THERMAL DEGRADATION BEHAVIOUR
OF SODIUM FIRE EXTINGUISHANT POWDER

R. K. Singh Raman[+], *F. C. Parida*[++] and *A. S. Khanna*[+]

[+]MATERIALS DEVELOPMENT LABORATORY,
[++]SAFETY RESEARCH LABORATORY, INDIRA GANDHI CENTRE FOR ATOMIC
RESEARCH, KALPAKKAM 603 102, INDIA

Although liquid sodium has proved to be a technologically superior and economically viable coolant in the heat-exchange circuits of fast reactors, it is fraught with the serious problems of fire hazards in the event of accidental leakages into the ambient air. For the rapid and effective suppression of sodium fires, sodium bicarbonate has emerged as a potential extinguishant. This paper attempts a description of the thermal decomposition behaviour of sodium bicarbonate fine powder in vacuum on the basis of thermogravimetry and differential thermal analysis. The analog percentage mass change data, transformed into dimensionless extents of reaction and calculated rates of reaction, are then analysed by a generalized computational technique. The results indicate that the most probable rate-controlling step is a process of three-dimensional contraction of the bicarbonate particle surface, with activation energy $E = 82.94$ kJ mol^{-1} and frequency factor $A = 34.73 \times 10^6$ s^{-1}. The decomposition temperature of sodium bicarbonate shows an upward trend with increasing heating rate.

Most of the experimental sodium loops and sodium circuits of fast reactor installations operate at a liquid sodium temperature far beyond its autoignition temperature in air. Hence, accidental spillages from these systems pose a potential fire hazard, which calls for rapid and effective control and extinguishment. In this context, a recent investigation [1] of powdered sodium bicaronate provides evidence that this is a promising extinguishant for liquid sodium pool fires.

Since the gaseous decomposition products of sodium bicarbonate, viz. CO_2 and water vapour, are known to undergo exothermic reactions with liquid sodium, its efficacy as a sodium pool fire extinguishant can be explained only if a detailed investigation is performed on the mechanism of the extinguishment phenomena. The striking features of the metal fire extinguishant powder include the removal of heat from the fire zone, the formation of a barrier between oxidants and the metal, and elevation of the ignition temperature of the metal. The heat removal/cooling process originates from the highly endothermic decomposition mechanism of sodium bicarbonate powder when applied to sodium fires. Although the

thermodynamic properties of sodiur: bicarbonate are well documented, the decomposition kinetics is still a subject of intensive study and there is a lack of reliable data in the literature.

The present experimental investigation is aimed at study of the behaviour of the peak decomposition temperature as a function of the heating rate, employing non-isothermal differential thermal analysis (DTA). The derivation of a possible mechanism has also been attempted from non-isothermal thermogravimetric (TG) data, with application of a generalized computational technique developed by Chen and Fong [4].

Experimental

Analar grade sodium bicarbonate (composition given in Table 1) was used in a sample size of 250 mg ($\pm 0.25\%$), 100 mesh. For sieving, we used a special type of spatula (supplied by Mettler) which preserves not only the mesh size but also the homogeneity in the compaction of samples in the TG balance crucible, which influences the kinetics. All the non-isothermal runs were performed on a simultaneous DTA/TG apparatus (Mettler TA1 balance), in dynamic vacuum mode, with an evacuation rate of (240 ± 10) cm^3 min^{-1} and a heating rate of 4 deg min^{-1}, allowing the recorder to be used at a sensitivity of 100 mg f.s.d. The non-isothermal temperatures are accurate to ± 5 degree. For peak dissociation temperatures at various heating rates ranging from 4 to 25 deg min^{-1}, only the

Table 1 Composition of sodium bicarbonate GR*

Constituents	Max. % (w/w)
Chloride	0.001
Nitrate	0.001
Phosphate	0.0005
Silicate	0.005
Sulphate	0.003
Ammonium	0.005
Arsenic	0.00004
Calcium	0.005
Heavy metal	0.0005
Iron	0.0005
Magnesium	0.005
Potassium	0.005
Water insoluble matter	0.01

* Sarabhai M. Chemicals Pvt. LTd.

DTA mode was employed. The instantaneous temperatures were obtained from the chart output by using a special scale supplied for that purpose by the manufacturer.

