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 (55°) 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 CIF 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 spectrum¹³ 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 dsp³ hybrids in the trifluorides and d²sp³ hybrids in the pentafluorides with the unshared electron pairs sterically active. The tendency of unshared pairs to occupy more space than expected from symmetry¹⁵ would then account for the angles F-X-F being 85-87° rather than right angles. It has been shown theoretically that when dorbitals 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 dipole¹⁶ 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.

Acknowledgment.—The authors are grateful to the Atomic Energy Commission for support of this work through Contract AT(11-1)-151.

(15) L. Helmholz and M. T. Rogers, *ibid.*, **62**, 1537 (1940); D. P. Stevenson and V. Schomaker, *ibid.*, **62**, 1267 (1940).

Stevenson and V. Schomaker, *ibid.*, **62**, 1267 (1940). (16) C. A. Coulson, "Valence," Oxford University Press, 1952, and private communication.

EAST LANSING, MICHIGAN

[CONTRIBUTION NO. 3733 FROM DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH LABORATORIES]

Thermal Decomposition of Sulfides

BY E. H. BRAYE,¹ A. H. SEHON² AND B. DEB. DARWENT³

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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 C₆H₅·CH₂-S·CH₃ 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 Darwent⁴ 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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(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. Szware, Chem. Revs., 47, 75 (1950).

at -195° . Any CH₄ and H₂ produced in the reaction were pumped continuously into a calibrated volume. For the analysis of H₂S and CH₃SH produced in the reac-

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_3S 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 CH₃SH 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

| | | | Dibenzyl | | |
|------------|----------------|-------------------|------------|----------------|---|
| Run no. | <i>Т</i> , °К. | $(CH_3SH + H_2S)$ | Run no. | <i>Τ</i> , °Κ. | $\frac{(CH_3SH + H_2S)}{(CH_3SH + H_2S)}$ |
| 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 H₂S, not exceeding 17% of the CH₃SH produced, some CH₄ and minute quantities of H₂ 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

$$C_{6}H_{5} \cdot CH_{2} \cdot S \cdot CH_{3} \longrightarrow C_{6}H_{5} \cdot CH_{2} \cdot + SCH_{3} \quad (1)$$

$$C_{6}H_{5} \cdot CH_{3} + \cdot SCH_{3} \longrightarrow C_{6}H_{5} \cdot CH_{2} \cdot + CH_{3}SH \quad (2)$$

$$2C_{6}H_{5} \cdot CH_{2} \cdot \longrightarrow C_{6}H_{5} \cdot CH_{2} \cdot CH_{2} \cdot C_{6}H_{5} \quad (3)$$

This scheme is analogous to the mechanism suggested by Sehon and Darwent⁴ for the thermal decomposition of benzyl mercaptan in a stream of toluene. The formation of H_2 and of some of the CH₄ produced can be explained as in the decomposition of mercaptans and benzyl bromide⁶ in a stream of toluene by reaction (4) between the radicals produced and dibenzyl

$$C_6H_5CH_2 \cdot CH_2 \cdot C_6H_5 + R \longrightarrow$$

 $C_{\delta}H_5\cdot CH_2\cdot CH\cdot C_{\delta}H_{\delta}+RH~~(4)$ followed by the decomposition of the radical so produced

 $C_{6}H_{5} \cdot CH_{2} \cdot CH \cdot C_{6}H_{5} \longrightarrow C_{6}H_{\delta} \cdot CH = CH \cdot C_{6}H_{\delta} + H \quad (5)$

to give stilbene and H atoms, reaction (5). Horrex and Miles' have suggested that even a benzyl radical might abstract an H atom from dibenzyl according to reaction (4).

According to Szwarc⁸ the H atoms produced in reaction (5) can then react with toluene to give H_2 and CH_4

$$C_{6}H_{5} \cdot CH_{3} + H \longrightarrow C_{6}H_{5} \cdot CH_{2} \cdot + H_{2} \qquad (6)$$

 $C_{6}H_{5} \cdot CH_{3} + H \longrightarrow C_{6}H_{6} + CH_{3} \cdot (7a)$ $C_{6}H_{5} \cdot CH_{2} + CH_{3} \cdot \longrightarrow C_{6}H_{5} \cdot CH_{2} + CH_{4} \quad (7b)$

Recently Blades and Steacie⁹ 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

$$CH_{3}S \longrightarrow CH_{3} + S$$
 (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.

$$C_{6}H_{5} \cdot CH_{3} + S \longrightarrow C_{6}H_{5} \cdot CH_{2} \cdot + HS \qquad (9a)$$

$$C_{6}H_{5} \cdot CH_{3} + HS \longrightarrow C_{6}H_{5} \cdot CH_{2} \cdot + H_{2}S \qquad (9b)$$

(ii) CH₃S might react with H atoms produced in reaction (5) to give a hot molecule of CH₃SH, which could then decompose to give methyl and SH radicals. These in turn would lead to production of methane and H₂S by reactions (7b) and (9b). Energetically, scheme (ii) would seem possible since on general grounds one would expect D(CH₃-SH) to be smaller than D (CH₃S-H).

