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THE SEARCH FOR PERBROMATE—I

THE THERMAL DECOMPOSITION OF BROMATES

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Abstract—Thermograms of the seventeen bromates that were thermally decomposed in a newly constructed apparatus are presented. The bromates decomposed to the bromide and/or the oxide depending on the cation. Although the thermograms of strontium bromate provided some evidence for perbromate formation, this was disproved by D.T.A. and infra-red analysis.

Relative free energies of decomposition and activation energies are calculated for the decompositions, the role of kinetics and thermodynamics in predicting the decomposition of bromates is discussed.

THE EXISTENCE and usefulness of perchlorates and periodates makes the non-existence of perbromates an interesting problem both theoretically and experimentally. The theoretical reasons proposed⁽¹⁻⁶⁾ have not satisfactorily explained this non-existence. Many experimental methods have been tried in an attempt to make perbromate: the action of Br₂ on HClO₄,⁽⁷⁾ the distillation of HBrO₃,⁽⁷⁾ the electrolysis of Br₂ and HBrO₃,⁽⁸⁾ the action of Br₂ on KClO₄ and NaIO₄,⁽¹⁾ the action of all the strongest oxidizing agents on bromates,⁽⁹⁾ and the thermal decomposition of bromates.⁽⁹⁻²⁰⁾ The latter method, which can be used to make perchlorates and periodates from chlorates and iodates, gave some small pieces of unexplainable evidence for formation of perbromate.

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HACKSPILL and WINTERER⁽¹⁰⁾ thermally decomposed calcium, strontium and barium bromates and followed the decompositions by measuring the pressure of oxygen evolved. They showed the possible existence of a perbromate over the temperature range 265° - 300° . They postulated the following reaction:

$$2\text{Ba}(\text{BrO}_3)_2 \rightarrow \text{Ba}(\text{BrO}_4)_2 + \text{Ba}\text{Br}_2 + 2\text{O}_2 \tag{1}$$

However, no plateau was formed which would indicate the formation of a compound. Hence their postulate does not seem to be adequately substantiated.

When DECOURSEY⁽⁹⁾ decomposed $Ba(BrO_3)_2$, a definite inflection point appeared at 340° in the thermogram. However, using wet analytical methods for detection, DECOURSEY could find no other evidence to substantiate his thermogram. X-ray, infra-red or D.T.A. could, however, have more clearly elucidated the structural changes at the inflection point.

ROCCHIOCCIOLI⁽¹¹⁾ used a Chevenard thermobalance to follow the weight changes when nine bromates were heated. He found no discontinuities in the decomposition curves. JACH^(12,13) has recently done a detailed study of the decomposition of sodium and potassium bromates and found no evidence for perbromate formation.

Because of the small pieces of evidence for perbromate formation, and because of the complete lack of information on the decompositions of lithium, rubidium, caesium, magnesium, cadmium and the rare earth bromates, a systematic and detailed study of the thermal decompositions of seventeen bromates has been undertaken using the apparatus previously described.⁽²¹⁾

To begin, it was felt that T.G.A. or T.B.G.A. would be most useful in detecting inflection points or plateaus due to perbromate formation, if HACKSPILL's reaction (Equation 1) or any other reaction is proceeding in which oxygen is evolved. However, MARKOWITZ *et al.*⁽²²⁾ have recently shown that the formation of perchlorate from chlorate proceeds without loss of weight, i.e.

$$MClO_3 \rightarrow \frac{3}{4}MClO_4 + \frac{1}{4}MCl \tag{2}$$

and thus T.G.A. might give no indication of perbromate, if formed. Thus we plan a detailed study of the D.T.A. of bromates. However, preliminary D.T.A. experiments on appropriate bromates will be briefly discussed in this paper.

EXPERIMENTAL

T.B.G.A. experiments⁽²¹⁾ up to 500°C were performed. After drying in a vacuum oven at about 80°C, each sample of about 100 mg was finely ground using a mullite mortar and pestle. Nearly all experiments were performed at a heating rate of about 1°C/min.

