

acid or water) varied according to the amount of adsorbed moisture on the glass walls of the reaction tubes. The permanency of the intermediate red precipitate formed when only small amounts of acetyl chloride were used was probably caused by the consumption of all the available hydrogen

chloride by reaction (i) thus leaving none for reaction (ii).

The author wishes to thank Professor A. D. Monro (University of New Zealand) for helpful discussions on many aspects of the present work.

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY]

Reactions of Chloramine with Anhydrous Primary and Secondary Amines

BY GEORGE M. OMIETANSKI,¹ A. DONALD KELMERS,² RICHARD W. SHELLMAN² AND HARRY H. SISLER³

RECEIVED MARCH 12, 1956

Chloramine produced by the gas phase reaction of chlorine and ammonia will, in general, react with various anhydrous primary and secondary amines to form N-substituted hydrazines. It has been found that good yields of alkyl hydrazines are obtained in the absence of gelatin and permanent base. Preparation of the following compounds has been realized by this method: methyl-, ethyl-, isopropyl-, unsymmetrical dimethyl-, and unsymmetrical di-isopropylhydrazine and N-aminopiperidine. Various identifying derivatives have been prepared. The reaction with diethylamine yields monoethylhydrazine. The results have been discussed in terms of recently proposed reaction mechanisms.

Introduction

By means of a modification of the Raschig synthesis, Audrieth and others have shown that chloramine reacts with primary^{4,5} and secondary^{6,7} amines in aqueous solution to produce the corresponding alkyl hydrazines. As reported for the Raschig synthesis of hydrazine itself,^{8,9} the production of monoalkyl hydrazines from the reaction of chloramine with primary amines in aqueous media is reported to proceed best in the presence of a permanent base and a metal deactivator such as gelatin.⁴ In the reactions of chloramine with aqueous secondary amines, the role of permanent base (sodium hydroxide) has not been defined; however, the presence of an inhibitor such as gelatin does not appear to be necessary in order to obtain good yields of the corresponding unsymmetrical disubstituted hydrazines.⁶

The rather remarkable success achieved in this Laboratory in synthesizing hydrazine by the reaction of chloramine with ammonia in liquid ammonia solution^{10,11} and in other solvents¹² in the absence of permanent base or other additive has led us to examine the reactions, under anhydrous conditions, of chloramine with alkyl-substituted ammonias, *viz.*, the amines. It has been found that chloramine reacts with anhydrous primary and secondary amines to form the corresponding alkyl hydrazines

in good yield in the absence of permanent base or other additives. This work is reported in this paper.

As reported in a previous publication from this Laboratory, chloramine has also been found to react with anhydrous tertiary amines to form hydrazinium chlorides of the type $[R_3N-NH_2]^+Cl^-$,¹³ clearly demonstrating its versatility as an N-aminating agent in anhydrous media.

Experimental¹⁴

Materials and Apparatus.—All of the amines were commercially available. The piperidine and diethylamine were dried over barium oxide and purified by fractionation through an efficient column packed with glass helices. Eastman Kodak Co. white label isopropyl- and di-isopropylamine and Matheson anhydrous methyl-, dimethyl- and ethylamine were used without further purification. The chloramine supply for study was produced by the gas phase reaction of ammonia and chlorine.¹⁰ All of the other chemicals were of reagent grade and the apparatus has been previously described.¹⁵

Analytical Methods.—The reaction mixture was diluted to 500 ml. with CO₂-free distilled water and 50-ml. aliquots were taken. Separate aliquots were used for the chloramine and alkyl hydrazine determinations. The amount of chloramine originally added was obtained by determining the chloride present in the solution, using modified Volhard procedure for chloride analysis.¹⁶ The alkyl hydrazines were determined as follows: the aliquot was neutralized with concentrated hydrochloric acid and sufficient excess acid was added so that the solution would be 7 N in hydrochloric acid at the end of the titration with potassium iodate: 15 ml. of chloroform was added and the solution was chilled to 0°. The standard potassium iodate (0.01667 f) was then added until the color of the chloroform layer changed from a dark brown to a light pink. At this point the iodate was added dropwise and the solution was shaken after the addition of each drop. Care was taken so that at no time did the temperature of the solution become greater than 5°. The endpoint was the disappearance of the iodine color in the chloroform layer. This method is essentially that given by Hull and Kruse.¹⁷

Effect of Variables on the Yield of Alkyl Hydrazines.—In order to evaluate the effect of chloramine concentration on the yield of alkyl hydrazines, a standardized experimen-

(1) Taken in part from the dissertation submitted for the degree of Doctor of Philosophy by George M. Omietsanski.

