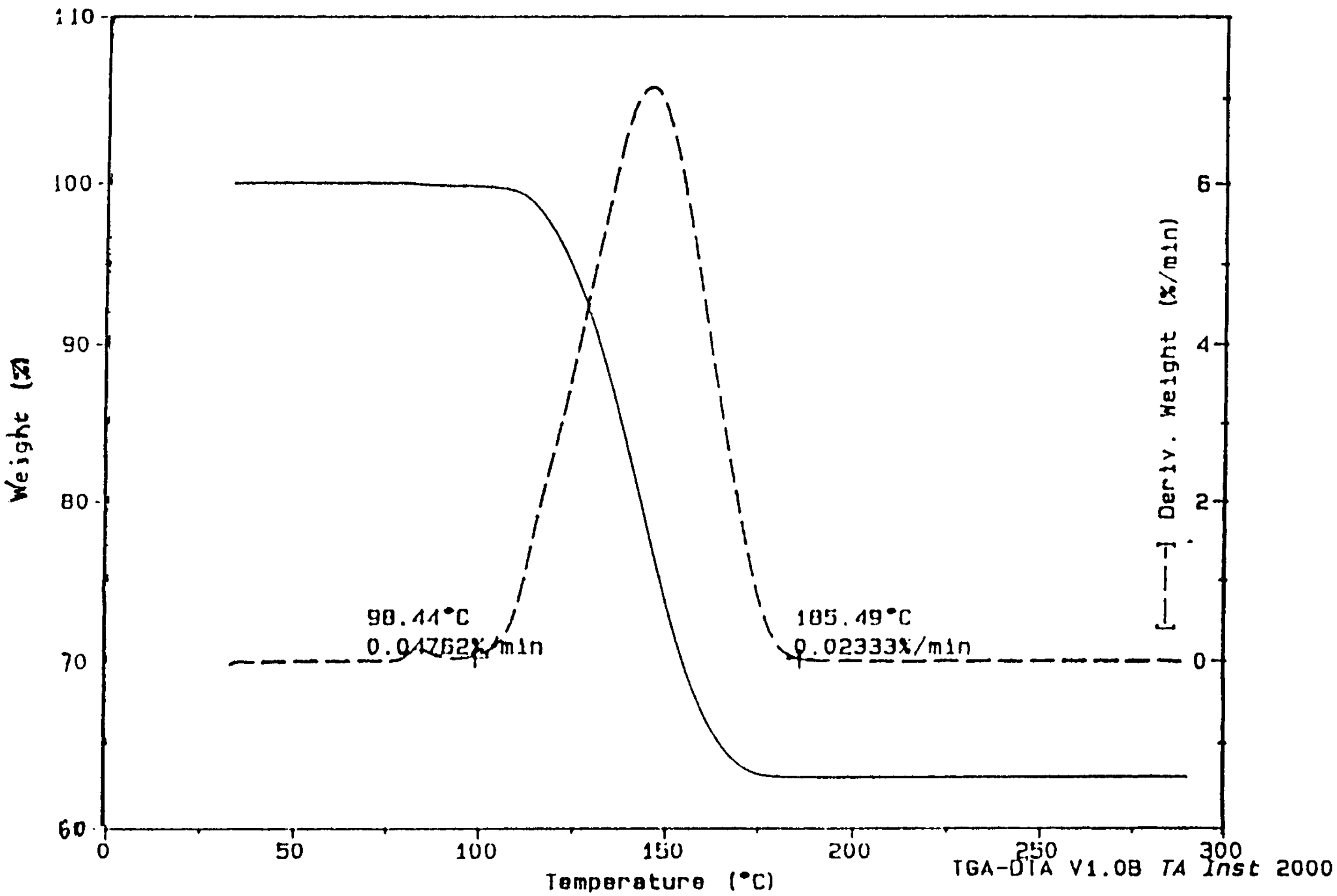

Fig. 1. TGA/DTG plot of sodium bicarbonate.

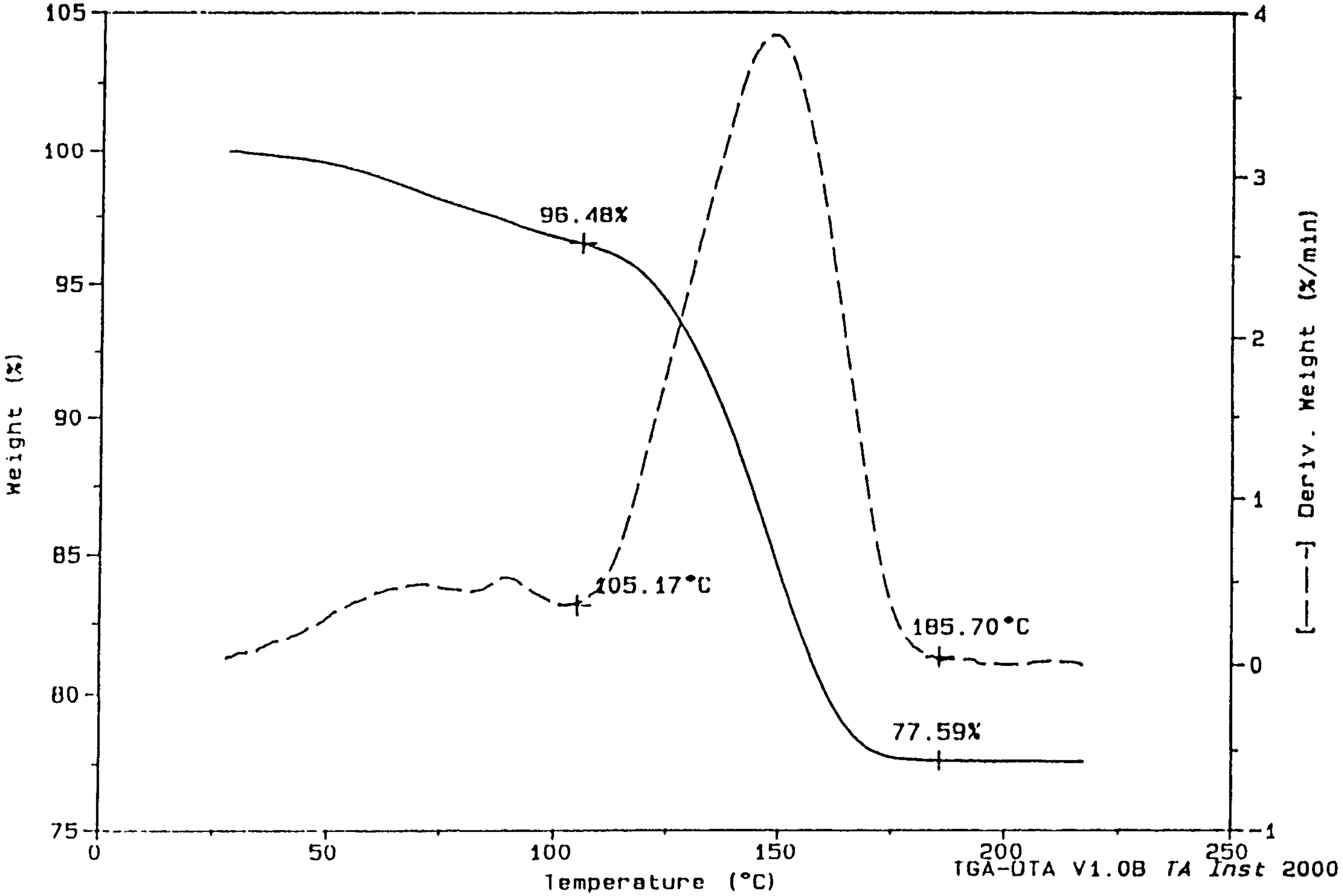

Fig. 2. TGA/DTG plot for the binary mixture, $NaHCO_3$: Na CMC.

