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EFFECTS OF ADMIXTURES OF POTASSIUM BROMIDE ON THE THERMAL DECOMPOSITION OF POTASSIUM BROMATE

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The effects of admixtures of potassium bromide (2.5% and 5%) on the thermal decomposition of potassium bromate were studied within the temperature range 653–683 K. The fraction decomposed (α) *vs.* time (t) relations revealed (i) initial gas evolution, (ii) acceleratory and (iii) decay steps. The data were analysed on the basis of the first-order law with two rate constants k_1 and k_2, k_1 being the rate constant for the initial, slow first-order process (0.02, 0.26), and k_2 being the rate constant for the subsequent faster process, holding within the range 0.21 to 0.98. Upon increase of the concentration of added potassium bromide to 5%, the range for the slow and faster processes became 0.01 to 0.16 and 0.1 to 0.98, respectively. At a given temperature, k_1 increased with increasing bromide concentration, whereas k_2 almost identical for pure potassium bromate and its mixtures (2.5% and 5% bromide).

The isothermal decomposition of potassium bromate has been studied in detail by Jach [1]. At low temperatures the decomposition proceeds in the solid phase, whereas at high temperature the substance melts well below the melting point, due to the formation of a eutectic between potassium bromate and potassium bromide. Solymosi [2] observed that the decomposition of potassium bromate was enhanced by the addition of potassium bromide and that the decomposition proceeded in the solid phase in the presence of the catalyst CuO. The discontinuity observed in the Arrhenius plot was attributed to the melting of potassium bromate during decomposition. The present work deals with the effects of admixtures of potassium bromide (2.5% and 5%) on the thermal decomposition of potassium bromate.

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Experimental

Analar grade potassium bromate and potassium bromide were dried for 3 hours at 403 K in a thermostated electric hot air oven [1]. Dry potassium bromide was powdered, and weighed quantities of potassium bromate and potassium bromide were mechanically mixed thoroughly to prepare two mixtures, one with 2.5% and the other with 5% potassium bromide. Both mixtures were again thoroughly dried at 403 K and were stored over P_2O_5 in desiccators.

Isothermal studies were made at different temperatures in the range 653–683 K. The details were reported earlier [3].

TG and DTG studied were performed in a model OD 103 Metrimpex derivatograph, which photographically recorded the DTA, DTG, and T curves simultaneously. The heating rate was 10 deg/min and the curves were obtained from ambient to 1273 K.

Results and discussion

The isothermal decomposition of potassium bromate proceeds through three stages. The initial gas evolution is enhanced slightly by increase of temperature as seen from the data below:

Temp., K	653	658	663	673	683
α	0.009	0.009	0.010	0.020	0.029

The acceleratory and decay stages are also shortened by the increase of temperature (Fig. 1). The decomposition of potassium bromate proceeds according to the reaction [2]:

$$KBrO_3 = KBr + 1.5\,O_2$$

During the acceleratory stage, the formation of a eutectic makes the reacting mass homogeneous and lower the melting point of the mixture [1]. In this stage potassium bromate melts partially, owing to the presence of excess potassium bromide. In this homogeneous semimolten state, the decomposition is enhanced more strangely by increase of temperature:

Temp., K	653	658	663	673	683
$\alpha_{10\,\mathrm{min}}$	0.076	0.090	0.115	0.318	0.694

This may be due to the fact that bromide ions catalyse the reaction. Being electron donors, bromide ions attract oxygen atoms from the neighbouring bromate ions thereby generating bromite and hypobromite ions, which decompose simulta-

