THE EFFECT OF INITIAL MIXTURE TEMPERATURE ON BURNING VELOCITY

Sir:

The effect of initial mixture temperature on the burning velocity of ethylene–air mixtures has been determined as an extension of the work done with propane–air mixtures.[1] The burning velocities were based on the inner edge of the shadow cast by the Bunsen cone and were computed by a total area method.[1] The data were smoothed by a method in which flame surfaces were related to heights, similar to the graphical method of Bollinger and Williams.[2] The maximum burning velocity was obtained with mixtures containing approximately 7.5% ethylene by volume for each of the initial temperatures, which ranged from 34 to 344°. These results are plotted in Fig. 1, along with curves predicted on a relative basis by the thermal theory as presented by Semenov[3] and by the square root law of Tanford and Pease.[4] These theoretical equations were used in the same manner as they were used for propane,[1] except that the temperature dependence of the Tanford and Pease equation has been re-evaluated and certain inconsistencies[5] have been eliminated. The corrected expression for predicting the relative effect of temperature on flame speed by the square root law is

$$u_f \propto \sqrt{(\Sigma k_1 p_1 D_{i,r}) T_o{}^2 T_f{}^{-1.33}} \qquad (1)$$

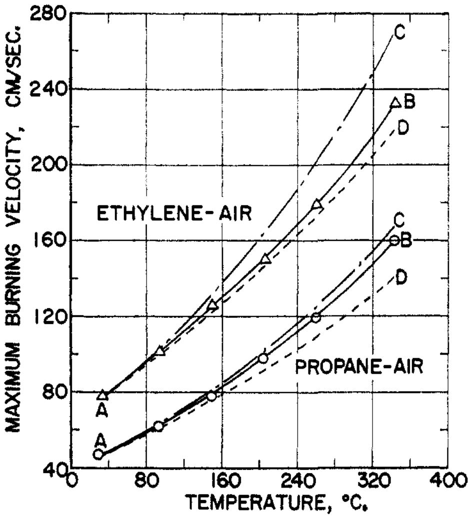

Fig. 1.—Effect of temperature on burning velocity: AB, experimental; AC, thermal theory; AD, square root law, $\Sigma_i p_i D_{i,r} = 6.5\, p_H + p_{OH} + p_O$.

The temperature dependence of k_i, the rate constant for interaction between active particles and combustible material, has been neglected in plotting the curves in Fig. 1. Constant values of k_i were used by Tanford[6] for variations in flame temperature of the order of magnitude considered in this paper. If the temperature dependence of k_i is represented by $\exp(-E/RT_f)$, the temperature effect on flame speed due to k_i will be small, since the activation energies for active-radical–fuel-molecule reactions are small. For example, using activation energies for reactions between hydrogen atoms and hydrocarbon molecules of 8.6 kcal./g.-mole for propane[7] and 2.6 kcal./g.-mole for ethylene[8] would raise the square-root law curves for the two gases by 10 cm./sec. and 4 cm./sec. at 344°, respectively. From another viewpoint, the activation energies which are required to give the best fits to the experimental curves (geometric mean values of computations for 5 temperature increments) are 9.9 and 8.3 kcal. for propane and ethylene, respectively.

The author gratefully acknowledges the suggestion of Dr. Robert N. Pease that the Tanford-Pease equation should be extended by substituting an Arrhenius expression for the rate constant.[9]

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[1] Dugger, THIS JOURNAL, **72**, 5271 (1950).

[2] Bollinger and Williams, Natl. Adv. Comm. Aeron. Report No. 932, 1949.

[3] Semenov, *Progress of Phys. Sci.* (*USSR*), **24**, No. 4 (1940). Translation appears as Natl. Adv. Comm. Aeron. Technical Memorandum No. 1026, 1942. The thermal theory curves are based on the equation for bimolecular reactions, since the same equation predicts that flame velocity should be independent of pressure, as was found for ethylene by Linnett according to Gaydon and Wolfhard, *Fuel*, **29**, 15 (1950), and for propane by Huebner and Wolfhard, Volkenrode Monograph, Die Verbrennung in Grossen Hoehen, Issued by Technical Information Bureau for Chief Scientist, Ministry of Supply, 1946.

[4] Tanford and Pease, *J. Chem. Phys.*, **15**, 861 (1947).

