2866 J. Org. Chem. 1980, 45, 2866-2874

Accelerated Decomposition of Benzoyl Peroxide by Dibenzenesulfenimide: One-Electron Transfer or Nucleophilic Substitution?[1]

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Received February 4, 1980

Dibenzenesulfenimide $(PhS)_2NH$ reacts with many organic peroxides in solution at room temperature to produce radical as well as nonradical intermediates. The stable dibenzenesulfenimidyl radical $(PhS)_2N\cdot$ is a key intermediate and provides a convenient means for monitoring these reactions. We have studied the reaction of $(PhS)_2NH$ with benzoyl peroxide (BPO) in detail, and we find this sulfenimide to be among the most effective species in inducing the decomposition of BPO known to date. The BPO is quantitatively converted to benzoic acid; $(PhS)_2NH$ gives diphenyl disulfide, N_2, and tar. The kinetics of the appearance of the sulfenimidyl radical are complex. Interestingly, although the sulfenimidyl radical is clearly formed, the dibenzenesulfenimide/benzoyl peroxide reaction is ineffective as an initiator of styrene polymerization. A mechanism for the interaction of the sulfenimide and benzoyl peroxide that involves the formation of a tetravalent sulfur compound is proposed. This reaction and other related systems from the literature are discussed in terms of competing one-electron-transfer and/or nucleophilic-substitution reaction mechanisms.

Chemists have long been fascinated by the possibility that some processes that involve the ultimate transfer of a pair of electrons occur in discrete one-electron steps and involve free-radical intermediates. In 1939, Michaelis suggested that this is common in biological systems in his dramatic generalization that "...very often..., even regularly, free radicals...arise as intermediate products in reversible oxidation systems...".[2] Subsequent study has indicated that, while many biological redox systems give no evidence for radical intermediates,[3] many others do, in fact, involve radicals.[4] For example, the reduction of O_2 is known to proceed via the superoxide radical anion in many systems,[5] and the 1-electron reduction of oxygen, rather than being an exceptional event, is known to be a commonplace of normal aerobic metabolism.[5]

In the organic field, there is a rapidly growing volume of literature on reactions which were initially formulated as two-electron processes but which the evidence now suggests in fact occur via discreet one-electron steps.[6-8] Noteworthy examples include electrophilic[7a,b] and nucleophilic[7c] displacement in aromatic systems and nucleophilic substitutions at saturated carbon and oxygen.[8]

The distinction between one- and two-electron pathways is often extremely subtle. As a classic example, consider the acceleration of the decomposition of peroxides in the presence of nucleophiles. The mechanistic nature of this process has been the source of considerable controversy for 30 years. The central question is whether the initial reaction involves displacement on an oxygen atom of the peroxide by the nucleophile[9,10] (eq 1a) or a one-electron

$$\mathrm{Nu{:}} + \mathrm{ROOR} \xrightarrow{S_N} \mathrm{Nu^+{-}OR} + \mathrm{RO^-} \tag{1a}$$

$$\searrow \xrightarrow{ET} \mathrm{Nu^{+}\cdot} + \mathrm{RO\cdot} + \mathrm{RO^-} \tag{1b}$$

transfer (ET) from the nucleophile (which is also an electron donor) to the peroxide (eq 1b).[1b,11-13] This has been a very difficult question to answer unambiguously in almost all of the systems studied thus far, and both S_N and ET mechanisms have been postulated to rationalize the data for particular systems. Since bimolecular kinetics and similar (or identical) ultimate products are expected for both mechanisms, it has been necessary to resort to such indirect methods as kinetic isotope effects[1c] or the independent synthesis of reactive intermediates[14] to distinguish between nucleophilic-substitution and electron-transfer pathways.

Dibenzenesulfenimide (1) is a particularly intriguing compound in this context. It is readily oxidized (eq 2) to

$$\underset{\mathbf{1}}{(\mathrm{PhS})_2\mathrm{NH}} \rightarrow \underset{\mathbf{2}}{(\mathrm{PhS})_2\mathrm{N}\cdot} \tag{2}$$

the sulfenimidyl radical **2**,[15,16] a species that has been reported to be stable in solution for a week at room temperature and in the presence of air.[16] Furthermore, as a class, nitrogenous compounds with sulfur–nitrogen bonds tend to be relatively poor nucleophiles (compared to amines, for example).[17-19] Thus, it seemed to us that the

