[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Thermodynamic Properties of Technetium and Rhenium Compounds. VII. Heats of Formation of Rhenium Trichloride and Rhenium Tribromide. Free Energies and Entropies[1,2]

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The heats of oxidation of $ReCl_3$(c) and $ReBr_3$(c) by basic hypochlorite have been determined. From these data the heats of formation at 25° have been calculated to be: $ReCl_3$(c), -63.0 ± 0.8 kcal. mole^{-1} and $ReBr_3$(c), -39.3 ± 0.8 kcal. mole^{-1}. Free energy and entropy estimates also are given.

Very few heat of formation data are available for the important second and third row transition element halides. This follows from the fact that such data usually are obtained from the corresponding heats of solution in water to give the simple and well-defined aqueous ions. However, the heavier transition element halides frequently form only poorly defined and characterized species on solution; indeed in some cases the presence of polymers and complexes has been reported. The only other source of heats of formation data is from high temperature dissociation vapor pressure measurements and such measurements are not simple.

It has been observed that basic hypochlorite solutions will quantitatively oxidize many of these transition element halides in clean cut reactions to well defined oxidation states and this communication describes the application of this technique to rhenium trichloride and tribromide. The recent[4,5] thermodynamic characterizations of hypochlorite make such measurements reliable.

Experimental

Materials.—Rhenium trichloride was prepared by two separate methods. The first of these was the thermal decomposition of rhenium pentachloride[6] which had been prepared by the direct reaction of metallic rhenium and dry chlorine.[7] The rhenium metal used was high purity powder (prepared from ammonium perrhenate) obtained from the University of Tennessee. The second method involved the thermal decomposition of silver hexachlororhenite(IV)[8] which was precipitated from an acidic solution of K_2ReCl_6[9] with silver nitrate. The Ag_2ReCl_6 so obtained was washed with water, 95% alcohol and finally, ether, and dried over P_2O_5. The material was heated gradually up to 400–450° in a previously degassed Pyrex combustion tube, which was part of a vacuum line. A mixture of the tri- and penta-chlorides, and some traces of oxychloride was first formed in the cooler portion of the tube. The mixture then was heated somewhat below 400°, whereby part of the pentachloride was further decomposed into $ReCl_3$ and chlorine. In both methods the trichloride was purified by repeated sublimation at 450–500°. Analyses were carried out to determine both the oxidation state and percentage composition: the former by addition of an excess of slightly basic standardized hydrogen peroxide followed by back titration with standard permanganate[10] and the latter by reduction to the metal with hydrogen.[11] Representative analyses on three separate samples gave these oxidation state values for the rhenium: 3.10, 3.05, 3.12. The percentage compositions of these same samples were: Re, calcd. 63.66%, obsd., 63.30, 63.79, 63.51%; Cl, calcd., 36.34%; obsd., 36.70, 36.49, 36.21%.

Rhenium tribromide was prepared by the thermal decomposition of silver hexabromorhenite(IV) under vacuum. Silver hexabromorhenite(IV) was prepared by addition of the potassium salt[12] to an excess of slightly acidic silver nitrate solution. Purification procedures were similar to those for rhenium trichloride. Typical analyses of the rhenium content were: Re, calcd., 43.73%, obsd., 43.95, 43.86, 43.48%; Br calcd. 56.27%, obsd. 56.05, 56.14, 56.52%.

Sodium hypochlorite solutions were prepared by passing purified chlorine through sodium hydroxide solutions (0.1–0.2N) for varying lengths of time. These stock solutions were stored in polyethylene containers under refrigeration and diluted with distilled water for use. The actual hypochlorite concentration was determined iodometrically with standard thiosulfate just prior to use.[13] Sodium bromide was oven dried (110°) reagent grade.

Apparatus.—The solution calorimeter was a glass submarine-Dewar type with a thermistor for temperature measurements and fitted for electrical calibration. It has been referred to and will be described[5] as laboratory calorimeter SC-2. The calorie has been taken as 4.184 abs. joules.

Procedure.—A small glass bulb containing a weighed amount of the anhydrous halide was sealed on the tip of the glass calorimeter heater rod with paraffin wax in a dry box. The calorimeter was filled with a known amount (~300 ml.) of the standardized basic hypochlorite solution. After assembly and immersion in the 25.00° thermostat, an electrical calibration of the effective heat capacity was made before, as well as after, the chemical reaction was over. On breaking the bulb, the reaction of the rhenium trichloride was observed to be fairly rapid and the stoichiometry was proven to be as given in equation 1 by determination of the final hypochlorite concentrations

$$ReCl_3(c) + 4OH^- + 2OCl^- \longrightarrow ReO_4^- + 2H_2O + 5Cl^- \quad (1)$$

The situation for rhenium tribromide was more complicated. Although the potentials[14] clearly indicate that any

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1525. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] For the previous publication of this series see THIS JOURNAL, **79**, 1559 (1957).

