[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN, AND SUMMIT RESEARCH LABORATORY, CELANESE CORPORATION OF AMERICA]

Azo Compounds. XXXII.[1] Kinetics of the Thermal Decomposition of Phenylphenylsulfonyl Diimide

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

RECEIVED JUNE 9, 1959

A study was made of the thermal decomposition of phenylphenylsulfonyl diimide. Decomposition rates in benzene and alkylbenzenes were followed by nitrogen gas evolution, and by a colorimetric procedure based on the formation of phenylazo-β-naphthol; the reaction was autocatalyzed by an acidic product; the autocatalyzed decomposition was inhibited by calcium oxide suspended in the solvent. The decomposition rate constant in benzene increases twofold on going from 60 to 70° and fourfold from 70 to 78°. The rates measured at low diimide concentration in toluene, xylene and ethyl benzene at 70° were the same as in benzene, but increased at higher concentrations while the rate in benzene remained constant. The addition of oxygen, iodine, trinitrobenzene, chloranil, styrene, vinyl acetate and acrylonitrile further accelerated the decomposition of the diimide. Three alternative mechanisms are proposed to account for the accelerated decomposition rate in the presence of radical scavingers: a bimolecular reaction of scavenger with the diimide; a radical induced decomposition of order 1.0; a capture by the scavenger of "caged" free radicals which otherwise have a high probability of recombination to undissociated diimide. Our data make no absolute distinction among these alternatives; however we are inclined to favor the latter.

Introduction

Phenylphenylsulfonyl diimide (diazosulfone), formed by mixing aqueous solutions of benzenediazonium chloride and sodium benzene-sulfinate, was recognized as a sulfone by Koenigs.[3] The diimides are covalent compounds, soluble in organic solvents and insoluble in water. It is generally conceded that they exist in the *trans* configuration.[4] They decompose on melting or warming in solution with the evolution of nitrogen gas.[5] They have been reported to initiate the emulsion polymerization of butadiene–styrene,[6] and to initiate other vinyl polymerizations in solution.[7] These features suggested that free radical fragments might be generated in solution.

The present work was undertaken to study the course of the thermal decomposition of phenylphenylsulfonyl diimide in solution. The data obtained show evidence for a spontaneous free radical decomposition, an autocatalyzed ionic decomposition, induced decomposition by attack of solvent-derived free radicals, and the possible occurrence of a diffusion-controlled free radical recombination process.

Experimental

Materials.—Sodium benzenesulfinate was prepared from benzenesulfonyl chloride by reduction with zinc dust by the method of Whitmore and Hamilton.[8] Phenylphenylsulfonyl diimide, m.p. 77.0–77.5°, was prepared by the method described by Hantzsch,[9] by mixing equimolar portions of benzenediazonium chloride in aqueous hydrochloric acid, free of excess nitrous acid, and sodium benzenesulfinate in water at 5° (75–76°[3]; 78°[4]). The crude yield was quantitative when based on diazotized aniline and using an excess of sodium benzenesulfinate of uncertain assay.

The nitrogen gas used for deaeration of the solutions used for kinetic measurements was "prepurified" quality, supplied by the Matheson Co.

The best available solvents were obtained commercially. Benzene, toluene, ethylbenzene, and *p*-xylene were washed with cold concentrated sulfuric acid, followed by distilled water, and dried and distilled over sodium. *p*-Xylene was further purified prior to drying by fractional freezing until a constant melting fraction at 13.5° was obtained. All other solvents were dried over potassium carbonate or calcium sulfate. All the solvents were fractionally distilled through a 90 by 2.5 cm. column packed with $^1/_8$ inch, single turn glass helices. In each case a middle fraction was collected which had a maximum boiling range of 0.1°. Diphenylmethane, styrene, methyl methacrylate and acrylonitrile were distilled at reduced pressure in a nitrogen atmosphere.

Iodine (Baker Analyzed Reagent) was used without further purification. Trinitrobenzene (Eastman Kodak Co.) was recrystallized from ethanol, m.p. 122.5°. Chloranil (Matheson, Coleman and Bell) was recrystallized from benzene, m.p. 290° (subl.).

Kinetic Measurements.—The decomposition of phenylphenylsulfonyl diimide in solution could be followed by nitrogen gas evolution, or by development of a color by reaction of unconsumed diimide with β-naphthol. In a few experiments the reaction was followed by the absorption of oxygen gas.

In the gas evolution method, 150 ml. of solvent was contained in a 3-necked 200-ml. flask immersed in a pigmented oil-bath, the temperature of which was kept constant to ±0.05°. A motor driven stirrer passed through a mercury seal in the center neck. A combination gas-inlet sparge and gas-outlet was fitted into a second neck. The gas outlet was connected through capillary tubing to a drying tube containing "indicating" calcium sulfate, then to a 100-ml. gas buret and a water-leveling bulb. The third neck was equipped with a solenoid to hold an 8 mm. × 12 mm. deep sample cup by its iron core, sealed-in-glass, handle. The entire apparatus was operated in a constant temperature room at 25.0 ± 0.5°. Prepurified nitrogen was bubbled through the solvent at a slow rate for a minimum of 15 minutes prior to starting a reaction. The reaction was started in the sealed and equilibrated system by releasing the solenoid-held sample into the solvent. The volume of gas evolved was then measured as a function of time. In determining the nitrogen gas yield, corrections were made for the vapor pressures of the solvent and water, and for changes in barometric pressure. Initial concentrations of diimide between 0.005 and 0.05 M could be handled by this procedure.

For following the diimide concentration colorimetrically, the color-developing solution was prepared from 900 ml. of reagent methanol, 100 ml. of distilled water, 2 g. of β-naphthol, 5 ml. of acetic acid and 10 g. of sodium acetate. The decomposition reaction was started as described above. At intervals, appropriate size aliquots were transferred from the reaction flask into 25.00 ml. of the β-naphthol solution; prepurified nitrogen was bubbled through the reaction flask whenever it was necessary to open it for removal of the ali-

---

(1) This is the 32nd in a series of papers related to the chemistry of azo compounds; for the previous paper in this series, see C. G. Overberger, M. P. Mazzeo and J. J. Godfrey, *J. Org. Chem.*, **24**, 1407 (1959); please address correspondence to C. G. Overberger.

(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.

(3) W. Koenigs, *Ber.*, **10**, 1531 (1877).

(4) H. C. Freeman, R. J. W. LeFevre, J. Northcott and I. Youhotsky, *J. Chem. Soc.*, 3381 (1952).

(5) R. L. Schlessinger, U. S. Patent 2,588,885, March 11, 1952.

(6) R. W. Brown, U. S. Patent 2,527,393, October 24, 1950.

(7) C. W. Theobold, U. S. Patent 2,564,306, February 5, 1952.

