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## THE DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF IRON OXIDE

F. E. BROWN AND W. C. ORR WHITE

The decomposition temperature of potassium chlorate is known to be lowered by the presence of varying quantities of different substances, especially oxides, which act in the capacity of catalytic agents in causing the evolution of oxygen. In most instances chlorine is also liberated.

This investigation on the effect of iron oxide was begun as one of a series of experiments to determine the effectiveness of various oxides in catalyzing the decomposition of potassium chlorate.

Considerable work has been done on this subject by English investigators, probably the most extensive on the effect of iron oxide being that of Fowler and Grant<sup>1</sup>; Baudrimont<sup>2</sup>; and Mills and Donald<sup>3</sup>. In their experiments with ferric oxide, Fowler and Grant reach the conclusion that water of hydration materially affects the spontaneous decomposition temperature of potassium chlorate. The data submitted show that a mixture of one part  $\text{Fe}_2\text{O}_3$  to six parts  $\text{KClO}_3$  decomposes at a temperature of  $380^\circ$  while a mixture of one part  $\text{Fe}_2(\text{OH})_6$  to two parts  $\text{KClO}_3$  decomposes at  $440^\circ$ . These results are not concordant with those obtained by Baudrimont who states that  $\text{Fe}_2\text{O}_3$  prepared in the wet way acts with much more facility than ferric oxide obtained by ignition, the inference being that the presence of water of hydration lowers the decomposition temperature rather than raises it. Temperatures as low as  $110^\circ$ — $120^\circ$  is given by Aug. Neumark<sup>4</sup> at which the decomposition may take place.

The apparatus at first used consisted of a brick furnace made by bricking in a ten inch length of three inch gas pipe placed vertically on a sand bath supported by a tripod. The furnace was heated by one or two quadruple gas burners and the top was covered with sheet asbestos.

The mixture of potassium chlorate and iron oxide was heated

<sup>1</sup> Trans. Chem. Soc., 57, 278, 1890.

<sup>2</sup> Jour. Chem. Soc., 24, 1152, 1871.

<sup>3</sup> Trans. Chem. Soc., 41, 18, 1882. Jour. Chem. Soc., 41, 18, 1882.

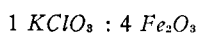
<sup>4</sup> Chem. and Met., 9, 641.

in a large hard glass test tube provided with a side tube which was connected to an inverted two and one-half liter bottle (A) filled with water. The exit tube of the bottle consisted of a siphon after the type found on a Soxhlet extractor and was connected to a second inverted empty bottle (B) about one liter in size. This bottle served to confine the water as it spurted from the mouth of the exit tube so that it might be collected in a beaker below and its volume ascertained. This corresponded to the volume of gas liberated by the decomposition of the potassium chlorate. Subsequently, a cylindrical vertical electric furnace the heating unit of which was made by winding chromel wire on a frame work of asbestos board, was substituted for the gas furnace. The temperature of the electric furnace was controlled by a rheostat. Two thermometers were used in both types of furnace; number one registered the temperature of the furnace, and number two was placed thru a one hole stopper in the test tube and imbedded in the mixture of potassium chlorate and iron oxide.

Wilkens-Anderson's C. P. potassium chlorate was used and it was ground to pass thru a 200 mesh sieve. The ferric oxide was Sargent's C. P. grade and it was likewise ground to pass thru a 200 mesh sieve. Each was dried in a 160° oven. Molecular ratios were taken for given mixtures, varying from 1 mole  $KClO_3$  : 4 moles  $Fe_2O_3$  to 64 moles  $KClO_3$  : 1 mole  $Fe_2O_3$ . Four experiments were run for each mixture. The spontaneous decomposition temperature was recorded as that temperature at which gas was evolved rapidly enough to cause a spurting of water from the exit tube into bottle (B). A rapid rise of the mercury in the thermometer whose bulb was imbedded in the mixture, was concomitant with the spurting of water. The rise in temperature caused by the exothermic reaction varied from 26° to 98° in a 1 : 1 mixture, averaging 62° for sixteen determinations.

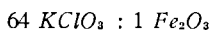
In all mixtures in which the ratio of potassium chlorate to ferric oxide was between 32  $KClO_3$  : 1  $Fe_2O_3$  and 1  $KClO_3$  : 4  $Fe_2O_3$ , a spontaneous decomposition took place. With the former mixture the temperature was elevated 10°; with the latter, there was seen to be a gradual increase in the evolution of gas but no sharp decomposition temperature was observed. This is shown in the following tables:—

TABLE NO. I



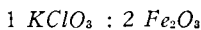
TEMPERATURE FURNACE	TEMPERATURE MIXTURE	VOLUME GAS CC'S	TIME
271	236	0	2:59
279	—	6	3:01
282	—	5	3:03
284	—	5	3:05
288	281	5	3:07
293	287	5	3:09
298	292	6	3:11
305	299	7	3:13
310	305	8	3:15
317	312	10	3:17
323	319	12	3:19
330	326	19	3:21
336	338	57	3:23
343	344	66	3:25
348	348	62	3:27
354	352	65	3:29
359	357	78	3:31
364	362	75	3:33

