

## EFFECT OF METAL OXIDE CATALYSTS ON THERMAL DECOMPOSITION OF POTASSIUM BROMATE

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Kinetic studies on the effect of metal oxide catalysts, (25% w/w) such as  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ , on the thermal decomposition of  $\text{KBrO}_3$  have been carried out. The kinetic parameters of the catalysed and uncatalysed decompositions were calculated by the Freeman–Carroll, Coats–Redfern and Horowitz–Metzger methods. It has been found that  $\text{Al}_2\text{O}_3$  is almost as good a catalyst as any other oxide used unlike in the thermal decomposition of  $\text{KClO}_3$ . In the case of  $\text{TiO}_2$  there was an increase in the activation energy of decomposition. Of the other oxides  $\text{Cr}_2\text{O}_3$  underwent reaction and was converted to dichromate and so the parameters of the reaction were not calculated. The effect of varying amounts of  $\text{Al}_2\text{O}_3$  on the thermal decomposition was also studied.

The oxysalts of halogens such as  $\text{KClO}_3$ ,  $\text{KClO}_4$  etc., are widely used in explosives and pyrotechnics. As such, studies on the thermal decomposition and high temperature properties of oxyhalogen salts are important and a review on this has recently been published [1]. The effect of metal oxide catalysts on the thermal decomposition of  $\text{KClO}_3$  was investigated by Rudloff and Freeman by TG and DTA [2], but the extent of catalysis was not interpreted in terms of kinetic parameters of the reaction. Bancroft and Gesser [3] studied thermal decomposition of several bromates by thermobarogravimetry. So far there seems to be no report on the effect of metal oxides on the thermal decomposition of  $\text{KBrO}_3$ , and this prompted us to investigate the work detailed below. In this paper the kinetics of the catalysed and uncatalysed thermal decomposition of  $\text{KBrO}_3$  have been studied by thermogravimetry. The oxides used as catalysts are  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . Of these  $\text{Cr}_2\text{O}_3$  underwent reaction and so the kinetics was not followed. The kinetic parameters were calculated by three well known methods viz., the differential method of Freeman and Carroll [4], the integral method of Coats and Redfern [5] and the approximation method of Horowitz and Metzger [6]. All the oxides except  $\text{TiO}_2$  behaved similarly with respect to the decrease in energy of activation. The effect of  $\text{Al}_2\text{O}_3$  was rather unexpected as it was unlike the case of  $\text{KClO}_3$ .

## Experimental

### Chemicals

Potassium bromate (May and Baker R grade) was dried at 120° for several hours and kept in a desiccator before use. The metal oxides Cr<sub>2</sub>O<sub>3</sub>, CuO, MnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were of BDH Laboratory Reagent Grade and had purity above 98%. The oxides were ignited at 500°, and kept in a desiccator before use. The metal oxides and KBrO<sub>3</sub> were of mesh size 200–240. In all experiments 0.2000 g of KBrO<sub>3</sub> was used. The metal oxides in required amounts were added and mixed intimately before the TG curves were taken.

### Apparatus

A Stanton recording thermobalance model TR-1 was used for recording TG traces. The heating rate was 4°min<sup>-1</sup> and chart speed was 6in. hr<sup>-1</sup>. The atmosphere was static air. The samples were taken in tall narrow crucibles to avoid loss by spattering.

In all the experiments except that with Cr<sub>2</sub>O<sub>3</sub> the amount of KBr left behind after decomposition agreed with the instrument reading. The recorded total weight loss in all cases except with Cr<sub>2</sub>O<sub>3</sub> was 58 ± 1 mg for 0.2000 g of KBrO<sub>3</sub>.