(8) A. H. Blatt, Editor, "Organic Syntheses," Second Edition, Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 492.

(9) A. Hantzsch and M. Singer, *Ber.*, **30**, 312 (1897); **31**, 641 (1898).

quots. At least three hours was allowed for formation of the phenylazo-β-naphthol color. Concentrations were then estimated from transmittance measurements made at 490 mμ with a Lumetron model 402-E photoelectric colorimeter. In some reaction mixtures containing monomers, polymer precipitates had to be filtered out before measuring the transmittance. In reaction mixtures containing chloranil a correction had to be made for the color which developed by interaction of chloranil and β-naphthol. This technique permitted the measurement of diimide decomposition rates at starting concentrations as low as 7×10^{-5} *M*.

Results and Discussion

Autocatalytic Decomposition.—The decomposition of phenylphenylsulfonyl diimide was first studied in toluene at 90° in a nitrogen atmosphere by the nitrogen gas evolution method. The rate of nitrogen evolution did not obey a simple first-order rate law (curve A in Fig. 1 is typical), nor was the final volume of nitrogen evolved, V_∞, ever as much as the theoretical volume. Table I shows that the initial rate of nitrogen evolution was indeed proportional to the initial diimide concentration, but the rate at the half-life, and the total nitrogen yield, increased with increasing initial diimide concentration.

TABLE I

PHENYLPHENYLSULFONYL DIIMIDE IN 160 ML. OF TOLUENE AT 90°: NITROGEN EVOLUTION RATE *versus* INITIAL CONCENTRATION

Initial diimide concn., *M*	Initial nitrogen evolution ml./min.	Nitrogen evolution at $t_{1/2}$, ml./min.	Ratio $\frac{\text{init. rate}}{\text{init. concn.}}$	Ratio $\frac{t_{1/2}\text{ nitrogen evol.}^a}{\text{init. nitrogen evol.}}$	Total nitrogen yield, %
0.0079	0.8	0.5	1.0	0.63	67
.0115	1.4	1.0	1.2	.71	79
.0301	3.7	3.1	1.2	.84	79
.0332	4.0	3.4	1.2	.85	77
.0455	5.6	5.2	1.2	.93	80

[a] Expected value 0.50 for pure first-order reaction.

Evidence for an autocatalysis mechanism was obtained by dropping a fresh portion of diimide into a spent solution of decomposition products and observing an appreciably greater decomposition rate (curve B *versus* curve A in Fig. 1), and a higher nitrogen gas yield than would be obtained in pure solvent. The spent solution after a decomposition reaction is acidic. The addition of benzenesulfonic acid greatly accelerates the decomposition rate. If the developed acidity is buffered by the presence of suspended calcium oxide the nitrogen evolution rate can be represented by a first-order rate law, such as curve C in Fig. 1, and the total nitrogen yield is reduced. The isolation of calcium benzenesulfinate from the calcium oxide phase is described in our following paper.[10] Unless it is noted otherwise all the following kinetic measurements were made with calcium oxide suspended in the solvent.

Oxygen Absorption.—When nitrogen flushing is omitted from a diimide decomposition in toluene there is an initial gas volume shrinkage (Fig. 2, curve B) and the final net gas volume increase is appreciably less than when the nitrogen flush is used (Fig. 2, curve A). The decrease in gas yield, 14 ml., was estimated to be equal to the volume of oxygen contained in the air inside the reaction flask. Figure 2, curve C, shows a smooth gas volume shrinkage for a decomposition followed in an excess of pure oxygen. A plot of log $(V_\infty - V)/V_\infty$ *versus* *t* for the oxygen absorption data produces a straight line with a first-order rate constant of 7.6×10^{-4} sec.$^{-1}$ at 80°, 15% faster than the rate constant observed for the same reaction in a nitrogen atmosphere. Absorption of the excess oxygen in pyrogallol solution after completion of the run corresponding to curve C, Fig. 2, revealed the presence of 38 ml. of nitrogen, so that the actual oxygen consumption was 104 ml. or 2.2 moles/mole of diimide.

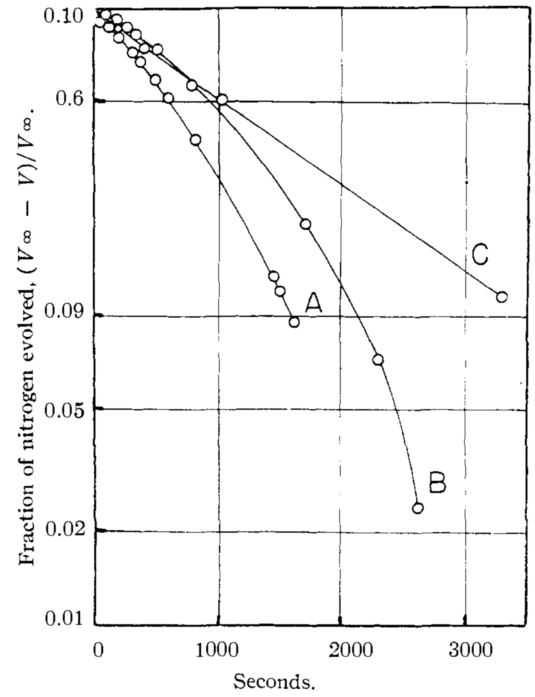


Fig. 1.—First-order rate plots for decomposition of phenylphenylsulfonyl diimide in toluene at 90°: A, 0.0298 *M* diimide, fresh solvent, 82% nitrogen evolved; B, 0.0302 *M* diimide, exhausted solution from A, 86% nitrogen evolved; C, 0.0097 *M* diimide, 0.13% w./v. CaO in suspension, 69% nitrogen evolved.

Decomposition in an excess of oxygen, but in the absence of calcium oxide, produced the results shown in curve D, Fig. C, which after correcting for the volume of nitrogen evolved corresponds to only 1.1 moles of oxygen consumed/mole of diimide decomposed. This lower oxygen consumption is attributed to the fact that the part of the diimide which was decomposed by acidic autocatalysis did not produce oxygen-absorbing radicals.

Russell[11] has also reported oxygen absorption kinetics and shows no effect of oxygen on the rate of α,α'-azobisisobutyronitrile decomposition in cumene or ethylbenzene, and a retardation of the decomposition of benzoyl peroxide in cumene. This is in contrast to the acceleration we have observed with phenylphenylsulfonyl diimide.

---

(10) C. G. Overberger and A. J. Rosenthal, THIS JOURNAL, **82**, 117 (1960).

(11) G. A. Russell, *ibid.*, **78**, 1044 (1956).

