

By comparison, closely spherical molecules such as tetramethylmethane and hexamethylethane show a single large transition well below the melting point, a relatively high melting point and a very short liquid range.

We wish to thank Dr. F. D. Rossini for furnishing the extremely pure samples of 2,2-dimethylbutane and Drs. Waddington and Huffman for giving us the results of their calorimetric measurements in advance of publication.

Summary

The heat capacity of 2,2-dimethylbutane has been measured from 15 to 280° K. and the vapor

pressure from 211 to 290° K. The following values were obtained: heats of transition, 1289.2 ± 3 cal./mole at 126.81° K.; 67.7 ± 1 cal./mole at 140.88° K.; heat of fusion 138.5 ± 0.5 cal./mole at 174.16° K.; entropy at 298.16° K., 65.13 ± 0.15 for the liquid and 85.72 ± 0.2 cal./degree mole for the ideal gas.

A vibrational assignment is made and the average potential barrier to internal rotation calculated to be 4375 cal./mole. The experimental entropy agrees very satisfactorily with the value calculated by one of us in 1940, which supports the general method employed then.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MONTANA STATE COLLEGE]

Heats of Formation of Liquid Methyl Sulfoxide and Crystalline Methyl Sulfone at 18°

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The properties of coördinate and of d-orbital bonds are of considerable interest, not only in the theory of molecular structure but by virtue of their occurrence in many well-known compounds. Although thermochemical studies have provided the energies of such bonds in many inorganic compounds, this information is lacking for the majority of the corresponding simple organic compounds, whose study seems particularly inviting because of the relative stability and apparent electromeric simplicity of the bonds attaching the aliphatic radicals.

Both of these bond types probably make major contributions to the structures of the sulfur-oxygen bonds in sulfoxides and sulfones. The heats of formation of methyl sulfoxide and methyl sulfone, hitherto unreported but given in this paper, can later be combined with their heats of vaporization, now being determined by the author, to give what may be formally designated as the sulfur-oxygen bond energies of these two compounds. These values may throw light on the large dipole moment¹ and the unusually short sulfur-oxygen bonds² of methyl sulfone.

Because the molar heats of combustion of even such simple organic compounds as these are large, it was thought that more accurate values of their heats of formation from methyl sulfide could be calculated from heats of oxidation by suitable reactions in solution, provided there were employed in each case one oxidant or reductant whose heat of formation had previously been determined accurately by two or more independent workers. This paper reports the results of measuring (1) the heat of oxidation of methyl sulfide to methyl sulfoxide by hydrogen peroxide, and (2) the heat of oxida-

tion of methyl sulfoxide to methyl sulfone by permanganate. The accuracy of the measurements was checked by determining the heat of neutralization of hydrochloric acid by sodium hydroxide.

Experimental

Methyl Sulfide.—Eastman Kodak Co. methyl sulfide was allowed to stand over sodium metal for several days. On distilling, a large middle fraction was collected, b. p. (637 mm.) 32.30–32.32°.

Methyl Sulfoxide.—A small excess of methyl sulfide, mixed with an equal volume of glacial acetic acid, was treated at 0–10° with 30% hydrogen peroxide. The solution was made alkaline and extracted with chloroform. A product was obtained which was 99.8% pure as determined from freezing point measurements and oxidation with permanganate, and showed no appreciable tendency to decompose. Cooling curves indicated 18.5° to be the m. p. of the pure compound.

Methyl Sulfone.—Methyl sulfide was treated with an excess of a 6% solution of potassium permanganate. After separation from the salts by solution in chloroform, the product was recrystallized twice from water. Only one crystalline form appeared, m. p. 108.1–108.5° (cor.).

Apparatus and Calorimetric Method.—Solutions of the required molalities were prepared and standardized using the usual methods and precautions. All weights were corrected to a vacuum basis.

A non-adiabatic calorimetric method was employed, the calorimeter vessel being a closed silvered dewar flask. In each run the reacting solutions other than the first were introduced from the jacket water-bath, which was thermostated to $\pm 0.001^\circ$ when necessary. Small unavoidable differences in temperature were properly corrected for. Temperatures were measured by Beckmann thermometers, and the temperature rise was corrected by use of the Regnault-Pfaundler equation,³ the thermal leakage modulus being redetermined in each run. The electrical calibrations were so conducted as to make the calorimetric method a substitution one. All measuring instruments were accurately calibrated, and each standard of potential and resistance was believed to be accurate to $\pm 0.01\%$. The time of electrical heating was automatically measured to 0.1 second.

