The Journal of the American Chemical Society

with which has been incorporated
The American Chemical Journal
(Founded by Ira Remsen)

VOL. 48 JULY, 1926 No. 7

A STUDY OF THE OXIDES OF POTASSIUM AND SODIUM

By Charles A. Kraus and Earle F. Whyte

Received July 20, 1925 Published July 6, 1926

Introduction

Although numerous investigators have studied the oxides of potassium and sodium, our knowledge of these oxides is still far from complete. Harcourt[1] showed that the highest product of direct oxidation of potassium is K_2O_4. Holt and Sims[2] confirmed the results of Harcourt. They found indications of the existence of the dioxide K_2O_2 and of the trioxide K_2O_3, the latter being obtained through the extended oxidation of metallic potassium by nitrous oxide. Lupton[3] claimed to have obtained the oxide K_2O_2 by the direct oxidation of potassium but his work is uncertain. The compound K_2O_2 has not been definitely established as a result of the direct oxidation of potassium.

Harcourt obtained sodium peroxide, Na_2O_2 as a final direct oxidation product of sodium and this result has been confirmed by Holt and Sims as well as others. Rengade[4] obtained the suboxides Na_2O and K_2O as well as the corresponding oxides of cesium and rubidium by direct oxidation in the presence of excess metal and subsequent removal of this excess by distillation in a vacuum.

Joannis,[5] oxidizing the metals in liquid ammonia, obtained the oxide of sodium, Na_2O_2 and, as he believed, a trioxide Na_2O_3. He also obtained a product corresponding to the formula $Na_2O.NH_3$, which was doubtless a mixture of sodium hydroxide and sodium amide (Rengade[4]). He likewise recorded the oxides of potassium K_2O_2, K_2O_3 and K_2O_4.

Rengade made a careful study of the oxidation of cesium and rubidium

[1] Harcourt, *J. Chem. Soc.*, **14**, 267 (1862).

[2] Holt and Sims, *ibid.*, **65**, 432 (1894).

[3] Lupton, *ibid.*, **30**, 565 (1870).

[4] Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907).

[5] Joannis, *Compt. rend.*, **110**, 1370 (1893).

in liquid ammonia and established the existence of the oxides corresponding to the formulas M_2O_4, M_2O_3 and M_2O_2. He states that with potassium similar results were obtained but gives no numerical data. Rengade showed that in the case of cesium and rubidium the product of oxidation in liquid ammonia depends upon the rate. With rapid oxidation the initial product corresponds to M_2O_2 and the final product to M_2O_4. On slow oxidation the initial product is a mixture of the hydroxide MOH and the amide MNH_2. The amide is further oxidized with the formation of nitrite and hydroxide.

According to deForcrand,[6] potassium tetroxide loses oxygen above its melting point with the formation of the trioxide, K_2O_3. Holt and Sims[2] found that the final product, on heating the tetroxide in glass, corresponds to the formula K_2O, reaction presumably taking place between the oxide and the glass.

The purpose of the present investigation was to determine the nature of the oxidation products obtained with sodium and potassium in liquid ammonia, to establish the reversibility of the dissociation of potassium tetroxide at higher temperatures and, if possible, to determine the equilibrium pressure of this process.

Oxidation of Potassium and Sodium in Liquid Ammonia

Apparatus and Procedure.—A detailed description of the apparatus employed in carrying out the oxidation of sodium and potassium in liquid ammonia may be omitted for the sake of brevity. The method consisted essentially in passing a controlled stream of oxygen through a solution of the metal in liquid ammonia contained in a weighed tube at liquid-ammonia temperatures. The volume of oxygen absorbed was measured and the weight of the products of reaction was determined by weighing the containing tube at the end of the reaction. The metal employed was melted in a vacuum and run into small sealed tubes of known weight. These tubes were broken just prior to introduction into liquid ammonia. The initial end-point of the reaction was indicated by the disappearance of the blue color characteristic of the free metal. The final end-point was obtained by passing oxygen through the solution until no further absorption occurred. In the rapid oxidation of the metal, a rapid stream of oxygen was passed through the solution under a considerable external pressure (20 cm.). In slow oxidation, a slow stream of oxygen was passed through the solution together with a stream of ammonia, the ammonia passing out under practically atmospheric pressure.

Mechanism of the Oxidation Process.—If the oxidation of potassium corresponds to that found by Rengade for rubidium and cesium we should expect the following reactions to occur.

---

[6] deForcrand, *Compt. rend.*, **158**, 991 (1914).