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(1) Part 11: "Radical Production from the Interaction of Closed-Shell Molecules". Previous papers in this series are: (a) Part 1, W. A. Pryor, J. H. Coco, W. H. Daly, and K. N. Houk, *J. Am. Chem. Soc.*, **96**, 5591 (1974); (b) part 2, W. A. Pryor and W. H. Hendrickson, Jr., *ibid.*, **97**, 1580 (1975); (c) part 3, W. A. Pryor and W. H. Hendrickson, Jr., *ibid.*, **97**, 1582 (1975); (d) part 4, W. A. Pryor, M. Iino, and G. R. Newkome, *ibid.*, **99**, 6003 (1977); (e) part 5, W. A. Pryor, W. D. Graham, and J. G. Green, *J. Org. Chem.*, **43**, 526 (1978); (f) part 6, W. A. Pryor and W. D. Graham, *ibid.*, **43**, 770 (1978); (g) part 7, W. A. Pryor in "Organic Free Radicals", W. A. Pryor, Ed., American Chemical Society, Washington, DC, 1978, pp 33–62; (h) part 8, W. A. Pryor and M. E. Kurz, *Tetrahedron Lett.*, 697 (1978); (i) part 9, M. E. Kurz and W. A. Pryor, *J. Am. Chem. Soc.*, **100**, 7953 (1978); (j) part 10, W. D. Graham, J. G. Green, and W. A. Pryor, *J. Org. Chem.*, **44**, 907 (1979).

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ease of oxidation and low nucleophilicity of dibenzenesulfenimide should favor its behaving as an electron donor in reactions with organic peroxides. It was our initial hope that because of these factors, dibenzenesulfenimide would exhibit interesting properties in its reaction with peroxides that might provide general insights into nucleophile/peroxide reactions. It was also our hope that dibenzenesulfenimide and a peroxide would prove to be a convenient means of initiating low-temperature free-radical polymerizations.

Unfortunately, neither of these expectations has been realized. Not only are the kinetics of the reaction of dibenzenesulfenimide and benzoyl peroxide extremely complex but the sulfenimidyl radical produced by this reaction also appears to act as an inhibitor of polymerization rather than as an initiator. Nevertheless, this system is an interesting one, since radical intermediates are produced faster by this nucleophile/peroxide system than by any other that has yet been investigated.

Results

Properties of the Dibenzenesulfenimidyl Radical (2). As reported by previous workers,[15,16] we found that dibenzenesulfenimide can be readily oxidized in solution with lead dioxide. The sulfenimidyl radical **2** that is formed has the same ESR parameters (a triplet with $a_N = 11.4$ G, $g = 2.0078$) and the same absorption maximum (535 nm) as reported earlier.[16]

The dibenzenesulfenimidyl radical (**2**) is insensitive to both air and light. The parent sulfenimide, while also not affected by air, is extremely sensitive (in solution) to light, undergoing a facile photoinduced oxidation to the sulfenimidyl radical. This sensitivity presented a problem when the radical concentration was used to monitor reactions of dibenzenesulfenimide, and solutions containing the sulfenimide were carefully protected against ambient light to prevent the photooxidation process from occurring.

The sulfenimidyl radical readily reacts with nitroso compounds to give stable nitroxide radicals. For example, 2-nitroso-2-methylpropane added to a solution of the sulfenimidyl radical gives an ESR spectrum that is a triplet of triplets ($a_N = 2.1$ G); this spectrum is consistent with a trapped sulfenimidyl radical. (Interestingly, however, the sulfenimidyl radical is not trapped at all by a nitrone spin trap such as phenyl-*tert*-butylnitrone.)

Trapping of the sulfenimidyl radical by nitrosobenzene was utilized to determine the extinction coefficient of the radical. Nitrosobenzene has an absorption in the visible region at 764 nm that disappears as the nitroso compound is converted to nitroxide. Thus, the extinction coefficient of the sulfenimidyl radical was determined by measuring the absorbance of a solution of the radical at 535 nm and then adding a known amount of nitrosobenzene to trap the radical. The amount of nitrosobenzene that reacted, and consequently the amount of the sulfenimidyl radical that was present, can be determined from the change in the absorbance at 764 nm. With this technique, the extinction coefficient of the sulfenimidyl radical at 535 nm is 1220 M^{-1} cm^{-1}.

Reactivity of Dibenzenesulfenimide toward Peroxidic Compounds. The reactivity of dibenzenesulfenimide toward a variety of organic peroxides, hydroperoxides, and peresters at room temperature was determined by measuring the initial rate of sulfenimidyl radical appearance. The data (Table I) indicate that benzoyl peroxide reacts one to two orders of magnitude faster than either *tert*-butyl perbenzoate or dilauroyl peroxide. Hydroperoxides and tertiary dialkyl peroxides apparently do not react.[20] The significance of the reduction potentials shown in Table I will be considered in the discussion section.

