THE TEMPERATURE OF THE CYANOGEN-OXYGEN FLAME

Sir:

We have recently determined[1] the temperature of the H_2–F_2 flame to be 4300 ± 150°K. at 1 atm. pressure, using a modified line-reversal technique, with the sun in the heavens as the comparison radiator.

A much higher flame temperature is to be expected from thermodynamic considerations for the cyanogen–oxygen flame, according to the reaction

$$(CN)_2(g) + O_2(g) \longrightarrow 2CO(g) + N_2(g)$$

This reaction is exothermic to the extent of 126,680 cal. at 298°K. Furthermore, the thermal stability of the CO and N_2 molecules is even greater than that of the HF molecule.

Although the $(CN)_2$–O_2 flame was studied many years ago,[2,3] its flame temperature has never been measured directly. This year Thomas, Gaydon and Brewer[4] measured the vibrational "temperature" of the flame molecules and obtained a "temperature" of 4800 ± 200°K. at the stoichiometric composition. The calculated flame temperature reported by these authors was 4850 ± 30°K., using the high value, *i.e.*, $\Delta H_0^0 = 226{,}000$ cal./mole or 9.76 ev., for the dissociation energy of N_2. They pointed out that by using the lower dissociation energy, *i.e.*, $\Delta H_0^0 = 170{,}240$ cal./mole or 7.38 ev., the calculated flame temperature was 4325°K., thus fixing the dissociation energy of N_2 at 9.76 ev. However, the vibrational "temperature" is not considered sufficiently representative of the true thermodynamic temperature of the flame. This conclusion was reached in connection with our work on the H_2–F_2 flame. The vibrational "temperature" of this flame was measured in our laboratory by Drs. W. S. Benedict, S. Silverman and B. W. Bullock[5] of the National Bureau of Standards and it was found that the precision and reliability of direct flame measurements by the line-reversal method was greater than that of vibrational "temperature" measurements.

Our modified line-reversal method[1] was again employed. The metered $(CN)_2$[6] and O_2 streams were premixed in a 6-mm. glass tee filled with 20-mesh quartz chips. A short length of quartz tubing acted as a torch tip. This tip was also filled with quartz chips and attached to the free end of the premixing tee by means of a piece of rubber tubing. The small oval-shaped opening in the face of the quartz torch tip measured 0.134″ × 0.031″. Small needle valves in the inlet gas lines made it possible to vary the rate of either gas.

The shape and structure of the flame varied with feed gas composition. Near the composition corresponding to one mole of cyanogen per mole of oxygen the flame consisted of two zones; the inner zone was a brilliant white comparable to that of a carbon arc. The outer zone had the blue color characteristic of the carbon monoxide flame in oxygen. In this work the outer zone was about 1″ long and the inner zone $^1/_4$″ to $^1/_8$″ in length. These dimensions correspond to a total gas rate of about 200 cc. per minute. In these instances the flame burned right at the tip of the torch.

The theoretical flame temperature as a function of inlet gas composition was calculated using the latest thermodynamic data[7,8,9,10,11] (ΔH_0^0 for $(CN)_2$-dissociation = 114 kcal./mole).[10] These results together with the experimentally determined flame temperatures for various gas compositions are given in Table I.

TABLE I

Vol. %, O_2, $(CN)_2$	Experimental temp., °K.	Theoretical temp., °K.
25.3, 74.7	2580, 2640	..
26.8, 73.2	3090, 3120	..
33.3, 66.7	3270	3200
36.5, 63.5	3333	..
50.0, 50.0	4640	4810
62.0, 38.0	4453	..
66.7, 33.3	4003, 4043, 4073, 4143	3700

The maximum experimental flame temperature was observed at the stoichiometric point (50 vol. % $(CN)_2$) in line with the above equation and equals 4640° ± 150°K. Thus at one atmosphere total pressure it is 340°K. higher than the hydrogen–fluorine flame and is therefore the highest directly measured flame temperature recorded to date.

The theoretical flame temperature for the stoichiometric composition is calculated to be 4810 ± 50°K. using the high value for the dissociation energy of nitrogen. A temperature of 4375°K. was obtained using the low value. The experimental flame temperature is in good agreement with the higher theoretical flame temperature and as such represents the first direct measurement of the cyanogen–oxygen flame temperature.

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AMICETIN, A NEW STREPTOMYCES ANTIBIOTIC

Sir:

A *Streptomyces* sp., isolated from a soil sample collected near Kalamazoo, Michigan, was found to inhibit a number of bacteria when grown on an agar streak plate. *Mycobacterium tuberculosis* var. *hominis* (ATCC 607), *Proteus vulgaris*, *Escherichia coli*, and *Staphylococcus aureus* were markedly inhibited when cross-streaked against this new isolate. When the organism was grown in submerged culture in a medium containing cerelose, yeast extract, soya flour and inorganic salts, the filtered fermentation liquor was found to inhibit Gram-negative and Gram-positive bacteria and particularly certain mycobacteria in both broth-dilution and agar plate assays. From these filtrates a crystalline antibiotic with pronounced antituberculous activity has been isolated and given the generic name amicetin.

