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EXAMINATION OF THE DECOMPOSITION OF $CaBr_2$ WITH THE METHOD OF SIMULTANEOUS TG, DTG, DTA AND EGA

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The thermal behaviour of anhydrous $CaBr_2$ in N_2 and O_2 atmospheres containing H_2O was investigated with the method of simultaneous TG, DTG, DTA and EGA (derivatograph). A method for the continuous determination of the amounts of Br_2 and HBr evolved from the heated sample was elaborated in the presence of each other, and the course of the gas evolution was followed. It was found that water vapour does not react with $CaBr_2$ in either a N_2 or an O_2 atmosphere, and no HBr is liberated. Under the given conditions $CaBr_2$ completely decomposed in an O_2 atmosphere between 500 and 1000°, with the formation of CaO and Br_2, while in a N_2 atmosphere between 700 and 1000° the material lost about 3 % of its original weight, due to evaporation.

In the literature [1], contradictory data can be found regarding the thermal behaviour of anhydrous $CaBr_2$. According to certain authors $CaBr_2$ boils at a temperature slightly higher than its melting point (730°). However according to other researchers, boiling does not start even at 1550°. By using a copper block calorimeter, Dvorkin and Bredig [2] found the melting point in air to be 742°. They did not observe any decomposition. According to Amirova and coworkers [3] boiling occurs at 750° with a slight Br_2 evolution. One of us [4] found the behaviour of anhydrous $CaBr_2$ to differ, depending on the heating rate and the sample amount. Measurements carried out in flowing air showed a weight-loss in the vicinity of the melting point. However, the views also differ as to whether the compound reacts with water vapour or not. If HBr were formed, then according to the literature data this should dissociate only above 800°. However, the reaction of O_2 and HBr is very slow even at 600°. Therefore, the probability of the simultaneous occurrence of any of the following processes can not be excluded:

$$CaBr_{2(l)} = CaBr_{2(g)} \tag{1}$$

$$CaBr_2 + 0.5\,O_2 = CaO + Br_2 \tag{2}$$

$$CaBr_2 + H_2O = CaO + 2\,HBr \tag{3}$$

It is easy to see that, by means of the conventional thermoanalytical methods, only the occurrence of the above processes can be established. However, which of the above processes have actually occurred, and to what extent they overlapped one another, can only be determined with the help of one of the EGA methods.

We found the method for simultaneous TG, DTG, DTA and TGT (thermogastitrimetry) [5,6] to be suitable for the clarification of this problem [7]. In our present paper we wish to report on further results of these examinations.

Experimental

Chemicals

Anhydrous $CaBr_2$ was prepared from p.a. $CaBr_2 \cdot 4\,H_2O$ (Merck) by thermal dehydration. In the course of dehydration the possible loss of bromine was checked with the help of the method to be described. The amount of sample was about 100 mg $CaBr_2$.

Instrument

The examinations were carried out by means of a derivatograph (Hungarian Optical Works, Budapest) complemented with the thermogastitrimetric device. The essence of this technique [5, 6] lies in the following. The gaseous decomposition products liberated in the course of the simultaneous TG, DTG and DTA are quantitatively collected and conducted by a carrier gas into an absorber vessel where they are absorbed by water. The changes taking place in the composition of the solution are followed by titrating with a suitable reagent and applying a potentiometric end-point indication. The amounts of the titrant consumed, added in an automatic way, are recorded as a function of temperature and yield the TGT titration curve. The heating rate was 10°/min. The sample holder was an open Pt crucible.

Method

According to Eqs 1–3, the formations of Br_2, HBr and gaseous $CaBr_2$ are all possible, and we therefore carried out two subsequent different kinds of thermogastitrimetric examinations. First, the changes in the amount of Br_2, and then those in that of $Br_2 + HBr$, were measured and recorded. We determined the amount of $CaBr_2$ evaporating in an indirect way, by difference calculations performed on the basis of the TG and TGT curves. In all probability $CaBr_2$ vapour did not reach the absorber vessel at all, but was condensed on the cooler parts of the apparatus. However, even if it had passed into the absorber vessel, it would not have interfered with the determination of Br_2 or HBr.

