anism). It is, of course, also true that high dielectric constant of the solvent will favor the reaction

$$NH_3 + NH_2Cl \longrightarrow NH_4^+ + NHCl^-$$
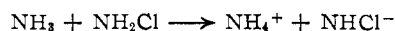
postulated by Audrieth, et al.[28] It is, therefore, apparent that the above order of solvents does not sharply distinguish between the two proposed mechanisms.

The reaction of chloramine with diethylamine to produce ethylhydrazine rather than 1,1-diethylhydrazine was unexpected, but there is no question as to its occurrence. This is in contrast to the reported production of 1,1-diethylhydrazine by the reaction of chloramine with diethylamine in aqueous solution.[30,31]

(30) R. A. Rowe, ref. 6, p. 89.

(31) R. A. Rowe and L. F. Audrieth, THIS JOURNAL, **78**, 563 (1956).

COLUMBUS 10, OHIO

Terbium Oxides. II. The Heats of Formation of Several Oxides[1]

BY C. T. STUBBLEFIELD, H. EICK AND L. EYRING

Three stable oxides of terbium were prepared, including two of non-stoichiometric composition, and their heat of reaction measured in an adiabatic microcalorimeter. The heats of reaction at 25° of $TbO_{1.500}$, $TbO_{1.71}$ and $TbO_{1.80}$ in 6.00 M HNO_3 containing a small concentration of Na_2SiF_6 were found to be -47.2 ± 0.3, -42.3 ± 0.5 and -39.2 ± 0.5 kcal. mole^{-1}, respectively. These values when combined with other data yielded the corresponding molal heats of formation for TbO_x of -218.4 ± 1.0, -223.3 ± 1.0 and -226.4 ± 1.0 kcal. mole^{-1}, respectively.

Introduction

Guth and Eyring[2] have made a phase study including an X-ray and differential thermal analysis of the terbium oxide system. These studies revealed two oxides stable over a wide temperature and pressure range of non-stoichiometric composition of $TbO_{1.71}$ and $TbO_{1.80}$, above $TbO_{1.50}$.

It was desired to know the heat of formation and the integral heats of oxidation of terbium sesquioxide and of these interesting non-stoichiometric oxide phases, but no thermochemical data were available on any terbium oxides. Existing supplementary thermochemical data, together with the measured heats of reaction of these oxides with nitric acid solutions, make possible the desired calculations.

The data were obtained using the adiabatic microcalorimeter described in a previous paper,[3] and may be compared to the results previously reported[4] for the praseodymium oxide system.

Experimental Methods

Preparation and Properties of the Oxides.—The starting material for the preparation of all the samples was obtained from Johnson, Matthey Co., Ltd., London, labeled Tb_4O_7. The purity was greater than 98% with gadolinium the principal impurity. The oxygen used was obtained from the thermal decomposition of $KMnO_4$ as previously described.[5] The atomic weight of terbium used was 159.2 and the defined calorie was assumed equal to 4.1840 absolute joules.

The conditions for preparation of the oxides, and a full description of the apparatus used, are given by Ferguson, Guth and Eyring.[5] Each oxide was quenched[6] after equilibrium was established at the predetermined pressure and temperature in order to freeze the oxide at a specific composition. The exact composition was determined by weight change. White $TbO_{1.500}$ which has a body centered cubic lattice with $a = 10.729 \pm 0.006$ Å., and two brown oxides, $TbO_{1.710}$ (rhombohedral) and $TbO_{1.805}$ (face centered cubic with $a = 5.286 \pm 0.003$) were prepared for the calorimeter runs. These terbium oxides dissolved very slowly in nitric acid to produce the trivalent terbium ion in solution. To facilitate solution, the nitric acid was made 0.01 M in Na_2SiF_6.

The addition of a small concentration of Na_2SiF_6 to the solvent made no difference, within the limits of the experimental error of the present work, in the heat of reaction of PrO_x[4] or $ThCl_4$.[7] It was assumed, therefore, that the small quantities of Na_2SiF_6 required for these measurements did not change the heat of reaction. Of course it would have no effect anyway on the integral heat of oxidation of the various phases but only in fixing the heat of formation of $TbO_{1.500}$.

