[CONTRIBUTION NO. 50 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

The Structure of the Organoboron Oxides

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In the preceding paper it was stated that the dehydration of the organoboric acids increased their molecular weights, indicating that the products of the reaction, the organoboron oxides, do not have the simple boronyl structure RBO arbitrarily assigned to them. Consequently an elucidation of their molecular structure is necessary in order to understand their behavior. The molecular weights of several organoboron oxides are recorded in the table. The oxides were prepared by heating the corresponding boric acid derivative for thirty-three hours in a drying oven held at 110°. The products were then analyzed for boron and their molecular weights determined cryoscopically in nitrobenzene.

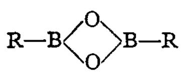
TABLE I

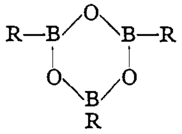
Derivative of boron oxide	% Boron Calcd.	% Boron Found		Mol. wt. Calcd.	Mol. wt. Found	
Phenyl	10.42	10.25	10.29	103.9	307	272
p-Tolyl[a]	9.18	9.15	9.11	117.9	312	249
m-Chlorophenyl[a]	7.82	7.65	7.59	138.3	581	573
p-Chlorophenyl[a]	7.82	7.73	7.69	138.3	406	462
p-Bromophenyl	5.92	5.79	5.68	182.8	331	342
α-Naphthyl[a]	7.03	7.38	7.24	153.9	391	435

[a] The acids from which these oxides were prepared were obtained from the Chemical Laboratory of the University of California through the courtesy of Dr. D. L. Yabroff.

Conclusions

A consideration of the data shows that the organoboron oxides cannot have the simple formula RBO. The variations in the values for duplicate molecular weight determinations probably indicate that mixtures of double, triple and perhaps higher molecular weights are produced. Without doubt the structure of the oxides may be compared to that of boron oxide (boric anhydride) in which at least one oxygen bridge is present (OBOBO). Since boron oxide as ordinarily prepared is a glass it is likely that it has a molecular weight higher than boric oxide, and that a number of boron atoms are linked together through oxygen. Such a comparison leads to the suggestion of the formulas below rather than to merely associated molecules.





The trimolecular formula is similar to those accepted for the trimers of the aldehydes, thioaldehydes and thioketones.

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The Polarity of the Nitrogen Tetroxide and Nitrogen Dioxide Molecules

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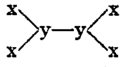
The structure of the molecules nitrogen tetroxide and nitrogen dioxide is incompletely understood at the present time, in spite of renewed activity in the investigation of the infra-red absorption spectra involved.[1] Thus, in the case of nitrogen tetroxide the data of Sutherland were interpreted to be exactly in accord with the expectation for a molecule of the type  in which all six atoms are co-planar, but Harris and King found some features of the spectrum which seemed to be in favor of the existence of molecules where the NO_2 groups do not lie in the same plane. The nitrogen dioxide molecule is usually assumed to be triangular rather than linear in shape, but the value of the O–N–O angle is still a matter of some dispute.[2]

There exists a somewhat similar situation in the interpretation of the vapor dielectric constant and density data to give the polarity of these two molecules. Zahn[3] has understood his observations to require a higher electric moment for nitrogen tetroxide as compared to that for the nitro-

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[1] (a) Sutherland, *Proc. Roy. Soc.* (London), **A141**, 342, 535 (1933); (b) Schaffert, *J. Chem. Phys.*, **1**, 507 (1933); (c) Strong and Woo, *Phys. Rev.*, **42**, 267 (1932); (d) Harris and King, *J. Chem. Phys.*, **2**, 51 (1934); (e) Cassie and Bailey, *Nature*, **131**, 239 (1933).

[2] Sutherland, *Proc. Roy. Soc.* (London), **A145**, 278 (1934).

[3] Zahn, *Physik. Z.*, **34**, 461 (1933).