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.

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RECEIVED JULY 30, 1957

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.

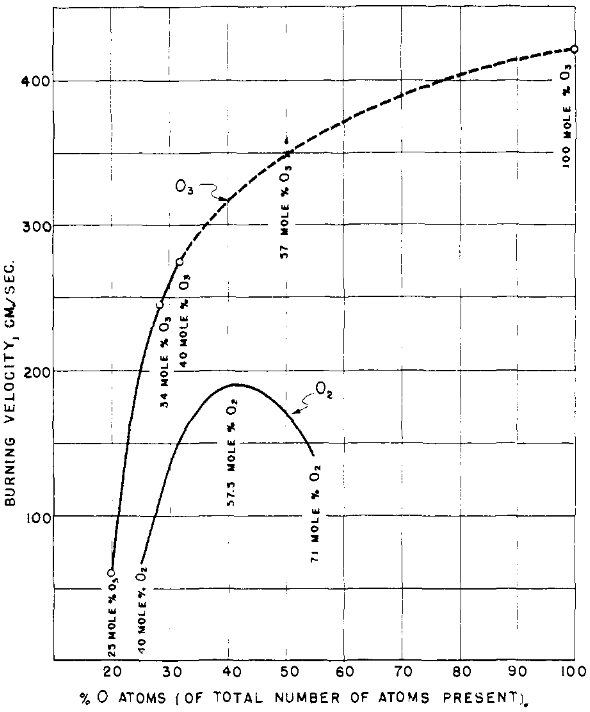

Fig. 1.—Burning velocities of $O_3 + (CN)_2$ and $O_2 + (CN)_2$ mixtures (at 0° initial gas temperature and 1 atm.).

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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RECEIVED AUGUST 26, 1957

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-

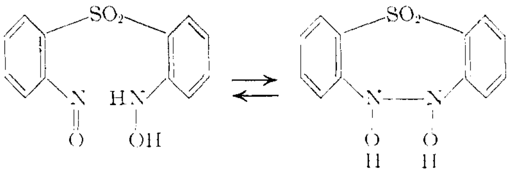
[1] H. H. Szmant and Y. L. Chow, THIS JOURNAL, **79**, 4382 (1957).

diazacyclohepta-2,4,6-triene. The purpose of this communication is to correct the erroneous conclusions which were published.

There exist two rather than three isomers of the cyclic azo and azoxy sulfones and they are the compounds which are referred to as IA, IB and IIA, IIC, respectively. The proposed conformational assignment of the isomers was shown correctly in the published Fig. 1.

The compound referred to as IC and later renamed III is the cyclic hydrazo sulfone and its ultraviolet spectrum was shown correctly in the published Fig. 2. The infrared spectrum of III shows strong absorption at 3430 cm.$^{-1}$ (N–H) and the published analytical data agree more satisfactorily when compared with those calculated for $C_{12}H_{10}O_2N_2S$ (C, 58.60; H, 4.09; N, 11.38; S, 13.00). The facile oxidation of the hydrazo compound III to IA under a variety of conditions explains the misunderstood "isomerizations" caused by perbenzoic acid and potassium permanganate (see footnote 9[1]).

The compound referred to as IIb and later renamed IV was obtained together with IIA by treating di-(*o*-aminophenyl) sulfone with peracetic acid. Compound IV is believed to be *o*-nitrosophenyl *o*′-hydroxylaminophenyl sulfone on the basis of its infrared spectrum (KBr disc) which showed a broad absorption band at 3500 cm.$^{-1}$ (O–H or N–H) and a sharp band at 1375 cm.$^{-1}$ (nitroso group). Also the analytical results agree more closely with those calculated for $C_{12}H_{10}O_4N_2S$ (S, 11.51; N, 10.07), found: S, 11.24; N, 10.07. The spatial proximity of the two nitrogen functions in IV suggests that this compound may partially exist in a cyclic state in analogy with cyclic dinitroso compounds.[2] In favor of this suggestion are the reported easy conversions of IV to IIA under dehydrating conditions and the reported reduction of IV to the cyclic hydrazo sulfone III by means of lithium aluminum hydride or zinc in acetic acid.



IV

In the published paper[1] there is described the reduction of di-(*o*-nitrophenyl) sulfide to what was thought to be the cyclic hydrazo sulfide (or dibenzo-1-thia-4,5-diazacyclohepta-2,6-diene) but which was later shown to be di-(*o*-hydroxylaminophenyl) sulfide. This compound can be crystallized from ethanol to give white plates, m.p. 119° dec., if care is taken to avoid excessive contact with air, and the material thus obtained gives the expected analytical results.

Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.00; H, 4.86; N, 11.28; S, 12.9. Found: C, 57.70; H, 4.65; N, 11.10; S, 13.0.

In this connection we wish to point out that it is now apparent that the reduction of di-(*o*-nitrophenyl) sulfone described in paper II of this series[3] also gave the corresponding hydroxylamino compound V[3] which upon oxidation in the presence of base gave the cyclic azoxy sulfone in accord with the observations of Jackson.[4]

Concerning the isomerizations of the two cyclic azoxy sulfones (II) it may be added that heating of either isomer in polar media (concd. sulfuric acid, acetic anhydride containing a few drops of concd. sulfuric acid) gave an apparent equilibrium mixture consisting predominantly of IIA, while prolonged heating in non-polar media (toluene) gives mixtures in which the other isomer predominates.

Also, it was possible to reduce IIA to IA by means of phosphorus tribromide according to the method of Ochiai.[5]

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(2) S. D. Ross and I. Kuntz, THIS JOURNAL, **74**, 1297 (1952).

(3) H. H. Szmant and R. L. Lapinski, *ibid.*, **78**, 458 (1956).

(4) E. L. Jackson, *ibid.*, **68**, 1438 (1946).

(5) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

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THE SPIN RELAXATION TIME OF TRIPHENYLMETHYL AT LOW TEMPERATURES[1]

Sir:

Recently Aston, Fritz and Seki[2] have reported that the paramagnetism of solid solutions of triphenylmethyl in several organic crystals disappears at temperatures of a few degrees Kelvin. This result is puzzling since the optical fluorescence and absorption spectra of the crystals clearly indicate the presence of monomeric triphenylmethyl molecules.[3] The purpose of this note is to report on the long relaxation times encountered in the crystals. Our results can account for the observations of Aston, Fritz and Seki without the necessity of postulating a decrease in static susceptibility. These authors used an inductance method (frequency not reported) for the measurements at low temperatures. At frequencies rapid compared with the reciprocal of spin-lattice relaxation time T_1 the susceptibility measured by this method is smaller than the static susceptibility (approximately by the square of the ratio of $1/T_1$ to frequency).[4]

We obtained the relaxation time T_1 from observation of the magnetic resonance behavior of a solution of triphenylmethyl in triphenylamine. At 300 and 77°K. we observed the saturation of the electron resonance with increasing microwave power under slow passage conditions. At 4.2 and 1.2°K. we observed directly the increase in magnetization with time subsequent to turning on

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(1) This work has been supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part for any purpose of the United States Government is permitted.

(2) J. G. Aston, J. J. Fritz and S. Seki, THIS JOURNAL, **79**, 1000 (1957).

(3) S. I. Weissman, *J. Chem. Phys.*, **22**, 155 (1954).

(4) This result may be obtained from the Bloch equations. A similar result was demonstrated by Debye for electric susceptibilities of polar molecules.