TABLE NO. II



TEMPERATURE FURNACE	TEMPERATURE MIXTURE	VOLUME IN CC.	TIME
275	—	0	11:10
295	292	8	11:10
313	312	11	11:20
319	319	7	11:22
324	325	10	11:24
329	331	19	11:26
334	337	56	11:28
339	347	133	11:30
345	388	215	11:32

TABLE NO. III



TEMPERATURE FURNACE	TEMPERATURE MIXTURE	VOLUME OF WATER DISPLACED IN CC.	TIME
281	237	0	2:43
286	—	10	2:45
288	—	11	2:47
290	284	11	2:49
293	290	10	2:51
297	295	10	2:53
303	300	12	2:55
307	305	12	2:57
312	310	15	2:59
318	315	19	3:01
323	322	25	3:03
325	324	violent spurting	

The results and averages of the various proportions are as follows :

PROPORTIONS	DECOMPOSITION TEMPERATURES	AVERAGE
1 $KClO_3$ : 2 $Fe_2O_3$	324°	324°
	323	
	324	
	325	
	312°	
1 $KClO_3$ : 1 $Fe_2O_3$	329	323°
	326	
	325	
	324	
	320	
	329°	
	326	
2 $KClO_3$ : 1 $Fe_2O_3$	332	326°
	324	
	321	
	318°	
	327	
4 $KClO_3$ : 1 $Fe_2O_3$	324	323°
	322	
	321°	
	324	
8 $KClO_3$ : 1 $Fe_2O_3$	323	323°
	325	
	326°	
	324	
	323	
16 $KClO_3$ : 1 $Fe_2O_3$	323	324°
	323	
	336°	
	335	
	331	
32 $KClO_3$ : 1 $Fe_2O_3$	334	334°
	331	
	334	
	347°	
64 $KClO_3$ : 1 $Fe_2O_3$	347°	347°

In the last mixture no sharp rise in the mercury was seen altho an increase in the volume of gas evolved took place in the neighborhood of 347° as shown in table II.

The effect of ferrosiferrous oxide upon the decomposition of potassium chlorate was also studied.  $Fe_3O_4$  was formed by heating  $Fe_2O_3$  to a temperature between 1000° and 1100°<sup>5</sup>. The product was dark red in color and non-magnetic. Very little catalytic action was observed in a mixture of 1  $KClO_3$  : 1  $Fe_3O_4$  at temperatures below 374°. The results are shown in the table below.

Another sample of  $Fe_3O_4$  was made by heating  $Fe_2O_3$  to a temperature of about 970° for two to three hours in a carbon monoxide atmosphere. The product, which was black, lustrous, hard, and crystalline, was ground to pass thru a 120 mesh sieve, and the

<sup>5</sup> Mellor's Inorganic Chemistry, p. 497.

TABLE NO. IV

TEMPERATURE FURNACE	TEMPERATURE MIXTURE	VOLUME GAS EVOLVED	TIME
380	300	—	5:53
380	315	1	5:54
380	338	1	5:55
380	347	3	5:56
379	357	5	5:57
378	361	5	5:58
376	362	6	5:59
374	368	6	6:00
372	371	6	6:01
370	374	6	6:02
368	374	5	6:03
364	372	4	6:04
362	370	4	6:05
360	362	4	6:06
358	365	3	6:07
355	364	3	6:08
352	359	2	6:10
347	356	2	6:09
342	351	2	6:11
339	348	2	6:12
336	345	1	6:13
332	343	1	6:14
327	343	1	6:15

decomposition temperature of a 1  $\text{KC1O}_3$  : 1  $\text{Fe}_3\text{O}_4$  mixture was determined. In this case a steady and rapid rise of the mercury took place at approximately  $370^\circ$ .

A third sample of  $\text{Fe}_3\text{O}_4$  was prepared by passing steam over iron powder heated to redness in an electric combustion furnace. It was magnetic. The proportions used were the same as before. This oxide apparently exerted a slight catalytic action at temperatures above  $360$  degrees.