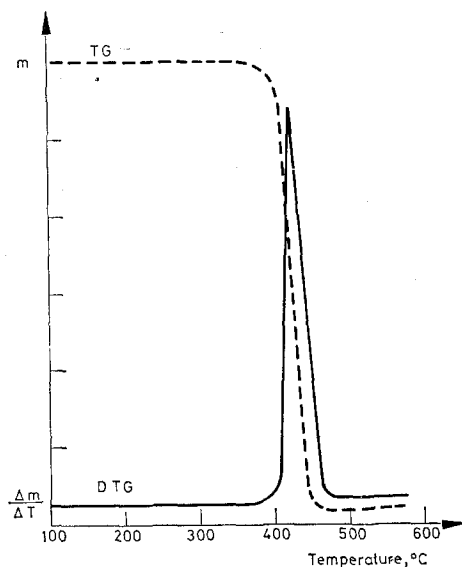
### Treatment of data

The recorded TG traces were redrawn as mass versus temperature (TG) curves and also as rate of loss of mass versus temperature (DTG) curves. The curves were drawn using standard curve sets. Typical TG and DTG curves are presented in Fig. 1.

All the TG curves were essentially of the same pattern except that in the catalysed decompositions the reaction proceeded to completion immediately after the peak temperatures were reached. Therefore, the kinetics of such reactions were followed

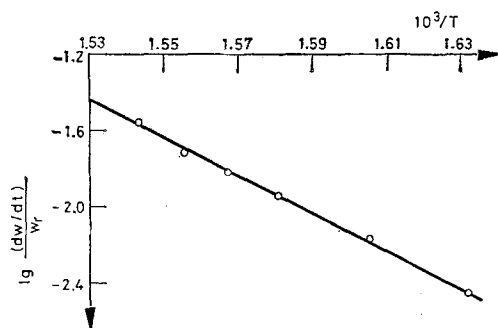
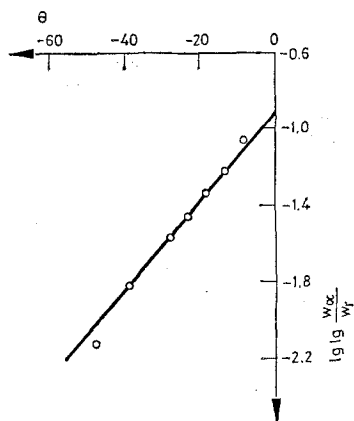
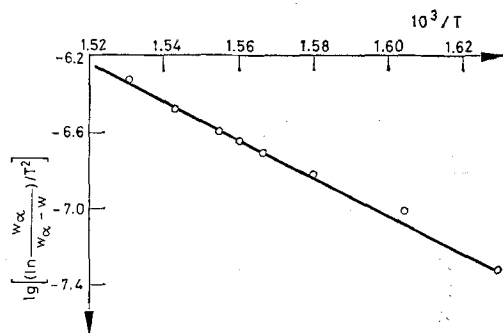
Table 1  
Thermal decomposition data and kinetic parameters

Substance	T <sub>i</sub> , K	T <sub>f</sub> , K	T <sub>s</sub> , K	E*, KJ mole <sup>-1</sup>		
				Freeman Carroll	Coats Redfern	Horowitz Metzger
KBrO <sub>3</sub>	643	723	693	456	433	453
KBrO <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub> (25% w/w)	523	583	582	—	—	—
KBrO <sub>3</sub> + MnO <sub>2</sub> (25% w/w)	573	633	625	197	186	194
KBrO <sub>3</sub> + CuO (25% w/w)	583	648	645	163	168	167
KBrO <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> (25% w/w)	598	663	661	187	191	188
KBrO <sub>3</sub> + TiO <sub>2</sub> (25% w/w)	643	693	670	578	561	598

Fig. 1. TG and DTG of  $\text{KBrO}_3$ 

rom the temperature of inception of reaction to the peak temperature. The emperature of inception ( $T_i$ ), temperature of completion ( $T_f$ ), and peak temperature of decomposition ( $T_s$ ) for  $\text{KBrO}_3$  and mixtures of  $\text{KBrO}_3$  and the metal oxides (25% w/w) are presented in Table 1. The energy of activation ( $E^*$ ), the frequency factor ( $Z$ ), and the entropy of activation ( $\Delta S^*$ ) for  $\text{KBrO}_3$  and the mixtures were calculated by the three different methods mentioned above and the values are given in Table 1. Representative plots are presented in Figures 2, 3 and 4. The values of  $E^*$  for varying amounts of  $\text{Al}_2\text{O}_3$  added to a fixed amount of  $\text{KBrO}_3$  were calculated using Horowitz–Metzger method only. These values along with the values of  $Z$ ,  $\Delta S^*$ ,  $T_i$ ,  $T_f$  and  $T_s$  are given in Table 2. The kinetic order of the thermal decomposition of  $\text{KBrO}_3$  has been evaluated using Freeman–

