An Electron Diffraction Investigation of the Molecular Structure of Antimony Triiodide

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The crystal structure of the addition compound containing antimony triiodide and molecular sulphur in the proportion 1:3 has recently been determined.[1] A reliable comparison of the structure parameters of antimony triiodide with those of the free molecule was desired, and a reinvestigation of the vapour was therefore carried out using the Oslo electron diffraction unit.[2] The distances chosen between diffraction point and photographic plate were 19 and 48 cm and the temperature of the vapour was kept at 195 ± 5°C during exposure. Four of the plates were selected for each distance for the structure determination and the photometric measurements carried out using a Leeds and Northrup recording photometer and oscillating the plates. The data thus obtained were treated as described in previous communications from this institute.[3] The background was worked out using an empirical approach. The intensity curve thus obtained and ranging from $s = 2.50$ to $s = 41.0$ is reproduced in Fig. 1. The radial distribution curve

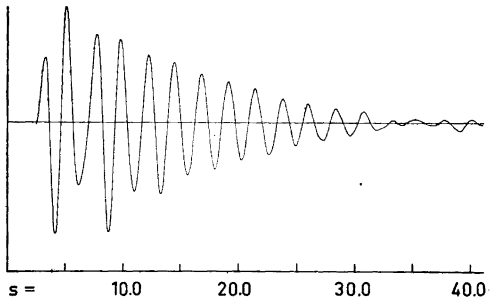

Fig. 1.

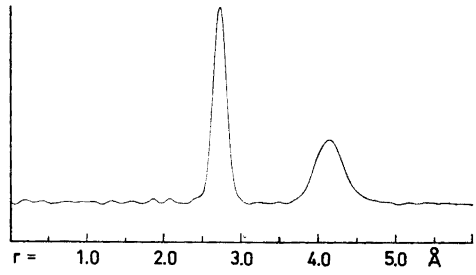

Fig. 2.

presented in Fig. 2 was calculated using an artificial damping factor k equal to 0.0015. The two observed peaks are slightly asymmetrical, with the steepest slope on the shorter distance side. This in probably due to the anharmonicity in the molecular vibration, and for the I—I peak, the effect of the bending vibration is also significant. The mean amplitude of vibration, $u = [(\overline{r-r_0})^2]^{1/2}$ for the Sb—I and I—I distance are 0.0660 and 0.173 Å. The internuclear distances are given in Table 1, where they are compared with the corresponding values for the addition compound. The standard deviations are given in parentheses.

Table 1.

	SbI_3	$SbI_3 \cdot 3S_8$
Distances	Sb—I 2.719 (0.0015) Å	2.747 (0.002) Å
	I—I 4.138 (0.0020) Å	4.101 (0.002) Å

From earlier investigations [4-6] a Sb—I distance of 2.71 Å and a I—Sb—I angle close to 99° appeared to be the most probable.

A lengthening of the Sb—I distance from 2.719 Å to 2.747 Å due to the formation of a bond between iodine and sulphur is thus observed. At the same time the I—I distance is decreased from 4.138 to 4.101 Å, corresponding to a decrease in the I—Sb—I angle from 99.1 to 96.6°. The decrease in the I—I distance may even be greater than this would indicate, because of the effect of the rather strong bending vibration which should lead to a decrease in the measured I—I distance as compared with that expected for the vibrational ground state. It may be added that the distances in the addition compound have not been corrected for bond length errors due to anisotropic atomic vibrations;[7] the correc-

tions are 0.0053 (0.0013) Å and 0.0080 (0.0020) Å, respectively for the Sb—I and I—I distance assuming the antimony triiodide molecule to be a rigid body.

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Received November 6, 1963.