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Oxygen¹⁸ as Tracer in the Catalytic Decomposition of Potassium Chlorate¹

By F. E. Brown and J. D. Woods

INTRODUCTION

There is evidence that the catalytic action of manganese on the decomposition of potassium chlorate involves an alternate oxidation and reduction of the manganese. This evidence can be tested by enriching the oxygen of the catalyst with oxygen¹⁸ isotope. Oxygen liberated from chlorate decomposition with an enriched catalyst should contain oxygen¹⁸.

Recently Forkushima et al (1) carried out a similar experiment. They enriched potassium chlorate with oxygen¹⁸ and decomposed it with MnO₂.H₂O containing ordinary oxygen. Water was formed from successive portions of the liberated oxygen. The density of this water was less than the density of water prepared from oxygen liberated from KClO₃ without a catalyst. They concluded that some unstable compound is formed between KClO₃ and MnO₂, and that oxygen is liberated from this compound. They further concluded that only a limited portion of the catalyst is used in the reaction.

In the present experiment the manganese dioxide was enriched with oxygen¹⁸, and the KClO₃ was normal. Isotopic ratios of liberated oxygen were determined directly by use of a mass spectrograph.

EXPERIMENTAL

PREPARATION OF OXYGEN¹⁸ ENRICHED MANGANESE DIOXIDE

Water enriched with oxygen¹⁸ was obtained. It was thought to electrolyze the water and react the resulting oxygen with powdered manganese metal to prepare the MnO₂¹⁸. Preliminary experiments, however, revealed that MnO_{0.9} was the highest oxide obtainable by this method.

Tompkins (2) prepared manganese dioxide by reacting manganese chloride with potassium permanganate according to the following reactions:



According to the mechanism of this reaction, as proposed by Tompkins, a part of the oxygen in the resulting MnO₂ comes from the water. Therefore, oxygen¹⁸ enriched manganese dioxide was

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prepared according to this reaction, by carrying out the precipitation in water enriched with oxygen¹⁸.

Equivalent quantities of anhydrous $MnCl_2$ and $KMnO_4$ (0.7550 g. and 0.6322 g., respectively) were mixed and stirred into 3.0 ml. of water enriched with oxygen¹⁸. A brown precipitate formed which was filtered and washed with two 1 ml. portions of H_2O^{18} . The wash water contained no permanganate.

The precipitate was dried in a desiccator connected to a vacuum pump for $\frac{1}{2}$ hour. Then the evacuated desiccator was placed in an oven at $115^\circ C.$ for 15 hours. At the end of this time the desiccator was again connected to a vacuum pump for $\frac{1}{2}$ hour.

Analysis by the bismuthate method showed 0.1000 g. of the oxide to contain 0.0569 g. of Mn. This corresponds to the formula, $MnO_{2.6}$, or nearly $MnO_2 \cdot H_2O$. That the oxide obtained was not exactly MnO_2 is not surprising, since Sakui et al (3) prepared manganese dioxide by eight methods and obtained eight formulas varying from $MnO_{1.28}$ to $MnO_{1.92}$.

COLLECTION OF OXYGEN SAMPLES

A 0.2098 g. sample of oxygen¹⁸ enriched catalyst was placed in the end of a 12 mm. x 10 cm. pyrex glass tube extending into a small electric furnace. The other end of the tube was connected by ground glass joints to a gas sampling tube, which in turn was connected to a high vacuum system. The gas sampling tube was a 12 mm. x 8 cm. pyrex glass tube with a high vacuum stopcock at each end, and with ground glass joints for connecting into the system. An acetone-dry ice trap was in the system to collect any moisture that might be liberated from the catalyst. A manometer, connected to the vacuum system, provided a measure of the pressure. The total volume of the vacuum system was approximately 60 ml.