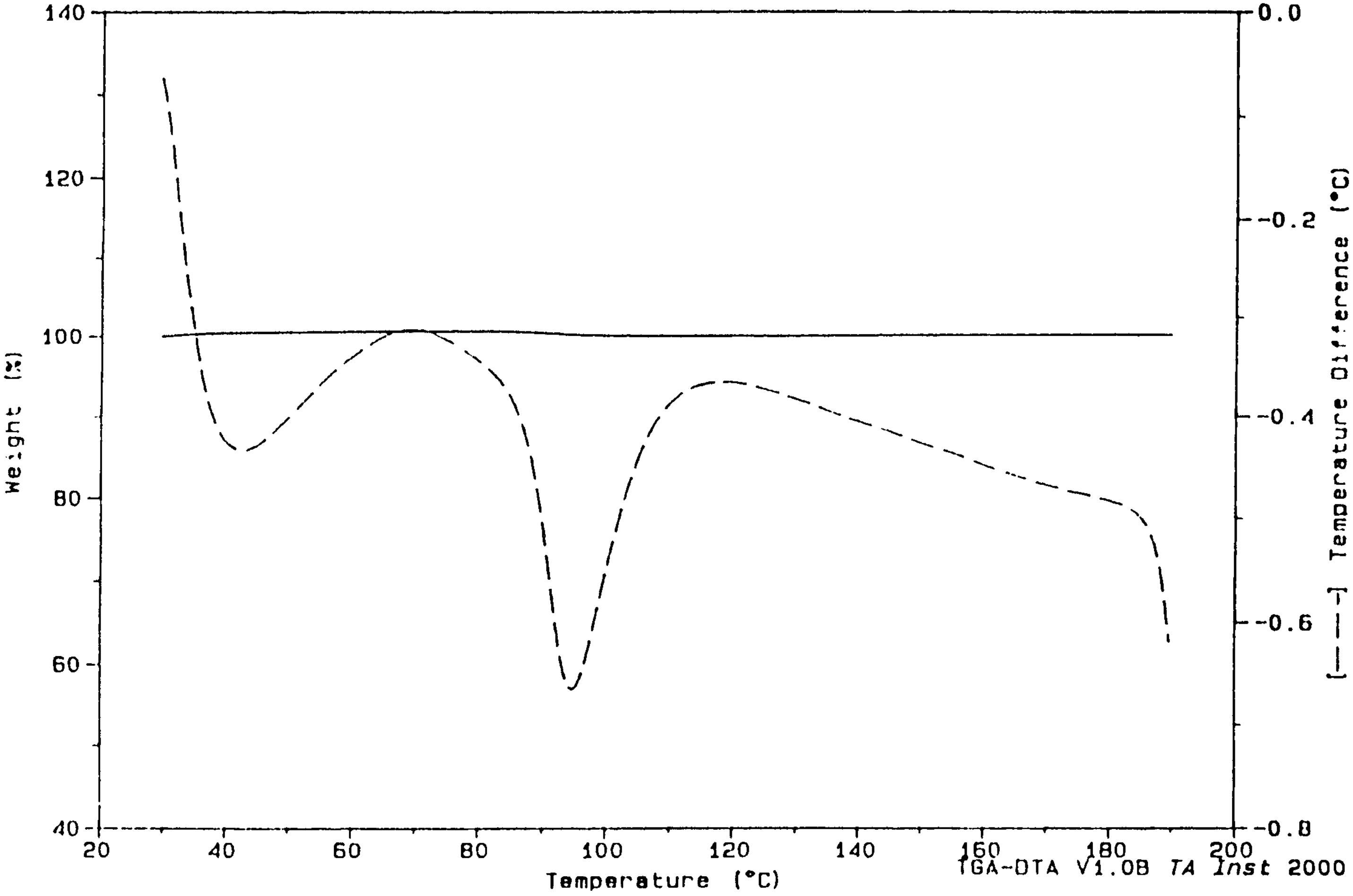

Fig. 3. TGA/DTG plot of sodium lauryl sulfate.

