above in the case of boron trimethyl the carbon radius in this structure would be about 0.10 Å. less than the tetrahedral radius. In resonance with the triple-bonded structure the carbon–oxygen distance would be unaffected, but the single bond distance between tetrahedral boron and carbon atoms would be decreased by about 0.08 Å. With this allowance the observed boron–carbon distance gives a boron radius of 0.88 Å.

The values for the boron radius listed in Table VI lie within 0.04 Å. of 0.89 Å. with two exceptions. In the first, boron trimethyl, the bonds are of a different type from those in the other compounds; and in the second, boron trifluoride, the anomalies observed in other fluorides make it difficult to interpret the observed distance with any assurance. The general agreement among the other data lends support to the value first obtained by extrapolation from the other first row elements. In the three compounds in which boron–boron distances have been observed there exists an insufficient number of electrons to form electron-pair bonds in every bond position. While this deficiency undoubtedly affects the character of the bonds, it is not evident that the bond distances are materially affected since the average of the three observed radii is 0.89 Å.

We are indebted to Professor Anton Burg of the University of Chicago for the sample of boron trimethyl, to Dr. S. H. Bauer for data on triborine triamine, borine trimethylammine, and borine carbonyl, and to Professor Linus Pauling for consultation and advice.

Summary

The electron diffraction investigation of the molecular structures of boron trimethyl, trifluoride, trichloride, and tribromide shows that these molecules are planar with the distances B–C = 1.56 ± 0.02 Å., B–F = 1.30 ± 0.02 Å., B–Cl = 1.73 ± 0.02 Å., and B–Br = 1.87 ± 0.02 Å., respectively.

These data together with those from six other boron compounds listed in Table VI support a value of 0.89 Å. for the single bond radius of boron surrounded by an octet of electrons and of 0.79 Å. for boron with only six electrons.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Photo-oxidation of Acetone Vapor

BY PAUL FUGASSI[1]

It was observed that when acetone vapor, containing some oxygen, is exposed to ultraviolet light (3130 Å.), a sharp change from blue fluorescence to green fluorescence occurs when all the oxygen is consumed.[2] This test was made the means of analyzing for traces of oxygen.[3] The work has been extended to include a measurement of the quantum efficiency of the photo-oxidation.

A small rectangular cell of quartz was equipped with a side chamber holding several thin-walled bulbs ranging from 0.4 to 1.0 cc. in volume. The bulbs had been sealed previously to a vacuum line and filled with air at varying pressures.

The air bulbs and the magnetic hammer were placed in position and the cell was filled partially with purified acetone and evacuated till only a few drops of liquid remained. The sealed cell was then placed in a thermostat at 25°, and the vapor was radiated with a beam of light of 3130 Å. from a capillary mercury arc lamp and a large monochromator.[4]

Usually an exposure for one to two minutes was sufficient to change the fluorescence of the vapor from blue to green, showing that most of the oxygen had been pumped off.

The bulbs of oxygen were then broken one at a time and the period of radiation necessary to change the color from blue to green was measured for each bulb. The data are listed in Table I.

The energy values employed in the calculation of ϕ were measured with an integrating thermopile which had been calibrated against a standard lamp from the U. S. Bureau of Standards. The transmission of the reaction cell alone was determined in each experiment by taking light in-

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[1] Present address: Department of Chemistry, Carnegie Institute of Technology.

[2] Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933).

[3] Damon, *Ind. Eng. Chem., Anal. Ed.*, **7**, 133 (1935).

[4] Heidt and Daniels, THIS JOURNAL, **54**, 2382 (1932).

TABLE I

PHOTO-OXIDATION OF ACETONE

Partial pressure of oxygen, mm.	Time, mm.	Molecules per quantum, ϕ
0.11	10	0.23
.24	17	.30
.53	58	.26
.76	81	.24
1.57	220	.19
	Average	0.24

tensity measurements with a duplicate "dummy" cell substituted for the reaction cell.

The data are shown graphically in Fig. 1, where the straight line shows that the time required to remove the oxygen is directly proportional to the concentration of oxygen. The intensity of light and the partial pressure of acetone were maintained constant. The rate of photo-oxidation is seen to be independent of the concentration of oxygen. A zero-order reaction with respect to the non-absorbing molecule has been noted for many photochemical reactions.[5]

It is interesting to note that this low quantum yield is the same as that obtained for the decomposition of acetone.[2] Experiments by Mr. David F. Mason in this Laboratory have shown that the ratio of oxygen consumed to acetone oxidized is approximately unity although the products of the photo-oxidation are complex. The factors which determine the number of activated molecules or fragments of molecules appear to be the same in both cases. An activated molecule (or fragment) will react with oxygen if oxygen is present, otherwise, it will produce decomposition.

Additional experiments were tried with electrical activation using a small Tesla coil. Acetone in an ordinary Pyrex tube was evacuated and cooled with salt and ice giving a vapor pressure of about 25 mm. When the tube (without electrodes) was touched with the Tesla coil, a blue fluorescence was produced when oxygen was present and a green fluorescence when oxygen was absent. The Tesla coil technic is much simpler, and it is satisfactory in showing whether or not oxygen is present, but it is not practical for determining the amount of oxygen, because the time for the color change cannot be determined quantitatively. In these experiments the oxidation induced by the electrical discharge was roughly 360 times faster than the photo-oxidation using the monochromator. Another disadvantage of the electrical method of analysis for oxygen lies in the fact that the colored discharge is quenched by the addition of about 10 mm. more gas, whereas the fluorescence produced by the ultraviolet light is only slightly diminished by an atmosphere of added gas.

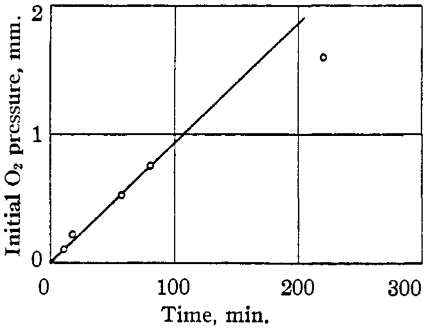

Fig. 1.

The author is glad to acknowledge the suggestions for this work given by Professor Farrington Daniels and financial aid given by the Wisconsin Alumni Research Foundation.

Summary

1. In the photo-oxidation of acetone vapor 0.24 mole of oxygen is consumed for each quantum of ultraviolet light absorbed by the acetone. Assuming that one molecule of oxygen reacts with one molecule of the acetone, the quantum yield for the oxidation of acetone is the same as that for its decomposition.

2. The oxidation of acetone vapor is produced in a similar manner in an electrical discharge.

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[5] Griffith and McKeown, "Photo-processes in Gaseous and Liquid Systems," 1929, p. 401.