COMPARISON OF THERMAL PROPERTIES AND KINETICS OF DECOMPOSITIONS OF NaHCO$_3$ AND KHCO$_3$

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The thermodynamics and kinetics of the thermal decompositions of NaHCO$_3$ and KHCO$_3$ were studied by means of simultaneous TG–DSC. Analysis of the isothermal mass-change traces indicated that the thermal decompositions of NaHCO$_3$ and KHCO$_3$ follow an Avrami–Erofeyev $A_{1.5}$ law. The $A_{1.5}$ law was tentatively explained by assuming a combination of the A_1 and A_2 laws.

It was illustrated that KHCO$_3$ is more stable than NaHCO$_3$ as concerns the thermodynamics and kinetics of the thermal decompositions. The apparent activation energies for the decompositions of the two hydrogencarbonates were a little larger than the corresponding enthalpy changes.

The kinetics of the thermal decompositions of NaHCO$_3$ and KHCO$_3$ have been studied by many workers, and these compounds have often been used as primary standards in thermoanalytical investigations [1, 2]. However, the results are not always concordant, and only few investigations have dealt with a kinetic comparison of the decompositions of the two hydrogencarbonates [3].

Examinations of the effects of deuteration on the dehydration stages of CuSO$_4 \cdot$ 5H$_2$O has recently demonstrated that thermal analysis is particularly useful for a comparison of the kinetics of solid-state reactions of homologous pairs [4]. It is thus of interest to compare the kinetics of the decompositions of sodium and potassium hydrogencarbonates by means of thermal analysis, assuming that the decompositions of these compounds are similar kinetically, irrespective of the different structures [5]; the two materials form a kinetically homologous pair [4].

In the present study, a systematic comparison is made of the thermodynamics and kinetics of the thermal decompositions of NaHCO$_3$ and KHCO$_3$, under identical experimental conditions, by means of simultaneous TG–DSC and isothermal mass-change determination. The thermal decompositions of NaHCO$_3$ and KHCO$_3$ each proceed in a single step to give the solid carbonate, gaseous water and carbon dioxide.

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Experimental

Reagent grade $NaHCO_3$ and $KHCO_3$ from Katayama Chemical Co. were ground manually in a mortar and sieved to a fraction of 170–200 mesh. TG–DSC traces were recorded on a Rigaku Thermoflex TG–DSC 8085E1 system. Samples of 1.00×10^{-4} mol were used, at a heating rate of ca. 0.50 deg/min, in flowing N_2 at a rate of 30 ml/min throughout. Ignited Al_2O_3 was used as reference material. Isothermal mass-change traces were obtained under identical conditions as for the TG–DSC runs.

Results and discussion

Isothermal method. The twelve kinetic model functions $F(\alpha)$ were examined in connection with the isothermal decompositions of $NaHCO_3$ and $KHCO_3$. The appropriate $F(\alpha)$ can be estimated to some extent by plotting all the $F(\alpha)$ against time t, assuming the following equation:

$$F(\alpha) = kt$$

where k is the rate constant [6].

Figure 1 shows the isothermal mass-change traces for the thermal decompositions of $NaHCO_3$ and $KHCO_3$ at various temperatures. In view of the correlation coefficients of linear regression analysis of the $F(\alpha)$ vs. t plots in the α range 0.1–0.9, $A_{1.41}$ and $A_{1.43}$ laws were appropriate for the decompositions of $NaHCO_3$ and $KHCO_3$, respectively. These laws may theoretically be $A_{1.5}$, but the
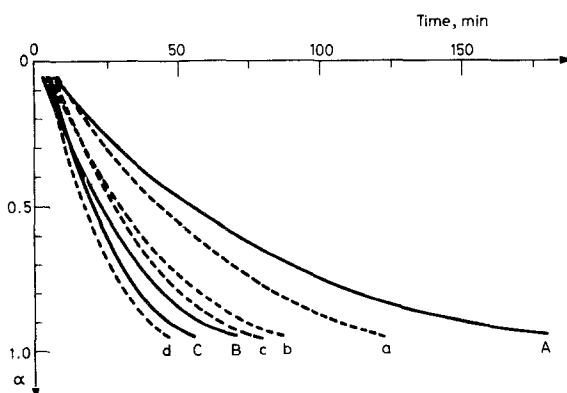
Fig. 1 Isothermal mass-change traces for the decompositions of $NaHCO_3$ (———) and $KHCO_3$ (- - - -). A, B, and C: At temperatures of 109.5, 121.0, and 123.7 °C; a, b, c, and d: At temperatures of 121.5, 127.7, 129.8, and 136.4 °C, respectively

