[BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Infrared Emission of $B_2O_3(g)$

BY DAVID A. DOWS AND RICHARD F. PORTER

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The emission spectrum of $B_2O_3(g)$ in the vicinity of 2000 cm.$^{-1}$ has been measured. The sample consisted of B_2O_3 in an alundum tube heated to 1500–1750°K. The effect of substituting B^{10} was studied. The isotope shift is in agreement with that predicted by the bipyramidal (D_{3h}) model of B_2O_3.

Recent mass spectrometric studies[1,2] have shown that liquid boric oxide vaporizes predominantly as $B_2O_3(g)$ molecules, while concentrations of such species as BO(g) and $B_2O_2(g)$ in the vapor are small provided the liquid is vaporized under non-reducing conditions. It is of interest to determine the structure of the $B_2O_3(g)$ molecule. In the crystal, each boron atom has been reported to be surrounded by a tetrahedron of oxygen atoms,[3] while in the liquid there still appears to be some question as to the structure.[4,5] Since the vapor pressure[1] can be brought to about one millimeter at 1700°K. it has been possible to observe the infrared emission of the gas.

Experimental

Boric oxide was heated in an alundum tube furnace by two globars, to a temperature of 1500–1750°K. The temperature was measured with a platinum–platinum-rhodium thermocouple in contact with the outside of the tube. The optical path length through the vapor was roughly 10 cm. Boric oxide is liquid throughout the temperature range studied.

Alternatively, boric oxide was prepared by oxidizing boron in the tube, the ends of which were at all times open to the atmosphere. The results were identical to those obtained in the first method. This method was used to prepare $B_2^{10}O_3$ from pure B^{10}.

The spectra were obtained with a Perkin–Elmer model 13 spectrometer, using single beam, and with the tube furnace as the source. Dispersing elements were a sodium chloride prism and a Merton-N.P.L. 7500 line per inch grating, the latter used in place of the Littrow mirror and with a potassium bromide prism in place to maintain the geometry of the optics.

Results

The emission spectrum of natural $B_2O_3(g)$ containing 19% B^{10} and 81% B^{11} consisted of one band, at 2013 cm.$^{-1}$, with a shoulder at 2059 cm.$^{-1}$. There appeared to be another band at 3770 cm.$^{-1}$, but this region was extremely complex: H_2O absorption lines were superimposed on the small amount of blackbody radiation from the furnace walls which entered the slit despite all efforts to exclude it. Thus the existence of this high frequency band is doubtful, though it should be noted that it apparently was shifted to higher frequency upon isotopic substitution.

When 97% B^{10} [6] was put in the furnace and oxidized to B_2O_3, an emission peak at 2114 cm.$^{-1}$ appeared. Small amounts of boric oxide with the natural abundances of the boron isotopes were then added and spectra were taken after each addition. Three peaks (at 2114, 2059 and 2013 cm.$^{-1}$) were observed, as expected for a molecule containing two boron atoms, and the intensities of the peaks changed as expected with increasing amounts of B^{11}.

The emission was studied over the spectral range 4000 to 700 cm.$^{-1}$, and except for the bands mentioned above no features were seen, even at the highest temperature, 1750°K.

Discussion

The appearance of the emission as a function of isotopic concentration clearly indicates that the emitter contains two boron atoms. This is the only experimental proof that its identity is B_2O_3, aside from the mass spectrometric data. The uncertain band at about 3770 cm.$^{-1}$ suggested the presence of hydrogen in the emitter. However, alternately flowing dry oxygen and water vapor over the sample failed to change the intensity of emission except for a slight flushing effect. This indicates the absence of hydrogen in the molecule. The lack of effect of oxygen on the intensity rules out B_2O_2 as the emitting species, since this molecule can exist only in a reducing atmosphere.[1] Since no other reasonable molecules with two borons can be thought of, it is concluded that B_2O_3 is the emitter. The band at about 3770 cm.$^{-1}$ may be a combination band of B_2O_3.

At temperatures above 1200° the vapor in the furnace also emitted in the green region of the spectrum. This radiation was photographed with a small glass spectrograph and was found to be due to the bands associated with $B_2O_3(g)$ by Soulen and Margrave.[7] The intensity of the green bands increased with the infrared emission as the temperature of the tube was raised.

The intensity of infrared emission was measured over the temperature region mentioned, and a plot of log IT *vs.* $1/T$ gave a heat of vaporization for $B_2O_3(g)$ of about 60 kcal. The position of the thermocouple outside the tube made temperature measurement quite uncertain, so this value may not be considered accurate. It may be compared with the value 78 kcal. obtained elsewhere.[7,8]

It is perhaps of value to comment that the optical density of the sample is probably low enough so that the emission intensity will be directly proportional to the density of emitters, since the rotational lines are broadened by one atmosphere total pressure. This is not necessarily always the case.[9]

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(1) M. G. Inghram, R. F. Porter and W. A. Chupka, *J. Chem. Phys.*, in press.

(2) P. Bradt, NBS Report 3016, Jan. 1, 1954.

(3) Sven V. Berger, *Acta Chim. Scand.*, **7**, 611 (1953).

(4) K. Fajans and S. W. Barber, THIS JOURNAL, **74**, 2761 (1952).

(5) J. D. Mackenzie, *J. Chem. Phys.*, **24**, 925 (1956).

(6) Obtained from U. S. Atomic Energy Commission, Oak Ridge, Tenn.

(7) J. R. Soulen and J. L. Margrave, private communication, 1956. J. R. Soulen, P. Sthapitanonda and J. L. Margrave, *J. Phys. Chem.*, **59**, 132 (1955).

