TABLE III

COMPOSITION OF THE PERRHENATES

Compound		Found, %	Calcd., %
$AgReO_4$	Ag	30.0	30.1
	ReO_4	69.9	69.9
$TlReO_4$	Tl	44.2	44.9
	$TlReO_4$	100.0	100.0
$Cu_2(ReO_4)_2$	Cu	19.9	20.3
	ReO_4	81.3	79.7
$Hg_2(ReO_4)_2$	Hg	45.5	45.5
	ReO_4	56.1	55.5
$Hg_2O{\cdot}Hg_2(ReO_4)_2$	Hg	61.0	60.8
	ReO_4	39.1	38.0

rhenate analyses are consistently a little higher than the calculated values. This could be due to the precipitation of some complex mercurate ion with the perrhenate ion on the addition of the tetraphenylarsonium chloride reagent.

The cuprous perrhenate gave values for copper lower than the theoretical and higher values for perrhenate. A small amount of cupric perrhenate still present would account for this difference. The possibility that the substance was cupric rhenate, which would have the same composition, was considered. Cupric rhenate should be more paramagnetic than cupric perrhenate since both the cupric and rhenate ions are paramagnetic while the perrhenate ion is diamagnetic. The product obtained was less paramagnetic than cupric perrhenate. Since cuprous perrhenate should exhibit diamagnetism, the paramagnetism of the product may be due to some cupric perrhenate being present.

Summary

The univalent heavy metal perrhenates have been prepared and analyzed to verify the formulas. The compounds containing cuprous and mercurous ions have not been previously reported with one possible exception.[5] These salts have been further characterized as to color, solubility in water or reaction with water, heat of solution, optical properties in plane polarized light, density and freezing point.

KNOXVILLE, TENNESSEE RECEIVED MAY 12, 1950

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

A Contribution to the Chemistry of the Alkali Metal "Ozonates"

BY THOMAS P. WHALEY AND JACOB KLEINBERG

The nature of the products formed by reaction between ozone and alkali metal hydroxides has long been the subject of investigation.[1-6] The deep yellow to orange materials formed as a result of this reaction were at one time considered to be derivatives of a hypothetical "ozonic acid," H_2O_4, and hence were given the name "ozonates."[7]

It has recently been discovered by Kazarnovskii, Nikolskii and Abletsova[6] that potassium "ozonate" is soluble in liquid ammonia with the formation of a red solution; evaporation of the ammonia leaves a red solid which was reported to consist mainly of compound having the formula KO_3. This substance which apparently slowly decomposes to potassium superoxide and oxygen, was named potassium ozonide.

Repetition of the work of Kazarnovskii, Nikolskii and Abletsova in this Laboratory confirmed their results in large measure. Cesium "ozonate" also was found to be soluble in liquid ammonia, and a red solid was obtained upon evaporation of the solvent. Analysis of this red solid, however, gave data which could not be explained solely on the basis of the formulation CsO_3, and the existence of another, as yet unknown, substance is indicated. In the case of both potassium and cesium, the extracted products were found to decompose violently in water, with an accompanying liberation of energy in the form of light, and to liberate iodine from acidified potassium iodide solution. The product of ozonization of sodium hydroxide was found to be insoluble in liquid ammonia, and isolation of the pure ozonate was not accomplished. However, the data obtained from magnetic and chemical analysis of the gross product of ozonization are best explained by the assumption of the formation of a compound of the formula NaO_3. A similar interpretation appears to be valid with respect to ozonated cesium hydroxide.

Experimental

The alkali metal hydroxides used in these investigations were C. P. materials, the principal contaminant being water of hydration. The sodium and potassium hydroxides were found to contain about 10 and 20%, respectively, of water of hydration. Anhydrous cesium hydroxide was obtained by heating the monohydrate, manufactured by Mackay Chemical Co., in a nickel crucible at 450° for about 5 hours in a stream of dry nitrogen. The anhydrous potassium hydroxide used in the extraction studies was prepared in a similar manner, but at 300°. The liquid ammonia used in the extraction expts. was obtained by the condensation of gaseous ammonia from a commercial cylinder into the extraction vessels to be described later. Ozone-containing oxygen was obtained from two sources: (1) a commercial "Ozonator," manufactured by Ozone Processes, Inc., which produced ozone-containing oxygen with an ozone concentration of about 5% by weight at flow rates of 10 to 20 liters per hour, and (2) a laboratory ozonizer, which utilized a 10,800 volt transformer and was a modification of an apparatus described by Smith.[8] The latter ozonizer produced an ozone concentration of 7.5 to 8.0% at flow rates of 10 to 20 liters per hour.