$Z, \text{sec}^{-1}$			$\Delta S^*, \text{J mole}^{-1}\text{K}^{-1}$		
Freeman Carroll	Coats Redfern	Horowitz Metzger	Freeman Carroll	Coats Redfern	Horowitz Metzger
$2.1 \times 10^{31}$	$9.4 \times 10^{29}$	$9.6 \times 10^{31}$	347.7	310.3	360.4
—	—	—	—	—	—
$4.6 \times 10^{13}$	$7.9 \times 10^{12}$	$6.6 \times 10^{13}$	10.4	-4.1	13.5
$1.3 \times 10^{10}$	$3.8 \times 10^{10}$	$1.2 \times 10^{11}$	-58.0	-48.8	-39.5
$5.3 \times 10^{11}$	$1.3 \times 10^{12}$	$2.5 \times 10^{12}$	-27.1	-19.8	-14.2
$3.6 \times 10^{42}$	$1.9 \times 10^{41}$	$4.1 \times 10^{44}$	563.0	538.0	602.3

Fig. 2. Freeman-Carroll (modified) plot for  $\text{KBrO}_3 + \text{Al}_2\text{O}_3$  (25% w/w)Fig. 3. Horowitz-Metzger plot for  $\text{KBrO}_3 + \text{Al}_2\text{O}_3$  (25% w/w)Fig. 4. Coats-Redfern plot for  $\text{KBrO}_3 + \text{Al}_2\text{O}_3$  (25% w/w)

Carroll method. The methods of calculation based on the three different equations are briefly given below.

*The differential equation of Freeman and Carroll [4]*

The Freeman–Carroll equation used was in the following form

$$\frac{\Delta \log (dw/dt)}{\Delta \log w_r} = \frac{(-E^*/2.303 R) \Delta(T^{-1})}{\Delta \log w_r} + n$$

where  $w_\alpha = w_a - w$ ;  $w_c$  is mass loss at the completion of the reaction,  $w$  = mass loss up to time  $t$ ;  $T$  = absolute temperature at time  $t$ ;  $n$  = order of reaction;  $R$  = gas constant in  $\text{kJ mole}^{-1}$ . The temperature slopes  $dw/dt$  were converted into time slopes  $dw/dt$  using the relation

$$(dw/dt) = (dw/dT)(dT/dt) = (dw/dT)\phi$$

where  $\phi$  is the heating rate.

A plot of  $\frac{\Delta(T^{-1})}{\Delta \log w_r}$  versus  $\frac{\Delta \log (dw/dt)}{\Delta \log w_r}$  was drawn and was found to be linear.

The order of the reaction was almost unity. The usual first order rate law expression

$$(dx/dt) = k(a - x)$$

can be put in the following form using the terms  $w$  and  $w_r$

$$(dx/dt) = Kw_r.$$

Combining this with the Arrhenius equation, we get

$$\log (dw/dt)w_r = (-E^*/2.303 RT) + \log Z.$$

A plot of left hand side of the expression against  $(T^{-1})$  was found to be linear in all cases;  $E^*$  and  $Z$  were calculated from the slope and intercept respectively. The entropy of activation  $\Delta S^*$  was obtained from the equation.

$$Z = (KT_s/h) \exp (\Delta S^*/R)$$

where  $K$  is Boltzmann constant and  $h$  is Planck's constant. A typical plot is given in Figure 2. The  $\Delta S^*$  values were calculated at the respective peak temperatures of decomposition.

