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Comparison of Manganese and Rhenium Compounds in the Catalytic Decomposition of Potassium Chlorate

By F. E. BROWN AND J. D. WOODS

INTRODUCTION

Several compounds of manganese, particularly manganese dioxide, are known to be catalysts for the decomposition of KClO_3 . The mechanism of the catalytic action has not been fully elucidated, though there is evidence that the manganese is alternately oxidized and reduced during the reaction (1). The decomposition of KClO_3 with compounds of rhenium, in the same periodic family as manganese, has not been reported.

In this study several manganese catalysts, each with manganese in a different initial oxidation state, were used to decompose KClO_3 under identical conditions. Also several rhenium compounds, with rhenium in different initial oxidation states, were used to decompose KClO_3 under the same conditions. Determination of the fate of the manganese and the rhenium in these reactions, and comparison of the catalytic effects of manganese and rhenium give data which help to explain the mechanism of the catalysis.

EXPERIMENTAL

Catalysts Used

Six manganese catalysts, manganese metal, manganous oxide, manganese trioxide, manganese dioxide, specially prepared manganese dioxide, and potassium permanganate, were used in this study. The manganous oxide and manganese trioxide were prepared by a method of Meyers and Kanters (2). The special manganese dioxide was a special catalyst prepared by the Fischer Scientific Company (3). The other manganese catalysts were reagent grade chemicals.

Five rhenium catalysts, rhenium metal, rhenium dioxide, rhenium trioxide, rhenium heptoxide and potassium perrhenate, were used in this study. The oxides were prepared from rhenium metal by methods found in the literature (4). The potassium perrhenate was prepared by reacting Re_2O_7 with water, titrating with KOH and evaporating to dryness.¹

¹Details of the preparation and analysis of the catalysts are reported in the thesis, "Action of Manganese and Rhenium Compounds in the Decomposition of Potassium Chlorate," by Joe Woods, on file in the Iowa State College library.

Preparation of Reaction Mixtures

In order that the catalytic activities of the various compounds might be compared, each reaction sample was made to contain the same mole per cent of manganese or rhenium. A composition of 1.4 mole per cent manganese or rhenium was used. This composition corresponds to 1% manganese dioxide by weight, a type of mixture known to produce measurable amounts of permanganate in the reaction residues (5). The reaction mixtures were of such size that each contained exactly one gram of KClO_3 . To prepare these mixtures 10.000 grams of KClO_3 and enough catalyst to contain 0.0115 moles of manganese were mixed and ground together in an agate mortar. The mixture was placed in a ground glass stoppered bottle and shaken thoroughly. Later samples large enough to contain 1.000 grams of KClO_3 were weighed out of these prepared batches.

Since the supply of rhenium catalysts was limited, an individual sample for each run was prepared. A 1.000 gram sample of KClO_3 was weighed out. Then enough rhenium catalyst to contain 0.00115 moles of rhenium was weighed out and mixed with the KClO_3 by grinding together in an agate mortar.

It is significant to note that as the Re , ReO_3 , and Re_2O_7 were being ground with the KClO_3 , a faint chlorine-like odor was observed. The ReO_3 and Re_2O_7 mixtures took up moisture while grinding and caused the powdered KClO_3 to pack somewhat.

Measurement of Reaction Rates

The rate of decomposition of KClO_3 in each sample was measured at constant temperature by placing the weighed sample in a reaction tube suspended in a constant temperature furnace by a pyrex glass rod hanging from the beam of an automatic recording balance (6). The reaction tubes for manganese mixtures were 11-12 mm pyrex tubes, 15 cm long. For rhenium mixtures the tubes were 20 cm long. The extra length extended above the furnace so that in the event a rhenium oxide should volatilize it could be detected as it would condense on the cool portion of the tube.

Loss of oxygen as a function of time was automatically plotted on graph paper by the balance recorder. Runs were considered to be completed when no more than one milligram of oxygen was liberated per hour. In some cases reactions were stopped before this point. In other cases the tubes were left in the furnace for several hours after this rate was reached. This was done to observe changes that might occur in the reaction residues after the oxygen evolution ceased. The reaction tubes were then removed from the furnace, cooled, and weighed. The difference in weight before and after heating served as a check on the total weight of oxygen liberated as shown on the chart paper. Agreement within 2% was usual.

Reaction rates for mixtures with each catalyst were measured at two temperatures: 366°C and 340°C.