Table I. Reaction of Dibenzenesulfenimide with Organic Peroxides and Peresters[a]

peroxide/perester	rate[b]	reduction potential[c]
$PhCO_2$-O_2CPh	5.2×10^{-7}	0
$PhCO_2$-$OC(CH_3)_3$	2.0×10^{-8}	-0.95
RCO_2-O_2CR[d]	7.0×10^{-9}	-0.15
$(CH_3)_3COOH$[f]	0[e]	-1.15
$(CH_3)_3CO$-$OC(CH_3)_3$	0[e]	not reduced

[a] Temperature 23 °C; solvent is benzene. The initial concentration of both the sulfenimide and the peroxide is 0.020 M. [b] Rate of appearance of $(PhS)_2N\cdot$ followed by its 535-nm absorbance (in M s^{-1}). [c] E. J. Kuta and F. W. Quackenbush, *Anal. Chem.*, 32, 1069 (1960). [d] Lauroyl peroxide; R = $CH_3(CH_2)_{10}$. [e] Too slow to be measured; oxidation of radical by ambient light becomes significant. [f] *tert*-Butyl hydroperoxide.

Table II. Products of Reaction between Dibenzenesulfenimide and Benzoyl Peroxide in Benzene[a]

product	rel amt,[b] mol	% recovery[c]				
		C	H	N	S	O
$PhCO_2H$	1.99	53.6	56.9			99.5
PhSSPh	0.45	20.8	21.4		45.0	
N_2	0.18			36.0		
$PhCO_2Ph$	0.01	0.5	0.5			0.5
PhPh	trace					
tar[d]		25.2	26.0	58.0	54.5	
total %		100.1	104.8	94.0	99.5	100.0

[a] These data are compiled from several experiments. In each case, the initial reactant concentrations were in the range 0.01-0.03 M, and the dibenzenesulfenimide and benzoyl peroxide concentrations were equal. [b] Per 1 mol of each of the reactants. [c] These recovery percents were determined from the amount of each element present in each product divided by the total amount of that element present in the two reactants. [d] After the five discrete products were pumped off under high vacuum, a nonvolatile, tarry material was left. The elemental percent shown results from analysis of this tar. See the Results for details.

Products of the Reaction of Dibenzenesulfenimide and Benzoyl Peroxide. The major products of the reaction of dibenzenesulfenimide and benzoyl peroxide in benzene are benzoic acid, diphenyl disulfide, and molecular nitrogen (N_2). In addition, trace amounts of phenyl benzoate and biphenyl were detected (see Table II). The remaining material was recovered as a nonvolatile tar, the elemental analysis of which is given in the Experimental Section. Since all of the benzoyl peroxide is accounted for as benzoic acid, the tar must be derived from dibenzenesulfenimide. We have, therefore, assumed in the calculations given in Table II that the tar is comprised of thiophenoxy moieties and some form of bound nitrogen.

The data in Table II account for all of the reactants. The recovered yields for each element, determined from the data in Table II, are as follows: carbon, 100%; hy-

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(20) Even when a sulfenimide solution is carefully shielded from ambient light, the absorbance increases by as much as 0.01 absorbance unit over a period of 2 h inside the spectrophotometer cell compartment. Thus, there is a lower limit of about (1-2) $\times 10^{-9}$ M s^{-1} for rates determined in this manner.

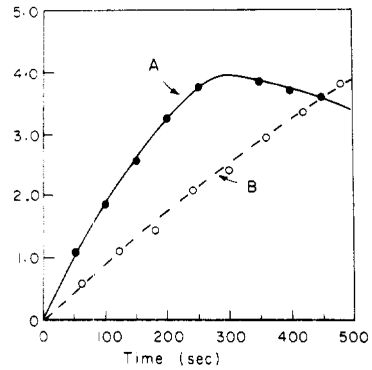

Figure 1. Comparison of the appearance of the sulfenimidyl radical (curve A) with the disappearance of benzoyl peroxide (curve B) during their reaction in benzene at 35 °C. The ordinate for the radical curve gives the concentration of the radical directly. For the peroxide, the ordinate gives the amount by which the peroxide concentration has decreased at a given time. This was done to make the visual comparison of the rates of appearance and disappearance easier.

drogen, 105%; nitrogen, 94%; sulfur, 100%; oxygen, 100%.

