fluoride would be about 0.25 D lower than the Br–F moment in bromine monofluoride.

The high value of the electric moment of iodine pentafluoride (2.18) excludes the trigonal bipyramidal or pentagonal planar configuration for the molecule. A distorted octahedral arrangement with the iodine atom below the plane of the four fluorine atoms, on the side opposite the fifth fluorine atom, (giving four angles F–I–F of about 85°) was proposed on the basis of an electron diffraction investigation.[12] This structure would account satisfactorily for the dipole moment. The I–F bond moment should be about 1.6 (by analogy with the known ClF and BrF moments) and, if the bond moments in iodine pentafluoride were all equal, this would lead to the observed moment for the molecule. However, the nuclear magnetic resonance spectrum[13] indicates that one bond differs from the other four so it might be expected by analogy with chlorine trifluoride that the unique I-F bond moment would be smaller than the other four. While a pentagonal pyramidal configuration would also account for the dipole moment it appears to be ruled out by the infrared spectrum,[14] and it is certainly eliminated by the nuclear magnetic resonance data.

(12) M. T. Rogers, A. L. Wahrhaftig and V. F. H. Schomaker, Paper presented before the Division of Physical and Inorganic chemistry of the American Chemical Society, Atlantic City, New Jersey, April, 1947.

(13) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(14) R. C. Lord, M. A. Lynch, W. C. Schumb and E. J. Slowinski, This Journal, **72**, 522 (1950).

The interpretation of the electric moments of the halogen fluorides is particularly difficult. The σ-bonds in these molecules might be considered to be dsp^3 hybrids in the trifluorides and d^2sp^3 hybrids in the pentafluorides with the unshared electron pairs sterically active. The tendency of unshared pairs to occupy more space than expected from symmetry[15] would then account for the angles F–X–F being 85–87° rather than right angles. It has been shown theoretically that when d-orbitals are used the contribution of the lone pairs of electrons to the dipole moment of a molecule is very sensitive to the amount of d-character in the bonds and may be quite large.[16] Since additional orbitals are available for π-bond formation in these molecules, and the bonds are known not to be equivalent, this factor may also be of importance. It is therefore difficult to even predict theoretically the direction of the total moment. Since the homopolar dipole[16] and the electronegativity differences both favor the conventional direction of the bond moment we have assumed this in the above discussion. A detailed analysis of the electron distribution in these molecules, however, will require in addition data obtained by other techniques.

Thermal Decomposition of Sulfides

BY E. H. BRAYE,[1] A. H. SEHON[2] AND B. deB. DARWENT[3]

RECEIVED APRIL 30, 1955

The thermal decomposition of methyl benzyl sulfide has been investigated, in a flow system, in the presence of a large excess of toluene as a carrier gas and a free-radical trap. The decomposition is a homogeneous, first-order free-radical process with an activation energy of 51 ± 2 kcal. mole^{-1}, which has been identified with the dissociation energy of the $C_6H_5 \cdot CH_2$–S·CH$_3$ bond. Preliminary results show that dimethyl sulfide decomposes by a free radical process and dimethyl disulfide by a molecular rearrangement.

Introduction

From the results of the recent kinetic study of the thermal decomposition of benzyl, methyl and ethyl mercaptans in a stream of toluene, Sehon and Darwent[4] derived the C–S bond dissociation energies and proposed a value of about 32 kcal./mole for the heat of formation of the SH radical.

Those studies have been extended, in the present investigation, to benzyl methyl sulfide, dimethyl sulfide and dimethyl disulfide in an attempt to determine the relevant C–S bond dissociation energy and the heat of formation of the SCH$_3$ radical.

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(3) Catholic University of America, Washington, D. C.

(4) A. H. Sehon and B. deB. Darwent, THIS JOURNAL, **76**, 4806 (1954).

Materials.—The toluene used was the Phillips Petroleum Company's research grade product; dimethyl sulfide and dimethyl disulfide were commercial Eastman Kodak samples and were used without further purification. Methyl benzyl sulfide was prepared by Eastern Chemicals and was purified by distillation under reduced pressure (12 mm.) through a Stedman fractionation column, only the middle fraction being used for pyrolysis.

