[CONTRIBUTION NO. 92 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM RESEARCH CENTER, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR, BARTLESVILLE, OKLAHOMA]

Sulfuric Acid: Heat of Formation of Aqueous Solutions by Rotating-bomb Calorimetry[1]

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Rotating-bomb calorimetry of rhombic sulfur, mixed with hydrocarbon oil in widely varying proportions, led to a more accurate value of the heat of combustion. The heat of formation of aqueous sulfuric acid was calculated from the measured value of the heat of combustion. For formation of $H_2SO_4\cdot 115H_2O$(liq.) from rhombic sulfur, gaseous hydrogen and oxygen, $\Delta Hf^\circ_{298.16}$ is -212.17 ± 0.06 kcal. mole^{-1}. Discrepancies in previous determinations may have stemmed in part from failure to detect and correct for N_2O in the reaction products.

The presently accepted values for the heat of formation of aqueous sulfuric acid solutions[2] depend upon experimental work that is relatively old, however accurate, and experimental paths that are indirect. The path generally followed had been oxidation of rhombic sulfur to gaseous sulfur dioxide, followed by oxidation of either gaseous or aqueous sulfur dioxide to aqueous sulfuric acid. Measurements of many workers have been evaluated and weighted several times[2-4] to arrive at the most reliable value of the heat of formation. Although an accurate value exists for the heat of oxidation of rhombic sulfur to gaseous sulfur dioxide,[5] the heat of oxidation of sulfur dioxide to aqueous sulfuric acid is not well known. It is noteworthy that the "accepted" value for the heat of formation of aqueous sulfuric acid has changed about 4 kcal. mole^{-1} in 25 years.

When the rotating-bomb method of combustion calorimetry made possible accurate measurements of heat of combustion for organic sulfur compounds,[6-8] it became important anew to select the best possible value for the heat of formation of aqueous sulfuric acid, one of the principal combustion products, to obtain more accurate values of heat of formation for organic sulfur compounds. It was found that rhombic sulfur mixed with an auxiliary hydrocarbon oil could be burned in oxygen to form a solution of aqueous sulfuric acid.[6,7] Thus, it became possible to determine a value for the heat of formation of sulfuric acid depending only upon precision oxygen-bomb calorimetry. Bomb calorimetry at the University of Lund and at the Bartlesville Petroleum Research Center[6-8] did give new values, between which, however, there was a discrepancy large enough to be disconcerting. An extensive series of measurements to resolve this discrepancy now has been done by the Bureau of Mines. These measurements of the heat of formation of sulfuric acid and the more reliable value obtained for this important thermochemical datum are reported herein.

Experimental

Apparatus and Procedures.—The apparatus (calorimeter BMR II and bomb Pt3b)[9,10] and procedures[7,8] have been described. Briefly, the combustion reaction took place in a platinum-lined bomb initially containing 10 g. of water and charged to 30 atm. with purified oxygen. One atmosphere of air (5 atm. in certain experiments as explained later) was left in the bomb to cause formation of oxides of nitrogen necessary to catalyze the complete oxidation of sulfur to the hexavalent state. By-products of the reaction were moderate amounts of aqueous nitric acid, small amounts of aqueous nitrous acid and, under certain conditions, small amounts of nitrous oxide. The energy equivalent of the calorimeter, $E_{Calor.}$, was determined by combustion of benzoic acid (National Bureau of Standards standard sample 39g certified to evolve 26.4338 ± 0.0026 abs. kj. per gram mass when burned under specified conditions).

Operation of the rotating-bomb calorimeter differed in one respect from that previously described for organic sulfur compounds.[6-8] Specifically, rotation of the bomb was continued from the mid-time to the end of a calorimetric experiment.[9] This procedure was used to assure thorough equilibration of gaseous and aqueous phases.

Reduction to Standard States.—Reduction of the results to standard states followed the method of Hubbard, Scott and Waddington.[11] The adequacy of the reduction to standard states and, also, the adequacy of equilibration between aqueous and gaseous phases when the bomb is rotated to the end of the experiment were corroborated in a recent investigation by the Bureau of Mines. In that investigation, the energy equivalent of the calorimeter was determined by benzoic acid calibrations made alternately with 1 g. and 10 g. of water initially in the bomb. Six calibration experiments of each kind gave average values for the energy equivalent that differed by only 0.004%. Significant inadequacy of the reduction to standard states or of the equilibration between phases would have produced a much greater difference.

Materials.—The sample of rhombic sulfur, laboratory designation USBM-Plb, was provided by the National Bureau of Standards through the courtesy of Thomas J. Murphy.[12] Another sample prepared in the same way was used recently for heat capacity measurements[13] and found to have a liquid-soluble, solid-insoluble mole fraction impurity of only 1.3×10^{-5}.

