imide in benzene at higher temperatures. The system

$$C_6H_5SO_2N_2C_6H_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} [C_6H_5SO_2\cdot \mid C_6H_5N_2\cdot] \xrightarrow{k_3} C_6H_5\cdot + N_2 + C_6H_5SO_2\cdot$$

leads to the kinetic rate law

$$-\frac{\mathrm{d(P)}}{\mathrm{d}t} = \left(\frac{k_1k_3}{k_2 + k_3}\right)\mathrm{(P)}$$

so that

$$k_{\text{observed}} = \frac{k_1k_3}{k_2 + k_3}$$

It is reasonable to expect that k_1 and k_3 will have *positive* energies of activation, even if that for k_3 may be small. It then becomes apparent that the only condition under which k_{obsd} can exhibit a higher temperature coefficient at higher temperatures is if k_2 has a negative temperature coefficient, and if k_2 decreases more with increasing temperature than k_3 increases. This is a reasonable conclusion, because higher temperatures should reduce the probability of recombination of the radical fragments for reasons proposed by Franck and Rabinowitch, *i.e.*, the dissipation of the dissociation energy to energetic solvent molecules becomes more difficult, and the fragments will travel further apart after dissociation before coming to rest.

An alternative explanation can be based on the assumption that an induced decomposition with kinetic order 1.0 does occur in benzene solution. The spontaneous decomposition will dominate over the induced decomposition at higher temperature because it is a higher activation energy process; this will be reflected in a greater temperature coefficient at higher temperatures.

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Azo Compounds. XXXIII.[1] Products of the Thermal Decomposition of Phenylphenylsulfonyl Diimide

BY C. G. OVERBERGER AND A. J. ROSENTHAL[2]

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The products of the thermal decomposition of phenylphenylsulfonyl diimide were studied and found to be consistent with a mechanism which involved some decomposition of the starting material into phenylazo and phenylsulfonyl radicals. Phenylphenylsulfonyl diimide initiated the polymerization of styrene, methyl methacrylate, vinyl acetate and acrylonitrile, and under suitable conditions high molecular weight polymers were obtained. A polystyrene was obtained which contained azo and sulfone groups.

Our preceding paper[1] described the thermal decomposition rates for phenylphenylsulfonyl diimide in alkaryl solvents and in the presence of monomers. From the kinetic data it was inferred that the principal decomposition route was by separation into free radical fragments; that there was induced decomposition by radicals derived from the solvents; and that an autocatalyzed ionic decomposition could be suppressed by a base. This paper presents the isolation and characterization of the thermal decomposition products of phenylphenylsulfonyl diimide, and of the polymers produced using this material as initiator.

Experimental

Materials.—The preparation of phenylphenylsulfonyl diimide, and the purifications of solvents and monomers have been described previously.[1]

Phenyl *p*-methylbenzyl sulfone, not previously reported, was prepared as a reference sample by heating 5 g. (0.025 mole) of sodium benzenesulfinate with 5 g. (0.027 mole) of α-bromo-*p*-xylene in 8 g. of ethanol under reflux for 5 hours. The solid mass which formed was washed with water, recrystallized three times from aqueous ethanol to obtain 2.5 g. (40%) of white needles, m.p. 149°.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.25; H, 5.73. Found: C, 68.00; H, 5.75.

Decomposition of Phenylphenylsulfonyl Diimide in Benzene.—A solution of 24.6 g. (0.10 mole) of phenylphenylsulfonyl diimide in 2500 ml. (27.8 moles) of benzene, containing 10.0 g. (0.18 mole) of calcium oxide, was deaerated with purified nitrogen and then maintained at a reflux temperature at atmospheric pressure for 7 hours. The introduction of nitrogen was continued throughout the reflux period to prevent the entrance of any oxygen. After cooling the solution and removal of the calcium oxide phase, an aliquot of the solution was evaporated to dryness in a stream of nitrogen gas. The brown tar residue was fractionated by steam distillation and the fractions were developed on an activated alumina column with petroleum ether–benzene mixtures and benzene–acetone mixtures to obtain identified products in the yields shown in column 1 of Table I.