Analysis of Residues

The residues from the reactions with manganese catalysts were analyzed for permanganate in the soluble portion and for manganese in the insoluble portion. The residue of a sample was scraped from the reaction tube and ground in an agate mortar. A weighed sample of the residue was treated with water and filtered in a weighed, sintered glass filtering crucible. The residue in the crucible was washed with water and the washings added to the filtrate. The filtrate was diluted to a measured volume.

Permanganate in the pink filtrate was determined colorimetrically with a Beckman D.U. spectrophotometer by measuring percentage transmittancy of the solution at 520 m μ . Permanganate in parts per million was calculated to percentage of total manganese. Complete absorption spectra in the visible range were measured in a few of the solutions to confirm the assumption that the color was due to permanganate.

Manganese was determined in the insoluble portion of the residue in the filtering crucible by the bismuthate method. From the analysis the weight of manganese was calculated. From the weight of manganese and the weight of the residual oxide the ratio of manganese atoms to oxygen atoms was calculated.

Residues from samples containing rhenium, with few exceptions, contained no insoluble portions. In the absence of a method for precipitating or determining perrhenate in the presence of chlorate and perchlorate, rhenium was not determined. However, absorption spectra in the ultraviolet were taken of solutions of the residues to prove the presence of perrhenate in each case. To do this the residue from a reaction was dissolved from the reaction tube, diluted to a measured volume, and the absorption spectra determined on the Beckman D. U. spectrophotometer.

Rhenium heptoxide melts at 220°C and sublimates at 450°C. The comparatively low sublimation point for this oxide made it imperative to insure that the weight loss recorded by the automatic recording balance was due to oxygen loss only, and not due to loss of rhenium by vaporization. Therefore the long reaction tubes were used. In no case, however, was there any deposit of rhenium oxide observed on the cool portion of the reaction tubes. For a further check, the residues from the reactions were analyzed for chloride by titrating measured volumes of the solutions with standard silver nitrate. From the weight of chloride, was calculated the weight of oxygen liberated. This weight of oxygen was then compared with the loss in weight as recorded on the chart paper. Only in the case of Re_2O_7 was there any significant loss of weight greater than the weight of oxygen as calculated from chloride. In all other cases oxygen calculated from chloride agreed with the

recorded oxygen loss within 2%. Thus it was known that in all cases, except where Re_2O_7 was used, rhenium catalysts were not lost by vaporization during the reactions.

RESULTS

Comparison of Catalytic Activities

Figures 1 and 2 show the decomposition curves copied on a smaller scale from curves recorded by the balance at 366°C and 340°C , respectively. The curves are reproduced on this scale so that the manganese and rhenium catalysts might be compared. The actual curves for the reactions with manganese extended

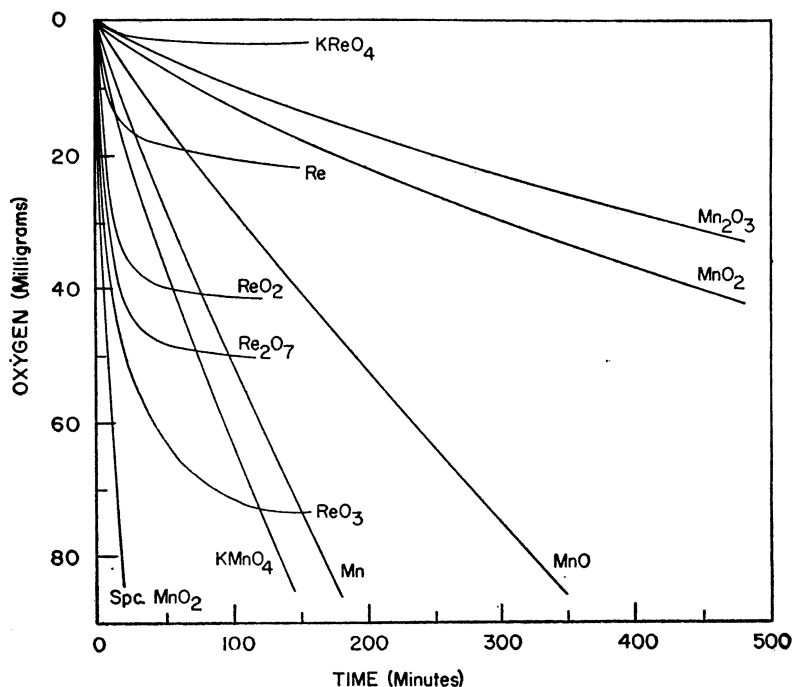


Figure 1. DECOMPOSITION of KClO_3 with VARIOUS Mn and Re CATALYSTS at 366°C .