Kinetic Methods. The reaction of dibenzenesulfenimide with benzoyl peroxide was followed by two methods. In the first, peroxide concentration was monitored by the peroxide carbonyl stretching band at 1792 cm^{-1} in the infrared region. This technique was effective only for initial peroxide concentrations in the range 0.010–0.040 M. A major problem with this method, aside from the restrictions on the peroxide concentration, was its insensitivity to small changes in concentration. Since we were particularly interested in measuring initial rates and wished to monitor the first 5% of the reaction, we sought alternative methods of analysis. The appearance of the dibenzenesulfenimidyl radical can be followed spectrophotometrically at 535 nm. This proved to be a much more sensitive probe, allowing the use of initial sulfenimide concentrations as low as 0.001 M and up to 0.030 M. The reproducibility was quite good, generally being within ±5%.

In Figure 1, typical data on the disappearance of benzoyl peroxide and appearance of the sulfenimidyl radical are shown. From the appearance curve (A), it can be seen that the radical concentration initially increases rapidly, peaks out, and begins to slowly decrease. The initial rate of disappearance of the peroxide (curve B) is half that of the rate of appearance of the radical, within experimental error. Thus, the two methods give the same result, aside from the factor of 2 rate difference which will be discussed below.

Effect of Concentration Variations and the Rate Expression. The rates of radical appearance at 35 °C for various reactant concentrations are shown in Table III. These data indicate a first-order dependence of the rate upon benzoyl peroxide concentration. This is shown in Figure 2, where the logarithm of the initial rate of radical appearance is plotted against the logarithm of the initial benzoyl peroxide concentration. Only one point, corresponding to run 7, falls noticeable off the line. In that experiment, the peroxide concentration was considerably larger than the sulfenimide concentration, and it is possible that a large excess of peroxide oxidizes the radical as soon as it is formed.[21] The slope of the best line through the remaining points is 0.98 ± 0.06, indicating an order in peroxide of unity.

Table III. Rate of Radical Appearance as a Function of Reactant Concentrations[a]

run no.	$(PhS)_2NH$, M	BzOOBz, M	BzOH, M	styrene, M	rate,[c] M s^{-1} × 10^6
1	0.008	0.002			0.4
2	0.008	0.004			0.9
3	0.008	0.006			1.1
4	0.008	0.008			1.4
5	0.008	0.010			1.8
6	0.008	0.015			2.8
7	0.008	0.020			1.6
8	0.0044	0.0077			0.4
9	0.0066	0.0077			0.9
10	0.0080	0.0077			1.2
11	0.010	0.0077			1.8
12	0.015	0.0077			3.4
13	0.020	0.0077			5.3
14	0.025	0.0077			7.2
15	0.013	0.013	0.0006		6.3
16	0.013	0.013	0.0013		4.3
17	0.013	0.013	0.0016		6.2
18	0.013	0.013	0.0022		6.1
19	0.013	0.013	0.0025		3.2
20	0.013	0.013	0.0030		2.7
21	0.013	0.013	0.0033		3.2
22	0.013	0.013	0.0038		1.9
23	0.013	0.013	0.0049		1.8
24	0.0039	0.0080		0.22	0.3
25	0.0060	0.0082		0.22	0.6
26	0.008	0.0083		0.22	1.4
27	0.011	0.0080		0.22	2.0
28	0.015	0.0081		0.22	3.4
29	0.020	0.0077		0.22	5.6
30	0.025	0.0082		0.22	7.2
31	0.0039	0.0087		4.37	0.2 (0.6)
32	0.0060	0.0087		4.37	0.4 (0.8)
33	0.0081	0.0087		4.37	0.6 (1.4)
34	0.010	0.0087		4.37	1.0 (2.4)
35	0.015	0.0087		4.37	1.6 (3.8)
36	0.023	0.0087		4.37	3.2 (7.1)
37	0.025	0.0087		4.37	3.5 (7.9)
38	0.030	0.0087		4.37	4.7 (10.6)
39	0.0034[b]	0.0084			0.1
40	0.0049[b]	0.0084			0.3
41	0.0070[b]	0.0084			0.6
42	0.010[b]	0.0086			1.4
43	0.014[b]	0.0086			2.7
44	0.020[b]	0.0086			4.5
45	0.029[b]	0.0086			7.8

[a] The temperature is 35 °C; the solvent is benzene. [b] $(PhS)_2ND$. [c] Observed rate of radical appearance; corrected rate of radical appearance in parentheses (see text).

