in methanol) was obtained. (*Anal.* Found: C, 68.19; H, 5.64; P, 5.07). Metathesis with ammonium iodide gave the levorotatory phosphonium iodide, m.p. 158–159°, $[\alpha]^{25}\text{D}$ −23.8° (*c*, 0.927 in methanol). (*Anal.* Found: C, 51.75; H, 5.18; P, 8.34; I, 34.35.)

The availability of the enantiomorphic phosphonium iodides will enable studies on the stereochemical course of important reactions, including the conversion of the corresponding phosphonium hydroxides to asymmetric phosphine oxides and reductions by lithium aluminum hydride, to be carried out. Studies in these areas are in progress in this Laboratory.

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THE HIGH TEMPERATURE REACTION BETWEEN SULFUR DIOXIDE AND BENZENE

Sir:

The principal volatile decomposition products in the pyrolysis of diphenyl sulfone are sulfur dioxide and benzene.[1] When the decomposition is carried to completion at temperatures of 500° and higher there is a noticeable decrease in the concentrations of these products This communication reports the results of a short experimental investigation of the reaction between sulfur dioxide and benzene.

TABLE I

THE REACTION OF SO_2 AND C_6H_6

			Concentration, cc.-atm., STP					
			Reactants		Products			
Run	Temp., °C.	Time, hr.	SO_2	C_6H_6	SO_2	C_6H_6	Other condensables	Non-condensables
1	540	15	20.5	20.5	5.8	7.2	2.2[a]	NA
8	540	15	20.3	20.3	8.6	NA	0.9	0.1
7	528	2	20.2	20.0	20.4	19.3	0.2	0.1
4	510	15	20.5	20.5	17.8	15.5	0.3	0
6	493	15	20.2	20.2	18.7	17.2	0.4	0
5[b]	490	15	20.9	20.9	15.6	17.7	0.3	0
5	481	15	20.5	20.5	20.0	20.0	0.3	0
2	400	15	20.5	20.3	20.5	19.9	...	0

[a] Mass spectrometer analysis of this fraction in %: CO_2 53.35; COS, 39.0; SO_2 3.5; O_2, 1.3; C_6H_6, 0.9; CS_2, 0.7; H_2S, 0.2; H_20, 0.5–1.0. [b] This reaction was run in the presence of polymeric residue obtained from a previous decomposition of diphenyl sulfone.

Equimolar mixtures of sulfur dioxide and benzene reacted in sealed Pyrex bulbs between 400 and 540°. The principal decomposition products are not volatile at room temperature. Yellow and white crystals were separated from a dark polymeric residue by distillation under vacuum at 450°. The yellow product was identified as sulfur by melting point determination and the white crystals as dibenzothiophene by infrared analysis. The volatile products were analyzed by standard high-vacuum techniques. Results in the accompanying table show a significant reaction between sulfur dioxide and benzene at temperatures above 480°.

With the exception of Run 7, all of the reactions were carried out for 15 hours so that a preliminary investigation of the reaction kinetics might be attempted. If one assumes from the data that sulfur dioxide and benzene react by a second-order process, then for an equimolar mixture the consumption of either reactant is expressed as

$$1/C - 1/C_0 = kt$$

Since time was constant for these runs, the term $(1/C - 1/C_0)$ is proportional to the rate constant for the reaction, if the kinetics are independent of extent of reaction. One can then determine the temperature dependency or apparent activation energy by plotting the log $(1/C - 1/C_0)$ against $1/T$. An apparent activation energy calculated on this basis is approximately 88 kilocalories per mole. Since the dissociation energy of the S–O bond in sulfur dioxide[2] is 92 kcal./mole and the C–H bond in benzene is 102 kcal./mole,[3] the activation energy for this reaction may be representative of the breaking of an S–O bond in sulfur dioxide.

Summarizing, sulfur dioxide and benzene are shown to react at approximately 500° by a process compatible with second order kinetics forming sulfur, dibenzothiophene, a polymeric residue, carbon dioxide, carbonyl sulfide, oxygen, and traces of carbon disulfide, hydrogen sulfide, and water.

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(2) L. P. Blanchard and P. LeGoff, *Can. J. Chem.*, **35**, 89 (1957).

(3) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955, p. 15.