Pulverized materials were used in order to expose the maximum surface to the ozone-containing stream of oxygen.

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(1) Wurtz, "Dictionnaire de Chimie pure et appliquee," Vol. II, p. 721, 1868.

(2) Baeyer and Villiger, *Ber.*, **35**, 3038 (1902).

(3) Manchot and Kampschulte, *ibid.*, **40**, 4984 (1907).

(4) Traube, *ibid.*, **45**, 2201 (1912); **49**, 1670 (1917).

(5) Strecker and Thieneman, *ibid.*, **53**, 2096 (1920).

(6) Kazarnovskii, Nikolskii and Abletsova, *Doklady Akad. Nauk, S. S. S. R.*, **64**, 69 (1949).

(7) Although present evidence indicates that these substances are not derivatives of "ozonic acid," the name "ozonates" is a convenient one and is employed in the present communication.

(8) Smith, THIS JOURNAL, **47**, 1850 (1925).

The hydroxide sample was finely powdered within an airtight dry-box which contained phosphorus pentoxide and magnesium perchlorate as drying agents. A portion of pulverized hydroxide was transferred to the ozonization cell (K of Fig. 1) and ozone-containing oxygen passed through the sample for several hours. The sample was stirred by periodically opening stopcock F and permitting the back pressure of the gas to be released through the sintered glass filter in K. The calcium oxide tower C and the potassium iodide tower D served as ozone destroyers. When the sample appeared to be ozonated as completely as possible, dry oxygen was passed through the system for approximately one-half hour in order to remove all traces of residual ozone. The ozonated hydroxide was then either transferred to the dry-box in preparation for analysis, or permitted to remain in the ozonization chamber for extraction with liquid ammonia.

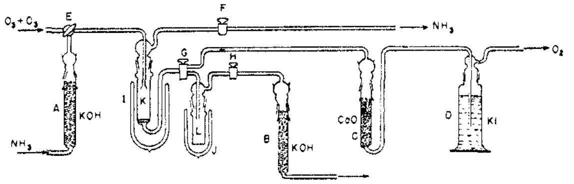

Fig. 1.—Apparatus used for liquid ammonia extraction of alkali metal "ozonates."

For the analysis of the gross product of ozonization, the sample was first transferred, within the dry-box, to a weighing tube for determination of magnetic susceptibility.[9] After magnetic measurements had been made, a weighed portion of the sample was decomposed with a known volume of standard hydrochloric acid and the volume of oxygen and carbon dioxide in the evolved gases determined. Titration with standard alkali of the solution remaining after decomposition permitted the estimation of alkali in the product of ozonization.

In the liquid ammonia extraction of the ozonates, ammonia was passed from a commercial cylinder, through a potassium hydroxide drying tower (A of Fig. 1), and into the ozonization chamber where it condensed above the ozonated hydroxide which was maintained at about −70° by a bath of Cellosolve and solid carbon dioxide in the dewar vessel I. After approximately 10 ml. of liquid ammonia had been collected in the ozonization chamber, stopcocks H and G were opened so that the solution was free to pass into the collection vessel L. Stopcock F was then closed, and the cooling bath I surrounding the solution was removed. The pressure of the ammonia from the cylinder forced the solution into the collection vessel, where it was permitted to evaporate to dryness by removal of the cooling bath J and passage of dry oxygen through the system. When all traces of ammonia had been removed, the collection flask (which was not lubricated) was quickly stoppered and weighed. The sample was then decomposed by means of either water or acidified potassium iodide solution, and the liberated oxygen measured. The solution remaining after decomposition was then analyzed titrimetrically for alkali content or iodine content, depending upon whether water or acidified potassium iodide solution had been used as the decomposant.

Results and Discussion

Inasmuch as sodium ozonate was found to be insoluble in liquid ammonia and the usual organic solvents, the method used to interpret the experimental data was necessarily an indirect one. The ozonate proved to be paramagnetic; therefore, application of the Wiedemann law for additivity of magnetic susceptibilities[10] permitted the calculation of the susceptibility of pure sodium ozonate, the value found, however, depending upon the formula assigned to this substance. The gross product of ozonization of sodium hydroxide was a mixture of 4 components, sodium ozonate, sodium carbonate, water[11] and unreacted sodium hydroxide; hence, the additivity law assumed the form

$$\chi_{\text{mix.}} = \chi_1 P_1 + \chi_2 P_2 + \chi_3 P_3 + \chi_4 P_4$$

where $\chi_{\text{mix.}}$ is the gram susceptibility of the mixture, χ_1, χ_2, χ_3 and χ_4 are the respective gram susceptibilities of the 4 components, and P_1, P_2, P_3 and P_4 are the respective weight fractions. $\chi_{\text{mix.}}$ P_{NaOH}, $P_{\text{Na}_2\text{CO}_3}$ and $P_{\text{H}_2\text{O}}$ were determined experimentally, and the values for χ_{NaOH} $\chi_{\text{Na}_2\text{CO}_3}$ and $\chi_{\text{H}_2\text{O}}$ were readily available in the literature.[12] Thus, if P_{ozonate} were known, the value of χ_{ozonate} could be calculated.