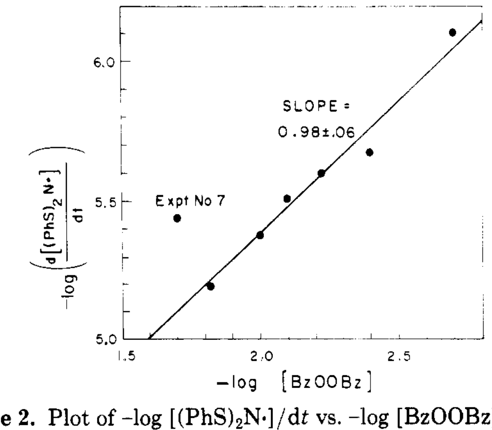

Figure 2. Plot of $-\log [(PhS)_2N\cdot]/dt$ vs. $-\log$ [BzOOBz] for the reaction of dibenzenesulfenimide and benzoyl peroxide in benzene at 35 °C. The data are from runs 1–7 of Table III. The initial sulfenimide concentration is 0.008 M in all runs.

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[21] Oxidation of the sulfenimidyl radical by excess oxidizing agent was noted in the original paper discussing this species. See ref 15.

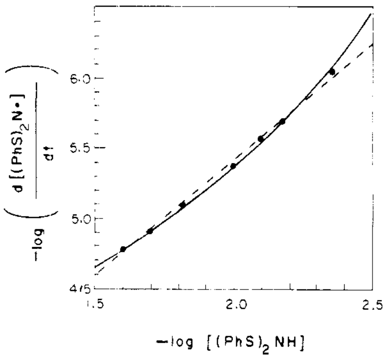

Figure 3. Plot of $-\log\ [(PhS)_2N\cdot]/dt$ vs. $-\log\ [(PhS)_2NH]$ for the reaction of dibenzenesulfenimide and benzoyl peroxide in benzene at 35 °C. The initial benzoyl peroxide concentration is 0.008 M in all runs. The solid curve shows that the kinetic order in peroxide varies over the concentration range studied (see text).

The relationship between the sulfenimide concentration and the rate of radical appearance is not so clear-cut. When $\log\ (d[(PhS)_2N\cdot]/dt)$ is plotted against $\log\ [(PhS)_2NH]$ for experiments 8–14 (Table III), the plot appears at first to be a straight line with a slope of 1.67 ± 0.03. (See the dashed line in Figure 3.) However, on closer examination, this plot shows curvature, suggesting a change in order with respect to the sulfenimide over the concentration range studied. The solid line in Figure 3 shows that the slope at the lower concentration limit is 1.85, while at the upper limit it is 1.51.

This behavior suggests that the rate equation for the reaction of dibenzenesulfenimide and benzoyl peroxide has the form shown in eq 3. The term in the denominator

$$\frac{d[(PhS)_2N\cdot]}{dt} = \frac{2k[(PhS)_2NH]^2[BzOOBz]}{k'[(PhS)_2NH] + k''} \qquad (3)$$

containing the sulfenimide concentration would account for the curvature seen in the log–log plot of Figure 3. (A factor of 2 has been included here to account for the difference between the rate of disappearance of the peroxide and the rate of appearance of the sulfenimidyl radical. See the Discussion section.)

Evaluation of the Rate Constants. Due to the restricted range over which we were able to measure radical concentrations, we could not evaluate the rate equation (eq 3) at the limits where the sulfenimide concentration term in the denominator either predominates or is negligible. Therefore, in order to estimate the rate constants k, k', and k'', we utilized a nonlinear, Gauss–Newton, curve-fitting technique.[22] This program fits the data (initial reactant concentrations and the corresponding rates) to the empirical rate equation (eq 3) and determines the "best" values of k, k', and k''. This technique gave the following values for the rate constants in eq 3: $k = 0.48 \pm 0.01\ M^{-2}\ s^{-2}$, $k' = 15.1$ (no limits found)[23] $M^{-1}\ s^{-1}$; $k'' = 0.27 \pm 0.02\ s^{-1}$.

Effect of Benzoic Acid on the Reaction of Dibenzenesulfenimide with Benzoyl Peroxide.[24] Several kinetic experiments were carried out with a carboxylic acid added to the initial reaction mixture. The data shown in Table III (no. 15–23) indicate that the rate of radical appearance is retarded when benzoic acid (BzOH) is added. Figure 4 shows a plot of rate^{-1} vs. [BzOH]. This treatment would be expected to yield a straight line whenever the dependence on acid concentration appears as a term in the denominator of a rate expression (e.g., eq 4). For initial rates with no added benzoic acid, eq 4 reduces to the empirically determined expression, eq 3.