Determination of Br_2 by redox titration

The determination is based on the fact that the amount of iodine set free from the iodide-containing solution by bromine can be titrated with arsenious acid solution at an appropriate pH value against a potentiometric equivalence point indication.

The absorption solution was an acetate buffer of pH 5 containing 1.5% KI. Iodine solution was added to this solution so that its I_2 content should be 10^{-4} *N*. We selected as equivalence point the potential value measured in the absorption solution prepared in this way, i.e. we adjusted the titrating device so that it should start with the titration when the potential differs from this preselected value. This operation was necessary because, due to the high sensitivity of the system, the working of the titrating device would have become uncertain if the potential of the iodine-free solution were selected as equivalence point. The response threshold value of the device was about 6 mV, corresponding to a concentration change of the iodine (expressed in terms of bromine) of about 0.6 mg Br_2/l. Platinum and calomel electrodes were used in the measurements, and 0.1 *N* H_3AsO_3 solution prepared according to Winkler served as titrant.

Alkalimetric titration of Br_2 and HBr in the presence of one another

Hydrogen bromide being a strong acid ($p_{Br^-} = 2.6$), it can easily be determined in an alkalimetric way by the application of potentiometric end-point indication. However, the titration becomes somewhat complicated if Br_2 is liberated simultaneously with HBr. In the presence of water, HBr and HBrO are formed from Br_2. The presence of HBrO makes the alkalimetric titration impossible, since it is not only a weak acid but a very unstable one. Therefore, the titration must be performed in the presence of an excess of H_3AsO_3, because this reduces HBrO to HBr. Since H_3AsO_3 is a weak acid ($p_{H_2AsO_3^-} = 9.2$), it does not interfere with the titration carried out at pH = 4.2.

H_3AsO_4 is formed in the course of the reaction

$$Br_2 + H_2O + H_3AsO_3 = 2\,HBr + H_3AsO_4 \qquad (4)$$

As a monobasic acid ($p_{HAsO_4^{2-}} = 7.1$), this also consumes titrant and must be taken into account in the calculation of the results.

Hence, the joint amount of HBr and Br_2 can be determined. However, from the results obtained in the Br_2 determination, the amount of HBr can also be computed, i.e. the curve demonstrating the process of the departure of HBr can be constructed.

The absorption solution was 0.02 *N* arsenious acid solution, the pH of which was adjusted to 4.2. This pH value was selected as equivalence point. The response threshold value of this device at pH 0.1 was also 6 mV in this case, which corresponded to about 0.6 mg Br_2/l. The changes in pH were measured by means of a glass-calomel electrode couple.

Carrier gas

The examinations were performed by applying four different kinds of carrier gas atmospheres.

N_2 atmosphere: N_2 was made oxygen-free with the help of BTS catalyst (Badische Anilin u. Sodafabrik A. G., Ludwigshafen am Rhein) and dried with P_2O_5.

N_2 atmosphere saturated with water vapour: After the N_2 was made free of oxygen, it was saturated with water vapour at room temperature by conducting the gas through a washing bottle filled with water.

O_2 atmosphere: O_2 was dried with P_2O_5.

O_2 atmosphere saturated with water vapour: O_2 was saturated with water vapour at room temperature, as in the case of N_2.

The flow rate of the carrier gas was 10 l/hour in every case.