Infra-red analysis was performed with KBr pellets using a Perkin Elmer Model 21 spectrometer.

Preliminary D.T.A. experiments were performed in a 3-holed brass block. Samples for these experiments weighed about 50 mg and were placed in a 3 mm od glass tube which fitted snugly into the holes.

Compounds

Fischer certified NaBrO₃ was used as the starting material in the preparation of all the bromates. Silver bromate and barium bromate were made from sodium bromate as follows:

AgBrO₃. Prepared by adding 100 g of AgNO₃ to the stoichiometric amount of hot NaBrO₃.

(*1) G. M. BANCROFT and H. D. GESSER. J. Inorg. Nucl. Chem. 27, 1537 (1965).
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The precipitated AgBrO₃ was washed several times to eliminate any NaNO₃. The AgBrO₃ was then dried under vacuum at 80°C.

Ba(BrO₃)₂:H₂O. Prepared by dissolving 100 g of BaCl₂ in water and adding the stoichiometric amount of NaBrO₃. The precipitated Ba(BrO₃)₂:H₂O was washed several times to eliminate any NaCl. The Ba(BrO₃)₂:H₂O was then dried under vacuum at 80°C.

The remainder of the bromates were prepared from $AgBrO_3$ or $Ba(BrO_3)_2 H_2O$ in one of the following two ways:

Experi- ment no.	Compound	Purity bromate (%)	Weight of sample (g)	$\begin{array}{c} T_s \\ (^{\circ}C \pm 2^{\circ}) \end{array}$	Heating rate (°C/min)	Temper- ature range (°C ± 2°)	% Br- in residue wt. %
1	LiBrO ₃	 99·8	0.084	251	1	236-256	95
2	NaBrO ₃	100	0.112	343	1	298-368	100
3	KBrO ₃	100	0.114	390	1	366-395	100
4	RbBrO ₃	97·2	0.137	403	3	328-416	100
5	RbBrO ₃		0.129	406	1	335-410	100
6	CsBrO ₃	99·0	0.155	366	2.5	265-388	100
7	CsBrO ₃		0.155	355	1	258-385	100
8	$Mg(BrO_3)_2$	98.9	0.060	316	1	245-329	5
9	Ca(BrO ₃) ₂	98.9	0.092	256	1	245-270	100
10	$Sr(BrO_3)_2$	98.7	0.100	265	1	248-275	100
11	$Sr(BrO_3)_2$		0.095	273	1	257-280	100
12	Ba(BrO ₃) ₂	100	0.119	317	1	267-328	100
13	Ba(BrO ₃) ₂		0.118	324	1	276-330	100
14	AgBrO ₃	99.3	0.161	272	1	212-292	100
15	CŎ(BrO₃)₂·2H₂O	96·2	0.055	110	1	73-115	3
16	Ni(BrO ₃) ₂	99·2	0.067	195	2	168-221	7
17	$Zn(BrO_3)_2$	97.3	0.055	190	1	160-205	1
18	$Cd(BrO_3)_2$	98·3	0.072	299	1	240-310	2
19	Nd(BrO ₃) ₃ ·9H ₂ O	99.8	0.02	220	1	207–227	20
20	Pr(BrO ₃) ₃ ·9H ₂ O	101-2	0.028	202	1	188-210	36
21	Y(BrO ₃) ₃ ·9H ₂ O	100-2	0.054	214	1	172-227	15

TABLE 1.-DECOMPOSITION DATA FOR THE BROMATES

1. The stoichiometric amount of MCl was added to about 3 g of AgBrO₃ dissolved in 500 ml H_2O with AgBrO₃ in slight excess. The AgCl was filtered and the large volume was evaporated at 80°C under vacuum to about 20 ml. Any excess AgBrO₃ precipitated out and was filtered. The solution was then evaporated to dryness at 80°C under vacuum and three to four grams of the bromate was obtained.

