with monohydrofluoboric and methoxyfluoboric acids. It is also of interest to note the decrease in melting points with increased carbon chain length; tetramethyl-, 417–419°; tetraethyl-, 365–367°; tetra-*n*-propyl-, 249–251° and tetra-*n*-butylammonium fluoborate, 153–155°.

Experimental

Preparation and Characterization of Tetramethylammonium Fluoborate.—In order to obtain the melting point, 418 ± 1°, a sample of this compound was prepared by reaction of tetramethylammonium hydroxide with 40% fluoboric acid.

Anal.[4] Calcd. for $(CH_3)_4NBF_4$: C, 29.84; H, 7.51; F, 47.22. Found: C, 30.12, 29.94; H, 7.59, 7.49; F, 47.61, 47.27.

Preparation of Tetraethylammonium Fluoborate.—The addition of fluoboric, monohydroxyfluoboric and methoxyfluoboric acid to either an aqueous solution of tetraethylammonium bromide or the solid salt resulted in the liberation of hydrogen bromide and the formation of tetraethylammonium fluoborate. The reactions with monohydroxyfluoboric and methoxyfluoboric acid were carried out at 10°, with fluoboric acid at room temperature. It was necessary in each instance to concentrate the reaction solution, followed by addition of ether to the solution, precipitating tetraethylammonium fluoborate, m.p. 365–367°. Analytical data are presented below for the fluoborate formed from the reaction of tetraethylammonium bromide with methoxyfluoboric acid.

Anal. Calcd. for $(C_2H_5)_4NBF_4$: C, 44.29; H, 9.23; F, 35.03. Found: C, 44.72, 44.50; H, 9.54, 9.70; F, 35.08, 34.74.

Preparation of Tetra-*n*-propylammonium Fluoborate.—Although the preparation of tetra-*n*-propylammonium fluoborate has not been previously reported it was assumed that the quaternary hydroxide would react with fluoboric acid, to produce the quaternary fluoborate. The addition of tetra-*n*-propylammonium hydroxide to excess fluoboric acid resulted in immediate precipitation of white crystals. Recrystallization from hot methanol yielded tetra-*n*-propylammonium fluoborate, m.p. 249–250°.

Anal. Calcd. for $(C_3H_7)_4NBF_4$: C, 52.75; H, 10.33; F, 27.82. Found: C, 52.28, 52.37; H, 10.05, 10.12; F, 27.18, 27.28.

Solid tetra-*n*-propylammonium iodide added to methoxyfluoboric acid yielded hydrogen iodide and tetra-*n*-propylammonium fluoborate. It was necessary to add ether to precipitate the quaternary fluoborate from the reaction mixture. The precipitated fluoborate was recrystallized from hot methanol. Addition of ether aided in crystallization. The purified tetra-*n*-propylammonium fluoborate melted at 251° in good agreement with the sample prepared as described above.

Anal. Calcd. for $(C_3H_7)_4NBF_4$: C, 52.75; H, 10.33; F, 27.82. Found: C, 53.24, 53.09; H, 10.66, 10.45; F, 27.47, 27.14.

Subsequent reactions of tetra-*n*-propylammonium iodide with monohydroxyfluoboric and fluoboric acid and tetra-*n*-propylammonium hydroxide with monohydroxyfluoboric and methoxyfluoboric acids produced tetra-*n*-propylammonium fluoborate, identified by melting point.

Preparation of Tetra-*n*-butylammonium Fluoborate.—The addition of fluoboric, monohydroxyfluoboric and/or methoxyfluoboric acid to tetra-*n*-butylammonium hydroxide resulted in the immediate precipitation of a white solid, tetra-*n*-butylammonium fluoborate, m.p. 153–155°, lit.[2] 161°, which gave a positive nitron test.

Anal. Calcd. for $(C_4H_9)_4NBF_4$: C, 58.36; H, 11.03; F, 23.08. Found: C, 58.05, 58.24; H, 11.02, 10.84; F, 23.34, 23.06.