Another fresh solution of 1.0 g. (0.004 mole) of phenylphenylsulfonyl diimide in 130 g. (1.7 moles) of benzene containing 1.0 g. (0.018 mole) of calcium oxide was flushed with prepurified nitrogen, and then stirred 48 hours at 70° in a sealed apparatus; 1.16 g. of the calcium oxide phase recovered by filtration of the benzene solution contained only an insignificant trace of calcium benzenesulfinate when tested by attempting a coupling of a water extract of the calcium oxide with benzenediazonium chloride. The benzene solution after removal of the calcium oxide was concentrated to 5 ml. in a stream of nitrogen under vacuum at room temperature. The concentrate was developed on a silica gel column "pre-wetted" with benzene. The sequence of solvents used, in gradually changing mixtures of adjacent pairs, was benzene, ethyl acetate, ethanol, methanol. Some of the fractions were resolved further by repeated chromatography. Identified products were isolated in the yields shown in column 2 of Table I.

Decomposition of Phenylphenylsulfonyl Diimide in *p*-Xylene.—*p*-Xylene was chosen as a decomposition solvent because monosubstitution in the ring could produce only one isomer. A solution of 12.3 g. (0.05 mole) of phenylphenylsulfonyl diimide in 65 g. of *p*-xylene was added over a 5-minute period to an agitated mixture of 10.0 g. (0.18 mole) of calcium oxide in 517 g. (total of 5.6 moles) of refluxing *p*-xylene which was maintained oxygen-free by a slow stream

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[1] This is the 33rd in a series of papers related to the chemistry of azo compounds; for the previous paper in this series, see A. J. Rosenthal and C. G. Overberger, THIS JOURNAL, **82**, 108 (1960).

[2] A portion of a thesis by A. J. Rosenthal submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

TABLE I

PHENYLPHENYLSULFONYL DIIMIDE DECOMPOSITION PRODUCTS

Column	1	2	3	4
Solvent	Benzene	Benzene	*p*-Xylene	*p*-Xylene
Temp., °C.	78	70	138	75
Compound	Moles per mole of phenylphenylsulfonyl diimide			
Benzene[a]	Solvent	Solvent	0.20	0.22
Biphenyl[b]	0.45	0.50	..	..
2,5-Dimethylbiphenyl[c]	..	..	.26	.10
Azobenzene[d]	.02	.05	..	.012
Phenyl-*p*-biphenyldiimide[e]	.005	.005	..	..
Diphenyl disulfide[f]	..	.04	.01	..
Phenyl sulfone[g]	.05	..	.03	..
Diphenyl disulfone[h]	..	..	.022	..
Benzene sulfinic acid[i]	.27[k]	..	.013	.13
Phenyl *p*-methylbenzyl sulfone[j]	..	..	.16	..
Nitrogen	.85	.85	.95	.40

[a] Isolated by fractionation of *p*-xylene reaction solvent; identified by boiling point, refractive index and infrared spectrum. [b] M.p. 68° (69°)[3]; a mixed m.p. with authentic diphenyl, 69°. [c] B.p. 283°, n^{25}_D 1.5753, λ_{max} 283 mμ (cyclohexane), most likely 2,5-dimethyldiphenyl, not previously described; the ultraviolet absorption spectrum is almost identical with that of 2-methylbiphenyl and showed none of the characteristic ultraviolet absorptions of diphenylmethane. *Anal.* Calcd. for $C_{14}H_{14}$: C, 92.24; H, 7.76. Found: C, 92.25; H, 7.69. [d] M.p. 67–68°; mixed m.p. with authentic azobenzene, m.p. 67–68°. [e] M.p. 152–153° (150–151°),[4] tentative identification. [f] Recrystallized from ethanol, m.p. 60°. An authentic sample of diphenyl disulfide melted at 61–62°, mixed m.p. 60.5–62°. *Anal.* Calcd. for $C_{12}H_{10}S_2$: C, 66.00; H, 4.61. Found: C, 66.4; H, 4.43. [g] Recrystallized from aqueous ethanol, m.p. 127–130°, mixed m.p. with authentic phenyl sulfone m.p. 128–130°, m.p. 127–129° (128–129°).[5] [h] Recrystallized from ethanol, m.p. 192–194° (193–194°).[6] *Anal.* Calcd. for $C_{12}H_{10}S_2O_4$: C, 51.04; H, 3.57. Found: C, 51.35; H, 3.62. [i] Isolated as calcium salt, coupled with benzenediazonium chloride to yield phenylphenylsulfonyl diimide, m.p. 76°; a mixed m.p. with an authentic sample, m.p. 77°, melted at 76°. [j] Recrystallized from aqueous ethanol, then ligroin, m.p. 148.5–149.5°; a mixed melting point with an authentic sample, m.p. 149°, melted at 149°.