The system was evacuated and the furnace was set at $360^\circ C.$ No oxygen was liberated from the catalyst at this temperature as was noted by the manometer. The temperature was then raised to approximately $600^\circ C.$ At this temperature the oxide decomposed enough to yield an oxygen pressure of 12.5 cm. The stopcocks on the sampling tube were closed and the sampling tube of oxygen was removed from the system to be analyzed (Sample 1, Table 1). A trace of frost formed in the acetone-dry ice trap while collecting the sample.

A mixture of 0.2450 g. $KClO_3$ and 0.2098 g. of enriched catalyst was placed in a reaction tube extending into another electric furnace. The reaction tube was connected by ground glass joints to a Y tube leading to two parallel gas sampling tubes. The other

Table I
Results of Oxygen¹⁸ Tracer Experiment

Sample	0-32 (mv.)	0-34 (mv.)	N-28 + N-29 + N-30 (mv.)	$\frac{0-34}{0-32} \times 10^3$	Factor x Normal
1	3.187	0.063	0.0255	19.7	6.2
2	3.442	0.0131	0.0247	3.76	1.2
3	3.570	0.0153	0.0256	4.23	1.4
4	3.410	0.0527	0.0304	15.4	4.8
5*	3.256	0.0112	0.0318	3.20	1.00
6†	1.439	0.0057	8.43
7	3.722	0.0109	0.0387	2.93	.92
8	2.452	0.0109	0.3963	4.45	1.4

*Tank oxygen.

†Sample of air.

ends of the sampling bulbs were connected to a Y tube leading to a vacuum system with a manometer. The volume of the vacuum system was approximately 150 ml.

The system was evacuated through a stopcock to a vacuum pump line. Then one sampling tube was closed off and the other was left open. The furnace was set at 340° C. When the pressure of the system rose to 14.0 cm. Hg., the first sampling tube was closed off and the second was opened. With the reaction still in progress the pressure of the system was pumped down to a few mm. Hg. The vacuum pump was closed off until the pressure rose to 5 cm. Hg., and again was turned on to pump the pressure to a few mm. Hg. Finally the pump was again shut off and the reaction continued until no more oxygen could be liberated at 366° C. The oxygen pressure was 9.5 cm. in the system. The second sampling tube was then closed off. The sampling tubes of oxygen were then removed to be analyzed on the mass spectrograph. They furnished samples 2 and 3, Table I. The collecting of samples 2 and 3 required approximately 10 minutes.

The residue was heated to 450° C. to be sure that all the $KClO_3$ was decomposed. Then the residue was heated to approximately 650° C. in an evacuated system containing another gas sampling tube. An oxygen pressure of 8 cm. developed from the decomposition of the residual manganese oxide. The sampling tube was shut off and the sample of oxygen was analyzed by the mass spectrograph (Sample 4, Table I).

For determination of the normal $\frac{0-34}{0-32}$ ratio in oxygen a sample of ordinary tank oxygen was analyzed (Sample 5, Table I). For correcting for air leaks into the samples the oxygen-32, nitrogen ratio in air was determined by analysis of a sample of ordinary air (Sample 6, Table I).

In order to check for isotopic exchange between oxygen of the manganese oxide and surrounding oxygen, another experiment was carried out. Ordinary tank oxygen was placed over 0.200 g. of the oxygen¹⁸ enriched manganese oxide in a pyrex tube connected to a 60 ml. system for 1 hour at 340° C. A sampling tube of this oxygen was analyzed for O¹⁸ (Sample 7, Table I).

Fresh tank oxygen was then placed over this same sample of oxygen¹⁸ enriched manganese oxide for a much longer period of time, 15 hours, at 340° C. A sampling tube of this oxygen was analyzed for O¹⁸ (Sample 8, Table I).

MASS SPECTROGRAPH ANALYSES OF SAMPLES

The sampling tubes, containing oxygen collected as shown above, were one by one connected to the high vacuum system of a mass spectrograph and analyzed for $\frac{0-34}{0-32}$ ratios according to a method described by Svec (4). Results of the analyses were automatically recorded as a series of voltage peaks versus mass numbers. The height of the peaks were a function of the mole fractions of any molecular weight species in the samples.