much beyond the portions shown. In most cases reactions were carried out until no more than one milligram of oxygen was liberated per hour. In the case of Curve 1 (Figure 1) for MnO_2 this rate was not reached until 4400 minutes, at which point 111 milligrams of oxygen (27% decomposition of KClO_3) had evolved. In the case of Curve 5 (Figure 1) for KMnO_4 this rate was reached in 1520 minutes, at which point 67.8% of the oxygen from the KClO_3 had evolved.

At 366°C (Figure 1) the order of increasing reactivity of the manganese catalysts was Mn_2O_3 , MnO_2 , MnO , Mn , KMnO_4 , and special MnO_2 . At 340°C (Figure 2) the order is somewhat altered. The significant fact to note, however, is that all curves with manganese catalysts show a continued type reaction.

At both temperatures with rhenium catalysts all curves show a rapid evolution of oxygen for a short time with an abrupt stop. Different catalysts and the different temperatures show different amounts of oxygen before the break in the curves. The significant

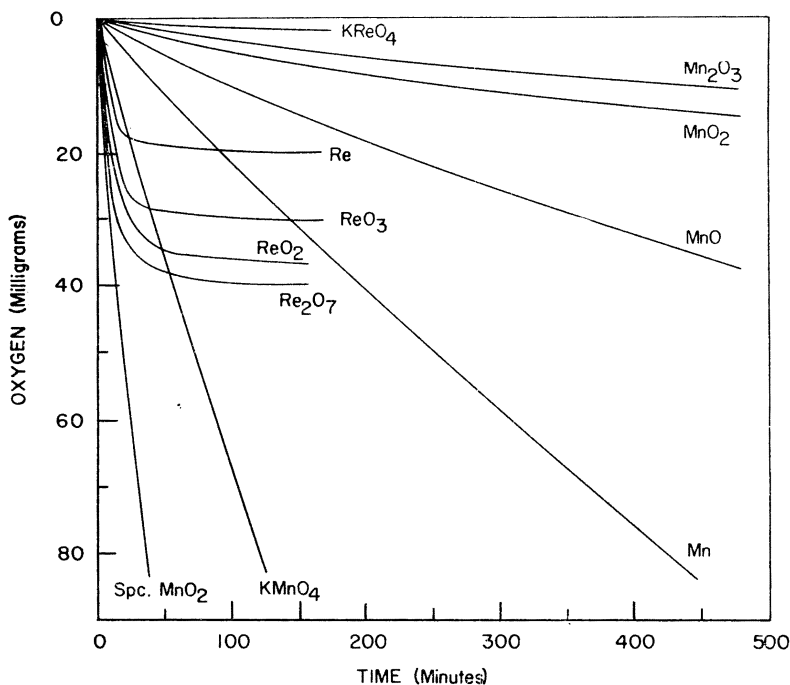


Figure 2. DECOMPOSITION of KClO_3 with VARIOUS
Mn and Re CATALYSTS at 340° C.

fact, however, is that these rhenium compounds do not cause a continued decomposition of KClO_3 as do manganese compounds.

Fate of the Manganese Catalysts

Table I is a summary of the results of analyses for manganese and for permanganate in the residue from the decomposition of KClO_3 with manganese catalysts. The catalysts used, temperatures of the runs, and the total time of heating are in the first three columns. The percentage of oxygen evolved shows how far each reaction progressed before slowing to approximately 1 milligram

of oxygen per hour. In a few cases data for reactions that were stopped before reaching this stage are included. The fifth column shows the ratio of oxygen atoms to manganese atoms in the insoluble portions of the residues. The last column shows the fraction of the manganese that was extracted from the residue as permanganate.

Inspection of Column 5, Table I, reveals a series of oxides with manganese to oxygen ratios from $\text{MnO}_{1.2}$ to $\text{MnO}_{2.0}$. The method of analysis of these small samples was not accurate enough to make a clear distinction between the small differences in ratios. However, the column as a whole indicates that most of the manganese, regardless of its oxidation state at the start, ends up with an intermediate oxidation state of 3 to 4. Manganese metal and MnO were oxidized. KMnO_4 was reduced.