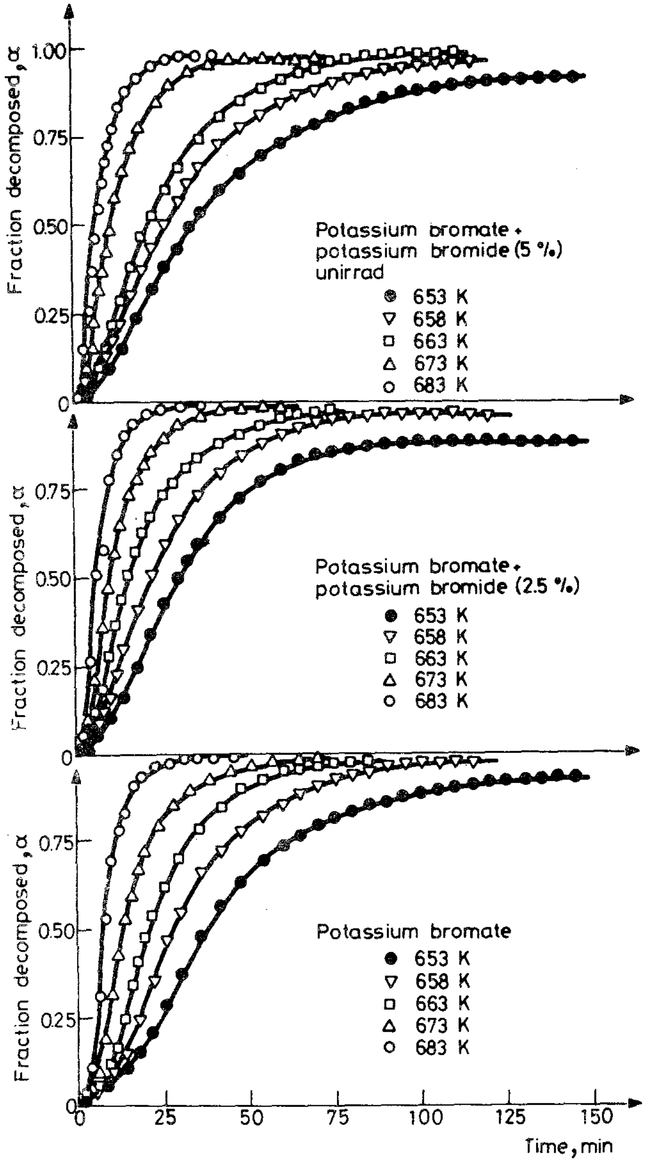

Fig. 1 Isothermal decomposition curves of potassium bromate containing different amount of potassium bromide

neously and instantaneously [1, 2]. Here, the mixtures remain in equilibrium and the system passes completely into the molten stage. The acceleratory reaction occurs in the molten and semimolten condition, with no topochemical aspects involved [4]. The data given below shows that the higher temperature of decomposition, the lower the value of α at which the initial, slow first-order reaction with constant k_1 changes into the second, faster first-order reaction with constant k_2 (Fig. 2).

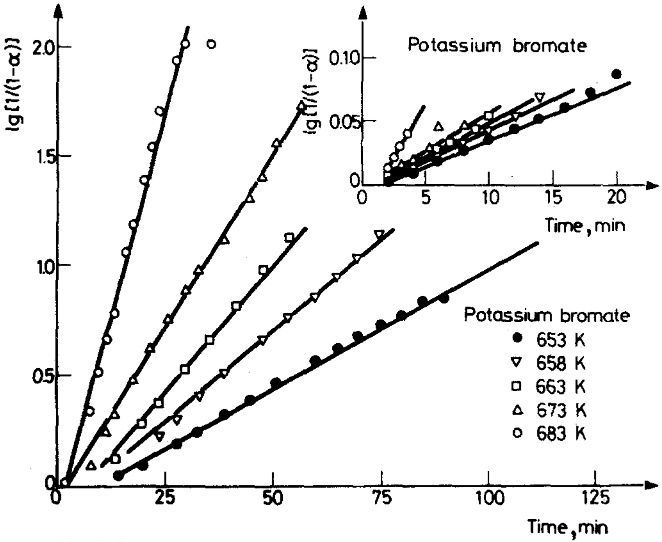

Fig. 2 Log/1/(1 − α)/vs. time curves of potassium bromate

Temp., K	653	658	663	673	683
$\alpha_{k_1-k_2}$	0.21	0.18	0.12	0.10	0.10

It is evident that the change is associated with complete melting, for at a higher temperature a lower concentration of bromide ions is sufficient to produce melting than that required at a lower temperature [4]. The TG and DTA show that the melting point of potassium bromate is lowered from 703 K to 673 K [5, 6], where it also starts to decompose.

Addition of a small amount of potassium bromide (2.5% and 5%) slightly increases the values α of at a given temperature. The data below show the comparative values of α at 658 K for potassium bromate and the two mixtures 10 minutes after the start of the decomposition:

Starting material	$\alpha_{10\,\mathrm{min}}$
1 Potassium bromate	0.090
2 Potassium bromate + 2.5% potassium bromide	0.150
3 Potassium bromate + 5% potassium bromide	0.152

Table 1 Temperature-dependence of velocity constants in the thermal decomposition of potassium bromate

Temp., K	First-order		Prout–Tompkins		Contracting cube	
	k_1	k_2	k_{1a}	k_{2a}	k_{1b}	k_{2b}
653	0.40	1.10	3.50	1.24	—	0.74
658	0.50	1.65	3.90	2.20	—	0.95
663	0.56	2.00	7.40	2.90	—	1.30
673	0.60	3.12	11.20	3.50	—	2.10
683	1.77	6.23	20.00	8.00	—	4.00
$E_{1,2}$	218	218	222	223	—	221

$E_{1,2}$, kJ mol^{-1}; $k_{1,2}$, 10^2 min^{-1}; $k_{1a,b}$, $k_{2a,b}$, 10^2 min^{-1}.

Table 2 Effects of admixtures of potassium bromide on the thermal decomposition of potassium bromate

Temp., K	$KBrO_3$ (pure)		$KBrO_3+KBr$ (2.5%)		$KBrO_3+KBr$ (5%)	
	k_1	k_2	k_1	k_2	k_1	k_2
653	0.40	1.10	0.54	1.22	0.65	1.10
658	0.50	1.65	0.83	1.82	1.01	1.60
663	0.56	2.00	0.94	2.27	1.11	2.00
673	0.60	3.12	1.34	4.31	2.05	3.84
683	1.77	6.23	4.30	8.15	5.45	7.41
$E_{1,2}$	218	222	230	237	220	224

$E_{1,2}$, kJ mol^{-1}; $k_{1,2}$, 10^2 min^{-1}

The DTA and T data show that the addition of 2.5% potassium bromide lowers the melting point of potassium bromate to 653 K, which also marks the onset of decomposition [8]. The added bromide therefore enhance the rate of the reaction.