Experimental

The thermal decomposition of the sulfides was studied in a flow system in the presence of excess toluene using the technique developed by Szwarc.[5] The apparatus used was essentially the same as that described previously.[4] Minor alterations were made in the method of separating and analyzing the products of reaction. The products together with undecomposed sulfide and toluene were made to flow, after passage through the furnace, through one trap kept at 0° and two traps at −195°. Most of the dibenzyl produced crystallized out in the trap at 0°, the other condensable products, toluene and undecomposed sulfide, being removed

(5) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

at −195°. Any CH_4 and H_2 produced in the reaction were pumped continuously into a calibrated volume.

For the analysis of H_2S and CH_3SH produced in the reaction, the liquid air traps were connected to a gas fractionating apparatus consisting of a Ward Still, a Toepler pump and gas buret. The liquid air surrounding the traps was removed and the volatile products distilled over into a Ward Still in which H_2S was readily separated from CH_3SH. The CH_3SH, and some undecomposed sulfide and toluene, which had been trapped in the Ward Still, were then condensed into an evacuated bulb at −195° containing a known amount of $AgNO_3$. The bulb was sealed off and the contents allowed to melt. The silver mercaptide was filtered off and the excess silver nitrate back-titrated with ammonium thiocyanate.

All experiments were preceded by blank runs with toluene alone to establish the extent of its decomposition at the appropriate temperature.

Methyl Benzyl Sulfide

Results.—The thermal decomposition of methyl benzyl sulfide in an excess of toluene was investigated over the temperature range 742 to 917°K. The products of pyrolysis were primarily CH_3SH and dibenzyl. Most of the dibenzyl was isolated in the trap cooled to 0° and some of it could also be detected in the first trap at −195°, which contained the undecomposed sulfide, toluene and minute amounts of some solid sulfur containing material. Ultraviolet analysis of the dibenzyl showed that it was slightly contaminated with stilbene (2–10%). Quantitative determination of the dibenzyl was not attempted in all experiments. Table I shows the ratio of dibenzyl, recovered only from the trap cooled at 0°, to $CH_3SH + H_2S$. In view of the inherent losses in the recovery of dibenzyl it seems reasonable to consider that the ratio involving all the dibenzyl actually produced was approximately unity.

TABLE I

PYROLYSIS OF METHYL BENZYL SULFIDE PRODUCTS OF THE REACTION

Run no.	T, °K.	$\dfrac{\text{Dibenzyl}}{(CH_3SH + H_2S)}$	Run no.	T, °K.	$\dfrac{\text{Dibenzyl}}{(CH_3SH + H_2S)}$
58 P	818	0.75	38	855	0.77
39	834	.62	62 P	903	.72
40	836	.63	57	906	.63
42	844	.77	63 P	917	.75

Small amounts of H_2S, not exceeding 17% of the CH_3SH produced, some CH_4 and minute quantities of H_2 were also formed (Table II).
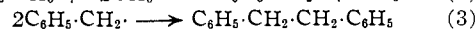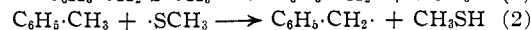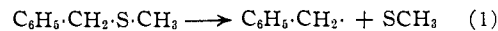
The rate constants were calculated on the assumption that the process was first order, the percentage decomposition being calculated on the assumption that each molecule of CH_3SH or H_2S produced corresponded to a molecule of benzyl methyl sulfide decomposed.

The data of Table II show that the rate constant was essentially independent of changes in reaction parameters such as pressure of sulfide and toluene, time of contact, and surface to volume ratio of the reaction vessel. The dependence of the rate constant on the temperature is also shown in Table II. All rate constants given in Table II are represented graphically in Fig. 1 and, as seen, most of the points lie close to a straight line. This is considered supporting evidence for the first-order character and homogeneity of the pyrolysis of benzyl sulfide.