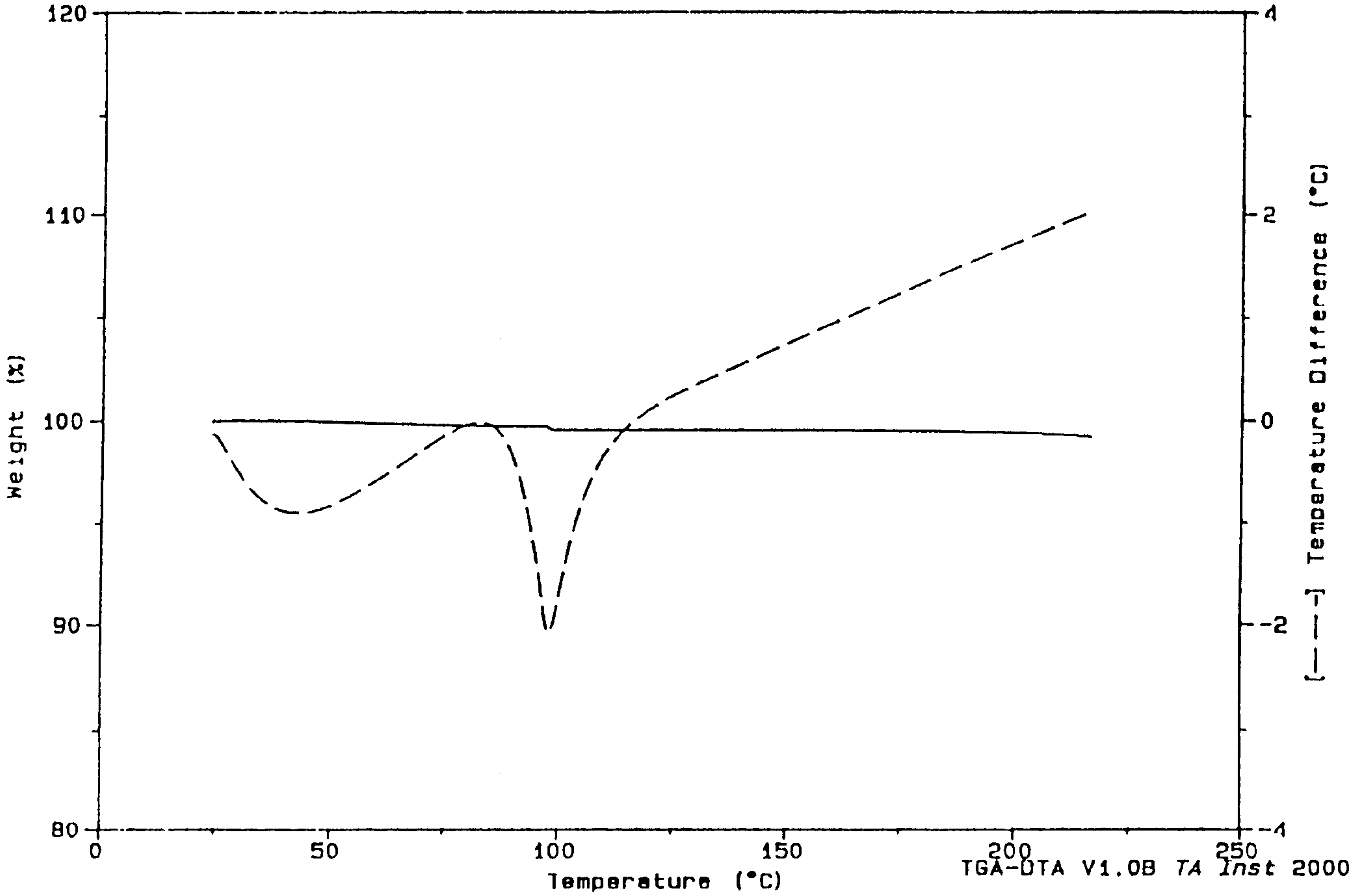

Fig. 4. TGA/DTG plot of crystalline sorbitol.

Table 2
Kinetic analysis[a] results for the *binary mixtures* using the single-heating-rate differential method with respect to the first order deceleratory mechanism, $f(\alpha) = (1 - \alpha)$, under an atmosphere of dry nitrogen

Binary mixtures (1 : 1 w/w)	Activation energy, E(kJ mol^{-1})	Frequency factor, A(s^{-1})	Regression factor (R)	Standard error (SE)
$NaHCO_3 : CaCO_3$ (AB)	108.2	2.2×10^{11}	0.992	0.174
$NaHCO_3 : CaHPO_4$ (AC)	114.7	1.5×10^{12}	0.990	0.193
$NaHCO_3$: SMFP (AD)	115.9	2×10^{12}	0.987	0.202
$NaHCO_3$: Na CMC (AE)	99.8	2×10^{10}	0.995	0.131
$NaHCO_3$: SLS (AF)	134.1	3.2×10^{14}	0.978	0.278
$NaHCO_3 : TiO_2$ (AG)	101.7	3.2×10^{10}	0.990	0.191
$NaHCO_3$: Sorbitol (AH)	95.1	2×10^{9}	0.972	0.357

[a] From Refs. [13–16]; the function $f(\alpha) = 1 - \alpha$ chosen by using the "recognition procedures" outlined in the above references by Dollimore et al.

Sorbitol and TiO_2 were not used in making the tertiary and quaternary mixtures. Sorbitol, though stable once it melts around 100°C up to 220°C as seen in Fig. 4, starts decomposing as sodium bicarbonate decomposes, as was seen in the TGA/DTG plot for the binary mixture, AH ($NaHCO_3$: Sorbitol). Moreover, sorbitol is used in the form of a 70% solution as a sweetening agent and a glossing agent. TiO_2 is used in very small quantities, approximately 0.25–0.5% in the dental formulations and does not melt up to 1800°C. In other words, it does not really affect the reactivity of sodium bicarbonate in the dental formulations in such low quantities in the temperature range of interest.

The onset and final temperatures for the decomposition reaction of sodium bicarbonate are marked on the DTG curves for all the mixtures. The onset temperature for the mixtures containing sodium carboxymethylcellulose and sorbitol were judged using the DTG tables on the computer work station. The TGA/DTG plots for the binary mixtures are shown in Fig. 2. The single step thermal decomposition of sodium bicarbonate was distinctly seen in all the plots of the mixtures.

The single-heating-rate differential and integral methods of kinetic analysis were used in order to obtain the Arrhenius parameters for the thermal decomposition of sodium bicarbonate in the mixtures of sodium bicarbonate with other solid excipients as used in dental formulations with respect to the first order deceleratory mechanism. The results for the binary mixtures are given in Tables 2 and 3; for the tertiary mixtures in Tables 4 and 5; and for quaternary mixtures in Tables 6 and 7.

From these tables it can be seen that the activation energies for the binary mixtures of sodium bicarbo-

Table 3
Kinetic analysis results[a] for the *binary mixtures* using the single-heating-rate integral method with respect to the first order deceleratory mechanism, $G(\alpha) = -\ln(1 - \alpha)$[b], under an atmosphere of dry nitrogen

Binary mixtures (1 : 1 w/w)	Activation energy, E (kJ mol^{-1})	Frequency factor, A (s^{-1})	Regression factor (R)	Standard error (SE)
$NaHCO_3 : CaCO_3$ (AB)	123.7	2×10^{13}	0.993	0.177
$NaHCO_3 : CaHPO_4$ (AC)	134.3	4.5×10^{14}	0.987	0.249
$NaHCO_3$: SMFP (AD)	145.3	9.8×10^{15}	0.980	0.296
$NaHCO_3$: Na CMC (AE)	117.9	3.8×10^{12}	0.990	0.214
$NaHCO_3$: SLS (AF)	166.3	3.8×10^{18}	0.977	0.349
$NaHCO_3 : TiO_2$ (AG)	118.1	3.7×10^{12}	0.992	0.204
$NaHCO_3$: Sorbitol (AH)	104.4	2.8×10^{10}	0.997	0.119

[a] From Refs. [13–16].

[b] $G(\alpha)$ is the integral form of $f(\alpha)$.

Table 4
Kinetic analysis[a] results for the *tertiary mixtures* from the single-heating-rate differential method with respect to the first order deceleratoy mechanism, $f(\alpha) = (1 - \alpha)$ under an atmosphere of dry nitrogen

Tertiary mixtures (1 : 1 : 1 w/w)	Activation energy, E(kJ mol^{-1})	Frequency factor, A(s^{-1})	Regression factor (R)	Standard Error (SE)
$NaHCO_3$: $CaCO_3$: $CaHPO_4$ (ABC)	112	6.5×10^{11}	0.994	0.146
$NaHCO_3$: $CaCO_3$: SMFP (ABD)	108.3	1.1×10^{11}	0.973	0.340
$NaHCO_3$: $CaCO_3$: Na CMC (ABE)	97.1	9.2×10^{9}	0.991	0.183
$NaHCO_3$: $CaCO_3$: SLS (ABF)	116.7	2.1×10^{12}	0.955	0.366
$NaHCO_3$: $CaHPO_4$: SMFP (ACD)	128.6	6.8×10^{13}	0.955	0.468
$NaHCO_3$: $CaHPO_4$: Na CMC (ACE)	108.8	2.7×10^{11}	0.964	0.381
$NaHCO_3$: $CaHPO_4$: SLS (ACF)	127.6	5.2×10^{13}	0.969	0.335
$NaHCO_3$: SMFP : Na CMC (ADE)	110	3.1×10^{11}	0.963	0.362
$NaHCO_3$: SMFP : SLS (ADF)	121.4	7.1×10^{12}	0.926	0.454
$NaHCO_3$: Na CMC : SLS (AEF)	118.9	3.6×10^{12}	0.947	0.426

[a] From Refs.[13–16].