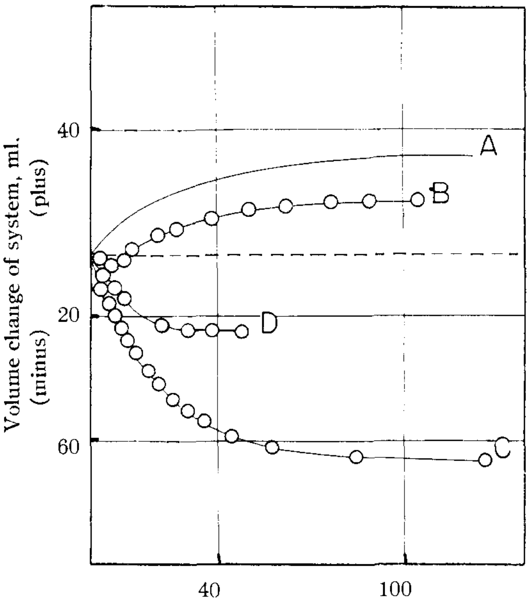


Fig. 2.—Effect of atmosphere on decomposition of phenylphenylsulfonyl diimide in 160 ml. of toluene at 90°: initial concentration 0.011 *M;* 1.3% w./v. CaO in suspension. Atmosphere above reaction mixture: A, nitrogen; B, air; C, oxygen; D, oxygen (0.016 *M;* no CaO used).

All the following kinetic data were obtained by decompositions under nitrogen.

Solvent Radical Induced Decomposition.—Table II shows first-order rate constants and nitrogen gas yields for the decomposition of phenylphenylsulfonyl diimide at 70° in a series of alkaryl hydrocarbons. The salient features of the data are that at very low initial diimide concentrations, $\sim 10^{-4}$ M, the rate constants are about the same in all the solvents except diphenylmethane; but at higher concentrations there is considerable divergence in rates and nitrogen yields, and only the rates in benzene and diphenylmethane remain constant.

Some parallels exist between phenylphenylsulfonyl diimide decomposition kinetics and benzoyl peroxide decomposition kinetics; the latter has been the subject of much recent work. Nozaki and Bartlett[12] showed that in addition to the unimolecular dissociation of the peroxide to form two $C_6H_5COO\cdot$ radicals, there was also a chain decomposition induced by radicals derived from either the peroxide or the solvent. Nozaki and Bartlett, and Swain, *et al.*,[13] showed that, depending on which radicals were attacking the peroxide molecules, and the nature of the chain carrier termination step, the order x of the induced decomposition, with rate constant k_i, could vary between 0.5 and 2.0.

$$- d(P)/dt = k_1(P) + k_i(P)^x \qquad (1)$$

(P) = concentration of phenylphenylsulfonyl diimide

The induced decomposition mechanism appears appropriate to the phenylphenylsulfonyl diimide system. Figure 3 shows the first-order decomposition rate constant for phenylphenylsulfonyl diimide in toluene at 70° as a function of diimide concentration. This straight line relationship establishes the order of the induced decomposition, *i.e.*, x in eq. 1, to be 2. The intercept provides an estimate of $k_1 = 0.22 \times 10^{-4}$ sec.$^{-1}$, and the slope provides an estimate of $k_i = 0.15 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. A similar analysis for the other alkaryl solvents provides the data shown in the last two columns of Table II.

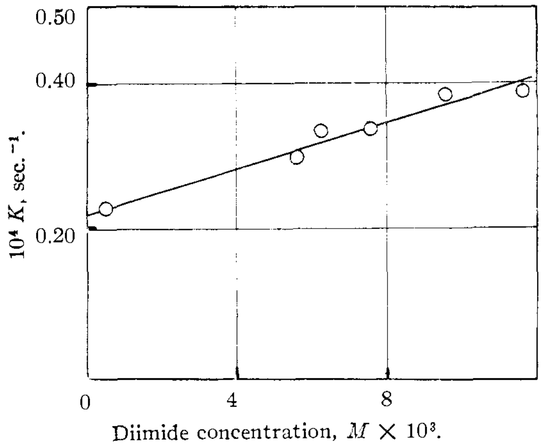


Fig. 3.—First-order rate constants *versus* phenylphenylsulfonyl diimide concentration in toluene at 70°: 0.33% w./v. CaO suspension; nitrogen atmosphere.

TABLE II

PHENYLPHENYLSULFONYL DIIMIDE IN ALKARYL SOLVENTS AT 70°: FIRST-ORDER DECOMPOSITION RATE CONSTANTS *versus* DIIMIDE CONCENTRATION

(0.33% w./v. calcium oxide; nitrogen atmosphere)

Solvent	Diimide, $M \times 10^3$	k_{obsd}, 10^4 sec.$^{-1}$	Nitrogen yield, %	k_1, 10^4 sec.$^{-}$	k_i, 10^{-2} l. mole^{-1} sec.$^{-1}$
Benzene	13.5	0.21[e]	91	[a]	[b]
	7.9	.22			
	1.17	.26			
	0.73	.26			
	.58	.26			
	.45	.24		0.25	0
Toluene	14.8	.29[e]	63		
	12.0	.39			
	0.52	.23		.22	0.15
p-Xylene	11.0	.40			
	7.8	.36			
	7.6	.38[e]	65		
	0.14	.29		.28	.11
Ethylbenzene	14.7	.52[c,e]	40		
	11.0	.46			
	0.14	.24		.24	.20
Diphenyl-methane	15.0	.072[e]	81		
	15.0	.080			
	0.14	.077		.076	0
Ethyl acetate[d]	4.55	.46			
	0.16	.22		.19	0.55

[a] Obtained from intercept of plot k_{obsd} *versus* diimide concentration. [b] Obtained from slope of plot k_{obsd} *versus* diimide concentration. [c] Not a straight line first-order plot; average rate over first half-life. [d] Included for comparison with vinyl acetate data of Fig. 8. [e] Rate followed by nitrogen gas evolution; all other rates are initial slopes from colorimetric data.

---

[12] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

[13] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

Diphenylmethane shows no induced decomposition term and the smallest spontaneous decomposition constant k_1. It is usually accepted that the lowest decomposition rate observed in any solvent comes closest to representing the spontaneous decomposition. However, the large number of estimates of k_1 in the other solvents coming close to the k_1 estimate for the decomposition rate in benzene leads one to suspect some other explanation for the low rate in diphenylmethane. Based on data presented later in the paper it is possible that the bulky viscous diphenylmethane solvent molecules act as an effective cage to prevent separation of primary fragments thus promoting recombination to starting material.

