detonation velocity in equimolar cyanogen-oxygen mixtures with the measurements of Dixon.[8] Serious objections can be raised to those calculations and the measurements, but the finding that the dissociation energy is higher than 7.383 ev. is correct.

Our measurements, made with piezoelectric gates,[9] since improved, included tubes of 1.2 to 10 cm. diameter in 180 cm. lengths. No change of detonation velocity with the distance was apparent within the high precision of these measurements (±5 m./sec.), ruling out effects of rarefaction, which tends to *lower* detonation velocity. Figure 1 shows the effect of tube diameter and makes clear that infinite wave has been closely approximated.

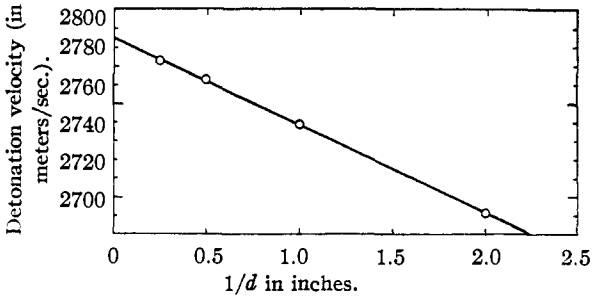

Fig. 1.—Detonation velocity plotted against the reciprocal of pipe diameter: 50% C_2N_2 + 50% O_2 at 1 atm. initial pressure.

Calculations of thermodynamic equilibria used the new heat of combustion of cyanogen[10] and Bureau of Standards Thermodynamic Tables, extrapolated by us to 5600–6400°K., the temperatures involved in the detonation of equimolar cyanogen-oxygen mixtures. We allowed for equilibria between CO, N_2, CN, C, N, O, since concentrations of NO, C_2N_2, O_2, C_2, CO_2 were shown by rougher calculations to be too low to affect the results significantly. The values in Fig. 2 are based on 170 kcal. for the sublimation heat of carbon and on 101 or alternately on 140 kcal. for the reaction $C_2N_2 \rightarrow 2$ CN. Recent measurements[2] indicate an intermediate value. The velocity for 8.573 ev. has been interpolated on the curves and the slope of the upper curve is estimated from rougher calculations. Dotted lines give total error limits for the experimental value. Table I compares calculated and measured detonation velocities for three total pressures and for a mixture containing additional nitrogen.

TABLE I

OBSERVED AND CALCULATED DETONATION VELOCITIES

Initial conditions	C_2N_2	49.9 %	C_2N_2	49.9 %	C_2N_2	49.9 %	C_2N_2	42.3 %
	O_2	49.9	O_2	49.9	O_2	49.9	O_2	42.3
	A	0.2	A	0.2	A	0.2	A	0.2
							N_2	15.2
	P = 0.5 atm.		P = 1 atm.		P = 1.5 atm.		P = 1 atm.	
V meas. meters/sec.	2745 ± 5		2773 ± 5		2780 ± 5		2678 ± 5	
V calcd. meters/sec.[a]	2742		2769		2780		2678	

[a] Using D_{N_2} = 225 kcal.; λ_0 = 170 kcal.; $C_2N_2 \rightarrow 2CN$ + 140 kcal.

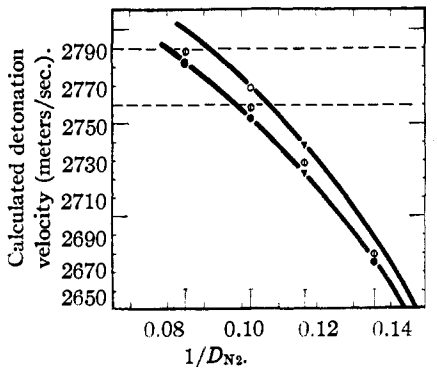

Fig. 2.—Comparison of calculated and measured detonation velocities: O, calculated assuming $D_{C_2N_2}$ = 140 kcal.; ●, calculated assuming $D_{C_2N_2}$ = 101 kcal.; ▼, interpolated for D_{N_2} = 8.573 ev.; ⊙, interpolated taking $D_{C_2N_2}$ = 114 kcal.[3]; dotted lines indicate limits of experimental uncertainty.

