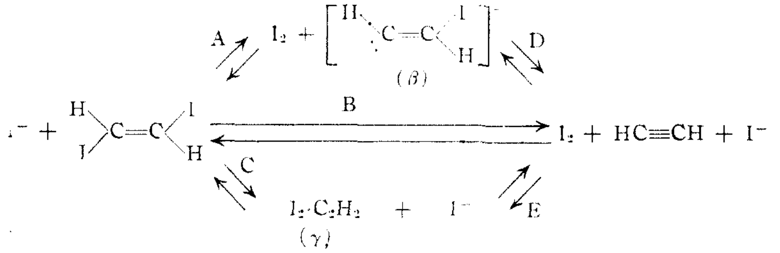

The kinetics require that the transition state for these reactions lies along path A, B or C, whichever is appropriate, and does not lie along path D or E. James and Sudborough[14] observed that ortho- and para-nitrophenyl propiolate ions add iodine under these conditions more slowly than phenyl propiolate ion does. This observation indicates that the free energy of activation is increased by groups which withdraw electrons from the reacting carbon atoms; therefore, we consider that the electron density at these carbon atoms is less in the transition state than it is in the original acetylene.[15] This condition is presumably fulfilled for a transition state lying along path C; it is fulfilled for a transition state lying along path A or B only if either the C–I or I–I bond is more nearly broken than the C–I_2 bond.

Two arguments serve to render the sequence A–D implausible. In the first place, it is doubtful that an ionic intermediate like species β would be formed at significant rate by the direct attack of iodide ion on an acetylenic carbon.[16] In the second place, we observe that the rate of *cis* elimination is very much smaller than the rate of *trans* elimination. We find it hard to believe that an intermediate like species β could retain a stereospecific configuration at these temperatures, and the free energy of formation would be nearly the same from either isomer of diiodoethylene. These conditions require that *trans* elimination proceeds through a transition state which is unattainable for the *cis* isomer and which has a lower free energy than the transition state for the formation of species β.

We know of no compelling arguments to favor path B or sequence C–E. Acetylene and iodine probably tend to form a complex like species γ, whether or not it is an intermediate in these reactions. Either of the two mechanisms could be formulated to account plausibly for the stereospecificity of the reactions if we accept theories that the electronic configuration is most favorable when bond making or breaking occurs on opposite sides of adjacent carbon atoms.[3,17] The only restriction which we can apply is that the concerted mechanism (path B) is permissible only if the C–I or I–I bond in the transition state is more nearly broken than the C–I_2 bond.

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[14] T. C. James and J. J. Sudborough, *J. Chem. Soc.*, **91**, 1037 (1907).

[15] This argument is suggested by the recent treatment of substituent effects by C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951).

[16] M. J. Murray, *ibid.*, **60**, 2662 (1938).

[17] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2117 (1948).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heats of Combustion of Thorium and Uranium[1,2,3]

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RECEIVED FEBRUARY 8, 1952

Precise measurements of the heats of combustion of thorium, uranium and uranium dioxide have been made and from the results the heats of formation of ThO_2, UO_2 and U_3O_8 have been calculated. The final values for the various materials are listed as follows: Thorium: heat of combustion in 25 atm. oxygen = 5274 ± 7 joules/g.; heat of formation of ThO_2, $\Delta H_{25}° = -1{,}226.9 \pm 1.5$ kjoules./mole. Uranium dioxide: heat of combustion in 25 atm. oxygen = 389.23 ± 0.46 joules/g.; heat of the reaction $3UO_2 + O_2 = U_3O_8$, $\Delta H_{25}° = -318.01 \pm 0.37$ kjoules. Uranium: heat of combustion to U_3O_8 in 25 atm. oxygen = 4984.7 ± 9.7 joules/g.: heat of formation of U_3O_8, $\Delta H_{25}° = -3570.9 \pm 6.9$ kjoules./mole. It was necessary to cut the uranium into small pieces and mix it with UO_2 in order for it to oxidize completely to U_3O_8. The heat of formation of UO_2 calculated from the above results is $\Delta H_{25}° = -1{,}084.3 \pm 2.5$ kjoules./mole.