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(1) Coop and Sutton, *Trans. Faraday Soc.*, **35**, 507 (1939).

(2) Lister and Sutton, *ibid.*, **35**, 497 (1939).

(3) White, "The Modern Calorimeter," Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1928, p. 41, equation (13).

TABLE I
 DETAILED THERMOCHEMICAL DATA (18.0°C.)

Scheme and step (see Table II)	Limiting reactant	Moles present	ΔT (cor.) (reaction)	Detns. of C_p	C_p (mean) (kcal. per deg.) [†]	Heat of step reaction, kcal. [‡]
1	HCl	0.06883	3.002	3	0.3160	13.78
1	HCl	.06883	2.999	5	.3158	13.76
1	HCl	.06883	3.002	2	.3163	13.80
2a	H ₂ O ₂	.014780	3.7475	3	.2448	62.07
2a	H ₂ O ₂	.014885	3.7675	3	.2449	61.99
2a	H ₂ O ₂	.014959	3.7785	2	.2452	61.94
2a	H ₂ O ₂	.014852	3.7565	2	.2448	61.92
2b	0.1045	3	.2427	1.71
2b1065	0	(.2427)	1.74
2c	(CH ₃) ₂ SO	.01469	.201	0	(.2429)	3.32
2c	(CH ₃) ₂ SO	.01457	.198	0	(.2429)	3.30
2c	(CH ₃) ₂ SO	.01462	.2005	0	(.2429)	3.33
2d	(CH ₃) ₂ S(l)	.01426	-.072	2	.1905	-0.96
2d	(CH ₃) ₂ S(l)	.01426	-.0735	0	(.1907)	-0.98
3a	(CH ₃) ₂ SO	.009145	3.3665	2	.3103	114.23
3a	(CH ₃) ₂ SO	.009145	3.367	3	.3107	114.39
3a	(CH ₃) ₂ SO	.009145	3.3715	2	.3108	114.58
3a	(CH ₃) ₂ SO	.009145	3.3665	2	.3105	114.30
3b	(CH ₃) ₂ SO ₂	.009145	3.1505	2	.3106	107.00
3b	(CH ₃) ₂ SO ₂	.009145	3.1485	3	.3107	106.97
3c	I ₂	.0442	-0.0685	0	(.2406)	-0.37
3c	I ₂	.0493	-.075	2	.2406	-0.37
3d	(CH ₃) ₂ SO	.01464	.1765	2	.3319	4.00
3d	(CH ₃) ₂ SO	.01464	.1755	0	(.3325)	3.99
3e	(CH ₃) ₂ SO ₂	.01334	-.217	0	(.3318)	-5.40
3e	(CH ₃) ₂ SO ₂	.01298	-.214	1	(.3322)	-5.48
3e	(CH ₃) ₂ SO ₂	.01253	-.204	0	(.3318)	-5.40

Results

In Table I are given all the essential thermochemical data obtained experimentally in this investigation, each line corresponding to a single determination. The temperature before mixing took place was 18.0° in each case. The column entitled " C_p (mean)" gives the value of the effective heat capacity used in the calculation of the heat of that particular determination. In each determination having a major temperature change for the reaction, this value of C_p was the mean from the calibrations accompanying that determination alone⁴ (with an average deviation from the mean of 0.04%). However, calibrations were made following only one of a set of determinations of the same reaction if the temperature change was very small and hence did not require as accurate a value of the heat capacity.

The reactions given by the equations in Table II are those which actually occurred in the calorimeter, except that the quantities of reactants indicated by the equations lead to the production of exactly one mole of substance in each net reaction. The mole compositions of the separate phases which were mixed are enclosed in brackets and separated by plus signs. In each equation these phases are given in the order in which they were introduced into the calorimeter. Each

(4) In most cases this procedure led to cancellation of some of the error due to small errors in the amounts of solutions introduced.

value given for ΔH is the mean of the values of Table I for that step and was obtained experimentally in this investigation, with the following exceptions: the heats of reaction for Step *e* of Scheme 2 and for Step *f* of Scheme 3 were calculated by interpolation from the tables of Bichowsky and Rossini.⁶

The mean value obtained experimentally for the heat of neutralization of hydrochloric acid with sodium hydroxide was in exact agreement with that calculated from data listed by Bichowsky and Rossini.⁶

In Table III are given the calculated values of the heats of formation of methyl sulfide, methyl sulfoxide, and methyl sulfone. The accuracy of these values is limited by the accuracy of the value for methyl sulfide, which is based on an old combustion value⁸ of Thomsen and on the heat of vaporization calculated from recent accurate data.⁷

Validity of the Thermochemical Schemes

Certain tests were performed to determine whether the reactions of Table II proceeded quantitatively and to completion in the calorimeter.