The kinetic model functions $F(\alpha)$ listed in Table 2 were examined [6] for the decomposition stages of solid sodium bicarbonate with the method developed by Chen and Fong [4]. The method consists of two steps. Degree of decomposition (α), temperature (T) and ΔW values obtained from TG traces were first employed to estimate kinetic parameters by linear least squares (LSS) fitting, using the five types of mechanisms (m, n, p, mn and np types) indicated in Table 2. Different sets of simultaneous equations were formulated for the different mechanisms, and these were solved using the Gauss–Jordan method to obtain kinetic parameters such as activation energy (E), frequency factor (A) and the type of mechanism.

Table 2 Kinetic model functions for solid decompositions

$F(\alpha)$	Mechanism type	Rate controlling process
m	m	Nucleation, linear growth of nuclei and linear diffusion
$(1-\alpha)^n$	n	Phase boundary reaction and unimolecular decay law
$[-\ln(1-\alpha)]^p$	p	Diffusion
$\alpha^m(1-\alpha)^n$	mn	Nucleation, latter stages of linear growth of nuclei and diffusion
$(1-\alpha)^n[-\ln(1-\alpha)]^p$	np	Growth of nuclei and diffusion

Results and discussion

One of the simultaneous TG–DTA curves is depicted in Fig. 1. Line AB represents the baseline of the TG curve, which shows no decomposition before the sample attains a certain temperature at B. Weight changes ΔW were recorded from the differences between a particular point on the TG curve and the base line. The degree of decomposition α was calculated from the expression

$$\alpha = \Delta W_t / \Delta W_\infty$$

where ΔW_t = weight loss of the sample at time t, and
          ΔW_∞ = weight loss of the sample when the decomposition is complete.

α values were traced against the corresponding temperature for two out of four experimental results. As shown in Fig. 2, the data are quite close for the various traces. All the analyses performed are based on the following solid-state reaction
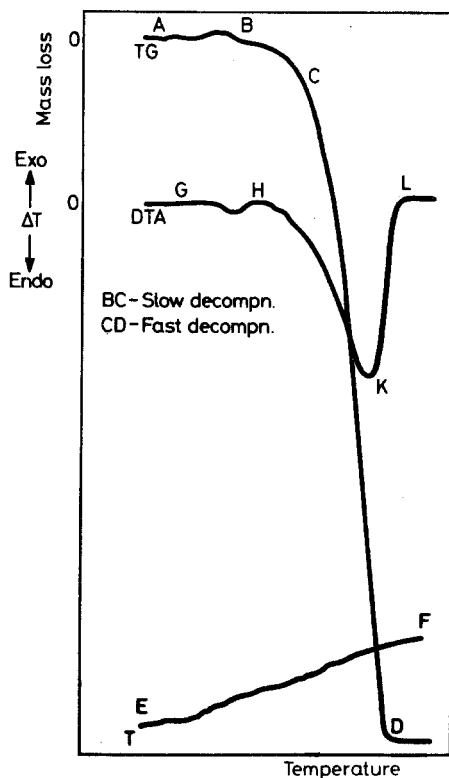
Fig. 1 Simultaneous TG–DTA traces of sodium bicarbonate

rate law:

$$d\alpha/dt = K\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p$$

$$K = A \exp(-E/RT)$$

where K denotes the rate constant, which is a function of absolute temperature T, activation energy E and frequency factor A. m, n and p are arbitrary numbers to determine the type of mechanism the particular reaction follows, as described in Table 3.