of prepurified nitrogen. Heating was continued for an additional 15 minutes (the half-life of the reaction at this temperature was known to be 9 seconds), the reaction mixture was cooled and filtered free of calcium oxide. Evaporation of a 5-ml. aliquot showed the presence of 10.3 g. of non-volatile decomposition products. The decomposition solution in *p*-xylene was concentrated by fractional freezing of the *p*-xylene. The "pure" *p*-xylene frozen out by this method was found, surprisingly, to contain 0.32 g. (0.0011 mole) of a solid, recoverable by evaporation of the *p*-xylene. This solid was recrystallized from ethanol to obtain dense granular white crystals of diphenyl disulfone, m.p. 192–194° (193–194°).[12] The brown tar was again resolved by chromatographic separation into the products whose yields are shown in column 3 of Table I.

Another portion of 25.0 g. (0.1 mole) of phenylphenylsulfonyl diimide was decomposed in 500 ml. of deoxygenated *p*-xylene and 10.0 g. of calcium oxide at 75° for 21 hours. The calcium oxide phase was filtered from the solution, washed with *p*-xylene and extracted with water. Evaporation of the water extract produced 2.6 g. (0.013 mole) of calcium benzenesulfinate. This salt coupled with benzenediazonium chloride to give phenylphenylsulfonyl diimide, m.p. 77–77.5° from ethanol; a mixed melting point with an authentic sample melted at 77–77.5°.

Half of the *p*-xylene decomposition solution was distilled to dryness at 3 mm. pressure. The distillate, collected in a −70° trap, was refluxed in a 2.5 × 90 cm. helices packed column to a constant head temperature of 123°. A 1.0-ml. fraction boiling from 123–127° was shown by an infrared analysis to be 38% benzene and 62% *p*-xylene. Successive 1.0-ml. cuts contained 25, 20 and 10% benzene for a total of 0.9 g. (0.011 mole).

The residue after removing *p*-xylene, 13.0 g., was extracted with petroleum ether. The 2.0 g. of petroleum ether-soluble portion was developed on an alumina column to yield 0.9 g. (0.005 mole) of 2,5-dimethylbiphenyl, identified as described in Table I. Further development produced 0.11 g. (0.0006 mole) of azobenzene, m.p. 63–66°, which on recrystallization from aqueous ethanol had a m.p. 67°; a mixed melting point with an authentic sample, m.p. 67°, was not depressed, m.p. 67–67.5°. After removal of several trace fractions of orange, yellow and red oils by further development with petroleum ether, benzene development eluted 0.20 g. of a red tar and methanol eluted another 0.05 g. of red tar fraction. These latter two fractions were combined with the petroleum ether-insoluble portion.

The petroleum ether-insoluble portion, 0.5 g., was developed on an alumina column with petroleum ether–benzene mixtures to produce red, yellow, orange and green oils and tars in trace quantities, none greater than 0.005 g. A fraction, 0.085 g. of red tar, crystallized on standing, m.p. 150–154°, which on analysis gave an appreciable nitrogen content (5.5%) and left an ash on ignition.

Polystyrene Formation.—Styrene was polymerized by the decomposition of 0.516 g. of phenylphenylsulfonyl diimide in 10 ml. of styrene, 140 ml. of benzene and 0.50 g. of calcium oxide at 70° under nitrogen. After 24 hours, 8% of the theoretical amount of nitrogen was evolved, no undecomposed diimide was detected by a β-naphthol color test, and 1.95 g. of polystyrene was obtained by precipitation with methanol. The polystyrene was reprecipitated from benzene by pouring into methanol and washed with hot methanol. The purified polymer was bright yellow.

Anal. Found: N, 1.28; S, positive. The infrared spectrum of the polymer contained absorptions at 2.33, *7.58*, *7.65*, 7.93, *8.68*, *8.80*, 9.20 and 12.5 microns which were not present in a thermally polymerized polymer. Those values italicized correspond to sulfone absorptions.

To obtain a high molecular weight polystyrene, 29 mg. of diimide was decomposed in 150 ml. of styrene at 70°. After 2 hours, 3.0 g. of polystyrene was recovered by precipitation with methanol which had an intrinsic viscosity in benzene of 0.44.

