

nylamid,¹ and again indicate the relationship between these *meso*-ionic systems and the isoelectronic sydnones.

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The Gas Phase Electron Diffraction Pattern of Beryllium Borohydride

KRISTEN BRENDHAUGEN, ARNE HAALAND* and DAVID P. NOVAK

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Despite extensive investigations by a variety of techniques¹⁻⁹ there remain some puzzling aspects to the structure of gaseous beryllium borohydride. These are perhaps most clearly brought out by the electron diffraction experiments¹⁻⁴ from which at least two types of intensity curves have been obtained. A possible, but we feel unlikely, explanation for this difference is gross impurities in the solid sample used in one of the studies. A second possibility is that two or more species of gaseous molecule can be obtained from solid BeB_2H_6 in amounts depending on the state of the sample. This explanation gains plausibility from the fact that BeB_2H_6 is known to exist as polymeric chains in the crystal.¹⁰ Indeed one type of diffraction pattern is known to have been obtained from freshly sublimed material kept at liquid N_2 temperature until just before the experiments were performed,³ another from an aged sample.⁴ Moreover, the infrared and Raman spectra of gaseous and matrix isolated BeB_2H_6 have been interpreted as evidence for the presence of two forms of monomeric BeB_2H_6 in equilibrium in the gas phase.⁷

We have carried out experiments designed to test the hypothesis described above. These involve solid samples of different histories and an all-glass nozzle-inlet system to eliminate the possibility of sample decomposition by contact with metal.

The BeB_2H_6 had been prepared by Dr. T. H. Cook at the University of Wyoming from B_2H_6 and $\text{Be}(\text{CH}_3)_2$. All the material used came from the same preparation and had been carefully purified by sublimation.

An all-glass inlet system was designed for Balzers Eldigraph KD-G2 which permitted the reservoir containing the solid sample to be kept outside the diffraction chamber. The diffraction patterns were recorded with a nozzle-to-plate distance of 327.3 mm and an electron wavelength of 0.0585 Å. Sufficient vapor pressure was obtained by submerging the reservoir in an oil bath maintained at 55°C. In order to prevent condensation in the inlet system and particularly at the glass nozzle tip the latter was heated to 60–70°C.

First the scattering pattern was recorded with a sample of BeB_2H_6 consisting of large clear colorless crystals. Then crystalline BeB_2H_6 was distilled into a liquid N_2 cooled cold finger and kept in liquid N_2 until 2 or 3 min before the diffraction pattern was recorded. Then

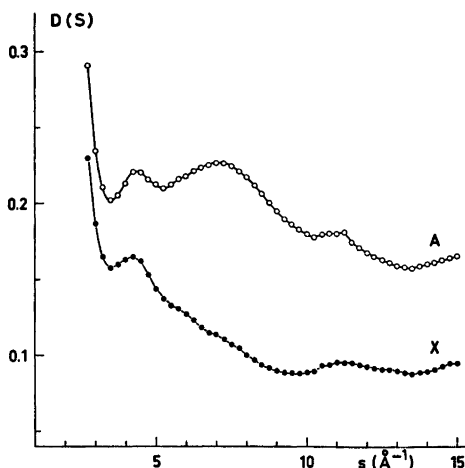


Fig. 1. Gas phase electron scattering patterns of beryllium borohydride. Scattering patterns obtained with crystalline solid sample (X) and with solid sample condensed at liquid N_2 temperature (A).

the liquid N_2 was withdrawn, the reservoir inserted in the hot oil bath and the data recorded as soon as it warmed up.

The difficulties associated with the recording of the diffraction pattern of BeB_2H_3 have been described.⁴ Here we shall only add that the charging effect with the consequent deflection of the primary beam appeared even more pronounced with a glass than a metal nozzle. Nevertheless three reasonably good plates were obtained from each run. The scattering pattern on the three plates obtained in each run were very similar.

The uncorrected optical densities of one plate obtained with the amorphous white solid resulting when gaseous BeB_2H_3 is condensed at liquid N_2 temperature (A) and one plate obtained with a crystalline solid sample (X) are shown in Fig. 1. It is at once clear that the two curves are significantly different. Curve X resembles the intensity curve obtained by Gundersen *et al.*⁴ in that it contains one peak with maximum around $s = 5$ and a broad shoulder on the high s side. Curve A resembles the intensity curve obtained by Almenningen *et al.*³ in that it contains two clearly separated peaks at $s = 4$ and 7 \AA^{-1} , though the latter peak appears to be greater in curve A.

Before proceeding we must point out that there also appears to be a perplexing difference in the "backgrounds" of the two molecular intensity curves in Fig. 1, the background to curve A being higher in the region from about $s = 4$ to about $s = 10 \text{ \AA}^{-1}$. Since the photographs themselves have circular symmetry, it is unlikely that the difference is due to

extraneous scattering. The difference could be explained if it is assumed that the gas jet contained different amounts of the constituent atoms, B, Be, and H, in the two experiments leading to a real difference in the atomic intensity. But this appears unlikely since no solid residues indicating decomposition, was observed in either run, and since the plates obtained in each run were consistent. Another possible explanation could be luminescence from the scattering region during experiment A.

Whatever the reason for the difference in backgrounds, it is clear from the difference in the diffraction patterns obtained that at least two different species of gaseous molecule may be obtained from solid BeB_2H_3 and that their relative amounts depend on the state of the solid sample.

Since it cannot be taken for granted that each of the two or more species have the exact composition " BeB_2H_3 ", reliable information about the chemical composition of the gas jet is needed before firm conclusions regarding structure can be drawn from the electron diffraction data.

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