On initial rapid oxidation the dioxide is formed according to the equation,

$$K_2 + O_2 = K_2O_2 \qquad \text{(I)}$$

and, on further oxidation of this product, the tetroxide, according to the equation,

$$K_2O_2 + O_2 = K_2O_4 \qquad \text{(II)}$$

On slow oxidation, the dioxide is probably first formed and then reduced to the suboxide by excess metal present, the net result of these reactions being expressed by the equation,

$$K_2 + \tfrac{1}{2}O_2 = K_2O \qquad \text{(III)}$$

This oxide, being a salt of the very weak acid KOH, ammonolyzes according to the equation,

$$K_2O + HNH_2 = KOH + KNH_2 \qquad \text{(IV)}$$

On further introduction of oxygen, the amide is oxidized to nitrite according to the equation,

$$2KNH_2 + \tfrac{3}{2}O_2 = KOH + KNO_2 \qquad \text{(V)}$$

If K_2O_3 is formed it should appear as an intermediate product between Reactions I and II. In the case of sodium, Reaction II does not occur.

Slow Oxidation of Potassium.—Preliminary experiments with potassium, in which the volume of oxygen absorbed was measured, indicated the initial formation of K_2O_2 on rapid oxidation, and of a mixture of compounds on slow oxidation. The weight of the reaction product as determined in a series of experiments is given in Table I.

TABLE I

INITIAL PRODUCT OF SLOW OXIDATION OF POTASSIUM

Potassium, g.	0.1908	0.2757	0.1611
Product found, g.	.2795	.3961	.2296
Product calcd. for KOH + KNH_2, g.	.2713	.3921	.2291

As may be seen from the table, the weight of the product formed is in substantial agreement with that required for the formation of potassium hydroxide and potassium amide according to Equations III and IV. The products of initial oxidation were identified by separating the two materials. A weighed quantity of potassium was oxidized in one limb of a two-legged tube, the potassium amide formed, being soluble in liquid ammonia, was decanted into the second limb of the tube, the two limbs were separated and their contents weighed. Following are the results obtained: 0.3558 g. of potassium gave 0.2484 g. of KOH and 0.2625 g. of KNH_2, that required is, 0.2553 g. and 0.2507 g., respectively. The slight excess in the weight of potassium amide was doubtless due to the presence of a small quantity of hydroxide carried over in decanting the solution of the former. The liquid ammonia soluble product was identified as potassium amide by treating with water.

Oxidation of Potassium Amide.—If, after disappearance of the blue color due to potassium, a stream of oxygen is passed through the solution further absorption of oxygen occurs. On completion of this oxidation process and evaporation of the solvent, the residue consists of a mixture of white and slightly yellow materials. A number of reactions were carried out in which the volume of oxygen absorbed and the weight of the final products of oxidation were determined. The results are given in Table II.

TABLE II

FINAL PRODUCTS OF SLOW OXIDATION OF POTASSIUM

K, g.	O_2 calcd., cc.	O_2 used, cc.	$KOH + KNO_2$, g. Calcd.	$KOH + KNO_2$, g. Found
0.1890	81.2	75.6	0.3413	0.3326
.2621	..	..	.4733	.4645
.2457	105.6	101.0	.4438	.4395
.2003	86.0	85.8	.3618	.3606

As may be seen, the volumes of the oxygen absorbed and the weights of the final products of oxidation are in substantial agreement with those required for the formation of potassium hydroxide and potassium nitrite according to Equations III, IV and V. The weights found as well as the volumes of oxygen used are a trifle lower than those required. This is probably due to incomplete oxidation. The final product was readily soluble in water and answered to tests for nitrite and hydroxide.

A weighed quantity of potassium amide was oxidized in one limb of a two-legged tube and, on completion of the oxidation process, the products were separated by decanting the solution of potassium nitrite from the hydroxide; 0.3401 g. of potassium converted to amide yielded, after oxidation and separation, 0.2526 g. of KOH, while that required is 0.2440 g. A portion of the potassium nitrite that separated in this reaction was lost on evaporating the solution. Titration with potassium permanganate showed that this product consisted primarily of potassium nitrite.

An attempt was made to oxidize potassium amide in the absence of ammonia. On slowly admitting oxygen absorption occurred, the color of the material changing to bright yellow and then to orange. After the initial reaction, the rate of absorption was slow and the weight of the materials indicated that the reaction was incomplete, at the end of 12 hours. The contents of the tube answered to the tests for potassium nitrite, and a measurable quantity of ammonia was recovered with the excess oxygen. These facts indicate that the oxidation of potassium amide in the dry state is similar to that in liquid ammonia. The color changes are rather puzzling.

