

Reaction of  $\alpha$ -Phenethyl Radical in Liquid Sulfur DioxideMasashi IINO,\*<sup>1</sup> Tsutomu ENOMOTO and Niichiro TOKURA

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Squire and Waters found that in the reaction of phenyl radical with sulfur dioxide diphenyl disulfone was formed by coupling reaction of benzene sulfonyl radicals, but diphenyl sulfone could not be obtained.<sup>1)</sup> On the other hand, in the reaction of methyl radical with sulfur dioxide both dimethyl disulfone and dimethyl sulfone were formed.<sup>2)</sup>

We have investigated the reaction of sulfur dioxide with  $\alpha$ -phenethyl radical formed by the decomposition of 1,1'-azo-bis-1-phenylethane or by the abstraction of  $\alpha$ -hydrogen atom from ethyl benzene.

We obtained neither disulfone ( $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{-SO}_2\text{SO}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3$ ) nor monosulfone ( $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{SO}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3$ ) in thermal or photochemical decomposition reaction of 1,1'-azo-bis-1-phenylethane in liquid sulfur dioxide, although 2,3-diphenylbutane, the coupling product of  $\alpha$ -phenethyl radicals, was obtained. The same results as described above have been obtained in the reaction of ethylbenzene and benzoyl peroxide in the presence of sulfur dioxide.

These results are interesting, contrasting with those of reactions of methyl and phenyl radical. It is reasonable to consider that  $\alpha$ -phenylethane sulfonyl radical is formed in these reactions, and has little reactivity toward coupling reaction, because in the radical copolymerization of styrene and sulfur dioxide<sup>3)</sup> styrene polysulfone ( $-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{SO}_2-$ ) is formed and a substituted  $\alpha$ -phenylethane sulfonyl radical ( $-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{SO}_2\cdot$ ) seems to be one of the chain carriers. At present, however, the reason why we have obtained neither disulfone nor monosulfone is not clear.

## Experimental

**Materials.** 1,1'-Azo-bis-1-phenylethane was prepared from acetophenone.<sup>4,5)</sup> 1,1'-Azo-bis-1-phenylethane obtained was recrystallized three times from 99%

ethanol. Found: C, 79.93; H, 7.24; N, 12.22%. Calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_2$ : C, 80.67; H, 7.56; N, 12.22%. mp 70.2—73.0°C (lit<sup>5)</sup> 72.3—72.9°C),  $\lambda_{\text{max}}$  355—357  $\mu$ .

Liquid sulfur dioxide was dehydrated with phosphorus pentoxide and distilled. Ethylbenzene was washed with concentrated sulfuric acid and water successively, dried with anhydrous magnesium sulfate, and then distilled. Commercial benzoyl peroxide was used without further purification.

**Reaction of 1,1'-Azo-bis-1-phenylethane with Sulfur Dioxide (Thermal Decomposition of 1,1'-Azo-bis-1-phenylethane in Liquid Sulfur Dioxide).**

Into a glass pressure vessel (about 300 ml capacity)<sup>6)</sup> charged with 1,1'-azo-bis-1-phenylethane (3 g), liquid sulfur dioxide (45 g) was introduced by using a pressure resistant buret<sup>6)</sup> after the replacement of oxygen in the vessel by nitrogen stream. This reaction vessel was then immersed in boiling water (95—97°C) and kept for eight hours. Sulfur dioxide in the vessel was then evaporated under reduced pressure. Extraction with petroleum ether from the residue (3.2 g) and removal of the solvent from the extract (petroleum ether-soluble part) gave a viscous oil (2.1 g). This oil was then dissolved in about 10 ml of petroleum ether and chromatographed on an alumina column. Elution with petroleum ether gave colorless crystals of 2,3-diphenylbutane (0.1 g), which were recrystallized from methanol. Found: C, 91.44; H, 8.56%. Calcd for  $\text{C}_{16}\text{H}_{18}$ : C, 91.37; H, 8.63%. mp 123.5—124.5°C (lit<sup>5)</sup> 125.3—125.9°C). Elution with benzene gave yellow crystals of acetophenone-azine (1.0 g), mp 122—123°C (recrystallized from ethanol) (lit<sup>5)</sup> 122.2—123.0°C), which showed no depression of melting point by mixing with an authentic specimen. Further elution with benzene gave a yellow liquid of acetophenone (small amount) which was identified by its transformation into 2,4-dinitrophenylhydrazone.