(2) Taken in part from theses submitted for the degree Master of Science by A. Donald Kelmers and by Richard W. Shellman.

(3) Department of Chemistry, University of Florida, Gainesville, Florida.

(4) L. F. Audrieth and L. H. Diamond, *THIS JOURNAL*, **76**, 4869 (1954).

(5) L. H. Diamond, Univ. Microfilms (Ann Arbor, Michigan) Publication No. 10466, p. 77 (1954).

(6) R. A. Rowe, *ref. 5*, Publication No. 11531, p. 94 (1955).

(7) M. O. Forster, *J. Chem. Soc.*, **107**, 267 (1915).

(8) M. M. Jones, L. F. Audrieth and E. Colton, *THIS JOURNAL*, **77**, 2701 (1955).

(9) R. S. Drago and H. H. Sisler, *ibid.*, **77**, 3191 (1955).

(10) R. Mattair and H. H. Sisler, *ibid.*, **73**, 1619 (1951).

(11) H. H. Sisler, F. T. Neth and F. R. Hyrley, *ibid.*, **76**, 3909 (1954).

(12) H. H. Sisler, C. E. Boatman, F. T. Neth, R. Smith, R. W. Shellman and D. Kelmers, *ibid.*, **76**, 3912 (1954).

(13) G. M. Omietsanski and H. H. Sisler, *ibid.*, **78**, 1211 (1956).

(14) All melting points are uncorrected. The microanalyses are by Galbraith Laboratories, Knoxville, Tennessee.

(15) H. H. Sisler, F. T. Neth, R. S. Drago and D. Vaney, *THIS JOURNAL*, **76**, 3906 (1954).

(16) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 38 (1935).

(17) L. Hall and H. Kruse, *NOTS TM No.* 1635, August 10, 1954.

TABLE I
 ALKYL HYDRAZINE DERIVATIVES

Alkyl hydrazine	Reaction temp., °C.	Formula of derivative	M.p., °C.	Analyses, %					
				C	Calcd. H	N	C	Found H	N
Methyl-	-25	C ₂₃ H ₂₃ N ₄ ^a	99-103 ^a	77.53	6.74	15.73	77.46	6.64	15.75
Ethyl-	-25 to -45	C ₂ H ₅ N ₂ ·H ₂ SO ₄ ^d	118-122 ^b	15.18	6.38	17.71	15.27	6.28	17.56
		C ₂ H ₅ N ₂ ·2HCl ^h	Dec. ^c	18.04	7.57	21.05	17.98	7.73	21.12
Isopropyl-	-20	C ₁₇ H ₁₈ O ₂ N ₂ ^d	165.5-166 ^d	72.08	6.76	9.89	72.11	6.58	9.71
<i>unsym</i> -Dimethyl-	-30	C ₂ H ₅ N ₂ ·H ₂ C ₂ O ₄	143-144 ^e	32.07	6.71	18.66	32.08	6.71	18.72
<i>unsym</i> -Diisopropyl-	-10 to 0	C ₆ H ₁₆ N ₂ ·H ₂ C ₂ O ₄	132-133	46.58	8.79	13.58	46.73	8.73	13.79
N-Aminopiperidine	21-27	C ₈ H ₁₂ N ₂ ·HCl	159-162 ^f	44.10	9.55	20.60	43.93	9.30	20.70

^a Reported m.p. for tribenzalmethylhydrazine: 109°, C. Harries and T. Haga, *Ber.*, **31**, 62 (1898). ^b Lit., 125°, see ref. 4. ^c E. Fischer, *Ann.*, **199**, 282 (1879). ^d Lit., 164.5-165°, for dibenzoylisopropylhydrazine, K. Taipale, *Ber.*, **56**, 954 (1923). ^e Lit., 142-143°, C. Harries and T. Haga, *Ber.*, **31**, 56 (1898). ^f Lit., 162°, L. Knorr, *Ann.*, **221**, 299 (1883). ^g *Anal.* for S: calcd., 20.24; found, 20.14. ^h *Anal.* for Cl: calcd., 53.34; found, 53.21.

tal procedure was adopted. The amount of chloramine added to a known volume of the liquid amine at a fixed temperature was controlled by varying the length of time the chloramine from the chloramine generator was allowed to pass into the amine. The reaction mixture was allowed to stand for a fixed period (usually one hour) at a fixed temperature. The reaction mixture was then diluted with distilled water and aliquots were immediately analyzed for chloride and alkyl hydrazine. The yields of alkyl hydrazines decreased as the no. of moles of chloramine added per liter of solution was increased. The range of yield of various hydrazines for the range of about 0.05 to about 0.25 mole of chloramine added per liter of solution was as follows: ethylhydrazine, 68 to 40%; isopropylhydrazine, 50 to 29%; methylhydrazine, 49 to 30%; *unsym*-dimethylhydrazine, 71 to 58%.