Rapid Oxidation of Potassium.—The dioxide K_2O_2 is formed when potassium is rapidly oxidized in liquid ammonia and the process of oxidation is interrupted as soon as the free metal has disappeared. The dioxide is white, but at times is tinted faintly yellow, probably owing to the presence of a trace of the tetroxide. The dioxide does not react with liquid ammonia even on long standing. It is readily oxidized to the tetroxide on passing oxygen through its liquid ammonia suspension.

The results of a series of experiments are given in Table III.

Table III

Products of Rapid Oxidation of Potassium

K, g.	O_2 for K_2O_2, cc. Calcd.	O_2 for K_2O_2, cc. Obs.	O_2 for K_2O_4, cc., Calcd.	O_2 for K_2O_4, cc., Obs.	K_2O_2, g. Calcd.	K_2O_2, g. Obs.	K_2O_4, g. Calcd.	K_2O_4, g. Obs.
0.1840	...	...	...	...	...	...	0.3346	0.3274
.1946	55.7	55.0	111.4	112.0	...	...	.3539	.3540
.1979	...	...	113.4	114.0	...	...	.3599	.3547
.3362	96.3	95.0	...	...	...	...	.6115	.6056
.2520	72.2	74.3	144.4	145.0	...	...	.4583	.4564
.2411	69.1	68.7	...	...	...	...	.4385	.4340
.2762	79.1	77.5	...	...	0.3993	0.3951	...	...
.4123[a]	118.1	106.0	...	...	.5811	.5683	...	...
.5147[a]	147.5	138.0	...	...	.7253	.7094	...	...
.4336[a]	124.2	113.0	...	...	.6162	.6037	...	...

[a] Weighed in air.

The volumes of oxygen absorbed and the weights of the resulting products correspond with those required for the oxides K_2O_2 and K_2O_4. No evidence was found indicating the existence of the intermediate oxide K_2O_3. At times, the precipitate had a slightly reddish tint but the volume of oxygen absorbed and the weights indicated a mixture of two or more oxides. Under the conditions of the present experiments, no product could be separated corresponding to the formula K_2O_3.

The tetroxide K_2O_4 is comparatively stable; it is not affected by dry air but it reacts slowly with moisture. On treating it with water, one molecule of oxygen is evolved according to the equation

$$K_2O_4 = K_2O_2 + O_2 \tag{VI}$$

This confirms the observations of the earlier investigators.

The dioxide is extremely reactive. In one case, on admitting air into a tube containing about 0.5 g. of this oxide, the product turned orange-red with evolution of considerable heat. On admitting water an explosion occurred. In another case the product turned reddish-brown on admission of air, after which explosion occurred. After explosion the products in various parts of the tube were colored red, yellow and purple. Holt and Sims prepared a product corresponding to the formula K_2O_3 by treating metallic potassium with nitrous oxide. This product they found to be extremely reactive with respect to oxygen.

An attempt was made to oxidize finely divided potassium in pure oxygen. The metal was obtained in a finely divided state by dissolving it in liquid ammonia and then evaporating the solution rapidly. On admitting oxygen, rapid absorption took place, at first, but the rate slowed with time. At the end of six weeks 0.2239 g. had absorbed only 0.0792 g. of oxygen. On initial admission of oxygen (at low pressure) the surface of the metal turned blue and after standing some time a red color developed at certain points. At the end of a week a cream-colored product made its appearance. On longer standing it was observed that the initial product gradually turned red and that this in turn passed over into the cream-colored material.

Oxidation of Sodium in Liquid Ammonia.—On rapid oxidation of sodium the peroxide Na_2O_2 is formed. This oxide is stable in liquid ammonia. No evidence was found of the formation of an oxide of oxygen content higher than Na_2O_2. This is contrary to the observations of Joannis who claimed to have obtained an oxide Na_2O_3. The results of several experiments, in which the volume of absorbed oxygen was measured, follows: sodium, 0.1370 and 0.2080 g.; O_2 absorbed, 69.8 and 104.2 cc.; O_2 required, 66.7 and 101.3 cc.

On slow oxidation, sodium hydroxide and sodium amide are initially formed according to Equations III and IV. On further treatment with oxygen, the amide is converted to a mixture of sodium hydroxide and sodium nitrite according to Equation V. The results of several experiments follow: 0.1482 g. of sodium slowly oxidized absorbed 38.5 cc. of oxygen at the end of the first stage and 91.0 cc. at the end of the final stage of oxidation. The final product weighed 0.3028 g. Corresponding to Equations III, IV and V, the volumes required are 36.1 and 90.2 cc., respectively, and the final weight, 0.3044 g.