Table 5
Kinetic analysis[a] results for the *tertiary mixtures* from the single heating rate integral method with respect to the first order deceleratory mechanism, $G(\alpha) = -\ln(1 - \alpha)$[b], under an atmosphere of dry nitrogen

Tertiary mixtures (1 : 1 : 1 w/w)	Activation energy E (kJ mol^{-1})	Frequency factor (A^{a})	Regression factor (R)	Standard error (SE)
$NaHCO_3$: $CaCO_3$: $CaHPO_4$ (ABC)	125.7	3.7×10^{13}	0.995	0.137
$NaHCO_3$: $CaCO_3$: SMFP (ABD)	111.5	2.6×10^{11}	0.999	0.074
$NaHCO_3$: $CaCO_3$: Na CMC (ABE)	108.7	2.7×10^{11}	0.996	0.135
$NaHCO_3$: $CaCO_3$: SLS (ABF)	152.4	6.1×10^{16}	0.982	0.293
$NaHCO_3$: $CaHPO_4$: SMFP (ACD)	143	5.1×10^{15}	0.992	0.195
$NaHCO_3$: $CaHPO_4$: Na CMC (ACE)	125.4	3.5×10^{13}	0.991	0.197
$NaHCO_3$: $CaHPO_4$: SLS (ACF)	148.8	2.3×10^{16}	0.983	0.2778
$NaHCO_3$: SMFP : Na CMC (ADE)	135.3	4.9×10^{14}	0.9856	0.269
$NaHCO_3$: SMFP : SLS (ADF)	171.4	1.2×10^{19}	0.966	0.423
$NaHCO_3$: Na CMC : SLS (AEF)	150.5	3.3×10^{16}	0.983	0.299

[a] From Refs. [13–16].
[b] $G(\alpha)$ is the integral form of $f(\alpha)$.

Table 6
Kinetic analysis[a] results for the *quaternary mixtures* from the single-heating-rate differential method with respect to the first order deceleratory mechanism, $f(\alpha) = (1 - \alpha)$, under an atmosphere of dry nitrogen

Quarternary mixtures (1 : 1 : 1 w/w)	Activation energy E (kJ mol^{-1})	Frequency factor A (s^{-1})	Regression factor (R)	Standard error (SE)
$NaHCO_3$: $CaCO_3$: $CaHPO_4$: SMFP (ABCD)	112.3	6.1×10^{11}	0.960	0.419
$NaHCO_3$: $CaCO_3$: $CaHPO_4$: Na CMC (ABCE)	98.8	1.4×10^{10}	0.989	0.209
$NaHCO_3$: $CaCO_3$: $CaHPO_4$: SLS (ABCF)	114	1×10^{12}	0.973	0.324
$NaHCO_3$: $CaCO_3$: SMFP : Na CMC (ABDE)	97.8	9.6×10^{9}	0.965	0.382
$NaHCO_3$: $CaCO_3$: SMFP : SLS (ABDF)	122.8	1.1×10^{13}	0.953	0.410
$NaHCO_3$: $CaCO_3$: Na CMC : SLS (ABEF)	107	1.3×10^{11}	0.976	0.271
$NaHCO_3$: $CaHPO_4$: SMFP : Na CMC (ACDE)	124.8	2.1×10^{13}	0.950	0.466
$NaHCO_3$: $CaHPO_4$: SMFP : SLS (ACDF)	128.1	4.8×10^{13}	0.935	0.446
$NaHCO_3$: $CaHPO_4$: Na CMC : SLS (ACEF)	125.2	2.4×10^{14}	0.941	0.480
$NaHCO_3$: SMFP : Na CMC : SLS (ADEF)	–	–	–	–

[a] From Refs. [13–16].

Table 7
Kinetic analysis[a] results for the *quaternary mixtures* using the single-heating-rate integral method with respect to the first order deceleratory mechanism, $G(\alpha) = -\ln(1-\alpha)$[b], under an atmosphere of dry nitrogen

Quarternary mixtures (1 : 1 : 1 : 1 w/w)	Activation energy E (kJ mol^{-1})	Frequency factor A (s^{-1})	Regression factor (R)	Standard error (SE)
$NaHCO_3$: $CaCO_3$: $CaHPO_4$: SMFP (ABCD)	123.1	1.4×10^{13}	0.995	0.148
$NaHCO_3$: $CaCO_3$: $CaHPO_4$: Na CMC (ABCE)	107.8	1.9×10^{11}	0.997	0.110
$NaHCO_3$: $CaCO_3$: $CaHPO_4$: SLS (ABCF)	128.4	6.8×10^{13}	0.994	0.166
$NaHCO_3$: $CaCO_3$: SMFP:Na CMC (ABDE)	107.7	1.8×10^{11}	0.997	0.118
$NaHCO_3$: $CaCO_3$: SMFP : SLS (ABDF)	150.9	3.8×10^{16}	0.984	0.283
$NaHCO_3$: $CaCO_3$: Na CMC : SLS (ABEF)	132.5	2×10^{14}	0.989	0.224
$NaHCO_3$: $CaHPO_4$: SMFP : Na CMC (ACDE)	143.9	5.5×10^{15}	0.988	0.254
$NaHCO_3$: $CaHPO_4$: SMFP : SLS (ACDF)	170.2	7.9×10^{19}	0.974	0.363
$NaHCO_3$: $CaHPO_4$: Na CMC : SLS (ACEF)	149.1	2.4×10^{16}	0.988	0.254
$NaHCO_3$: SMFP : Na CMC : SLS (ADEF)	166.9	2.8×10^{18}	0.974	0.381

[a] From Refs. [13–16].
[b] $G(\alpha)$ is the integral form of (α).

nate with sodium carboxymethylcellulose (AE), and with sorbitol (AH), are less when compared to the other binary mixtures, in other words, sodium bicarbonate is seen as a more reactive substance in these mixtures. This can be attributed to the fact that the sodium carboxymethylcellulose starts decomposing before the decomposition of sodium bicarbonate begins and decomposes throughout the range of the decomposition reaction of sodium bicarbonate. Whereas, sorbitol melts around 100°C and starts decomposing as sodium bicarbonate decomposes. In both these cases, the amount of weight loss in the decomposition range of sodium bicarbonate is the sum of the weight lost by sodium bicarbonate and the other excipient forming the binary mixture.