At a given temperature, the value of k_1 increases with increase of the potassium bromide content, whereas the k_2 value does not show any such regularity (Table 2). The initial part of the reaction at lower temperatures, viz. 653–663 K, becomes shorter and faster, due to the catalytic effect of the added bromide ions. With the progress of the reaction and the accumulation of bromide ions, the added concentration becomes negligible and hence its influence during the faster process becomes insignificant. With the progress of the decomposition, potassium bromide separates out as a solid [9] and the decomposing mass solidifies due to the presence of excess bromide ions. As a result, the escape of oxygen becomes restricted, which explains the gap between the 663 K and 673 K isotherms for the mixtures (Fig. 1).

The activation energy values obtained via the first order law, Prout–Tompkins and contracting cube equations (Table 1) are very similar and close to the Br–O strength (209 kJ mol^{-1}) [7]. Similar activation energy values were likewise obtained from analysis of the two mixtures by the above methods (Table 2). This may be due to simple Br–O bond rupture taking place in the decomposition of pure potassium bromate and the potassium bromate–bromide mixtures. The plot of α against the reduced time t' (Fig. 3) gives a superimposable curve, suggesting that the same chemical process is involved [10].

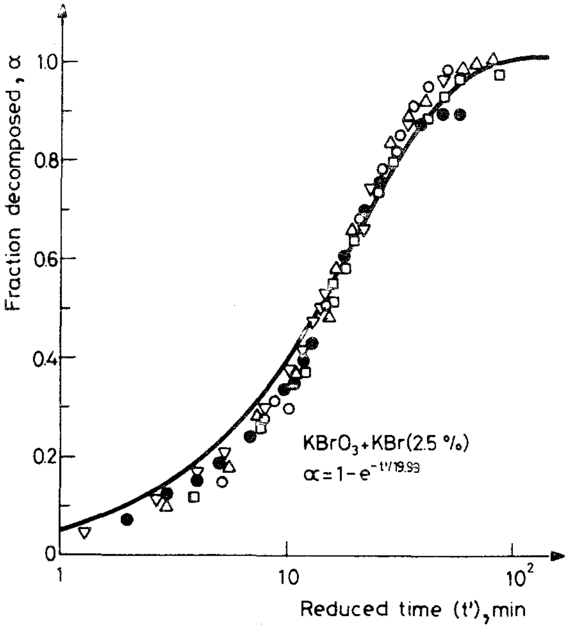

Fig. 3 α *vs.* reduced time curves

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The work is dedicated to the memory of the late Prof. S. R. Mohanty.

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Zusammenfassung — Im Temperaturbereich von 653–683 K wurde der Einfluß von Beimengen von Kaliumbromid (2,5% und 5%) auf die thermische Zersetzung von Kaliumbromat untersucht. Die Funktion der zersetzten Menge (α) in Abhängigkeit von der Zeit (*t*) weist eine anfängliche Gasentwicklung (i), eine beschleunigte (ii) und eine abklingende Stufe (iii) auf. Die Daten wurden auf der Grundlage einer Kinetik erster Ordnung mit den zwei Geschwindigkeitskonstanten k_1 und k_2 durchgeführt, wobei k_1 die Geschwindigkeitskonstante für den einleitenden, langsameren Schritt erster Ordnung ist (0,02, 0,26) und k_2 die Geschwindigkeitskonstante für den darauffolgenden schnelleren Vorgang mit Werten zwischen 0,21 und 0,98. Bei Erhöhung der Konzentration von Kaliumbromid auf 5% betrug der Bereich für den langsameren und den schnelleren Vorgang 0,01 bis 0,16 bzw. 0,10 bis 0,98. Bei gegebener Temperatur steigt k_1 mit zunehmender Kaliumbromidkonzentration an, während k_2 für reines Kaliumbromat und seine Mischungen mit 2,5% und 5% Kaliumbromid fast identisch bleibt.

Резюме — В температурном интервале 653–683 К изучено влияние добавок бромида калия (2,5 и 5%) на термическое разложение бромата калия. Температурные зависимости степени разложения показали стадии первоначального выделения газа, ускорения и затухания реакции. Анализ полученных данных проведен на основе реакции первого порядка с двумя константами скорости k_1 и k_2, где первая является константой скорости начального медленного процесса первого порядка (со значениями от 0,02 до 0,26), а вторая–константой скорости последующего быстрого процесса со значениями в интервале 0,21–0,98. При увеличении концентрации бромида калия до 5% интервал значений k_1 и k_2 становится равным, соответственно, 0,01–0,16 и 0,1–0,98. При данной температуре k_1 увеличивается с увеличением концентрации бромида калия, тогда как k_2 почти одинакова как для чистого бромата калия, так и его смесей (2,5 и 5%) с бромидом калия.