The results corresponding to the correct type of mechanism obtained from the LSS method are listed in Table 3 for the two traces. A cursory examination of Table 3 suggests that the only possible mechanism for the thermal decomposition of sodium bicarbonate is of n type, because the derived parameters for other types of mechanisms (viz. m, p, nm and np) involve large deviations in E, A and n values
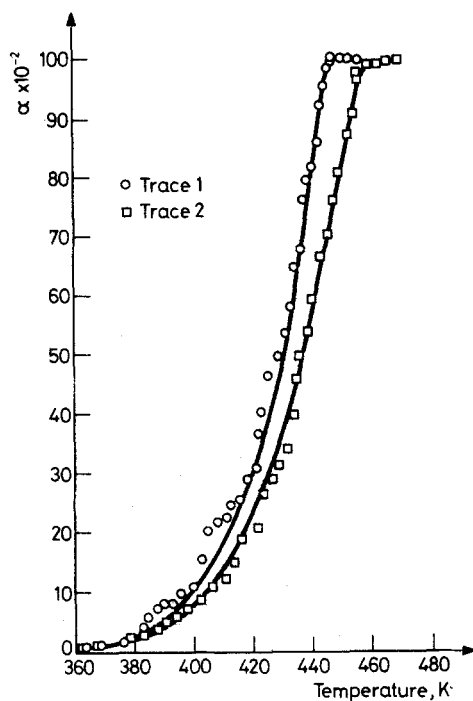
Fig. 2 Degree of decomposition (α) as a function of temperature for thermal decomposition of sodium bicarbonate

Table 3 Kinetic results from LLS procedure

$f(\alpha) \rightarrow$	α^m	$(1-\alpha)^n$	$[-\ln(1-\alpha)]^p$	$(1-\alpha)^n\alpha^m$	$(1-\alpha)^n \cdot [-\ln(1-\alpha)]^p$
Trace I					
A, s^{-1}	34.7×10^{-11}	42.3×10^6	39.1×10^2	32.2×10^{-10}	14.2×10^{-11}
E, kJ^{mol-1}	-57.82	85.48	53.21	-49.86	-60.76
n	—	.1930	—	.0412	.5615
m	1.7087	—	—	1.6330	—
p	—	—	.237	—	1.69
Trace II					
A, s^{-1}	12.4×10^{-6}	25.1×10^6	77.6×10^{23}	11.8×10^{15}	14.7×10^{27}
E, kJ mol^{-1}	-18.89	76.68	234.22	160.06	262.71
n	—	.3094	—	.4061	$-.0955$
m	1.0463	—	—	-1.0837	—
p	—	—	-1.91	—	-2.29

Averaged values for the accepted $(1-\alpha)^n$ mechanism

A, s^{-1}	E, kJ mol^{-1}	n
$(34.73 \pm 7.52) \times 10^6$	82.94 ± 4.49	$.2491 \pm .0486$

Table 4 Comparison of present results with reported values

Method	A, s^{-1}	E, kJ mol^{-1}	n	(Test atmosphere, temperature, gas flow rate)
Wang Hu et al. [2]	—	102	—	Helium flowing at 2.2 cc min^{-1}, 373–473 K
Ball, Mathew [3]	10^5	~64	—	Nitrogen mixed with moisture and carbon dioxide
	$10^{13.5}$	~130	—	flowing at 5 cc min^{-1}, 360–500 K
Present	34.73×10^6	82.94	.2491	Self-generated at 1 atm evacuation rate at 240 cc min^{-1}, 400–500 K

among the various results. This mechanism leads to averaged values of E, n and A of (82.94 ± 4.49) kJ mol^{-1}, (0.2491 ± 0.0486) and $(34.73 \pm 7.52) \times 10^6$ s^{-1}, respectively. It reveals the fact that a process of three-dimensional contraction of the bicarbonate particle surface is operative in the most probable rate-determining step.

Table 4 compares the present results with those reported in the literature. Wang Hu et al. [2] performed isothermal and non-isothermal thermogravimetric experiments in the temperature range 373–473 K, to study the thermal decomposition of NaHCO$_3$ powder (sample size 50 mg) in helium flowing at a rate of 2.2 cm^3 min^{-1}. They obtained average values of 102 kJ mol^{-1} and 1.43×10^{11} s^{-1} for the activation energy and frequency factor respectively. Ball et al. [3] have reported that, when the thermal decomposition of solid NaHCO$_3$ (40 mg) is studied by isothermal TG at temperatures varying between 360 and 500 K in nitrogen flowing at 5 cm^3 min^{-1}, the reaction follows two distinct mechanisms, depending on the temperature region of the test. Above 440 K, the reaction obeys contracting cube kinetics, with an activation energy of 32 kJ mol^{-1} and a frequency factor of 10^1 s^{-1}, showing insensitivity towards the presence of moisture and carbon dioxide. Below 390 K, the reaction follows first-order kinetics, with an activation energy of 64 kJ mol^{-1} and a frequency factor of 10^5 s^{-1} in nitrogen atmosphere. They also confirmed that an increase of the carbon dioxide concentration in the nitrogen pushes the activation energy up to 130 kJ mol^{-1} and the frequency factor to $10^{13.5}$ s^{-1}. Our results clearly fall in the range of values for E and A reported by the above investigators. However, the observed variations of our results from the others can be attributed to the larger sample size (~ 250 mg) and the higher evacuation rate (240 cm^3 min^{-1}) employed in the present experiment.