These data eliminate the two lower values of the dissociation energy. A clear-cut decision between 9.764 and 11.8 ev. is not yet possible, but Herzberg[11] has adduced such strong evidence against the higher value that the 9.764 ev. (225 kcal.) value appears to be proven. The 170 kcal. for the sublimation energy of carbon[12] is indirectly supported by these data since the dissociation energy of nitrogen must be raised by a commensurate amount, if a lower figure is taken for carbon, to bring calculation and experiment into agreement again.

Further data pertinent to energies of nitrogen dissociation and sublimation of carbon will be published later.

(8) H. B. Dixon, *Phil. Trans.*, **A184**, 97 (1894).

(9) D. J. Berets, E. F. Greene and G. B. Kistiakowsky, THIS JOURNAL, **72**, 1080 (1950).

(10) Private communication from Dr. E. J. Prosen of the Bureau of Standards.

(11) G. Herzberg, paper delivered before Am. Phys. Society Meeting, Pittsburgh, March, 1951.

(12) L. Brewer, P. W. Gilles and F. A. Jenkins, *J. Chem. Phys.*, **16**, 797 (1948).

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RESOLUTION INTO OPTICAL ISOMERS OF SOME AMINO ACIDS BY PAPER CHROMATOGRAPHY

Sir:

We have attempted to resolve several amino acids by means of paper chromatography, using *l*-methyl-(β-phenylisopropyl)-amine ($[\alpha]_D$ −17.8°) as a solvent.

The results are shown in Fig. 1.

While the *d*- and *l*-forms of leucine gave the same R_f values (a), those of the acidic amino acids, glutamic acid (b), and tyrosine (c) gave differences in R_f values from 0.02 to 0.03. In the case of *d*- and *l*-isomers of tyrosine-3-sulfonic acid (d, e), the difference in R_f values was 0.21, and the racemic mixture was also completely resolved.

We had anticipated that the R_f values of *d*- and *l*-amino acids should be reversed when the *d*-solvent was used. However, identical results were observed using *d*-, *l*- and *dl*-solvents. The tendency to resolve was also observed when in-

active solvents such as *n*-butanol and acetic acid (h) or lutidine mixture (i) were used.

Thus it became clear that the resolution was not due to the optical character of the solvent. For confirmation, a chromatopile separation was carried out in which a solution of 250 mg. of *dl*-tyrosine-3-sulfonic acid was dried on 20 sheets of 9 cm. No. 2 (Toyo) filter paper. The 20 disks were incorporated at 100 disks from the top of a 700 sheet pile packed in 15 cm. After 27 hours, the solvent (*n*-butanol:water:acetic acid:*l*-methyl-(β-phenylisopropyl)-amine, 15:5:1:1) reached the