For these experiments interest was centered on mass numbers 32 and 34, corresponding to O¹⁶-O¹⁶ and O¹⁶-O¹⁸ molecules. Since the ratio of O¹⁶ to O¹⁸ in ordinary oxygen is only about 1 to 500 (5), O¹⁸-O¹⁸ combinations are rare. Peaks for mass number 36, therefore, did not occur.

Comparisons of the amount of O¹⁸ enrichment were made by comparing the $\frac{0-34}{0-32}$ ratio of each sample to that of ordinary oxygen. Since ratios were used for values, the units employed were not critical. Therefore, the ratios are ratios of millivolts readings from the calibrated peaks on the recorded chart paper.

Corrections were made for traces of air that leaked into the oxygen samples. In ordinary air the ratio $\frac{0-32}{N-28 + N-29 + N-30}$ is $\frac{1}{5.85}$. Assuming that any nitrogen present was proportional to the amount of air in the samples, one could solve for the 0-32 in the air in a sample and subtract it from the 0-32 voltage read from the chart. A similar correction for the 0-34 can be applied. However, this correction proved to be practically negligible and was not applied in these results.

RESULTS AND DISCUSSION

The results of these experiments are shown in Table I. Sample

5 was ordinary tank oxygen, giving .0032 for the normal ratio of $\frac{0.34}{0.32}$. The factor times normal column was obtained by dividing the $\frac{0.34}{0.32}$ ratios of other samples by .0032.

Sample 6 was a sample of air, confirming the correction factor $\frac{0.32}{N-28 + N-29 + N-30}$ to be $\frac{1}{5.85}$

Sample 1 contained 6.2 times the normal $\frac{0.34}{0.32}$ ratio, showing that the method of enriching the manganese oxide with ¹⁸O was successful.

Sample 2, the first of the oxygen liberated from the mixture of KClO₃ and manganese oxide, was enriched in ¹⁸O by a factor of 1.2 times normal. This showed that some of the oxygen liberated came from the catalyst.

Sample 3, the last part of the oxygen liberated during the catalytic decomposition of the KClO₃, was enriched in ¹⁸O by a factor of 1.4 times normal. Sample 4, obtained by decomposing the residual oxide, showed that the ¹⁸O content of the catalyst decreased during the reaction.

Sample 7 shows no ¹⁸O enrichment of the 60 ml. of tank oxygen that was in contact with 0.200 g. of the ¹⁸O enriched manganese oxide for 1 hour at 340° C. This is evidence that the ¹⁸O liberated during the 10 minutes of potassium chlorate decomposition was not just a result of isotopic exchange between oxygen liberated from the chlorate and oxygen in the catalyst. However, Sample 8 does show that some isotopic exchange had occurred after oxygen had been in contact with the catalyst for a 15-hour period at 340° C. Whether or not the water of hydration, probably present in the manganese oxide, was involved in this exchange was not determined.

These results prove that some of the manganese loses oxygen and then regains oxygen from the chlorate during catalytic decomposition of KClO₃. Not all the manganese atoms present, however, are involved in the catalysis when such large amounts of catalyst are present.

It appears that the manganese is undergoing a cyclic oxidation and reduction process. Once an ¹⁸O atom is set free from the manganese, it is replaced by an ¹⁶O from the chlorate. The next cycle involving this manganese atom, therefore, liberates ordinary oxygen. Oxygen¹⁸ enrichment of the liberated oxygen did not decrease during the decomposition; in fact, it increased slightly. This can be explained by the fact that only a part of the catalyst takes part in the reaction. As the reaction continues, the tiny particles of catalysts are broken into smaller particles, thus

exposing more new manganese atoms at the surfaces. This accounts for the continued enrichment of the liberated oxygen.

The original catalyst was enriched with O¹⁸ by a factor of 6.3 times normal. The residual oxide still contained 4.8 times the normal enrichment. This further indicates that only about 20% of the manganese was involved in the decomposition of 50 mole percent KC10₃.

These results are in agreement with the work of Forkushima et al (1).

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