

ANALOGUES OF THE ACTIVE AND INACTIVE SODIUM CARBONATE

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The reactivity of the anhydrous carbonates of alkaline metals with sulphur dioxide has been studied experimentally in dependence both on the nature of the cation and on the way of preparation of the anhydrous carbonate. The carbonates were prepared either by thermal decomposition of hydrogen carbonates or by thermal dehydration of carbonate hydrates. The carbonates of lithium, sodium, potassium, rubidium and caesium have been investigated. Kinetic measurements were carried out in a flow reactor in the integral regime at 423 K under atmospheric pressure, with a gas containing 0.2 vol.% of sulphur dioxide and 2.0 vol.% of water vapour in the nitrogen as a carrier gas. The reactivities have been compared on the basis of time dependence of the conversion of carbonate to sulphite.

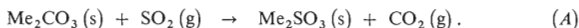
The present investigation represents an extension of kinetic studies¹⁻⁷ pursuing the reactivity of the anhydrous solid sodium carbonate with the gaseous sulphur dioxide which resulted in the discovery of the existence of two forms of the solid anhydrous sodium carbonate differing impressively one from the other in their reactivity in dependence on the way of preparation. The anhydrous sodium carbonate prepared by thermal decomposition of the sodium hydrogen carbonate exhibits in reaction with the sulphur dioxide an extremely high reactivity as compared with the anhydrous sodium carbonate prepared by thermal dehydration of the corresponding hydrate. In terms of effective rate constants, the difference amounts to two to three orders of magnitude. For instance at contact times of the gas with the solid carbonate in hundredths of a second and at temperatures of about 423 K, the active form is able to remove more than 99% of the sulphur dioxide from a gas stream of an inlet concentration of 0.2 vol.%. The other form of the anhydrous sodium carbonate reacts slowly and incompletely with a degree of conversion of the solid of about 5% under the same conditions.

A necessary condition of the high reactivity of the active form is the presence of water vapour acting as a gaseous catalyst which is fed together with the sulphur dioxide in the stream of the carrier gas. The dependence of the reaction rate on the concentration of water vapour exhibits a saturation character, whereas in the reaction of the inactive form the effect of the water vapour is negligible.

The mentioned facts yielded not only physico-chemical backgrounds of a potential desulphurization process of high efficiency but led also to the prediction of the existence of two analogous forms of anhydrous carbonates even with other alkaline metals forming under normal conditions both solid hydrogen carbonates and hydrates of carbonates which are at higher temperatures transformed by decomposition or by dehydration into the corresponding anhydrous carbonate. Thus the experimental verification of this prediction became the main aim of the present paper. Kinetic measurements of reactivities of the anhydrous carbonates with the sulphur dioxide

in dependence on the way of their preparation have been carried out with the carbonates of lithium, potassium, rubidium and caesium. Kinetic data of the anhydrous sodium carbonate have been taken from previous papers^{6,7}.

The heterogeneous reaction of a solid anhydrous carbonate of an alkaline metal with the sulphur dioxide may be described as

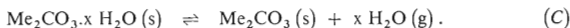


The reaction takes place without any change in the number of molecules and with regard to its substitutional nature, the heat of reaction is not very significant – *e.g.* with sodium it amounts to 54 kJ or with potassium to 36 kJ per unit extent of reaction under standard conditions. An important factor, however, which affects the course of the mentioned reaction with most of the alkaline metals, consists in the way of preparation of the solid anhydrous carbonates which can be prepared in two basic ways, either by thermal decomposition of hydrogencarbonates or by thermal dehydration of the hydrates of carbonates.