The onset and final temperatures also effect the kinetic parameters (Table 8). This aspect can be seen in the binary mixture of sodium bicarbonate with sodium lauryl sulfate (AF), in which the activation energy is more when compared to that of the other binary mixtures.

All these aspects can again be clearly seen in all the tertiary and quaternary mixtures incorporating the excipient sodium carboxymethylcellulose and sodium lauryl sulfate.

In general, the activation energy for the decomposition reaction of sodium bicarbonate increases as the number of solids in the mixture increases, or in other words, the reactivity of sodium bicarbonate decreases.

Table 8
The onset and final temperatures of reaction, the surface areas, and the ratio of the reactivity parameters for various ground samples of sodium bicarbonate

Grinding time (h)	Onset temp. of the reaction (°C)	Final temp. of the reaction (°C)	Surface area (m^2/g)	Reaction temp. (°C) for $\alpha = 0.5$	Reaction extent (α) at 140°C	α_s/α_r	T_s/T_r
0[a]	99.6	180.0	6	142.6	0.443	1.000	1.000
1	95.5	178.4	14	138.2	0.550	1.242	0.969
2	92.8	175.4	22	133.9	0.650	1.467	0.934
3	90.5	172.0	31	129.9	0.750	1.693	0.911
4	89.3	170.0	35	128.1	0.780	1.761	0.898
5	88.8	167.0	40	126.1	0.817	1.844	0.884
6	87.7	166.0	43	125.0	0.841	1.898	0.877
7	87.8	166.2	43	125.4	0.831	1.876	0.879
8	87.9	166.3	43	125.5	0.821	1.876	0.880

[a] Commercially acquired sample used as a reference.

The assumption of a pre-existing mechanism of reaction is false when there is a change in the textural properties of the samples. This is due to the fact that the mechanism of reaction varies with changes in the particle size and shape for the ground samples. The presence of excipients with different textural properties and thermal behavior affect the thermal behavior of sodium bicarbonate and the mechanism cannot be preset. Solid state reactivity could be expressed in terms of the conventional kinetic parameters, but there are three terms to consider, namely the reaction rate equation, the activation energy and the pre-exponential term. A change in any one of these can cause a corresponding change in the other two. This makes comparison of the solid state reactivity difficult.

The change in the thermal behavior of the solid samples due to a change in their pre-history, etc. could be assessed by use of comparative methods as described below. Two such methods were developed during the course of this project. In these methods the reactivity could be assessed by comparing a thermal behavioral property of the sample with that of the reference. This overcomes the difficulty of comparing Arrhenius parameters which are three interdependent terms that need to be quoted.

3.1. The (α_s–α_r) and (T_s–T_r) methods for assessing reactivity

A thermogravimetric (TGA) plot is obtained for the reference sample, and then similar TGA plots are obtained for various samples prepared by altering the pre-history of the sample using identical conditions and the same thermogravimetric unit. The solid state reactivity can then be assessed from plots of ($\alpha_{\mathrm{reference}}$), the extent of decomposition of the reference substance, against the values of (α) for various samples labeled as (α_{sample}) to denote the extent of decomposition values for various prepared samples. The values for appropriate couples of (α_{sample}) and ($\alpha_{\mathrm{reference}}$) at different temperatures T_1, T_2, T_3, ... T_n, allows an (α_{sample}–$\alpha_{\mathrm{reference}}$) plot to be constructed from which the solid state reactivity may be assessed. Similarly, the solid state reactivity could be assessed from the plots obtained by choosing appropriate couples of (T_{sample}) and ($T_{\mathrm{reference}}$) at different values for (α).

If the solid state reactivity of the ground samples matches that of the reference, the result will be a linear plot showing coincidence of (α_{sample}) and ($\alpha_{\mathrm{reference}}$) at all values of ($\alpha$). If the solid state reactivity of the ground samples exceeds that of the reference or in other words if the sample is more reactive than the reference then the lines plotted will be on one side of the coincidence line, while if they are less reactive than the reference sample, they will be on the other side as seen in Fig. 5. A similar argument can be made while comparing the other reactivity parameter, the reaction temperature, as shown in Fig. 6.

The (α_{s}–α_{r}) method of assessing the solid state reactivity was used in order to assess the solid state thermal behavior of sodium bicarbonate in the presence of the solid excipients of dental formulations. A 7.5 mg sample was used as the reference in comparing the reactivity of sodium bicarbonate in the binary mixtures of 15.0 mg size. Similarly, a 5.0 mg sample was used for the tertiary mixtures and a 3.75 mg sample was used for the quaternary samples of 15.0 mg size each. This was done in order to make sure that when the reactivity of the sample was compared, the reference sample had the same amount of sodium bicarbonate as that in the mixture. Moreover, as the reactivity decreases with a decrease in the sample size, the comparison of the reactivity would be better justified and unbiased.

The (α_{s}–α_{r}) plots for each of the binary mixtures were prepared and a typical plot is given in Fig. 7, in order to more vividly see the change in the solid state reactivity of sodium bicarbonate in the presence of another substance. Figs. 8–10 show the (α_{s}–α_{r}) plots for all the binary, tertiary and quaternary mixtures, respectively.

In general, the solid state decomposition of sodium bicarbonate is delayed in the presence of other excipients. The onset temperature of decomposition of sodium bicarbonate is significantly high in the presence of sodium lauryl sulfate and sorbitol. This could be attributed to a transition in sodium lauryl sulfate around 100°C and due to the melting of sorbitol in the presence of sodium bicarbonate around 100°C. The reactivity seems to be increasing in the presence of sodium carboxymethylcellulose. This may be due to the weight loss of sodium carboxymethylcellulose itself.

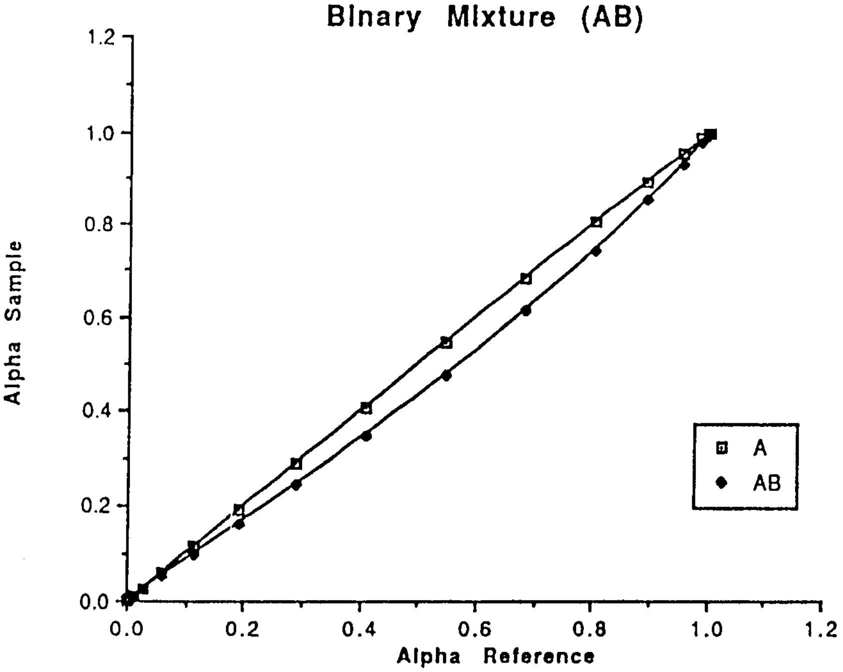

Fig. 5. A typical (α_s–α_r) plot.

