of the labeled reaction partner. These activities were measured on samples of barium sulfate, prepared from S, H_2S and SO_2 by oxidation, and were corrected for self-absorption.[4] The results are given in Table I.

TABLE I

Reactant labeled with S^{35}	Reactant used in excess	Ratio (as %) of specific activities of elementary sulfur and of labeled react. partn.
H_2S	H_2S	61, 64
SO_2	H_2S	34, 32, 34
SO_2	SO_2	31, 28
H_2S	SO_2	71, 70, 67, 66
		68, 74, 74, 70

The conditions in each series of experiments have been varied widely; reactants were sometimes added as solutions, sometimes in gaseous form, either undiluted, or diluted with nitrogen. Occasionally an excess of 0.1 *N* HCl was present, in which case the reactants were added as solutions of their sodium salts.

Lanthanum nitrate was added, sometimes before, sometimes after the reactants were mixed, to precipitate the sulfur. In most cases the elementary sulfur was filtered off within two hours but occasionally it was left in the solution overnight. In all experiments the mixing of the reactants was performed in less than one hour, in order to reduce the effect of reactions between the added compound and the reaction products, like polythionic acids.

Our results indicate that under all circumstances the main portion of the elementary sulfur originates from H_2S and SO_2 in the ratio 2:1. This conclusion is in agreement with all theories on the subject, in which the partial reaction responsible for the sulfur formation does not simultaneously produce other sulfur compounds.[1,5,6,9]

There is also formal agreement with the mechanism proposed by Zil'berman,[7] but only if the primary reaction is supposed to be really termolecular—as it is written by him—which is highly improbable. The reaction-mechanism of von Deines and Grassmann[2] could be made to agree with our results by introduction of several suppositions not explicitly made by these authors. Our observations exclude the mechanism proposed by Heinze.[8]

Another conclusion which may be derived from our results is that no appreciable exchange of sulfur between H_2S and SO_2 occurs within the time required for the formation of sulfur. The absence of such an exchange rules out the rapid formation of an intermediate compound in equilibrium with both reactants, unless the former compound contains sulfur atoms in positions which are not equivalent.

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RECEIVED JANUARY 5, 1953

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(4) A. H. W. Aten, Jr., *Nucleonics*, **6**, No. 1, 68 (1950).

(5) F. Foerster and A. Hornig, *Z. anorg. allgem. Chem.*, **125**, 86 (1922).

(6) H. Stamm and M. Goehring, *cf.* the review by the latter, *loc. cit.*

(7) Ya. I. Zil'berman, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1257 (1940).

(8) E. Heinze, *J. Prakt. Chem.*, **99**, 109 (1919).

(9) H. Basset and H. G. Durrant, *J. Chem. Soc.* (London), 1401 (1927).

β-RAY INITIATION OF POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE

Sir:

The effect of β-radiation as an initiator of polymerization of pure styrene, pure methyl methacrylate and an equimolar mixture of these monomers has been studied.

The source of β-particles was an equilibrium mixture of anhydrous $Sr^{90}Cl_2$ and $Y^{90}Cl_3$ (half life of 19.9 years) giving a spectrum of electrons with a maximum energy of 2.24 Mev. The source was placed in a small glass bulb of about 2 mm. diameter. It was held by a rigid stem at the center of the spherical end of a small distilling flask which had a capacity of 8 cc. and which was filled with the monomer to be studied. The total energy of the particles entering the monomers was $5.0 \times 10^{-6} \pm 0.5 \times 10^{-6}$ cal./sec. and was completely absorbed by the surrounding monomer. The range of the 2.24 Mev. β-particles is *ca.* 11.5 mm. (depending upon the density of the material); the inner radius of our monomer-containing bulb was 12.4 mm.

The rates of β-ray induced polymerization of styrene, methyl methacrylate and the equimolar mixture were all measured at 30.5° in the vessels described above. Control experiments were made under identical conditions to measure the purely thermal rate. The results are shown in Table I.

TABLE I

POLYMERIZATION AT 30.5°

% CONVERSION PER HOUR

β-Ray induced	Monomer	Thermal
0.019	Styrene (S)	0.007
.26	Methyl methacrylate (MMA)	.11[a]
.039	Equimolar mixture (S) and (MMA)	.016

[a] This rate is somewhat high due probably to adventitious peroxides remaining after our purification procedure.

Each result given in Table I is the average of at least three runs—the maximum deviation being approximately 10% in the case of the β-ray induced polymerization. Air was found to be a powerful inhibitor of the β-ray induced polymerization and the thermal polymerization.

The composition of the copolymers was determined by C–H analysis and calculation of the % methyl methacrylate. The result of the determination[1] gave a methyl methacrylate content in the copolymer of 50.2% ± 4.0.

Walling, *et al.*,[2] have shown that an equimolar solution of styrene and methyl methacrylate gives a copolymer containing 49% methyl methacrylate

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(1) Clark Microanalytical Laboratory, Urbana, Ill., and Joseph F. Alicino, Metuchen, N. J.

(2) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, THIS JOURNAL, **72**, 48 (1950).

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.

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[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.

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[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-

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[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.