Results and Conclusions

Heats of Reaction.—The enthalpy changes upon reaction of $TbO_{1.500}$, $TbO_{1.710}$ and $TbO_{1.805}$ with oxygen saturated 6.00 M HNO_3 made 0.01 M in Na_2SiF_6 at 25° were determined in the microcalorimeter to be -47.2 ± 0.3, -42.3 ± 0.5 and -39.2 ± 0.5 kcal./mole, respectively. Sample size varied from 6 to 16 mg. No correction was made for the isomorphous replacement of terbium by the small amount of gadolinium in the oxide crystals. It was expected that such a correction, if it could be made, would be negligible.

The samples were weighed with an Ainsworth FDJ, Optical lever, microbalance (sensitivity: 2.5 μg. per division). The enthalpy change was not corrected for the vaporization of water into the liberated oxygen because this correction (less than

(1) These data were reported at the 126th meeting of the American Chemical Society at New York City in September, 1954, and were included in a dissertation submitted by C. T. Stubblefield to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree. The work was supported by the Atomic Energy Commission through the Research Contracts Division.

(2) E. D. Guth and L. Eyring, THIS JOURNAL, **76**, 5242 (1954).

(3) G. Machlan, C. T. Stubblefield and L. Eyring, ibid., **77**, 2975 (1955).

(4) C. T. Stubblefield, H. Eick and L. Eyring, ibid., **78**, 3018 (1956).

(5) R. Ferguson, E. Daniel Guth and L. Eyring, ibid., **76**, 3890 (1954).

(6) E. Daniel Guth, J. R. Holden, N. C. Baenziger and L. Eyring, ibid., **76**, 5239 (1954).

(7) L. Eyring and E. F. Westrum, Jr., ibid., **72**, 5555 (1950).

0.04 kcal. per mole for $TbO_{1.81}$) is small compared to the experimental error.

The reaction which occurred in the calorimeter may be represented by equation 1

$$TbO_x(c) + yHNO_3 \cdot zH_2O = Tb(NO_3)_3 \cdot (y - 3)$$
$$HNO_3 \cdot (z + 3/2)H_2O + 1/2(x - 1.5)O_2(g) \quad (1)$$
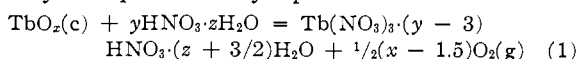
Heats of Formation.—The heats of formation of the oxides correspond to equation 2
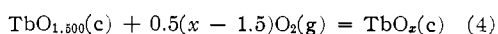
$$Tb(c) + 0.5xO_2(g) = TbO_x(c) \quad (2)$$
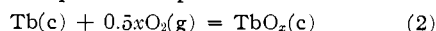
when the reactants and the products are in their standard states.

The heat of solution of the sesquioxide is given by equation 3

$$TbO_{1.500}(c) + yHNO_3 \cdot zH_2O = Tb(NO_3)_3 \cdot$$
$$(y - 3)HNO_3 \cdot (z + 3/2)H_2O \quad (3)$$
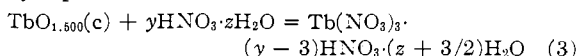
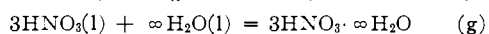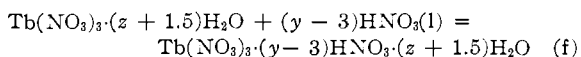Subtraction of (1) from (3) gives (4), which is the equation for the oxidation of the sesquioxide to a higher oxide