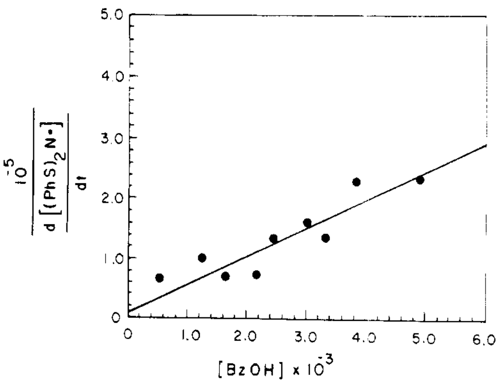

Figure 4. Plot of the inverse of the rate of sulfenimidyl radical appearance vs. [BzOH] for the reaction of dibenzenesulfenimide and benzoyl peroxide in benzene at 35 °C. The initial sulfenimide and peroxide concentrations are both 0.013 M.

$$\frac{d[(PhS)_2N\cdot]}{dt} = \frac{2k[(PhS)_2NH]^2[BzOOBz]}{k'[(PhS)_2NH] + k'' + k'''[BzOH]} \qquad (4)$$

In another study, p-toluic acid was added to the initial reaction mixture. Analysis of unreacted benzoyl peroxide gave no evidence that any mixed peroxide (p-toluoyl benzoyl peroxide) had been formed. This rules out the possibility that the peroxide and acid are involved in an equilibrium reaction and suggests that the acid retards the reaction by reacting with some intermediate species.

Effect of Styrene on the Reaction of Dibenzenesulfenimide with Benzoyl Peroxide. Surprisingly, the addition of styrene to a dibenzenesulfenimide/benzoyl peroxide reaction mixture has no effect upon the rate of radical appearance (Table III, runs 24–38). Consider, for example, the rates when both reactant concentrations are initially about 0.008 M. The rates with 0.0 and 0.22 M styrene (2.7 and 3.1 M s^{-1}; runs 10 and 26) are the same after allowing for small differences in actual reactant concentrations. At 4.37 M styrene, the rate of radical appearance (1.3 M s^{-1}; run 33) is about half what it is in the absence of styrene. However, we will show in the following paragraphs that the apparent decrease in the rate results from the addition of the sulfenimidyl radical to styrene, and that when this reaction is taken into account, the actual rate of radical appearance (3.1, in parentheses) in the presence of 4.37 M styrene is the same as in the absence of styrene.

There are two possible side reactions that might occur when styrene is present. Firstly, the styryl radical (M·) formed by the addition of any radical in the system to styrene could abstract the N-hydrogen of the sulfenimide (eq 5), leading to an apparent increase in the rate of appearance of the nitrogen radical. The second possibility is the addition of a sulfenimidyl radical to styrene monomer (eq 6), giving an apparent decrease of the rate.

$$M\cdot + (PhS)_2NH \xrightarrow{k_5} MH + (PhS)_2N\cdot \qquad (5)$$

$$(PhS)_2N\cdot + PhCH_2{=}CH_2 \xrightarrow{k_6} (PhS)_2NCH_2{-}\dot{C}HPh \qquad (6)$$

To determine the importance of reaction 5, the chain-transfer constant of dibenzenesulfenimide in the polym-

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[22] Part of the SAS computer program package by A. J. Barr, J. H. Goodnight, J. P. Sall, and J. T. Helwig of the SAS Institute, Raleigh, NC 27605.

[23] The quality of "the fit" was insensitive to changes in the value of this parameter. The value given represents a very shallow minimum of the residuals.

[24] We wish to thank a referee for helpful suggestions regarding this experiment.

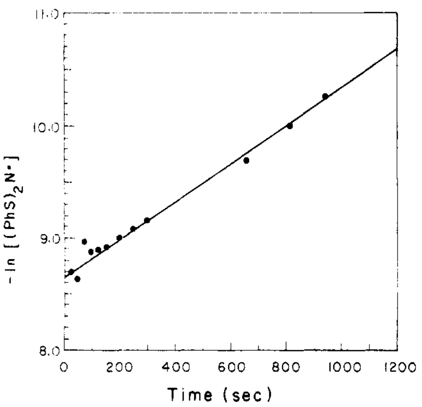


Figure 5. First-order plot of radical concentration after styrene was added. The temperature is 35 °C, and the solvent is benzene. The styrene concentration is 2.91 M.

