and 51% styrene when initiated by typical free radical catalysts such as benzoyl peroxide at 60°; for typical cationic initiators such as $SnCl_4$ a copolymer containing more than 99% styrene is obtained; for typical anionic initiators the copolymer contains more than 99% methyl methacrylate. Thus, the composition of the copolymer formed from β-ray initiation indicates that a free radical mechanism is operative.

By polymerizing pure styrene at 30° with various concentrations of 2-azobisisobutyronitrile, we have shown that the monoradical line[3] at 30° is given by: $1/D.P. = 2.0 \times 10^{-5} + 69.2\, R_p$ (R_p = rate of polymerization in moles liters^{-1} sec.$^{-1}$). For the β-ray induced polymerization the value of R_p is 4.16×10^{-7} (see Table I) and the $D.P.$ is 1.07×10^4. This point falls on the monoradical line, which constitutes another proof of the free radical mechanism.

The rate of initiation of polymer chains for the β-ray induced polymerization can be computed from R_p and the slope of the monoradical line.[2] It is equal to 2.40×10^{-11} mole liter^{-1} sec.$^{-1}$ A similar calculation was made for methyl methacrylate.

If the β-ray induced polymerization, which we have proved to proceed via radicals, occurs homogeneously throughout the medium, and if the energy to produce the initiating radicals be estimated at 50 kcal./mole, we compute that 0.19% of the absorbed radiant energy is effective in producing initiating radicals in the case of styrene and 2.3% of the energy is effective in producing initiating radicals in methyl methacrylate.

(3) D. H. Johnson and A. V. Tobolsky, THIS JOURNAL, **74**, 938 (1952).

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RECEIVED DECEMBER 18, 1952

THE REACTION OF HYDRAZINE AND SYMMETRICAL DIMETHYLHYDRAZINE WITH DIBORANE

Sirs:

The reaction of diborane with hydrazine and with symmetrical dimethylhydrazine in ethereal solution at −80° produces white, crystalline, somewhat ether-soluble 1:1 adducts of the formula $H_3BNHRNHRBH_3$ in which R is either hydrogen or a methyl radical.[1] These formulas are based on the stoichiometry of the reagents and on the fact that hydrolysis of the adducts regenerates the original hydrazine. Furthermore, pyrolysis of these compounds generates one mole of hydrogen per gram atomic weight of nitrogen, in analogy with the pyrolysis of dimethylamine borine, $(CH_3)_2HNBH_3$. Both hydrazine adducts continue to generate hydrogen at a greatly reduced rate after the initial loss. The solid product of pyrolysis of the unsubstituted hydrazine-diborane adduct at 130° was not isolated; the pyrolysis of the dimethylhydrazine adduct at 69° yielded hydrogen, a slightly volatile liquid, discussed below, and small amounts of free dimethylhydrazine and diborane. These facts suggest that decomposition of the adduct is accompanied by slight dissociation.

The hydrazine–diborane adduct was analyzed by hydrolysis, measurement of the evolved hydrogen and subsequent titration of boric acid and hydrazine.[2] *Anal.* Sample weight 0.0780. Calcd. for $N_2H_4 \cdot B_2H_6$: B, 36.15; N_2H_4, 53.59; H, 10.12. Found: B, 36.28; N_2H_4, 53.59; H, 10.12. Similar analysis of the symmetrical dimethylhydrazine adduct gave a B:H ratio of 1:3, and a qualitative identification of symmetrical dimethylhydrazine as its hydrochloride. Quantitative determination of symmetrical dimethylhydrazine awaits development of a satisfactory method of analysis.

Trimethylamine displaces hydrazine from an ethereal solution of its diborane adduct forming trimethylamine borine, $(CH_3)_3NBH_3$. The adduct does not react with either excess diborane or excess hydrazine but is slightly soluble in the latter reagent.