*The approximation method using the Horowitz–Metzger equation [6]*

The Horowitz–Metzger equation applicable to first order kinetic proceeds in the form:

$$\log \log w_\alpha/w_r = E^*\Theta/2.303RT_s^2 - \log 2.303;$$

where  $\Theta = T - T_s$  and the other terms are as described earlier. A plot of  $\log \log w_\alpha/w_r$  versus  $\Theta$  was drawn and was found to be linear; from the slope of which  $E^*$  was calculated, typical plot is given in Fig. 3. The pre-exponential factor  $Z$  was calculated from the equation  $E^*/RT_s^2 = Z/\phi \exp -E^*/RT_s$ . The

entropy of activation  $\Delta S^*$  was calculated from the equation used earlier for the purpose.

*The integral method using Coats–Redfern equation [5]*

For first order processes Coats–Redfern equation may be written in the form

$$\log \left( \ln \frac{w_\alpha}{w_\alpha - w} \right) / T^2 = \log \left[ \frac{ZR}{\phi E^*} \left( 1 - \frac{ZRT}{E^*} \right) \right] - \frac{E^*}{2.303RT}$$

since  $1 - (2RT/E^*) \approx 1$ , a plot of left-hand side of the equation against  $T^{-1}$  was drawn (Figure 4) and  $E^*$  was calculated from the slope and  $Z$  was found out from the intercept. Entropy of activation at the peak temperature was calculated from the equation given above. Other kinetic models ( $\log n \neq 1$ ) did not give linear plots.

The slopes and intercepts of all the plots obtained by the three methods were calculated by the method of least squares and  $E^*$  values were evaluated therefrom. The correlation coefficients were in the range 0.98–0.99. The parameters are given in Table 1 and 2.

Table 2

Effect of  $\text{Al}_2\text{O}_3$  on thermal decomposition of  $\text{KBrO}_3$

Percentage (w/w) of $\text{Al}_2\text{O}_3$ used with 0.2000 g of $\text{KBrO}_3$	$T_i$ , K	$T_f$ , K	$T_s$ , K	$E^*$ , KJ mole <sup>-1</sup>	$Z$ , sec <sup>-1</sup>	$\Delta S^*$ , mole <sup>-1</sup> K <sup>-1</sup>
0	643	723	693	453	$9.6 \times 10^{31}$	360.4
5	608	693	673	342	$2.2 \times 10^{24}$	214.2
10	608	683	668	232	$6.2 \times 10^{15}$	50.7
20	608	668	659	202	$3.6 \times 10^{13}$	7.9
25	598	663	661	188	$2.5 \times 10^{12}$	-14.2
35	598	658	656	160	$1.6 \times 10^{10}$	-55.9
43	598	658	655	155	$7.3 \times 10^9$	-62.7
60	598	658	655	158	$1.1 \times 10^{10}$	-59.1
100	598	658	656	151	$2.8 \times 10^9$	-70.6

### Discussion

Jach studied the decomposition kinetics of  $\text{KBrO}_3$  by gas evolution method from 615 K onwards [7]. It was found that two different kinetic behaviours were observed in the ranges 615 – 640 K and 652 – 685 K with a transition region in between. The reaction was first order over both the ranges but the activation energies were 260 and 221 KJ mole<sup>-1</sup> respectively. Duval [8] and Bancroft and Gesser [3] found the temperature of inception of decomposition to be at 643 K

by thermogravimetry which is supported by the present investigation also. The activation energy according to Bancroft and Gesser obtained using Horowitz–Metzger method was  $494 \text{ KJ mole}^{-1}$ . The average value of  $E^*$  calculated by different methods in this study is  $447.5 \text{ KJ mole}^{-1}$ . The decreased value of  $E^*$  may be explained as due to increased sample size and greater rate of heating used in the present study.

While studying the effect of metal oxide catalysts on the thermal decomposition of  $\text{KClO}_3$  and  $\text{KClO}_4$ , Rudolff and Freeman [2] based their arguments on the temperature of inception of reaction ( $T_i$ ) and peak temperature of decomposition ( $T_s$ ) and the changes in  $E^*$  values on the addition of catalysts were not evaluated. Further, basing their arguments on the semiconductive properties of the oxides used, they concluded that *p*-semiconductive oxides like  $\text{CuO}$ ,  $\text{NiO}$  and  $\text{Cr}_2\text{O}_3$  are good catalysts whereas *n*-semiconductive oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  are poor catalysts. Though a *n*-semiconductor  $\text{Fe}_2\text{O}_3$  was found to be a good catalyst and  $\text{MnO}_2$  could be considered either as *p*-semiconductive or as *n*-semiconductive. Thus it remains that the principle based on semiconductive properties is not applicable to all metal oxide catalyses. It seems that the effect of metal oxide catalysts on thermal decomposition can be better understood from a knowledge of  $E^*$  and  $\Delta S^*$  than from  $T_i$  and  $T_s$ .