The formation of an anhydrous carbonate of the alkaline metal by thermal decomposition of the pertinent hydrogen carbonate can be described in general as



With all the hydrogen carbonates of alkaline metals, the reaction (B) is an endothermic process and the heat consumed lies under standard conditions in the range from 125 to 168 kJ per unit extent of reaction. If the decomposition is carried out in a fixed layer under adiabatic conditions, a lowering of the temperature of the reaction space can thus take place in consequence of the endothermicity of the process, and if the tension of water vapour formed by decomposition exceeds the equilibrium value of the pertinent hydrate, a hydration of the recently formed anhydrous carbonate can take place under formation of a hydrate according to the equation



In the sequence of Li – Na – K – Rb – Cs the following hydrates are stable under laboratory conditions⁸⁻¹⁶: $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$; $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$; $\text{RbCO}_3 \cdot 1.5 \text{H}_2\text{O}$; and $3 \text{Cs}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ (the lithium carbonate is anhydrous). Even though accurate data of equilibrium tensions of water vapour above the corresponding solid phase in dependence on temperature are lacking with most of the carbonates of alkaline metals, it is stated⁸⁻¹⁶ that the hydrates mentioned above are transformed on heating in an inert atmosphere under atmospheric pressure (sometimes under transient formation of lower hydrates) into the corresponding anhydrous salts between the temperatures of 373–403 K. In contrast to this, the decomposition

temperatures of hydrogen carbonates under atmospheric pressure increase in the sequence Na — K — Rb — Cs in the following way: NaHCO_3 — 373.7 K; KHCO_3 , — 430.1 K; RbHCO_3 — 437.4 K, and CsHCO_3 — 448.4 K. By comparison the decomposition temperatures of carbonate hydrates with those of hydrogen carbonates it is seen, that a transient formation of hydrates cannot take place in the decomposition of the pertinent hydrogen carbonates in the case of potassium, rubidium and caesium, especially in a suitable experimental arrangement, since their decomposition temperatures at atmospheric pressure are at least 20–50 K above the temperatures, above which the hydrates cannot exist under given conditions. With the sodium, where the decomposition temperature of hydrogen carbonate and the dehydration temperature of the carbonate hydrate are rather close (385.7 and 373.7 K), the mentioned problem has been successfully solved already previously⁵. It can be said in general that the potential, even transient formation of a hydrate of carbonates can be prevented by means of a suitable experimental arrangement, especially by using a flow system with a dry inert gas enabling an instantaneous dilution and removing the gaseous products of decomposition, and, further on, by using an optimum heating regime of the reaction space so that no sudden release of the water vapour and of the carbon dioxide can take place.

The transformation of the hydrates of carbonates into anhydrous salts according to the equation (C) takes place without interfering effects, only the hydrates of potassium, rubidium and of cesium are known^{10,13,14} to retain the last traces of water very resistantly at the end of the thermal dehydration.

If the reaction (A) is performed in a flow reactor with a fixed layer, it is possible to describe its course by means of dimensionless parameters Y , W and M , defined in the following way⁵:

$$Y = y_r/y_0, \quad (1)$$

$$W = (y_0 F \tau)/n_s, \quad (2)$$

$$M = (k P n_s)/F, \quad (3)$$

where Y denotes the relative concentration of the sulphur dioxide at the reactor outlet and W represents the degree of the stoichiometric loading of the layer (*e.g.* when a stoichiometric amount of sulphur dioxide passes through the fixed layer of the solid carbonate, W equals to one). The parameter M characterizes the working regime of the reactor. Under the assumption that the chemical reaction takes place in the kinetic region under isothermal and isobaric conditions, it is possible to find the relationship between the parameters of Y , W , and M , if the kinetic equation is known. In the case of reaction of the anhydrous, active sodium carbonate with the

sulphur dioxide for which the following kinetic equations is valid¹

$$r = k \cdot p_{\text{SO}_2} \cdot x^{1/2} \cdot (1 - x)^{3/2}, \quad (4)$$

the relevant solution has been found in an algebraic form already previously². Since the resulting relations do not allow to express the parameter M , and even the effective rate constant k as an explicit function of Y and W , it is convenient to treat the primary kinetic data graphically in a form of the dependence of Y on W , and to use as a parameter the ratio $M/k = Pn_s/F$ instead of M . The quantities Y , W , and M/k are experimentally very easy accessible. Besides, it is also convenient to define the mean degree of conversion of the solid as

$$\bar{x} = \int_0^W (1 - Y) dW \quad (5)$$

which can be visualized graphically in the dependence of Y vs W obtained by experiment as an area delimited by the experimental points, the coordinate of $Y = 1$, and by the value of W for which the \bar{x} is required.