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- (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).

| | THE TH | ERMAL DEC | COMPOSIT | ION OF METHYL | BENZYL SULF | IDE EFFECT OF | CONDITION | S ON THE R | ATE |
|--------------|--------|------------------|------------------|--|---|---|--------------|-------------|----------------------------|
| Expt. no. | (°K.) | Toluene (mm.) | Sulfide (mm.) | $\begin{array}{r} H_2S \times 10^2 \\ C H_3SH + H_2S \end{array}$ | $\frac{\mathrm{CH_4}\times10^2}{\mathrm{CH_3SH}+\mathrm{H_2S}}$ | $\frac{H_2 \times 10^2}{CH_3 SH + H_2 S}$ | % Decomp. | 7 (sec.) | $k 	imes 10^2$ (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 meas | ured | 5.42 | 1.03 | 5.40 |
| 30 | 758 | 15.1 | 0.9 | | Not meas | ured | 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 meas | ured | 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 measu | ired | 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 | 1.2 | 8 | 24 85 | 71 | 40.25 |
| 37 | 814 | 8.5 | 3 | 1.07 | Not measu | tred. | 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 | 011 | 18.5 | 1.07 | 37 4 | 745 | 62.8 |
| 9 | 819 | 12.7 | 0.6 | | 13.9 | 18 1 1 1 F | 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 | 73 | 11.5 | 96 | 60.8 | 72 | 130 |
| 39 | 834 | 9.8 | 4 | 1.0 | 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 | 10.0 | 2.56 | 91 | 42 1 | 35 | 156 |
| 31 | 838 | 11.9 | 6 | | Not measu | ired | 32 | 36 | 107 |
| $60P^a$ | 838 | 22 1 | 1.2 | 14 6 | 16 4 | 94 | 64 9 | 65 | 161 |
| 42 | 844 | 9.2 | 04 | 11.0 | 10.2 | 68 | 48 2 | 36 | 180 |
| 38 | 855 | 77 | 2 | | 7 99 | 1 16 | 57 2 | 37 | 229 |
| 32 | 863 | 10.2 | | 13 3 | Not measu | red | 74 | 36 | 374 |
| 33 | 870 | 10.0 | 2 | 9 1 | 10.3 | 2 19 | 74 5 | 36 | 379 |
| 55 | 877 | 4 7 | 2 | 0.1 | 10.2 | 9.97 | 41 1 | 125 | 422 |
| 56 | 878 | 5.7 | | | 9.35 | 1 11 | 45 1 | 118 | 507 |
| 54 | 878 | 8.0 | 4 | | Not measu | red | 75.2 | 335 | 417 |
| 34 | 884 | 10.2 | . 1 | | 11 0 | 1 68 | 81.2 | 37 | 452 |
| 35 | 889 | 9.5 | . 1 | 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 | 1. I | 12.6 | 2 1 | 91.2 | . 11 | 2210 |
| $63P^a$ | 917 | 7.9 | .1 | 6.9 | 12.1 | 1.95 | 72.8 | .108 | 1205 |
| | ~ ~ 1 | | | V 1 U | * - * * | | | | |

TABLE II THE THERMAL DECOMPOSITION OF METHYL BENZYL SULFIDE EFFECT OF CONDITIONS ON THE

 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 CH₃SH molecules produced by reaction (2) might undergo further decomposition to give CH₃ and SH radicals and these, as in scheme (ii), would lead to the formation of methane and H₂S. This is, however, untenable under the present experimental conditions in view of the results obtained by Sehon and Darwent⁴ in the thermal decomposition of methyl mercaptan.

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

 $C_6H_5 \cdot CH_2 \cdot S \cdot CH_3 \longrightarrow C_6H_5 \cdot CH_2 \cdot CH_3 + S$ (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 (CH₃SH + H₂S) 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

$$C_{6}H_{5} \cdot CH_{2} \cdot S \cdot CH_{3} \longrightarrow C_{6}H_{5} \cdot CH_{2} \cdot S + CH_{4} \quad (11)$$

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 SCH₃ with benzyl radicals or to a dimerization of the SCH₃ 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 \pm 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 CH₃S and benzyl radicals is equal to zero, it follows that D (C₆H₅·CH₂-S·CH₃) 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 CH₃S radical on the basis of the value proposed here for $D(C_{6}H_{5}\cdot CH_{2}-$ SCH₃).

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 CH₄, CH₃SH, H₂S 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 CH₃SH, H₂S, CH₄, H₂, CH₂=CH₂, CH₃CH₃ and heavier sulfur compounds.

Ottawa, Canada

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES] On the Question of the Existence of a Crystalline SiO

By S. Geller and C. D. Thurmond

RECEIVED APRIL 4, 1955

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 SiO₂ 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 SiO₂ 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