$$TbO_{1.500}(c) + 0.5(x - 1.5)O_2(g) = TbO_x(c) \quad (4)$$
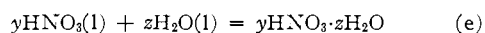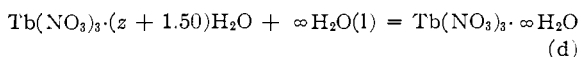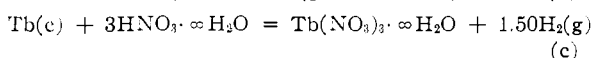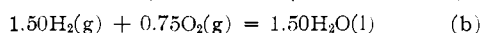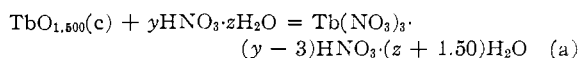
It follows that if the heat of formation of the sesquioxide is known, the heat of formation of TbO_x is

$$\Delta H_f^0[298°K., TbO_x(c)] = \Delta H_4^0 + \Delta H_f^0$$
$$[298°K., TbO_{1.5} (c)]$$

The heat of formation of the sesquioxide is represented by equation 5

$$Tb(c) + 0.75 O_2(g) = TbO_{1.5}(c) \quad (5)$$
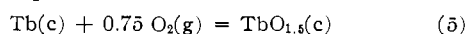
Also it is given by a combination of the following seven reactions

$$TbO_{1.500}(c) + yHNO_3 \cdot zH_2O = Tb(NO_3)_3 \cdot$$
$$(y - 3)HNO_3 \cdot (z + 1.50)H_2O \quad (a)$$

$$1.50H_2(g) + 0.75O_2(g) = 1.50H_2O(l) \quad (b)$$

$$Tb(c) + 3HNO_3 \cdot \infty H_2O = Tb(NO_3)_3 \cdot \infty H_2O + 1.50H_2(g)$$
$$(c)$$

$$Tb(NO_3)_3 \cdot (z + 1.50)H_2O + \infty H_2O(l) = Tb(NO_3)_3 \cdot \infty H_2O$$
$$(d)$$

$$yHNO_3(l) + zH_2O(l) = yHNO_3 \cdot zH_2O \quad (e)$$

$$Tb(NO_3)_3 \cdot (z + 1.5)H_2O + (y - 3)HNO_3(l) =$$
$$Tb(NO_3)_3 \cdot (y - 3)HNO_3 \cdot (z + 1.5)H_2O \quad (f)$$

$$3HNO_3(l) + \infty H_2O(l) = 3HNO_3 \cdot \infty H_2O \quad (g)$$

The standard heat of formation at 298°K. for the sesquioxide is

$$\Delta H_f^0{}_{298}(TbO_{1.50}) = -\Delta H_a + \Delta H_b + \Delta H_c - \Delta H_d - \Delta H_e + \Delta H_f + \Delta H_g$$

ΔH_a is the heat of reaction of the sesquioxide in 6.00 M HNO_3.

ΔH_b is the heat of formation of liquid water (N.B.S. Circular 500).[8]

ΔH_c is the heat of formation of the aqueous trivalent ion obtained by interpolation from the data of Spedding and Flynn.[9]

ΔH_d is the heat of infinite dilution of the aqueous trinitrate solution which is assumed to be the same as the heat of infinite dilution for the lanthanum trichloride solution of the same concentra-

(8) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards.

(9) F. H. Spedding and J. P. Flynn, THIS JOURNAL, 76, 1474 (1954).

tion. The assumption is probably valid because it is observed from N.B.S. Circular 500[8] that the difference in the heats of solution of two concentrations of a chloride is about the same as the difference for the same concentrations of the corresponding nitrate. This is especially true within the range of low concentrations which are of interest here.

Also, it is known that all the rare earth trichlorides have nearly the same values for these heats of dilution for the same changes in concentration.

ΔH_e to ΔH_g are the heats of solution of HNO_3 (1), the concentration of the rare earth trinitrate in equation (f) being negligible as compared to that of the acid. Their values are listed in N.B.S. Circular 500.[8] The values of ΔH_b to ΔH_g (in kcal.) are given below

ΔH_b	-102.48	ΔH_e	-3035.31
ΔH_c	-161.9	ΔH_f	-3013.37
ΔH_d	-0.78	ΔH_g	-23.90

When these heats of reaction are properly combined with the heat of reaction of the oxide in 6.00 M HNO_3, ΔH_a, the heat of formation of the sesquioxide, is obtained.