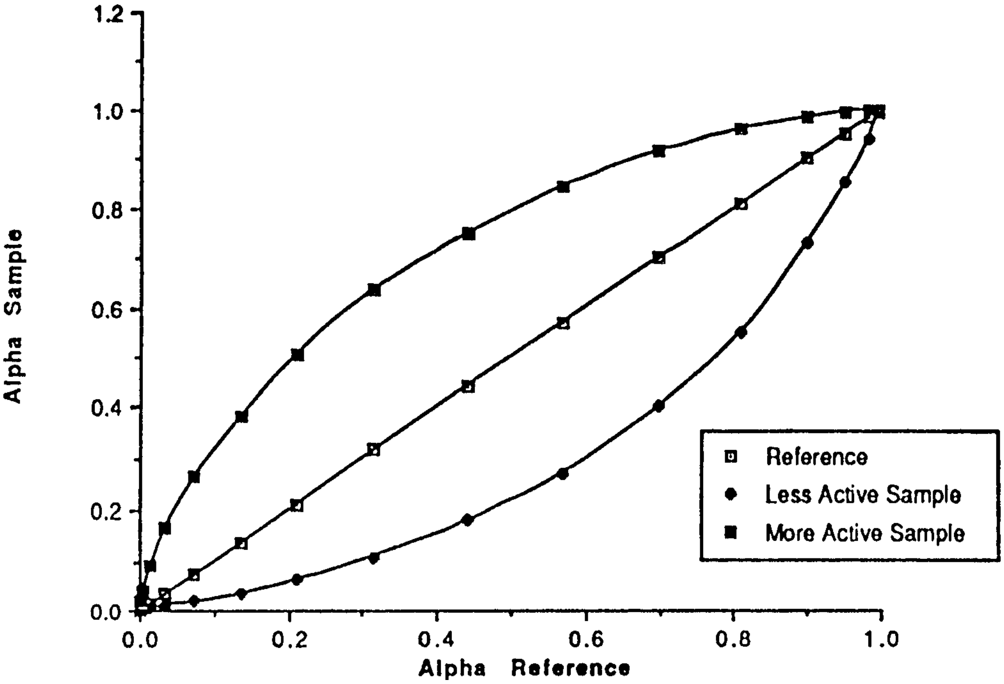

Fig. 6. A typical (T_s–T_r) plot.

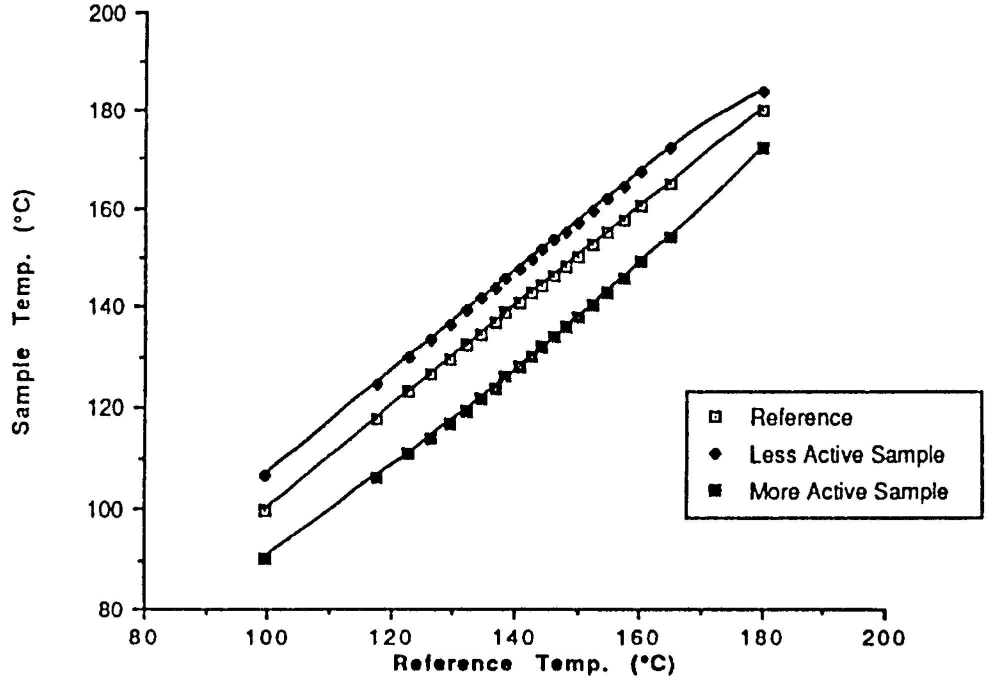

Fig. 7. An (α_s–α_r) plot for the binary mixture, $NaHCO_3 : CaCO_3$.

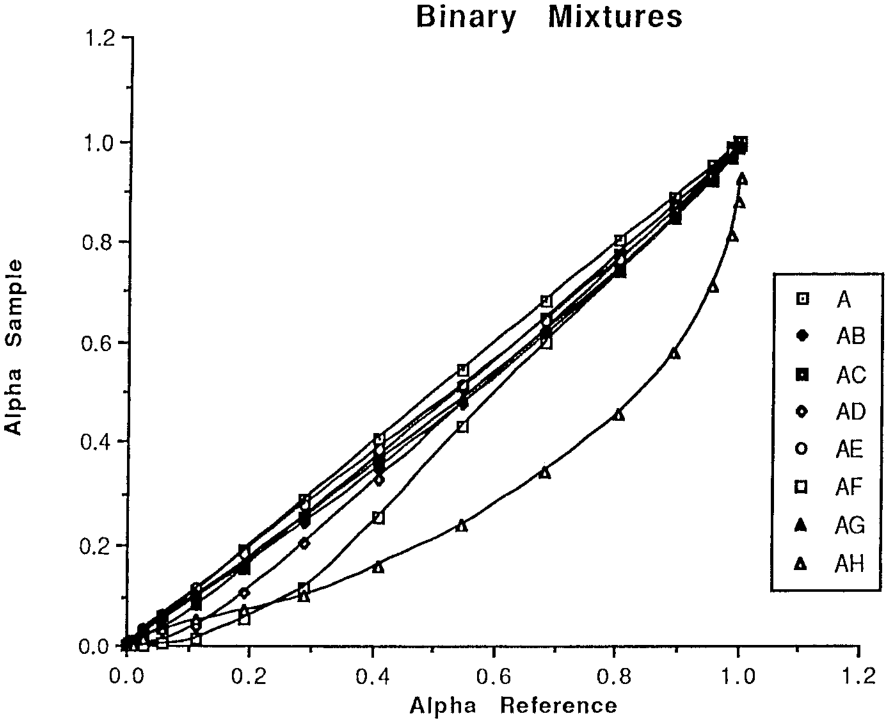

Fig. 8. An (α_s–α_r) plot for all the binary mixtures.