erization of styrene was determined by standard methods.[25,26] At 60 °C, its value was found to be about 0.4.[27] The chain-transfer constant, C_S, is equal to the ratio, eq 7, of the rate constants for chain transfer (k_5) to that for

$$C_S = k_5/k_p \tag{7}$$

propagation (k_p). Using a value for k_p of 177 $M^{-1}\ s^{-1}$, we can calculate k_5 at 60 °C to be approximately 70 $M^{-1}\ s^{-1}$.[28]

This k_5 value is greater than the value at 35 °C, the temperature of our experiments; however, we can use it to estimate an upper limit for the rate of appearance of the nitrogen-centered radical due to hydrogen abstraction by styryl radical in our system. (The fact that our chain-transfer constant itself is an upper limit[27] does not affect this argument.) Taking the concentration of styryl radicals[29] to be 1×10^{-8} M and a maximum sulfenimide concentration of 3×10^{-2} M, the upper limit for the rate of appearance of the radical by this route is $k_5[M\cdot][(PhS)_2NH] = 2 \times 10^{-8}\ M\ s^{-1}$. This is at least 2 orders of magnitude less than the rate of appearance of nitrogen radical in the absence of styrene; therefore, radical production from eq 5 is too slow to occur in this system.

The rate constant for the addition of dibenzenesulfenimidyl radical (generated by treatment of the sulfenimide with PbO_2) to styrene (eq 6) was evaluated by following the disappearance of the sulfenimidyl radical in the presence of excess styrene (Table III). Since styrene was in large excess, the disappearance of the radical should follow first-order kinetics. A first-order plot of ln $[(PhS)_2N\cdot]$ vs. time is shown in Figure 5. The slope of this plot, equal to k_6[styrene], is $1.68 \times 10^{-3}\ s^{-1}$; since [styrene] = 2.91 M, $k_6 = 5.76 \times 10^{-4}\ M^{-1}\ s^{-1}$. Then when [styrene] = 4.37 M and $[(PhS)_2N\cdot] = 2.0 \times 10^{-3}$ M (the maximum values in our kinetic runs), the rate of disappearance of the nitrogen-centered radical via its addition to styrene is $k_6[\text{styrene}][(PhS)_2N\cdot] = 5.0 \times 10^{-6}\ M\ s^{-1}$. This is a significant value, amounting to about 40% of the observed rate, and must be taken into account. The adjusted values are shown in parentheses in Table III, and the method used to make this correction is described in the Appendix. When [styrene] = 0.22 M, only about 2% of the radical disappears by this route, and therefore reaction 6 can be neglected for these runs.

Initiation of Polymerization. To test the dibenzenesulfenimide/benzoyl peroxide system as an initiator of free-radical polymerization, we allowed a styrene solution containing about 0.05% each of the sulfenimide and peroxide to react for 96 h at 60 °C; less than 2% of the styrene was converted to precipitable polymer. For comparison, styrene alone is thermally polymerized to 2% conversion after just 20 h at 60 °C. The lack of initiation of polymerization by the peroxide–sulfenimide pair probably is due to the fact that the combination of a sulfenimidyl radical with a styryl radical is much faster than the addition of the sulfenimidyl radical to styrene to initiate polymerization. This sort of behavior is observed, for example, with DPPH (a model for the sulfenimidyl radical) which is a far better inhibitor than it is an initiator.[30]

Isotope Effects. The rates of appearance of the nitrogen-centered radical have also been determined by using dibenzenesulfenimide-*N-d* (Table III, runs 39–45). It is immediately evident that the overall rates of radical appearance are slower for deuterated material than for the nondeuterated compound. However, the computer curve-fitting procedure gave values for the individual rate constants k, k', and k'' that are *higher* in the case of deuterated substrate. The values obtained for the rate constants are as follows: $k_D = 0.44 \pm 0.03\ M^{-2}\ s^{-2}$, $k_D' = 15.1$ (no error limits found)[23] $M^{-1}\ s^{-1}$, $k_D'' = 0.40 \pm 0.06\ s^{-1}$. These isotope effects will be discussed below.

Discussion

Dibenzenesulfenimide is remarkably reactive; in fact, as we shall discuss below, the sulfenimide is one of the most effective nucleophiles studied thus far at accelerating the rate of decomposition of benzoyl peroxide.