2. The stoichiometric amount of MSO₄ was added to about 4 g of $Ba(BrO_3)_2 H_2O$ dissolved in 200 ml hot water, with $Ba(BrO_3)_2 H_2O$ in slight excess. The $BaSO_4$ precipitated out and was filtered. The solution was evaporated to about 10 ml. Any excess $Ba(BrO_3)_2 H_2O$ precipitated and was filtered. The solution was then evaporated at 80°C (except for cobalt bromate which was evaporated at 40°C) under vacuum and about 4 g of the bromate was obtained.

Analysis of bromates

All the bromates were analysed for bromate purity by the method of BRITTON and BRITTON.⁽²³⁾ About 0.1 g of bromate was dissolved in 75 ml of water and 8 ml of concentrated H_3SO_4 and titrated with a 0.1 N KI standard solution. An average of two results is shown in Table 1.

Those bromates that were made from $Ba(BrO_3)_3 H_2O$ were tested for the presence of barium ion with H_3SO_4 ; those that were made with AgBrO₃ were tested for the presence of silver ion with HCl.

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None of the bromates was contaminated with either cation. The only other impurity could be the oxide or bromide. A small amount (less then 0.5 mole % of bromide was found in the bromates of zinc, rubidium, and cobalt, but *no oxide* was present in any of the bromates. Recrystallization did not decrease the bromide content. KASHOULIS⁽²⁴⁾ noted that a small amount of LiCl had little effect on the rate of decomposition of LiClO₄. As will be seen in the results a small amount of bromide added to strontium and barium bromates (experiments 10 and 12) had little effect on the rate of the trate of decomposition. The inaccuracies in the bromate results could be due to the fact that BRITTON's method had been used to analyse for bromate in potassium bromate and perhaps other cations interfere.

After the bromates were decomposed, the oxygen evolved was pumped into a gas burette and measured. The solid residue was analysed for bromide content potentiometrically using 0.025 N AgNO₃ as the titrant. The insoluble oxides in the residue were determined gravimetrically in some cases, and were shown to agree with the stoichiometry of the reaction and therefore oxide determinations were redundant.



FIG. 1.—Thermograms for the decompositions of the alkali bromates (experiments 1, 2, 3, 5, 7).

RESULTS

For convenience, just the weight readings are plotted as a percentage of the total weight loss. The time chosen as t = 0 is completely arbitrary and has no significance even when activation energies are calculated.

The thermograms of the bromates are shown in Figs. 1-4. Table 1 summarizes the results of the decompositions and Table 2 shows the accuracy of the weight and pressure measurements. T_s is defined as the temperature at which

$$\frac{w_0 - w_f}{w - w_f} = \frac{1}{e} \quad \text{and} \quad \theta = T - T_s$$

where $w_0 = initial$ weight

 $w_r =$ final weight after decomposition

w = weight at time t

e = base of natural logarithms.

Even though most of the bromates crystallize as hydrates, every attempt was made to completely dehydrate these bromates before decomposition to the bromide or oxide.

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FIG. 2.—Thermograms for the decompositions of the alkali earth bromates (experiments 8, 9, 11, 13).



FIG. 3.—Thermograms for the decompositions of transition metal bromates (experiments 14, 15, 16, 17, 18).



FIG. 4.—Thermograms for the decomposition of the hydrated rare earth bromates (experiments 19, 20, 21).

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Contrary to the work of ROCCHIOCCIOLI,⁽¹¹⁾ the bromates of zinc and nickel were completely dehydrated before decomposition to the bromide or oxide ensued. However cobalt bromate evolved two water molecules with bromine and oxygen as ROCCHIOCCIOLI noted. Anhydrous bromates of zinc and nickel were probably obtained because these experiments were done at low pressures, whereas his were done at atmospheric pressure.