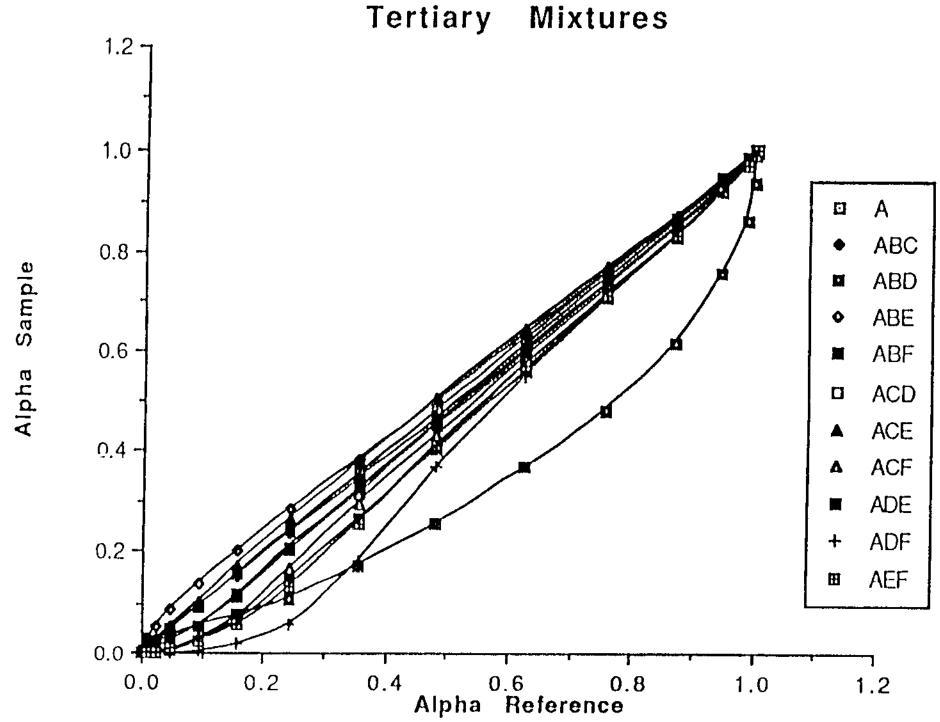

Fig. 9. An ($\alpha_s$$-$$\alpha_r$) plot for all the tertiary mixtures.

3.2. The (W_t–W_a) method of assessing reactivity

Another approach, which is believed to be more powerful than the (α_s–α_r) method for comparing reactivity of different samples is described in this section. This method could be substantially expanded in any future work. When the TG signals for the excipients interfere with the peaks for sodium bicarbonate, the (α_s–α_r) method cannot exactly predict the change in the reactivity of the sample except to say whether it is decreasing or increasing. In the present study, this aspect can be observed with the excipients sodium carboxymethylcellulose and sorbitol. In the mixtures containing these excipients the onset temperature of reaction seems to be a little biased even though it is based on a practical choice using a computer work station. The extent of reaction values for the decomposition reaction (α_is) are deemed faulted since they are based on the weight loss while the excipients mentioned above also lose weight along with the substance under analysis. Therefore, even though the reactivity of sodium bicarbonate seems to be increasing in the presence of these excipients, it may or may not actually be happening. Hence, a different approach is required in order to assess and compare the reactivity which takes into consideration the individual TG signals from both the substance under analysis as well as the excipient.

In this new approach, the theoretical or calculated TGA curves are constructed by combining individual TGA curves for the substance under analysis, here sodium bicarbonate, and the excipient (s). The calculated or theoretical curves can then be superimposed over the actual TGA curves for the mixtures in order to compare their reactivity. In an extension of this method, the ratio of the wt% actual (W_a) to the wt% theoretical (W_t) and the difference in the wt% actual (W_a) and the wt% theoretical (W_t) could be plotted against the temperature. If the reactivity of the substance under analysis is unchanged in the presence of the excipients, then the ratio should always be equal to unity and the difference should always be equal to

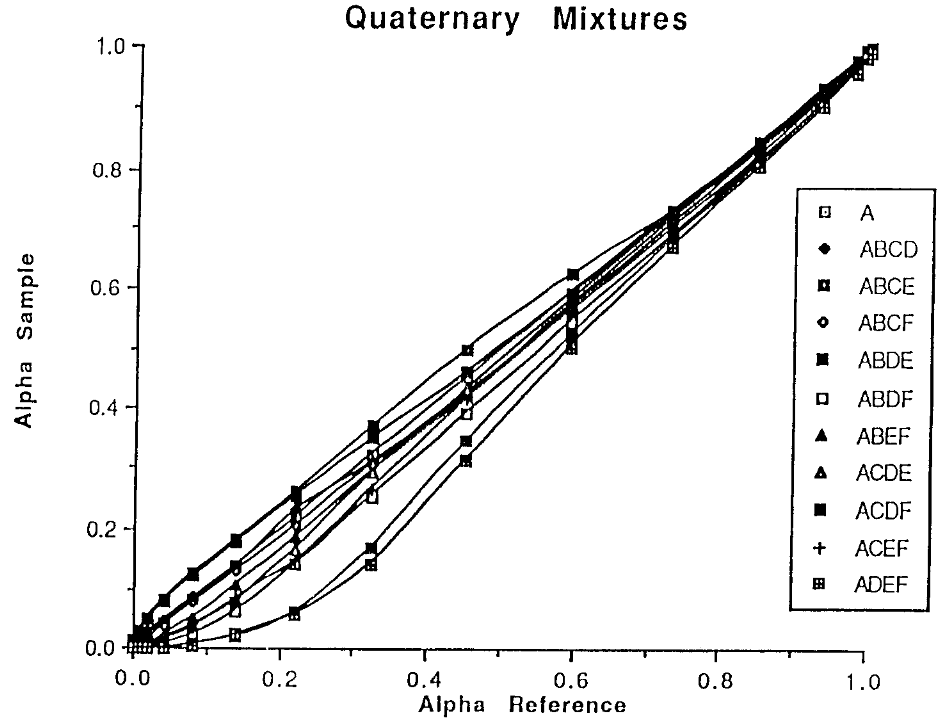

Fig. 10. An (α_s–α_r) plot for all the quaternary mixtures.