Oxidation of Sulfide to Sulfoxide (Scheme 2).—It was found that under the conditions pre-

(5) One kcal. = 4.1833 international kilojoules.

(6) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(7) Osborne, Doescher and Yost, *THIS JOURNAL*, **64**, 171 (1942).

TABLE II
THERMOCHEMICAL SCHEMES AND MEAN EXPERIMENTAL HEATS OF REACTION

Scheme 1		ΔH (mean)
$\left[\begin{array}{c} 1 \text{ HCl} \\ 200 \text{ H}_2\text{O} \end{array} \right] + \left[\begin{array}{c} 1 \text{ NaOH} \\ 40 \text{ H}_2\text{O} \end{array} \right] \longrightarrow \left[\begin{array}{c} 1 \text{ NaCl} \\ 241 \text{ H}_2\text{O} \end{array} \right]$		$-13.78 \pm 0.02 \text{ kcal. (18.0}^\circ)$
Scheme 2		
Step	Reaction of the step	ΔH (mean) for step reaction (kcal.)
a	$\left[\begin{array}{c} 8.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 311.9 \text{ H}_2\text{O} \end{array} \right] + \left[\begin{array}{c} 1 \text{ H}_2\text{O}_2 \\ 184.2 \text{ H}_2\text{O} \end{array} \right] \longrightarrow \left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO} \\ 7.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 497.1 \text{ H}_2\text{O} \end{array} \right]$	-61.98 ± 0.1
b	$\left[\begin{array}{c} 7.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 311.9 \text{ H}_2\text{O} \end{array} \right] + [185.2 \text{ H}_2\text{O(l)}] \longrightarrow \left[\begin{array}{c} 7.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 497.1 \text{ H}_2\text{O} \end{array} \right]$	-1.72 ± 0.02
c	$\left[\begin{array}{c} 7.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 497.1 \text{ H}_2\text{O} \end{array} \right] + [1 \text{ (CH}_3)_2\text{SO(l)}] \longrightarrow \left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO} \\ 7.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 497.1 \text{ H}_2\text{O} \end{array} \right]$	-3.32 ± 0.02
d	$\left[\begin{array}{c} 7.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 311.9 \text{ H}_2\text{O} \end{array} \right] + [1 \text{ (CH}_3)_2\text{S(l)}] \longrightarrow \left[\begin{array}{c} 8.0 \text{ (CH}_3)_2\text{S} \\ 193.4 \text{ CH}_3\text{COOH} \\ 311.9 \text{ H}_2\text{O} \end{array} \right]$	$+0.97 \pm 0.02$
e	$\left[\begin{array}{c} 1 \text{ H}_2\text{O}_2 \\ 184.2 \text{ H}_2\text{O} \end{array} \right] \longrightarrow [185.2 \text{ H}_2\text{O(l)}] + [1/2 \text{ O}_2 \text{ (g)}]$	(-22.71 ± 0.05)
<hr/> <p>Net reaction: $1 \text{ (CH}_3)_2\text{S(l)} + 1/2 \text{ O}_2 \text{ (g)} \longrightarrow 1 \text{ (CH}_3)_2\text{SO(l)}; \Delta H = -33.26 \pm 0.1 \text{ kcal. (18.0}^\circ)$</p>		
Scheme 3		
Step	Reaction of the step	ΔH (mean) for step reaction (kcal.)
