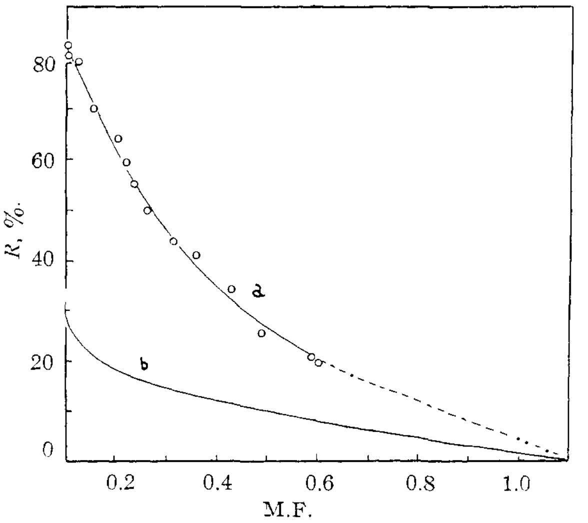

Fig. 1.—Retention of solid ethyl bromide (curve "a") and liquid ethyl bromide (curve "b") as a function of the molar fraction of bromine.

The purpose of experiment (a) was to determine whether free organic radicals were trapped in the solid. The constancy of the retention indicates either that such radicals do not exist or, that they react before mixing with the scavenger solution. The reproducibility of the results obtained using the second method of freezing bromine–ethyl bromide mixtures was checked by repeating a number of experiments at the same bromine concentration. No variations beyond statistical limits were observed, even though the freezing time varied from 3 to 5 minutes.

These preliminary results show that the drop in retention caused by the addition of small quantities of bromine is less sharp than that observed in liquid ethyl bromide (Fig. 1b). To clarify the nature of the processes involved we are now carrying out experiments to identify the radioactive products obtained and to determine the comparative behavior of the bromine isotopes produced by (n, $\gamma$) processes.

The author wishes to thank Professor H. Halban (Paris) for encouragement and support, to Professor J. Willard (Wisconsin) and Dr. P. F. D. Shaw (Oxford) for helpful discussions.

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## RHOMBOHEDRAL ELEMENTAL BORON

*Sir:*

The simultaneous occurrence of two widely dissimilar external forms for single crystals of pure boron growing[1] on a hot filament was thought[1,2] for a time to reflect true structural polymorphism, but comprehensive diffraction studies[3] show that, at least in the work cited,[1] a single structural type is represented: namely, the atomic arrangement based upon a fifty-atom *tetragonal* unit earlier described.[2] That there exists, nevertheless, a second, and probably more commonly obtained modification of boron has seemed certain from published powder diffraction data. For example, the interplanar spacings listed[4] for prominent powder lines given by a sample of better than 99% purity (unspecified method of preparation) are wholly incompatible with our tetragonal cell. Recently we have obtained from independent sources two preparations of boron briefly characterized as follows: the stated purities are 99.4 and 99.5% B but the preparative chemical methods are withheld; both are aggregates of small single crystals resulting from crystallization of the melt, and both afford specimens suitable for single crystal study; and they give a common powder diagram which includes the lines listed by Godfrey and Warren.[4] Dr. S. Geller of the Bell Telephone Laboratories provided us with Preparation I. Amorphous boron, supplied by Cooper Metallurgical Associates, was melted partially in a "Heliarc" furnace and allowed to crystallize in a helium atmosphere by E. Corenzwit of the Bell Laboratories. Preparation II, received within the fortnight, came to us from the United States Borax & Chemical Corporation through the good offices of Professor A. W. Laubengayer.

