A Study on the Mechanism of the Catalytic Action of Manganese Dioxide on the Decomposition of Potassium Chlorate by Use of Heavy Oxygen as an Isotopic Tracer

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Introduction

It is a well-known fact that various metallic oxides, especially manganese dioxide, show a remarkable catalytic action for the thermal decomposition of potassium chlorate.(1) Thus, the potassium chlorate, which melts at 370°C. without chemical change in the absence of catalyst, decomposes at such low temperature as 235~290°C.(2), when it is mixed with manganese dioxide which alone does not evolve oxygen gas below 520°C.

Ever since the reaction was studied by Döbereiner(3) in 1832, various hypotheses have been proposed for the mechanism of the catalytic action of manganese dioxide. But among these hypotheses the one which postulates the formation of an intermediate compound is presumably most probable.(4) According to this hypothesis, primarily an unstable intermediate compound is formed between potassium chlorate and manganese dioxide, and the subsequent decomposition of this intermediate compound is accompanied by the evolution of oxygen gas and the production of potassium chloride, manganese dioxide being regenerated. Although this hypothesis seems very probable from the recent point of view about the general mechanism of catalytic reactions, only few direct verifications for this mechanism have been found in the literatures so far as we know.

If, however, oxygen is evolved through the intermediate formation of an unstable compound between potassium chlorate and manganese dioxide, the evolved oxygen must contain oxygen atoms which are originated not only from potassium chlorate but also from manganese dioxide used as catalyst. And this may easily be shown by an isotopic analysis of the evolved gas, if either the oxygen atoms of potassium chlorate or those of manganese dioxide are labeled with heavy oxygen as an isotopic tracer. From this point of view, we studied the isotopic composition of oxygen gas evolved when potassium chlorate labeled with heavy oxygen was decomposed in the presence of an ordinary manganese dioxide.

Experimental

The potassium chlorate labeled with heavy oxygen was prepared by the anodic oxidation of potassium chloride in the solution of heavy water, of which content of heavy oxygen had been whose increased above its natural abundance by fractional distillation.

The product was purified by repeated recrystallizations in aqueous solution of ordinary water for the exchange reaction of oxygen atoms between water and chlorate ion can be ignored.(5)

The heavy potassium chlorate prepared in such a way was decomposed by heating in the presence of an ordinary manganese dioxide under various conditions as described below and the evolved oxygen was converted into the form of water by recombining with an ordinary tank hydrogen by the aid of a copper catalyst. At the same time a part of the same heavy potassium chlorate was non-catalytically decomposed in the absence of manganese dioxide catalyst by heating at 650°C. and the evolved oxygen gas was converted into the form of water in the same way as above, using the same tank hydrogen.

Another sort of water was also prepared by reducing, with the same tank hydrogen, a part of the same manganese dioxide which was used for the decomposition of heavy potassium chlorate as the catalyst. Although in this case manganese dioxide was to be reduced only to manganese monoxide, the isotopic separation between oxygen atoms contained in the produced water and those which remained in manganese monoxide was ignored.

The densities of these three sorts of water were then compared by the ordinary sinker

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(1) Gmelin, "Handbuch der anorganischen Chemie", Kalium **22**, 473: Chlor, **6**, 342.

(2) Brown, Burrow and McLaughlin, *J. Am, Chem. Soc.*, **45**, 1843 (1923): Neville, ibid., **45**, 2331 (1923): Burrow and Brown, ibid., **48**, 1790 (1926): Balarew, *Kolloid-Z.*, **66**, 317 (1934).

(3) Döbereiner, *Ann.*, **1**, 236 (1832).

(4) McLeod, *J. Chem. Soc.*, **55**. 184 (1889); Sodeau, *J. Chem. Soc*., **81**, 1066 (1902): *Proc. Chem. Soc.*, **18**, 136 (1903); Dhar, *J. Phys. Chem.*, **28**, 953 (1924): Deniges, *Bull. trav. Soc. pharma. Bordeaux*, **74**, 93 (1936); Bhatnagar, et al, *J. Indian Chem. Soc.*, **17**, 124 (1940).