It may be noted that, although non-isothermal TG techniques have been widely used in recent years for the evaluation of kinetic parameters of solid-phase reactions, due to the adaptation of various numerical methods and diversified computer programming, their efficiency is yet to be tested for universal application

to most of the solid-phase systems, as pointed out by Elder et al. [7]. They observed that a difference in calculation procedures can modify the values of the kinetic parameters. In the present study, the technique developed by Chen and Fong [4] has been adopted, because it can simultaneously take up the five types of mechanisms described earlier and then process the non-isothermal TG data for concurrent evaluation of the activation energy, the frequency factor and the type of mechanism, rendering the process convenient and labour-effective.

The peak decomposition temperature is considered to be the temperature corresponding to the apex of the endothermic DTA curve in a set of experimental conditions. Figure 3 depicts the DTA traces of thermal decomposition of sodium bicarbonate, which was subjected to various heating rates. It also incorporates the experimental values of peak decomposition temperatures (T_p) and heating rates (β). The plot of β vs. T_p is shown in Fig. 4 (a). The upward trend of peak temperature with enhanced heating rate is mainly ascribable to the following points:

The rate of dynamic evolution of CO_2 and moisture during the decomposition is
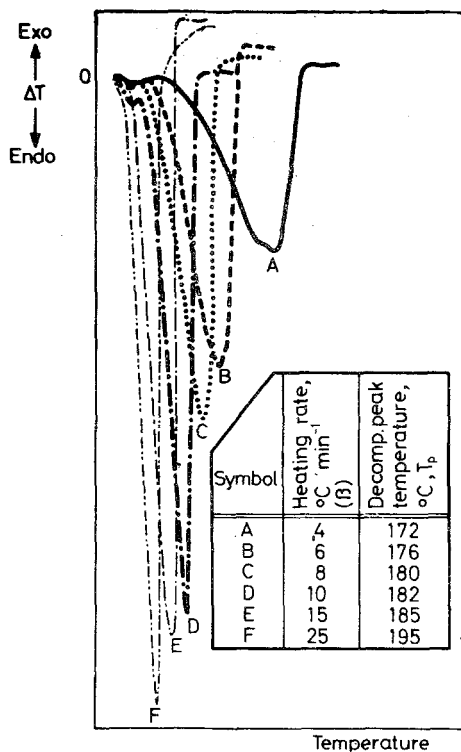

Symbol	Heating rate, $^\circ C \cdot min^{-1}$ (β)	Decomp. peak temperature, $^\circ C$, T_p
A	4	172
B	6	176
C	8	180
D	10	182
E	15	185
F	25	195

Fig. 3 DTA traces of sodium bicarbonate decomposition at various heating rates (β), inset, β and corresponding peak decomposition temp. (T_p) values
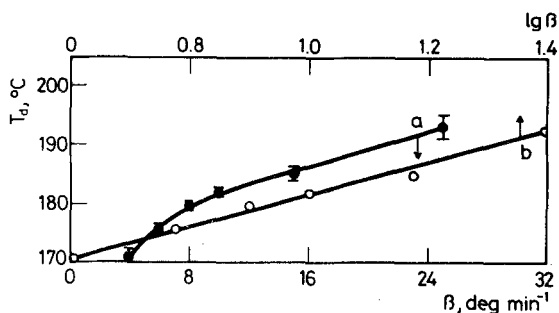
Fig. 4 Plots of peak decomposition temperature (T_p) vs. (a) heating rate (β); (b) log β

maintained constant for a given heating rate. In the region of high heating rates, the rates of generation of CO_2 and H_2O gases outweigh their evacuation rates, and thereby increase the partial pressures of these gases at the sample site. The equilibrium constant would then require a higher reaction temperature for a higher heating rate.