EXPERIMENTAL

Procedures

Experimental procedures of kinetic measurements did not differ from the procedures described previously^{5,6} either instrumentally nor methodically^{5,6}. For preparation of a defined and uniformly dense arrangement of particles of the solid reactant (diameter of 0.25–0.33 mm) in the fixed layer, a feeding equipment has been used which has been constructed especially for this purpose. Both the decomposition and the dehydration of parent substances have been carried out *in situ* in a stream of an inert gas (nitrogen for lamps). In the sequence of Na–K–Rb–Cs, from the potassium hydrogen carbonate beginning, higher temperatures than 324 K for the decomposition to anhydrous carbonates under atmospheric pressure are required. Consequently, this process has been carried out after previous tests at 458 K, with potassium, at 493 K with rubidium and at 503 K with the caesium. At the end of the decomposition, the temperature has been lowered to 423 K, at which the actual kinetic experiments have been carried out. The total pressure during the measurements amounted to the level of the atmospheric pressure, the tension of the sulphur dioxide in the feed was about 0.2 kPa, and the tension of the water vapour was also constant, namely 2.06 kPa. The working regime of the reactor was selected in such a way that the value of $Pn_s/F = M/k$ remained constant during all the experiments and amounted approximately to 340 kPa.s.

The preparation of carbonate hydrates and of the hydrogen carbonates of alkaline metals used in the present study proceeded in such a way that the final preparation steps were analogous to those in the preparation of sodium carbonate and hydrogen carbonate used in previous kinetic measurements^{4,5}. The reagents for preparations were mostly of a R.G. quality and the water used was always a distilled one. The hydrates of carbonates have been obtained by crystalliza-

tion from their aqueous solutions. The hydrogen carbonates have been precipitated from the solutions of corresponding carbonates by means of the carbon dioxide gas up to a neutral reaction to phenolphthalein. The prepared samples have been dried, crushed, and screened. For kinetic measurements, a size fraction of 0.25–0.33 mm has been used. If not used immediately, the samples were preserved in sealed glass ampoules (the carbonates) or in tight wide-mouth bottles (the hydrogen carbonates).

Preparation of Carbonates

Lithium carbonate. The warm solutions of lithium hydroxide and ammonium carbonate (in a slight excess) were mixed up, transferred to a Petri dish and evaporated to dry. To eliminate an eventual effect of the escaping ammonia, the evaporation residue has been redissolved in water and reevaporated in a drying oven to dry. The sample contained 99.98% by wt. of Li_2CO_3 .

Potassium hydrogen carbonate. The solution of potassium carbonate was continuously saturated with the carbon dioxide gas. The precipitated solid phase contained after rinsing and drying 99.90% by wt. of KHCO_3 . In the preparation, it is necessary to prevent the formation of a double salt of $\text{K}_2\text{CO}_3 \cdot 2 \text{KHCO}_3 \cdot 1.5 \text{H}_2\text{O}$ by a selection of optimum concentration of the initial carbonate solution (about 40% by wt.)¹⁷.

Potassium carbonate. The commercial potassium carbonate was dissolved in warm water, filtered, cooled, and the separated solid phase has been filtered off and dried on air in a drying oven. The sample contained 94.9% by wt. of K_2CO_3 , and was evidently already partially dehydrated.

Rubidium hydrogen carbonate. From a solution of the rubidium sulphate, the sulphate ions have been removed by conversion to rubidium hydroxide by means of barium hydroxide. After filtering off the barium sulphate, the solution of the rubidium hydroxide has been concentrated and saturated with carbon dioxide gas up to the separation of the solid hydrogen carbonate. The purity of the sample after rinsing and drying amounted to 99.97% by wt.

Rubidium carbonate. The hydrogen carbonate from the preceding preparation has been decomposed thermally at 503 K in a stream of nitrogen. The formed rubidium carbonate has been dissolved in water and dried at 413 K. The purity of the anhydrous salt amounted to 99.20% by wt.

