

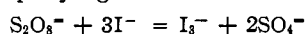
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Production of Atomic Iodine in the Reaction of Peroxides with Iodide Ion

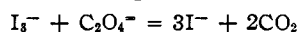
BY HENRY TAUBE

For many reactions in which peroxides act as catalysts or reagents, the experimental results suggest that these substances produce free radicals in their reactions with reducing agents (*e. g.*, unsaturated compounds, SO_3^- , halides).¹ In the present paper the results of a study to determine whether selected peroxides [persulfate, acetyl peroxide (Ac_2O_2) peracetic acid (AcOOH) and hydrogen peroxide] react with I^- in aqueous solution by a one electron process, to produce atomic iodine and a peroxide free radical in the first step, or by a two electron process, to produce HIO and a stable residue, are presented and discussed. The rate laws for the reactions of the peroxides with I^- are consistent with either mechanism.

In the method used $\text{C}_2\text{O}_4^{2-}$ was added to the reaction mixture containing I_3^- , I^- and the peroxide. Photochemical experiments² have shown that atomic iodine reacts with $\text{C}_2\text{O}_4^{2-}$. Since the peroxides studied and the HIO ³ react with $\text{C}_2\text{O}_4^{2-}$ at a rate which is negligible compared to the rate of reaction with I^- , and since the rate of reaction of $\text{C}_2\text{O}_4^{2-}$ and iodine is relatively slow (and can be allowed for), any appreciable oxidation of $\text{C}_2\text{O}_4^{2-}$ accompanying the reaction



can be taken as evidence that atomic iodine is an intermediate. The evidence is made stronger by a study of the variation of the amount of induced reaction with the concentration factors, and by a quantitative comparison with the photochemically induced reaction of iodine and $\text{C}_2\text{O}_4^{2-}$. Experimentally, the effect is detected by fact that the I_3^- formed is less than the equivalent of the peroxide added; since the induced reaction can exceed in extent the amount of peroxide added, it is best described by the equation

**Experimental**

In performing an experiment, an accurately known volume of solution containing potassium oxalate (and oxalic

(1) An extensive review of this subject containing references to other work in this field is by Mayo and Walling, *Chem. Rev.*, **27**, 351-412 (1940).

(2) Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **29**, 382-95 (1933).

(3) According to the experiments of Griffith and McKeown, *ibid.*, **28**, 752-760 (1932), HIO does not react with $\text{C}_2\text{O}_4^{2-}$, but only with HC_2O_4^- .

acid for some experiments), potassium iodide, and iodine at the desired concentrations was placed in a darkened stoppered bottle and immersed in a constant temperature bath at 25°. Aliquot portions were withdrawn and the iodine content determined by titration (for acid solutions, standard sodium thiosulfate solution was used, otherwise standard sodium arsenite). Then a known volume of the peroxide solution, the strength of which was also determined, was added and the time of mixing noted. After sufficient time had elapsed to ensure reduction of the peroxide, samples were withdrawn at long intervals and analyzed for total iodine. These values were plotted against time and extrapolated to zero time. This extrapolation corrects approximately for the slow but measurable thermal reaction between I_3^- and $\text{C}_2\text{O}_4^{2-}$. In most experiments, the peroxide reacted almost completely (>99.7%) in six hours; the thermal reaction in such cases was always less than 10% of the effect sought. Subtracting the extrapolated value from the initial iodine plus iodine equivalent of the peroxide added, the amount of $\text{C}_2\text{O}_4^{2-}$ oxidized, $\Delta(\text{C}_2\text{O}_4^{2-})$, is obtained.

In the experiments with acetyl peroxide, a stock solution was not prepared due to the rapid hydrolysis of this substance. The procedure was modified by introducing the acetyl peroxide as a liquid, with a capillary pipet, into the potassium oxalate solution, mixing thoroughly and withdrawing samples for analysis, then adding the potassium iodide-iodine solution. The samples were analyzed by running them into concentrated potassium iodide; under these conditions, the reaction of I^- with acetyl peroxide (and $\text{S}_2\text{O}_8^{2-}$) is quantitative even in the presence of $\text{C}_2\text{O}_4^{2-}$.