interpretation of the exponent in the Avrami–Erofeyev functions is difficult since the actual decompositions of solids, particularly in the case of crystalline powders, are very complex [7]. Alternatively, it may be that the decompositions proceed in a combination of A_1 and A_2 laws. The present kinetic result on the decomposition of $NaHCO_3$ corresponds to some extent with that of other workers [8].

The fact that practically the same law is followed for the isothermal decompositions of $NaHCO_3$ and $KHCO_3$ suggests that the decompositions are kinetically similar. The very different structures of the two hydrogencarbonates [5] may not be so important here, but the kinetics appears to depend on the nucleation of the product and its growth in the bulk as well as on the surface.

A linear regression analysis of the $\ln k$ vs. $1/T$ plot yields the activation energy E and frequency factor A. Table 1 shows the values of E and A, together with the rate constant k and correlation coefficient r. It follows that $KHCO_3$ is kinetically more stable than $NaHCO_3$ as regards isothermal decomposition.

Table 1 Arrhenius parameters and rate constants k^{*1} for the isothermal decompositions of $NaHCO_3$ and $KHCO_3$ in terms of $A_{1.41}$ and $A_{1.43}$, respectively

Compound	Kinetic parameter			Temp. range, °C	$-r^{*2}$
	E, kJ/mol	$\log A$, 1/s	$k \cdot 10^4$ 1/s		
$NaHCO_3$	109 ± 5	11.1 ± 0.7	6.08	109.5–123.7	0.9988
$KHCO_3$	92.8 ± 5.7	8.22 ± 0.74	0.957	121.5–136.4	0.9962

*1 Value at a temperature of 123.0 °C
*2 Correlation coefficient of linear regression analysis

Non-isothermal method. Figure 2 shows typical TG–DSC traces recorded simultaneously for the decompositions of $NaHCO_3$ and $KHCO_3$. We see from Fig. 2 that $KHCO_3$ is kinetically more stable than $NaHCO_3$ with respect to thermal decomposition, though the onset temperature of the former is slightly lower than that of the latter. The onset temperature largely depends on the formation and growth of nuclei of the decomposition product on the surface in an initial stage. It is interesting to note that the main portion of the TG curve of $KHCO_3$ corresponds approximately to that of $NaHCO_3$, but shifted by ca. 10 deg to a higher temperature. This may imply that the two hydrogencarbonates decompose in a kinetically similar way, with $NaHCO_3$ reacting more rapidly than $KHCO_3$. Table 2 shows a comparison of the decomposition temperatures of the two hydrogencarbonates according to TG. Table 3 gives the decomposition temperatures according to DSC. It is clear from Tables 2 and 3 that $KHCO_3$ is thermally more stable than $NaHCO_3$.

The kinetic parameters can be derived more easily using TG, assuming that the

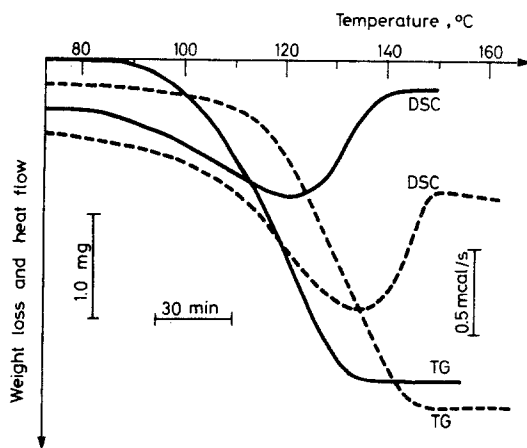**Fig. 2** Typical traces of TG–DSC recorded simultaneously for the decompositions of NaHCO$_3$ (——) and KHCO$_3$ (————)