The value for P_{ozonate} was determined by assigning various formulas to the ozonate and calculating the quantity of NaO_3, NaO_2, $NaOH{\cdot}O_2$ and $(NaOH)_2{\cdot}O_2$[13] that would give rise to the volume of oxygen that had been measured gasometrically. The quantity of sodium carbonate was determined directly from the gasometric data, and the amount of unreacted hydroxide was determined titrimetrically. (Since part of the hydrochloric acid decomposant was neutralized in decomposing the ozonate and the carbonate in addition to reacting with free hydroxide, the calculated per cent. of unreacted sodium hydroxide in the sample depended upon the formula assigned to the ozonate.) The amount of water was determined by difference. Multiplication of the calculated gram susceptibility of the ozonate by the assigned formula weight gave the molar susceptibility; from this value the magnetic moment of the ozonate could be determined by use of the well-known expression $\mu^2 = 8\chi_{\text{m}}T$. Similar treatment of the gross product of ozonization of cesium hydroxide was also carried out. The formula which leads to a calculated value of μ most nearly consistent with the corresponding structure may then be regarded as most probable.

The formulas $MOH{\cdot}O_2$ and $(MOH)_2{\cdot}O_2$ would demand either that the substance contain two unpaired electrons per formula weight, or that it be diamagnetic. Since the magnetic moments calculated on the basis of these formulas were scarcely half the theoretical value of 2.84 Bohr magnetons for two unpaired electrons, these formulas were not acceptable. Magnetic moments calculated on the

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[9] The apparatus and procedure used for determining magnetic susceptibility were the same as reported by Stephanou, Schechter, Argersinger and Kleinberg, THIS JOURNAL, **71**, 1819 (1949), the only modification being the replacing of the standard analytical balance by a semi-micro balance.

[10] Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 231.

[11] The water contained in the sample was unquestionably present in the form of water of hydration. The assumption was made throughout these calculations that the hydrated hydroxide (or carbonate) could be treated as a mixture of water and the anhydrous material, *i. e.*, that the magnetic susceptibilities of water and the anhydrous materials were additive and could be so utilized in the application of the Wiedemann additivity law. Recently, Prasad, Dharmatti, Kanakar and Biradar (*J. Chem. Phys.*, **17**, 813 (1949)) have reported that hydration does cause some deviation from linearity. However, their data indicate a maximum deviation of only about 8%, with an average deviation of about 4%. A deviation of even 8% would not appreciably alter the results obtained from these calculations.

[12] Hodgman (Editor), "Handbook of Chemistry and Physics," 25th ed., Chemical Rubber Publishing Co., Cleveland, 1941, pp. 1873–1883.

[13] These formulas correspond to those which have been suggested by Kazarnovskii, Nikolskii and Abletsova,[6] Baeyer and Villiger,[2] and Traube,[4] respectively, for potassium ozonate. The formulas $NaHO_2$ and Na_2O_2 were not considered since these substances are diamagnetic.

basis of MO_2 were much lower than the theoretical value of 1.73 Bohr magnetons for one unpaired electron; this fact, coupled with the observation that sodium ozonate did not give a positive peroxide test, as do the superoxides, when decomposed with water, served to eliminate this formula from consideration. The data were found to be best accounted for by assigning the formulas NaO_3 and CsO_3 (Table I), which imply one unpaired electron per formula weight. In view of the small percentage of ozonate present in the mixture, the agreement between the calculated value of μ and the theoretical value for one unpaired electron is entirely satisfactory. The observation that solutions remaining after decomposition of ozonated cesium hydroxide samples contained a substance which liberated iodine from acidified potassium iodide solution did not alter the results calculated for cesium ozonate, since quantitative determinations showed that the amount of iodine liberated was almost negligible with respect to the amount of oxygen evolved.

