2. The dioxide, K_2O_2, is formed as initial product of rapid oxidation of potassium in liquid ammonia. On further oxidation this yields the tetroxide, K_2O_4. No evidence was found indicating the formation of the trioxide, K_2O_3, in liquid ammonia.

3. The products of slow oxidation of sodium in liquid ammonia correspond to those of potassium. On rapid oxidation, the dioxide, Na_2O_2, is formed. No evidence was found indicating the formation of the trioxide, Na_2O_3.

4. Potassium tetroxide, K_2O_4, dissociates at temperatures above 300°. This process is reversible but the pressures appear to depend on the oxygen content of the solid phase. The final product of dissociation has a composition corresponding to the formula, K_2O_3.

5. Potassium tetroxide exposed to the action of moisture loses oxygen irreversibly between 100° and 200°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE DECOMPOSITION OF POTASSIUM CHLORATE. II. THE SPONTANEOUS DECOMPOSITION TEMPERATURES USING VARIOUS PROPORTIONS OF MANGANESE DIOXIDE, AND OF FERRIC OXIDE, AND OF A MIXTURE OF MANGANESE DIOXIDE AND FERRIC OXIDE AS CATALYSTS[1]

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Spontaneous decomposition temperatures for potassium chlorate-manganese dioxide mixtures,[2] and for iron oxide-manganese dioxide mixtures[3] have been reported. Spontaneous decomposition temperature was defined as the temperature at which the mixture began to evolve oxygen violently with a rapid rise of temperature due to the heat of reaction. The catalysts used for the determinations previously reported were not especially purified. The manganese dioxide may have contained some ferric oxide which Neville[4] has shown acts as a promoter for manganese dioxide in catalyzing the decomposition of potassium chlorate. The ferric oxide either had been heated to high temperatures, which destroys much of its catalytic activity, or contained ammonium chloride which according to Hodgkinson and Lowndes[5] lowers the decomposition point of potassium chlorate.

[1] This paper is an abstract of a thesis presented by J. Austin Burrows in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Iowa State College.

[2] Brown, Burrows and McLaughlin, THIS JOURNAL, **45,** 1343 (1923).

[3] Brown and White, *Proc. Iowa Acad. Sci.,* **31,** 291 (1924).

[4] Neville, THIS JOURNAL, **45,** 2330 (1923).

[5] Hodgkinson and Lowndes, *Chem. News,* **58,** 309 (1888); **59,** 63 (1889).

The object of the present work is to determine the spontaneous decomposition temperatures of potassium chlorate with the individual catalysts, using carefully purified oxides, and to find the correlation between the promoter action of ferric oxide reported by Neville and the effect of ferric oxide-manganese dioxide mixtures in causing spontaneous decomposition of potassium chlorate.

Materials

The potassium chlorate used was the C. P. grade of the Baker and Adamson Chemical Company which had been analyzed by Dr. H. M. McLaughlin in this Laboratory and found free from chlorides, heavy metals, calcium bromates, nitrates and sulfates, and except for a small amount of adsorbed moisture was pure potassium chlorate.

The manganese dioxide was prepared from Merck's highest purity C. P. carbonate by heating it in air to 255–260° during frequent stirring, until free from carbonate. After it had been washed thoroughly with dil. hydrochloric acid and water, it was found to be free from iron, nickel, silver and ammonium compounds. The oxidizing power was determined by dissolving it in sulfuric acid, adding an excess of oxalic acid, and titrating back with potassium permanganate; 0.4 g. required 72.82 cc. of 0.0981 N oxalic acid as compared with 91.5 cc. required for pure manganese dioxide. The total manganese content was determined by the bismuthate method; 0.01 g. of the manganese dioxide oxidized 11.76 cc. of 0.0496 N ferrous sulfate solution, as compared with 11.59 cc. required for pure ferrous sulfate. This discrepancy is probably due to the presence of moisture and lower oxides of manganese. A lower oxide of manganese would not be an impurity for our purpose as alternate oxidation and reduction of the catalysts is believed to occur,[5] and we find manganese carbonate almost as effective a catalyst as manganese dioxide.

The ferric oxide was prepared from Merck's reagent ferric chloride by precipitation with sodium hydroxide in an iron container, washing by decantation, and drying for two weeks at 110°. The sodium hydroxide had been freed from carbonates by filtering through iron filings in a paraffined Gooch crucible. The iron content of the oxide indicated 98.5% ferric oxide. It was free from manganese, silica, nickel and chlorides.