The auxiliary oil was a sample of redistilled mineral oil, laboratory designation USBM-P3a, empirical formula $CH_{1.891}$. The value of $\Delta Ec^\circ/M$ for this material, as deter-

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(2) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," N.B.S. Circular 500, 1952.

(3) "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, pp. 178, 212.

(4) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936, pp. 28-29, 198-199.

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(6) S. Sunner, (a) *Svensk Kem. Tid.*, **58**, 71 (1946); (b) Thesis, University of Lund (1949).

(7) W. N. Hubbard, C. Katz and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

(8) G. Waddington, S. Sunner and W. N. Hubbard, "Experimental Thermochemistry," F. D. Rossini, Editor, Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 7, pp. 149-179.

(9) W. D. Good, D. W. Scott and G. Waddington, *J. Phys. Chem.*, **60**, 1080 (1956).

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(11) W. N. Hubbard, D. W. Scott and G. Waddington, "Experimental Thermochemistry," F. D. Rossini, Editor, Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 5, pp. 75-128.

(12) T. J. Murphy, W. S. Clabaugh and R. Gilchrist, *J. Research Natl. Bur. Standards*, **64A**, 355 (1960).

(13) E. D. West, THIS JOURNAL, **81**, 29 (1959).

mined in a series of experiments done concurrently with those reported here, is −10,984. 1 cal. g.$^{-1}$.

Units of Measurements and Auxiliary Quantities.—All data reported are based on the 1951 International Atomic Weights[14a] and fundamental constants[14b] and the definitions 0°C. = 273.16°K.; 1 cal. = 4.1840 abs. j. Measurements of mass were referred to standard devices calibrated at the National Bureau of Standards.

For use in reducing weights in air to *in vacuo*, in correcting the energy of the actual bomb process to the isothermal bomb process and in correcting to standard states, the values tabulated were used for density, ρ, specific heat, c_p, and $(\partial E/\partial P)_T$ of the substances.

	ρ, g. ml.$^{-1}$	c_p, cal. deg.$^{-1}$ g.$^{-1}$	$(\partial E/\partial P)_T$, cal. atm.$^{-1}$ g.$^{-1}$
Rhombic sulfur	2.07	0.168	−0.00077
Auxiliary oil	0.87	0.53	−0.00614

Heat of Combustion of Rhombic Sulfur.—Combustion experiments were made with samples of three different compositions, that is, with atom ratios of carbon to sulfur (C/S) of 8, 5 and 2. Results selected as typical of experiments with each composition are summarized in Table I. The values of $\Delta Ec°/M$ in Table I are for the reaction

$$S(c, rhombic) + 3/2O_2(g) + 116H_2O(liq.) = H_2SO_4 \cdot 115\ H_2O(liq) \quad (I)$$

In the experiments with the higher mass of sulfur (approximately 0.575 g.) it was necessary to charge the bomb with 5 atm. of air (instead of the 1 atm. normally used) to effect complete oxidation of sulfur to the hexavalent state. This circumstance accounts for the larger quantities of nitrogen acids observed in these experiments.

Table I

Summary of Typical Combustion Experiments[a]

m'(rhombic sulfur), g.	0.18926	0.28493	0.57552
$\Delta t_c = t_f - t_i - \Delta t_{cor.}$ deg.	2.01539	2.01807	2.02538
E(calor.)($-\Delta t_c$), cal.	−8065.13	−8075.85	-8105.1^0
E(cont.)($-\Delta t_c$),[b] cal.	−26.95	−26.95	-27.1^0
ΔE_{ign}, cal.	0.59	0.45	0.96
$\Delta E^f_{dec.}$ ($HNO_3 + HNO_2$), cal.	13.47	12.04	28.78
ΔE, cor. to st. states,[c] cal.	3.83	1.97	−5.26
$-m''\Delta Ec°/M$ (auxiliary oil), cal.	7226.07	6814.32	5538.20
$-m'''\Delta Ec°/M$ (fuse), cal.	3.97	3.61	3.73
$m'\Delta Ec°/M$ (rhombic sulfur), cal.	−844.15	−1270.41	−2565.79
$\Delta Ec°/M$ (rhombic sulfur), cal.	−4460.26	−4458.67	−4458.21

[a] The symbols and abbreviations in this table are those of ref. 11, except as noted. [b] E^i(cont.)(t_i −25°) + E^f(cont.)(25° − t_f + $\Delta t_{cor.}$). [c] Items 81–85, incl., 87–91, incl., 93 and 94 of the computation form of ref. 11.