Introduction

The heats of formation of the oxides of thorium and uranium are of interest for thermodynamic calculations. Since it is only recently that these metals have become available in high purity, an experimental redetermination of their heats of combustion was thought desirable. The heat of combustion of uranium dioxide was also redetermined.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the material in question with oxygen at a known pressure in a bomb calorimeter. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid, and the heat of combustion was evaluated from this value and the measured temperature rise per unit mass of metal. The details of the method and apparatus have been described.[4]

Units and Precision.—The results of this work are expressed in absolute joules. For purposes of comparison with the older literature the results are also expressed as calories using the definition 1 calorie = 4.1840 absolute joules.

The unit of mass is the gram mass *in vacuo*. The materials to be burned were weighed to the nearest 0.0001 g. The water for the calorimeter was weighed to the nearest 0.01 g.

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[1] This work was done under the auspices of the A.E.C.

[2] Presented before the Section on Physical and Inorganic Chemistry, XIIth International Congress of Pure and Applied Chemistry, at New York, N. Y., September 13, 1951.

[3] For detailed table order Document 3576 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 x 8 inches) readable without optical aid.

[4] Charles E. Holley, Jr., and Elmer J. Huber, Jr., THIS JOURNAL, **73**, 5577 (1951).

The uncertainty intervals attached to the final average values are taken as twice the corresponding standard deviations.

Calibration of the Calorimeter.—The calibration of the calorimeter has been described.[4] The value obtained for the energy equivalent was 10,095.4 ± 4.2 joules/°C. An additional series of fifteen calibration runs was made using benzoic acid. The average value obtained was 10,095.0 ± 5.1 joules/°C. From these two values, the energy equivalent, based on twenty-seven runs, was taken to be 10,095.2 ± 3.4 joules/°C.

The Combustion of Thorium.—The thorium metal used was in the form of 0.010 inch sheet and 0.005 inch wire. A precise analysis of a portion of the sheet showed that it contained 0.12% oxygen, 0.01% carbon, less than 0.01% of iron and beryllium, and no other metallic impurities in significant amounts.

The thorium was burned on sintered ThO_2 discs supported on a platinum platform. Two strands of 0.005 inch thorium wire were used as fuse wire. Correction was made for the electrical energy used in igniting the wire. The total energy equivalent of the calorimeter and contents was used taking account of the disc, the platinum, and the difference in energy equivalent between the thorium dioxide formed and the oxygen used up. The combustion took place in oxygen at 25 atmospheres pressure. The initial temperature was 24.6° and the average temperature rise was 1.3°.

Completeness of combustion was determined by treating the combustion products with 6 *N* HCl and measuring the hydrogen evolved. Since thorium metal does not dissolve completely in 6 *N* HCl, an insoluble residue of unknown composition being formed, an empirical correction factor was determined from the gas evolved in the reaction of acid with weighed samples of thorium metal. In this manner it was found that 88% of the theoretical amount of hydrogen was evolved. Since the combustion was very nearly complete, a small error in determining this correction factor would be negligible in the final result.

The results obtained with thorium may be summarized as follows: number of runs, 16; mass of thorium, 1.90 to 2.97 g.; % burned, 99.74 to 99.99; firing energy 2.1 to 6.7 joules; temperature rise, 0.98 to 1.53°; energy from thorium, 5201.0 to 5253.5 joules/g. with an average value of 5230.9 joules/g.; average deviation from the mean, 10.2 joules/g.; standard deviation of the mean, 3.4 joules/g.

The correction to be applied to these results because of the impurities is somewhat uncertain. If it is assumed that the oxygen is all present as ThO_2 and that the other impurities contribute according to the corresponding heat of combustion of the element, the corrected result for the heat of combustion of thorium is 5274 ± 7 joules/g. This neglects any heat of formation of carbides or alloys. The statistical uncertainty includes the uncertainty in the energy equivalent.