Amicetin was purified by extracting the clarified fermentation broth with *n*-butanol at *p*H 7.5, removing the solvent by distillation, leaching the activity from the residue with water, lyophilizing the aqueous solution, fractionating the freeze-dried preparation by countercurrent distribution between water and methylene chloride, and finally crystallizing from water. Amicetin is a basic compound with pK_a's about 7. The crystals melted at 160–165°. On warming to 50–70° in methanol or water suspension, they were converted to a granular high-melting crystal form of the free base with the properties: m.p. 243–244°; $[\alpha]^{24}\text{D}$ +116.5° (*c*, 0.5 in 0.1 *N* hydrochloric acid); solubility in water at 25°, 1–2 mg. per ml.; only slightly soluble in common organic solvents. Amicetin exhibits characteristic ultraviolet absorption: in neutral aqueous solution at the maximum $E^{1\%}_{1\,\text{cm.}} = 465$ at 305 mμ; in 0.1 *N* hydrochloric acid, $E^{1\%}_{1\,\text{cm.}} = 433$ at 316 mμ; and in 0.1 *N* sodium hydroxide, $E^{1\%}_{1\,\text{cm.}} = 470$ at 322 mμ. Titration data and analyses indicate the formula $C_{29}H_{44}N_6O_9$ for the free base. (*Anal.* Calcd. for $C_{29}H_{44}N_6O_9$: C, 56.11; H, 7.15; N, 13.54. Found: C, 55.98; H, 6.92; N, 13.18).

The *in vitro* activity of crystalline amicetin free base against several bacteria is shown in Table I.

TABLE I

ANTIBACTERIAL ACTIVITY OF CRYSTALLINE AMICETIN AS COMPARED WITH STREPTOMYCIN AND THE CULTURE BROTH FROM WHICH AMICETIN WAS EXTRACTED

Dilutions are expressed in microliters of broth or micrograms of solids per ml. required for complete inhibition of the test organism.

Organism	Culture broth	Amicetin	Streptomycin
Mycobacterium tuberculosis (H37Rv)[1]	..	0.5	1.0
Mycobacterium tuberculosis (ATCC-607)	1.0	1.0	1.0
Staphylococcus aureus (FDA-209)	0.1	2.0	0.2
Bacillus subtilis (Ill.)	0.04	4.0	0.1
Klebsiella pneumoniae (PCI-602)	0.1	>20.0	0.2
Escherichia coli (ATCC-26)	1.0	>20.0	1.0
Bodenheimer's cocco-bacillus (PCI-3)	1.0	>20.0	>40.0

It is apparent that amicetin is active mainly against certain acid-fast and Gram-positive bacteria in contrast to the culture filtrates which have good Gram-negative activity as well. This is one of several indications that the *Streptomyces* sp. in question produces antibacterial activity in addition to that of amicetin.

Crystalline amicetin has been found to be active *in vivo* against *Mycobacterium tuberculosis* H37Rv when tested in infected mice.[1] However, on a weight basis, amicetin does not appear to be as effective as streptomycin sulfate when tested in this species. Preliminary studies indicate that the toxicity[2] of amicetin varies considerably with the species. The acute intravenous LD_{50} of amicetin as the citrate complex at *p*H 6 in mice is approximately 90 mg. per kg.; the subcutaneous LD_{50}, 600–700 mg. per kg. In rats the acute intravenous LD_{50} is approximately 200 mg. per kg. and the subcutaneous LD_{50}, about 600 mg. per kg. Amicetin is especially toxic to guinea pigs: by the subcutaneous route it is about forty times as toxic as streptomycin, but on the other hand only about one-tenth as toxic as penicillin to this same species. In contrast to streptomycin, amicetin does not appear to cause eighth-nerve damage when studied according to the procedure of Fowler and Feind.[3]

Detailed accounts of these studies are in preparation.

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(2) Determined by O. F. Swoap, E. S. Feenstra, R. J. Cole, and P. M. Brockie, Pharmacology Department, The Upjohn Company.

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SYNTHESIS AND BIOCHEMISTRY OF 5- AND 7-HYDROXYTRYPTOPHAN AND DERIVATIVES[1]

Sir:

The reported occurrence of serotonin (5-hydroxytryptophan) in serum,[2] in intestinal mucosa (enteramin)[3] and blood platelets (thrombocytin)[4] as well as in the parotid glands of *Bufo marinus*[5] suggests, as mentioned previously,[6] the possibility of a direct hydroxylation of the benzene ring in tryptophan prior to any reaction on the pyrrole part of the molecule. The alternative formation of serotonin from 5-hydroxyindole *via* 2,5-dihydroxyphenylalanine[7] is unlikely, since the introduction of a β-side chain into indole is a process unknown in animals. We now have synthesized 5- and 7-hydroxytryptophan and their derivatives of actual and potential physiological importance.

Catalytic debenzylation of 5-benzyloxytryptophan (m.p. 280°, dec.), obtained *via* condensation of 5-benzyloxygramine[8] with diethylformaminomal-

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