[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PROMOTER ACTION IN THE DECOMPOSITION OF POTASSIUM CHLORATE

BY HARVEY A. NEVILLE

RECEIVED JULY 26, 1923

Introduction

In an extensive research upon the catalytic decomposition of potassium chlorate[1] it was discovered that commercial manganese dioxide, or pyrolusite, was more active than the pure material in accelerating the evolution of oxygen. Analysis of the pyrolusite showed the presence of 8.8% of ferric oxide, Fe_2O_3, as an impurity. A mixture of pure manganese dioxide and ferric oxide in the proportions given by the analysis was then made and used as a catalyst. This mixture showed almost exactly the same activity as the pyrolusite, indicating that ferric oxide exerts a promoter action upon manganese dioxide in catalyzing the decomposition of potassium chlorate. The activities of these oxides separately and mixtures of the two as catalysts were measured at three different temperatures and the action of cupric oxide as a promoter with manganese dioxide was also studied.

Experimental Part

Apparatus.—The apparatus and method used in these experiments did not differ essentially from that described in other recent papers on this decomposition. The apparatus is indicated in Fig. 1. The reaction tube was heated by the condensation of the vapor of a constant-boiling substance. The decomposition of potassium chlorate is exothermic and such a method of heating tends to act as a thermostatic arrangement; when the temperature of the reaction mass begins to rise above the boiling point of the liquid, heat is absorbed by the vaporization of liquid condensed on the reaction tube, which should be of thin glass for this reason.

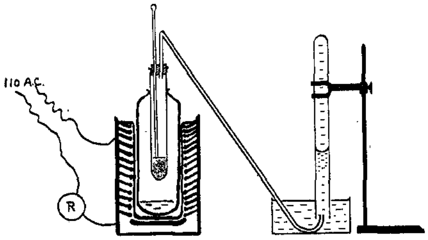

Fig. 1.—Apparatus

Materials.—Fine crystals of the purest potassium chlorate were used. The catalyst materials were finely ground pyrolusite, pure manganese dioxide made by the method of Georgen,[2] and cupric oxide made by oxidizing the pure metal, dissolving this oxide in nitric acid and decomposing the nitrate at 300°. Mixtures of catalysts were made both directly and by mixing the nitrate of one metal with the oxide of the other and heating to decomposition. The latter method gave more consistent results.

---

[1] The recent report of a similar investigation makes a complete presentation of results inadvisable at present. Compare Brown, Burrows and McLaughlin, THIS JOURNAL, **45,** 1343 (1923).

[2] Georgen, *Compt. rend.*, **88,** 797 (1879).

Procedure.—A sample for an experiment was prepared as follows. The potassium chlorate and catalyst in weighed proportions were finely ground, thoroughly mixed, moistened with water and dried. In this way the catalyst and potassium chlorate were brought into very intimate contact. A sample consisted of 6 g. of potassium chlorate plus an amount of the catalyst calculated as a certain percentage of the total weight. In the study of promoter action the catalyst was always 25%; that is, the mixture contained 6 g. of potassium chlorate and 2 g. of catalyst.

Results.—The results of the experiments at 328° are graphically represented in Figs. 2 and 3. The decomposition at this temperature is fairly steady and rapid and the temperature is safely below the melting point of potassium chlorate. At the other temperatures used (235° and 300°) the effects are exactly analogous, though less pronounced. The three oxides indicated are the only ones which have a marked catalytic activity at these temperatures. Above the melting point of potassium chlorate any finely divided solid accelerates the decomposition. As a basis for comparison it is to be noted that pure potassium chlorate at 328°, under the conditions of these experiments, evolves oxygen at the rate of 1 cc. per minute.

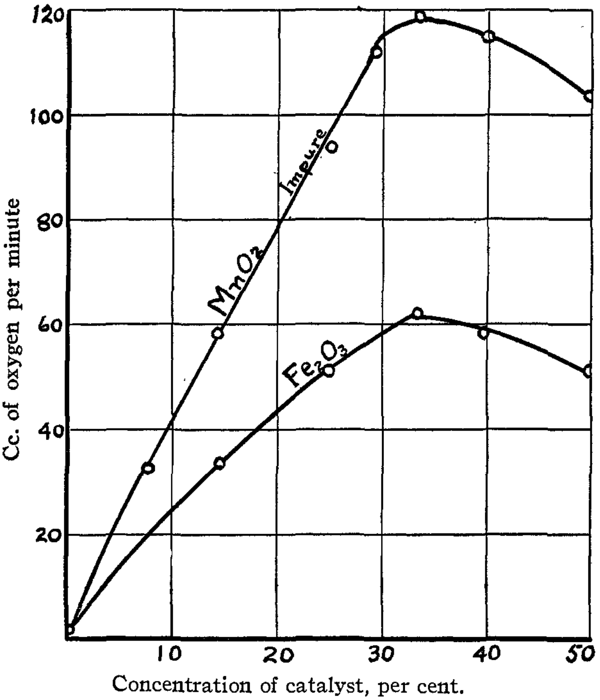

Fig. 2.—Rate of oxygen evolution with different amounts of catalyst

Discussion

The figures given for the rate of decomposition of potassium chlorate are not claimed as absolute values but are relative only. They are closely reproducible under the conditions of these experiments. The results obtained in any set of experiments will depend upon so many variable factors that no agreement will be possible except under those exact conditions. Purity, melting point and previous treatment of the potassium chlorate, physical condition of the catalyst method of mixing and rate of heating are especially important factors.