Nitrogen Gas Evolution.—The lower nitrogen gas yield observed in the alkaryl solvents as compared to benzene suggests that the induced decomposition term, $k_i(\mathrm{P})^2$, is responsible for the less than quantitative yields of nitrogen gas. Carrying the benzoyl peroxide analogy further, Barnett and Vaughan have reported that the carbon dioxide yield from the thermal decomposition of benzoyl peroxide increases with increasing dilution and consequent diminution of the induced decomposition in that system.[14] The decomposition rate of phenylphenylsulfonyl diimide could be followed by either nitrogen gas evolution or by colorimetric estimation of the remaining diimide. When the second-order induced decomposition term is appreciable the two methods do not give equivalent results. The gas evolution data generally give first-order rate plots which can be fitted by straight lines, which, it can be shown, are fortuitous. The colorimetric data show a faster initial rate and a slight curvature, indicating a reduction in decomposition rate as the reaction proceeds. The latter is in agreement with the form of eq. 1.

Free Radical Scavengers.—Nozaki and Bartlett showed that the rate of benzoyl peroxide decomposition in solution is slower in the presence of oxygen, hydroquinone or picric acid. Hammond and Soffer[15] used iodine to inhibit the induced decomposition and to effectively trap $C_6H_5COO\cdot$ radicals. Swain, *et al.*,[13] did the most extensive study of inhibitors for the induced decomposition of benzoyl peroxide and found stilbene, acrylonitrile, styrene, 3,4-dichlorostyrene, 1,4-diphenylbutadiene, iodine, methyl methacrylate and trinitrobenzene to be the best and equally effective in inhibiting the chain decomposition of benzoyl peroxide in dioxane. The convergence of their rate data to a limiting slow value with these eight inhibitors suggested that these inhibitors successfully captured all, or nearly all, radicals in solution to yield in their place radicals which are almost incapable of attacking peroxide.

The addition of a free radical scavenger appeared attractive as a means for inhibiting the chain-induced decomposition of phenylphenylsulfonyl diimide and determining whether the observed decomposition rate in benzene, or in diphenylmethane, represented the spontaneous unimolecular decomposition rate. Table III shows results obtained when 0.83 *M* styrene was added to each of the alkaryl solvents considered in Table II. The presence of styrene, instead of causing a reduction in decomposition rate, caused an appreciable acceleration of the diimide decomposition in the entire series of solvents.

TABLE III

FIRST-ORDER RATE CONSTANTS FOR DECOMPOSITION OF 0.016 *M* PHENYLPHENYLSULFONYL DIIMIDE IN ALKARYL SOLVENTS CONTAINING 0.83 *M* STYRENE AT 70°

0.33% w./v. calcium oxide; nitrogen atmosphere

Solvent with 0.83 *M* styrene	k, 10^4 sec.$^{-1}$	Nitrogen yield, %
Benzene	0.79	0
Toluene	.85	17
p-Xylene	.78	20
Diphenylmethane	.42	0

Table IV presents the effects of a number of radical scavengers on the decomposition rate of the diimide in benzene. In this table the rates are presented as the time to first half-life because some of the data did not fit first-order plots. Each of the additives accelerated the decomposition reaction, the most outstanding effect occurring in the presence of iodine. At this point the parallelism between the phenylphenylsulfonyl diimide system and the benzoyl peroxide system breaks down. In an attempt to gain an understanding of the phenomenon a number of the free radical scavenger systems were studied in detail.

TABLE IV

HALF-LIFE OF 0.01 *M* PHENYLPHENYLSULFONYL DIIMIDE IN BENZENE CONTAINING FREE RADICAL SCAVENGERS AT 70°

Scavenger	Scavenger concn., *M*	Half-life, hr.
None	...	8.7[a]
Trinitrobenzene	0.094	4.3[b]
Vinyl acetate	1.10	2.8[a]
Styrene	0.83	2.4[a]
Chloranil	.054	2.3[a]
Iodine	.016	0.013[b]

[a] Colorimetric measurements. [b] Gasometric measurement.

Iodine.—Table V summarizes the rate data obtained for the decomposition of the diimide in benzene in the presence of iodine. The entire set of data corresponds to a bimolecular rate equation

$$-\mathrm{d(P)}/\mathrm{d}t = 0.162 \times \text{mole}^{-1}\ \text{sec.}^{-1}\ \mathrm{(P)(I_2)} \quad (2)$$

Figure 4 shows the goodness of fit to a second-order plot for two of the runs in which the starting concentrations of the reactants were not equal.

Styrene.—The diimide decomposition kinetics in benzene–styrene mixtures are summarized in Fig. 5. These data show a dependence of the first-order rate constant on the initial diimide concentration, and the induced decomposition equation of Nozaki and Bartlett, eq. 1, again appears appropriate. In this case the best fit is obtained with x = 1.5, *i.e.*, the plots in Fig. 5 of observed first-order rate constant *versus* square root of phenylphenylsulfonyl diimide concentration, $\mathrm{(P)}^{0.5}$, yield straight lines with intercept k_s and slope k_i.

$$-\mathrm{d(P)}/\mathrm{d}t = k_s\mathrm{(P)} + k_i\mathrm{(P)}^{1.5}$$

$$k_{\text{obsd}} = k_s + k_i\mathrm{(P)}^{0.5}$$

---

[14] B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926 (1947).

[15] G. S. Hammond and L. M. Soffer, THIS JOURNAL, **72**, 4711 (1950).

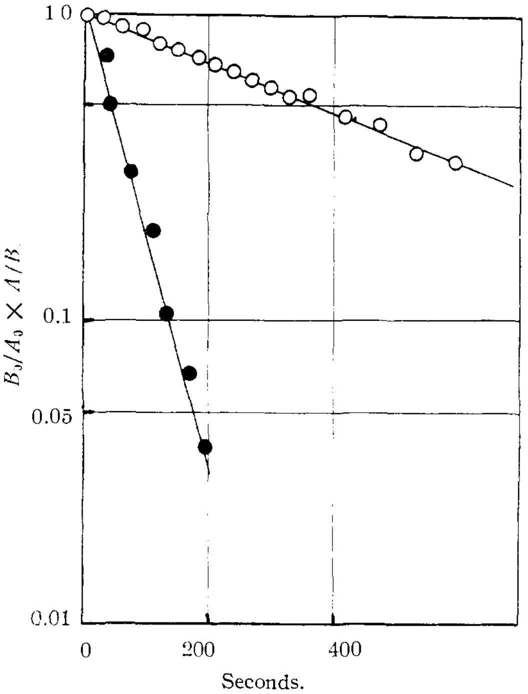


Fig. 4.—Second-order rate plot for decomposition of phenylphenylsulfonyl diimide in benzene containing iodine at 70°: 0.33% CaO, nitrogen atmosphere; gasometric method. Initial concentrations of diimide, iodine and rate constants: white circles, 0.141 *M*, 0.0250 *M*, 0.174 l. mole^{-1} sec.$^{-1}$; black circles, 0.0143 *M*, 0.125 *M*, 0.154 l. mole^{-1} sec.$^{-1}$