Oscillation, Weissenberg, and precession photographs of single crystals from Preparation I establish a *rhombohedral* lattice having $a = 10.12$ Å, $\alpha$ 65°28′; the associated triply primitive hexagonal cell has $A = 10.95$, $C = 23.73$ Å, accurate to 0.2%. The experimental density, 2.35 ± 0.01 g./cc., is equally consistent with 107 or 108 atoms within the rhombohedral unit. The diffraction symmetry and lack of glide plane vanishings indicate $R\bar{3}m$, R32, or R3m as the space group. Spectrometrically measured intensity data (using both Cu K$\alpha$ and Mo K$\alpha$ radiations) have been obtained for two zones, *i.e.*, with the hexagonal $A$ and rhombohedral $a$ as zone axes. The statistical distribution of intensities is centrosymmetric[5] for the first zone, hypercentric[6] for the second, thus supporting the unique choice of $R\bar{3}m$ as the space group. We note that boron carbide[7] also crystallizes in $R\bar{3}m$, with $a = 5.19$ Å, $\alpha = 65°18'$ so that all lattice translations are approximately half the corresponding values in rhombohedral boron. However, there is no suggestion in the boron data of a pseudo-unit comparable in volume or obviously related in structure to the boron carbide unit. Although undoubtedly belonging to a more complex structural type, our rhombohedral boron affords intensity data showing little or no evidence for the presence of the large and variable concentrations of short-range defects which seem to characterize[3] all actual specimens of tetragonal boron as grown

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(1) A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

(2) J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).

(3) J. L. Hoard, R. E. Hughes and D. E. Sands, to be submitted to THIS JOURNAL.

(4) T. N. Godfrey and B. E. Warren, *J. Chem. Phys.*, **18**, 1121 (1950).

(5) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(6) H. Lipson and M. M. Woolfson, *ibid.*, **5**, 680 (1952).

(7) H. K. Clark and J. L. Hoard, THIS JOURNAL, **65**, 2115 (1943); G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U.R.S.S.*, **32**, 432 (1941).

in the large thermal gradient normal to the surface of the hot filament. We are confident of success in determining the atomic arrangement in rhombohedral boron when we shall have completed the quantitative measurement of the numerous *h k l* intensity data.

Thanks are due Dr. Gordon S. Smith and Mr. D. B. Sullenger for taking some of the photographs.

[8] Now at Radiation Laboratory, University of California, Livermore, California.

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## THE PREMIXED OZONE-CYANOGEN FLAME[1,2]

*Sir:*

The pure ozone decomposition flame to oxygen[3] and the premixed ozone–hydrogen flame[4] were recently described. A premixed pure ozone flame with a *carbon* compound, namely, cyanogen, has now been achieved.

It was first established, in static experiments, that cyanogen and pure ozone can be mixed and stored for a considerable time without reaction. Thus the mixture $3(CN)_2 + 4O_3$ was kept in a 100-cc. Pyrex vessel, at 1000 mm. at 0° for 2.0 hours with no noticeable change in pressure; after this time cyanogen was frozen out at −78°, the $O_3$ pumped off and the volumes of the separated gases were found to be essentially equal to their original volumes. Identical results were obtained with the mixture $3(CN)_2 + 2O_3$.

The results of our laminar flame measurements are given in Fig. 1 and compared with $O_2$. Burning velocities of $(CN)_2$–$O_3$ mixtures containing 25.0, 33.3, 40.0 and 100.0 mole % $O_3$ were, respectively, 60 ± 3, 242 ± 12, 285 ± 6 and 420 ± 6 cm./sec. A mixture beyond the stoichiometric point, on the $O_3$-rich side, containing 50.0 atom % O detonated immediately upon ignition. The same apparatus was used as in the $O_3$–$H_2$ measurements[4]; the desired mixture was stored over water in a Pyrex gas holder, dried by passing through a trap cooled to −19°. ($H_2O$-content of gas = 0.11 mole %) and ignited by a hot Pt-wire from an aluminum burner tip (i.d. = 0.66 mm.). Since flame velocities of $(CN)_2$–$O_2$ flames are increased by traces of $H_2O$,[5] we used the same apparatus and the same conditions to measure $(CN)_2$–$O_2$ flames.