Apparatus

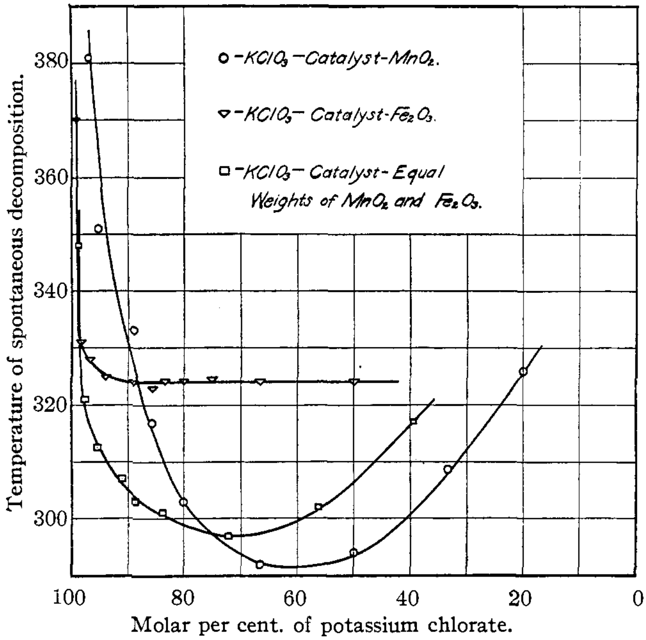
The apparatus was essentially the same as that used by Brown, Burrows and McLaughlin.[2] The furnace was electrically heated and regulated. In the bottom of the furnace was placed a vessel containing a low-melting alloy which reduced the fluctuations of temperature. The temperatures were taken by mercury thermometers, one imbedded in the reacting mixture and another suspended in the furnace near the tube containing the reacting mixture.

Experimental

Each ingredient was dried at 110°, pulverized, and sifted through a 200-mesh sieve. The mixtures were made by sifting proper proportions of the ingredients together once through a 200-mesh sieve and twice through a 150-mesh sieve. The resulting mixtures appeared uniform.

Manganese Dioxide as Catalyst

Mixtures were prepared in which the number of moles of manganese dioxide per hundred moles of mixture were 3.0, 5.9, 11.1, 14.3, 20.0, 33.3, 50.0, 66.7 and 80.0. Portions of each of the mixtures containing 2 g. of potassium chlorate were placed in a hard glass, side-arm test-tube 2.5 cm. in diameter. The tube was lowered into the furnace which had been heated to a temperature such that the insertion of the tube would lower it to approximately the spontaneous decomposition temperature. The spontaneous decomposition temperature is marked by a sudden acceleration of temperature rise in the reaction tube and a spurting of water from the collecting bottle due to rapid evolution of oxygen. Three or more portions of each mixture were heated and the spontaneous decomposition temperature reported is the average of the temperatures observed for that mixture. These temperatures are plotted against molal composition in Fig. 1, each point being indicated by a circle.



Ferric Oxide as Catalyst

Mixtures were prepared in which the moles of ferric oxide per 100 moles of mixture were 0.8, 1.6, 3.0, 5.9, 11.1, 14.3, 16.7, 20.0, 25.0, 33.3, 50.0, 66.7, 80.0, 83.3, 85.6 and 88.8. When 100 moles of mixture included as much as 66.7 moles of ferric oxide no sudden rise in temperature or spurting of water occurred. In Fig. 1 is a graph of the spontaneous decomposition temperatures of the other mixtures plotted against molar composition, each point being indicated by a triangle.

Mixtures of Manganese Dioxide and Ferric Oxide as Catalyst

Equal weights of manganese dioxide and ferric oxide[6] were intimately mixed. Portions of this mixture were then mixed with potassium chlorate in such proportions that the moles of combined catalysts in 100 moles of the final mixtures were 1.2, 2.4, 4.6, 8.8, 11.4, 16.2, 27.9, 43.6 and 60.6. The spontaneous decomposition temperatures with the mixed catalyst are plotted against the molar concentrations in Fig. 1, the points being indicated by squares.