In the present investigation some typical *p*-semiconductive and *n*-semiconductive metal oxides were used to study their effect on the thermal decomposition of  $\text{KBrO}_3$ . The kinetic parameters are used to assess their relative merits as catalysts as against the explanation based on  $T_i$  and  $T_s$  [2]. The oxides, viz.  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}_3$  lowered the values of  $T_i$ ,  $T_f$  and  $T_s$  for the decomposition of  $\text{KBrO}_3$ . With  $\text{TiO}_2$  there was practically no change in  $T_i$ ; but  $T_s$  and  $T_f$  were lower compared to the uncatalysed decomposition. Therefore all these oxides may be considered as positive catalysts with respect to  $T_s$  and  $T_f$ . The  $E^*$  values for the uncatalysed thermal decomposition of  $\text{KBrO}_3$  evaluated by the different methods correspond to nearly  $447.5 \text{ KJ mole}^{-1}$  on the average. Addition of (25% w/w)  $\text{CuO}$ ,  $\text{MnO}_2$  and  $\text{Al}_2\text{O}_3$  decreased this values to 166, 192.5 and 189  $\text{KJ mole}^{-1}$  respectively. So the catalytic effects of these oxides are almost similar. On the other hand  $\text{TiO}_2$  increased  $E^*$  to  $579 \text{ KJ mole}^{-1}$ . If the semiconductive properties were the deciding factor,  $\text{Al}_2\text{O}_3$  must not have decreased the  $E^*$  value this much extent. It is inferred by comparing the TG traces that  $\text{TiO}_2$  has effect only after melting of  $\text{KBrO}_3$  while the other oxides catalyse the decomposition even before melting.

Perusal of the  $\Delta S^*$  values suggests that the entropy of activation for the catalysed reaction excepting that with  $\text{TiO}_2$  is lowered by about  $360 - 400 \text{ J mole}^{-1} \text{ K}^{-1}$ . In the presence of  $\text{TiO}_2$  there is an actual increase in  $\Delta S^*$  to the extent of about  $200 \text{ J mole}^{-1} \text{ K}^{-1}$ . This would suggest that in the presence of the other catalysts a more ordered transition state is formed. The entropy decrease, observed in the catalysed processes, though unfavourable for enhanced reaction rate, is more than compensated for by the decrease in the  $E^*$  values. It is likely that some chemisorbed complexes are formed in the process of formation of the transition state with oxides showing negative  $\Delta S^*$ . The increase in entropy with added  $\text{TiO}_2$

rules out the chance of such a transition state formation. The increase in  $E^*$  by the addition of  $\text{TiO}_2$  is not sufficiently compensated by the increase in  $\Delta S^*$ . Hence  $\text{TiO}_2$  cannot be considered as a catalyst for the decomposition though it decreases the value of  $T_s$ .

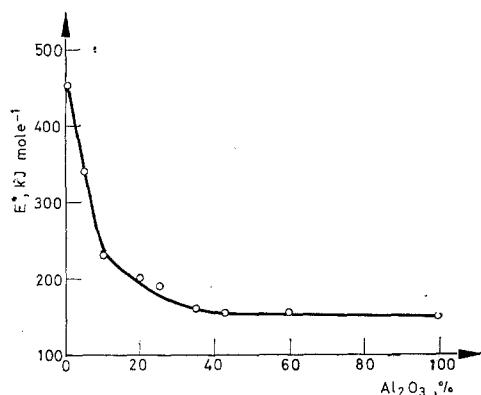


Fig. 5. Effect of varying amounts of  $\text{Al}_2\text{O}_3$  on  $E^*$  of  $\text{KBrO}_3$