The Heat of Formation of ThO_2.—The corrected heat of combustion reported above gives a value of $\Delta E_{24.6°} = -1{,}224.2$ kjoules./mole for the reaction in the bomb. The correction of this value to 25° is less than the uncertainty in the result. To get the heat of formation, ΔH, it is necessary to correct for the deviation of oxygen from the perfect gas law and to convert from ΔE to ΔH. According to Rossini and Frandsen[5] the value of $(\partial\Delta E/\partial\Delta P)_{301°\mathrm{K}}$ for oxygen is −6.51 joules/atm./mole. Using this value and taking $\Delta H = \Delta E + \Delta(PV)$ we have for the heat of formation of ThO_2, $\Delta H_{25°} = -1{,}226.9 \pm 1.5$ kjoules./mole. In defined calories this is −293.2 ± 0.4 kcal./mole.

This value is in good agreement with the value of −292.6 ± 1.4 kcal./mole obtained by Roth and Becker.[6]

The Combustion of Uranium Dioxide.—Preliminary experiments showed that uranium dioxide, UO_2, burned in oxygen to give U_3O_8. The formula of the combustion products was determined by igniting them in oxygen at 800°, under which conditions U_3O_8 should be formed, and noting the change in weight.

The UO_2 used was of C.P. grade obtained from Mallinckrodt. It was of the highest purity, the main impurities being less than 0.01% each of calcium, silicon and carbon. Its formula, determined by ignition to U_3O_8, was about $UO_{2.03}$. By heating it at 1200° in hydrogen it could be reduced to $UO_{2.006}$, and this is the material which was burned in the calorimeter.

The UO_2 was burned on a ThO_2 disc and ignited by a strand of U fuse wire. The total energy equivalent was computed including a correction for the U_3O_8 formed and the oxygen used up in the combustion. The heat of combustion of the uranium was taken to be 4984.7 joules/g., the value reported later in this paper. The combustion took place in oxygen at 25 atmospheres pressure. The initial temperature was 24.6° and the average temperature rise was 1.0°.

The results may be summarized as follows: number of runs, 12; mass of UO_2, 24.97 to 27.01 g.; mass of U, 0.0620 to 0.0690 g., average formula of product, $U_3O_{8.036 \pm 0.006}$; firing energy, 5.7 to 6.5 joules; temperature rise, 0.99 to 1.07°; energy from UO_2, 388.08 to 390.83 joules/g. with an average value of 389.23 joules/g.; average deviation from the mean, 0.60 joules/g.; standard deviation of the mean, 0.22 joules/g. The final result, including the uncertainty in the energy equivalent, is 389.23 ± 0.46 joules/g.

The Heat of the Reaction $3UO_2 + O_2 = U_3O_8$.—From the above result the value of ΔE for the reaction $3UO_2 + O_2 = U_3O_8$ is −315.36 ± 0.37 kjoules. When corrected for gas imperfection and converted to ΔH the value is $\Delta H_{25°} = -318.01 \pm 0.37$ kjoules./mole or −76.01 ± 0.09 kcal./mole.

The Combustion of Uranium.—It was found in preliminary experiments that uranium when burned in oxygen at pressures from 5 to 55 atmospheres did not give U_3O_8 but rather a product of the composition $UO_{2.5-2.6}$. However, when the uranium was cut into small pieces, mixed with UO_2, and burned, the resulting combustion product was U_3O_8.

The uranium was in the form of 0.010 inch sheet and 0.010 inch wire using two different sheets. One gave on analysis 0.02% carbon, 0.01% oxygen, and less than 0.01% silicon and iron. The other gave 0.01% or less of carbon, oxygen, aluminum, silicon, iron, copper and calcium. Because of the rather large uncertainties in the final combustion results no corrections were made for these small amounts of impurities.

In preparing the metal for combustion, the desired amount of uranium sheet was cut into pieces about 1 mm. square and mixed with the proper amount of uranium dioxide. The combustion was carried out as in the case of uranium dioxide. The ratio of uranium to uranium dioxide was varied over wide limits. When more than 0.7 of the energy came from the uranium the resulting heat of combustion was low and the ratio of oxygen to uranium in the combustion product was also low. If less than 0.7 of the energy came from the uranium the combustion product was U_3O_8. The composition was determined by ignition in oxygen at 800° as described above.

