the hexadecylpyridonium salt. Accordingly, the Λ_0 values for the octadecyltrimethylammonium and octadecylpyridonium must sulfamates lie around 57–58. It is thus clear that, except for hexadecyltrimethylammonium sulfamate, in which case the maximum value of Λ is approximately the same as that of Λ_0, the values of Λ at the maxima lie appreciably above the limiting equivalent conductances. The values of $(\Lambda_{\text{max.}} - \Lambda_0)$ for octadecyltrimethylammonium, octadecylpyridonium and hexadecylpyridonium sulfamates are approximately 5, 8 and 1, respectively. Kraus and others[13] have reported values of 7 and 10.7, respectively, for $(\Lambda_{\text{max.}} - \Lambda_0)$ in the cases of octadecyltrimethylammonium bromate and formate in 10% acetone–water mixture. The conductances of the bromate and formate ions are 55.8 and 54.6, respectively. It therefore appears that the height of the conductance peak is not dependent entirely on the conductance of the gegenion since in view of the lower conductance of the sulfamate ion we might expect a higher maximum. It is interesting to note that the position of the maximum appears to depend only on the nature of the long chain—it occurs at about $2 \times 10^{-3}\ N$ for the hexadecyl chain and at about $9 \times 10^{-4}\ N$ for the octadecyl chain.

It is concluded that while the sulfamate ion is not sufficiently slow to allow of the existence of conductance maxima in water its size and other properties are such that unusual aggregation effects are evident in acetone–water mixtures. An interpretation of these phenomena awaits the presentation of more extensive data.

Summary

1. The conductances of dilute aqueous solutions of sulfamic acid, silver, potassium and ammonium sulfamates have been measured at 25°.

2. The dissociation constants of sulfamic acid and silver sulfamate in water at 25° have been calculated.

3. The limiting conductance of the sulfamate ion has been determined.

4. The conductances of dilute solutions of *n*-octadecyltrimethylammonium, *n*-hexadecyltrimethylammonium, *n*-octadecylpyridonium and *n*-hexadecylpyridonium sulfamates in water and in 10% acetone–water mixtures have been measured at 25°.

5. In water the usual breakpoint in the $\Lambda/\sqrt{C}$ curves is observed.

6. In 10% acetone–water mixture all four salts show maxima in the $\Lambda/\sqrt{C}$ plots.

WILLIAMSTOWN, MASSACHUSETTS RECEIVED JULY 7, 1950

---

[13] Young, Grieger and Kraus, THIS JOURNAL, **71**, 309 (1949).

[CONTRIBUTION NO. 94 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Salts of Perrhenic Acid. III. Univalent Heavy Metals[1]

BY WM. T. SMITH, JR.

Preparation of the Salts.—Water solutions of thallous sulfate and potassium perrhenate, on mixing produced relatively insoluble thallous perrhenate. This white salt was purified by repeated washing and digesting with boiling water. Kraus and Steinfeld[2] have reported this compound and because of its insolubility have suggested its use in the estimation of rhenium.

Silver perrhenate was prepared by treating freshly precipitated silver oxide with a water solution of perrhenic acid. This salt which is more soluble than thallous perrhenate was purified by recrystallization from water. The white salt when pure is not decomposed by sunlight although impure samples darkened slowly. Hönigschmid and Sachtleben[3] reported the preparation of this salt by several metathetical reactions in water solution and found it to be insoluble in concd. nitric acid and soluble in concd. ammonium hydroxide. The salt has been used by Geilmann and Wrigge[4] in a determination of the atomic weight of rhenium.

Freshly prepared cuprous oxide when treated with a perrhenic acid solution produced a blue solution of cupric perrhenate. The very soluble cupric perrhenate was recrystallized from water. The water of crystallization was removed by heating in an oven at 110° and the white anhydrous salt decomposed by heating at 400 to 500° for several days. Rhenium heptoxide and oxygen were volatile products of the decomposition. The brownish-pink residue, similar in color to the hexahydrate of cobalt chloride, remaining after decomposition had ceased was cuprous perrhenate. This salt has not been previously reported.

A water solution of mercurous nitrate on the addition of a solution of potassium perrhenate produced a white basic or oxy-mercurous perrhenate. This substance was digested and washed with hot water. After drying over calcium chloride the substance lost no weight in an oven at 110°. On heating the white solid turned orange at approximately 400° and then melted to a black liquid which decomposed with the evolution of mercury and oxygen. The melt was held between 550 and 600° until no further signs of decomposition were evident and cooled to produce a red solid which changed to orange then yellow and finally to white mercurous perrhenate as the temperature fell. An insoluble mercurous perrhenate has been reported[5] but not quantitatively characterized.

Freezing Point.—The freezing points of the salts were determined[6] from cooling curves obtained with a Brown potentiometer and a chromel–

---

[1] Presented at the Symposium on the Less Familiar Elements at the A. C. S. Meeting in Detroit, April 17, 1950.

[2] Kraus and Steinfeld, *Z. anorg. Chem.*, **197**, 52 (1931).

[3] Hönigschmid and Sachtleben, *ibid.*, **191**, 207 (1930).

[4] Geilmann and Wrigge, *ibid.*, **199**, 65 (1931).

[5] Heyne and Moers, *Z. anorg. allgem. Chem.*, **196**, 129 (1931).

[6] Smith and Long, THIS JOURNAL, **70**, 354 (1948).

alumel thermocouple which had been checked against a calibrated couple furnished by the Brown Instrument Co. and guaranteed to give standard potentials to within 3°F. over the range 0–1200°F. The constancy of freezing point obtained after successive recrystallizations or after prolonged heating for those compounds produced by thermal decomposition was used as an indication of purity.