Discussion of Results

The data given strengthen the conclusions which the authors established in their previous paper, namely, that the spontaneous decomposition tem-

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[6] Neville, Ref. 4, found this to be the most effective proportions.

perature of mixtures of potassium chlorate and manganese dioxide depends upon the percentage composition of the mixture and that those containing too much manganese dioxide as well as those containing too little manganese dioxide suffer no spontaneous decomposition. This is believed to be due in the former case to the fact that the heat given off by the potassium chlorate which would otherwise be utilized in increasing the rate of its decomposition is not sufficient to do this as well as to increase the temperature of the large amount of inert material which is present. In the latter case no spontaneous decomposition is produced due to the fact that much of the potassium chlorate is not in contact with the catalyst since too little catalyst is present.

In general it is noted that ferric oxide is not as efficient as a producer of spontaneous decomposition as manganese dioxide although at some of the concentrations in which very little catalyst was present, the ferric oxide gave a spontaneous decomposition temperature lower than manganese dioxide. This is very probably due to the fact that the ferric oxide was in a very much finer state of division than the manganese dioxide since much of it was practically colloidal. This gave an enormous surface and, therefore, the small amount of the ferric oxide could be in contact with a large amount of potassium chlorate and thus catalyze its decomposition. This work, as well as that of Brown and White, establishes the fact that for a wide variety of mixtures of potassium chlorate and ferric oxide there is a constant spontaneous decomposition temperature. The reason for this has not been determined.

Neville has shown[4] that at constant temperatures ferric oxide added to mixtures of potassium chlorate and manganese dioxide acts as a promoter of the catalysis. The most efficient proportion is ferric oxide and manganese dioxide in equal weights. Our data show that such a mixture is a more efficient producer of spontaneous decomposition of potassium chlorate than manganese dioxide alone or ferric oxide alone when the proportion of catalyst is less than 25%. But a potassium chlorate-manganese dioxide mixture containing between 25 and 55% of manganese dioxide has a lower spontaneous decomposition point than any mixture containing potassium chlorate and equal weights of ferric oxide and manganese dioxide. It is difficult to think of ferric oxide as a promoter of this particular phenomenon, spontaneous decomposition of potassium chlorate in the presence of manganese dioxide at all concentrations. If a mixture of 20 moles (1738.6 g.) of manganese dioxide with 80 moles of potassium chlorate is chosen, the spontaneous decomposition temperature is about 303°. If 1738.6 g. (10.9 moles) of ferric oxide is added there will be $(30.9/110.9) \times 100 = 27.9$ moles of catalyst per hundred moles of mixture and the spontaneous decomposition temperature is 297°. If 1738.6 g. (20 moles) of manganese dioxide is added to a similar mixture there will be (40/120) × 100 = 33.3 moles of catalyst per hundred moles of mixture and the spontaneous decomposition temperature is 292°. That is, the addition of manganese dioxide to manganese dioxide produces almost twice as great a lowering of the spontaneous decomposition point as is produced by the addition of an equal weight of ferric oxide, a supposed promoter. It is just as evident from an inspection of Fig. 1, that doubling the manganese dioxide content in manganese dioxide–potassium chlorate mixtures containing less than 10 moles of manganese dioxide per 100 moles lowers the spontaneous decomposition point less than it would be lowered by doubling the weight of catalyst by adding ferric oxide.

The authors wish to express their appreciation to Dr. H. M. McLaughlin for helpful suggestions during the progress of the work.

Summary

1. For a wide range of mixtures manganese dioxide produces a lowering of the decomposition temperature of potassium chlorate and the amount of heat produced by the decomposition of part of it is sufficient to cause spontaneous decomposition of the remainder. This spontaneous decomposition takes place at very definite temperatures for each mixture under defined conditions.
2. Ferric oxide also causes spontaneous decomposition of potassium chlorate over a wide range of mixtures.
3. The spontaneous decomposition temperature for ferric oxide mixtures is quite constant for a wide variety of mixtures.
4. When manganese dioxide is present in mixtures of that substance with potassium chlorate in proportions less than 25% of the total number of molecules, the substitution of ferric oxide for one-half of the weight of manganese dioxide present produces a lowering of the spontaneous decomposition temperature; when more than 25% of the molecules in the mixture are manganese dioxide, the substitution of ferric oxide for one-half of the weight of manganese dioxide produces a rise in spontaneous decomposition temperature.
5. The substitution of manganese dioxide for one-half of the ferric oxide in mixtures of that substance with potassium chlorate lowers the spontaneous decomposition point for all proportions of catalyst except those containing very little catalyst.

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