[3] From the Ph.D. thesis of J. P. King, Purdue University (1959).

[4] R. E. Connick and Yuan-tsan Chia, THIS JOURNAL, **81**, 1280 (1959).

[5] J. P. King and J. W. Cobble, to be published.

[6] H. S. Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 182.

[7] *Ibid.*, p. 180.

[8] J. G. F. Druce, "Rhenium," University Press, Cambridge, 1948, pp. 49–52.

[9] H. S. Booth, ref. 6, p. 178.

[10] The trichloride was first dissolved in a standardized hydrogen peroxide solution toward which the solid is reasonably ineffective as a catalyst in the self decomposition of H_2O_2. The resulting solution is pink; dropwise addition of 0.1N sodium hydroxide to this solution will cause the pink color to disappear. The solution now shows only the characteristic perrhenate spectrum, can be acidified and the excess peroxide titrated with permanganate. Such a procedure minimizes, but does not completely prevent, the catalytic decompositions of the peroxide.

[11] The reduction was most satisfactory if the temperature of the tube furnace, which contained the sample in a quartz combustion tube, was gradually raised from 350 to 800° over many hours. Otherwise some $ReCl_3$ will tend to be lost by volatilization.

[12] John Walton, Ph.D. thesis, Purdue University, 1957.

[13] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," 3rd Ed., Macmillan Co., New York, N. Y., 1952, p. 608.

[14] W. M. Latimer, "Oxidation-Reduction Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952, p. 51.

bromine valence state eventually will be oxidized to bromate by an excess of basic hypochlorite, it was apparent that the actual situation under the conditions of concentration in these experiments was modified by certain kinetic considerations. On mixing $ReBr_3$ or sodium bromide with excess basic hypochlorite, a pale yellow color suggestive of hypobromite results. Some bromate may be formed but there does not appear to be any accurate method to determine the final stoichiometry of a mixture of hypochlorite, hypobromite and bromate. Further, bromate is not spectrally active between 2000–8000 Å.

In practice, the final oxidation state of bromine need not be known, since separate calorimetric determinations of the hypochlorite oxidation can be made on a soluble bromide whose heat of formation is known. It then follows that with the assumption that the amounts of each of the final oxidation states in each experiment are the same, the difference in the heats of the soluble bromide and rhenium tribromide can be determined.

Separate calorimetric experiments are recorded in Table I on the heat of oxidation of NaBr(c) to the reference oxidation state.

TABLE I

HEAT OF OXIDATION OF NaBr(c) WITH ClO^- AT 25°

Run	$[OH^-]$ (normal)	$[ClO^-]$ (normal)	Ionic str., μ	NaBr(c), g.	ΔH_2, kcal./mole NaBr
19	0.05	0.0465	0.14	0.03268	−7.72
20	.05	.0465	.14	.10209	−7.91
23	.05	.0440	.14	.11197	−7.86
25	.017	.0130	.043	.11924	−7.95
				Av.	−7.88 ± 0.03[a]

[a] Standard deviation.

The heat, ΔH_2, in Table I will be assigned to the reaction

$$NaBr(c) + (3 - 2x)ClO^- \longrightarrow Na^+ + xBrO^- + (1 - x)BrO_3^- + (3 - 2x)Cl^- \quad (2)$$

where x is the fraction of the total bromine oxidized to hypobromite.[15] At this ionic strength of 0.14 the heat of solution of solid sodium bromide is zero, so that $\Delta H_2 = -7.88 \pm 0.03$ kcal.mole^{-1} can also be assigned to reaction 3.

$$Br^- + (3 - 2x)\ ClO^- = xBrO^- + (1 - x)\ BrO_3^- + (3 - 2x)\ Cl^- \quad (3)$$

Corrected to zero ionic strength, $\Delta H_3^0 = -7.9 \pm 0.1$ kcal. mole^{-1}.

Experimental Results

Table II is a summary of the heat of oxidation of $ReCl_3(c)$ as given by equation 1.

TABLE II

THE HEAT OF OXIDATION OF $ReCl_3(c)$ BY HYPOCHLORITE AT 25°

Run	$[OH^-]$ (normal)	Init. $[ClC^-]$ (normal)	Ionic[a] str., μ	$ReCl_3(c)$, g.	$-\Delta H_{(1)}$, kcal./mole
13	0.20	0.07571	0.35	0.02397	190.7
14	.10	.08987	.28	.02672	191.2
16	.050	.04474	.14	.03032	191.0
18	.050	.04464	.14	.03305	190.5
				Av.	190.7 ± 0.2

[a] The inert salt is sodium chloride.