		Tota	al wt. loss		· · · · · · · · · · · · · · · · · · ·	
	(mg)			Pressure gain in		
		Ву	•	с	m Hg	
Experi-	Compound	thermo		Ву	÷	
ment	decomposed	balance	Theoretical	gauge	Theoretical	
1	LiBrO ₃	splattering		3.9	3.95	
2	NaBrO ₃	41·0 Î	36.7	5.0	5.6	
3	KBrO3	sp	lattering	5.1	5.1	
4	RbBrO ₃	28.5	28.9	4.0	4 ⋅0	
5	RbBrO ₃	31.0	30.8	5.4	5.2	
6	CsBrO ₃	29.5	28.6	4.1	4 ·1	
7	CsBrO ₃	30.0	29.4	4 ·7	4.7	
8	$Mg(BrO_3)_2$	36.0	36.9	2.4	2.4	
9	Ca(BrO ₃) ₂	34.0	30.0	4.2	4.2	
10	Sr(BrO ₃) ₂	26.5	26.5	3.6	3.7	
11	Sr(BrO ₃) ₂	25.5	24.9	3.6	3.6	
12	Ba(BrO ₃) ₂	29.5	28.5	4.1	4.1	
13	$Ba(BrO_3)_2$	29.0	28.4	4 ∙1	4.2	
14	AgBrO ₃	32.0	31.7	4 ⋅8	4.8	
15	Co(BrO ₈) ₂ ·2H ₂ O	32.0	35.6	adsorption		
16	Ni(BrO ₈) ₂	35.0	36-1	2.3	2.4	
17	$Zn(BrO_3)_2$	32.0	31.1	2.2	2.0	
18	$Cd(BrO_3)_2$	40 ·0	41 ·2	2.7	2.6	
19	Nd(BrO ₈) ₃ ·9H ₂ O	no	not reliable adsorr		orption	
20	Pr(BrO ₃) ₃ ·9H ₂ O	33.0	34.4	adsorption		
21	Y(BrO ₃) ₈ ·9H ₂ O	not	not reliable adsorption		orption	

TABLE 2.—OPERATION OF THE BALANCE AND PRESSURE GAUGE

The theoretical and thermobalance readings in Table 2 coincided well except in the following two general cases:

1. When splattering occurs. This splattering was troublesome with lithium, sodium and potassium bromates due to melting before decomposition (as found from D.T.A.).

For lithium, splattering was eliminated when the temperature was held at 214°C.

2. Bromates which liberated water, oxygen and bromine simultaneously. The water and bromine when present in the gaseous products tended to be absorbed by the core in some cases, making the weight and pressure readings too low. Except for the above two cases the difference between the theoretical and thermobalance readings was less than 3 per cent of the total weight loss or pressure increase.

Except for lithium bromate, the pressure reading gives no additional information in these decompositions except that it is a good check on the weight reading especially in the case of $Sr(BrO_3)_2$. The bromates of magnesium, nickel, zinc, cadmium, cobalt and the rare earths decomposed to the oxide and the bromide. However, for cobalt and the rare earths, the T.B.G.A. method could not be used because a third gas, water, is evolved while the bromates decompose. For the first four bromates mentioned above, such a small amount of bromide (less than 1 mg) was formed, that it was outside the accuracy limits of the apparatus to attempt to estimate the rates of the two competing reactions. However, if the latter four decompositions were done under different conditions such that more bromide was formed, then the T.B.G.A. method would be useful.