Caesium hydrogen carbonate. The caesium chloride has been fumed off with sulphuric acid and the residue has been dissolved in water. The formed solution of caesium sulphate has been converted to that of caesium hydroxide by means of the barium hydroxide, the sulphate ions being precipitated. After the barium sulphate has been filtered off, the solution of caesium hydroxide has been concentrated and saturated with a carbon dioxide gas up to the separation of the solid hydrogen carbonate. The purity of the sample amounted to 99.97% by wt.

Caesium carbonate. The hydrogen carbonate from the preceding preparation has been decomposed thermally at 503 K in a stream of nitrogen. The formed anhydrous caesium carbonate has been dissolved in water and dried at 413 K. The anhydrous sample contained practically 100% by wt. of Cs_2CO_3 .

RESULTS AND DISCUSSION

The primary experimental data from kinetic measurements of the reaction (A) yielded the following informations: the value of total pressure in the fixed layer (P), the initial amount of the submitted solid (n_s), the total feed (F) and the feed of the sulphur

dioxide (F_g), the final conversion of the solid, and the time dependence of the cumulative increase of the amount of the sulphur dioxide passed through the fixed layer without having reacted (the record of a high-speed recorder). From these data, the partial pressure of the sulphur dioxide in the feed and the value of the parameter of M/k (according to the equation (3)) have been computed. The time dependence of the relative concentration of the sulphur dioxide at the reactor outlet $Y(\tau)$ and the time dependence of the stoichiometric loading $W(\tau)$ of the fixed layer have been evaluated from the curve of the cumulative increase of the amount of sulphur dioxide (in the case of $Y(\tau)$ by numerical derivation). A preliminary evaluation of every kinetic experiment consisted in obtaining the dependence of Y vs W , by means of which it is possible (according to the equation(5)) to find easily by planimetry or by some method of numerical integration the mean degree of the solid phase conversion $\bar{x}(\tau)$ belonging to an arbitrary $W(\tau)$. From the total amount of the fed and unreacted sulphur dioxide, and further on, from the amount of the submitted and unreacted carbonate, a material balance has been computed for every kinetic experiment, which was on the average somewhere within an interval of $\pm 2.5\%$ and served as one of the measures of accuracy of the performance of kinetic experiments.

The dependences of Y versus W are demonstrated in Fig. 1 for anhydrous sodium, potassium, rubidium, and caesium carbonates prepared by thermal decomposition of the corresponding hydrogen carbonates. Experimental conditions of measurements with individual carbonates differed only very little. It is seen that the reactivity of this form of anhydrous carbonates with the sulphur dioxide differs in the sequence

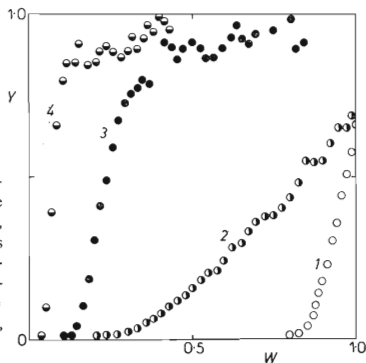


FIG. 1

Dependence of the relative outlet concentration of the sulphur dioxide, Y , on the degree of stoichiometric loading of the fixed layer, W , in reaction (A) for anhydrous carbonates of alkaline metals prepared by thermal decomposition of corresponding hydrogen carbonates; $T = 423$ K, $p_{\text{SO}_2} = 0.2$ kPa, $p_{\text{H}_2\text{O}} = 2.06$ kPa, $M/k \approx 340$ kPa.s: 1 Na_2CO_3 , 2 K_2CO_3 , 3 RbC_2O_3 , 4 Cs_2CO_3

Na - K - Rb - Cs rather significantly. For instance, an 80% removal of sulphur dioxide from the feed ($Y = 0.20$) is attained in the mentioned sequence at values of the stoichiometric loading of the layer equal to 0.90 for Na, 0.55 for K, 0.18 for Rb, and 0.05 for Cs. The mean degree of conversion of the carbonate to sulphite at a unit stoichiometric loading of the fixed layer with sulphur dioxide ($W = 1$) is given in Table I, where the lowering of \bar{x} from sodium carbonate to caesium carbonate illustrates the decrease of the reactivity of the mentioned sequence of carbonates towards sulphur dioxide.