Although there are no reliable heat of dilution data available at present on aqueous sodium perrhenate solutions, the corresponding data for sodium perchlorate[16] probably can be used as a satisfactory substitute. Under those conditions and using previous auxiliary heat data,[16] the heats of dilution cancel within the experimental error quoted. Thus $\Delta H^0_{(1)}$ is also -190.7 ± 0.2 kcal. mole^{-1}. With the new value[17] for the heat of formation of hypochlorite of -25.92 kcal. mole^{-1}, and the most recent one for the perrhenate ion[18] of -189.2 ± 0.8 kcal. mole^{-1}, the heat of formation of $ReCl_3(c)$ becomes -63.0 ± 0.8 kcal. mole^{-1}. Brewer[19] has estimated a value of -55 ± 10 kcal. mole^{-1}; there are so few similar heavy transition element halides known upon which to make an estimate that the values can be considered in essential agreement. The limits of error can be reduced by about a factor of two when the heat of formation of perrhenate is fixed more precisely.

The heat of oxidation data for $ReBr_3(c)$ are given in Table III.

TABLE III

THE HEAT OF OXIDATION OF $ReBr_3(c)$ BY HYPOCHLORITE AT 25°

The ionic strength in these experiments was $\mu = 0.27$.

Run	$[OH^-]$ (normal)	Init. $[ClO^-]$ (normal)	$ReBr_3(c)$, g.	$-\Delta H_{(4)}$, kcal./mole
38	0.10	0.0838	0.03688	204.0
43	.10	.0838	.05295	206.5
48	.10	.0838	.06239	203.5
49	.10	.0838	.07962	204.8
50	.10	.0838	.06492	204.4
			Av.	204.7 ± 0.5

In the absence of conclusive proof of the exact stoichiometry of the final oxidation states of bromine, we shall write for the heat of reaction given in Table III

$$ReBr_3(c) + 4OH^- + (11 - 6x)ClO^- = ReO_4^- + 2H_2O + 3xBrO^- + (3 - 3x)BrO_3^- + (11 - 6x)Cl^- \quad (4)$$

Since the heats of dilution are again small and tend to cancel, $\Delta H^0_4 = -204.7 \pm 0.5$ kcal. mole^{-1}. It can be shown that the heat of formation of $ReBr_3(c)$ then is given by

$$\Delta H^0_{ReBr_3} = 3\Delta H^0_{(3)} - \Delta H^0_{(4)} + \Delta H^0_{ReO_4^-} + 2\Delta H^0_{H_2O} + 2\Delta H_{Cl^-} + 3\Delta H^0_{Br^-} - 2\Delta H^0_{ClO^-} - 4\Delta H_{OH^-} \quad (5)$$

TABLE IV

THERMODYNAMIC FUNCTIONS FOR THE FORMATION OF RHENIUM HALIDES AT 25°

	ΔF^{0a}	ΔH^{0a}	S^{0b}
$ReCl_3(c)$	−47.8	−63.0	(38)
$ReBr_3(c)$	−33.6	−39.3	(44)

[a] In kcal. mole^{-1} and based on the normal liquid standard state for bromine. [b] Calculated from estimates made in ref.[19]

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(15) An actual fact, the data of Table I indicate all of the bromine is oxidized to hypobromite, although the heats of formation of both BrO^- and BrO_3^- are not accurately enough known to make this a certainty. This conclusion is supported by the fact that changes in the relative concentration of ClO^- and initial bromide do not, within experimental error, indicate any significant change in the heat, and therefore stoichiometry, of the reaction. This conclusion is in agreement with the kinetic studies of others in this *p*H range. See L. Farkas, M. Lewin and R. Bloch, THIS JOURNAL, **71**, 1988 (1949). We are indebted to a referee of this paper for calling this work to our attention.

(16) "Selected Values of Chemical Thermodynamic Properties," U. S. Bureau of Standards, Washington, D. C., 1948.

(17) The authors of ref. 4 list −25.94 kcal. mole^{-1} which involves an estimated but small temperature correction from 18 to 25°; the calorimetrically determined value referred to in ref. 5 was −26.2 kcal. mole^{-1}; the value of −26.2 kcal. mole^{-1} is adopted for these calculations.

(18) J. W. Cobble, G. D. Oliver and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5786 (1953).

(19) L. Brewer, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," edited by L. L. Quill, McGraw-Hill Book Co., New York, N. Y., 1950, p. 133.

The value so calculated is $\Delta H^0_{\mathrm{ReBr_3}} = -39.3 \pm 0.8$ kcal. mole^{-1}. Brewer[19] had estimated a value of -40 ± 15 kcal. mole^{-1} for this heat.