DISCUSSION

The search for perbromate

As seen in the thermograms, only strontium bromate shows a distinct discontinuity in the decomposition curve. This decomposition is readily reproducible. The decomposition curves for $Ba(BrO_3)_2$ at different temperatures showed no discontinuity as found by DECOURSEY.⁽⁹⁾ If the reaction proposed by HACKSPILL and WINTERER⁽¹⁰⁾ occurred for strontium bromate, i.e.

$$Sr(BrO_3)_2 \rightarrow \frac{1}{2}Sr(BrO_4)_2 + \frac{1}{2}SrBr_2 + O_2$$
(3)

then the perbromate would form after one-third of the total oxygen had been liberated. The break in the decomposition curves at about $\frac{1}{3}$ of the total oxygen evolved could be due to perbromate formation. An infra-red spectrum was taken at the inflection point using a KBr pellet. This spectrum was found to be identical to that of the anhydrous bromate before decomposition. By analogy with the chlorate and perchlorate, and the iodate and periodate⁽²⁵⁾ a small shift should be observed in the two peaks at 11.80 and 12.65 μ if perbromate was formed. It is possible, but not probable that the structure of the sample changed when cooled or when the potassium bromide disc was made under high pressure. Ideally, infra-red spectra should be taken as the sample is heated. In this way structural changes could be followed continuously.

Preliminary D.T.A. experiments on strontium and barium indicate no formation of perbromate prior to decomposition as MARKOWITZ found for his alkali chlorates.⁽²²⁾ Thus the discontinuity in the thermogram must be due to a change in the topochemical mechanism of the decomposition.

THERMODYNAMICS AND KINETICS

MARKOWITZ⁽²⁶⁾ used thermodynamics to predict the decomposition products when metal perchlorates are heated. As is the case with metal perchlorates, bromates decompose to leave a residue of either the oxide, the halide, or a mixture of both the oxide and the halide. From the results on the decomposition of bromates, the following two overall reactions are competing:

$$MBrO_3 \rightarrow MBr + \frac{3}{2}O_2 \tag{4}$$

$$MBrO_{3} \to \frac{1}{2}M_{2}O + B_{2}^{1}r_{2} + \frac{5}{4}O_{2}$$
(5)

Since the free energies of formation of the bromates are not known (except for $KBrO_3$) then

$$(\Delta F_{fMBr} - \Delta F_{fMO})_{equiv.} = \Delta F_{D_4} - \Delta F_{D_5}$$
(6)

If $\Delta F_{D_4} - \Delta F_{D_5}$ is negative, then thermodynamically the bromide should form; if positive, the oxide should form.

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This method considers only the relative stabilities of the final products in predicting the decomposition products. Thermodynamics can usually predict the equilibrium concentrations of a particular reaction. However, the time taken to reach this equilibrium is dependent on the rate of the reaction which is of course determined by the kinetic parameters. The nature of these decompositions as with most thermogravimetric decompositions seems to be irreversible and equilibrium does not seem likely either between the bromate and the decomposition products or between the bromide and oxide, i.e.

$$MO + Br_2 \rightleftharpoons MBr_2 + \frac{1}{2}O_2 \tag{7}$$

Because of the irreversible nature of the decompositions, it would seem reasonable that the kinetics should play an important role in determining the decomposition products. Thus kinetic parameters E^* , the activation energy and A, the pre-exponential factor were calculated using the simple integral method of HOROWITZ and METZGER.⁽²⁷⁾ This method was used because other recent methods to extract kinetic parameters^(28, 29) involve either graphic or numerical differentiation of the thermogram, a procedure which is very cumbersome and subject to large errors. In HOROWITZ' method

$$\ln \ln \frac{w_0 - w_f}{w - w_f}$$

is plotted vs. θ which should give a straight line whose slope is E^*/RT^2 for any first order reaction in which the total number of moles is a constant.

However, it should be noted that MARKOWITZ was able to predict the decomposition products of the perchlorates except for magnesium just using $(\Delta F_{fCl^-} - \Delta F_{fO^-})_{equiv}$. For all the perchlorates noted except magnesium, $(\Delta F_{fCl^-} - \Delta F_{fO^-})_{equiv}$, is either more negative than 15 kcal. or more positive than 5 kcal. For the decompositions of the bromates of lithium, calcium, cadmium, cobalt, nickel and zinc is between -15 kcal and +5 kcal. Thus the bromates should test the thermodynamic predictions more severely than the perchlorates.