The reagents potassium oxalate, oxalic acid, potassium persulfate, potassium iodide, iodine and hydrogen peroxide (inhibitor free) were C. P. quality, and used without purification. The acetyl peroxide (Ac_2O_2) was prepared as described by Gambarjan.⁴ The product obtained by simple recrystallization was of uneven quality, and melting points ranged from 29 to 19°.

All experiments were done at 25°; the units time in minutes and concentrations in moles per liter are used throughout.

Results and Discussion

The results obtained in a study of the variation of the consumption of ($\text{C}_2\text{O}_4^{2-}$), $\Delta(\text{C}_2\text{O}_4^{2-})$, with ($\text{S}_2\text{O}_8^{2-}$)₀, (I_3^-), (I^-), ($\text{C}_2\text{O}_4^{2-}$) and (H^+) are presented in Table I. The numbers in column 7, experiments 1 to 12, show that over the 8-fold range of (I^-), 3-fold range in (I_3^-)₀, 10-fold range in ($\text{S}_2\text{O}_8^{2-}$)₀ and 4-fold range in ($\text{C}_2\text{O}_4^{2-}$) studied, $\Delta(\text{C}_2\text{O}_4^{2-}) \propto (\text{C}_2\text{O}_4^{2-})\sqrt{(\text{S}_2\text{O}_8^{2-})_0}/\sqrt{(\text{I}^-)^3}$. Accurate results can be obtained only for a limited range of variation of the concentration factors. At low ($\text{C}_2\text{O}_4^{2-}$) and high (I^-) and ($\text{S}_2\text{O}_8^{2-}$), the effect be-

(4) Gambarjan, *Ber.*, **42**, 4010 (1909).

comes small compared to the total titration and the percentage error becomes high; on the other hand, when (I^-) is reduced to increase the effect, the thermal correction becomes so great as to make proper allowance impossible without a much more detailed study. The figures which show the greatest deviation from the mean in column 7 are always for extreme conditions.

TABLE I

THE VARIATION OF $\Delta(C_2O_4^{2-})$ WITH (I^-) , $(S_2O_8^{2-})$, $(C_2O_4^{2-})$, (I_3^-) AND (H^+)

Zero subscripts refer to initial concentration. $(I^-)_m$ is the mean value of iodide in concentration in an experiment. $(I_3^-)_0 = ca. 10^{-8} M$ except in 6 where it is $0.33 \times 10^{-8} M$. $F = (\Delta(C_2O_4^{2-})\sqrt{(I^-)_m})/((C_2O_4^{2-})\sqrt{(S_2O_8^{2-})_0})$.

	$(C_2O_4^{2-})$	$(S_2O_8^{2-})_0 \times 10^4$	$(I^-)_0 \times 10^2$	$(I^-)_m \times 10^2$	$\Delta(C_2O_4^{2-}) \times 10^5$	$F \times 10^5$
1	0.200	2.14	3.94	3.91	3.39	9.0
2	.200	5.34	3.89	3.81	6.13	9.9
3	.204	5.51	3.94	3.86	6.53	10.3
4	.202	10.02	3.94	3.79	8.52	9.8
5	.200	19.81	3.74	3.44	15.41	11.0
6	.204	5.51	4.01	3.93	6.10	9.7
7	.200	2.71	0.91	0.87	34.10 ^a	8.4
8	.200	2.71	1.92	1.88	11.84 ^a	9.2
9	.200	2.71	3.89	3.85	4.38 ^a	10.1
10	.200	2.71	7.90	7.86	1.50 ^a	10.0
11	.100	2.71	3.89	3.85	2.35 ^b	10.8
12	.050	2.71	3.89	3.85	1.06 ^b	9.7
13	. ^d	2.71	3.89	3.85	-.02	ca. 0
14	.100	10.26	3.92	3.77	5.60 ^c	12.0
15	.100	10.26	3.92	3.77	5.50 ^c	12.6

^a μ was kept constant with KNO_3 as KI was varied.

^b μ was kept equivalent to 0.2 M $K_2C_2O_4$ with K_2SO_4 .

^c With 0.1 M $Na_2C_2O_4$, 0.01 M $NaHC_2O_4$. ^d With 0.2 M KHC_2O_4 .