The difference between ΔH_a and the corresponding heat of solution of TbO_x yields the heat of oxidation of $TbO_{1.5}$ to give TbO_x. The sums of the heat of formation of $TbO_{1.5}$ and the heat of oxidation gives the heat of formation of TbO_x. These calculated values are shown in Table I.

TABLE I

ENTHALPY CHANGES FOR PRASEODYMIUM[4] AND TERBIUM OXIDES AT 298°K. IN KCAL. MOLE^{-1}

Substance	$-\Delta H_{reaction}$	$-\Delta(\Delta H$ reaction)	$-\Delta Hf_{M_xO}$	$-\Delta Hf_{M_xO}$
$PrO_{1.5}$	53.0 ± 0.1	5.8 ± 0.4	218.4 ± 0.8	145.6 ± 0.5
$TbO_{1.5}$	$47.2 \pm .3$		218.4 ± 1	$145.6 \pm .7$
$PrO_{1.70}$	$47.9 \pm .1$		223.5 ± 0.8	$131.2 \pm .5$
$TbO_{1.71}$	$42.3 \pm .5$	5.3 ± 0.7	223.3 ± 1	$130.6 \pm .7$
$PrO_{1.72}$	$47.4 \pm .4$		224.0 ± 0.9	$130.5 \pm .5$
$PrO_{1.80}$	$44.9 \pm .1$	5.7 ± 0.5	226.5 ± 0.8	$125.6 \pm .5$
$TbO_{1.80}$	$39.2 \pm .5$		226.4 ± 1	$125.4 \pm .7$
$PrO_{1.833}$	$43.8 \pm .1$		227.6 ± 0.8	$124.2 \pm .5$

The heat of formation of the "C" form sesquioxides (Table I) are higher by about one kilocalorie than might be expected from an extrapolation of the data of Huber and Holley[10-12] on the sesquioxides of Nd, Sm and Gd. This difference is somewhat outside the limit of error of both measurements and hence should be considered real. The higher heat of formation of praseodymium and terbium oxides is consistent with the fact that only these two oxides of the five considered form stable higher oxides.

The difference between the heats of reaction of the sesquioxides of praseodymium and terbium is -5.8 kcal. mole^{-1} which is precisely the difference between the heat of formation of $Pr^{+3}(aq)$ and an interpolated value for $Tb^{+3}(aq)$ from the data of Spedding and Flynn.[9] This would seem to justify the equivalent treatment of Tb^{+3} and Pr^{+3}

(10) E. J. Huber, Jr., and C. E. Holley, Jr., ibid., 74, 5530 (1952).

(11) E. J. Huber, Jr., C. O. Matthews and C. E. Holley, Jr., ibid., 77, 6493 (1955).

(12) E. J. Huber, Jr., and C. E. Holley, Jr., ibid., 77, 1444 (1955).

in correcting to the standard state from the calorimeter solutions and results in no difference in the heat of formation of oxides of praseodymium and terbium of the same composition.

Heat of Reaction of Irradiated Graphite with Potassium[1]

BY W. PRIMAK AND L. A. QUARTERMAN

The heats of reaction of fast neutron irradiated graphite samples and potassium were determined. The difference between the specific heats of reaction of irradiated and unirradiated graphite (excess heat of reaction) was in all cases much smaller than the difference between the specific heats of combustion of the respective irradiated graphite samples and unirradiated graphite (excess heat of combustion; energy content). The excess heat of reaction as a function of irradiation was found to saturate sooner than the energy content. A single determination indicated that hydrocarbons are produced in small quantity in the hydrolysis of the irradiated graphite–potassium compound but not in the hydrolysis of the unirradiated graphite–potassium compound suggesting the formation of some potassium carbide in the reaction of irradiated graphite and potassium.