(5) T. Titani and K. Goto, This Bulletin, **13**, 667 (1938).

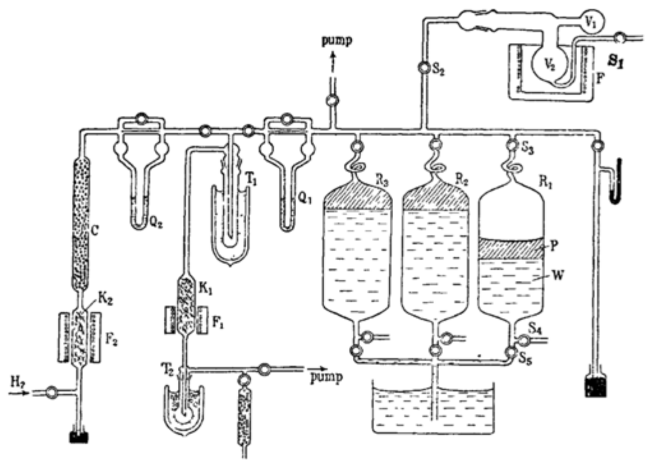

Fig. 1.

method, after a careful purification by heating with a small quantity of caustic soda and potassium permanganate and vacuum distillations. For each measurement, 0.5∼0.8 ml. of water was needed.

The apparatus used for the thermal decomposition of heavy potassium chlorate in the presence and the absence of manganese dioxide is shown in Fig. 1 and the details of each run of the experiments are given below, where $KClO_3$* denotes the potassium chlorate whose oxygen is labeled with heavy oxygen, and $MnO_2\cdot H_2O$ the manganese dioxide used as catalyst, because the manganese content of the catalyst determined by pyrophosphate method corresponds to that of this formula.

Exp. I.—Carefully powdered samples of 0.051 mole of $KClO_3$* and 0.045 mole of $MnO_2\cdot H_2O$, were placed separately in V_1 and V_2. $KClO_3$* was dried in a vacuum for three hours at 20°C. and $MnO_2\cdot H_2O$ was dried first in dry air current passed through S_1 and S_2 for two hours at 320°C. then in a vacuum for three hours at 20°C. Then, two reagents were mixed thoroughly in V_2 in a vacuum and the mixture was heated carefully by means of an electric furnace F at the desired temperature, which was measured by a thermocouple placed closely to the wall of the reaction vessel V_2. Oxygen gas was found to evolve at moderate rate at 320°C. and it took about fifty minutes until the reaction was completed, during this period the temperature inside the furnace being kept constant within a range of ±3°C. All of the evolved oxygen was collected in receiver R_1 by opening stopcocks S_2, S_3 and S_5. A thick layer of liquid paraffin P was placed to cover the surface of water W in the receiver in order to isolate the sampled oxygen from the air dissolved in the water. Then the oxygen gas was pushed out of R_1 to the catalyst tube K_1 through the flowmeter Q_1 and the dry ice trap T_1 by applying a hydropressure through S_4. The catalyst tube K_1 was filled with copper catalyst and heated at 400°C. in an electric furnace F_1. On the other hand, an excess quantity of tank hydrogen, which was freed from oxygen and water vapor by passing through the heated copper catalyst tube K_2 and the calcium chloride tube C and the dry ice trap T_1, was introduced into the catalyst tube K_1, the flow rate being checked by flowmeter Q_2. And thus the water, which was formed in the catalyst tube K_1 by the combination of the sample oxygen and the tank hydrogen, was collected in the ice water trap T_2.

Exp. II.—The experimental procedures and conditions were the same as Exp. I, except that 0.053 mole of $KClO_3$* was taken.