A summary of all calorimetric results is given in Table II. As discussed in a later section, a small correction is applied in this table for the formation of nitrous oxide in the experiments with larger sulfur samples. The agreement of the results from experiments with samples of widely different composition is good evidence that the chemistry of the combustion reaction is described correctly.

Table II

Summary of Calorimetric Results

Atom ratio of C/S	8	5	2
$-\Delta Ec°/M$, cal. g.$^{-1}$	4460.26	4458.67	4458.21
	4456.76	4466.25	4460.41
	4462.55	4461.01	4456.34
	4456.77	4454.08	4456.92
	4460.58	4457.36	4455.26
	4456.65	4459.28	4458.59
	4460.26	4464.04	4455.97
	4457.04	4453.19	4459.74
		4457.49	4457.87
			4455.55
			4455.65
			4457.20
Mean and std. dev.	4458.86 ± 0.82	4459.04 ± 1.42	4457.31 ± 0.49
Correction for N_2O	....	....	0.73 ± 0.73
Corrected mean and std. dev.	4458.86 ± 0.82	4459.04 ± 1.42	4458.04 ± 0.88

Heat of Formation of Aqueous Sulfuric Acid.—Combination of results of all experiments summarized in Table II leads to a value of −142.96 ± 0.06 kcal.mole^{-1} for $\Delta Ec°$ for reaction I. The uncertainty expressed is the uncertainty interval equal to twice the over-all standard deviation of the mean. It reflects uncertainties in the calibration experiments and in the heat of combustion of the auxiliary oil as well as in the heat of combustion of rhombic sulfur. The value of $\Delta Hc°$ is −143.85 ± 0.06 kcal. mole^{-1}. This value and that for the heat of formation of liquid water[2] were added to obtain the heat of formation of $H_2SO_4 \cdot 115\ H_2O$(liq) according to reaction II

$$S(c, rhombic) + 2\ O_2(g) + H_2(g) + 115\ H_2O(liq.) = H_2SO_4 \cdot 115\ H_2O(liq.) \quad (II)$$

$$\Delta Hf°_{298.16} = -212.17 \pm 0.06 \text{ kcal. mole}^{-1}$$

Discussion

Sources of Error.—Earlier workers who attempted combustion experiments with mixtures of rhombic sulfur and hydrocarbon oil were disturbed by changes in the appearance of the surface of the platinum crucible after a combustion experiment.[8] Frequent failure of these experiments to produce the anticipated energy led to concern about the possibility of reaction between platinum and sulfur. Although slight surface effects of the kind described were noted in occasional experiments of the group described here, no accompanying energy effect was detected. Constancy of weight of the platinum crucibles, weighed before and after such experiments, is good evidence that the phenomenon observed was merely a slight surface effect.

Present indications are that the low evolution of energy observed earlier[8] was caused either by formation of nitrous oxide—an oxidation product that has previously escaped detection—or possibly by non-equilibration of the gaseous and aqueous phases. Mass and infrared spectroscopic examination of the gases from combustion experiments reported here failed to produce evidence of sulfur-containing compounds such as COS or CS_2. The only hitherto undetected oxidation product was N_2O, present in thermally significant amounts only in those experiments in which the sulfur sample was relatively large and 5 atm. of air was used in the bomb. Samples of combustion gases were passed through a liquid-nitrogen trap, and the condensable gases were examined by mass spectroscopy. There was evidence of N_2O, but positive identification was difficult because of interference by CO_2. Repeated passage of the gases over Ascarite to remove CO_2 produced a gas whose infrared spectrum matched perfectly that of pure N_2O. Semiquantitative analyses from the mass

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(14) (a) E. Wichers, This Journal, **74**, 2447 (1952); (b) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

spectra indicated the formation of about 2×10^{-5} mole of N_2O in the combustion gases from experiments with large amounts of sulfur and 5 atm. of air. Nitrous oxide presumably formed when higher oxides of nitrogen were reduced in the oxidation of SO_2 to aqueous sulfuric acid. As indicated in Table II, a correction for formation of N_2O, based on the value of the heat of formation from ref. 2, was applied to the results for $C/S = 2$.

The amount of N_2O in the final state probably depends on reactions on the surface of the hot crucible. In experiments in which a fused-silica crucible instead of a platinum crucible was used, significant amounts of N_2O sometimes were formed, and the evolution of energy was lower than when platinum crucibles were used. The results obtained with fused-silica crucibles were rejected and are not reported here.

The effect of differences in purity of sulfur samples also could explain the difference between the values of the present investigation and those listed in ref. 8.