[5] Tanford and Pease assumed diffusion coefficients to be proportional to T^2 rather than $T^{1.67}$ as used by the author and had converted diffusion coefficients at combustion zone temperature to those at room temperature on this basis. Further, they assumed the mean combustion zone temperature to be proportional to flame temperature, T_f, hence concentrations should be proportional to T_f, rather than the arithmetic average $(T_o + T_f)/2$ used by the author.

[6] Tanford, "Third Symposium on Combustion, Flame and Explosion Phenomena," The Williams and Wilkins Company, Baltimore, Md., 1949, pp. 140–146.

[7] Steacie, *J. Chem. Phys.*, **16**, 361 (1948).

[8] Computed from data of Melville and Robb, *Proc. Roy. Soc.* (*London*), **A196**, 445 (1949), assuming a steric factor of 0.1.

[9] Dr. Hartwell F. Calcote's helpful criticism is also acknowledged.

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TESTS WITH LYXOFLAVIN FOR VITAMIN ACTIVITY

Sir:

L-Lyxoflavin has been examined biologically for vitamin activity. In a rat assay for unidentified vitamins in liver and other source materials, L-lyxoflavin has shown growth-promoting or vitamin-like activity.

In 1949, Pallares and Garza[1] isolated from human heart myocardium a pentose-flavin, which was found to be identical with synthetic L-lyxoflavin. Lyxoflavin differs from riboflavin only in the configuration of the groups about C_4 of the pentose side chain. The significance of the presence of lyxoflavin in human heart muscle was not discussed[1], but another paper[2] considers it as "stereoisomerism of vitamin B_2."

α-Ribazole[3] (1-α-D-ribofuranosido-5,6-dimethylbenzimidazole) is a unit of the vitamin B_{12} molecule. Vitamins B_2 and B_{12} and lyxoflavin contain a 1,2-diamino-4,5-dimethylbenzene moiety linked through nitrogen to a pentose. It seemed *a priori* that lyxoflavin might be a new member of the vitamin B complex with a biological role different from

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[1] Pallares and Garza, *Arch. Biochem.*, **22**, 63 (1949).

[2] Pallares and Garza, *Arch. Inst. Cardio. Mex.*, **19**, 735 (1949).

[3] Brink, Holly, Shunk, Peel, Cahill and Folkers, THIS JOURNAL, **72**, 1866 (1950).

that of vitamin B_2, B_{12}, and other known vitamins. Nicotinic acid is one precedent for a substance being known chemically before recognition as a vitamin. Besides vitamin tests, lyxoflavin was desired for tests on the growth of lymphosarcoma transplants in mice, since 6,7-dichloro-9-(1′-D-sorbityl)-isoalloxazine[4] enhanced regression and yet was not an inhibitor of riboflavin.

Our tests show that synthetic lyxoflavin[5] is devoid of riboflavin activity in rats by the standard assay as it should be if it is a distinct vitamin-entity.

Ershoff[6] found that a water-insoluble liver fraction counteracted the growth depressing effect of a casein diet containing thyroid powder. Addition of vitamin B_{12} did not give a growth response in this test.

We have maintained rats on a deficient diet consisting of soybean meal, dextrose, minerals, the known vitamins and 0.5% thyroid powder which enhances development of a deficiency state. After depletion for twenty-eight days, vitamin B_{12} was added to the basal ration. When natural sources of unidentified vitamins were added, a weight gain resulted (Table I).

TABLE I

RAT ASSAY FOR UNIDENTIFIED VITAMINS

Dietary groups	No. male rats	15-day weight gain
Basal	50	64 g.
Defatted liver powder (10%) Viobin Corp.	30	77 g.
Menhaden fish meal (10%)	20	79 g.
Water insoluble liver solids (10%)	10	83 g.

We have found in two assays (Table II) that supplementation with lyxoflavin resulted in weight gains comparable with those observed with liver and fish meal, namely, 20–35% above that of the control groups.

TABLE II

TESTS ON LYXOFLAVIN FOR GROWTH ACTIVITY IN RATS

Groups of rats (9–11 males each)	15-day weight gain, g.
Basal (expt. 1)	64
Plus 150 μg. lyxoflavin daily (expt. 1)	78
Basal (expt. 2)	64
Plus 150 μg. lyxoflavin daily (expt. 2)	88

Thus, it appears that lyxoflavin has growth-promoting or vitamin-like activity in rats. These tests are being extended with rats and with microorganisms, chicks and other animals.