In summary, new thermodynamic functions are given for rhenium trichloride and rhenium tribromide at 25° in Table IV.

This method for obtaining heats of formation appears to be quite general and can be applied to fluorides and iodides as well. Thus it should be applicable to the halides of molybdenum, technetium, ruthenium tungsten, osmium and perhaps zirconium and hafnium iodides and bromides.

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The Preparation of the Anhydrous Zirconium Trihalides

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A new process for preparing pure, anhydrous zirconium trichloride, tribromide and triiodide is described. The appropriate tetrahalide vapor is mixed with hydrogen at a pressure of 3–4 mm. and passed through a glow discharge. The zirconium trihalide which is formed is subsequently freed from adsorbed or unreduced contaminants by heating *in vacuo.*

The important role which zirconium trichloride can play in the separation of zirconium and hafnium[1] has drawn attention to the paucity of thermodynamic data concerning not only the trichloride but also the analogous tribromide and triiodide. One obstacle to the accurate study of the properties of these compounds has been the absence of a method for preparing them in the pure anhydrous state.

The first preparation of a zirconium trihalide was attempted by Ruff and Wallstein[2] who reduced zirconium tetrachloride with aluminum, but their product was contaminated with 2.5–4% aluminum; moreover, the brown color of the compound which these early workers described indicated that partial hydrolysis had occurred. Larsen and Leddy[3] eliminated the aluminum contamination but, even under the most favorable reaction conditions, the trichloride which they prepared contained 15% unreacted zirconium. The brown color of their product also showed that they were unable to avoid a certain amount of hydrolysis. Larsen and Leddy pointed out that their trihalides were formed as a layer on the surface of finely-divided zirconium, and Newnham[4] has shown that the caking which occurs under these conditions makes complete elimination of the zirconium metal an extremely slow process.

Young[5] realized that one of the first essentials in the preparation of the pure trihalides was their complete isolation from the reactants. By making use of the St. Claire-Deville "hot-cold" tube, he prepared zirconium tribromide in a part of the apparatus not occupied by the aluminum reducing agent. Unfortunately he was not able to control the degree of reduction of his tetrabromide, so that the blue-black powder which he obtained was a mixture of tribromide, dibromide and finely divided zirconium metal. Young found that his tribromide turned brown when subjected to a slight amount of hydrolysis, and his prediction that the trichloride should be blue-black rather than brown subsequently was confirmed by Newnham.[4]

From the foregoing it is apparent that any method for preparing the pure trihalides must eliminate contamination by the reductant, closely control the degree of reduction and guard against any trace of hydrolysis. Since the trihalides are comparatively involatile, it is obvious that contamination can be avoided by using a gaseous reductant. Hydrogen presents itself as a likely choice in view of the work of Schumb and Sundström[6] on the analogous reduction of titanium tetrachloride by hydrogen. However, attempts to prepare zirconium trichloride by either Schumb's method or by the closely related technique of Young[5] have proved unsuccessful, and attention therefore has been directed to the possibility of using atomic hydrogen as the reductant. The dissociation of hydrogen into free atoms in an electric glow discharge was first described by Wood,[7] and Poole[8] has made a thorough study of the energy efficiency when atomic hydrogen is produced in this way. It has not proved practicable to adopt all the recommendations of these earlier workers (for example, they used hydrogen which had been saturated with water-vapor), but a careful adaptation of their technique has led to the development of a new process for preparing the pure zirconium trihalides.

Experimental

Raw Materials.—Zirconium tetrachloride was prepared by chlorinating reactor-grade zirconium at 500°. Since the reaction between chlorine and zirconium can be quite violent, the chlorination was initiated with a 10% mixture of chlorine in oxygen-free nitrogen, and the ratio of chlorine to nitrogen was increased as the reaction proceeded. Both gases were dried by passing them through magnesium per-

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[1] I. E. Newnham (a) *Research*, **10**, 424 (1957); (b) U. S. Patent 2,791,485, *C. A.*, **51**, 11227 (1957).

[2] O. Ruff and R. Wallstein, *Z. anorg. Chem.*, **128**, 96 (1923).

[3] E. M. Larsen and J. J. Leddy, THIS JOURNAL, **78**, 5983 (1956).

[4] I. E. Newnham, *ibid.*, **79**, 5415 (1957).

[5] R. C. Young, *ibid.*, **53**, 2148 (1931).

[6] W. C. Schumb and R. F. Sundström, *ibid.*, **55**, 596 (1933).

[7] R. W. Wood, *Phil. Mag.*, **44**, 538 (1922).

[8] H. G. Poole, *Proc. Roy. Soc.*, **163A**, 424 (1937).