TABLE I

ANALYSIS OF OZONATED SODIUM AND CESIUM HYDROXIDE SAMPLES

The first 6 rows are data for sodium hydroxide, the remainder for cesium hydroxide

$\chi_{mix.}$ c. g. s. unit/g. $\times 10^{-6}$	MOH,[a] %	M_2CO_3, %	H_2O, %	MO_3,[b] %	μ,[c] Bohr magnetons; theoretical for MO_3, 1.73
+0.54	58.8	9.8	26.7	4.5	2.0
− .01	74.7	9.2	12.5	3.6	1.6
− .17	92.2	0.7	4.6	2.3	1.7
+ .85	46.4	21.8	20.9	10.2	1.5
+ .45	47.0	32.2	8.8	11.0	1.2
− .03	80.5	10.0	8.0	3.2	1.7
− .07	87.8	0.0	9.9	2.3	1.8
− .04	84.3	.4	12.8	2.5	2.0
− .15	84.4	.0	13.2	2.2	1.5
− .23	85.1	.0	13.3	1.6	1.2
− .11	83.8	1.5	13.2	1.5	1.7

[a] The magnetic susceptibility of sodium hydroxide is given in the literature (see ref. 11) as -0.59×10^{-6} c.g.s. unit/g. The susceptibility of cesium hydroxide was determined experimentally by application of the Wiedemann additivity law, utilizing the analytical data for the hydrated cesium hydroxide starting material. The value for the hydroxide was determined to be -0.203×10^{-6} c.g.s. units/g. [b] Calculated on the basis of complete decomposition to M_2O and O_2. All samples which were found to contain less than 1.5% (calculated) MO_3 were rejected, since the least reliable data (magnetic data) were found to be reliable to about this extent. [c] Average value of μ is $1.6_3 \pm 0.2_8$.

Although sodium ozonate is decomposed in water or acid with the evolution of oxygen, neither the solid material nor the solution remaining after acidic decomposition gives a positive peroxide test. Sodium ozonate which has been prepared at room temperature is insoluble in liquid ammonia and the common organic solvents; however, a very small amount of yellow solid is extracted by liquid ammonia from pulverized sodium hydroxide which has been treated with ozone at −50°. The ozonate is apparently stable at room temperature; no decomposition was noted in samples which had stood for 18 months. It decomposes at temperatures above 100° to produce oxygen and the hydroxide. No indication of decomposition to superoxide was obtained.

Potassium and cesium ozonates are colored orange and orange-red, respectively. Both decompose in water or acid with liberation of oxygen; both liberate iodine from acidified potassium iodide solution. The ozonates appear to be readily soluble in liquid ammonia, but not in any of the common organic solvents. Ozone-treated potassium hydroxide is decolorized on standing at room temperature after several hours, whereas the corresponding cesium material is partially decolorized under the same conditions only after several days.

The role of the moisture in the reactions between ozone and the alkali metal hydroxides is important. Ozone-containing oxygen does not color anhydrous sodium hydroxide, so that it is necessary to use partially hydrated material in the preparation of the sodium ozonate. Although ozone reacts with the anhydrous hydroxides of potassium and cesium, the reaction is much slower than with the hydrated materials. When the ozone-containing stream of oxygen is carefully dried by passage through magnesium perchlorate, no reaction is noted with either the hydrated or anhydrous materials. (The effluent gases were tested with potassium iodide solution to make certain that the ozone had not been destroyed by the drying agents.) It thus appears that a trace of water is necessary to catalyze the reaction.

The role of water in the extraction of ozonated potassium and cesium hydroxides with liquid ammonia was found to be important also. Any moisture present in excess of that required for formation of stable hydrates with the hydroxide reactants is absorbed by the liquid ammonia; this precludes the obtaining of a dry product after evaporation of the ammonia. Since moisture is one of the products of the ozonization reaction (as observed experimentally), it was necessary to provide a means for preventing absorption of this water by the extracting solvent. This was accomplished by utilizing a relatively high column (3 to 4 cm.) of partially dehydrated hydroxide, so that the water formed during the course of the reaction was absorbed by the anhydrous or partially dehydrated hydroxide in the lower portion of the column to form a stable hydrate, and was thus not available for absorption by the liquid ammonia.

The red solid products obtained from the liquid ammonia extraction of ozonated potassium and cesium hydroxides liberated iodine from acidified potassium iodide solution, but immediately after preparation gave negative peroxide tests. The potassium product gave a positive peroxide test after standing for several days at room temperature; when the liquid ammonia extract was maintained at 50° for one hour, the red color gave way to a mixture of white and yellow, and the residue gave a positive peroxide test when decomposed by water. The yellow color and the positive peroxide test are indicative of the formation of superoxide. The extracted cesium material showed no apparent decomposition after standing in a closed vessel for seven days at room temperature, and gave a negative test for peroxide; however, when heated at 170° for an hour and a half, the red solid decomposed to a mixture of white and yellow solids which gave the tests that would be expected of cesium superoxide. Both the potassium and cesium extracts decompose violently in water, with flashes of light accompanying the decomposition.