[4] Holly, Peel, Mozingo and Folkers, *ibid.*, **72**, 5416 (1950).

[5] Heyl, Cates, Koniuszy and Folkers, *ibid.*, **73**, in press (1951).

[6] Ershoff, *Proc. Soc. Exp. Biol. Med.*, **73**, 459 (1950).

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RECEIVED MARCH 19, 1951

THE SEPARATION OF MONOSACCHARIDES BY ION EXCHANGE[1]

Sir:

The biosynthetic preparation of C^{14}-labeled sugars requires a method for the separation of individual monosaccharides from their mixtures The methods used up to the present time have, in general, been based upon adsorptive chromatography and both columnar and paper partition chromatography.[2] In many cases they are nonquantitative, or difficult, or impossible to apply to preparative isolations, or include undesirable manipulative procedures and chemical conversions.

Since borate ion reacts with sugars to produce negatively charged sugar–borate complexes,[3] it occurred to us that such sugar–borate complexes might be separable by the technique of ion exchange in a fashion similar to that used in separating nucleotides and related compounds.[4]

It was found that fructose, glucose, mannose and galactose, dissolved in weak sodium borate solutions, are quantitatively adsorbed on strong-base anion exchangers. Elution was carried out with dilute sodium borate solutions and the effluent fractions were analyzed for sugar by the quantitative anthrone method of Dreywood[5] as developed by Morris.[6] Identification of the sugars was accomplished by paper chromatography.[7]

A separation of glucose, galactose and fructose on a strong-base anion exchanger is shown in Fig. 1. Recoveries of the individual sugars were essentially quantitative.

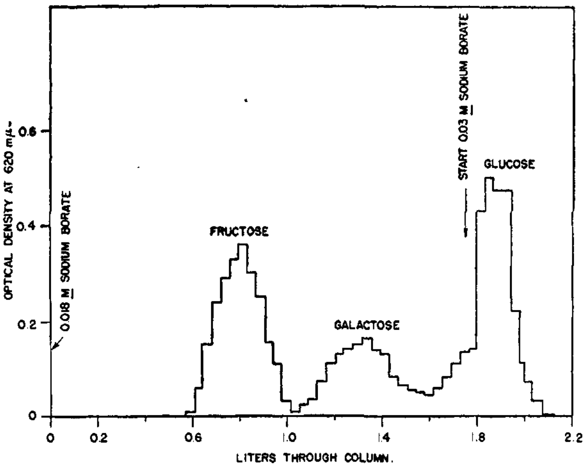

Fig. 1.—Exchanger, 0.85 sq. cm. × 11 cm. Dowex-1, *ca.* 300 mesh, borate form; eluting agent; sodium borate as shown at 1 ml./min.; test material, 10 mg. fructose, 12.5 mg. galactose, 12.5 mg. glucose in 10 ml. of 0.01 *M* sodium borate; recovery, ~99%, based on optical density at 620 mμ.

While a number of variables remain to be explored and the method has not yet been extended to in-

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[1] Work performed under Contract Number W-7405-Eng-26 for the Atomic Energy Commission.

[2] S. Udenfriend and M. Gibbs, *Science*, **110**, 708 (1949); W. W. Binkley and M. L. Wolfrom, "Chromatography of Sugars and Related Substances, Sugar Research Foundation, Inc., Scientific Report Series No. 10 (1948); B. W. Lew, M. L. Wolfrom and R. M. Goepp, Jr., THIS JOURNAL, **68**, 1449 (1946); G. R. Noggle and R. A. Bolomey, *Plant Physiol.*, in press.

[3] J. Böeseken, *Advances in Carbohydrate Chem.*, **4**, 189 (1949); H. S. Isbell, J. F. Brewster, N. B. Holt and H. L. Frush, *J. Res. Nat. Bur. Standards*, **40**, 129 (1948); Y. Tuzuki, *Bull. Chem. Soc., Japan*, **16**, 23 (1941).

[4] W. E. Cohn, THIS JOURNAL, **72**, 1471 (1950); E. Volkin, J. X. Khym and W. E. Cohn, *ibid.*, **73**, 1533 (1951).

[5] R. Dreywood, *Ind. Eng. Chem., Anal. Ed.*, **18**, 499 (1946).

[6] D. L. Morris, *Science*, **107**, 254 (1948).

[7] S. M. Partridge, *Biochem. J.*, **42**, 238 (1948).