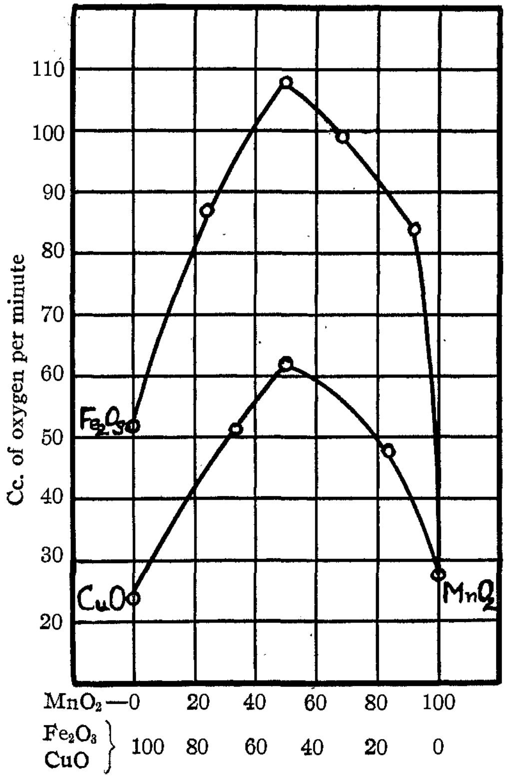

Fig. 3.—Percentages of oxides in mixture and rate of gas evolved at 328° from 6 g. of potassium chlorate mixed with 2 g. of catalyst

In a recent article on promoter action A. Pickles[3] suggested that if the atomic number of the metal present in a catalyst be even, the promoter should contain a metal of odd atomic number, and *vice versa*. A number of instances were cited where this is true. There are, however, many obvious exceptions, but it is apparent from a consideration of the law of probability that in 50% of all the cases of promoter action the rule must hold true even if there be no relation between atomic number and promoter action. The atomic numbers of the metals under consideration are Mn (25), Fe (26), Cu (29)—so the rule holds in the combination Fe_2O_3-MnO_2, but does not in the case of CuO-MnO_2.

A comparison of Figs. 2 and 3 discloses the fact that while impure manganese dioxide is a much better catalyst than ferric oxide, the pure substance is slightly more than half as good but is very susceptible to promotion by ferric oxide. In Fig. 3 the fact that pure manganese dioxide and cupric oxide have about the same activity and nearly the same molecular weights would lead one to expect a 50–50 mixture of the two to give the

[3] Pickles, *Chem. Age* (London), 8, 232 (1922).

best result. Such a mixture contains nearly twice as many molecules of manganese dioxide as of ferric oxide; and, although a molecule of ferric oxide is about four times as active as a molecule of manganese dioxide, this is balanced by the fact that the latter is more improved by a promoter than is the former.

Part of the experimental work for this paper was performed by Myron A. Snell, to whom acknowledgement is hereby made.

Summary

The fact that commercial manganese dioxide is a more effective catalyst than the C. P. material in the decomposition of potassium chlorate is ascribed to the presence of 8.8% of ferric oxide in the former.

Experiments with mixtures of these two oxides confirm this view and show that each oxide is a promoter for the other.

The action of cupric oxide and manganese dioxide as mutual promoters is also demonstrated.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PROFESSOR EDWARD KREMERS]

A STUDY OF AMINO AND OXIMO DERIVATIVES OF THYMOQUINONE[1]

BY RALPH M. HIXON[2]

RECEIVED NOVEMBER 20, 1922

The study of the reaction of the amines with the quinones dates from the time of Hofmann's report[3] of the isolation of a compound of the composition $C_6H_2O_2.N(C_6H_5)H$ from the reaction mixture of aniline and benzoquinone. Some years later, the reaction was studied thoroughly by Zincke.[4] He concluded that the amines reacted with the quinones in different ways under different conditions, giving the formulas of the following reaction products as proof of his statement.

Phenanthraquinone + methyl amine give $(C_{14}H_{13})(:N—CH_3)=O$ and $(C_{14}H_{18})(:N—CH_3)_2$ (1)

Phenanthraquinone + ammonia give $(C_{14}H_{18})(:N—H)=O$ (2)

Benzoquinone + aniline give $(C_6H_2O_2)_2(NHC_6H_5)_2$ (3)

In 1881, Zincke[5] concluded that the amines reacting with the quinones, replace a hydrogen atom of the quinone nucleus. This conclusion rested

---

[1] This communication is a portion of a thesis submitted to the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Fritzsche Brothers Fellow.

[3] Hofmann, *Jahresber.*, **1863,** 415.

[4] Zincke, *Ber.*, **12,** 1641 (1879).

[5] Zincke, *Ber.*, **14,** 92 (1881).