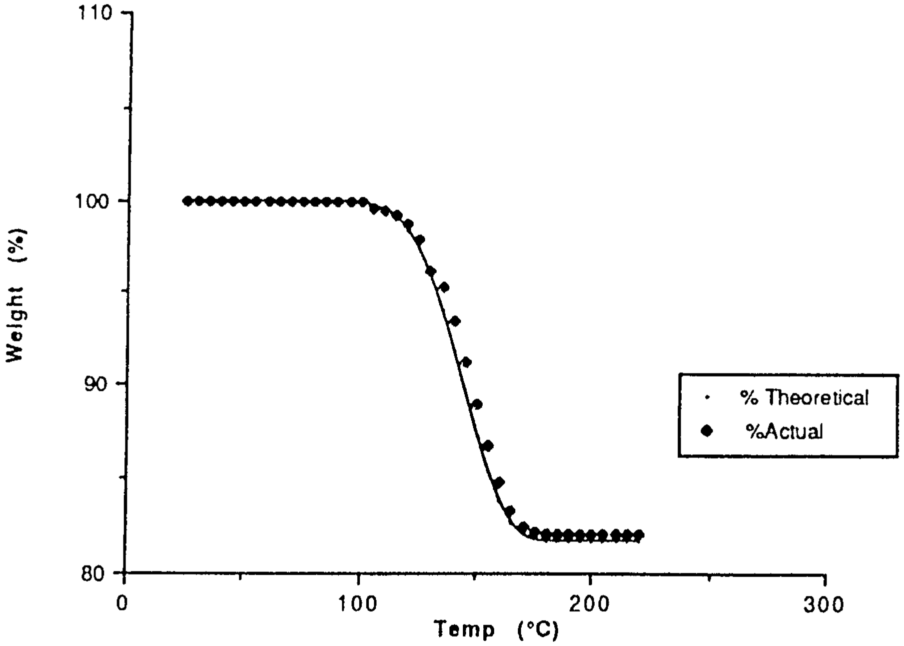

Fig. 11. Plot of the theoretical TG curve against the actual TG curve for $NaHCO_3 : CaCO_3$.

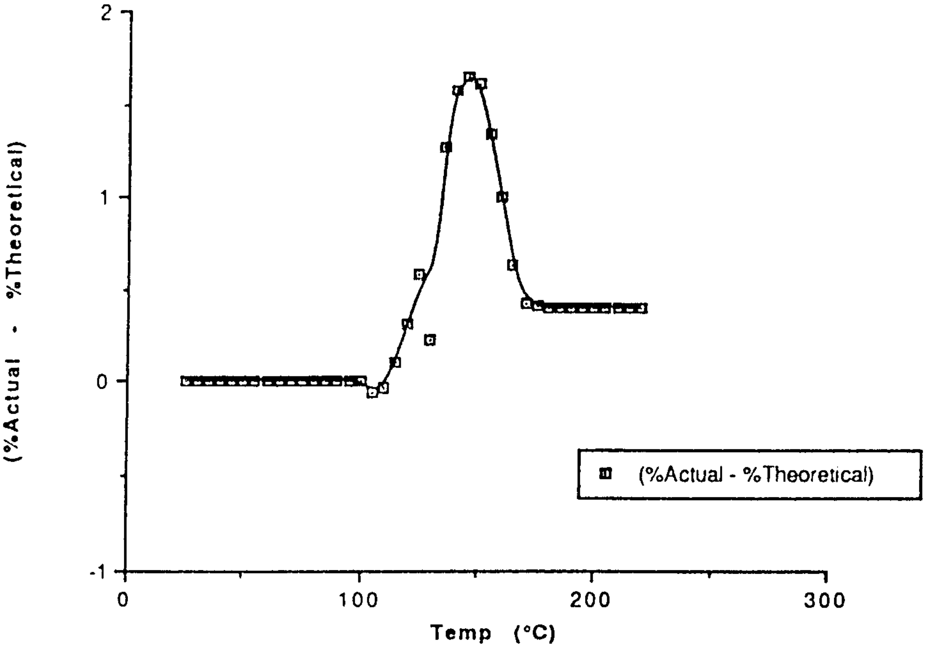

Fig. 12. The difference in weight (W_a–W_t) plotted against the temperature for $NaHCO_3$: $CaCO_3$.

zero. The plot of the difference against temperature is a better approach to this problem since it also gives the percentage error in the sampling procedure.

The above mentioned method was applied to all the binary mixtures. The superimposed calculated (or theoretical) and actual TGA curves were prepared and a typical plot is given in Fig. 11. The differences between the wt% actual (W_a) and the wt% theoretical (W_t) plotted against temperature were prepared and a typical plot is given in Fig. 12.

It can be observed that all the figures obtained by plotting the difference between the wt% actual (W_a) and the wt% theoretical (W_t) against temperature start at zero. However, after the decomposition range of sodium bicarbonate they do not end at zero. This can be attributed to the errors incurred in the sample preparation. If the difference in the wt% on the vertical axis is greater than zero, then the amount of sodium bicarbonate in the binary mixture was less than 50%. If it is less than zero, then the amount of sodium bicarbonate in the binary mixture is more than 50%. In the binary mixture with sorbitol, wherein the sorbitol decomposes simultaneously with sodium bicarbonate once it is melted around 100°C, it cannot be said that the amount of sodium bicarbonate is less than 50%, because the difference in wt% as observed may be only partially due to the above mentioned reasoning. In other words of the difference in wt% for this particular mixture of sodium bicarbonate and sorbitol is due to the simultaneous decomposition of sorbitol along with sodium bicarbonate.

4. Conclusions

1. From the kinetic analysis of the mixtures it can be observed that the activation energy for the decomposition reaction of sodium bicarbonate increases as the number of solids in the mixture increases, or in other words, the reactivity of sodium bicarbonate decreases.
2. The assumption that a pre-existing mechanism exists for the reaction in the estimation of the kinetic parameters for the mixtures of sodium bicarbonate with other solid excipients as used in dental formulations is false.
3. The assessment of the solid state reactivity by the (α_{sample}–$\alpha_{\text{reference}}$) plots proves to be a reliably

simple method for measuring the reactivity between components of the formulation.

4. From the (α_s–α_r) method for analysis of the binary, tertiary and quaternary mixtures in this study, it can be concluded that the solid state decomposition of sodium bicarbonate is delayed in the presence of other excipients.
5. The analysis of mixtures can be repeated with different proportions of excipients. It makes more sense to assess the reactivity of a substance with the exact proportion of excipients as used in the formulation than from the equivalent ratio of (w/w) mixtures. It should be noted that the equivalent (w/w) ratio mixtures give a good indication of the general behavior of the reactivity of a given substance with another in the formulation.
6. The "recognition procedure" for establishing the mechanism for the kinetic analysis and (α_s–α_r) method for reactivity, cannot clearly show the exact changes in the reactivity of a substance when the TGA signals from other substances which may interfere with the TGA signals for that substance. Therefore, the (W_t–W_a) method must be adopted in such cases and will lead to a resolution which is free from extraneous erroneous parameters.

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