A plot of log β against T_p is linear, as exhibited in Fig. 4 (b), resembling the endothermic dehydration of kaolinite observed by Langen and Kerr [5]. When sodium bicarbonate powder is sprinkled over a sodium fire, it experiences rapid heating as the temperature of the flame zone of an open sodium fire is 850°, far above the peak decomposition temperature, 195°, at the highest heating rate, i.e. 25 deg min^{-1}. The rapid endothermic decomposition of the bicarbonate cools the combustion zone. The reaction product, sodium carbonate, is a reasonably stable solid ($T_p \sim 860°$), and hence it either forms a protective layer between the sodium and the atmospheric oxygen to extinguish the fire or, if decomposed, again consumes heat to cause further cooling, as the reaction is endothermic. These factors join together to help quench the flame and effect extinguishment.

Conclusions

This investigation was a preliminary attempt to understand the mechanisms through which sodium fires are extinguished by using sodium bicarbonate powder, and the results are encouraging enough to warrant further detailed study. The salient observations of the present work are:

1. The small value of the activation energy (E) and the large one of the pre-exponential factor (A) render the decomposition kinetics rapid enough to extract heat from the fire zone and hence speed up the extinguishment process.

2. The elevation of the decomposition peak temperature of sodium bicarbonate

with increasing heating rate is insignificant compared to the temperature in the fire zone. Hence, the efficacy of sodium bicarbonate powder is reasonably substantiated.

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Zusammenfassung — Obwohl flüssiges Natrium als technologisch überlegenes und ökonomisch beständiges Kühlmedium im Wärmeaustausch von schnellen Reaktoren angesehen wird, verbirgt es viele ernste Probleme an Feuergefährlichkeit im Falle eines unfallverursachten Austrittes in die Luft der Umgebung. Zur schnellen und effektiven Unterdrückung von Natriumfeuern ist Natriumbikarbonat als potentieller Auslöscher hervorgetreten. Vorliegende Arbeit versucht mittels Thermogravimetrie und Differentialthermoanalyse das thermische Zersetzungsverhalten von feinem Natriumbikarbonatpulver in Vakuum zu beschreiben. Die entsprechenden Angaben von prozentualer Massenveränderung, transformiert in dimensionslose Reaktionsgrössen sowie von errechneten Reaktionsgeschwindigkeiten werden dann mittels einer verallgemeinerten Rechenmethode ausgewertet. Die Ergebnisse zeigen, daß den geschwindigkeitsbestimmenden Schritt am wahrscheinlichsten ein dreidimensionaler Oberflachen-kontraktionsvorgang der Bikarbonatpartikel mit der Aktivierungsenergie $E = 82.94$ kJ/mol und dem Häufigkeitsfaktor $A = 34.73 \cdot 10^6$ s^{-1} darstellt. Mit anwachsender Aufheizgeschwindigkeit zeigt die Zersetzungstemperatur von Natriumbikarbonat eine steigende Tendenz.

Резюме — Хотя жидкий натрий оказался технологически превосходным и экономически выгодным охладителем в теплообменниках быстрых реакторов, использование его чревато серьезными проблемами, связанными с воспламенением его при случайной утечке на воздух. Бикарбонат натрия всплыл как потенциальный гаситель для быстрого и эффективного подавления горения натрия. В связи с этим, предприняты попытки описания термического

разложения тонкого порошка бикарбоната натрия в вакууме, исходя из ТГ и ДТА измерений. Аналоговые данные процентного изменения веса, преобразованные до безразмерных степеней реакции и вычисленные скорости реакции, затем анализировались обобщенным вычислительным методом. Результаты показали, что наиболее вероятной стадией, определяющей скорость реакции, является процесс трехмерного сжатия поверхности частиц бикарбоната натрия с энергией активации равной $E = 82,94$ кдж·моль$^{-1}$ и частотным множителем $A = 34,73 \cdot 10^6$ сек$^{-1}$. Температура разложения бикарбоната натрия с увеличением скорости нагрева показывает тенденцию к повышению.