The slope of the Arrhenius line corresponds to an activation energy of 51.5 ± 2 kcal./mole.

Discussion

The formation of dibenzyl is considered proof for the radical mechanism of the decomposition of benzyl methyl sulfide. The similar rates of production of CH_3SH and dibenzyl, the principal products of reaction, can be most readily explained by the reactions

$$C_6H_5 \cdot CH_2 \cdot S \cdot CH_3 \longrightarrow C_6H_5 \cdot CH_2 \cdot + SCH_3 \quad (1)$$
$$C_6H_5 \cdot CH_3 + \cdot SCH_3 \longrightarrow C_6H_5 \cdot CH_2 \cdot + CH_3SH \quad (2)$$
$$2C_6H_5 \cdot CH_2 \cdot \longrightarrow C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5 \quad (3)$$

This scheme is analogous to the mechanism suggested by Sehon and Darwent[4] for the thermal decomposition of benzyl mercaptan in a stream of toluene. The formation of H_2 and of some of the CH_4 produced can be explained as in the decomposition of mercaptans and benzyl bromide[6] in a stream of toluene by reaction (4) between the radicals produced and dibenzyl
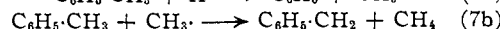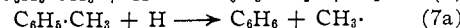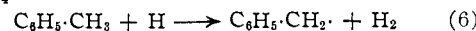
$$C_6H_5CH_2 \cdot CH_2 \cdot C_6H_5 + R \longrightarrow$$
$$C_6H_5 \cdot CH_2 \cdot CH \cdot C_6H_5 + RH \quad (4)$$
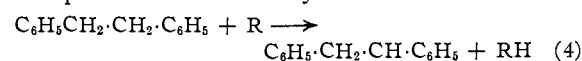
followed by the decomposition of the radical so produced

$$C_6H_5 \cdot CH_2 \cdot CH \cdot C_6H_5 \longrightarrow C_6H_5 \cdot CH=CH \cdot C_6H_5 + H \quad (5)$$
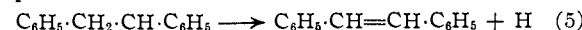
to give stilbene and H atoms, reaction (5). Horrex and Miles[7] have suggested that even a benzyl radical might abstract an H atom from dibenzyl according to reaction (4).

According to Szwarc[8] the H atoms produced in reaction (5) can then react with toluene to give H_2 and CH_4

$$C_6H_5 \cdot CH_3 + H \longrightarrow C_6H_5 \cdot CH_2 \cdot + H_2 \quad (6)$$
$$C_6H_5 \cdot CH_3 + H \longrightarrow C_6H_6 + CH_3 \cdot \quad (7a)$$
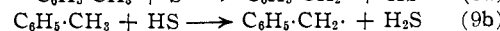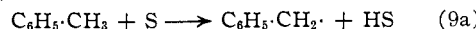$$C_6H_5 \cdot CH_3 + CH_3 \cdot \longrightarrow C_6H_5 \cdot CH_2 + CH_4 \quad (7b)$$

Recently Blades and Steacie[9] have obtained experimental proof substantiating reactions (6) and (7).

The formation of the bulk of methane and of H_2S can be explained by one of the following side reactions.

(i) Some of the CH_3S radicals might undergo further decomposition

$$CH_3S \longrightarrow CH_3 \cdot + S \quad (8)$$
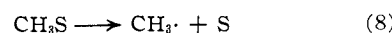
to give methyl radicals and sulfur atoms, which would then react with toluene to give methane as in reaction (7b) and H_2S, via the intermediary of HS radicals.

$$C_6H_5 \cdot CH_3 + S \longrightarrow C_6H_5 \cdot CH_2 \cdot + HS \quad (9a)$$
$$C_6H_5 \cdot CH_3 + HS \longrightarrow C_6H_5 \cdot CH_2 \cdot + H_2S \quad (9b)$$

(ii) CH_3S might react with H atoms produced in reaction (5) to give a hot molecule of CH_3SH, which could then decompose to give methyl and SH radicals. These in turn would lead to production of methane and H_2S by reactions (7b) and (9b). Energetically, scheme (ii) would seem possible since on general grounds one would expect D (CH_3–SH) to be smaller than D (CH_3S–H).