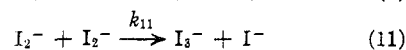
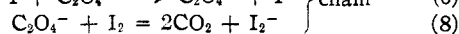
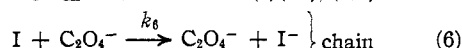
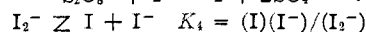
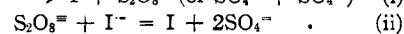
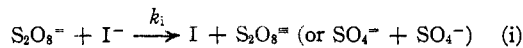
Experiment 13 shows that the effect is not observed for $HC_2O_4^-$. To test whether the effect was strongly dependent on pH , an experiment was carried out with a mixture containing the 0.2 M $C_2O_4^{2-}$ but with 0.02 M $HC_2O_4^-$ added; while the experiment was not conducted with the same care as the others and not included in the table, it was sufficiently accurate to show that essentially the same result was obtained as in the others (cf. also Expts. 14 and 15). It is concluded that H^+ exerts an influence only by reducing the concentration of $C_2O_4^{2-}$.

Experiment 7 shows that the amount of $C_2O_4^{2-}$ oxidized can exceed the amount of $S_2O_8^{2-}$ added. As is evident from the results for the variation of the effect with (I^-) , the induction factor can probably be increased to high values by lowering (I^-) .

To make the work comparable with that of Griffith, McKeown and Winn,² experiments 14 and 15 were carried out using 0.1 M $Na_2C_2O_4$. For these

experiments, the specific rate of interaction of $S_2O_8^{2-}$ and I^- was also measured ($k_i = 0.253$ and 0.247). Since the amount of iodine liberated at any time is less than the peroxide consumed when $C_2O_4^{2-}$ is present, the function in column 7 was used to calculate $\Delta(C_2O_4^{2-})$, and thus the true value of (I_3^-) for any concentration of $S_2O_8^{2-}$ during an experiment.

The results of Table I are completely interpreted by a mechanism in which the reaction between $S_2O_8^{2-}$ and I^- produces atomic iodine; the following reactions are identical with those proposed by Griffith, *et al.*,² for photochemically produced iodine atoms, and for convenience in comparison the same numbers are given. Rate determining steps are represented by arrows.



By the usual process for reactions with intermediates at low concentration, it may be shown that

$$\frac{-d(C_2O_4^{2-})}{dt} = k_6 K_4 \sqrt{\frac{k_1 (S_2O_8^{2-})}{k_{11} (I^-)}} (C_2O_4^{2-})$$

Consistent with what Griffith, *et al.*, appear to have done, the rate of disappearance of I_2^- in reaction 11 is defined as $2k_{11}(I_2^-)$.²

$$-d(S_2O_8^{2-})/dt = k_1(S_2O_8^{2-})(I^-)$$

$$d(C_2O_4^{2-}) = \frac{k_6 K_4 (C_2O_4^{2-}) d(S_2O_8^{2-})}{\sqrt{k_1 k_{11} (I^-)^2} \sqrt{(S_2O_8^{2-})}}$$

For any one experiment, the only variable is $(S_2O_8^{2-})$, since all the other reagents are present in excess. Hence

$$\Delta(C_2O_4^{2-}) = (C_2O_4^{2-})_0 - (C_2O_4^{2-})_t = \frac{2k_6 K_4 (S_2O_8^{2-})_0^{1/2}}{\sqrt{k_1 k_{11} (I^-)_m^2}} (C_2O_4^{2-})$$

The variation of $\Delta(C_2O_4^{2-})$ predicted by this mechanism is experimentally observed; furthermore, on the basis of an iodine atom mechanism, it is expected that $HC_2O_4^-$ should not give an effect.⁵ These facts make it reasonable to conclude that atomic iodine is indeed produced when $S_2O_8^{2-}$ and I^- react in aqueous solution.

