SPACE GROUP OF CYCLOHEXANONE AT −180°C

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ABSTRACT. The Debye-Scherrer pattern of frozen cyclohexanone at −180°C has been photographed and analysed. It has been found that the crystal is orthorhombic with the unit cell dimensions $a = 10.38$ A.U., $b = 7.34$ A.U. and $c = 15.09$ A.U. The density of cyclohexanone at −180°C has been measured and it has been found that there are 8 asymmetric molecules in the unit cell. The space group Q_h^1 is assigned to the crystal.

INTRODUCTION

Hassel and Sommerfeldt (1938) studied the habits of crystals of cyclohexane and its monosubstituted compounds like cyclohexanone, cyclohexanol, chlorocyclohexane with a polarising microscope and reported that the crystals of all the substances mentioned above belong to the cubic system at a temperature just below their respective melting points. They found the lattice constant of cubic crystal of cyclohexanone at −55°C to be 8.61 A.U. by photographing the Debye-Scherrer pattern. It was, however, pointed out by them that the measurement of the lattice constant is subject to much uncertainty due to limited number of reflections observed and also because of the large width of the rings in the pattern. They further reported that in the case of cyclohexanone the cubic lattice of the crystals found at temperature of −55°C does not retain its physical shape at temperatures lower than −55°C. But they did not study the Debye-Scherrer pattern of the crystal at lower temperatures. An attempt has, therefore, been made to study the space group of the crystals of cyclohexanone at −180°C by photographing the Debye-Scherrer pattern of the crystals at that temperature and the results obtained are discussed below.

EXPERIMENTAL

Pure cyclohexanone, distilled under reduced pressure, was used for studying the Debye-Scherrer pattern of the substance at −180°C. The pattern of the crystals at −180°C was photographed by the method described earlier (Krishna Murti and Sen, 1956), using a camera of special design (Biswas, 1958).

A Seifert X-ray tube running at 32 KV, 26 mA was used to photograph the pattern. The X-ray tube was provided with a copper target and a nickel filter was used to cut off the Kβ radiation. An exposure of about 3 hours was sufficient to record the pattern with moderate densities. The radius of the camera

was measured by photographing the Debye-Scherrer pattern of aluminium powder and was found to be 4.5 cms.

RESULTS AND DISCUSSION

The Debye-Scherrer pattern obtained for the crystal at −180°C is reproduced in Figure I. The spacings and the values of $\sin^2\theta$ calculated from the rings of the Debye-Scherrer pattern for the crystal at −180°C are given in Table I, in which the spacings observed by Hassel and Sommerfeldt (1938) for the crystal at −55°C are also included for comparison.

It can be seen from Table I that the structure of crystals of cyclohexanone at −180°C is different from that of the substance at −55°C and also the pattern for the crystal at −180°C does not fit in with a cubic lattice.

Fig. 1 Debye-Scherrer pattern of cyclohexanone at—180°C

Lipson's method (1949) was applied to analyse the pattern and to find out whether the lattice was orthorhombic and it has been found that the crystal actually belongs to orthorhombic system. The values of $\lambda^2/4a^2$, $\lambda^2/4b^2$ and $\lambda^2/4c^2$ deduced from the values of $\sin^2\theta$ are 0.0055, 0.0110 and 0.002605 respectively. The unit cell dimensions of the crystal at −180°C calculated from the above constants are :

$$a = 10.38 \text{ A.U.}$$

$$b = 7.34 \text{ A.U.}$$

and

$$c = 15.09 \text{ A.U.}$$

It can be seen from the Table I that the values of $\sin^2\theta$ calculated from these unit cell dimensions agree well with those observed for the crystal at −180°C.

The density of frozen cyclohexanone at −180°C has been measured by the method used earlier in this laboratory (Biswas and Sirkar, 1957) and found to be 1.136. The number of molecules in the unit cell calculated with this value of density is 8. It can be seen from Table I that there is no restriction for the occurrance of reflections from the planes. The want of restriction leads to the conclusion that the space group is C_h^1 and as the number of asymmetric molecules in the unit cell of this space group is 8, it appears that the molecule of cyclohexanone at −180°C is asymmetric. The structure of the molecule is not known and it can have only a plane of symmetry containing the HCCO group, but the results, mentioned above, show that no such symmetry is utilised by the molecules in forming the crystals

TABLE 1

Debye-Scherrer rings of cyclohexanone at −180°C

Spacings in A.U.		Indices	Values of $\sin^2\theta$ at −180°C	
From Hassel & Sommerfeldt (1938) at −55°C	Observed at −180°C		Observed	Calculated
—	7.54 (w)	002	0.01042	0.01042
—	6.435 (m)	011	0.01410	0.01360
4.98 (vs)	5.15 (s)	200	0.02230	0.02200
4.305 (s)	4.30 (m)	202	0.03200	0.03243
—	4.13 (m)	013	0.03475	0.03444
—	3.77 (m)	004	0.04170	0.04170
—	3.68 (m)	212 020	0.04370	0.04342 0.04400
—	3.56 (w)	021 104	0.04670	0.04660 0 04720
—	3.45 (w)	300, 120	0.04970	0.04950
—	3.26 (vw)	213	0.05590	0.05640
—	3 12 (m)	310	0.06090	0.06050
—	2.905 (m)	105	0.07020	0.07060
2.84 (vw)	2.80 (vw)	015 222	0.07580	0.07610 0.07642
—	2.59 (s)	400	0.08850	0.08800
2.49 (w)	2.26 (w)	206	0.11590	0.11580
—	2.16 (w)	216	0.12650	0.12680
—	2.095 (w)	324	0.13560	0.13520
—	2.00 (w)	330 520	0.14800	0.14850 0.14790
—	1.885 (w)	008	0.16670	0.16670
—	1.755 (m)	142, 522 036, 416	0.19240	0.19190 0.19280
—	1.73 (m)	600, 240	0.19800	0.19800
—	1.685 (w)	242 610	0.20880	0.20840 0.20900
—	1.608 (w)	434	0.22900	0.22870

Hence it can be concluded that the crystal which is cubic at −55°C (Hassel and Sommerfeldt, 1938) has a low temperature modification of lower symmetry at −180°C.

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