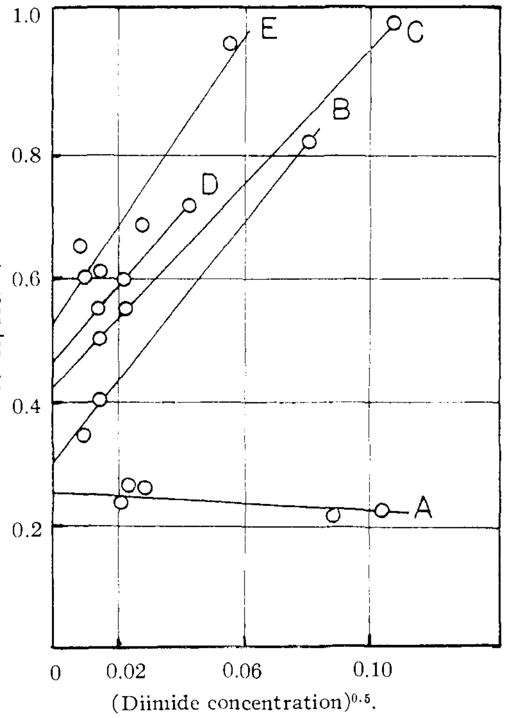


Fig. 5.—Phenylphenylsulfonyl diimide first-order decomposition rate constants in benzene–styrene mixtures at 70°. Solvents: curve A, benzene; curve B, 0.55 *M* styrene; curve C, 2.77 *M* styrene; curve D, 5.54 *M* styrene; curve E, 8.30 *M* styrene (bulk).

TABLE V

SECOND-ORDER RATE CONSTANTS[a] FOR DECOMPOSITION OF PHENYLPHENYLSULFONYL DIIMIDE IN PRESENCE OF IODINE IN BENZENE SOLUTION AT 70°

0.33% w./v. calcium oxide, nitrogen atmosphere

A_0, phenylphenylsulfonyl diimide, *M*	B_0, iodine, *M*	*k*, l. mole^{-1} sec.$^{-1}$	Nitrogen yield, %
0.0125	0.0125	0.157[b]	100
.0143	.0250	.174[c]	100
.0141	.1250	.154[c]	100
		Av. 0.162	

[a] Followed by nitrogen gas evolution. [b] Obtained from slope of plot of $1/C_A$ *versus* *t*. [c] Obtained from slope of plot of $\left(\frac{C_{B_0}}{C_{A_0}} \times \frac{C_A}{C_B}\right)$ *versus* $\left(\frac{C_{A_0} - C_{B_0}}{2.303}\right) t$.

where k_s is the spontaneous decomposition rate constant in the presence of scavenger and k_i is the induced decomposition rate constant. The intercepts in Fig. 5 provide the k_s values at zero concentration of diimide. These k_s values at zero concentration, plotted in Fig. 6 *versus* styrene concentration, show an initial high dependence on styrene concentration that appears to level off at about $k_s = 0.6 \times 10^{-4}$ sec.$^{-1}$. The same data plotted in Fig. 7 as a function of (styrene)$^{0.5}$ give an excellent straight line with intercept k_1 and slope k_2. Thus, an empirical equation for describing the rate of disappearance of diimide concentration in benzene–

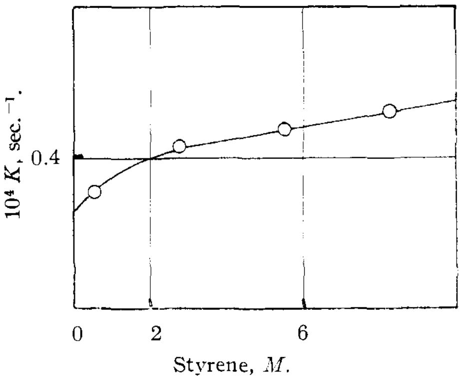


Fig. 6.—Phenylphenylsulfonyl diimide first-order decomposition rate constant *versus* styrene concentration at 70°: diimide concentration extrapolated to zero.

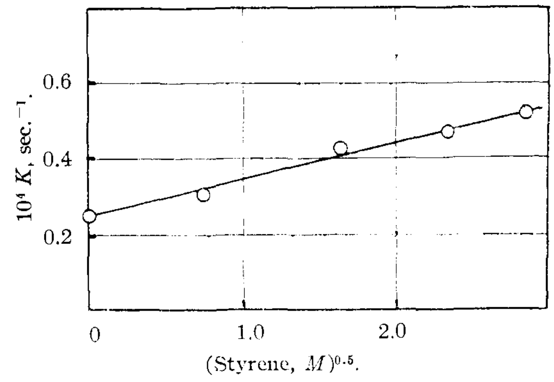


Fig. 7.—Phenylphenylsulfonyl diimide first-order decomposition rate constant *versus* (styrene)$^{0.5}$ at 70°: diimide concentration extrapolated to zero.

styrene mixtures (buffered by calcium oxide and extrapolated to zero diimide concentration) is

$$-\ (d(P)/dt)_{(P)\rightarrow 0} = k(P) = k_1(P) + k_2(P)(\text{styrene})^{0.5} \quad (3)$$

Vinyl Acetate.—The diimide decomposition kinetics in benzene–vinyl acetate mixtures are summarized in Fig. 8. This system also shows an induced decomposition with observed decomposition rates dependent on diimide concentration. Extrapolation to zero concentration of diimide, as shown in Fig. 8, yields a set of rate constants, k_s, which increase almost linearly with vinyl acetate concentration, as shown in Fig. 9.

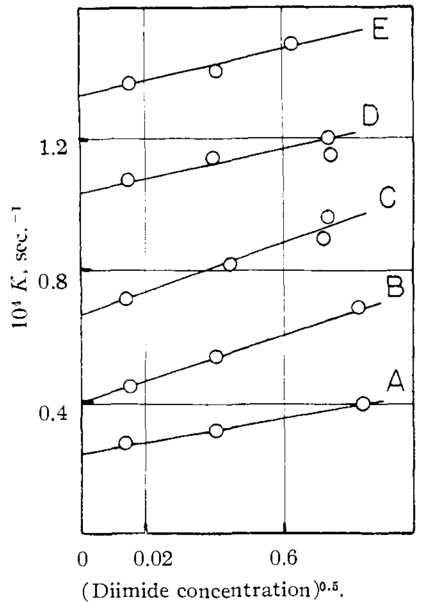


Fig. 8.—Phenylphenylsulfonyl diimide first-order decomposition rate constants in benzene–vinyl acetate mixtures at 70°. Vinyl acetate concentration in solvent: curve A, 0.11 *M*; curve B, 1.10 *M*; curve C, 3.60 *M*; curve D, 7.20 *M*; curve E, 11.0 *M* (bulk vinyl acetate).