a	$\left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO} \\ 11.23 \text{ H}_2\text{SO}_4 \\ 1185 \text{ H}_2\text{O} \end{array} \right] + \left[\begin{array}{c} 0.7881 \text{ KMnO}_4 \\ 299.3 \text{ H}_2\text{O} \end{array} \right] + \left[\begin{array}{c} 10.01 \text{ HI} \\ 1 \text{ I}_2 \\ 279.2 \text{ H}_2\text{O} \end{array} \right] \longrightarrow \left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO}_2 \\ 8.07 \text{ HI} \\ 1.970 \text{ I}_2 \\ 10.05 \text{ H}_2\text{SO}_4 \\ 0.3940 \text{ K}_2\text{SO}_4 \\ 0.7881 \text{ MnSO}_4 \\ 1765 \text{ H}_2\text{O} \end{array} \right]$	-114.38 ± 0.15
b	$\left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO}_2 \\ 11.23 \text{ H}_2\text{SO}_4 \\ 1185 \text{ H}_2\text{O} \end{array} \right] + \left[\begin{array}{c} 0.7881 \text{ KMnO}_4 \\ 299.3 \text{ H}_2\text{O} \end{array} \right] + \left[\begin{array}{c} 12.01 \text{ HI} \\ 278.2 \text{ H}_2\text{O} \end{array} \right] \longrightarrow \left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO}_2 \\ 8.07 \text{ HI} \\ 1.970 \text{ I}_2 \\ 10.05 \text{ H}_2\text{SO}_4 \\ 0.3940 \text{ K}_2\text{SO}_4 \\ 0.7881 \text{ MnSO}_4 \\ 1765 \text{ H}_2\text{O} \end{array} \right]$	-106.98 ± 0.05
c	$\left[\begin{array}{c} 10.01 \text{ HI} \\ 279.2 \text{ H}_2\text{O} \end{array} \right] + [1 \text{ I}_2 \text{ (c)}] \longrightarrow \left[\begin{array}{c} 10.01 \text{ HI} \\ 1 \text{ I}_2 \\ 279.2 \text{ H}_2\text{O} \end{array} \right]$	$+0.37 \pm 0.01$
d	$\left[\begin{array}{c} 11.23 \text{ H}_2\text{SO}_4 \\ 1185 \text{ H}_2\text{O} \end{array} \right] + [1 \text{ (CH}_3)_2\text{SO(l)}] \longrightarrow \left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO} \\ 11.23 \text{ H}_2\text{SO}_4 \\ 1185 \text{ H}_2\text{O} \end{array} \right]$	-4.00 ± 0.02
e	$\left[\begin{array}{c} 11.23 \text{ H}_2\text{SO}_4 \\ 1185 \text{ H}_2\text{O} \end{array} \right] + [1 \text{ (CH}_3)_2\text{SO}_2 \text{ (c)}] \longrightarrow \left[\begin{array}{c} 1 \text{ (CH}_3)_2\text{SO}_2 \\ 11.23 \text{ H}_2\text{SO}_4 \\ 1185 \text{ H}_2\text{O} \end{array} \right]$	$+5.43 \pm 0.05$
f	$\left[\begin{array}{c} 12.01 \text{ HI} \\ 278.2 \text{ H}_2\text{O} \end{array} \right] + [1/2 \text{ O}_2 \text{ (g)}] \longrightarrow \left[\begin{array}{c} 10.01 \text{ HI} \\ 279.2 \text{ H}_2\text{O} \end{array} \right] + [1 \text{ I}_2 \text{ (c)}]$	(-42.54 ± 0.05)
<hr/> <p>Net reaction: $1 \text{ (CH}_3)_2\text{SO(l)} + 1/2 \text{ O}_2 \text{ (g)} \longrightarrow 1 \text{ (CH}_3)_2\text{SO}_2 \text{ (c)}; \Delta H = -59.00 \pm 0.2 \text{ kcal. (18.0}^\circ)$</p>		