Hydrolysis of Polystyrene.—A tenth of a gram of the above polymer (1.28% N) was refluxed with 5 ml. of acetone and 0.1 ml. of 0.1 *N* hydrochloric acid for 1 hour, evaporated to dryness, dissolved in benzene, precipitated into methanol and washed with hot methanol. *Anal.* Found: N, 0.94. In a second attempt 0.2 g. of the polystyrene (1.28% N) was refluxed with 5 ml. of acetone, 0.1 ml. of concentrated hydrochloric acid for 48 hours and processed as above. *Anal.* Found: N, 0.17. The infrared spectrum of the recovered polymer showed that the absorptions at 7.93 and 12.5 μ had disappeared, all the other extra absorptions remained, and a new absorption band with a peak at 5.91 μ appeared.

Other Polymerization Reactions.—Methyl methacrylate was polymerized by decomposition of 0.133 g. of phenylphenylsulfonyl diimide in 15 ml. of monomer, 135 ml. of benzene and 0.50 g. of calcium oxide at 70°; 6.5 g. of polymer having an intrinsic viscosity of 0.24 was obtained after 6 hours by precipitation into methanol.

Vinyl acetate and acrylonitrile were also readily polymerized in bulk and in benzene solution.

Discussion

All of the decomposition products reported in Table I can be considered to be derived by spontaneous cleavage of phenylphenylsulfonyl diimide into phenylazo and phenylsulfonyl radicals, transfer of radical activity to solvent, induced decomposition by original or solvent derived radicals, and combination of all possible radicals. Attack on aromatic solvent can result by over-all displacement of hydrogen atoms and consequent formation of reduction products. The situation is complicated by the possibility of attack of the various free

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[3] J. H. Perry, Editor, "Chemical Engineers' Handbook," Second Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 288.

[4] L. P. Griess, *Ber.*, **9**, 132 (1876); E. Bandrowski and M. Prokopeczko, *Chem. Zentr.*, **75**, 1491 (1904).

[5] O. Hinsberg, *Ber.*, **43**, 290 (1910).

[6] T. Hilditch, *J. Chem. Soc.*, **93**, 1526 (1908).

radicals on the products accounted for above, thus producing the numerous small fractions isolated by chromatography for which identification was not completed.

Products in Benzene.—The formation of the products isolated from the decomposition of phenylphenylsulfonyl diimide in benzene can be accounted for by the following sequence of reactions. All reactions which indicate a hydrogen atom as a product are only to show the over-all process. As noted below, no hydrogen atoms are obtained as such.

Spontaneous cleavage:

$$C_6H_5N_2SO_2C_6H_5 \longrightarrow C_6H_5N_2\cdot + C_6H_5SO_2\cdot \tag{1}$$

Evolution of nitrogen:

$$C_6H_5N_2\cdot \longrightarrow C_6H_5\cdot + N_2 \tag{2}$$

Attack on solvent:

$$C_6H_5\cdot + C_6H_6 \longrightarrow C_6H_5C_6H_5 + H\cdot\ \text{(addition)} \tag{3}$$

The hydrogen atom is removed from the intermediate addition product by a radical or a radical acceptor.

$$C_6H_5SO_2\cdot + C_6H_6 \longrightarrow C_6H_5SO_2C_6H_5 + H\cdot\ \text{(addition)} \tag{4}$$

The hydrogen atom removed from intermediate addition by another radical or radical acceptor.

$$C_6H_5N_2\cdot + C_6H_6 \longrightarrow C_6H_5N{=}NC_6H_5 + H\cdot\ \text{(addition)} \tag{5}$$

Induced decomposition:

$$C_6H_5\cdot + C_6H_5N_2SO_2C_6H_5 \longrightarrow C_6H_5N{=}NC_6H_5 + C_6H_5SO_2\cdot \tag{6}$$

$$\longrightarrow C_6H_5SO_2C_6H_5 + C_6H_5N_2\cdot \tag{7}$$

$$C_6H_5SO_2\cdot + C_6H_5N_2SO_2C_6H_5 \longrightarrow C_6H_5SO_2SO_2C_6H_5 + C_6H_5N_2\cdot \tag{8}$$

