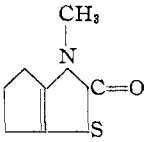
getics. This new substance is 2,3,5,6-tetrahydro-3-methyl-4(H)-cyclopentathiazolo-2-one (I).[6]



I

When α-chlorocyclopentanone is allowed to react with ethyl xanthamidate in boiling 1-propanol, there was obtained the crystalline compound, 2,3,5,6 - tetrahydro - 4(H) - cyclopentathiazolo - 2-one. Purification by recrystallization from water or water–ethyl alcohol (9:1) mixture gave product of m.p. 144–145°; *Anal.* Calcd. for C_6H_7NOS: C, 51.06; H, 5.02; N, 9.93; S, 22.60. Found: C, 51.02; H, 4.96; N, 9.96; S, 22.90. Ultraviolet absorption measurements at *p*H 7 gave $\lambda_{max}^{C_2H_5OH}$ 252 mμ, ϵ 4430; $\lambda_{min}^{C_2H_5OH}$ 229 mμ, ϵ 2500. Methylation of this thiazolone with methyl iodide in a basic medium gave rise to I which, after purification by crystallization from water, melted at 70–71°. *Anal.* Calcd. for C_7H_9NOS: N, 9.04; S, 20.68. Found: N, 8.90; S, 21.00. Absorption data in the ultraviolet are $\lambda_{max}^{C_2H_5OH}$ 253 mμ, ϵ 4170; $\lambda_{min}^{C_2H_5OH}$ 231 mμ, ϵ 2720.

The pharmacodynamic evaluation of this compound revealed a rather surprising activity in reducing experimental pain. The Wolf–Hardy principle for testing analgesia was employed in experimental animals according to a method described by Gross.[7] A beam of heat was directed against the tips of the tails of white mice and the reaction time measured from the onset of pain stimulus to the tail flick. Analgetic effects were expressed in terms of prolonged reaction time to the pain stimulus. With this method the above-mentioned compound produced a marked prolongation of the reaction time in the range of one-tenth to one-fifth of the LD50. It was characterized by a rapid onset of action and a maintenance of the analgetic effect for several hours following parenteral administration. Compared to aminopyrine the material was more potent, somewhat less toxic and devoid of antipyretic activity.

(6) According to *Chemical Abstracts*, an alternate name for I is N-methylcyclopentano-[d]4-thiazolin-2-one.

(7) F. Gross, *Helv. Physiol. Acta*, C31 (1947), *v5*.

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THE PURE OZONE TO OXYGEN FLAME[1]

Sir:

We live in a world of molecular oxygen and an overwhelming number of studies on combustion are devoted to oxidation with molecular oxygen. On the other hand, the active modification of the element, or ozone, has not been studied in the pure form.

Ozone has been known since 1785, when van Marum observed its formation in the electric spark discharge in oxygen. The highly sensitive nature of pure ozone and the extreme facility with which it explodes or detonates, has so far prevented combustion studies with pure ozone.

Before studies of the behavior of pure ozone with various fuel gases could be started profitably it was first necessary to achieve the combustion or decomposition flame of pure ozone to oxygen. It could be expected, since the exothermic heat (at constant pressure of 1 atm. and 291°K.) of the reaction $O_3 \rightarrow 1.5\ O_2$ equals $-$ 33,923 $\pm$ 180 cal./mole, that appreciable flame temperatures should be attained and that a stable ozone–oxygen flame should exist. Flame temperature calculations can be made with great accuracy since the enthalpy and the dissociation constants for the $O_2 \rightleftarrows 2O$ reaction are well known; these temperatures are, at initial conditions of 298°K. and 1.0 atm. pressure, for 100, 66.7, 40.0 and 18.2 mole % O_3 in O_2, respectively, 2677°, 2277°, 1687° and 1027°K.