0.1429 G. of sodium was converted to the amide and oxidized. There was absorbed 105.0 cc. of oxygen, and the final weight was 0.3243 g. According to Equation V, there are required 104.4 cc. and 0.3387 g., respectively. The solution of the final product answered to tests for nitrite.

The highest oxide of sodium in liquid ammonia is Na_2O_2. On slow oxidation, sodium, like potassium, is oxidized to hydroxide and nitrite.

Dissociation of Potassium Tetroxide at Higher Temperatures

Final Products of Dissociation.—Known weights of potassium tetroxide, usually in the form of pellets, were introduced into weighed Pyrex or soda-glass tubes and heated to the melting point of the oxide. Before being heated, the tubes were evacuated. The oxygen evolved on heating was removed by means of a Toepler pump and its volume determined. At the end of the reaction the tubes containing the material were detached and weighed.

When the tetroxide is heated for some time in contact with glass, reaction takes place, oxygen is evolved, and the weight of the final product corresponds to the formula K_2O. The results of several experiments follow: K_2O_4, 0.3205, 0.1914 g.; final product, 0.2276 and 0.1193 g.; required for K_2O, 0.2344 and 0.1269 g. These results are in agreement with earlier observations of Holt and Sims.

In several cases, particularly when the surface of contact between the oxide and the glass container was small, the weight of the final product was found to correspond to K_2O_2 and this product when dissolved in water answered to tests for hydrogen peroxide. The results of one of these experiments follow: K_2O_4, 0.2098 g.; final weight, 0.1694 g.; required for K_2O_2, 0.1626 g.

The evolution of oxygen at higher temperatures is greatly influenced by moisture. Potassium tetroxide which has been carefully guarded against the action of moisture shows practically no evolution of oxygen in a vacuum until the temperature is raised to 300° or higher. When the oxide has been exposed to the action of moisture, evolution of oxygen begins at about 100° and continues until approximately 200° is reached, when it ceases. The amount of oxygen evolved at these temperatures is dependent upon the extent to which the material was originally exposed to the action of moisture. Once this initial evolution of oxygen has taken place, further evolution of oxygen does not occur until a temperature of 300° is reached, after which the behavior of the material corresponds closely with that of dry potassium tetroxide. For example, in one case, 0.2601 g. of material when exposed to the action of water vapor at room temperature yielded 7.66 cc. of oxygen and, on heating to 270°, evolved 29.8 cc. of oxygen, while after heating to temperatures above 300°, yielded only an additional 8.4 cc. of oxygen. The weight of the residue on completion of the dissociation process was found to be 0.1959 g. as compared with 0.2100 g. required for K_2O_2. The total volume of gas evolved was 38.2 cc. as compared with 35.1 cc. required for K_2O_2 as final product. Just what part water plays in the dissociation of potassium tetroxide between 100° and 200° could not be determined from the present experiments.

In order to avoid the action between the oxide and the glass containing tube, pellets of dry tetroxide were placed in a gold or an aluminum cup in a weighed Pyrex tube. Gold was found to be much less resistant to the action of the oxide than is aluminum. A gold cup weighing 1.6503 g. lost 24.2 mg. after having been heated to the melting point of the tetroxide for about an hour. On the other hand, an aluminum cup exposed to the action of the tetroxide at 500° for more than an hour showed no appreciable loss in weight. However, on extended heating of the tetroxide in an aluminum cup (30 hours) the surface of the aluminum appeared to have suffered attack. Using an aluminum cup, the weight of the residual oxide was found to correspond approximately to that required for K_2O_3. It was noticeable that the color of the final product was markedly darker than that of the original tetroxide. At ordinary temperatures the tetroxide is distinctly yellow while the final product was of an orange color.

A pellet weighing 0.1173 g. lost 0.0175 g. on extended heating above the melting point and the residue weighed 0.0998 g.; the weight required for K_2O_3 is 0.1041 g. In another experiment, 0.1102 g. of K_2O_4 lost 0.0123 g., and the residue weighed 0.0950 g.; the weight calculated for K_2O_3 is 0.0977 g.

The weight of the final product is 7% below that required for K_2O_3. This may in part be due to a slight action of the oxide on the aluminum cup. Our observations with respect to K_2O_3 in general confirm the earlier work of deForcrand.

Reversibility of Dissociation Process.—A sample of the tetroxide in an aluminum cup was heated to 370°, 400° and 460°, first in a vacuum and then in the presence of oxygen at a pressure of one atmosphere. The loss and gain in weight of the oxide are given in Table IV. The total weight of tetroxide was 0.1102 g.

