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.