(8) R. Speiser, S. Naraitch and H. C. Johnston, THIS JOURNAL, **72**, 2578 (1950).

(9) See, *e.g.*, S. S. Penner, H. M. Ostrander and H. S. Tsien, *J. Appl. Phys.*, **23**, 256 (1952).

The isotope shift observed in going from the molecule containing only B^{10} to that containing only B^{11} was 101 ± 10 cm.$^{-1}$. Assuming a bipyramidal model (of symmetry D_{3h}), the isotope ratio for the A''_2 frequency and for the E′ frequency involving predominantly the boron atom motions is calculated to be 1.045, or a shift of 91 cm.$^{-1}$. The agreement is reasonable, and in particular much better than with any less condensed structure which might be proposed for B_2O_3. For example, models such as linear or bent O=B—O—B=O predict isotope shifts of 25 cm.$^{-1}$ or less.

A D_{3h} model predicts three infrared active fundamental frequencies, of which the observed band, at 2013 cm.$^{-1}$ is presumed to be of symmetry E′ and to involve primarily the B atoms. The other fundamentals will probably occur at considerably lower frequencies. It is estimated that under the conditions used in this study, an emission band *with the same absolute absorption intensity as the band at 2013 cm.*$^{-1}$ would not be detected if it occurred below 1000 cm.$^{-1}$ because of the frequency-cubed factor in the emission intensity. This may explain the absence of other bands, and indicates a need for absorption measurements.

ITHACA, N. Y.

[CONTRIBUTION NO. 460 FROM THE DEPARTMENT OF CHEMISTRY AND INSTITUTE FOR ATOMIC RESEARCH, IOWA STATE COLLEGE]

The Separation of Lithium from Alkali Metal Ions[1,2]

BY GERALD A. GUTER AND GEORGE S. HAMMOND

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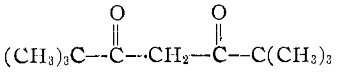
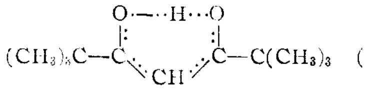
It has been found that dipivaloylmethane, DPM, binds lithium ions selectively and firmly under alkaline conditions. By use of an ether solution of the reagent as an extractant, it is possible to determine lithium in the presence of the other alkali metals. A small correction is necessary if large amounts of sodium are present.

Despite the increasing use of organic chelating agents in the separation and determination of metal ions, no reagents have heretofore been found which permit the separation of lithium from other metals except by tedious procedures which involve the stepwise removal of other ions from lithium. We have found that a new chelating agent, dipivaloylmethane, DPM (I), is applicable to the separation of lithium from sodium and potassium.



$$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-C(CH_3)_3$$

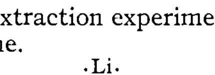
I



(1)

II

This compound, which is found to exist almost entirely in the form of the symmetrical enolic modification II in the pure liquid and in organic solvents, binds lithium firmly in the form of a lithium chelate which is soluble in ether and other organic solvents but is sparingly soluble in water. It is very probable that the chelate has structure III and that the specificity for the lithium ion is due to the small radius of that ion (0.60 Å.)[3] as compared with the sodium and potassium ions. In keeping with this view is the fact that sodium gives a minor interference in extraction experiments whereas potassium gives none.



III

We have found that ether is the best of the common organic solvents for use in extraction procedures. As is indicated by the data presented in the Experimental section, it is possible to extract substantially all of the lithium from alkaline aqueous solutions under conditions which lead to the removal of only minor amounts of sodium. Because only limited amounts of DPM were available at the outset of these studies, a large number of orienting experiments were carried out (and are reported) under conditions which were recognized not to be ideal for quantitative procedures.

Experimental

Dipivaloylmethane.—The compound was prepared by the method of Hauser and Adams.[4] It forms a white, gelatinous precipitate when shaken with lithium hydroxide solutions. The chelate is readily soluble in ether at room temperature and only slightly soluble in water. DPM dissolved in benzene, petroleum ether, butyl ether, carbon tetrachloride and chloroform would not extract the lithium chelate from alkaline solutions.

The diketone, a colorless oil which boils at 94.0–94.5° at 20 mm., has an absorption maximum at 275 mμ, which is attributed to the cyclic enol form. The molecular extinction coefficients at the maximum in three solvents are as follows: acetonitrile, 1.09 × 10^4; isoöctane, 1.27 × 10^4; water, 0.19 × 10^4; 0.1 *N* NaOH, 1.60 × 10^4 (max. = 294 mμ).

Acidity Constant of DPM.—The pK_a in water was determined spectrophotometrically at 25.0° and calculated[5] from the data in Table I.

Extraction Experiments.—An ether solution of DPM was shaken with aqueous solutions of metal ion. The amount of metal chelate in the ether was determined either by nonaqueous titration or by hydrolyzing an aliquot of the ether with neutral water and titrating the water–ether mixture as metal hydroxide. For the non-aqueous titrations an ali-

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] Abstracted from the doctoral dissertation of Gerald A. Guter. Presented at the National Meeting of the American Chemical Society, September, 1954.

[3] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, 2nd Ed., p. 346.

[4] C. R. Hauser and J. T. Adams, THIS JOURNAL, **66**, 1220 (1944).

[5] The absorbance of the solution containing no OH^- was used to calculate the extinction coefficient, ε, of the diketone at 295 mμ. The extinction coefficient, ε′, of the anion was estimated from a plot of log I_0/I *vs.* OH^- concentration as being 1.58 × 10^4 at 295 mμ. The data were then used to solve the two equations

$$\log(I_0/I)_{295\ m\mu} = \epsilon[AH] + \epsilon'[A^-]$$
$$1 \times 10^{-4} = [AH] + [A]$$