The presented kinetic data permit to compare the reactivity of the above sequence of anhydrous carbonates with sulphur dioxide on the basis of reaction rates. Since the kinetic measurements were carried out at integral conditions, at which the solid conversion, x , and of the partial pressure of sulphur dioxide, p_{SO_2} , generally change along the fixed layer at a given instant, it was necessary to introduce an approximation. This approximation consisted in an assumption that in the breakthrough region of sulphur dioxide the local values of the degree of conversion, x , and of the partial pressure of sulphur dioxide, p_{SO_2} , do not significantly differ from the corresponding mean values \bar{x} and \bar{p}_{SO_2} for the whole fixed layer. For calculations of the reaction rate in this region, it is possible to use a relation

$$r(\tau) = [1 - Y(\tau) F_g] / n_s, \quad (6)$$

currently applied in the treatment of kinetic data obtained under differential conditions. To each value of $r(\tau)$, the corresponding mean degree of conversion, $\bar{x}(\tau)$, and the corresponding value of the partial pressure of sulphur dioxide, $\bar{p}_{\text{SO}_2}(\tau)$, have been calculated. To reduce the comparison of reactivities of carbonates to a com-

TABLE I

Mean degree of conversion, \bar{x} , of anhydrous carbonates in reaction (A)^a in dependence on the nature of the cation and on the way of preparation of the corresponding anhydrous carbonate

Anhydrous carbonate	Li ₂ CO ₃	Na ₂ CO ₃	K ₂ CO ₃	Rb ₂ CO ₃	Cs ₂ CO ₃
from MeHCO ₃ , thermal decomposition	— ^b	0.94	0.77	0.37	0.11
from Me ₂ CO ₃ ·n H ₂ O thermal dehydration	0.00	0.06	0.16	0.20	0.29

^a $\bar{p}_{\text{SO}_2} = 0.25 \pm 0.03$ kPa, $p_{\text{H}_2\text{O}} = 2.05$ kPa, $T = 423$ K, $M/k = 340$ kPa.s; ^b Lithium hydrogen carbonate does not exist at laboratory conditions in a solid dry state.

mon basis, all the reaction rates, $r(\tau)$, have been referred to the reaction rate of the active anhydrous sodium carbonate with the sulphur dioxide, which has been computed according to the above approximation and for the same values of independent variables $\bar{x}(\tau)$ and $\bar{p}_{\text{SO}_2}(\tau)$ by means of the relation (4) with the value of the effective rate constant of $15.8 \pm 3.0 \text{ s}^{-1} \text{ kPa}^{-1}$ (Table II).

The ratios of reaction rates of the anhydrous, active sodium carbonate and of the compared anhydrous carbonate of the alkaline metals are given in Table II. They represent the averages for different values of $\bar{x}(\tau)$ and $\bar{p}_{\text{SO}_2}(\tau)$. To verify the plausibility of the mentioned procedure, the comparison of reaction rates has been first applied to samples of the anhydrous sodium carbonates differing in the way of preparation

TABLE II

Comparison of reaction rates and of effective rate constants of the reaction (A)^a for anhydrous carbonates of alkaline metals prepared by thermal decomposition of hydrogen carbonate

Anhydrous carbonate Me_2CO_3	Way of preparation	$\frac{r_{\text{Na}_2\text{CO}_3}^b}{r_{\text{Me}_2\text{CO}_3}}$	$k, \text{s}^{-1} \cdot \text{kPa}^{-1} \cdot 10^3$	
			estimated	calculated
Na_2CO_3	precipitated from Na_2CO_3 solution	1.15	13.7 ± 2.6	15.8 ± 3.0
Na_2CO_3	commercial A.G., imported (Bulg.)	1.8	8.8 ± 1.7	12.9 ± 3.2
Na_2CO_3	peletized (GFR)	4.9	3.2 ± 0.6	3.8 ± 1.2
Na_2CO_3	recrystallized	2.8	5.6 ± 0.5	12.8 ± 1.5
Na_2CO_3	inoculated	2.7	5.8 ± 1.1	8.1 ± 1.7
K_2CO_3	precipitated from K_2CO_3 solution	10.5	—	—
Rb_2CO_3	precipitated from Rb_2CO_3 solution	40	—	—
Cs_2CO_3	precipitated from Cs_2CO_3 solution	170	—	—