(6) M. Szwarc, B. N. Ghosh and A. H. Sehon, *J. Chem. Phys.*, **18**, 1142 (1950).

(7) C. Horrex and S. E. Miles, *Disc. Faraday Soc.*, **10**, 187 (1951).

(8) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

(9) H. Blades, A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 1142 (1954).

TABLE II

THE THERMAL DECOMPOSITION OF METHYL BENZYL SULFIDE EFFECT OF CONDITIONS ON THE RATE

Expt. no.	T (°K.)	Toluene (mm.)	Sulfide (mm.)	$\dfrac{H_2S \times 10^2}{CH_3SH + H_2S}$	$\dfrac{CH_4 \times 10^2}{CH_3SH + H_2S}$	$\dfrac{H_2 \times 10^2}{CH_3SH + H_2S}$	% Decomp.	τ (sec.)	$k \times 10^2$ (sec.⁻¹)
53	742	19.9	1.3	...	19	0.08	3.94	1.41	2.84
52	743	19.5	1.3	...	25.9	.38	3.74	1.59	2.39
26	745	15.4	0.2	...	Not measured		5.42	1.03	5.40
30	758	15.1	0.9	...	Not measured		4.33	0.99	4.46
28	758	14.8	1.0	...	14.1	.4	6.4	.99	6.65
29	758	13.9	1.3	...	22.4	.4	5.32	.98	5.55
27	763	14.4	0.6	...	Not measured		2.97	.96	3.14
51	764	17.1	1.6	...	25.6	.17	9.48	1.47	6.79
21	773	11.4	0.2	...	2.48	1.8	6.95	0.79	9.07
61P[a]	773	18.8	.5	...	17.4	1.16	...	...	.....
22	777	11.4	.8	...	18.8	0.75	7.8	0.77	10.55
50	779	18.3	.7	...	15.7	.66	17.7	1.39	13.96
49	790	15.3	.3	...	9.9	.65	29.8	1.51	23.4
16	799	13.9	.5	2.61	17.5	.67	19.83	0.74	29.8
18	799	11.3	.7	1.4	9.7	.51	16.5	.74	24.4
17	801	11.7	.7	0.8	Not measured		10.93	.79	14.68
19	804	11.7	.9	7.1	14.2	.53	22.38	.76	33.35
20	805	16.8	.3	1.3	4.8	.8	24.85	.71	40.25
37	814	8.5	.3	...	Not measured		14.52	.37	42.3
58P[a]	818	14.8	.8	3.1	16.2	0.79	41.45	.74	72.4
10	818	10.3	1.0	...	18.5	1.07	37.4	.745	62.8
9	819	12.7	0.6	...	13.9	..	39.6	0.585	86
25	821	11.4	.4	10.7	13.5	1.13	47.2	1.015	62.8
24	827	14.1	.3	3.1	10.6	1.11	59.55	0.94	96.2
23	827	12.5	1.0	8.8	19.0	0.91	55.65	.97	83.95
14	833	13.3	0.3	7.3	11.5	.96	60.8	.72	130
39	834	9.8	.4	...	7.7	.90	35.85	.36	123
15	834	11.8	.7	13.5	9.9	.81	54.4	.74	106
40	836	9.8	.3	...	2.56	.91	42.1	.35	156
31	838	11.9	.6	...	Not measured		32	.36	107
60P[a]	838	22.1	1.2	14.6	16.4	.94	64.9	.65	161
42	844	9.2	0.4	...	10.2	.68	48.2	.36	180
38	855	7.7	.2	...	7.99	1.16	57.2	.37	229
32	863	10.2	.3	13.3	Not measured		74	.36	374
33	870	10.0	.2	9.1	10.3	2.19	74.5	.36	379
55	877	4.7	.2	...	10.2	9.97	41.1	.125	422
56	878	5.7	.1	...	9.35	1.11	45.1	.118	507
54	878	8.0	.4	...	Not measured		75.2	.335	417
34	884	10.2	.4	...	11.0	1.68	81.2	.37	452
35	889	9.5	.3	16.6	16.1	3.0	65.0	.33	318
36	890	7.5	.3	16.2	15.3	2.35	71.9	.35	362
62P[a]	903	7.8	.1	4.1	12.2	1.63	76.2	.099	1450
57	906	5.9	.1	...	12.6	2.1	91.2	.11	2210
63P[a]	917	7.9	.1	6.9	12.1	1.95	72.8	.108	1205