RESULTS

Table 3 lists the thermodynamic data $(\Delta F_{fBr^-} - \Delta F_{f0^-})_{equiv}$ at different temperatures and at $T = T_s$. $(\Delta F_{vBr^-} - \Delta F_{f0^-})_{equiv}$ at $T = T_s$ was calculated from a linear interpolation of the other three values or in a few cases an extrapolation. The free energies of formation of the oxide and bromide were obtained from references.^(30,31,33) Because ΔF_{fBr^-} for the rare earths is not known, the thermodynamic and kinetic data for yttrium, neodynium and praeseodymium are not included. See M.Sc. thesis⁽³²⁾ for estimated values.

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	$(\Delta F_{f Br} - \Delta F_{f O})_{equiv}$ in kcal						
Bromate	(% Br-)	27°Č	227°C	727°C	<i>T</i> ,°*		
LiBrO ₃	90	13.8	- 12.9	-11.3	-12		
NaBrO ₃	100	- 36.2	- 35.2	-32.8	-35		
KBrO ₃	100	-51.8	-50.5	-46.9	-49		
RbBrO ₃	100	-55.8	-54.9	-	- 54		
CsBrO ₃	100	- 59.1		_	- 52		
Mg(BrO ₃) ₂	5	16.9	18-4	22.6	19		
Ca(BrO ₃) ₂	100	12.6	-9.9	-4.9	9		
Sr(BrO ₃) ₂	100	34.2	- 30.7	-26.2	-30		
$Ba(BrO_3)_2$	100	-49·0	-43·0	- 38.8	- 43		
$Zn(BrO_3)_3$	1	2.9	5.2	4.9	5		
Cd(BrO ₃) ₂	2	16-9	-14·1	- 8.5	13		
Co(BrO ₃) ₂ ·2H ₂ O	3	1.4	1.3	5.4	-0.		
AgBrO ₃	100	19-2			- 15		
Ni(BrO ₃) ₂	7	0.8	2.7	8.4	+2.		

TABLE 3.—FREE ENERGY DIFFERENCES $(\Delta F_{fBr} - \Delta F_{fO})_{equiv.}$

* Estimated from linear interpolation or extrapolation of the other three values. — not known.

Table 4 lists the kinetic parameters E^* and A for the decompositions. An example of the plot of $\ln \ln (w_0 - w_f)/(w - w_f)$ vs. θ for the bromates is seen in Fig. 5. Excellent straight lines were obtained for the first part of the Ba(BrO₃)₂ decompositions, but there was deviation near the end of the decomposition. Most of the bromates showed

Experi- ment no.	Compound	Heating rate (°C/min)	E* (kcal/mole)	A (min ⁻¹)
	LiBrO	1	277 p	8.0×10^{11}
2	NaBrO ₂	1	84 w	1.1×10^{29}
3	KBrO,	1	118 p	1.8×10^{88}
4	RbBrO ₂	3	54 w	7.8×10^{16}
5	RbBrO ₃	1	49 w	4.3×10^{14}
6	CsBrO ₃	2.5	33 w	2.4×10^{10}
7	CsBrO ₂	1	26 w	$4.4 imes 10^7$
8	Mg(BrO ₃) ₂	1	20 w	8·5 × 10⁵
9	Ca(BrO ₃) ₂	1	288 w	$4.0 imes 10^{11}$
10	Sr(BrO ₃) ₂	1	68 w	$8.1 imes10^{36}$
11	Sr(BrO ₃) ₂	1	65 w	$2.1 imes 10^{35}$
12	$Ba(BrO_3)_2$	1	52 w	1.9×10^{16}
13	$Ba(BrO_3)_2$	1	52 w	$1.1 imes 10^{18}$
14	AgBrO ₃	1	45 w	1.2×10^{17}
15	Co(BrO ₃) ₂ ·2H ₂ O	1	21 w	$8.5 imes 10^{10}$
16	Ni(BrO ₃) ₂	2	46 w	9·6 × 10 ²⁰
17	$Zn(BrO_3)_2$	1	46 w	$8.1 imes10^{20}$
18	Cd(BrO _s) ₂	1	38 w	$2.5 imes 10^{13}$