^a $p_{\text{SO}_2} = 0.25 \pm 0.03 \text{ kPa}$, $p_{\text{H}_2\text{O}} = 2.05 \text{ kPa}$, $T = 423 \text{ K}$, $M/k = 340 \text{ kPa.s}$; ^b $r_{\text{Na}_2\text{CO}_3}$ has been calculated by means of the equation (4), $r_{\text{Me}_2\text{CO}_3}$ from the equation (6).

of its parent substance (sodium hydrogen carbonate). The kinetic studies of these samples have been carried out already previously⁶ and they yielded relatively accurate values of effective rate constants given equally in Table II. Because for the anhydrous, active sodium carbonates in their reaction with the sulphur dioxide the kinetic equation (4) is valid, it is possible to estimate from the ratios of reaction rates even the values of effective rate constant (Table II, fourth column), which differ from the corresponding constants obtained previously^{5,6} at most by about one third of the order of magnitude. In the case of anhydrous carbonates of other alkaline metals given in Table II, with which the validity of the kinetic equation (4) cannot be assumed in advance, it is possible to evaluate only the ratios of reaction rates. It is seen that the corresponding reaction rates are by one to two orders of magnitude lower than with the active sodium carbonate.

In Fig 2, the dependences of Y versus W are plotted under identical experimental conditions for anhydrous carbonates of Na, K, Rb and Cs prepared by thermal dehydration of corresponding hydrates. The reaction course for the anhydrous lithium carbonate is not represented in the figure, since its degree of conversion was equal to zero, even for stoichiometric loading of the fixed layer of the carbonate with the sulphur dioxide exceeding units. On comparing the curves in Fig. 1 and Fig. 2, it is seen that the form of carbonates prepared from the hydrates does not exhibit differences in the reactivity as high as the form prepared by decomposition of hydrogen carbonates. The most reactive one is the caesium carbonate with the mean degree of conversion to sulphite of about 30% at a unit stoichiometric loading of the fixed layer with the sulphur dioxide.

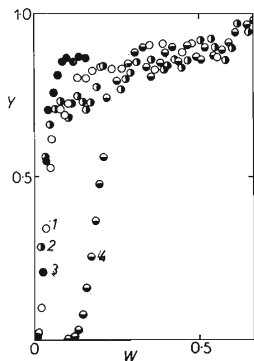


FIG. 2

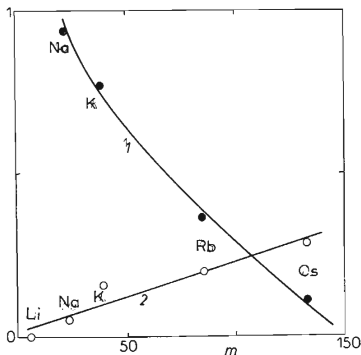
Dependence of the relative outlet concentration of the sulphur dioxide, Y , on the degree of stoichiometric loading of fixed layer, W , in reaction (A) for anhydrous carbonates of alkaline metals prepared by thermal dehydration of corresponding hydrates of carbonates; $T = 423$ K, $p_{\text{SO}_2} = 0.2$ kPa, $p_{\text{H}_2\text{O}} = 2.06$ kPa, $M/k \approx 340$ kPa.s: 1 Na_2CO_3 , 2 K_2CO_3 , 3 Rb_2CO_3 , 4 Cs_2CO_3