Several experiments were carried out in ethyl acetate to check on whether the polarity of the vinyl acetate or its unsaturation was responsible for its effect on the diimide decomposition rate. The results in the bottom group of data in Table II show a dependence on diimide concentration, but a k_1 value for spontaneous unimolecular decomposition about the same as in benzene.

Based on Fig. 9, the diimide decomposition rate in vinyl acetate benzene follows a rate law of the form

$$-\ (d(P)/dt)_{(P)\rightarrow 0} = k_s(P) = k_1(P) + k_9(P)(\text{vinyl acetate}) \quad (4)$$

Acrylonitrile.–Table VI summarizes the diimide decomposition kinetics in acrylonitrile–benzene mixtures. The lower molecular weight of this monomer permitted the use of higher scavenger concentrations than with the other monomers. These results show a pronounced increase in phenylphenylsulfonyl diimide decomposition rate at the higher acrylonitrile concentrations. The polymerization rate, obtained by weighing the polymer in aliquots of the reaction mixture as a function of time, paralleled the diimide consumption rate.

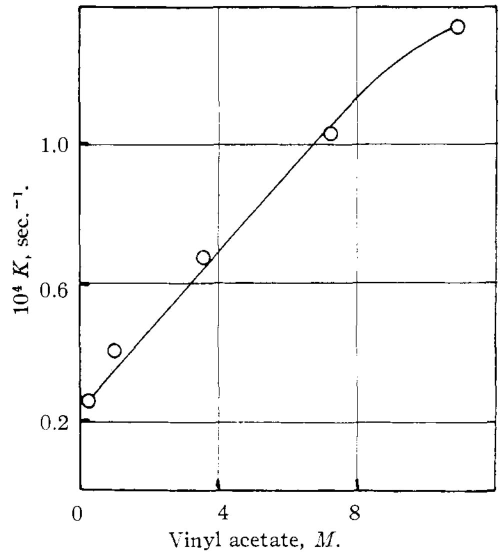


Fig. 9.—Phenylphenylsulfonyl diimide first-order decomposition rate constant *versus* vinyl acetate concentration at 70°: diimide concentration extrapolated to zero.

TABLE VI

FIRST-ORDER RATE CONSTANTS[a] FOR DECOMPOSITION OF PHENYLPHENYLSULFONYL DIIMIDE IN BENZENE–ACRYLONITRILE MIXTURES AT 70°

0.33% w./v. calcium oxide; nitrogen atmosphere

Acrylonitrile, *M*	Phenylphenylsulfonyl diimide, *M* × 10^3	k_{obsd}, 10^4 sec.$^{-1}$	Polymerization rate,[c] %/min.
5.0	0.13	0.51	0.037
10.0	.13	1.00	..
15.0	.13	16[b]	0.69

[a] Colorimetric analysis. [b] Some overheating; peak observed temperature in reaction flask 71.1°. [c] Initial rate.

The possibility exists that the increase in decomposition rate at high acrylonitrile concentrations is indicative of a shift from a radical to a polar decomposition mechanism. Such an effect is postulated by Tobolsky and Mesrobian for the decomposition of *p*-methoxy *p'*-nitrobenzoyl peroxide.[16] However, their compound polymerizes styrene and does *not* polymerize acrylonitrile, presumably because of the shift to a polar, non-radical decomposition route. The fact that the diimide does polymerize acrylonitrile makes the polar mechanism doubtful in the phenylphenylsulfonyl diimide case.

Chloranil.—The kinetic data for the decomposition of the diimide in benzene containing chloranil are summarized in Table VII. The observed rate constants show a complex dependence on both diimide and chloranil concentrations. Thus Fig. 10 shows the marked dependence of the observed rate constant on diimide concentration at low chloranil concentration, a lesser dependence on diimide concentration at an intermediate concentration, and a rate constant independent of diimide concentration at high chloranil concentration. A

---

(16) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 113.

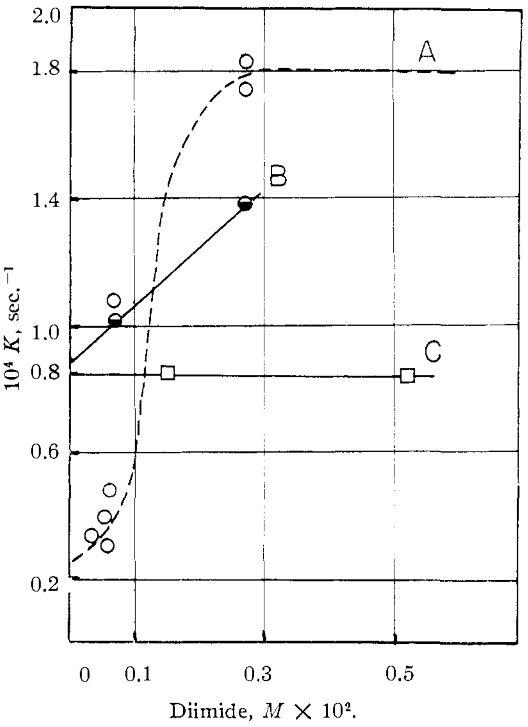


Fig. 10.—Phenylphenylsulfonyl diimide first-order decomposition rate constants in benzene-chloranil mixtures at 70°. Chloranil concentration: curve A, 0.0027 *M*; curve B, 0.0136 *M*; curve C, 0.0542 *M*.

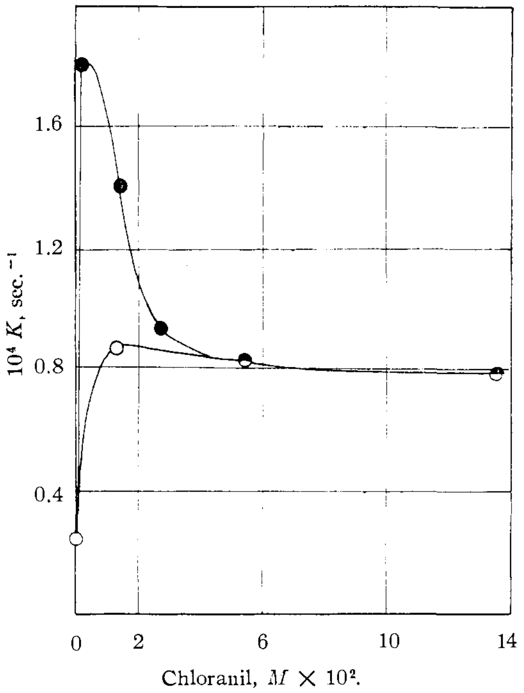


Fig. 11.—Phenylphenylsulfonyl diimide first-order decomposition rate constant *versus* chloranil concentration in benzene at 70°. White circles, diimide concentration extrapolated to zero; black circles, diimide concentration 0.003 *M*; half-black circles, superimposed data for both diimide concentrations.

plot of diimide decomposition rate constant *versus* chloranil concentration at two levels of diimide concentration in Fig. 11 shows a leveling off at about 0.8×10^{-4} sec.$^{-1}$. The upper curve passing through a maximum might be explained by the induced decomposition of diimide by semiquinone radicals formed by reaction of the chloranil with radicals from the diimide; the fall off from the maximum to the "level off" value can then be attributed to the scavenging of these semiquinone radicals by the large excess of chloranil, perhaps by formation of a quinhydrone adduct.