The monohydrate of ferrosiferrous oxide  $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$  was next prepared by dissolving magnetic  $\text{Fe}_3\text{O}_4$  in concentrated  $\text{HCl}$  and pouring the solution thus obtained into an excess of a solution of sodium hydroxide. The precipitate was filtered out, washed, dried in a  $115^\circ$  oven, and ground to pass thru a 120 mesh sieve. The monohydrate thus formed was magnetic. A spontaneous decomposition temperature of  $294^\circ$  was obtained as an average of three determinations, using a 1 : 1 mixture. The heat liberated by the decomposition of the 2 grams of  $\text{KC1O}_3$  used in the mixture caused a rapid rise in temperature varying from  $65^\circ$  to  $83^\circ$ . From these results it was apparent that the water of hydration must be influencing the decomposition temperature. With a view to ascertaining the extent of this influence in the case of ferric oxide, a sample of hydrated  $\text{Fe}_2\text{O}_3$  was prepared by neutralizing a solution of ferric chloride with ammonium hydroxide, filtering, wash-

ing and drying the precipitate for 5 to 6 hours in a 115° oven. Three experiments with this oxide in a 1 : 1 mixture gave 235° as the spontaneous decomposition temperature. The average rise in temperature caused by the heat liberated was 75°. It was significant also that there was a sudden evolution of gas at about 120°. This was largely chlorine, the test tube being filled with the yellowish green gas. The large amount of chlorine is attributed to the presence of ammonium chloride which was not completely removed by washing.

TABLE NO. V

 $1 KClO_3 : 1 Fe_2O_3$ 
 $Fe_2O_3$  heated to 150°—175° in a vacuum over for five hours

TEMPERATURE FURNACE	TEMPERATURE MIXTURE	VOLUME GAS IN CC.	TIME
131	48	—	10:35
149	69	4	10:37
171	96	6	10:39
192	118	38	10:41
	118	increased evolution of gas	
204	173	105	10:43
232	190	4	10:45
246	?	3	10:47
260	212	10	10:49
272	226	19	10:51
283	239	30	10:53
295	252	56	10:55
	255	sudden increase in evolution of gas	
	300	maximum temperature reached	
306	300	350	10:57
315	288	3	10:59

The  $Fe_2O_3$  was next placed in an electric furnace heated to 470° and the current turned off. This further dehydrated the sample and volatilized part of the ammonium chloride. The evolution of gas at 120° was much diminished and the decomposition temperature was found to be 248°, 253°, 255°, 248° for four runs; an average of 251°. The oxide was then heated in vacuo at a temperature of 150°-175° for five hours. The average decomposition temperature of three determinations was then found to be 265°; and finally, the ferric oxide was heated for five hours in an electric furnace at a temperature of 550°. There was no evolution of chlorine in the neighborhood of 120° and the decomposition temperature was again elevated, this time to 278°, as shown by the following table.

TABLE NO. VI

TEMPERATURE FURNACE	TEMPERATURE MIXTURE	VOLUME IN CC.	TIME
206	96	—	10:28
226	140	1	10:30
245	173	1	10:32
258	195 (?)	1	10:34
271	222	2	10:36
282	240	10	10:38
292	254	15	10:40
302	265	18	10:42
310	276	33	10:44
	278	increased evolution	
320	317	415	10:46
	Temperature reached	343°	
327	322	190	10:48
334	314	1	10:50

In order to establish the fact that ammonium chloride was the cause of evolution of gas at 120° a sample of  $\text{Fe}_2\text{O}_3$  that had been heated to 550° was intimately mixed with 8% of its weight of  $\text{NH}_4\text{Cl}$ , and sufficient  $\text{KClO}_3$  was added so that one charge would contain two grams of potassium chlorate. The ratio was 1  $\text{KClO}_3$ :1  $\text{Fe}_2\text{O}_3$  as before. The temperature at which the gas was evolved was about 130°. The evolution of gas then dropped to three cubic centimeters per two minutes at a temperature of 200° and a second increased evolution of gas occurred at a higher temperature as shown in table V.

This result is in accord with experiments conducted by Hodgkinson and Lowndes<sup>6</sup> who have shown that the chlorine of  $\text{NH}_4\text{Cl}$  is liberated quantitatively when ammonium chloride is heated with potassium chlorate. The low decomposition temperature of 110°-120° given by Neumark is therefore due to some impurity, such as  $\text{NH}_4\text{Cl}$  in the  $\text{Fe}_2\text{O}_3$ .

## SUMMARY

1. The minimum temperature for the "spontaneous decomposition" of potassium chlorate in the presence of ferric oxide does not vary with different proportions of these substances within certain limits.

2. These limits are between 32  $\text{KClO}_3$ :1  $\text{Fe}_2\text{O}_3$  and 1  $\text{KClO}_3$ :4  $\text{Fe}_2\text{O}_3$ , and the temperature was found to be approximately 324° using standard C. P. chemicals.

3. The history of the ferric oxide is an important factor in making a determination of the spontaneous decomposition temperature.

<sup>6</sup> Chem. News, 59, 63, 1889.



4. Water of hydration is shown to lower this temperature both with  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . With each degree of dehydration the temperature is raised a corresponding amount. This is in accord with the work of Baudrimont, but not in agreement with that of Fowler and Grant.

5. A decomposition temperature as low as  $120^\circ$  is due to the presence of ammonium chloride in the ferric oxide.

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