Hydroxyfluoboric acid was added to a solution of tetra-*n*-butylammonium iodide with immediate precipitation of tetra-*n*-butylammonium fluoborate. An attempt was made to recrystallize the salt from methanol; however, due to the high solubility of the salt in the alcohol it was necessary to add water and concentrate the solution on a steam-bath. Subsequent cooling produced crystalline tetra-*n*-butylammonium fluoborate, m.p. 156°, positive nitron test.

Methoxyfluoboric acid was added to solid tetra-*n*-butylammonium iodide. It was necessary to extract the fluoborate with chloroform, followed by evaporation of the solvent. The fluoborate was recrystallized from a 50% water–methanol solution yielding crystals melting 155°, positive nitron test.

Anal.[5] Calcd. for $(C_4H_9)_4NBF_4$: F, 23.08. Found: F, 22.92, 22.85, 22.74.

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[4] Unless otherwise noted all analyses were performed by Laboratory of Microchemistry, Dr. Carl Tiedcke, Teaneck, New Jersey.

[5] Fluorine detn. by nitron ppt. method: W. F. Hillebrand, *et al.*, "Applied Inorganic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 321.

COMMUNICATIONS TO THE EDITOR

THE PRODUCTION OF A FLAME TEMPERATURE OF 5000°K.

Sir:

We have recently measured the temperature of the $(CN)_2$–O_2 flame at the stoichiometric point (*i.e.*, 1:1 mole)[1] and found that it produces the highest temperature obtainable by a chemical reaction. This is due to its high exothermicity coupled with the fact that the products of combustion, *i.e.*, CO and N_2, are the most thermally stable molecules known. Our experimental flame temperature measurement (4640 ± 150°K.) checks the calculated temperature, *i.e.*, 4835 ± 50°K., within the error of both methods.

In order to produce higher temperatures we have recently operated this flame at pressures up to 100 p.s.i.a., as described below. Under pressure the dissociation of CO and N_2 is suppressed and the temperature of the flame is increased.

The pressure effect can be calculated with a high degree of reliability due to the precision of the heat content data now being published by the National Bureau of Standards,[2] coupled with W. M. Latimer's revised tables[3] of the free energy functions and dissociation constants of the CO and N_2 molecules up to 5000°K. Using the above data we

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[1] J. B. Conway, R. H. Wilson, Jr., and A. V. Grosse, THIS JOURNAL, **76**, 499 (1953).

[2] Circular of the National Bureau of Standards C-461, Washington, D.C., 1947, p. 228.

[3] W. M. Latimer, "Tables of Free Energy Functions for Elements and Compounds in the Range of 2000–5000°K.," MDDC-1462, revised **1952**.

have calculated the stoichiometric (1:1) flame temperature (± 50°K.) to increase with pressure as shown:

1 atm. = 4835°K.
2 atm. = 4900°K.
5 atm. = 4985°K.
6.8 atm. (= 100 p.s.i.a.) = 5015°K.
10 atm. = 5050°K.

We believe that at the present time these calculated values involve less error possibilities than direct measurements in this 200° range.

To avoid condensation of cyanogen at the higher pressures we have preheated the two gases to 100°. This increased the heat contents of the reactants by 2000 cal./mole and raised our actual flame temperature at 100 p.s.i.a. from 5015°K. to 5050°K. The temperature is not lowered by ionization since all the molecules and atoms involved have very high ionization potentials.

The premixed gases were burned off a torch installed in a pressure chamber.[4] The latter consisted of a 24-inch length of one-inch copper pipe; the top 18 inches of this vertically mounted cylinder were water-cooled. A sight-glass assembly was attached to the chamber just below the water-cooling jacket which allowed for visual observation of the flame during operation. The torch tube was inserted through a stuffing box and positioned in such a way that the flame or torch tip could be seen through the sight-glass. The torch tube was a 10-inch length of stainless steel tubing having an outside diameter of 0.25 inch and an inside diameter of 0.035 inch (= 0.89 mm.). The premixed gas was ignited as it left the tip of the torch by means of a hot tungsten wire igniter. Both gases were measured through Fischer and Porter Flowrators. The reaction chamber was pressurized with argon to the desired value. The combustion products left through a top purge line and a valve was throttled to maintain the desired operating pressure.

The combustion gases were analyzed and found to contain 0.110 mole per cent. CO_2 or less, based on the cyanogen burned. Thus the combustion to CO and N_2 was at least 99.89% complete.