As the petroleum ether-insoluble part was found to be acidic, about 30 ml of water was added into the substance and the resulting solution was neutralized by aqueous sodium hydroxide solution. The solution was then extracted with diethyl ether. Acetophenone (0.3 g) was obtained from the ethereal solution by evaporating ether and then distilling the residue under reduced pressure. Addition of aqueous barium chloride solution to water layer gave 0.3 g of barium sulfate.

Neither disulfone nor monosulfone could not be identified, and IR spectra of petroleum ether-soluble and insoluble parts did not show their presence.

On the other hand, acetophenone and sulfate ion obtained from the petroleum ether-insoluble part are considered to be formed by the decomposition of petro-

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TABLE 1. THERMAL REACTION OF 1,1'-AZO-BIS-1-PHENYLETHANE (APE) WITH SULFUR DIOXIDE

Reactant (g)		Solvent (g) ethyl- benzene	Reaction temp. (°C)	Reaction time (hr)	Product (mol%)*			
APE	SO <sub>2</sub>				2,2-diphenyl- butane	acetophenone azine	aceto-** phenone	SO <sub>4</sub> <sup>2-</sup> **
1.0		43	95-97	8	24.0			
3.0	47		70	72	3.0	12.4	6.6	9.1
3.0	45		95-97	8	3.0	35.0	11.6	11.6
3.0	15	78	95-97	8	9.4	7.4	19.6	6.8
3.0	30	69	95-97	8	8.3	2.1	16.5	7.5

\* This value was calculated from the molar ratio of product *vs.* APE.

\*\* Sulfate ion and probably a part of acetophenone was formed from the decomposition of an unidentified product by water.

TABLE 2. PHOTOCHEMICAL REACTION OF 1,1'-AZO-BIS-1-PHENYLETHANE (APE) WITH SULFUR DIOXIDE

Reactant (g)		Solvent (g) ethyl- benzene	Reaction temp. (°C)	Reaction time (hr)	Product (mol%)*			
APE	SO <sub>2</sub>				2,3-diphenyl- butane	acetophenone azine	aceto-** phenone	SO <sub>4</sub> <sup>2-</sup> **
2.9	45		room temp.	24	5.7	trace	19.8	16.3
3.0	15	82	room temp.	24	20.4	12.1	16.5	9.5

\* This value was calculated from the molar ratio of product *vs.* APE.

\*\* Sulfate ion and probably a part of acetophenone was formed from the decomposition of an unidentified product by water.

leum ether-insoluble product by water. This materials was at first a white solid and then turned into a yellow and sticky solid on exposure to air, and had the absorption near 2600 cm<sup>-1</sup> (broad) and 1200 cm<sup>-1</sup> which disappeared after the addition of water. Although the structure of the product is not yet established, it is considered to be neither disulfone nor monosulfone from its chemical behavior.

Similar experiments were carried out at different reaction temperatures, or by using solvents. The results are summarized in Table 1. Table 1 also shows that the decomposition of 1,1'-azo-bis-1-phenylethane in ethyl benzene gave 2,3-diphenylbutane. No reaction occurred at room temperature in the 1,1'-azo-bis-1-phenylethane-sulfur dioxide system, although mixing of the two reactants exhibited a yellow coloration due, probably, to the formation of a charge-transfer complex.

**Reaction of 1,1'-Azo-bis-1-phenylethane with Sulfur Dioxide under Irradiation of Ultraviolet Light.** 1,1'-Azo-bis-1-phenylethane has a strong absorption in the region of 320 mμ to 400 mμ ( $\lambda_{\max}$  355-357 mμ). The reaction vessel was a quartz cylindrical vessel equipped with a stainless steel joint connected by

a stopcock<sup>6)</sup> to a pressure-resistant buret.<sup>6)</sup> The reaction was carried out under irradiation by using a 300 W mercury lamp. Other details of the experimental procedure were the same as described in the case of the thermal decomposition of 1,1'-azo-bis-1-phenylethane in liquid sulfur dioxide and the results obtained are summarized in Table 2.

Table 2 shows that the same products as listed in Table 1 were obtained and no sulfone could be detected.

**Reaction of Ethylbenzene and Benzoyl Peroxide in the Presence of Sulfur Dioxide.** A Solution of benzoyl peroxide (30 g) in ethylbenzene (300 ml) in a 1 l round-bottomed flask was heated at 70°C under a reflux condenser, and sulfur dioxide was passed into slowly through an inlet glass tube extending to the bottom of the flask. Passage of sulfur dioxide was continued for 42 hr. The treatment of the reaction mixture afforded 14.2 g of benzoic acid, 0.4 g of 2,3-diphenylbutane and 4.5 g of low molecular-weight styrene-polysulfone, but no sulfone having  $\alpha$ -phenethyl group could be obtained.

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