A purified sample of the less volatile liquid obtained in the pyrolysis of the symmetrical dimethylhydrazine–diborane adduct had a melting point of about 0.4° and a molecular weight of 82 (83.8 calculated for $N_2(CH_3)_2 \cdot 2BH_2$) as determined by vapor density measurements at 38.4° and 45.9°. Vapor tensions observed at various temperatures and those calculated by the equation $\log_{10} P_{mm} = 7.8005 - (2027/T)$ were as follows:

T, °K.	273.2	282.5	286.0	291.5	303.6
P_{obs}	2.35	4.25	5.05	7.55	12.75
P_{calc}	2.44	4.22	5.16	7.03	13.30

The preceding facts suggest the structural formula $H_2BN(CH_3)N(CH_3)BH_2$ for the liquid decomposition product. At approximately 60° the liquid slowly produces what appears to be a solid polymer, since the change occurs without the generation of hydrogen, nitrogen or methane.

Data obtained from the reactions of hydrazine and its derivatives with trimethyl boron and boron trichloride as well as the reaction of ethylene diamine with diborane will be presented at a later date.

(1) The present investigation was begun before the article by H. J. Emeléus and F. G. A. Stone (*J. Chem. Soc.*, 840 (1951)) on the reaction of diborane with hydrazine had appeared. Their failure to obtain definite results was probably due to the facts that they used no solvent, and did not recrystallize their product.

(2) I. M. Kolthoff, THIS JOURNAL, **46**, 2009 (1924).

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RECEIVED JANUARY 21, 1953

L-HISTIDINE CONVERSION TO A URINARY GLUTAMIC ACID DERIVATIVE IN FOLIC-DEFICIENT RATS

Sir:

The previously reported[1] derivative of glutamic acid, excreted in the urine of folic-deficient rats, has been crystallized as a barium salt, containing one equivalent of glutamic and formic acids and ammonia.[2] A similar barium salt has been crys-

(1) (a) H. A. Bakerman, M. Silverman and F. S. Daft, *J. Biol. Chem.*, **188**, 117 (1950); (b) M. Silverman, R. C. Gardiner and H. A. Bakerman, *ibid.*, **194**, 815 (1952).

(2) M. Silverman, unpublished data.

tallized after the degradation of histidine by liver extracts[3]; both salts are converted to L-glutamic acid by *Pseudomonas fluorescens* extracts, which degrade L-histidine to L-glutamic and formic acids and ammonia.[4] The relationship of the excreted glutamic derivative to L-histidine metabolism was strengthened by the observation of a large increase in the excretion of bound (heat-labile) glutamic acid when histidine was added to the diet of folic-deficient rats.[5] The assay used[1,5] usually failed to detect any glutamic derivative in the urine of normal rats, even when histidine was added to the diet.[5]

To establish the origin of the glutamic acid derivative, L-histidine, labeled with N^{15} in the γ position,[6] was fed to five folic-deficient rats.[7] The barium salt of the glutamic derivative was crystallized from the pooled urines after chromatography on Dowex 50 and Dowex 1.

TABLE I

	Millimoles	Atom % excess N^{15} [a]
L-Histidine fed[b]	10.6	1.61 (in 3 N atoms)
Glutamic derivative excreted	4.6	1.37 (in 2 N atoms)

[a] We are indebted to Dr. Julius White for the N^{15} analyses. [b] Including the histidine of the dietary casein.

If the dietary N^{15} histidine were not diluted by body histidine, the N^{15} content of the glutamic derivative would have been 2.4 atom per cent. excess. The observed value of 1.37 therefore indicates that approximately 55% of this glutamic derivative excreted was derived from the dietary N^{15}-histidine. Crystalline L-glutamic acid ($[\alpha]^{20}D$ = 30.4° in 6 *N* HCl), isolated after hydrolysis of the barium salt with *Pseudomonas* extract, was found to contain essentially all of its N^{15} (2.5 atom % excess).

The major pathway of histidine degradation in both liver homogenates[8,9,10] and *Pseudomonas* extracts[11] has been shown to proceed via urocanic acid, rather than by a primary rupture of the imidazole ring[12]; the γ (rather than the α) nitrogen of the histidine persists in the glutamic acid ultimately found. The use of folic deficient rats has permitted demonstration of this pathway *in vivo*, as the glutamic acid moiety of the compound excreted contains the isotope of the nitrogen of the administered histidine. Although glutamic derivatives, obtained by incubating histidine with liver preparations, have been assigned various structures by other workers,[9,10,12,13] our synthetic and degradative studies do not yet permit an unequivocal structure to be written for our barium salts. The role of folic acid in the metabolism of histidine, and the relationship of the intermediates of histidine metabolism to one-carbon metabolism[14] remain to be determined.