Since the behaviour of  $\text{Al}_2\text{O}_3$  was rather unexpected with regard to the decrease in  $E^*$ , varying proportions of  $\text{Al}_2\text{O}_3$  were added to  $\text{KBrO}_3$  and the kinetics were followed. The  $E^*$  values were calculated using Horowitz – Metzger equation only and are given in Table 2. A plot of  $E^*$  values against percentage of  $\text{Al}_2\text{O}_3$  is presented in Fig. 5. It is found therefrom that the optimum amount of  $\text{Al}_2\text{O}_3$  is nearly 35% (w/w).

From these studies it seems that explanations for the behaviour of metal oxide catalysts on thermal decomposition reactions cannot be solely based on the semi-conductive properties of the oxides. This is due to the specificity of catalysts for each reaction.

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RÉSUMÉ — Des études cinétiques sur l'influence d'oxydes métalliques tels que  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$  et  $\text{TiO}_2$  comme catalyseurs (25 % en poids) de la décomposition thermique de  $\text{KBrO}_3$  ont été effectuées. Les paramètres cinétiques des réactions de décomposition catalysées ou non ont été calculés par les méthodes de Freeman—Carroll, Coats—Redfern et Horowitz—Metzger. On a établi que — contrairement à la décomposition thermique de  $\text{KClO}_3$  — l'oxyde  $\text{Al}_2\text{O}_3$  était un catalyseur presque aussi bon que n'importe quel autre oxyde utilisé. Dans le cas de  $\text{TiO}_2$  l'énergie d'activation de la décomposition se trouve augmentée. Parmi les autres oxydes,  $\text{Cr}_2\text{O}_3$  entre en réaction et se transforme en bichromate; c'est pourquoi les paramètres de la réaction n'ont pas été calculés. L'effet de quantités variables en  $\text{Al}_2\text{O}_3$  sur la décomposition thermique a également été étudié.

ZUSAMMENFASSUNG — Kinetische Untersuchungen bezüglich der Wirkung von Metalloxidkatalysatoren z. B. 25 Gew. %,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$  und  $\text{TiO}_2$  auf die thermische Zersetzung von  $\text{KBrO}_3$  wurden durchgeführt. Die kinetischen Parameter der katalysierten und nichtkatalysierten Zersetzungen wurden mit den Methoden von Freeman—Carroll, Coats—Redfern und Horowitz—Metzger errechnet. Es wurde festgestellt, dass — im Gegensatz zur thermischen Zersetzung von  $\text{KClO}_3$  —  $\text{Al}_2\text{O}_3$  ein beinahe so guter Katalysator ist wie jedes andere angewandte Oxyd. Im Falle von  $\text{TiO}_2$  trat eine Erhöhung der Aktivierungsenergie der Zersetzung auf. Von den anderen Oxiden trat  $\text{Cr}_2\text{O}_3$  in Reaktion und wurde zu Dichromat umgesetzt, deswegen wurden diese Reaktionsparameter nicht berechnet. Die Wirkung verschiedener Mengen von  $\text{Al}_2\text{O}_3$  auf die thermische Zersetzung wurde ebenfalls untersucht.

Резюме — Были проведены кинетические исследования влияния таких металлоокисных катализаторов (25 вес. %),  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$  и  $\text{TiO}_2$  на термическое разложение  $\text{KBrO}_3$ . Кинетические параметры каталитического и не каталитического разложений были вычислены с помощью методов Фримэна—Кэррола, Коутса—Рэдферна и Хоровиц—Мецгера. Найдено, что  $\text{Al}_2\text{O}_3$  является почти таким же хорошим катализатором, как и любой другой оксид, в отличие от того, что наблюдалось при термическом разложении  $\text{KClO}_3$ . В случае  $\text{TiO}_2$  происходило увеличение энергии активации разложения. Из всех оксидов только  $\text{Cr}_2\text{O}_3$  подвергался реакции и превращался в бихромат, вследствие чего параметры реакции не были вычислены. Было также изучено влияние различных добавок  $\text{Al}_2\text{O}_3$  на термическое разложение.