Table 2 Comparison of the decomposition temperatures (°C) as a function of the fraction decomposed α between NaHCO$_3$ and KHCO$_3$ by means of TG*

Compound	Fraction decomposed α				
	0.1	0.3	0.5	0.7	0.9
NaHCO$_3$	100.5 ± 1.2	110.8 ± 1.0	117.5 ± 0.8	123.3 ± 0.7	129.8 ± 0.7
KHCO$_3$	117.2 ± 1.5	125.3 ± 1.4	131.4 ± 1.2	136.7 ± 0.8	142.4 ± 0.6

* Mean of five-time measurements

Table 3 Comparison of the decomposition temperatures and enthalpy changes ΔH between NaHCO$_3$ and KHCO$_3$ by means of DSC

Compound	Peak temp., °C	ΔH, kJ/mol	
		obsd.	calcd.*
NaHCO$_3$	120.0 ± 2.6	71.8 ± 0.8	64.6
KHCO$_3$	135.7 ± 0.3	79.0 ± 1.3	66.7

* Calculated from standard heats of formation at 25 °C.

$F(\alpha)$ estimated isothermally is valid for the non-isothermal analysis. Table 4 lists the kinetic parameters derived using the modified equation of Coats and Redfern [9] in terms of the $F(\alpha)$ estimated isothermally.

We see that the kinetic parameters derived non-isothermally are comparable with those obtained isothermally and that KHCO$_3$ is more stable than NaHCO$_3$

Table 4 Arrhenius parameters and rate constants k^* for the decompositions of $NaHCO_3$ and $KHCO_3$ in terms of $A_{1.41}$ and $A_{1.43}$, respectively by means of TG^{*2}

Compound	E, kJ/mol	$\log A$, 1/s	$k \cdot 10^4$, 1/s
$NaHCO_3$	86.4 ± 2.2	8.23 ± 0.28	7.60 ± 0.65
$KHCO_3$	107 ± 6	10.5 ± 0.7	3.39 ± 0.62

*¹ Value at a temperature of 124.5 °C
*² Mean of five-time measurements

kinetically too. The fact that the activation energies E are greater than the corresponding enthalpy changes ΔH implies that the decomposition rate is regulated by the nucleation and growth mechanism [10]. It follows that neither the breaking of the hydrogen-bond structures of the two hydrogencarbonates nor the escape of the gaseous products H_2O and CO_2 is very important, but the rearrangement of the destroyed structures to form the crystals of the solid products plays a significant role in the decomposition kinetics of $NaHCO_3$ and $KHCO_3$.

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Zusammenfassung — Die Thermodynamik und Kinetik der thermischen Zersetzung von $NaHCO_3$ und $KHCO_3$ wurden mittels simultaner TG–DSC untersucht. Die Analyse des Verlaufs der isothermen Massenänderung ergab, daß die thermische Zersetzung von $NaHCO_3$ und $KHCO_3$ nach einem Avrami–Erofeyev $A_{1.5}$-Gesetz verläuft. Das $A_{1.5}$-Gesetz wurde versuchsweise mit der Annahme einer Kombination des A_1- und A_2-Gesetzes erklärt. Es wird gezeigt, daß $KHCO_3$, was die Thermodynamik und die Kinetik der thermischen Zersetzung betrifft, stabiler als $NaHCO_3$ ist. Die scheinbare Aktivierungsenergie der Zersetzung der zwei Hydrogencarbonate ist etwas größer als die entsprechende Enthalpieänderung.

Резюме — Совмещенным методом ТГ и ДСК изучена термодинамика и кинетика термического разложения гидрокарбонатов натрия и калия. Анализ изотермического микроизменения веса показал, что термическое разложение обоих соединений подчиняется закону $A_{1,5}$ Аврами-Ерофеева. Закон $A_{1,5}$ условно был объяснен на основе предполагаемой комбинации законов A_1 и A_2. Было показано, что относительно термодинамики и кинетики термического разложения гидрокарбонат калия более устойчив, чем гидрокарбонат натрия. Кажущиеся энергии активации реакций разложения обоих гидрокарбонатов были немного выше, чем соответствующие изменения энтальпии.