(3) A. Mehler and H. Tabor, unpublished.

(4) H. Tabor and O. Hayaishi, *J. Biol. Chem.*, **194**, 171 (1952).

(5) F. S. Daft, M. Silverman, H. Tabor and A. Mehler, in preparation.

(6) Synthesized essentially as described by C. Tesar and D. Rittenberg, *J. Biol. Chem.*, **170**, 35 (1947).

(7) The folic-deficient (succinylsulfathiazole-containing) diet was that previously used (1, 2, 5).

(8) A. Mehler and H. Tabor, *J. Biol. Chem.*, in press.

(9) K. Sera and D. Aihara, *J. Osaka Med. Soc.*, **41**, 745 (1942).

(10) Y. Oyamada, *J. Biochem. (Japan)*, **36**, 227 (1944).

(11) H. Tabor, A. H. Mehler, O. Hayaishi and J. White, *J. Biol. Chem.*, **196**, 121 (1952).

(12) S. Edlbacher, *Ergeb. Enzymforsch.*, **9**, 131 (1943).

(13) A. Abrams and H. Borsook, *J. Biol. Chem.*, **198**, 205 (1952).

(14) The metabolism of the 2C of histidine has been reviewed recently by M. Toporek, L. Miller and W. F. Bale, *ibid.*, **198**, 839 (1952).

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FACTORS AFFECTING MOLECULAR WEIGHT OF ENZYMATICALLY SYNTHESIZED DEXTRAN

Sir:

Dextrans, glucose polymers in which the α-1,6-glucopyranosidic linkage predominates[1,2] generally have molecular weights of 6 to 100 million when produced by conventional fermentation procedures.[3] Polymers in the same molecular weight range are produced in reaction mixtures containing initially 10% sucrose and dextransucrase,[3,4,5] the dextran-synthesizing enzyme. To be suitable as a blood plasma substitute, such dextran must be degraded to a molecular weight of *ca.* 75,000.[6,7] By variation of reaction conditions, part of the enzymatically synthesized dextran was obtained having a molecular weight of 400,000 or less. Dextransucrase used in our investigations was derived from *Leuconostoc mesenteroides* NRRL B-512.[8] Average molecular weights were determined either by ultracentrifugal or light scattering measurements.

As stated above, dextran with a high molecular weight is synthesized in reaction mixtures containing initially 10% sucrose. However, low molecular weight polysaccharide of *ca.* 8000 was synthesized in 70% sucrose reaction mixtures. The molecular weight distribution at intermediate sucrose levels was bimodal, a portion distributed about 40 million and the other about a varying molecular weight below 30,000. This effect was due at least partially to the influence of accumulated fructose on the course of the polymerization.

Reaction mixtures containing enzyme, sucrose, and certain glucosyl acceptors such as fructose or maltose yield oligosaccharides and low molecular weight dextran, as well as high molecular weight polymer.[9] The average molecular weight of the former was raised to its maximum of 35,000 by the

(1) T. H. Evans and H. Hibbert, "Advances in Carbohydrate Chem.," Academic Press, Inc., New York, N. Y., **2**, 203 (1946).

(2) Allene Jeanes and C. A. Wilham, THIS JOURNAL, **72**, 2655 (1950).

(3) F. R. Senti and N. N. Hellman, Amer. Chem. Soc., Abstract of Papers for 121st Meeting, 8O, (1952).

(4) E. J. Hehre, *Science*, **93**, 237 (1941).

(5) E. J. Hehre, "Advances in Enzymology," Interscience Publishers, Inc., New York, N. Y., **11**, 297 (1951).

(6) Military Medical Purchase Description, No. 1, May 24, 1951, Armed Services Medical Procurement Agency, Brooklyn 1, New York.

(7) E. J. Pulaski, *Chem. Eng. News*, **30**, 2187 (1952).

(8) H. M. Tsuchiya, H. J. Koepsell, J. Corman, G. Bryant, M. O. Bogard, V. H. Feger and R. W. Jackson, *J. Bacteriology*, **64**, 521 (1952).

(9) H. J. Koepsell, H. M. Tsuchiya, N. N. Hellman, A. Kazenko, C. A. Hoffman, E. S. Sharpe and R. W. Jackson, *J. Biol. Chem.*, in press.