Introduction

An account of the discovery of property changes in graphite exposed to energetic neutrons was given by Burton.[2] A review of this work is given by Burton and Neubert.[3] It was Szilard[4] who first suggested that energy should be stored in graphite under irradiation. The presence of stored energy in irradiated graphite was demonstrated by differential thermal analysis independently by Maurer and Ruder,[5] by Leaf and Novick,[6] and by Wheeler and O'Connor.[7] It was suggested by Neubert[8] that it would be desirable to find the change in energy content by means of heat of combustion measurements. It was arranged to have this work performed at the National Bureau of Standards by Rossini and Prosen.[9] Some of these results and many more recent ones obtained under Prosen's direction are given in a review paper by Woods, Bupp and Fletcher.[10] The increase in energy content, amounting to from several cal./g. to several hundred cal./g. is small compared to the heat of combustion of graphite (nearly 8000 cal./g.). The determination of the increase in energy content using the heat of combustion therefore requires very precise calorimetry. It was suggested by Gordon[11] that since the heat of reaction of graphite with potassium was much smaller (about 100 cal./g.) a much easier determination of the increase in energy content of graphite on irradiation could possibly be developed by the use of this reaction.

Experimental

The irradiated graphite samples were cut from pieces of irradiated AGOT-K graphite[10] remaining from other work

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) M. Burton, *J. Phys. Colloid Chem.*, **51**, 618 (1947).

(3) M. Burton and T. J. Neubert, *J. Appl. Phys.*, **27**, 557 (1956).

(4) L. Szilard, unpublished.

(5) R. J. Maurer and R. C. Ruder, *J. Appl. Phys.*, **27**, 571 (1956).

(6) B. Leaf and A. Novick, unpublished.

(7) J. A. Wheeler and J. J. O'Connor, unpublished.

(8) T. J. Neubert, unpublished.

(9) F. D. Rossini and E. J. Prosen, unpublished.

(10) W. K. Woods, L. P. Bupp and J. F. Fletcher, Paper A/Conf. 8/P/746, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," United Nations, New York, N. Y., 1956, Vol. 7, p. 455.

(11) S. Gordon was associated with the present work at its inception.

done by Neubert and his co-workers or from samples obtained from the General Electric Company (Hanford Atomic Products Operation). The heats of combustion of these samples had been determined at the National Bureau of Standards. The heat of reaction with potassium was determined in the manner described by Quarterman and Primak.[12] The rate of reaction of the irradiated graphite with potassium was very rapid, the temperature rises occurring more rapidly than the thermocouple e.m.f. recorder pen could move.

The hydrolysis, for which the results are given below, was performed in the following manner. Small samples of the graphite were introduced into the apparatus filled with purified helium at several mm. pressure. When the desired quantity of the graphite–potassium compound had been prepared, the apparatus was evacuated, and an excess of gasfree water was introduced. A sample of the evolved gases was dried by storing it over sublimed P_2O_5. A sample of the dried gas was then taken for mass-spectrometric analysis.

Results

Heats of reaction for a number of samples are given in Table I. The exposure units are described by Woods, Bupp and Fletcher,[10] and a further interpretation of them may be found in an article by Primak.[13] A comparison of the excess heat of reaction with the energy content[14] is also effected in Table I.

The hydrolytic products which were sought were hydrocarbons. A blank, 7.0 g. of potassium, and another blank, 7.6 g. of potassium and 3.79 g. of unirradiated graphite, both gave approximately 100% hydrogen. A run, 10.6 g. of potassium and 2.66 g. of graphite irradiated 1406 Mwd/aT, gave mass spectrometer peaks corresponding to 99.53% H_2, 0.38% CH_4, 0.09% C_2H_6.

Discussion

From the data given in Table I, it is seen that under the conditions maintaining in the Hanford test-holes, the energy content increases at first at a rate about 1 cal./g. per Mwd/aT and that within

(12) L. Quarterman and W. Primak, THIS JOURNAL, **74**, 806 (1952).

(13) W. Primak, submitted.

(14) The energy content is defined as the difference in the heats of reaction of an irradiated and an unirradiated sample when the end products are in the same state. It is thus the difference in the heat contents at the temperature at which the calorimetry is performed. The excess heat of reaction is used here to designate the difference between the specific heats of reaction with potassium of an irradiated and an unirradiated sample.