Exp. III.—The experimental procedures of this Exp. III, where 0.093 mole of $KClO_3$* and 0.095 mole of $MnO_2\cdot H_2O$ were taken, were different from preceding Exps. I and II in two respects. In the first place $MnO_2\cdot H_2O$ used in this experiment was pretreated under more severe conditions than in the preceding experiments. It was at first desiccated in the current of dry air for two hours at 480°C. and then treated for three hours in a vacuum at 320°C. By this severe treatment the catalytic activity of $MnO_2\cdot H_2O$ seemed to be somewhat injured, for with this $MnO_2\cdot H_2O$ the moderate rate of oxygen evolution was not observed until the temperature was raised up to 345°C. which is much higher than 320°C. the temperature used in the preceding experiments. The second characteristic of the procedure of this run was that the fractions of oxygen gas which were evolved at three different stages of the reaction were collected separately in three receivers, namely, the first fraction (1.05 l.) in R_1, the middle fraction (1.05 l.) in R_2 and the last fraction (0.35 l.) in R_3, and these three fractions of sampled oxygen were separately converted to water by use of the same tank hydrogen.

Exp. IV.—The purpose of this experiment was quite different from the purposes of the preceding Exps. I, II, and III and it is to investigate the possibility of a supposed secondary exchange reaction of oxygen atoms between manganese dioxide and gaseous oxygen which is evolved by the decomposition of potassium chlorate.

A gaseous oxygen which has the same isotopic composition as that of $KClO_3$* was prepared by the non-catalytic thermal decomposition of $KClO_3$*. The prepared heavy oxygen gas was then passed slowly through a reaction vessel which contains $MnO_2\cdot H_2O$ pad at 350°C. and at the rate of 1.85 l. per hour. The $MnO_2\cdot H_2O$ used in this experiment was preliminarily dried in the same way as in Exps. I and II, and the temperature of the reaction vessel (350°C.) was chosen much higher than the temperature (320°C.) at which the reaction mixture was heated in Exps. I and II. The heavy oxygen gas after being passed through the reaction vessel was converted to water in the same way as in the preceding experiments.

Results and Discussions

Results of the experiments are shown in Table 1; the third column gives the excess densities of recombined water due to the enrichment of heavy oxygen above the tap water in Osaka city,(6) and the last column the same, but with sample 1 taken as the standard. It will be seen from this table, by comparing the excess densities of samples No. 1 and 2, that the oxygen in $KClO_3$* is 47.5 p. p. m. heavier than that in $MnO_2 \cdot H_2O$. Accordingly the oxygen gas, which is evolved by the thermal decomposition of the mixture of $KClO_3$* and $MnO_2 \cdot H_2O$, must show the same excess density as that of $KClO_3$*, if the gas is exclusively originated from $KClO_3$*. But in fact the evolved gas has a much lower excess density than that of $KClO_3$*, as is seen from samples No. 3 to 5. On the other hand, the possibility of the secondary exchange reaction between evolved oxygen gas and $MnO_2 \cdot H_2O$ can be excluded by the result of Exp. IV, where the heavy oxygen, which was prepared by the noncatalytic decomposition of $KClO_3$* and passed over the same $MnO_2 \cdot H_2O$ as used in Exp. I and II, at higher temperature than that in these experiments, showed the same excess density as that of $KClO_3$* (see sample No. 8 in Table 1). From these experimental results, it can be concluded that a part of the oxygen gas, which is evolved by the catalytic decomposition of potassium chlorate in the presence of manganese dioxide, originates from the latter, presumably through an unstable compound, formed intermediately between the two substances. The result obtained in Exp. III is highly interesting, because it has been found there that the first fraction of the oxygen, which is evolved at the beginning of the reaction, shows the lower excess density than that of $KClO_3$*, as is seen in the preceding Exps. I and II, whereas the densities of the middle and last fractions agree with that of $KClO_3$* within the limit of the experimental error (see samples No. 5, 6 and 7 in Table 1). This result can, however, be explained under the following assumptions.