By using pure ozone, containing less than a few parts per million of organic impurities, as described originally by C. E. Thorp,[2] we have been able to burn ozone–oxygen mixtures to oxygen in the entire range from 17–100 mole % O_3. The all-Pyrex glass apparatus was extremely simple; it consisted of a narrow glass gasholder, from which any desired mixture of O_3–O_2 or pure O_3 could be delivered at any predetermined rate, by simple displacement with water. From the gasholder the gas mixture went to a Pyrex glass, quartz, or aluminum tip. Stopcocks greased with C_nF_{2n+2} or Kel-F, were used. The burning velocities were determined by the standard schlieren method. In the range of 17 to about 50 mole % O_3, the flame cannot be observed visually, but can be seen very easily on the screen of the schlieren apparatus. The flame is visible above this range. Pure 100% ozone burns with a faint, non-luminous flame, blue in color, with a typical pink cast. The experimental burning velocities, at 298°K. and 1.0 atm. pressure, are shown in Fig. 1.

The ozone flame is of particular theoretical interest since it is the simplest flame imaginable. Outside of the "fuel" O_3 and the "product of combustion" O_2, the only possible intermediates are oxygen atoms.

In recent years Drs. J. O. Hirschfelder,[3] Theodore von Kármán[4] and R. Sandri,[5] and their associates, have developed the theory of laminar flame propagation. Dr. von Kármán presented his results recently[6] and they are in essential agreement with Fig. 1. The more extensive data of Dr. Sandri[7] are given in Table I and are compared with our experimental results in Fig. 1. As can be seen,

(1) 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. 18(600)-1475.

(2) C. E. Thorp, U. S. Patent 2,700,648, Jan. 25, 1955; see also "Bibliography of Ozone Technology," Vol. II: "Physical and Pharmacological Properties," 1955, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill.

(3) J. O. Hirschfelder, C. F. Curtiss and D. E. Campbell, *J. Phys. Chem.*, **57**, 403 (1953); Proc. IVth International Symposium on Combustion, 1953, p. 197.

(4) T. von Kármán and S. S. Penner, "Selected Combustion Problems," (AGARD): Combustion Colloquium, Cambridge University, England, pp. 5–41 (1953), and *C. A.*, **48**, 10409e (1954).

(5) R. Sandri, *Canadian J. Chem.*, **34**, 313, 324, 331 (1956).

(6) T. von Kármán, Proc. VIth International Symposium on Combustion, held at Yale University, Aug. 19–24, 1956.

(7) An extension of Sandri's theory to ozone-rich mixtures will be published soon in *Canadian J. Chem.* (1957).

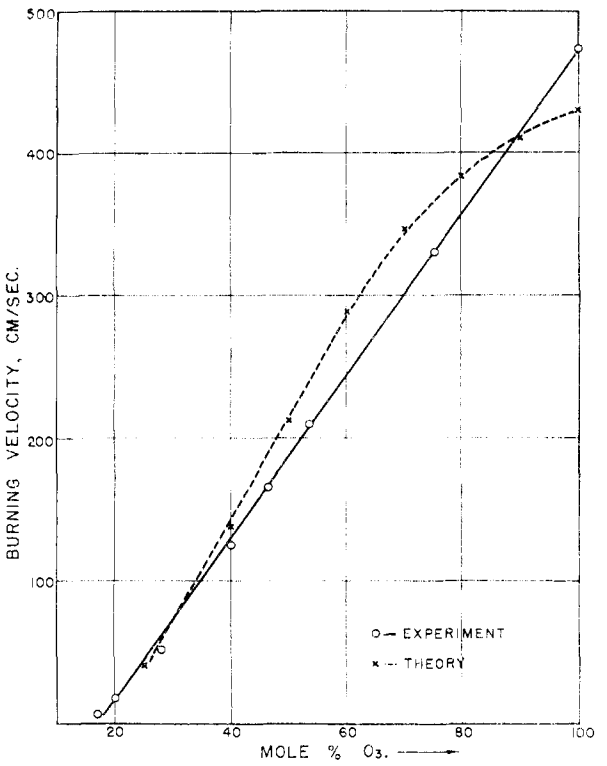

Fig. 1.—Burning velocities of ozone and ozone + oxygen mixtures (initial gas temperature = 298°K., pressure = 1 atm. abs).

pure ozone at 1 atm. pressure and at an initial temperature of 298°K. (25°C.) has a burning velocity of 472 (± 12) cm./sec.; at 195°K. it is 270 (± 7) cm./sec. Pure ozone can be burned to oxygen for substantial periods of time without explosion and detonation, like a regular combustible gas mixture.