Besides the argument presented in the introduction, the experimental fact that the effect

(5) Griffith, McKeown and Winn, *loc. cit.*, have concluded that the reaction of atomic iodine with $HC_2O_4^-$ is less than 2% of the reaction with $C_2O_4^{2-}$ at equal concentrations.

does not depend on pH argues against hypiodous acid as the intermediate producing the effect. A further argument against the reactive intermediate being any substance derived from I^- by a two-electron change is the fact that the induction factor can exceed unity. Hypiodous acid or an ion with the same oxidation number would be expected to react with $C_2O_4^{2-}$ by a two-electron change to give carbon dioxide as a stable product and a maximum of unity for the induction factor would be expected.

A quantitative comparison of these results with those obtained by Griffith, *et al.*,³ in their photochemical experiments can be made. Using the results of experiments 14 and 15 and the mean value of 0.250 liter moles⁻¹ min.⁻¹ for k_1

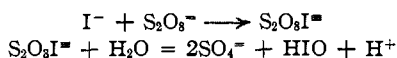
$$\frac{k_6 K_4}{\sqrt{k_{11}}} = \frac{\Delta(C_2O_4^{2-}) \sqrt{k_1 (I^-)^2}}{2 \sqrt{(S_2O_8^{2-})_0} (C_2O_4^{2-})}$$

is calculated to be 3.2×10^{-5} . This quotient may also be calculated from the results of Griffith, *et al.* (*loc. cit.* Table XIII, p. 384) by using the equation

$$\frac{k_6 K_4}{\sqrt{k_{11}}} = \frac{\gamma \sqrt{E} \sqrt{(I^-)_m} [(I^-)_m + (\alpha_1/\alpha_2) K_3] \sqrt{1000}}{\sqrt{k_2} 6.06 \times 10^{23} (C_2O_4^{2-})}$$

This is the relation derived by the authors from the mechanism for the photo reaction, except for the factor $\sqrt{1000}/6.06 \times 10^{23}$ which was introduced to make the units comparable to the present ones. The authors have concluded that k_2 is *ca.* 1 at $\lambda = 4360 \text{ \AA}$. On introducing this value and their recorded value for the numerator on the right-hand side, the value of $k_6 K_4/\sqrt{k_{11}} = 4.7 \times 10^{-5}$ is calculated. The approximate agreement with the value 3.2×10^{-5} from the present work is striking, and is regarded as additional support for the interpretation of the data.

However, the discrepancy seems somewhat outside the range of the combined experimental error of the present⁶ and the photochemical work. The possibility exists that $S_2O_8^{2-}$ does not oxidize I^- solely by a one electron path but that a two electron path, as suggested below, also contributes

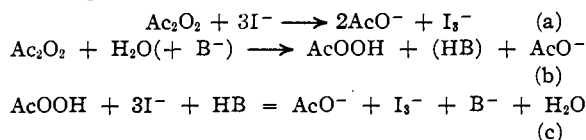


This would account for the low value of $k_6 K_4/\sqrt{k_{11}}$ since any peroxide reacting by this path would not induce oxidation of $C_2O_4^{2-}$. It is possible

(6) The present results contain a systematic error since the peroxide induced and the spontaneous thermal rates are not simply additive. A detailed calculation investigating this effect showed that the recorded value is too low by between 5 to 10%. This effect will also account for the drift in the values of F (Table I) as $(S_2O_8^{2-})$ is varied.

that the entire reaction proceeds through a single intermediate complex, $S_2O_8 I^{\bullet}$, which can dissociate into I and $S_2O_8^{\bullet -}$ or hydrolyze in part as suggested above.

In the experiments with acetyl peroxide, a complication arises from the fact that in aqueous solution this substance hydrolyzes fairly rapidly into peracetic acid, $AcOOH$, and acetic acid.⁷ With I^- added, the following reactions take place (B^- represents a buffer ion, here $C_2O_4^{2-}$).



(c) is a rapid follow reaction. Thus the rate law for the reaction between I^- and Ac_2O_2 has two terms corresponding to the paths (a) and (b):

$$-d(Ac_2O_2)/dt = k_a(Ac_2O_2)(I^-) + k_b(Ac_2O_2)$$

This is illustrated by the data in Fig. 1 which show the variation of $-d(Ac_2O_2)/dt(Ac_2O_2)$ with (I^-) . From these results $k_a = 0.276$ and $k_b = 0.0074$.