Two series of runs were made. In the first series the uranium oxide had a composition corresponding to the formula $UO_{2.03}$ and had a heat of combustion of 381.30 joules/g. In the second series the composition was $UO_{2.006}$ and its heat of combustion was 389.21 joules/g. as reported above. Those runs were omitted from the final average which had more than 0.7 of the heat coming from the uranium or in which the combustion product varied from U_3O_8. The remaining twenty runs may be summarized as follows: mass of U, 0.51 to 1.80 g.; mass of UO_2, 9.76 to 26.38 g.; average formula of product, $U_3O_{7.998 \pm 0.003}$; firing energy, 5.4 to 8.3 joules; temperature rise, 1.09 to 1.61°; energy from U, 4956.5 to 5021.4 with an average value of 4984.7 joules/g.; average deviation from the mean, 15.0 joules/g.; standard deviation of the mean, 3.9 joules/g. The final result, including the uncertainty in the energy equivalent and the uncertainty in the value used for UO_2, is 4984.7 ± 9.7 joules/g.

The Heat of Formation of U_3O_8.—From the above result the value of ΔE for the reaction $3U + 4O_2 = U_3O_8$ is −3560 ± 6.9 kjoules. When this is corrected for gas imperfection and converted to ΔH the value for the heat of formation of U_3O_8 is $\Delta H_{25°} = -3570.9 \pm 6.9$ kjoules./mole or −853.5 ± 1.6 kcal./mole.

The Heat of Formation of UO_2.—From the heat of formation of U_3O_8 and the heat of the reaction $3UO_2 + O_2 = U_3O_8$ it is possible to calculate the heat of formation of UO_2. The value so obtained is $\Delta H_{25°} = -1084.3 \pm 2.5$ kjoules./mole or −259.2 ± 0.6 kcal./mole.

Comparison with Previous Work on Uranium.—The only combustion values on uranium in the literature are those of Mixter[7] who measured the heats of reaction of U and UO_2

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(5) F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

(6) W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 1 (1932).

(7) W. S. Mixter, *Am. J. Sci.*, **34**, 141 (1912).

HEATS OF FORMATION OF URANIUM OXIDES

	ΔH kcal.		
	Mixter's values		
Reaction	Peroxide bomb	Oxygen bomb	This paper oxygen bomb
$3U + 4O_2 = U_3O_8$	−895.5	−845.2	−853.5 ± 1.6
$3UO_2 + O_2 = U_3O_8$	− 86.4	− 75.3	− 76.01 ± 0.09
$U + O_2 = UO_2$	−269.7	−256.6	−259.2 ± 0.6

with O_2 and of U, UO_2 and U_3O_8 with Na_2O_2. The values he obtained with oxygen do not agree with the values he obtained with sodium peroxide. Our values are in fair agreement with his oxygen values as can be seen in the adjoining table:

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NOTES

Some Inorganic Reactions of Nitryl Chloride

BY HARRY H. BATEY AND HARRY H. SISLER

RECEIVED FEBRUARY 18, 1952

The improvement in methods for the synthesis of nitryl chloride, which has made possible its convenient preparation in the laboratory, has resulted in a considerable increase in interest in its reactions and particularly in its possible use as a reagent in organic synthesis. By analogy with nitrosyl chloride it was at first considered to be a possible source of the nitronium (NO_2^+) group and of negative chlorine. Schmiesser,[1] however has reported that at very low temperatures in the liquid or solid phase, nitryl chloride reacts with ammonia to yield chloramine and ammonium nitrite. This would indicate that nitryl chloride behaves as a source of positive chlorine and negative nitrite. Schmiesser, however, gives very little information concerning his experiments. We were, therefore, interested in carrying out the reaction of nitryl chloride with ammonia under a variety of conditions, and further to observe the behavior of nitryl chloride toward a variety of other reagents which might give some indication concerning its polar characteristics.

Experimental

Preparation of Nitryl Chloride.—The method used was that of Dachlauer[2] as modified by Shechter and Kaplan.[3] This method involves the reaction, in the absence of moisture, of anhydrous nitric acid with chlorosulfuric acid. To the anhydrous nitric acid (1.4 moles), cooled to −0.5°, was added in a dropwise manner with vigorous stirring over a period of two hours, 1.4 moles of chlorosulfuric acid. Nitryl chloride distilled out of the mixture and condensed in at −80°. The receiver was disconnected as soon as the addition of chlorosulfuric acid was complete. A yield of 1.1 moles of NO_2Cl was obtained as a pale yellow liquid freezing at −145° (lit. −145°).