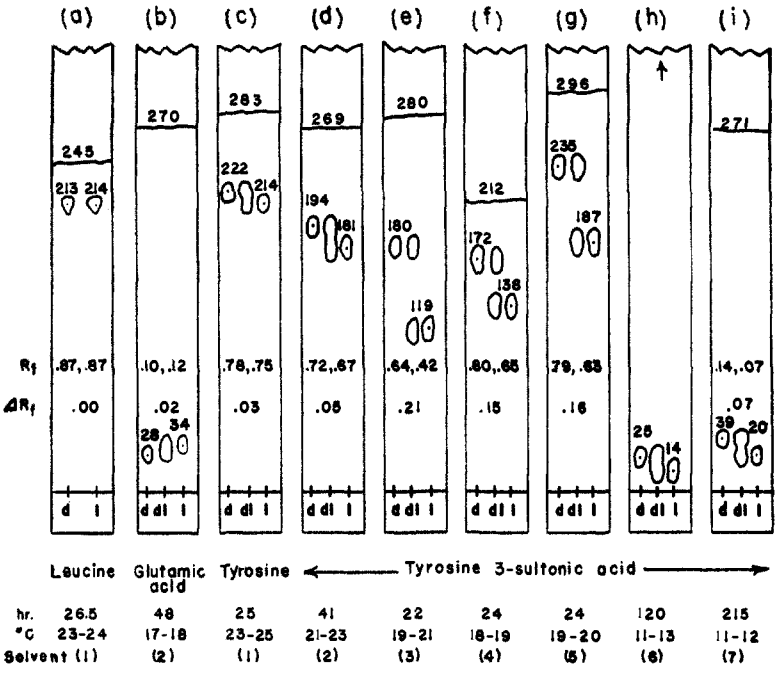

Fig. 1.—Uni-dimensional resolution of amino acids; solvent and compound excursion distances are recorded in mm.; solvent: (1) *l*-amine:AcOH:H_2O:*n*-BuOH, 1:1:1:1; (2) *l*-amine:water, 4:1; (3) *l*-amine:AcOH:H_2O: *n*-BuOH, 1:1:2:6; (4) *d*-amine: AcOH:H_2O:*n*-BuOH, 1:1:1:1; (5) *dl*-amine:AcOH:H_2O:-*n*-BuOH, 1:1:1:1; (6) *n*-BuOH:AcOH:H_2O, 4:1:1; (7) lutidine:AcOH:H_2O:-*n*-BuOH, 1:1:2:6.

bottom and a further 24 hours were required for a total of 733 g. of solvent.

After drying at room temperature, the approximate location of the two isomers was determined with ninhydrin. The amino acid was found in two parts, (I) at disks 180–255 and (II) at disks 275–330.

Each group of disks was eluted, and the amino acids were obtained as mercury salts which were decomposed with hydrogen sulfide to give crystalline products. The crystals from (I) tasted bitter and (II) very sweet. The rotation of (I) was $[\alpha]^{18}D$ −4.14° (2*N* NaOH, c = 1.69%); II, $[\alpha]^{18}D$ +4.47° (2*N* NaOH, c = 1.11%).

It is most reasonable to consider that these resolutions are due at least in part to the asymmetric character of the cellulose.

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FORMATION OF FORMALDEHYDE FROM GLYCEROL-C^{14} BY PROPIONIBACTERIUM[1]

Sir:

It has been previously reported that following the fermentation of glycerol as well as other substrates by *P. arabinosum* in the presence of C^{14} formaldehyde, the isolated propionate was completely labeled, the highest activity occurring in the carboxyl position.[2]

Using glycerol 1-C^{14} as a substrate in a similar fermentation it has now been possible to isolate labeled formaldehyde from the medium.[3]

Eighty micromoles of unlabeled formaldehyde and 2.4 millimoles of glycerol 1-C^{14} per 100 ml. were fermented with resting cells using phosphate-bicarbonate buffer. At the end of 18 hours the formaldehyde was separated by neutral distillation. Twenty-eight micromoles were recovered as determined by the chromotropic acid method.[4] To this 124 micromoles of carrier formaldehyde were added and the dimedon derivative was made and found to have a constant specific activity when recrystallized from aqueous acetone and from aqueous alcohol. The specific activity was 1560 cts./min./mM. of carbon or 8,600 cts./min./mM. carbon in the original undiluted formaldehyde obtained from the fermentation. The average activity of the 1- and 3-carbons of the added glycerol-C^{14} was 13,000. Similar results have been obtained in a second experiment. Formaldehyde added to glycerol-1-C^{14} and isolated without fermentation was found to be inactive.

The propionate formed by resting cells of *P. arabinosum* from glycerol 1-C^{14} also has been degraded. It was separated by steam distillation, chromatographed on a silica gel column and degraded,[5,6] after conversion to lactate through bromination. The distribution of activity expressed as cts./min./mM. was: CH_3-(4760)-CH_2-(4840)-COOH-(8100). The activity of the CO_2 and bicarbonate of the buffer was 1630. This distribution is strikingly similar to that found when formaldehyde C^{14} was fixed in the propionate.[2]

From the results of the above experiments it seems that formaldehyde is formed largely from the 1,3-carbons of glycerol. Whether or not the 2

(1) This work was supported by grant AT-30-1-1050 from the Atomic Energy Commission under the auspices of the Office of Naval Research. Acknowledgment of many helpful suggestions is due to Dr. H. G. Wood.

(2) F. W. Leaver, THIS JOURNAL, **72**, 5326 (1950).

(3) The 1-C^{14} glycerol was kindly furnished by Dr. M. L. Karnovsky of Harvard University.

(4) B. Alexander, G. Landweler and A. M. Seligman, *J. Biol. Chem.*, **160**, 51 (1945).

(5) H. G. Wood and C. H. Werkman, *J. Bact.*, **30**, 332 (1935); *Biochem. J.*, **30**, 618 (1936).

(6) L. F. Goodwin, THIS JOURNAL, **42**, 39 (1920).