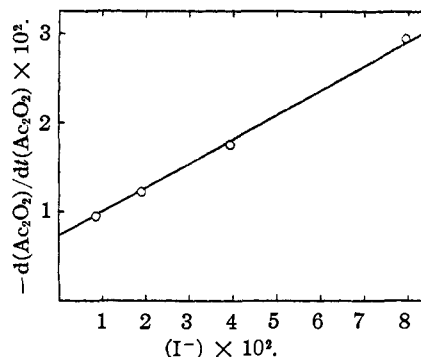


Fig. 1.—The rate of oxidation of I^- by Ac_2O_2 at 25°C: $(K_2C_2O_4) = 0.2 M$; $(KHC_2O_4) = 0.02 M$; $(Ac_2O_2)_0$ is *ca.* $7 \times 10^{-4} M$.

This value of k_b was checked by an experiment in which Ac_2O_2 was added to $K_2C_2O_4$ and KHC_2O_4 of the composition used before. At intervals the total $(Ac_2O_2) + (ACOOH)$ was determined by running a sample into concentrated potassium iodide; at the same time peracetic acid alone was determined by running another sample into cold dilute potassium iodide. From the difference (Ac_2O_2) at various times was obtained, and a value of $k_b = 0.0077$ was calculated. In this experiment, it was also observed that peracetic acid reacts slowly with $C_2O_4^{2-}$, but there was no indication of a direct reaction between Ac_2O_2 and $C_2O_4^{2-}$.

(7) Clover and Richmond, *Am. Chem. J.*, **39**, 179 (1903).

In Table II, the results of a series of experiments studying the variation of $\Delta(\text{C}_2\text{O}_4^{\cdot-})$ with Ac_2O_2 and with (I^-) are presented.

TABLE II

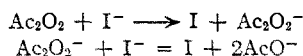
EFFECT OF VARIATION OF $(\text{Ac}_2\text{O}_2)_0$ AND $(\text{I}^-)_m$ ON $\Delta(\text{C}_2\text{O}_4^{\cdot-})$
AT $10^{-3} M(\text{I}_2^-)$, $0.200 M \text{C}_2\text{O}_4^{\cdot-}$, $0.02 M \text{HC}_2\text{O}_4^-$

No.	$(\text{Ac}_2\text{O}_2)_0 \times 10^4$	$(\text{I}^-)_m$	$\Delta(\text{C}_2\text{O}_4^{\cdot-}) \times 10^5$	$\frac{k_6 K_4}{\sqrt{k_{11}}} \times 10^5$
1	6.662	0.0383	2.6	1.7
2	2.93	.0388	1.8	1.8
3	6.78	.0182	5.6	1.7
4	7.05	.0780	1.1	1.6

The values of $k_6 K_4 / \sqrt{k_{11}}$ are recorded in the fifth column and are calculated from the relation

$$\frac{k_6 K_4}{\sqrt{k_{11}}} = \frac{\Delta(\text{C}_2\text{O}_4^{\cdot-})(\text{I}^-)_m (k_a \text{I}^- + k_b)}{2 \sqrt{k_a (\text{Ac}_2\text{O}_2)_0 (\text{C}_2\text{O}_4^{\cdot-})}}$$

This relation was derived in the same way as the similar expression for $\text{S}_2\text{O}_8^{\cdot-}$; the mechanism differed only in the initial reactions. It was assumed that the reaction of acetyl peroxide with I^- (reaction a) has a rate determining step in which atomic iodine is produced, *e. g.*,



but that the reaction of peracetic acid with I^- does not produce atomic iodine. The function describes the results with reasonable accuracy, as is seen by the constancy of the results. The deviation of the values is much greater if peracetic acid is also assumed to produce iodine atoms; it is therefore concluded that whereas acetyl peroxide produces atomic iodine in its reaction with I^- , peracetic acid probably does not.

The value of $k_6 K_4 / \sqrt{k_{11}}$ found for acetyl peroxide is much smaller than the photochemical value of 4.7×10^{-5} . It seems likely, therefore, that only part of the acetyl peroxide produces atomic iodine, and that the greatest part reacts with I^- by a two electron process (analogous to the process suggested for $\text{S}_2\text{O}_8^{\cdot-}$).