A comparison of the reactivity of both forms of anhydrous carbonates is well apparent from Table I and equally from Fig. 3 which illustrates an empirical correlation of the mean degree of conversion, \bar{x} (at a unit value of W), with the atomic weight of the cation. It is seen that the reactivity of anhydrous carbonates prepared from hydrogen carbonates exhibits a steep decrease in the direction from sodium to caesium, which is in agreement with the trend of ratios of reaction rates of these carbonates from Table II. In contrast to this, the carbonates prepared from the hydrates exhibit a reversed dependence. Here, the mean degree of conversion, \bar{x} , increases moderately in the direction from lithium to caesium. The reactivity trends of both carbonate forms is of such a character, that the difference in the attained degree of conversion, \bar{x} , decreases in the sequence Na - K - Rb - Cs monotonously in such a way that the caesium carbonate form prepared from the hydrate possesses even a higher reactivity than the form prepared from the hydrogen carbonate.

To explain the causes of different reactivities of both forms of anhydrous carbonates with the sulphur dioxide, it is possible to assume that the reaction mechanism is the same with all the carbonates. In this case we can adopt the original idea¹ devised for the reaction mechanism of the anhydrous, active sodium carbonate with the sulphur dioxide, according to which an activated complex acts as an intermediate in the conversion of the carbonate to sulphite. The activated complex has a probable composition of $\text{NaHSO}_3 \cdot \text{NaHCO}_3$ and it is formed after adsorption of molecules of the sulphur dioxide and of water from the gas phase on adsorption sites localized on the phase boundary between the carbonate and sulphite. This activated complex is decomposed into reaction products consisting of the newly formed sulphite, carbon dioxide, and water. In this reaction mechanism it is supposed that there

FIG. 3

Dependence of the mean degree of conversion of anhydrous carbonates of alkaline metals, \bar{x} , in reaction (A) for $W = 1$ on atomic weight of cation, m , for two ways of preparation: 1 thermal decomposition of hydrogen carbonates according to reaction (B), 2 thermal dehydration of hydrates of carbonates according to reaction (C)



are two types of adsorption sites, one for the sulphur dioxide and the other for water vapour, and that the rate determining step is the decomposition of the activated complex to the sulphite. In addition, it may be assumed that the reactivity of anhydrous carbonates of the alkaline metals will depend — the way of preparation being the same — first of all on the properties of cations, possibly even on the properties arising from the interaction of cations and anions, however, not on the properties of the anion alone; by X-rays structure analyses¹⁸⁻²⁰ it was verified that the shape and size of various complex anions containing oxygen is invariant with regard to the surrounding environment (nature of the cation). This statement is valid not only with the anions of ClO_4^- , SO_4^{2-} , PO_4^{3-} , SiO_4^{4-} , and with the NO_3^- , CO_3^{2-} , BO_3^{3-} , but also with the SO_3^{2-} .

One of the possible variants of interpretation of the mentioned mechanism which could contribute to explain the effect of the way of preparation of anhydrous carbonates on their reactivity, is the problem of the localization of adsorption sites of molecules of sulphur dioxide and of water on the phase boundary between the carbonate and sulphite. A high frequency of formation and decomposition of the activated complex and thereby the resulting fast reaction course are probably facilitated not merely by a sufficient number of adsorption sites but also by their suitable localization, *i.e.* both types of adsorption sites should be situated in accord with the dimensions and the shape of the activated complex being formed. In this way, the higher reactivity of carbonates formed from the hydrogen carbonates, especially of sodium and potassium, could be explained, where, after decomposition of the parent substance and desorption of the formed carbon dioxide and water, a certain preformation of the formed carbonate can be assumed consisting in a suitable localization of adsorption sites for the molecules of the sulphur dioxide and water. This concept is supported by the fact that the molecules of the carbon dioxide and sulphur dioxide are similar one to another as regards the shapes and dimensions.