The last column, Table I, indicates that in most cases a detectable or measurable fraction of the manganese can be extracted from the reaction residues as permanganate. From the residues from the special MnO_2 reactions little or no permanganate was extracted. However, when this catalyst was used, the decomposition of chlorate was complete, and any permanganate may have

Table I
Analysis of Decomposition Residues Showing
Fate of Manganese Catalysts.

Catalyst	Temperature of Run	Time (min.)	% Oxygen Evolved	Formula of Residue Oxide	% Mn in KMnO_4
Mn	366°	1000	83.4	$\text{MnO}_{1.2}$	0.4
MnO	366°	2622	76.5	$\text{MnO}_{1.8}$	Trace
	340°	1478	19.2	$\text{MnO}_{1.7}$	0.1
Mn_2O_3	366°	2620	21.0	$\text{MnO}_{1.7}$	0.3
	340°	276	1.7	$\text{MnO}_{1.8}$	0.2
	340°	2835	7.7	$\text{MnO}_{1.6}$	0.8
MnO_2 , B.&A.	366°	4440	27.0	$\text{MnO}_{1.7}$	0.1
	366°	2400	25.0	0.3
	340°	1311	4.1	$\text{MnO}_{2.0}$	0.0
MnO_2 , Fisher	366°	75	99.0	$\text{MnO}_{1.3}$	Trace
	340°	92	99.0	$\text{MnO}_{1.9}$	0.0
KMnO_4	366°	180	42.2	$\text{MnO}_{1.5}$	13.0
	340°	1265	60.8	$\text{MnO}_{2.0}$	24.0
	366°	1518	67.8	$\text{MnO}_{1.7}$	14.0

decomposed before the reactions were stopped. When a mixture with the special MnO_2 was heated only three minutes, the water extract of the residue contained permanganate.

The reaction mixtures with manganese catalysts usually appeared light grey-brown with a pink tint as they were taken from the furnace. They usually were partially melted at 366°C. At 340°C they remained unmelted but always appeared to have sintered. Occasionally, a residue appeared to have a green tint. This possibly indicated the presence of a trace of manganate, although

the decomposition temperature of manganate is only 190°C . When water was added to any green tinted residues, pink solutions resulted, showing that any manganate underwent disproportionation to yield KMnO_4 in solution.

That the pink water extracts were, indeed, permanganate is proved by curves of Figure 3. Curve 1 is the absorption spectrum of a solution of KMnO_4 . Curve 2 is the absorption spectrum of a solution containing the soluble portion of a reaction residue from KClO_3 decomposition with MnO_2 . The fact that both curves exhibit the three characteristic minima at $505\text{ m}\mu$, $525\text{ m}\mu$, and $548\text{ m}\mu$ leaves little doubt that solution 2 contains permanganate.

Fate of the Rhenium Catalysts

The residues from all the decompositions of KClO_3 with the various rhenium catalysts were partly or wholly melted when re-

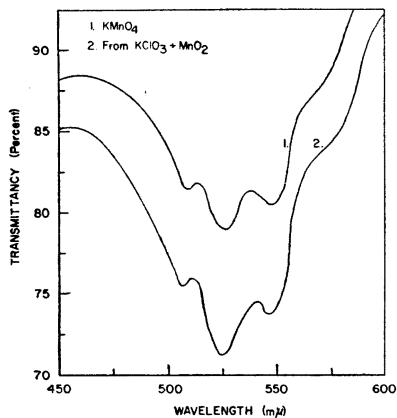


Figure 3. ABSORPTION SPECTRA OF SOLUTIONS CONTAINING MANGANESE

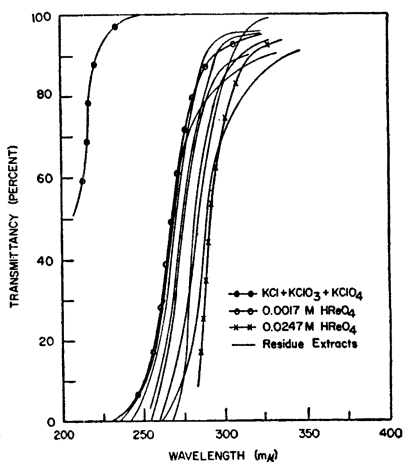


Figure 4. ABSORPTION SPECTRA OF SOLUTIONS CONTAINING RHENIUM

moved from the furnace at 366°C . At 340°C the residues appeared to be sintered. Evidently low melting point mixtures were produced.