The results quoted in Table II were obtained with a single preparation; while the magnitude of the effect varied somewhat (*ca.* 15%) from one preparation to another, the relations observed and the conclusions did not alter.

An experiment was also carried out with hydrogen peroxide. A buffer mixture containing $0.1 M \text{K}_2\text{C}_2\text{O}_4$, and $0.1 M \text{KHC}_2\text{O}_4$ was used in order to suppress the catalytic decomposition of hydrogen peroxide in the I^- - I_3^- mixture. In the experiment $(\text{H}_2\text{O}_2)_0 = 6.853 \times 10^{-4} M$, $(\text{I}^-)_m = 0.0160$, and $(\text{I}_3^-)_0 = 0.40 \times 10^{-3} M$, the specific rate of

interaction of I^- and hydrogen peroxide was found to be 0.486. $\Delta(\text{C}_2\text{O}_4^{\cdot-})$ for the experiment was zero, within experimental error,⁸ although an effect comparable to that observed in the experiments with $\text{S}_2\text{O}_8^{\cdot-}$ is expected, if hydrogen peroxide oxidizes I^- by a one-electron process. It seems likely that the two electron process suggested by Noyes,⁹ $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{IO}^- + \text{H}_2\text{O}$ describes the reaction. The present experiments only test the path for the reaction between hydrogen peroxide and I^- which is independent of (H^+) , since the (H^+) dependent path does not contribute appreciably to the total reaction at the acid concentration used.

Most of the peroxides of the type represented by $\text{S}_2\text{O}_8^{\cdot-}$ (*e. g.*, Ac_2O_2 , $\text{K}_4\text{P}_2\text{O}_8$, Bz_2O_2 , Pr_2O_2), react at measurably slow rates with I^- ; those of the type AcOOH (*e. g.*, H_2SO_5 , BzOOH , H_3PO_5) react very rapidly. The production of atomic iodine as an intermediate may be a property of all the members of the group to which $\text{S}_2\text{O}_8^{\cdot-}$ belongs.

The method used in this study can probably be applied to other reactions of I^- and I_2 —to reactions, in which I_2 is reduced as well as those in which I^- is oxidized. It is seriously limited in its application by the fact that the effect observed is measurable only for fairly slow reactions; to bring rapid reactions within the range of investigation, a substrate more sensitive to atomic iodine than $\text{C}_2\text{O}_4^{\cdot-}$ is required.

The author is grateful to Professor W. C. Bray for helpful discussions of this work.

Summary

Experiments were performed to determine whether oxidation of $\text{C}_2\text{O}_4^{\cdot-}$ is induced by the reaction of each of the peroxides $\text{S}_2\text{O}_8^{\cdot-}$, Ac_2O_2 , peracetic acid and hydrogen peroxide with iodide ion; the effect was observed only with $\text{S}_2\text{O}_8^{\cdot-}$ and acetyl peroxide, and was studied as a function of the concentration variables in these cases.

It was concluded that $\text{S}_2\text{O}_8^{\cdot-}$ and acetyl peroxide, but not peracetic acid or hydrogen peroxide, produce atomic iodine in their reaction with iodide ion.

The amount of reaction induced was com-

(8) It was necessary to make a correction of about 1% for the catalytic decomposition of hydrogen peroxide; the extent of this was determined by a blank experiment containing acetic acid and sodium acetate to give the same (H^+) , potassium iodide, iodine and hydrogen peroxide.

(9) Noyes and Scott, *Z. physik. Chem.*, **18**, 131 (1895). This mechanism has been accepted by Brode [*ibid.*, **49**, 208 (1904)], Bray [*ibid.*, **54**, 463-97 (1906)], and by other later workers in this field.

pared with that expected on the basis of published photochemical results; there appears to be an alternative two electron process for the

reactions of $S_2O_8^{2-}$ and acetyl peroxide with I^- .