TABLE I

1. FLAME VELOCITIES FOR INITIAL T = 298°K.

Mole % O_3	25	40	50	60	70	80	90	100
Burning velocity, V_0 (cm./s.)	41	139	214	290	349	386	411	430

Pure ozone was combusted with various fuel gases. The diffusion flame of pure ozone and cyanogen is extremely bright and produces a temperature of 5200°K. at 1.0 atm.

A detailed description of our experiments will be published elsewhere.[8]

(8) See (a) Proc. VIth International Symposium on Combustion, Aug. 19–24, 1956; (b) Proc. International Ozone Conference, Chicago, Ill., Nov. 28–30, 1956.

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A FACILE SYNTHESIS OF 2-SUBSTITUTED ADENINES[1]

Sir:

The conventional synthetic route to adenines involves the condensation of guanidine or thiourea with malononitrile to give a 4,6-diaminopyrimidine, which is then nitrosated, reduced, formylated and subsequently ring-closed.[2] The preparation of 2-alkyl- and 2-aryladenines is more cumbersome, since direct condensation of amidines with malononitrile proceeds anomalously[3] and the desired 2-substituted-4,6-diaminopyrimidines must be prepared by other methods.[4–7] The synthesis of derivatives such as isoguanine (2-hydroxy-6-aminopurine) is also circuitous, since urea does not condense satisfactorily with malononitrile and the 2-hydroxy group must be introduced indirectly.[7,8,9]

We now wish to describe a facile synthesis of 2-substituted adenines which would appear to be generally applicable. Thermal cyclization of amidine salts of isonitrosomalononitrile (I) (R = $-CH_3$; m.p. 141–142°. *Anal.* Calcd. for $C_5H_7N_5O$; C, 39.2; H, 4.6; N, 45.7. Found: C, 39.4; H, 4.4; N, 45.4. R = $-C_6H_5$; m.p. 148–150°. *Anal.* Calcd. for $C_{10}H_9N_5O$: C, 55.8; H, 4.2; N, 32.5. Found: C, 55.7; H, 4.0; N, 32.6. R = $-NH_2$; m.p. 157–158°. *Anal.* Calcd. for $C_4H_6N_6O$: C, 31.2; H, 3.9; N, 54.5. Found: C, 31.3; H, 3.9; N, 55.0) in 2-methyl-5-ethylpyridine yielded 2-substituted 4,6-diamino-5-nitrosopyrimidines (II) (R = $-CH_3$[5]; *Anal.* Found: C, 39.2; H, 4.6; N, 46.1: R = $-C_6H_5$: *Anal.* Found: C, 55.9; H, 3.9; N, 32.6: R = $-NH_2$;[10] *Anal.* Found: C, 30.7; H, 3.5; N, 55.0). The salts (I) were prepared readily in almost quantitative yield by mixing an amidine hydrochloride in ethanol solution with the silver salt of isonitrosomalononitrile,[11] removing silver chloride by filtration and concentrating the ethanol. In some instances, isolation of I was not necessary prior to cyclization; for example, heating guanidine carbonate with potassium isonitrosomalononitrile (III) (m.p. 209–211°; *Anal.* Calcd. for C_3N_3OK: N, 31.6. Found: N, 31.6) in dimethylformamide yielded 2,4,6-triamino-5-nitrosopyrimidine (II; R = $-NH_2$) in 88% yield, and condensation of III with urea in sodium ethoxide solution yielded 2-hydroxy-4,6-diamino-5-nitrosopyrimidine.[9,12]

Heating these 2-substituted 4,6-diamino-5-nitrosopyrimidines with a mixture of formamide, formic acid and sodium hydrosulfite[13] yielded 2-substituted adenines in high yield. In this manner, 2-methyladenine[5,14,15] was prepared in 74% over-

(1) This investigation was supported by a research grant (C-2551) to Princeton University from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) For a recent review of purine chemistry, see A. Bendich in "The Nucleic Acids, Chemistry and Biology," ed. by E. Chargaff and J. N. Davidson, Vol. 1, Academic Press, New York, N. Y., 1955, p. 81.

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