Results and discussion

Tables 1 and 2 show the results, each of five parallel experiments performed in an O_2 atmosphere, with the technique for simultaneous thermogravimetric and thermogastitrimetric measurements with the parallel application of redox and alkalimetric titrations. The mean values of the results of measurements in the three other kinds of carrier gas atmospheres are listed in Table 3. The weight change readable off the TG curve and the amount of Br_2 measured are given as percentages of the theoretical values calculated from the weight of anhydrous $CaBr_2$. The TG,

Table 1

Redox titration of Br_2 evolved in an O_2+H_2O atmosphere

According to TG curve			According to TGT curve		
Weight change, %	Mean, %	Deviation from mean value, %	Br_2, %	Mean, %	Deviation from mean value, %
103.4		+3.2	103.2		+3.4
97.8		−2.4	99.9		+0.1
100.3	100.2	+0.1	102.6	99.8	+2.8
101.7		+1.5	96.8		−3.0
97.9		−2.3	96.3		−3.5

Table 2

Alkalimetric-titration of Br+ HBr, evolved in an O_2+H_2O atmosphere

According to TG curve			According to TGT curve		
Weight change, %	Mean, %	Deviation from mean value, %	Br_2(+HBr), %	Mean, %	Deviation from mean value, %
101.9		+2.8	102.1		+1.3
97.1		−2.0	98.6		−2.2
97.4	99.1	−1.7	102.4	100.8	+1.6
99.9		+0.8	101.1		+0.3
99.4		+0.3	99.8		−1.0

Table 3

Decomposition of $CaBr_2$ in different atmospheres

Atmosphere	Weight change		Amount of evolving Br_2	
	from TG curves		from TGT curves	
	a	b	redoxtitration a	alkalimetric-titration b
	%			
N_2	2.5*	3.0*	—	—
N_2+H_2O	3.1*	2.9*	—	—
O_2	100.2	99.1	101.2	98.7
O_2+H_2O	99.5	98.7	99.8	100.8

* 3 % Weight loss up to 1000 °C due to evaporation of $CaBr_{2(l)}$.

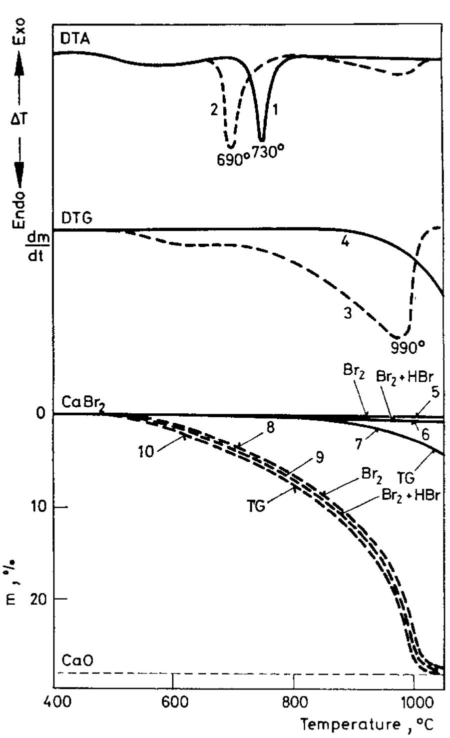

Fig. 1. Simultaneous TG, DTG, DTA and TGT curves of $CaBr_2$ in N_2 (curves 1, 4, 5, 6 and 7) and O_2 (curves 2, 3, 8, 9 and 10) atmospheres saturated with water vapour. Thermogastitrimetric curves obtained from redox-(curves 5 and 8) and alkalimetric-titrations (curves 6 and 9)

DTG, DTA and TGT curves obtained from experiments in O_2 and N_2 atmospheres saturated with water vapour at room temperature are shown in Fig. 1.

In the sense of Eq. 2, in an O_2 atmosphere the sample not only loses Br_2, but also takes up O_2. Accordingly, the TG curve (curve 10) demonstrates the resultant of these two processes. Therefore, in the selection of the scale of the TGT curves (curves 8 and 9), this circumstance was taken into consideration in order to be able to demonstrate that the TG and TGT curves can be brought into overlap.