vailing in the calorimeter, hydrogen peroxide does not oxidize methyl sulfide appreciably beyond the sulfoxide stage. Some of the solvent 193CH₃COOH:497H₂O was made approximately 0.04 M with respect to methyl sulfide and 0.1 M with respect to hydrogen peroxide. After the re-

TABLE III
HEATS OF FORMATION FROM THEIR ELEMENTS^a AT 18.0°

Compound	ΔH , kcal. per mole
Methyl sulfide, $(\text{CH}_3)_2\text{S}$ (liquid)	- 14.4
Methyl sulfoxide, $(\text{CH}_3)_2\text{SO}$ (liquid)	- 47.7
Methyl sulfone, $(\text{CH}_3)_2\text{SO}_2$ (crystalline)	-106.7

action occurring was calculated to be at least 99.99% complete, determination of the remaining hydrogen peroxide indicated that each molecule of the sulfide had acquired an average of 1.001 and 1.002 atoms of oxygen in two trials.

However, the reaction in the calorimeter was carried out with an excess of methyl sulfide, in order to obviate error due to the inevitable loss of a small part of the sulfide by evaporation. Theoretically it appears improbable but nevertheless conceivable that under that circumstance a considerable part of the oxidation may not have reached the sulfoxide stage before the exhaustion of the hydrogen peroxide, but may instead have produced a stable product other than the sulfoxide. In an attempt to test this possibility, the order of the reaction between methyl sulfide and hydrogen peroxide was determined rather roughly. The same solvent was used as in the calorimeter, and the initial concentrations of the two reactants were 0.05 and 0.4 *M*, in one test the sulfide being in excess and in the other the hydrogen peroxide. The progress of the reaction was followed by the temperature rise,⁹ and repetition at a lower temperature enabled calculation of the isothermal reaction velocities. After correcting for the small change of concentration of whichever reactant was present in excess, the average rates of reaction for half-minute intervals were calculated, and are represented in Fig. 1. The slopes of the graphs signify a second-order reaction. There is no particular indication of the occurrence during the reaction of a changing order, which might well have resulted had the methyl sulfide been oxidized in slow consecutive steps.

As another test of the probable simplicity of the reaction, a calorimetric redetermination of Step *a* was carried out except with the initial concentration of hydrogen peroxide only half the usual value. The molar heat was 0.04 kcal. higher than the mean for this step recorded in Table II.

The eleven-minute "experimental periods" of Step *a* proved adequate for completion of the reaction, for analysis of the temperature data showed that all but 0.01% of the hydrogen peroxide had reacted in the first nine minutes.

The question arose as to whether enough methyl sulfide evaporated from the solutions of this scheme to lead to appreciable thermal error. The

(8) The carbon as β -graphite.

(9) This widely applicable method, often the most convenient one available for following the progress of a reaction, does not seem to have received the attention it deserves. It is obvious that with a sufficiently dilute solution the whole temperature rise would be so small that for practical purposes the reaction occurring could be treated as isothermal.

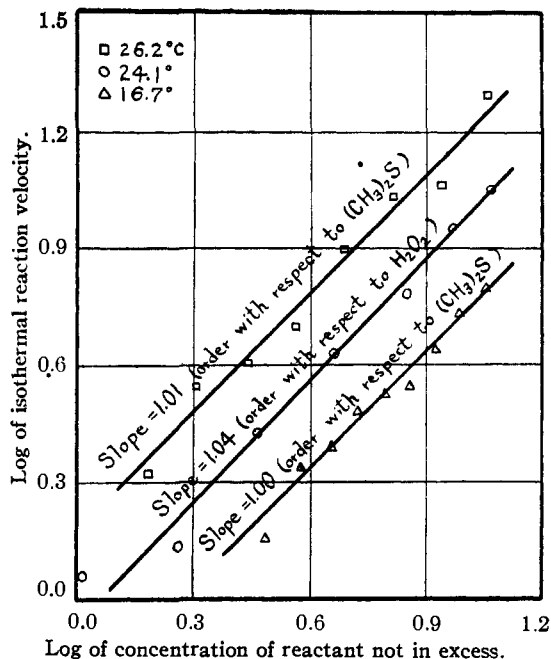


Fig. 1.—Order of the reaction between methyl sulfide and hydrogen peroxide in aqueous acetic acid solution. (The physical units of each graph are arbitrary and not comparable with those of the other graphs.)

partial pressures given in Table IV were roughly determined by passing air through samples of two typical solutions used in the calorimeter.¹⁰

TABLE IV
PARTIAL PRESSURES OF METHYL SULFIDE IN CERTAIN SOLUTIONS

Solution	Temperature, °C.	Pressure of methyl sulfide, mm.
$8(\text{CH}_3)_2\text{S}:193\text{CH}_3\text{COOH}:312\text{H}_2\text{O}^{11}$	0	37
	23	87
$8(\text{CH}_3)_2\text{S}:193\text{CH}_3\text{COOH}:497\text{H}_2\text{O}$	23	98

The absence of drift of successive calorimetric calibrations showed that insufficient sulfide vapor escaped from the calorimeter to lower the heat capacity appreciably. But the change of sulfide pressure which took place when the second reacting phase was added probably led to evaporation or condensation of enough methyl sulfide to produce an error of about 0.05 kcal. in each of several steps in Table II. However, it can be shown that this led to no systematic error in the heat of the net reaction. For if the equations given in Table II for Scheme 2 are corrected by adding after each solution a phase composed of a constant volume of methyl sulfide vapor at a pressure in equilibrium with that solution, all these vapor phases will can-

(10) Although the water content enhanced the partial pressure of the sulfide, the selection of these solvents minimized the heat of dilution involved in Steps *a* and *b*.