The flame is at its brightest at or very close to the stoichiometric point. It looks like an electric arc even at atmospheric pressure. It becomes more luminous at higher pressures because the combustion takes place in a smaller volume and at a higher temperature.

The way is now open to study the chemistry and physics of various substances in the neighborhood of 5000°K.

Acknowledgment is due to the Office of Naval Research, Department of the Navy (Contract N9-onr-87301) for the financial support of this project, and to the American Cyanamid Company for supplying us with a cylinder of pure cyanogen.

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(4) Details of construction and experimental techniques are fully described in the Final Report on Contract ONR (N9-onr-87301) by J. B. Conway and A. V. Grosse, July 1, 1954, pp. 30–43 and 45.

A NEW PANCREATIC PROTEINASE

Sir:

A previously unreported proteinase has been found in hog pancreas. Its general behavior is not ascribable to trypsin or chymotrypsin. The partially purified material shows considerably stronger hydrolytic activity than crystalline trypsin or α-chymotrypsin upon protein substrates. In Table I a preparation of the new enzyme, temporarily designated pankrin,[1] is compared with crystalline trypsin and α-chymotrypsin in proteolysis of several native (N) and denatured (D) proteins.

TABLE I

COMPARATIVE ENZYMATIC ACTIVITIES[a] AGAINST DIFFERENT SUBSTRATES

Substrate	Trypsin	α-Chymotrypsin	Pankrin	$\frac{\text{Pankrin}}{\text{Trypsin}}$	$\frac{\text{Pankrin}}{\alpha\text{-Chymotrypsin}}$
D Hemoglobin[b]	11.94	5.70	38.40	3.2	6.7
N Hemoglobin[b]	1.79	1.10	5.36	3.0	4.9
D Serum Albumin[c]	4.77	2.45	6.17	1.3	2.5
N Serum Albumin[c]	0.44	0.38	1.90	4.3	5.0
D Casein[d]	11.52	18.40	31.55	2.7	1.7
N Casein[d]	6.16	9.49	9.54	1.5	1.0

[a] Mg. tyrosine liberated per mg. enzyme in 10 minutes at 37°; Anson, *J. Gen. Physiol.*, **22**, 79 (1938). [b] Bovine hemoglobin substrate powder, Armour. [c] Crystalline bovine serum albumin, Armour. [d] "Vitamin Test" casein, Nutritional Biochemicals.

The markedly high proteolytic activity of pankrin is hard to explain without postulating: (a) a new proteinase; (b) activation of trypsin or α-chymotrypsin; (c) an "unmasking" of additional active centers of trypsin or α-chymotrypsin; or (d) a synergistic action of several proteinases acting at different substrate sites.

A rise in esterase activity of trypsin or α-chymotrypsin, resembling the rise in proteolysis, would be expected to accompany situations (b) and (c). The specific esterase activity of pankrin on *p*-toluenesulfonyl-L-arginine methyl ester (TSAME)[2] is 0.138 and on acetyl-L-tyrosine ethyl ester (ATEE)[3] it is 0.187, but these activities remain well below those of trypsin (TSAME activity = 0.448 and α-chymotrypsin (ATEE) activity = 0.396). Indeed, the ATEE potencies for six fractions of pankrin closely parallel the D hemoglobin potencies (Hb:ATEE = 192 ± 34), suggesting an intrinsic characteristic rather than a chymotrypsin impurity. Possibility (b) is further weakened by retention of activity after dialysis against distilled water and Versene and by the failure of other workers to find any activations of the order of magnitude required here. Possibility (d) fails when tested. Combinations of α-chymotrypsin plus trypsin and/or carboxypeptidase give specific activities (D hemoglobin) lower than that of trypsin. Moreover, pankrin displays vigorous proteinase activity—exceeding that of trypsin—

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(1) This name was adopted from the Greek *pankreas*.

(2) G. W. Schwert, H. Neurath, S. Kaufman and J. E. Snoke, *J. Biol. Chem.*, **172**, 221 (1948).

(3) S. Kaufman, H. Neurath and G. W. Schwert, *ibid.*, **177**, 793 (1949).