Analyses of the extracted potassium product indicate that the red solid contains about 55% K_2O and 45% available oxygen, *i. e.*, oxygen liberated upon complete decomposition, as compared with the values 54.1 and 45.9% calculated for the decomposition of KO_3. This fact would appear to substantiate to a large extent the findings of Kazarnovskii, Nikolskii and Abletsova[6] that the red solid is composed primarily of a substance having the formula KO_3; hence, it should be termed potassium ozonide. In addition, thermal decomposition of the material at 50° for one hour liberates approximately the quantity of oxygen calculated for the decomposition of KO_3 to KO_2 (found, 16.0; calcd., 18.4). Measurement of the oxygen and iodine liberated when acidified potassium iodide solution is used as a decomposant indicates that the oxygen–iodine ratio is about 2.5:1. The solution remaining after aqueous decomposition of the red solid retains a very weak oxidizing power. Inasmuch as the behavior of this red solid differs from that of the sodium ozonate in that the latter is incapable of oxidizing acidified potassium iodide, considerable doubt exists that the potassium extract is a single chemical species.

Analyses of the extracted cesium products proved very inconclusive. The per cent. of Cs_2O was much higher than that calculated on the assumption that the red cesium solid was CsO_3. As in the case of the extracted potassium material, the results of oxygen–iodine determinations showed the oxygen–iodine ratio to be approximately 2.5:1. However, in this instance the oxidizing power displayed by the solid was in no way affected by aqueous or acidic decomposition; the resulting solutions displayed the same amount of oxidizing action toward iodide ion as did the solid material. In this respect the behavior of the extracted potassium and cesium materials differ considerably. These observations would seem to lend weight to the thesis that the extracted material is not a single chemical species of the formula CsO_3, particularly in view of the fact that sodium ozonate does not oxidize iodide ion.

Acknowledgment.—The authors are indebted to Professor Arthur W. Davidson for his critical reading of this manuscript.

Summary

Ozone-treated sodium hydroxide decomposes in water with evolution of oxygen, but does not liberate iodine from acidified potassium iodide solution. Ozonated potassium and cesium hydroxides also evolve oxygen upon decomposition in water, but liberate iodine from acidified iodide solution. Analyses of the gross products of ozonization of sodium and cesium hydroxides produce data which are most reasonably explained by assigning the formulas NaO_3 and CsO_3 to the colored, paramagnetic materials.

The colored products of ozonization of potassium and cesium hydroxides are soluble in liquid ammonia; evaporation to dryness of the resulting solutions produces red solid substances which decompose violently in water with evolution of oxygen, and liberation of energy in the form of light. Although analysis of the material extracted from ozone-treated potassium hydroxide appears to indicate that the red solid consists mainly of the compound KO_3, chemical behavior would seem to indicate that the extract is not a single chemical species. Analysis of the extracted cesium material even more strongly suggests the presence of another substance.

LAWRENCE, KANSAS RECEIVED JUNE 7, 1950

[CONTRIBUTION NO. 89 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Ionization and Hydration Equilibria of Periodic Acid[1]

BY C. E. CROUTHAMEL, A. M. HAYES AND D. S. MARTIN

Introduction

Kinetic studies of the reaction between periodic acid and ethylene glycol[2] and other oxidation reactions involving periodate have large variations in their rates with temperature and hydrogen ion activity. A more detailed knowledge of the species present in solution should be of assistance in explaining these variations. The apparent ionization constants of periodic acid have already been evaluated at 25°.[3] No differentiation between the degree of hydration of ionic and molecular species was made, thus the apparent ionization constants written in more general form would be

$$(a_{H^+})\Sigma a_1/\Sigma a_0 = K_1' \qquad (1)$$

$$(a_{H^+})\Sigma a_2/\Sigma a_1 = K_2' \qquad (2)$$

where a_{H^+} is the hydrogen ion activity, and Σa_0, Σa_1 and Σa_2 are, respectively, the sums of the activities of undissociated forms, singly charged and doubly charged ionic species. Since the ionization of three hydrogen ions was observed, the acid was designated as the hydrated species, H_5IO_6.

In the first paper[2] it was established that the absorption maximum at 2225 Å. was caused by univalent ions. Further examination of this peak under various conditions was interpreted to in-

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[1] Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] Frederick R. Duke, THIS JOURNAL, **69**, 3054 (1947).

[3] C. E. Crouthamel, *et al.*, *ibid.*, **71**, 3031 (1949).