The shapes of the three $O_3$ flames described are widely different.[3,4] Although the $O_3$-rich side of the $O_3$–$H_2$ and $(CN)_2$–$O_3$ systems could not be explored due to their detonability, it is unlikely that the latter system will show the high peak of the $O_3$–$H_2$ system. All $(CN)_2$–$O_3$ mixtures burn comparatively slowly and even at the $2CO + N_2$ (*i.e.*, = 33.3 atom % O) point, the velocity is substantially below that of pure ozone.

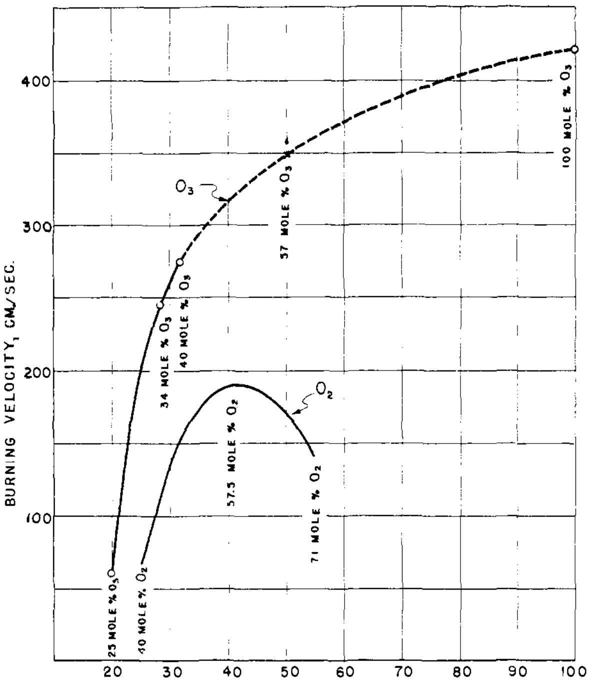

Fig. 1.—Burning velocities of $O_3 + (CN)_2$ and $O_2 + (CN)_2$ mixtures (at 0° initial gas temperature and 1 atm.).

All flames on the $(CN)_2$-rich side up to and including the mixture burning to $2CO + N_2$ burn uniformly, noiselessly, as brightly as an electric arc and with a pink-violet color. The $2(CN)_2 + O_3$ flame is particularly bright and has a different characteristic blue green color.

Their temperatures can be calculated[6] with great accuracy (± 2°K.); one of them is compared with the corresponding $O_2$ flame[7,8] below

| Gas composition | °D. | |
|---|---|---|
| | 1.0 Atm. | 10.0 Atm. |
| $(CN)_2 + O_2$ | 4856 | 5025 |
| $3(CN)_2 + 2O_3$ | 5208 | 5506 |

In these calculations the value of $\Delta H_f^{25°}$ for ozone = +33.98 and for cyanogen = +73.85 kcal./mole was used.

[1] Paper presented at the Sixteenth International Congress on Pure and Applied Chemistry, Paris, France, July 18–24, 1957.

[2] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF-18(600)-1475.

[3] A. G. Streng and A. V. Grosse, THIS JOURNAL, **79**, 1517 (1957).

[4] A. G. Streng and A. V. Grosse, *ibid.*, **79**, in press (1957).

[5] R. S. Prokaw and R. N. Pease, *ibid.*, **75**, 1454 (1953).

[6] Acknowledgment is made to the Reaction Motors, Inc., and to Mrs. Marianne Stoltenberg for their help with some of the calculations.

[7] J. B. Conway, R. H. Wilson, Jr., and A. V. Grosse, THIS JOURNAL, **75**, 499 (1953).

[8] J. B. Conway, W. F. R. Smith, W. J. Liddell and A. V. Grosse, *ibid.*, **77**, 2026 (1955).

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## DERIVATIVES OF 1-THIA-4,5-DIAZACYCLOHEPTA-2,4,6-TRIENE. III. CORRECTIONS AND ADDENDUM

*Sir:*

As a result of the unintentional return of an incompletely corrected proof, there are certain errors in our recent publication dealing with isomerism of derivatives of dibenzo-1-thia-4,5-

[1] H. H. Szmant and Y. L. Chow, THIS JOURNAL, **79**, 4382 (1957).