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The Heat Capacity, Entropy, Heats of Fusion, Transition, and Vaporization and Vapor Pressures of Methyl Mercaptan

By HORACE RUSSELL, JR., DARRELL W. OSBORNE AND DON M. YOST

Introduction.—Methyl mercaptan, $HSCH_3$, represents an interesting and relatively simple case in which one may expect to find hindered internal rotation. The comparison between the accurately determined calorimetric entropy and the entropy calculated from structural and spectroscopic data should give a reliable value of the barrier, since the calculation may now be carried out quite exactly.¹ By analogy with methyl alcohol,² a transition in the solid should be found, the investigation of which should throw further light on the nature of the two substances. In the present paper there are presented the results of an investigation of the thermodynamic and structural properties of methyl mercaptan as deduced from a low temperature study of the substance.

Purification of Methyl Mercaptan.—The material used was an Eastman Kodak Company product which was purified by two careful fractionations in a closed, meter and a half, vacuum-jacketed column packed with glass helices. The final distillation was done at a reflux ratio of 30:1. Ninety-four grams was collected from an original sample of 200 g. The mercaptan was dried with phosphorus pentoxide before each of the distillations. The substance reacts slightly with moist phosphorus pentoxide to give a yellow, non-volatile product. The air-free sample was sealed in a weighed bulb with a fragile tip and weighed. It was then distilled into the calorimeter through a single stopcock lubricated with Apiezon L grease. The liquid-soluble, solid-insoluble impurity as determined from the premelting was 0.05 mole %.

The Heat Capacities.—All measurements except the heat of vaporization were made in an adiabatic calorimeter (gold-plated copper calorimeter I) and the temperatures were measured with the strain-free platinum resistance thermometer of laboratory designation CT-26. The heat of vaporization was measured in a non-adiabatic calorimeter specially designed for such measurements, using thermometer CT-4. The construction and operation of the apparatus and the calibration of the thermometers are described elsewhere.³

The defined calorie of 4.1833 international joules was used throughout, and the ice-point was taken as 273.16°K.

TABLE I

MOLAL HEAT CAPACITY OF METHYL MERCAPTAN
0°C. = 273.16°K., molecular weight = 48.102, 1.9462 moles in calorimeter.

Run	T, °K.	C_p , cal./deg./mole	Run	T, °K.	C_p , cal./deg./mole
55	14.97	0.773	12	94.12	11.38
72	15.82	0.885	13	99.38	11.74
56	16.47	0.983	14	104.87	12.10
73	17.48	1.126	15	110.37	12.47
57	17.98	1.226	16	115.70	12.81
74	19.35	1.435	25	117.20	12.89
58	19.49	1.476	17	120.87	13.15
59	21.17	1.773	26	122.29	13.23
75	21.50	1.835	18	125.90	13.46
60	23.26	2.168	27	128.06	13.61
76	23.94	2.300	19	130.81	13.80
61	25.63	2.641	45	133.03	13.95
77	26.57	2.831	28	133.21	13.97
62	28.17	3.155	49	133.22	13.96
78	29.37	3.396		137.6	Transition
63	30.97	3.719	51	140.42	14.87 ^a
79	32.51	4.022	47	140.60	14.97 ^a
64	33.86	4.285	30	141.09	15.66 ^a
80	35.96	4.690	52	143.45	16.62 ^a
65	37.09	4.902	31	145.88	16.98 ^a
81	39.61	5.352	53	146.57	17.47 ^a
66	40.73	5.555		150.16	M. p.
82	43.61	6.038	85	154.16	21.27
67	44.40	6.170	33	155.62	21.27
83	48.08	6.763	86	160.50	21.17
68	48.30	6.798	34	162.07	21.12
69	52.64	7.435	87	166.80	21.07
84	53.04	7.486	88	174.47	20.97
35	56.72	7.948	89	184.11	20.87
70	57.46	8.038	90	194.31	20.80
36	61.86	8.548	91	204.51	20.75
71	62.53	8.625	92	214.63	20.71
37	67.00	9.106	93	224.68	20.70
38	72.15	9.600	94	234.63	20.73
39	77.34	10.09	95	244.48	20.81
40	82.58	10.51	96	254.23	20.88
41	87.89	10.93	97	263.89	21.00
11	88.84	10.99	98	271.06	21.13
42	93.26	11.33		279.12	B. p.

^a Not corrected for premelting.

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