Table VII

First-order Rate Constants[a] for Decomposition of Phenylphenylsulfonyl Diimide in Benzene–Chloranil Mixtures at 70°

0.33% w./v. calcium oxide; nitrogen atmosphere

Chloranil, $M \times 10^2$	Phenylphenylsulfonyl diimide, $M \times 10^3$	k_{obsd}, 10^4 sec.$^{-1}$
0.0271	0.44	0.30
.0605	0.59	0.30
.137	3.44	0.54
.271	10.0	1.75
	2.71	1.83
	2.71	1.75
	1.34	0.96
	0.68	1.07
	.63	0.47
	.60	.40
	.60	.39
	.57	.31
	.43	.33
1.36	2.71	1.38
	0.74	1.01
	0 (extrap.)	0.88
2.71	2.71	.92
	2.71	.96
5.42	5.32	.84
	1.49	.84
	0 (extrap.)	.84
13.6	3.52	.80

[a] Colorimetric analysis; correction made for chloranil-β-naphthol color by measurements at 490 and 590 mμ.

Temperature Coefficient.—The sharp increase in apparent energy of activation for the decomposition of phenylphenylsulfonyl diimide in benzene at higher temperatures, as shown in Fig. 12, is additional evidence for the complexity of the reaction. These data are explained in the Mechanism section in terms of radical-induced decomposition or diffusion recombination.

Mechanism

One method used to separate the spontaneous from the induced part of a decomposition reaction involves extrapolation of the rate data at several concentrations of initiator to zero concentration. This method was followed in the series of alkaryl solvents and led to an estimate of k_1, the spontaneous decomposition rate constant, which was about the same in all the solvents except diphenylmethane. A defect of this procedure is that if one of the significant induced decomposition–termination modes corresponds to a kinetic order of 1.0, its effect will still be included in the observed rate constant at zero initiator concentration.

The addition of known free radical scavengers offered a route for inhibiting the chain-induced decomposition, thus permitting an estimate of the spontaneous decomposition regardless of the kinetic order of the induced term. However, the data presented above have shown that every potential radical scavenger tried resulted in an increase in the rate of disappearance of phenylphenylsulfonyl diimide. Thus this device for isolating the spontaneous decomposition term by scavenger addition has proved inoperative in this system. In addition a possible new mode of decomposition of the diimide has been uncovered.

This additional route for accelerated decomposition in the presence of scavenger-type additives might be explained in terms of: (a) additional radical induced decomposition; (b) bimolecular reaction between diimide and additive; or (c) competition between scavengers and a diffusion–recombination system Our kinetic data cannot make a definite distinction among them, though some preferences are indicated in the following discussion.

First-order Radical Induced Decomposition.—The expected method of operation of the scavengers was that they would capture almost all the radicals in solution yielding in their place radicals which would be almost incapable of attacking the phenylphenylsulfonyl diimide molecule. The dependence of the apparent first-order rate constant on diimide concentration in the styrene, vinyl acetate and chloranil systems indicates that an induced decomposition route of kinetic order greater than 1.0 does occur in these systems; thus radicals capable of attacking the diimide molecule do form in these systems. The intermediate radical adduct with trinitrobenzene might also continue an induced decomposition chain since Price and Read have reported that dinitrobenzene can be found copolymerized in a styrene polymer.[17] Peroxy radicals, which would form in the decomposition of the diimide in the presence of oxygen, could also possibly be reactive enough to promote induced decomposition as evidenced by the formation of a styrene–oxygen copolymer.

Accordingly, it is possible that induced decomposition–termination modes having a kinetic order of about 1.0 can also occur in the presence of these additives, and the high first-order rate constants obtained even after extrapolation to zero concentration could be due in part to such radical-induced decomposition modes. The acceleration observed with molecular iodine could not be accounted for by a radical-induced decomposition mechanism.

Bimolecular Reaction.—An initial step of radical formation involving both peroxide and olefin has

$$ROOH + CH_2{=}CHC_6H_5 \longrightarrow ROO\cdot + CH_3\dot{C}HC_6H_5$$

been proposed by Walling to account for the high rates of decomposition and polymerization in the *t*-butyl hydroperoxide–styrene system.[18]

Schulz and Husemann had postulated initiation of polymerization by decomposition of a benzoyl peroxide–styrene complex,[19] but this now appears to be without foundation.

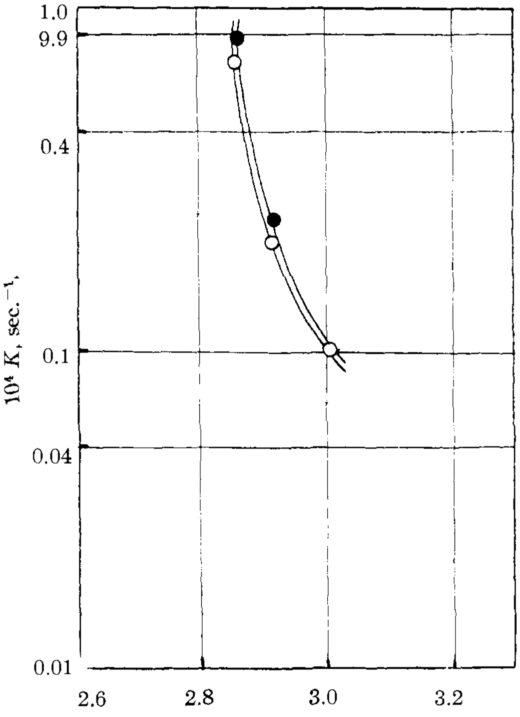


Fig. 12.—Arrhenius plot of phenylphenylsulfonyl diimide decomposition rate constants in benzene *versus* temperature: 0.33% w./v. CaO in suspension, nitrogen atmosphere. Initial diimide concentration: white circles, 0.009 *M;* black circles, 0.0009 *M;* half-black circles, superimposed data for both diimide concentrations.

Phenylphenylsulfonyl diimide may enter into a bimolecular reaction with some or all of the additives used whereby the diimide is decomposed and a free radical is formed, analogous to the process proposed by Walling for hydroperoxides. For example, one possibility might be

$$C_6H_5N_2SO_2C_6H_5 + CH_2{=}CHC_6H_5 \longrightarrow$$
$$C_6H_5N_2\cdot + C_6H_5SO_2\dot{C}H_2CHC_6H_5$$

This proposal can account for the second-order kinetic laws observed with some of the additives studied in detail. However, the styrene–benzene–diimide system followed a 1.5 order kinetic law (0.5 order with respect to styrene as seen in Fig. 7); and the chloranil–benzene–diimide system showed a "level-off" rate independent of chloranil at sufficently high chloranil concentration.