Comparison with Previous Work.—The result of this investigation for the heat of formation of $H_2SO_4 \cdot 115H_2O$ is compared with other values in Table III. If experiments in progress at the University of Lund confirm the preliminary value quoted in Table III, this important thermochemical datum will have been defined independently in two laboratories within ±0.1 kcal. mole^{-1}, or better.

TABLE III

COMPARISON WITH PREVIOUS WORK

Source	Sulfur sample	$\Delta Hf°_{298.16}$ ($H_2SO_4 \cdot 115\ H_2O$) kcal. mole^{-1}
NBS circular 500(1952)[a]		−211.63
USBM (1956)[b]	USBM P1[c]	−212.02
Lund (1956)[b]	SS[d]	−212.39
USBM (1959)[e]	USBM P1b[g]	−212.17
Lund (1959–1960)[f]	USBM P1b[g]	−212.24

[a] Value interpolated from table in ref. 2. [b] Values calculated from results listed in ref. 8, p. 171. [c] Sample described in ref. 7. [d] Sample prepared by S. Sunner, University of Lund. [e] This investigation. [f] Communicated by S. Sunner. This value is from preliminary results of experiments still in progress. [g] Sample described in this paper.

Effect on Values of the Heat of Formation of Organic Sulfur Compounds.—All heat of formation values previously reported by the Bureau of Mines were revised and placed on a more consistent basis by using the newly determined value for the heat of formation of $H_2SO_4 \cdot 115\ H_2O$. Most of the originally published values were changed by an amount less than the experimental uncertainty. The revised values will be given in comprehensive tabulations, now in preparation, of the thermodynamic properties of organic sulfur compounds.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ROCHESTER, ROCHESTER, NEW YORK]

Photochemical Production of Acetone-O^{18} in the System Acetone:O^{18}_2 at 3130 Å.[1]

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Acetone-O^{18} was observed to be formed on exposure of a mixture of acetone vapor and oxygen^{18} gas to light of 3130 Å. At the same time, no change in the isotopic composition of the oxygen was detected. Oxygen consumption and photo-oxidation of the ketone accompanied the labelling process. The rate of formation of acetone-O^{18}, when corrected for the dark reaction, was found to be independent of oxygen pressure (from 1 to 40 mm.) and temperature (up to 65°) at constant intensity. The quantum yield for the formation of acetone-O^{18}, which was 0.45, was unaffected by a ten-fold change in intensity. The quantum yield for the production of 3-pentanone-O^{18} in the system 3-pentanone:$O_2{}^{18}$ was 0.7. In the photolysis of a mixture of 3-pentanone, azoethane and $O^{18}{}_2$ by light which was absorbed only by azoethane, the formation of 3-pentanone-O^{18} was not observed. It is believed that the photochemical production of the labelled ketones may be a part of the photo-oxidation mechanism.

Introduction

It is known[2] that the phosphorescence of acetone vapor, which presumably arises from a triplet state, is quenched by oxygen. Some features of the quenching suggest that an exchange of an oxygen atom between the ketone and the oxygen molecule may accompany this process. The present study was undertaken to test the idea.

The photo-oxidation of acetone in an O^{18} enriched environment has been studied by Dunn and Kutschke,[3] but an isotopic analysis of the ketone or the oxygen at the end of the photolysis was not reported.

Experimental

Acetone (Eastman Kodak "Spectrograde") was dried over "Drierite" and distilled *in vacuo* before use. Oxygen^{18} (> 98% purity) obtained from the Weizmann Institute of Science, Israel, was used as such.

A conventional high vacuum system was used. In order to conserve materials, the volume of the cell and dead space were kept as small as possible. The quartz cell of 5.0 cm. dia. and 4.4 cm. length (82.5 ml.) was attached to a Toepler pump of about 300 ml. capacity. After the desired quantity of acetone and oxygen had been admitted to the cell, the mixture was stirred by repeated expansion into the large volume. About 60 such cycles were found to mix the reactants thoroughly. During a run the light beam was interrupted at regular intervals and the contents of the cell were stirred. A timer which operated a series of microswitches carried out these operations automatically and recorded the durations of the irradiation and stirring. It was observed that at low oxygen pressures, even at low intensities, the yield of acetone-O^{18} was lower in the absence of mechanical stirring, which suggested that diffusive mixing was not rapid enough to avoid local depletion of oxygen.

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(1) The authors wish to thank the National Science Foundation for a grant in support of this work.

(2) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951); J. Heicklen, THIS JOURNAL, **81**, 3863 (1959).

(3) J. R. Dunn and K. O. Kutschke, *Can. J. Chem.*, **36**, 421 (1958).