(11) From the heat of vaporization of methyl sulfide and the temperature coefficient of its partial pressure in this solution, a value of +0.8 kcal. was estimated for ΔH for Step *d*.

cel and there will result the same net reaction, since the latter contains no solutions.

Oxidation of Sulfoxide to Sulfone (Scheme 3).—By determining the iodine produced, Step *a* was shown to proceed strictly quantitatively. In the initial reaction of this step the sulfoxide reduced the permanganate to manganese dioxide only.¹²

Analysis of the calorimetric temperature data of Step *a* showed that 0.1–0.2% of the sulfoxide originally present may have remained unoxidized in the five minutes between adding the permanganate and adding the hydriodic acid. In that event a small equivalent amount of permanganate also remained, but was subsequently reduced by excess hydriodic acid with the evolution of about 90% of the heat which the unoxidized sulfoxide would have furnished, as shown by the relatively small difference between the heats of Steps *a* and *b*. Therefore the resulting net error in the heat of Step *a* did not exceed 0.01 kcal.

Uniformity of the Sulfoxide.—Attention was directed to the possibility that methyl sulfoxide may have existed in solution in a different form when its heat of solution was measured than when its heat of formation (in Scheme 2) or its heat of oxidation (in Scheme 3) was measured, with appreciable thermochemical error as a result. Such a lack of uniformity of solutes has apparently not been suspected in the great majority of thermochemical studies on record, and there is no evidence of its existence in the present case.

Several observed facts make it seem unlikely that in measuring the heats of Scheme 3 the methyl sulfoxide underwent an appreciable change from the time it was dissolved until the measurements of its heat of oxidation were completed several weeks later. During that time there was no detectable formation of sulfide (by self-oxidation–reduction), and the heat of oxidation (that produced before adding the hydriodic acid) remained extremely constant. This apparent sta-

(12) By adding standard ferrous sulfate solution in place of the hydriodic acid, and titrating the excess with permanganate, an indirect but very accurate method was found for determining methyl sulfoxide in the absence of other reductants.

bility of the sulfoxide in solution parallels the stability of the pure compound.

If the sulfoxide deviated from the structure $(\text{CH}_3)_2\text{SO}$ to exist as a polymer, a desmotope, a hydrate, or an ester, it appears that the resulting molecule could not be formulated without one or more d-orbital sulfur bonds. Such bonds would probably be relatively unstable, and might reasonably be expected to lead, through dissociation or hydrolysis, to mobile equilibrium with the above simple structure, thereby eliminating the kind of thermochemical error under discussion. The type of unstable compound here postulated is exemplified by $(\text{CH}_3)_2\text{SBr}_2$, which has been shown¹³ to hydrolyze completely and apparently immediately when dissolved in water.

Summary

Pure methyl sulfoxide (m. p. 18.5°) was prepared and found to be quite stable.

The heats of oxidation of methyl sulfide to methyl sulfoxide and of methyl sulfoxide to methyl sulfone were measured in solution in a non-adiabatic calorimeter. The sulfide was oxidized by hydrogen peroxide, and the sulfoxide was oxidized by permanganate with reduction of the excess oxidant by hydriodic acid. Relevant heats of solution also were measured.

The reaction between methyl sulfide and hydrogen peroxide in aqueous acetic acid solution was followed by the temperature rise, and is thereby shown to be second-order. Both oxidation reactions were found to be quantitative and sufficiently rapid for accurate calorimetric investigation, and the validity of the thermochemical schemes which were used is discussed.

The following mean values for the heat evolved at constant pressure at 18.0° were found: $\text{HCl (200 H}_2\text{O)} + \text{NaOH (40 H}_2\text{O)} = \text{NaCl (241 H}_2\text{O)} + \text{H}_2\text{O (l)}$, 13.78 ± 0.02 kcal.; $(\text{CH}_3)_2\text{S (l)} + \frac{1}{2} \text{O}_2 = (\text{CH}_3)_2\text{SO (l)}$, 33.26 ± 0.1 kcal.; $(\text{CH}_3)_2\text{SO (l)} + \frac{1}{2} \text{O}_2 = (\text{CH}_3)_2\text{SO}_2$ (crystalline), 59.00 ± 0.2 kcal.

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(13) Hantzsch and Hibbert, *Ber.*, **40**, 1514 (1907).