All the residues were completely soluble in water with the exception of runs with ReO_2 . The ReO_2 used in these experiments was known to be impure. The impurity was left as a small grey residue after water extraction. That the grey residue contained no rhenium was proved by the fact that it would not dissolve in 30% H_2O_2 as all rhenium oxides do (7). Of the catalysts used, only Re_2O_7 and KReO_4 are soluble. Therefore, all the other rhenium catalysts were converted to a soluble form during the decomposition reactions.

The absorption spectra in the ultraviolet region of solutions of

the reaction residues with rhenium catalysts are shown in Figure 4. Curve 2 is the ultraviolet absorption spectrum of 0.0017 M standard perrhenate. Curve 3 is a 0.0245 M perrhenate curve reproduced from data of Maum (8). The shapes of curves 2 and 3 are similar. There is only a small shift in position for a 100 fold change in concentration. Therefore, quantitative determinations for perrhenate were not possible.

Curve 1 is an absorption spectrum of a prepared solution of a chloride, chlorate, and perchlorate mixture. The position of absorption proves that these salts do not interfere with the perrhenate absorption band. The several curves represented by curve type 4, Figure 4, are absorption spectra of solutions of the residues of the several reaction mixtures of KClO_3 with rhenium catalysts. These curves all exhibit the perrhenate absorption spectrum. Since all the rhenium from each run was soluble, the conclusion can be made that all the rhenium is converted to perrhenate during decomposition of KClO_3 , regardless of its oxidation state at the beginning of the reaction.

DISCUSSION AND CONCLUSIONS

Results from the analysis of residues from the potassium chlorate decompositions with the various catalysts reveal significant facts. For the manganese catalysts, regardless of the oxidation state of manganese at the beginning of a reaction, at the end of the reaction the manganese existed in a mixture of states. Most of the manganese ended with an oxidation state of +3 to +4, but some small fraction of it ended in a portion extractable in water as permanganate. Potassium permanganate decomposes at 240°C , far below the reaction temperatures. Therefore, permanganate must form and decompose in the reaction mixtures. This conclusion is borne out by the fact that when KMnO_4 was used as a catalyst, as much as 14% of the manganese could be extracted as permanganate from the reaction residue, even after heating for 21 hours at a temperature 126°C above the decomposition point of KMnO_4 (Table I).

For the rhenium catalysts, regardless of the oxidation state of the rhenium at the beginning of a reaction, at the end of the reaction all the rhenium existed only as a water soluble compound giving the perrhenate absorption spectrum.

All the manganese catalysts, although showing a variety of activity, exhibited a continued type catalysis. Rhenium compounds, on the other hand, gave catalytic action for a short time only, and did not cause a continued type of chlorate decomposition.

The above facts can be explained by the theory that catalytic decomposition of KClO_3 occurs only during a change in oxidation state of the manganese or rhenium. Potassium perrhenate can be distilled at $1,370^\circ\text{C}$ without decomposition (9). Since perrhenate

is so stable, catalysis stops with the rhenium compounds as soon as the rhenium is oxidized to perrhenate. Since permanganate (or manganate) is relatively unstable, it decomposes as formed, and a cyclic oxidation and reduction of the active manganese atoms results so that a continued catalysis occurs.

Literature Cited

- (1) Brown and Woods, *Proc. Iowa Acad. Sci.*, 62, 258 (1955).
- (2) Myers and Kanters, *Z. Anorg. Chem.*, 185, 177 (1929).
- (3) U. S. Steel Corporation, "Sampling and Analysis of Carbon and Alloy Steels," Reinhold Publishing Co., New York, 1938, p. 48.
- (4) Nechamkin, Kurtz, and Hiskey, *J. Am. Chem. Soc.*, 73, 2828 (1951).
- (5) Woods, "Formation of Permanganate During Catalytic Decomposition of $KClO_3$," Unpublished M. S. Thesis, Ames, Iowa, Iowa State College Library, 1950.
- (6) Brown, Loomis, Peabody, Woods, *Proc. Iowa Acad. Sci.*, 59, 159 (1952).
- (7) Dobbin and Colehour, *J. Am. Chem. Soc.*, 56, 2054 (1934).
- (8) Maum, "Investigations in Chemistry of Rhenium," Ph. D. Thesis, California Institute of Technology, 1949. (Unclassified A. E. C. Report, N-P 1378).
- (9) Vorlander and Dalichau, *Berichte*, 66, 1534 (1933).

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