By keeping the amount of chloramine added to a fixed volume of amine nearly constant, and by varying the time the reaction mixture was allowed to stand (10 minutes to 46 hours) at a fixed temperature, it was found that under these conditions the data still fell on a curve based on a one hour reaction time, *i.e.*, the curve giving the yield of alkyl hydrazine as a function of added chloramine. On this basis it appears that the reaction of chloramine with ethyl- and dimethylamine is complete in less than 10 minutes.

Preparation of Alkyl Hydrazines.—In order to clearly identify the alkyl hydrazines produced in the chloramine-amine reactions, a standardized experimental procedure was adopted. During a period of about an hour about 0.039 mole of chloramine was added to about 100 ml. of the amine. The reaction mixture was allowed to stand for about 2 hours and filtered if it was necessary to free the reaction mixture from precipitated amine hydrochloride and/or ammonium chloride. The reaction mixture was distilled, and the alkyl hydrazine derivative was formed directly from the still-pot residue, or, if it was contaminated with amine, the oxalate salt of the alkyl hydrazine was prepared by the method outlined by Gever and Hayes.¹⁸ The data on the alkyl hydrazines are summarized in Table I.

The Diethylamine-Chloramine Reaction.—The chloramine was passed into 100 ml. of diethylamine for about 40 minutes at -10 to -20°. A series of 9 duplicate experiments was made. The reaction mixtures were combined, allowed to come to room temperature (25°) and filtered.

The solid residue was separated into two fractions by treatment with cold absolute alcohol. The alcohol insoluble fraction was recrystallized from water and gave qualitative tests for ammonium and chloride ions. *Anal.* Calcd. for NH₄Cl: Cl, 66.3. Found: Cl, 66.7. The alcohol soluble fraction was recrystallized from alcohol. The crystals melted at 223-224°. The *p*-toluenesulfonamide derivative melted at 59.5-60°. These data suggest that the solid was diethylamine hydrochloride.

The filtrate was distilled and the residue was treated by the method given by Gever and Hayes¹⁸ for the isolation of an alkyl hydrazine as the oxalate. The oxalate derivative was repeatedly recrystallized from an alcohol-ether mixture.

(18) G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

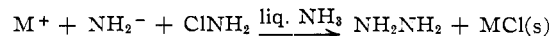
(19) I. Heilbron, "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, N. Y., 1953, p. 180; P. Walden, *et al.*, *Z. physik. Chem.*, **114**, 290 (1925).

(20) W. Marckwald and A. F. v. Droste-Huelshoff, *Ber.*, **31**, 3263 (1898).

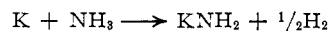
The crystals melted at 169-170° (lit. value for ethylhydrazine oxalate: 170-171°).¹⁸ There was no depression in a mixed melting point determination with a known sample of ethylhydrazine oxalate.

Anal. Calcd. for C₆H₁₀O₄N₂: C, 32.00; H, 6.71; N, 18.66. Found: C, 32.00; H, 6.62; N, 18.68.

The Potassium Amide-Chloramine Reaction in Liquid Ammonia.—The recently published studies by Jander²¹⁻²³ concerning the reactions of chloramine with liquid ammonia and with liquid ammonia solutions of potassium amide have prompted us to include in the present communication some previously unpublished data on these reactions which had been obtained in this Laboratory several years ago.²⁴ We had postulated that in the presence of considerable concentrations of amide ion the reaction



might be favored and that the hydrazine thus obtained might be better than that obtained from the reaction of chloramine and liquid ammonia. Potassium amide was selected because (1) it is appreciably soluble in liquid ammonia and (2) potassium chloride has only a very small solubility in liquid ammonia and thus would precipitate. The liquid ammonia solution of potassium amide was prepared by dissolving potassium metal in liquid ammonia in the presence of iron wire as a catalyst for the reaction