From the results of the above examinations it turned out that $CaBr_2$ does not decompose up to 1000° in a N_2 atmosphere if this was previously saturated at room temperature with water vapour. However, according to the TG curve (curve 7), the weight of the sample began to decrease after the melting at 730° and the sample lost about 3% of its original weight up to 1000°. This weight loss can be attributed solely to the evaporation of $CaBr_2$, since according to curves 5 and 6, neither Br_2 nor HBr were liberated. Experiments carried out in a dry N_2 atmosphere led to the same result.

In an O_2 atmosphere saturated at room temperature with water vapour, the slow decomposition of $CaBr_2$ began even in the solid state at about 500° (curves 3 and 10). In this case the sample melted earlier, i.e. at 600° (curve 2). The probable explanation of this phenomenon is that the CaO formed in the course of decomposition exerted a boiling point-reducing effect upon the $CaBr_2$. Under the given conditions the decomposition was complete at about 1000°. Since curves 8 and 9 became totally congruent, it can be stated that in the course of the experiment no HBr, but only Br_2 was formed. Accordingly, it is evident that water vapour does not play any role in the decomposition process. This is proved by the TG and TGT curves obtained in a dry O_2 atmosphere too, since their course became identical with those of curves 8, 9 and 10. The numerical data given in Tables 1, 2 and 3 also support the above statement.

If the data given in the Tables are considered from a methodological aspect, it can be stated that the two methods developed are of sufficient accuracy and can be qualified as suitable for the solution of similar problems.

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RÉSUMÉ — Le comportement thermique de $CaBr_2$ anhydre a été étudié dans des atmosphères N_2 et O_2 contenant H_2O par l'emploi simultané des méthodes TG, TGD, ATD et AGE (Derivatograph). On a élaboré une méthode à déterminer les quantités de Br_2 et HBr dégagées par l'échantillon chauffé en présence l'une de l'autre. Les auteurs ont trouvé que la vapeur d'eau ne réagit pas avec $CaBr_2$, ni en atmosphère d'azote ni en atmosphère d'oxygène et que HBr ne se dégage pas. Dans les conditions données, la décomposition complète de $CaBr_2$ a lieu entre 500 et 1000° en atmosphère d'oxygène tandis qu'en atmosphère d'azote elle se déroule entre 700 et 1000°. Les pertes de substance, dues à l'évaporation, s'élèvent à 3 % environ du poids initial.

ZUSAMMENFASSUNG — Das thermische Verhalten von wasserfreiem $CaBr_2$ in H_2O-haltigen N_2 und O_2 Atmosphären wurde mit der Methode der simultanen TG, DTG, DTA und EGA (Derivatograph) untersucht. Es wurde eine Methode für die Bestimmung der Mengen des aus der erhitzten Probe entwickelten Br_2 und HBr in Gegenwart von einander ausgearbeitet. Die Autoren fanden, daß Wasserdampf weder in N_2 noch in O_2 Atmosphäre mit $CaBr_2$ reagiert und daß kein HBr freigesetzt wird. Unter den gegebenen Bedingungen erfolgt die vollständige Zersetzung von $CaBr_2$ in O_2 Atmosphäre zwischen 200 und 1000° unter Bildung von CaO und Br_2, während dies in N_2 Atmosphäre zwischen 700 und 1000° erfolgt. Masseverluste durch Verdampfen betragen etwa 3 % des ursprünglichen Gewichts.

Резюме — Было исследовано термическое поведение безводного $CaBr_2$ в атмосфере азота и кислорода, содержащих воду. Методом одновременной регистрации ТГ, ДТГ, ДТА и ЭГА (Дериватограф), было определено количество выделенных Br_2 и HBr в присутствии друг друга и был прослежен ход выделения газа. Найдено, что пары воды не реагируют с $CaBr_2$ ни в атмосфере азота, ни в атмосфере кислорода. При данных условиях в атмосфере кислорода $CaBr_2$ полностью разлагался между 500—1000° с образованием CaO б Br_2, в то время как в атмосфере азота — между 700—1000°. Потеря материала, вследствии испарения, составляла около 3% первоначального веса.