The increase in freezing point with increase in atomic weight of the cation observed in Table I is not characteristic of other salts of these metals.

TABLE I

FREEZING POINT AND DENSITY OF PERRHENATES

Compound	F. p., °C.	Density, g./cc. at *ca.* 25°
$Cu_2(ReO_4)_2$	380	5.70
$AgReO_4$	455[a]	6.96[c]
$TlReO_4$	525[b]	6.89
$Hg_2(ReO_4)_2$	561	7.23
$Hg_2O{\cdot}Hg_2(ReO_4)_2$	Dec. 400	7.90

[a] Vorlander and Dalichau[7] report that silver perrhenate decomposes at 430° and decomposes actively at 455°. [b] Jaeger and Beintma[8] report the melting point of thallous perrhenate as 527 ± 3°. [c] Vorlander and Dalichau[7] report 7.05. Buschendorf[9] calculated the density to be 6.933 from X-ray diffraction data.

Density Determination.—All of these salts were found to be insoluble in benzene and the densities were measured[10] by displacement of benzene in a pycnometer. The pycnometer containing the salt and benzene was degassed in a vacuum desiccator which resulted in cooling below room temperature. The pycnometer was then placed in the balance case and weighed when its temperature reached room temperature, approximately 25°. The volume of benzene in the pycnometer was in all determinations corrected to 25° using the thermal expansion coefficient of the liquid. The densities increase with increasing atomic weight of the cation, see Table I, except that the order of silver and thallium are reversed. While the two densities differ by only 1%, the method is dependable to ±0.5%. The reversal of the order may indicate a difference in crystal structure.

Microscopic Examination of Crystals.—Crystals of all of the univalent heavy metal perrhenates including the oxy-mercurous salt were examined with a microscope using plane polarized light. In every case the salts exhibited anisotropic behavior.

Solubility Determination.—The solubilities were determined by evaporation of water from weighed quantities of saturated solutions.[11] The solubilities of silver and thallous perrhenates were determined at 0, 30 and 50° and the heats of solution calculated from the slope of the curve obtained by plotting the logarithm of the solubility against the reciprocal of the absolute temperature (see Table II).

TABLE II

SOLUBILITY AND HEAT OF SOLUTION OF PERRHENATES

Compound	Solubility, g./100 g. H_2O 0.0°	30.0°	50.0°	Heat of soln. ΔH (kcal./mole) ± 1%
$AgReO_4$	0.43	1.39	2.71	6.57
$TlReO_4$[a]	.115	0.298	0.555	6.44

[a] Jaeger and Beintma[8] reported 1.6 g. per liter at 20°.

Cuprous and mercurous perrhenates react when dissolved in water as

$$Cu_2(ReO_4)_2 \longrightarrow Cu + Cu(ReO_4)_2$$

$$2Hg_2(ReO_4)_2 + H_2O \longrightarrow Hg_2O{\cdot}Hg_2(ReO_4)_2 + 2HReO_4$$

Analysis of the Salts.—The method used for the determination of rhenium was a modification[6] of the method of Willard and Smith.[12] Silver and copper perrhenates presented no new difficulties. The less soluble thallous and mercurous salts were first oxidized with hydrogen peroxide to produce more soluble substances. The rhenium in the original thallous perrhenate was then determined simultaneously with the thallium by precipitation of both perrhenate and chlorothallate with tetraphenylarsonium chloride reagent.[13] The insoluble oxy-mercurous perrhenate was dissolved in concentrated hydrochloric acid and 30% hydrogen peroxide. The mercury was then partially precipitated by neutralizing with sodium hydroxide solution. After filtration the solution was neutralized with hydrochloric acid, and made strongly alkaline with ammonium hydroxide. The rhenium was then precipitated with tetraphenylarsonium chloride. The complex ion containing mercury does not precipitate with the reagent under these conditions. This modification of the method of analysis for rhenium in the presence of mercury was devised by Grover E. Maxwell.

Silver was determined as the chloride.[14] Thallium was estimated by oxidation with standard permanganate in the presence of hydrochloric acid[15] and also by the simultaneous precipitation of perrhenate and chlorothallate with tetraphenylarsonium chloride.[13] Mercury was determined by the standard thiocyanate method.[16] The precipitation of mercury with 8-hydroxyquinoline in buffered acetic acid solutions[17] gave low and inconsistent results possibly due to the use of hydrochloric acid in dissolving the samples. Copper was determined by the potassium iodide method.[18] The results of the analyses are included in Table III. The composition of the oxy-mercurous perrhenate corresponds closely to the composition of mercurous rhenate, Hg_2ReO_4, but the rhenate ion is paramagnetic, and the compound obtained is diamagnetic as the oxy-mercurous perrhenate should be. While the mercury analyses check the calculated values very closely, the per-

---

(7) Vorlander and Dalichau, *Ber.*, **65**, 535 (1932).

(8) Jaeger and Beintma, *Proc. Koninkl. Akad. Wetenschappen Amsterdam*, **36**, 523 (1933).

(9) Buschendorf, *Z. physik. Chem.*, **B20**, 237 (1933).

(10) Smith and Maxwell, THIS JOURNAL, **71**, 578 (1949).

(11) Smith, *ibid.*, **68**, 394 (1946)

(12) Willard and Smith, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 305 (1939).

(13) Smith, *Anal. Chem.*, **20**, 937 (1948).

(14) Scott, "Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 821.

(15) Hawley, THIS JOURNAL, **29**, 300 (1907).

(16) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 172.

(17) Pirrone, *Atti accad. Italia, Rend. classe sci. fis., mat. nat.* [7] **1**, 50 (1939), *C. A.*, **34**, 5450 (1940).

(18) Scott, "Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 368.

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.

---

(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).