The mixture of chloramine and ammonia gas was then passed into the potassium amide solution: a yellow color immediately appeared which disappeared as soon as the chloramine flow was stopped. In some instances the reaction mixture was held at temperature for a period of time. In other instances the ammonia was allowed to evaporate immediately. In either case the residue was dissolved in water and analyzed for chloride by the Volhard method²⁵ and for hydrazine by the direct iodate method.²⁶ The amounts of potassium amide in the reaction mixtures were calculated from the weights of potassium metal used and the amounts of chloramine added were determined from the chloride analyses. The results of several typical experiments are summarized in Table II. These results indicate quite clearly that, far from improving the yield of hydrazine, the presence of potassium amide in the liquid ammonia reduces the yield of hydrazine to zero or else to a value much lower than that obtainable in similar reactions with liquid ammonia alone (15% or higher).

Discussion of Results

We have demonstrated that the yields of alkyl hydrazines are sensitive to the amount of added

(21) J. Jander, *Z. anorg. allgem. Chem.*, **280**, 264 (1955).

(22) J. Jander, *ibid.*, **280**, 276 (1955).

(23) J. Jander, *Naturwiss.*, **42**, 178 (1955).

(24) R. W. Shellman, M. S. Thesis, The Ohio State University 1953.

(25) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, Rev. Ed., p. 573.

(26) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 157.

TABLE II
THE REACTION OF CHLORAMINE WITH SOLUTIONS OF POTASSIUM AMIDE IN LIQUID AMMONIA

KNH ₂ , moles	ClNH ₂ , moles	Vol. of soln., ml.	Temp. of soln., °C.	Time in coolant, hr.	Yield of N ₂ H ₄ , % ^a
0.01	0.00333	50	-50	0	0
.01	.00256	50	-33	0	0
.01	.00450	50	-78	12	0
.02	.00466	50	-70	1.3	0
.02	.00420	38	-70	0	4.5
.02	.00984	37	-70	12	6.0

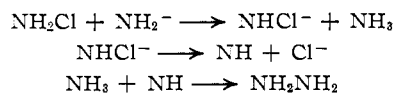
^a Hydrazine results are accurate to within ± 2 to 3%.

chloramine. Similar results have been obtained in the reactions of chloramine with liquid ammonia,¹¹ aqueous ammonia,¹² ammonia in cellosolve,¹² and alkyl amines in aqueous solution.⁴ Just as hydrazine is subject to further attack by chloramine,^{11,27} the decrease in per cent. yield of alkyl hydrazines with increasing amounts of added chloramine suggests that the alkyl hydrazines are subject to further attack by chloramine in the parent amine solutions.

Although the effluent gases from the chloramine generator contain considerable quantities of ammonia, and the ammonia was found to be quite soluble in the liquid amines at low temperatures, no evidence was obtained for the formation of hydrazine. This is consistent with the observation that the reaction of chloramine with those alkyl amines which are stronger bases than ammonia appears to be much more rapid than the reaction of chloramine with ammonia to produce hydrazine at the same temperature.^{4,11}

Two fundamentally different mechanisms have recently been proposed for the chloramine-ammonia reaction. The first of these mechanisms, postulated by Audrieth and co-workers,²⁸ assumes that the active intermediate in the chloramine-ammonia reaction in aqueous solution is the chloramide ion (NHCl⁻) or the imide molecule (NH). Since the *pK* value for chloramine as an acid is estimated to be about 15, Audrieth, *et al.*, postulate that the existence of the above species is possible only in strongly alkaline solutions, and state further as evidence for their mechanism that the formation of hydrazine in aqueous systems depends on the presence of hydroxide ion. This mechanism has been extended to the consideration of reactions of chloramine with alkyl amines in aqueous solution.⁴

In his recent papers, Jander²¹⁻²³ has proposed the transitory formation of chloramide ion and its decomposition into imide molecules in solutions of chloramine in liquid ammonia. He presents some qualitative results on solutions of chloramine in liquid ammonia as evidence for this point of view. In particular, he implies that the presence of potassium amide in the liquid ammonia improves the tendency to form hydrazine by producing imide molecules as indicated below

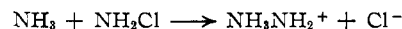


(27) J. W. Cahn and R. E. Powell, *THIS JOURNAL*, **76**, 2565 (1954).

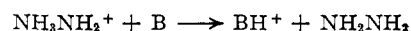
(28) L. F. Audrieth, E. Colton and J. Jones, *ibid.*, **76**, 1428 (1954).