Radical combination:

$$2C_6H_5\cdot \longrightarrow C_6H_5C_6H_5 \tag{9}$$

$$2C_6H_5SO_2\cdot \longrightarrow C_6H_5SO_2SO_2C_6H_5 \tag{10}$$

$$C_6H_5N_2\cdot + C_6H_5\cdot \longrightarrow C_6H_5N_2C_6H_5 \tag{11}$$

$$C_6H_5SO_2\cdot + C_6H_5\cdot \longrightarrow C_6H_5SO_2C_6H_5 \tag{12}$$

(intermediate addition product)

$$H\cdot + C_6H_5SO_2\cdot \longrightarrow C_6H_5SO_2H \tag{13}$$

In addition, radical attack on products could produce additional products in small yields.

$$C_6H_5\cdot + C_6H_5N{=}NC_6H_5 \longrightarrow C_6H_5C_6H_4N{=}NC_6H_5 \tag{14}$$

Products in *p*-Xylene.—The formation of products by decomposition in *p*-xylene includes additional reaction possibilities due to the alkyl side chains.

Attack on solvent:

$$C_6H_5\cdot + CH_3C_6H_4CH_3 \longrightarrow C_6H_6 + CH_3C_6H_4CH_2\cdot \tag{15}$$

$$\longrightarrow C_6H_5C_6H_3(CH_3)_2 + H\cdot\ \text{(addition)} \tag{16}$$

$$C_6H_5SO_2\cdot + CH_3C_6H_4CH_3 \longrightarrow C_6H_5SO_2H + CH_3C_6H_4CH_2\cdot \tag{17}$$

$$C_6H_5SO_2\cdot + CH_3C_6H_4CH_3 \longrightarrow C_6H_5SO_2C_6H_3(CH_3)_2 + H\cdot\ \text{(addition)} \tag{18}$$

$$C_6H_5N_2\cdot + CH_3C_6H_4CH_3 \longrightarrow C_6H_5N{=}NC_6H_3(CH_3)_2 + H\cdot\ \text{(addition)} \tag{19}$$

Induced decomposition:

$$CH_3C_6H_4CH_2\cdot + C_6H_5N_2SO_2C_6H_5 \longrightarrow CH_3C_6H_4CH_2N{=}NC_6H_5 + C_6H_5SO_2\cdot \tag{20}$$

$$\longrightarrow CH_3C_6H_4CH_2SO_2C_6H_5 + C_6H_5N_2\cdot \tag{21}$$

Radical combination:

$$C_6H_5\cdot + CH_3C_6H_4CH_2\cdot \longrightarrow C_6H_5CH_2C_6H_4CH_3 \tag{22}$$

$$C_6H_5N_2\cdot + CH_3C_6H_4CH_2\cdot \longrightarrow C_6H_5N{=}NCH_2C_6H_4CH_3 \tag{23}$$

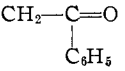
$$C_6H_5SO_2\cdot + CH_3C_6H_4CH_2\cdot \longrightarrow C_6H_5SO_2CH_2C_6H_4CH_3 \tag{24}$$

The introduction of the concept of diffusion recombination of radicals in a cage does not alter the expected products.

It is interesting to note the formation of azobenzene, phenyl sulfone and diphenyl disulfone in xylene solution. Phenyl sulfone may have been formed in a cage recombination reaction. The azobenzene and diphenyl disulfone most likely are products of induced decomposition by phenyl or phenylsulfone radical, eq. 7 and 9 (or its indistinguishable counterpart, capture of a caged radical), but the possibility exists that they could have been formed by random free radical combination.

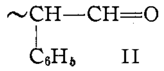
Polymer.—The Experimental section described the preparation and characterization of a polystyrene with $C_6H_5N_2-$ and $C_6H_5SO_2-$ end groups. The appearance of a strong infrared absorption at 5.91 μ on removal of the nitrogen end-group by hydrolysis is of particular interest because this absorption indicates aromatic ketone corresponding to a polystyrene with end-group structure I rather than II.

I



$$\sim CH_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}O$$

II



$$\sim\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}CH{=}O$$

According to established principles for the initiation of styrene polymerization, attack occurs at the β-carbon.[7] Thus the presence of carbonyl at the α-carbon is suggestive that a large portion of the $C_6H_5N_2-$ groups entered the polymer by attack of polystyrene radical on the diimide, *i.e.*, by induced decomposition of the diimide. The high diimide concentration, 0.014 *M*, used in this polymerization would be expected to favor the chain induced decomposition route considerably.

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[7] C. S. Marvel and E. C. Horning in H. Gilman, "Organic Chemistry," Second Edition, Vol. I, Chap. 8, John Wiley and Sons, Inc., New York, N. Y., 1943.