TABLE 4.—KINETIC PARAMETERS E^* and A for the decompositions

w-from weight readings.

p-from pressure readings.

the same type of kinetic plot. For all the bromates except those of lithium and calcium, a straight line was obtained for over two-thirds of the decomposition. In the case of lithium and calcium, linearity in the kinetic plot was obtained over about one-half of the decomposition.



DISCUSSION

The significance of the kinetics

The actual significance of the kinetic parameters in many solid decompositions is not known. JACH⁽¹³⁾ states that the rate constant for a solid state decomposition can be represented as

$$K = Na \exp\left(-E^*/RT\right)$$

where N is a number which varies with external features such as surface area and lattice type, and thus A could be significantly different for the two different modes of decomposition for one bromate. Thus the A values shown in Table 4 (A = Na)have no real physical significance. The activation energy E^* also varies with conditions. From Table 4 the higher the heating rate, the higher the apparent activation energy. Thus the calculated activation energy for the caesium bromate decomposition at a heating rate of 2.5° C/min is 33 kcal/mole whereas the calculated activation energy for the same compound at a heating rate of 1°C/min is 26 kcal/mole. A similar trend is also evident for rubidium bromate. Particle size is also very important in calculating E^* values and each sample was ground vigorously in a mullite mortar to ensure some uniformity of particle size. Since each bromate was treated in the same way and since the calculated activation energy for the decomposition of calcium oxalate monohydrate agreed well with that calculated by previous workers, then if a straight line kinetic plot is obtained, the calculated activation energies should be very close to the true values unless the assumption that n = 1 breaks down. Because of the complexity of these reactions, the significance of a first order reaction is not really known. This has obviously led to incorrect (high) values of E* for LiBrO₃, KBrO₃ and Ca(BrO₃)₂. Thus the activation energies will be used for comparative purposes only.

The role of thermodynamics and kinetics in predicting the decomposition products of bromates

In the decomposition of magnesium perchlorate, $(\Delta F_{fCl^-} - \Delta F_{fO=})$ is about zero and at equilibrium about equal amounts of oxide and chloride should be formed according to thermodynamics. However, depending on conditions mostly chloride or oxide was formed. To explain this deviation thermodynamically, an equilibrium was postulated:

$$MgO_{(s)} + Cl_{2(g)} \rightleftharpoons MgCl_{2(s)} + \frac{1}{2}O_{2(g)}$$
(8)

 $\Delta F_8 = RT \ln \frac{P_{\text{O}_2}^{1/2}}{P_{\text{C1}_2}}$

For this reaction, large local concentration in the body of the decomposing perchlorate might be a sufficient driving force to produce some oxide or chloride by reaction (8). Thus MARKOWITZ says,⁽²⁶⁾ "if appropriate control of the gas ratio $P_{O_2}^{1/2}/P_{Cl_2}$ could be maintained throughout a mass of decomposing magnesium perchlorate, the reaction products could be predetermined."

In the decomposition of the bromates several discrepancies in the thermodynamic approach arise. $(\Delta F_{fBr^-} - \Delta F_{fO=})_{equiv.}$ is --12 kcal for the lithium decomposition and 5 wt % oxide was found in the residue. For cadmium $(\Delta F_{fBr^-} - \Delta F_{fO=})_{equiv.}$ is -13 kcal and nearly all oxide is formed whereas for calcium $(\Delta F_{fBr^-} - \Delta F_{fO=})_{equiv.}$ is -9 kcal and only bromide is formed. For nickel, $(\Delta F_{fBr^-} - \Delta F_{fO=})_{equiv.}$ is +2.5 kcal and 7 per cent bromide is formed whereas for cobalt $(\Delta F_{fBr^-} - \Delta F_{fO=})_{equiv.}$ is -0.1 kcal and only 3 per cent bromide is formed. However, when $(\Delta F_{fBr^-} - \Delta F_{fO=})_{equiv.}$ is large (greater than 15 kcal), then, as MARKOWITZ found for the metal perchlorates, the decomposition products can be predicted thermodynamically. Thus the bromates of sodium, potassium, rubidium, caesium, strontium, barium and silver fall into this category.