On the other hand, the hydrates of alkaline carbonates which thermally treated, lose only water will presumably yield an anhydrous carbonate form with the majority of adsorption sites able to bind only water molecules. This will, in consequence, result in a lower reactivity towards sulphur dioxide. It cannot be excluded that the affinity of these anhydrous carbonates towards water in the gas phase leading to the formation of hydrates, will be proportional even to the reactivity of the corresponding anhydrous carbonates towards sulphur dioxide. For instance, lithium carbonate, which even at laboratory conditions exists in an anhydrous form (forms no hydrates) will, neither at elevated temperature, with a high probability contains on its phase boundary no adsorption sites able to bind water molecules, which is also in accord with its total inactivity towards sulphur dioxide. In contrast to this, rubidium and caesium carbonates form hydrates very readily, being in addition also very hygroscopic which again is in agreement with the higher reactivity of the corresponding anhydrous carbonate towards sulphur dioxide. The sodium and potassium analogues, where

the corresponding hydrates of carbonates are by far not so hygroscopic as the preceding ones assume also in their reactivity towards sulphur dioxide an intermediate position.

CONCLUSIONS

The prediction²¹ of the existence of two forms of anhydrous carbonates discovered already previously^{1-7,22} with the anhydrous sodium carbonate, has been experimentally verified with potassium, rubidium, and caesium. Both forms of carbonates differing significantly in their chemical reactivity, can be obtained by different ways of preparation, namely, either by thermal decomposition of the hydrogen carbonate or by thermal dehydration of the hydrate of carbonate. With lithium only one form can be obtained since lithium hydrogen carbonate does not exist at laboratory conditions in a solid and dry state.

With both forms of anhydrous carbonates, a strong influence of the nature of cation, on the reactivity of the carbonate anion towards sulphur dioxide has been proved. With carbonates prepared by the thermal decomposition of the corresponding hydrogen carbonates, the reactivity towards sulphur dioxide steeply decreases in the sequence Na - K - Rb - Cs, whereas the reactivity of anhydrous carbonates prepared by thermal dehydration of the corresponding hydrates moderately increases in the sequence Li - Na - K - Rb - Cs under the same conditions, the anhydrous lithium carbonate being entirely unreactive. The mutual course of reactivities of both forms assumes in this way an antagonistic character, so that for instance with sodium and potassium it is possible to distinguish an active and an inactive form of carbonates, whereas with rubidium and caesium the differences in reactivity of both forms are not by far so outstanding. With caesium, the form of carbonate prepared from the hydrate exhibits even a higher reactivity than the form prepared from the hydrogen carbonate.

The different reactivity of both forms of carbonates with regard to sulphur dioxide may be partially explained on a qualitative level by means of the theory of the activated complex, if it is assumed to be formed by an interaction of ions of the reacting solid on the phase boundary and the adsorbed molecules of water and sulphur dioxide from the gas phase, different adsorption sites being assumed for the two latter substances. The resulting reactivity of the anhydrous carbonate in dependence on the way of preparation and on the nature of the cation could be determined according to the proposed hypothesis by the location, density, prevalence or even absence of some kind of adsorption sites.

The practical application of the obtained results can be meanwhile expected only with the anhydrous sodium and potassium carbonates prepared from hydrogen carbonates, where a high reactivity towards sulphur dioxide together with a bearable economic accessibility create prerequisites for their applications in some of the dry processes for removing sulphur dioxide from waste gases.

LIST OF SYMBOLS

F	total gas feed into reactor, mol s^{-1}
F_g	feed of reacting gas component into reactor, mol s^{-1}
k	effective rate constant, $\text{kPa}^{-1} \text{s}^{-1}$
M	dimensionless parameter defined by equation (3)
m	relative atomic weights
n_s	amount of reacting solid, mol
P	total pressure, kPa
$p_{\text{H}_2\text{O}}$	partial pressure of water vapour in gas feed, kPa
p_{SO_2}	partial pressure of reacting gas component, kPa
p_{SO_2}	mean value of pressure of reacting gas component in fixed layer, kPa
r	reaction rate, s^{-1}
W	dimensionless parameter defined by equation (2)
x	local degree of conversion of reacting solid
\bar{x}	mean degree of conversion of reacting solid in fixed layer
Y	dimensionless parameter defined by equation (1)
y_0	mole fraction of reacting gas component at reactor inlet
y_f	mole fraction of reacting gas component at reactor outlet
τ	time, s

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