

Infrared Spectra of Methylboranes. The Examination of Unstable Substances using Multiple-scan Interference Spectroscopy

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DURING a study of diborane-trimethylboron equilibria we attempted to characterize various compounds isolated from equilibrium mixtures by comparing their infrared spectra with those reported previously.^{1,2} Certain discrepancies were noted, however, which indicate that further examination of the infrared spectra of alkyl-diboranes is warranted.

Methylated diborane equilibrium mixtures were carefully fractionated using the method of Fehlner and Koski,³ yielding fractions of the order of 10^{-7} mole. A small infrared cell was attached to the fractionation train. A selected, well-resolved fraction, or a portion of one, was frozen out in a liquid nitrogen-cooled capillary attached to the cell. The sample trapped within the cell could then be

vaporized or re-frozen at will. Infrared spectra over the range $2500\text{--}250\text{ cm}^{-1}$ were recorded at approx. 18 cm^{-1} resolution using a Block Engineering Model 200 interference spectrometer. The instrumentation is described in detail elsewhere.^{4,5}

Many of the spectra of supposedly pure methyl-diboranes recorded rapidly with the interference spectrometer differed significantly from those reported earlier^{1,2} or from those presently recorded with a Perkin-Elmer Model 521 spectrophotometer. The differences are attributed to the contamination and decomposition of samples during preparation, fractionation, or trapping steps of previous studies and, significantly, during the course of recording a spectrum. The spectra in the Figure show such a time effect.

A pure fraction, considered to be *cis*-1,2-dimethyldiborane was trapped by freezing it within the cruciform infrared cell. The refrigerant was removed, and 30 sec. thereafter the multiple-scan interference spectrometer was activated. A total of 50 consecutive scans, each of 1 sec. duration, were made and the resulting cumulative signal was processed^{4,5} to result in spectrum A of the Figure. The gaseous sample had consequently been at or near room temperature at a pressure of several hundred torr for approx. 80 sec. subsequent to the initial trapping. The sequence of spectra B—G were obtained with a second sample of the same compound by similar methods, but after the sample had been at or near room temperature for various periods of time. Significantly, spectra F and G are similar to a P.-E. 521 spectrum recorded in a 30-min. scan, using a fresh but much larger sample of the same compound.

The spectra in the Figure show that large and obvious changes occurred with the passage of time. For example, the band near 1600 cm^{-1} ascribed to a B—H¹ (bridge) stretching mode^{1,2} decreased significantly in intensity, indicating a disruption of the diborane skeleton. The decomposition products then gave rise to misleading spectra. Consequently, it is likely that trace A bears a close resemblance to the true spectrum of the pure compound. However, trace A must still be taken as an approximation, although a close one, because the sample must have changed slightly during the 50 sec. used to record the data. More serious distortions of band intensities and positions can, of course, be expected in spectra recorded with slow-scanning dispersion instruments. Similar, although not as pronounced, effects were found with the spectra of other pure compounds recorded with the interference spectrometer. The spectra of the six possible methyldiboranes will be discussed elsewhere.

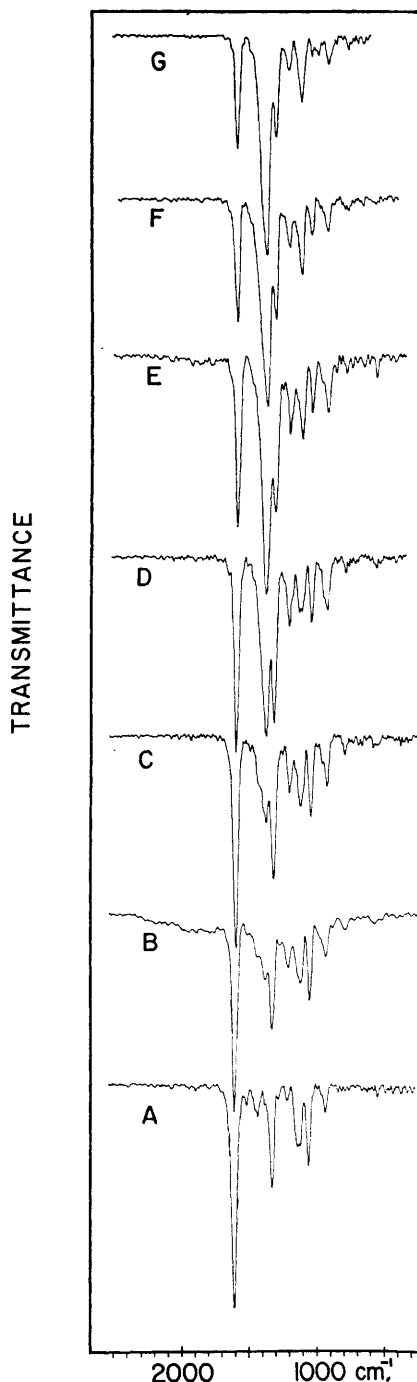


FIGURE. Effect of time on spectra. The total time in minutes the sample was at or near room temperature was: A, 1—5; B, 4; C, 7; D, 10; E, 13; F, 20; G, 40. Spectra A resulted from 50 scans of the interference spectrometer; 100 scans were taken for each of the other spectra. The ordinates are arbitrary and are displaced.

The discrepancies and changes of infrared spectra suggest that further consideration be given to the purity of methylboranes, as far as isolation procedures and the validity of physical measurements are concerned. Also, with initially pure alkylboranes and other compounds of limited stability in general, infrared spectra recorded with conventional dispersion spectrophotometers might be misleading. The scanning rate of such instruments can also be expected to be too low to permit the useful study of alkylborane disproportionation reactions, contrary to the suggestion of

Lehmann *et al.*,² unless the reactions were so slow that no significant change occurred in the composition of the sample during the course of the scan. As suggested by the evidence in the Figure an interference spectrometer capable of examining samples in the micromole range within seconds^{6,7} is more suitable for such purposes.

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¹ W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, 1960, **32**, 1088, 1786; 1960, **33**, 590; 1961, **34**, 476, 783.

² W. J. Lehmann, C. O. Wilson, J. F. Ditter, and I. Shapiro, "Advances in Chemistry", No. 32, American Chemical Society, Washington, D.C., 1961; pp. 139 ff.

³ T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, 1964, **86**, 581.

⁴ M. J. D. Low and I. Coleman, *Spectrochim. Acta*, 1966, **22**, 369.

⁵ M. J. D. Low, *J. Chem. Educ.*, 1966, **43**, 637.

⁶ M. J. D. Low, *Chem. Comm.*, 1966, 371.

⁷ M. J. D. Low and S. K. Freeman, *Analyt. Chem.*, in the press.