[a] The experiments denoted by P were carried out in a reaction vessel packed with quartz fibers. The surface to volume ratio was thus increased by a factor of 16.

(iii) Some of the CH_3SH molecules produced by reaction (2) might undergo further decomposition to give CH_3 and SH radicals and these, as in scheme (ii), would lead to the formation of methane and H_2S. This is, however, untenable under the present experimental conditions in view of the results obtained by Sehon and Darwent[4] in the thermal decomposition of methyl mercaptan.

(iv) It is also possible that some of the benzyl methyl sulfide might decompose by reaction (10)

$$C_6H_5 \cdot CH_2 \cdot S \cdot CH_3 \longrightarrow C_6H_5 \cdot CH_2 \cdot CH_3 + S \quad (10)$$
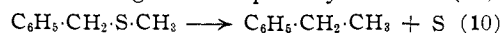
and that the sulfur atoms produced would give rise to H_2S by reactions (9a) and (9b). This scheme, however, does not account for the production of methane and therefore can be ruled out.

An examination of the influence of any of the reaction parameters on the formation of H_2S reveals that at a given temperature and contact time the ratio of H_2S to $(CH_3SH + H_2S)$ decreases with increasing ratio of toluene to sulfide concentration (e.g., compare experiments 14 and 15, 20 and 19, 23 and 24). This finding is in accordance with both schemes (i) and (ii) put forward above.

The formation of methane could be reconciled with a molecular mechanism for the decomposition of benzyl methyl sulfide to give thiobenzaldehyde and methane

$$C_6H_5 \cdot CH_2 \cdot S \cdot CH_3 \longrightarrow C_6H_5 \cdot CH_2 : S + CH_4 \quad (11)$$
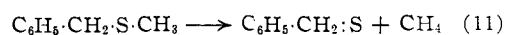
Thiobenzaldehyde does not exist by itself but polymerizes to give a trimer or a higher polymer. Thi

may explain, at least in part, the presence of a heavy sulfur compound isolated with dibenzyl.

In Fig. 1 the points corresponding to experiments 34, 35, 36, 54 and 55 fall below the Arrhenius line. By increasing the ratio of toluene to sulfide (runs 33 and 56), the rate constant in this temperature range, where the extent of decomposition was rather high (in the region of 75%), returned to the expected value. This is interpreted as being due to either a recombination of the SCH_3 with benzyl radicals or to a dimerization of the SCH_3 radicals, when the concentration of those radicals is exceedingly high.

In accordance with the foregoing interpretation of the mechanism of the thermal decomposition of benzyl methyl sulfide, the activation energy of 51.5 ± 2 kcal./mole, derived from the Arrhenius line of Fig. 1, is considered to represent the activation energy of reaction (1). The frequency factor for reaction (1) is calculated to be 3×10^{13} sec.$^{-1}$ within a factor of 3. Assuming that the activation energy of the reverse recombination reaction of the CH_3S and benzyl radicals is equal to zero, it follows that D ($C_6H_5 \cdot CH_2$—$S \cdot CH_3$) is equal to 51.5 ± 2 kcal./mole. Unfortunately the heat of formation of benzyl methyl sulfide has not yet been determined. When this becomes known, one will be able to calculate the heat of formation of the CH_3S radical on the basis of the value proposed here for $D(C_6H_5 \cdot CH_2$—$SCH_3)$.