This is in direct contradiction with the experimental results presented in this paper; this contradiction considerably weakens his argument for the chloramide ion-imide molecule mechanism.

The second mechanism was proposed by Cahn and Powell. In this mechanism it is postulated that chloramine reacts with ammonia by a simple bimolecular displacement reaction as

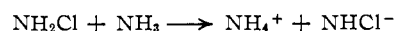


In the presence of additional base B (NH₃ or OH⁻, for example) the hydrazine is set free



This mechanism was based upon kinetic studies. Recent studies⁹ in this Laboratory, which have shown that the yield of hydrazine in aqueous solution is not favored by concentrations of hydroxide ion in excess of that required to react with the ammonium ion formed in the reaction, tend to favor the Cahn and Powell mechanism. This mechanism is also favored by our finding¹⁸ that chloramine reacts directly and rapidly with tertiary amines to give 1,1,1-trialkyl hydrazinium chloride in high yields. These hydrazinium chlorides are the postulated intermediates of the Cahn and Powell mechanism. Further, the results concerning the reaction of chloramine with primary and secondary amines presented in this paper are consistent with the Cahn and Powell type of mechanism.

Further basis for our preference for the Cahn and Powell mechanism is found in the fact that electrical conductances of solutions of chloramine in liquid ammonia are very low,²⁹ so low in fact as to make doubtful the occurrence in liquid ammonia of a protolysis reaction of the type



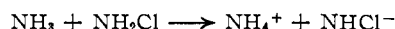
to any kinetically significant extent.

Moreover, chloramine has been found to react rapidly with tertiary amines which are relatively weak bases (*e.g.*, (C₆H₅)₂N, *pK*_b ≈ 9.6¹³) to form trisubstituted hydrazinium chlorides. The existence of appreciable concentrations of chloramide ion in such systems is highly unlikely. Furthermore, in the reaction of chloramine with tertiary amines,¹³ no evidence was obtained for the presence of chemical species of the type R₃N→NH or R₃NH⁺ even when the amines are strongly basic (*pK*_b ≈ 3.25).

Finally, in support of the chloramide ion-imide molecule mechanism, Jander²¹ states that the yield of hydrazine in the chloramine-ammonia reaction is directly dependent on the proton affinity of the solvent since the yield of hydrazine decreases in the solvent series NH₃ > H₂O > C₂H₅OH > (C₂H₅)₂O. This is, however, not the sequence of decreasing proton affinities, for ethyl ether has a higher proton affinity than ethyl alcohol. The order H₂O > C₂H₅OH > (C₂H₅)₂O is, however, the order of decreasing dielectric constant which would be the order of the decreasing tendency to favor a bimolecular displacement reaction yielding ions (in other words, the Cahn and Powell mech-

(29) F. N. Collier, Jr., private communication.

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



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 re-

ported production of 1,1-diethylhydrazine by the reaction of chloramine with diethylamine in aqueous solution.^{30,31}

Acknowledgment.—These studies have been supported in a large part by the Davison Chemical Company, a Division of W. R. Grace and Company, through a contract with The Ohio State University Research Foundation.

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

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

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Terbium Oxides. II. The Heats of Formation of Several Oxides¹

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

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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_{1.710} and TbO_{1.805} in 6.00 *M* HNO₃ containing a small concentration of Na₂SiF₆ 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 TbO₂ of -218.4 ± 1.0, -223.3 ± 1.0 and -226.4 ± 1.0 kcal. mole⁻¹, respectively.

Introduction

Guth and Eyring² 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_{1.710} and TbO_{1.805}, above TbO_{1.500}.

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 reported⁴ 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 Tb₄O₇. The purity was greater than 98% with gadolinium the principal impurity. The oxygen used was obtained from the thermal decomposition of KMnO₄ 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.

(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).

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 quenched⁶ 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 ± 0.006 Å., and two brown oxides, TbO_{1.710} (rhombohedral) and TbO_{1.805} (face centered cubic with *a* = 5.286 ± 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 Na₂SiF₆.

The addition of a small concentration of Na₂SiF₆ to the solvent made no difference, within the limits of the experimental error of the present work, in the heat of reaction of PrO₂⁴ or ThCl₄.⁷ It was assumed, therefore, that the small quantities of Na₂SiF₆ 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* HNO₃ made 0.01 *M* in Na₂SiF₆ 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

(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).