TABLE IV

LOSS AND GAIN IN WEIGHT OF K_2O_4 AT DIFFERENT TEMPERATURES

Temp., °C.	370	400	460
Loss, g.	0.0057	0.0099	0.0123
Gain, g.	0.0021	0.0099	0.0123

The loss corresponding to one atom of oxygen per molecule of K_2O_4 is 0.0125 g. At 370° the loss of 0.0057 g. was much below this value. On treating with oxygen, the original weight was not reëstablished. At 400° the loss was markedly higher although still below the amount required for K_2O_3 as final product. On treating with oxygen at 400° the initial weight, prior to heating in a vacuum, was reëstablished. At 460° the loss of 0.0123 g. corresponds closely to that required for K_2O_3 as final product. On heating the material in oxygen the additional weight was reëstablished. The weight of the final product, after evacuating at 470°, was 0.0950 g. as compared with 0.0977 g. for K_2O_3. This difference may have been due to the presence of a trace of moisture which would lead to the formation of K_2O_2 at temperatures between 100 and 200°. The final material exhibited a marked orange color. It is clear from these results that the process of dissociation of K_2O_4 at higher temperatures is a reversible one.

The Dissociation Pressure of K_2O_4.—Since the dissociation process is reversible, it might be expected that the equilibrium pressure could be determined. According to observations of deForcrand at 480°, the dissociation pressure is not fixed owing to the fact that the system contains only a liquid and a vapor phase and is therefore divariant. An attempt was made to determine the equilibrium pressure at temperatures below 400°, where apparently no liquid phase is present. It was found, however, that even at these temperatures, the pressure is dependent upon the volume of oxygen evolved.

A pellet of potassium tetroxide weighing 0.1271 g. was placed in a large aluminum cup within a Pyrex tube which was attached to a high-vacuum pump and to a calibrated McLeod gage. The tube containing the pellet was raised to 180° and thoroughly evacuated. It was then allowed to cool to room temperatures, after which the temperature was again raised and a series of pressure observations made. The results of the first series of observations are given in Table V.

TABLE V

DISSOCIATION PRESSURE OF POTASSIUM TETROXIDE AS INITIALLY MEASURED

t, °C.	100	120	155	195	237	247	300	305
p, mm. of Hg	0.035	0.055	0.095	0.295	0.465	0.532	1.47	1.61

At 200° the color of the oxide was orange while at 300° it was practically black. When the tube was pumped for a short time at 305°, the pressure returned to 0.170 mm. after standing for about an hour. The tube was allowed to cool without evacuating and left for 24 hours. At the end of that time the following series of pressure readings was made.

TABLE VI

PRESSURE OF K_2O_4 AT DIFFERENT TEMPERATURES AFTER PUMPING

t, °C.	24	60	100	160	205	263	280	300
p, mm. of Hg	0.010	0.011	0.012	0.015	0.018	0.071	0.114	0.206

After removing the evolved gas at 300°, the pressure returned practically to its original value but on continued pumping it returned to a lower value. After pumping had been continued for 16 hours at 300°, the pressure returned to 0.170 mm. The weight of the oxide at this time was found to be 0.1198 g. On further pumping for 17 hours at 300° the pressure returned to 0.128 mm. at the end of one hour. The weight was found to be 0.1073 g.

Corresponding to the equation

$$K_2O_4 = K_2O_3 + \frac{1}{2}O_2 \qquad \text{(VII)}$$

0.1271 g. of K_2O_4 should lose 0.0146 g. At the end of the first 16 hours' pumping at 200°, the loss was 0.0073 g. and at the end of another 17 hours the total loss was 0.0098 g. The total weight of oxygen removed was well below that required according to Equation VII. On the first pumping at 300° for a short time the pressure fell from 1.61 mm. to 0.170 mm. The loss in weight was not determined but on pumping for 16 hours at 300°, the pressure again returned to 0.170 mm., 0.0073 g. of oxygen having been lost. On pumping for another 17 hours at 300° with an additional loss of 0.0025 g. the pressure returned to 0.13 mm. in one hour. It appears that at 300° the equilibrium pressure of reaction (VII) may lie in the neighborhood of 0.17 mm. The observations recorded in Tables V and VI are not true equilibrium pressures.

Summary

1. On slow oxidation of potassium in liquid ammonia, potassium hydroxide and potassium amide result as initial products. On further oxidation, potassium amide yields potassium hydroxide and potassium nitrite.

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°.

PROVIDENCE, RHODE ISLAND

[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]

BY J. AUSTIN BURROWS WITH F. E. BROWN

RECEIVED SEPTEMBER 18, 1925 PUBLISHED JULY 6, 1926

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).