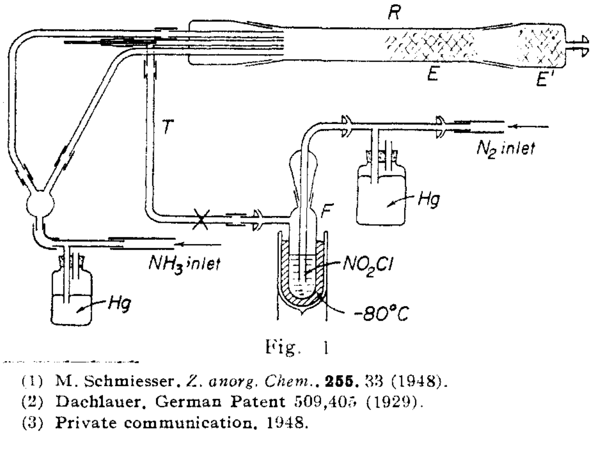

Fig. 1

Reaction of Nitryl Chloride with Ammonia in the Liquid Phase.—The addition of liquid nitryl chloride to liquid ammonia even at −75° results in a very violent reaction. The reaction takes place somewhat less violently but still very vigorously when gaseous ammonia, diluted with nitrogen gas, is passed into dilute solutions of nitryl chloride in inert solvents such as carbon tetrachloride, diethyl ether or petroleum ether. In all these cases the products of the reaction include chloramine, hydrazine, ammonium nitrite and ammonium chloride. In no case was an appreciable amount of nitrate found.

Reaction of Nitryl Chloride with Ammonia in the Gas Phase.—In order to reduce the vigor of the reaction the mixing of nitryl chloride (diluted with nitrogen) with an excess of ammonia was carried out in the gaseous state using the apparatus shown in Fig. 1. The outlet from E' was connected to a series of three traps, cooled to −80°. The residual gas was finally bubbled into water. Nitryl chloride contained in bubbler F was entrained in a stream of nitrogen gas and passed into reactor R (60 cm. long × 4.5 cm. in diameter) at 25° where it was mixed with a large excess of gaseous ammonia. The reaction which occurred was immediate but was not violent and there was no noticeable heating of the reaction chamber. The effluent gases gave strong tests for the presence of chloramine. The white solid formed was filtered out by the glass wool plugs at E and E'. Gases from the reactor tube were condensed at −80° in the traps and the water bubbler was used to remove the last traces of chlorine-containing substances.

The solid contents of the reactor were dissolved in water and analyzed for hydrazine and chloride, and tested qualitatively for nitrite and nitrate. No hydrazine or nitrate was ever detected in this portion of the system, but the presence of an abundance of nitrite was indicated. In a series of experiments carried out in this manner amounts of chloride corresponding to from 10 to 15% of the nitryl chloride were found in the glass wool plugs in the reactor. Mattair and Sisler[4] had found, in the reaction of chlorine with ammonia to produce chloramine in a similar reactor that up to about 10% of the chloramine produced by the chlorine–ammonia reaction decomposes to ammonium chloride in the reactor tube. Assuming that a similar proportion of chloramine might decompose in the nitryl chloride–ammonia reaction, we may conclude that the reaction of nitryl chloride and ammonia in the gaseous phase proceeds quantitatively to yield chloramine and ammonium nitrite; and that the chloride found in the reactor results from the secondary decomposition of a small portion of the chloramine so produced.

The liquid ammonia solutions of chloramine in the traps were allowed to stand at −75° overnight and then to evaporate. White solid residues composed of a mixture of hydra-

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(1) M. Schmiesser, *Z. anorg. Chem.*, **255**, 33 (1948).

(2) Dachlauer, German Patent 509,405 (1929).

(3) Private communication, 1948.

(4) R. Mattair and J. Sisler, THIS JOURNAL, **73**, 1619 (1951).