Diffusion Recombination.—Franck and Rabinowitch[20] proposed that when radical fragments are produced in pairs in a solution by a thermal or photochemical dissociation reaction, their excess energies are rapidly dissipated in collisions with solvent molecules and the two radical fragments stop within one or a few molecular diameters of each other. Thus in addition to the normal probability of recombination governed by the law of mass action there is an additional probability of "primary recombination" of two particles which have been parts of the same molecule before dissociation.

---

(17) C. C. Price and D. H. Read, *J. Polymer Sci.*, **1**, 44 (1946).

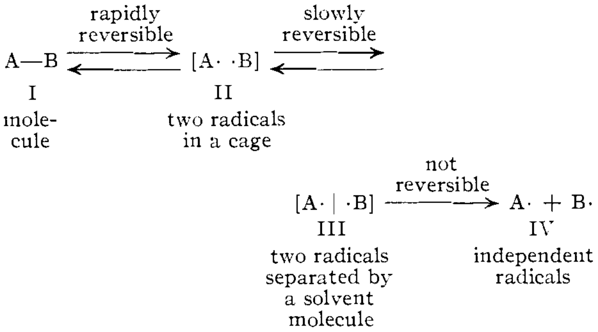
(18) C. Walling and Y. W. Chang, THIS JOURNAL, **76**, 4878 (1954).

(19) G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

(20) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

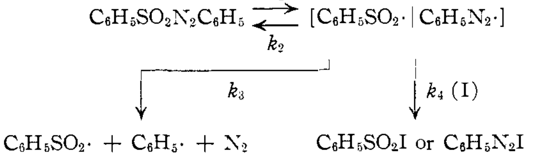
Noyes[21] has developed kinetic expressions for the competition between reactions of pairs of radical fragments and the reaction of a radical fragment with a "scavenger." He recognized three modes of radical pair combination. (1) "Primary recombination" in the "cage" in which they are formed. In this case, the fragments never attain a separation of as much as a molecular diameter and recombination takes place in a period of the order of a molecular vibration (10^{-13} sec.). Only very efficient scavengers at high concentrations can be expected to compete with primary recombination. (2) "Secondary combination" of fragments which escape the cage and which are undergoing $\sim 10^{11}$ random diffusion displacements per second of the order of a molecular diameter within a few molecular diameters of each other. (3) Radical fragments escaping both primary and secondary recombination may combine with fragments from other dissociations, and scavengers compete with this combination reaction by conventional kinetic processes.

The phenylphenylsulfonyl diimide decomposition data in the presence of free radical scavengers can be accounted for by assuming the occurrences of primary and secondary recombinations as detailed by Noyes, and that the various scavenger agents exhibit different reactivities such that some can compete with the primary recombinations and some only with the secondary recombinations. Thus the following scheme might illustrate the thermal decomposition in benzene where A· = $C_6H_5N_2\cdot$ and B· = $C_6H_5SO_2\cdot$



Almost all radicals in state IV will be consumed in some reaction other than recombination, even in the absence of scavengers. For example, the phenylazo radical is certain to liberate nitrogen gas making recombination impossible, and the resulting reactive phenyl radical will react with the solvent.

Most radical scavengers are reactive enough to capture some radicals in state III. This reaction can be treated by classical kinetics as (where (I) = radical scavenger concentration)



Application of the steady state principle to the concentration of caged radicals leads to an expression

$$-\frac{d(P)}{dt} = k_1\left(\frac{k_3 + k_4(I)}{k_2 + k_3 + k_4(I)}\right)(P) = k_s(P) \quad (5)$$

Equation 5 predicts a dependence of the composite first-order rate constant on scavenger concentration (I) which tends toward a plateau value, k_1, when the scavenger concentration is high, *i.e.*, when $k_4(I) >> k_2$. The fit of the data for the styrene and chloranil systems can be judged from Figs. 6 and 11. The approximately constant "level-off" value with both chloranil and styrene suggests that the value of k_1 is about 0.7×10^{-4} sec.$^{-1}$.

Noyes offers an alternate kinetic expression for competition between secondary recombination and reaction with scavenger which is based on diffusion considerations. His equation indicates, to a first approximation, that the increased consumption of diimide should vary as the square root of the concentration of scavenger.[21] Figure 7 shows that the styrene scavenger system does fit the Noyes derivation for competition of scavenger with secondary recombination, and this is the form of eq. 3.

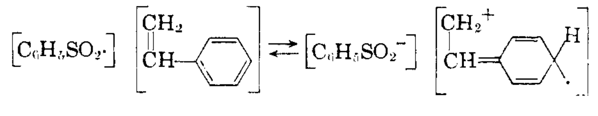
Very reactive scavengers, capable of reaction with radicals at almost every encounter, can begin to compete with primary recombination for capture of radicals in state II. We propose that the data obtained with iodine, vinyl acetate and acrylonitrile as scavengers are a manifestation of such a competition. The formation of the primary cage, state II, is a rapidly reversible process with cage fragments in equilibrium with undissociated diimide molecules. Thus the reaction between scavenger and state II can be described by

$$-\,d(P)/dt = k\,(I)(P)$$

When this scavenger rate term is large enough, as it is in the iodine system, the decomposition route not involving scavenger becomes insignificant, and pure second-order kinetics are observed.

Variations in propensity toward recombination could be due to the time available for primary recombination; this would be related to the rates of diffusion. The difference in decomposition rates observed in benzene *versus* diphenylmethane, in which no induced decomposition was apparent in either case, might be accounted for by the bulkier diphenylmethane molecules which exhibit considerably higher liquid viscosity.

The rate of reaction of a caged radical with monomer or other free radical scavenger in competition with recombination of fragments may be aided if it involves the rapid formation of a loose π-complex species.[22] In this case it would be



The formation of such a complex would require less activation energy than the reaction for radical addition to olefin and thus might be expected to facilitate the capture of a caged radical before it could enter recombination.

Temperature Coefficient.—Figure 12 shows a sharp increase in apparent energy of activation for the decomposition of phenylphenylsulfonyl di-

---

[21] R. M. Noyes, This Journal, **77**, 2042 (1955).

[22] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955).

imide in benzene at higher temperatures. The system

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

leads to the kinetic rate law

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

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.

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN, AND SUMMIT RESEARCH LABORATORY, CELANESE CORPORATION OF AMERICA]

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

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

RECEIVED JUNE 9, 1959

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

---

[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.