In the decomposition of lithium bromate, perhaps some of the oxide or bromide could be formed by the following reaction:

$$\frac{1}{2}\text{Li}_2\text{O} + \frac{1}{2}\text{Br}_2 \rightleftharpoons \text{LiBr} + \frac{1}{4}\text{O}_2 \tag{9}$$

For this reaction

$$\Delta F_9 = -12 - 2.73 \log_{10} \frac{P_{\text{O}_2}^{1/2}}{P_{\text{Br}_2}^{1/2}}$$

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It seems highly unlikely that reaction (9) can proceed thermodynamically from right to left to a significant extent. Since reaction (9) should not proceed thermodynamically from right to left and, however, since decomposition of the bromate to the oxide cannot be predicted thermodynamically, it may be concluded that the presence of a large amount of oxide in the residues after decomposition of lithium and cadmium bromates cannot be explained solely by thermodynamics.

Thus, it appears that kinetics does play an important role in these decompositions. It must be stressed that the molecular mechanism and rate controlling process are not known for these decompositions. Thus, it is assumed that each reaction has a single potential barrier (unknown) which must be reached by many bromate crystals if decomposition is to take place at a significant rate.

For the alkaline earths, the activation energy increases enormously from barium

to calcium and then drops off sharply when magnesium oxide is formed from magnesium bromate. This suggests that the activation energy for the bromate to bromide decomposition increases from barium to calcium until the rate becomes so slow that the oxide begins to form because of its lower activation energy. However, magnesium oxide would also be predicted thermodynamically since $(\Delta F_{fBr} - \Delta F_{fO})_{equiv}$ is 19 kcal. The same general trend in activation energies is noticed for the alkali metal bromates. The activation energies for sodium and potassium are slightly out of line in this trend, but the enormous activation energy for the lithium bromate decomposition indicates that although the bromide is favoured thermodynamically, some oxide is formed because of its smaller activation energy. This seems to be confirmed. (See Fig. 5, Ref. 21). The oxide is initially formed because of its lower activation energy, but due to some process (perhaps melting) the thermodynamically favoured bromide then forms.

Calcium decomposes to the bromide whereas cadmium decomposes to the oxide yet the activation energy for the bromate-bromide mode of decomposition for calcium is relatively high (280 kcal). However, reactions occur spontaneously only if they approach a state of lower free energy. If the oxide of calcium has a higher free energy than the bromate then the oxide should not form. However, for the cadmium bromate decomposition, the oxide probably has a slightly lower free energy than the bromate and because the bromate oxide mode of decomposition probably has a lower activation energy than the bromate-bromide mode, then the oxide forms. For potassium, this statement is verified since ΔF_{fBr_8} is -58.2 kcal/equiv. and ΔF_{fO-} is -30.5 kcal/equiv. However, free energy data for all the bromates would have to be determined before these conclusions could be verified.

From the results, two general conclusions may be stated on the use of thermodynamics and kinetics in predicting the decomposition products of metal bromates or other compounds of this type where equilibrium between solid and vapour is not readily achieved.

1. If $(\Delta F_{fBr} - \Delta F_{fO})_{equiv}$ is large (greater than ± 15 kcal) then thermodynamics can be used to predict the decomposition products.

2. If $(\Delta F_{fBr} - \Delta F_{fO})_{equiv}$ is smaller than ± 15 kcal then the kinetics of the reaction become important in predicting the decomposition products.

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