Dimethyl Sulfide and Dimethyl Disulfide

Only preliminary results on the thermal decomposition of these compounds have been obtained.

In the pyrolysis of dimethyl sulfide in a stream of toluene between 931 and 982°K. the products of the reactions were CH_4, CH_3SH, H_2S and dibenzyl. The formation of dibenzyl indicated that, at least in part, the thermal decomposition of dimethyl sulfide proceeded via a radical mechanism. The re-
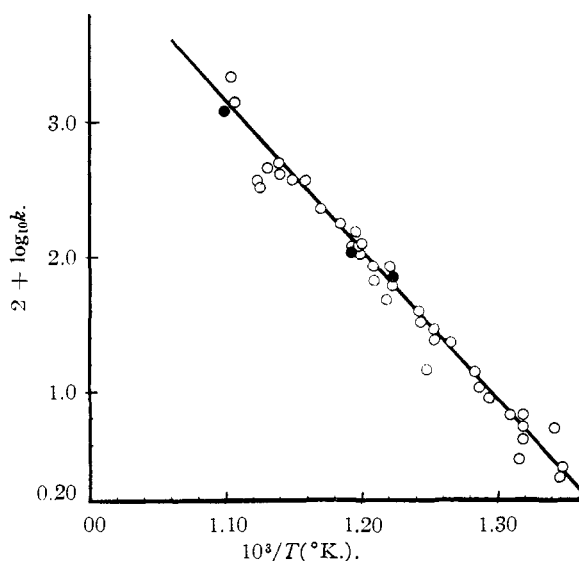

Fig. 1.—The thermal decomposition of methyl benzyl sulfide Arrhenius plot. Filled points denote experiments in packed vessel.

action was not studied sufficiently thoroughly to determine either the order of the reaction or the activation energy.

The thermal decomposition of dimethyl disulfide proceeded fairly vigorously at a much lower temperature, viz., 735 to 833°K., with a time of contact of about 0.4 second. Only traces of dibenzyl were detected which indicated that dimethyl disulfide decomposes thermally by a molecular mechanism and not via radicals. The products were CH_3SH, H_2S, CH_4, H_2, CH_2=CH_2, CH_3CH_3 and heavier sulfur compounds.

OTTAWA, CANADA

On the Question of the Existence of a Crystalline SiO

BY S. GELLER AND C. D. THURMOND

In a recent paper by Hoch and Johnston titled "Formation, Stability and Crystal Structure of Solid Silicon Monoxide,"[1] the existence of crystalline SiO is inferred from X-ray diffraction patterns obtained from mixtures of Si and SiO_2 heated in a high temperature camera. Some interesting features of the data published by Hoch and Johnston are pointed out and an alternative explanation of their data is presented. In addition, some experiments are described which substantiate the conclusion that crystalline SiO has not yet been identified, and that the pattern found by Hoch and Johnston and ascribed to SiO is actually from a mixture of β-cristobalite (high temp. form) and β-silicon carbide (cubic form).

Introduction

In a recent paper by Hoch and Johnston titled "Formation, Stability and Crystal Structure of Solid Silicon Monoxide"[1] the existence of crystalline SiO is inferred from X-ray diffraction patterns obtained from mixtures of Si and SiO_2 heated in a high temperature camera. We wish to point out some interesting features of the data published by Hoch and Johnston and then suggest an alternative explanation for these patterns. In addition, some experiments we have performed will be described

(1) M. Hoch and H. L. Johnston, THIS JOURNAL, **75**, 5224 (1953).

which substantiate our conclusion that crystalline SiO has not yet been identified, and that the pattern found by Hoch and Johnston, and ascribed to SiO is due to a mixture of β-cristobalite (high temperature form) and β-silicon carbide (cubic form).

Hoch and Johnston assert that they have studied the reaction of Si and vitreous SiO_2 at 1300° in a powder diffraction camera. The "disappearance of the Si diffraction lines and the appearance of a new set of diffraction lines, together with the fact that upon cooling the sample to room temperature this new set of lines was found to disappear