Table 1

Results of the Experiments

Number of the sample	Sample	Excess density due to heavy oxygen in the sample(6) (in p. p. m.)	Density difference (in p.p.m.)
1	$KClO_3$*	48.3±0.8	Standard
2	$Mn_2O \cdot H_2O$	0.8±0.5	−47.5
3	Oxygen gas evolved in Exp. I	32.6±1.0	−15.7
4	Oxygen gas evolved in Exp. II	34.6±1.0	−13.7
5	Oxygen gas evolved in the first stage of Exp. III	37.8±0.2	−10.5
6	Oxygen gas evolved in the middle stage of Exp. III	48.5±0.3	+ 0.2
7	Oxygen gas evolved in the last stage of Exp. III	46.5±2.6	− 1.8
8	Oxygen gas after exchange reaction in Exp. IV	48.0±0.2	− 0.3

Although the oxygen is liberated through the decomposition of the intermediate compound, which is formed between potassium chlorate and manganese dioxide, only a small part of the manganese dioxide has the activity to form such an intermediate compound, with potassium chlorate. It follows therefore that an isotopic exchange equilibrium is quickly established between the oxygen atoms contained in this active part of manganese dioxide and those of potassium chlorate through the repeated formation and decomposition of the intermediate compound between the two substances, when a limited quantity of manganese dioxide is heated with potassium chlorate. And when this equilibrium is once attained, the oxygen liberated from the mixture of both substances must have the same isotopic composition as that of potassium chlorate, whereas a part of the gas originates from manganese dioxide. This may be the reason why in Exp. III the oxygen, evolved after a certain period of the reaction, has the same excess density as that of potassium chlorate.

If it is so, the ratio of the number N of oxygen atoms contained in the active part to the total number N_0 of oxygen atoms contained in the whole manganese dioxide can be calculated from the quantity of potassium chlorate and manganese dioxide used in the experiment and the isotopic composition of the liberated oxygen and that contained in the potassium chlorate. The results of the calculation are shown in Table 2.

Although nothing can be said on the exact nature of this active part of manganese dioxide without further study, it may be a reasonable assumption that it would be a thin layer on the surface of each manganese dioxide particle. It has been found further by a microscopic observation that the manganese dioxide particles used in the present experiment may be

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(6) Corrected for the difference in the isotopic composition of hydrogen between the tank hydrogen and tap water.

Table 2

Ratio of the Active Part and Thickness of Active Layer of Manganese Dioxide

Sample	N/N_0	Thickness of active layer ($m\mu$)
$MnO_2 \cdot H_2O$ used in Exp. I	0.37	2.2
$MnO_2 \cdot H_2O$ used in Exp. II	0.32	1.8
$MnO_2 \cdot H_2O$ used in Exp. III	0.072	0.4

regarded as a sphere having a mean diameter of $30\,\mu$. The thickness of the active layer given in the last column of Table 2 has been calculated by using the ratio N/N_0 given in the second column of the table, under the assumption that the active part forms a complete shell layer on the surface of a spherical particle of manganese dioxide having a diameter given above. From the figures given in Table 2, it will be seen that the active part of $MnO_2 \cdot H_2O$ used in the last Exp. III is much smaller than those used in Exps. I and II. This result is, however, in good accordance with the experimental fact that $MnO_2 \cdot H_2O$ used in Exp. III has a much weaker activity than those used in the other experiments as has already been stated. And if it is taken into consideration that $MnO_2 \cdot H_2O$ used in Exp. III has been pretreated under more severe conditions than in other experiments, namely, heated in a vacuum at much higher temperatures than others, it may be concluded that a large portion of the active part of manganese dioxide catalyst has been lost or destroyed by this severe treatment.

Summary

By use of heavy oxygen as an isotopic tracer, the following facts have been found;

1. At the catalytic decomposition of potassium chlorate in the presence of manganese dioxide, an unstable compound is formed between potassium chlorate and manganese dioxide, and oxygen gas is liberated by the decomposition of this intermediate compound.
2. The active part of manganese dioxide capable of composing such an intermediate compound with potassium chlorate is only a limited small portion of the particle.
3. Such an active part is readily destroyed by such a severe treatment as the heating of the catalyst in a vacuum at high temperature.

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