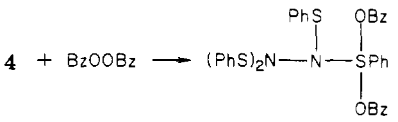
Reaction Scheme. A scheme that accounts for both the observed products and kinetics is shown in eq 8–12,

$$(PhS)_2NH + BzOOBz \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \underset{\mathbf{3}}{PhSNHS(OBz)_2Ph} \tag{8}$$

$$\mathbf{3} + (PhS)_2NH \xrightarrow{k_9} 2(PhS)_2N\cdot + 2BzOH \tag{9}$$

$$2(PhS)_2N\cdot \rightleftarrows \underset{\mathbf{4}}{(PhS)_2NN(SPh)_2} \tag{10}$$

$$\mathbf{4} \rightarrow 2PhSSPh + N_2 \tag{11}$$



$$\mathbf{4} + BzOOBz \longrightarrow (PhS)_2N\text{—}\overset{PhS}{\overset{|}{N}}\text{—}\underset{\underset{OBz}{|}}{\overset{\overset{OBz}{|}}{S}}Ph \tag{12}$$

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(25) (a) For a discussion of chain-transfer constants and how to determine them, see: G. Odian, "Principles of Polymerization", McGraw-Hill, New York, 1970, pp 203 ff; (b) Since the sulfenimide also inhibited styrene polymerization, the chain-transfer constant could not simply be determined from the plot of $1/\bar{P}_n$ vs. $[(PhS)_2NH]/[\text{styrene}]$. A term including the observed rate of polymerization must be considered, and the chain-transfer constant is the slope of the plot of $1/\bar{P}_n - k_t R_P/k_p^2[\text{styrene}]^2$ vs. $[(PhS)_2NH]/[\text{styrene}]$, where all of the symbols have their standard meanings. This treatment is similar to that of W. A. Pryor and T. Huang, *Macromolecules*, **2**, 70 (1969), and J. C. Bevington and H. G. Troth, *Trans. Faraday Soc.*, **59**, 127 (1963).

(26) For a discussion of the determination of the degree of polymerization from intrinsic viscosities, see: R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 2373 (1948); D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry", 2nd ed., McGraw-Hill, New York, 1967, pp 278–286.

(27) The value of the chain-transfer constant that we have determined here is an apparent value, due to the rate retardation effect of the sulfenimide; thus, it is greater than the true value. However, this apparent value for the chain-transfer constant is no more than tiwce the true value. See J. T. Clarke, R. O. Howard, and W. H. Stockmayer, *Makromol. Chem.*, **44**, 427 (1961).

(28) M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).

(29) The radical concentration was calculated by using the relationship between radical lifetime and radical concentration, (ref 25, p 232). The values for the constants and radical lifetimes were taken from Gregg and Mayo.[26]

(30) See the discussion of the use of DPPH in polymerization studies in A. R. Forrester, J. N. Hay, and R. H. Thomsen, "Organic Chemistry of Stable Free Radicals", Academic Press, New York, 1968, pp 153–156.

where BzOOBz is benzoyl peroxide. (These reactions are not necessarily elementary processes and will be discussed in more detail below.) The form of the empirically derived rate expression (eq 3) requires a reversible process followed by an irreversible one, and reactions 8 and 9 were written to satisfy this requirement. Note, also, that in eq 8 and 9 two sulfenimidyl radicals are produced for every peroxide destroyed. This accounts for the factor of 2 rate difference between the rate of disappearance of peroxide and that of the appearance of sulfenimidyl radical. Also, since styrene does not affect the rate of sulfenimidyl radical appearance (see Results), scavengable radicals cannot be intermediates in this scheme; this implies that free benzoyloxy radicals (BzO·) are not significantly involved in the pathways leading to the sulfenimidyl radical.[31] (However, see the following paragraph.) Intermediate **3** is suggested as a reasonable possibility, since it allows us to satisfactorily explain the observed products and kinetics. Although there is no direct evidence for this species in the current study, analogous intermediates resulting from oxidative additions to sulfur[32] and selenium[33] have been reported.

As we have said, the absence of any effect on the rate of radical appearance by added styrene is evidence against the involvement of benzoyloxy radicals in the formation of the sulfenimidyl radical. However, trace amounts of biphenyl and phenyl benzoate are observed after the reaction of dibenzenesulfenimide and benzoyl peroxide in benzene, clearly indicating the presence of low concentrations of benzoyloxy radicals. (Biphenyl and phenyl benzoate are major products from the homolytic decomposition of benzoyl peroxide in benzene.[34]) One possible source of benzoyloxy radicals is an induced decomposition of benzoyl peroxide by the sulfenimidyl radical (eq 13).

$$\underset{\textbf{6}}{(PhS)_2N\cdot + BzOOBz \rightarrow (PhS)_2NOBz + BzO\cdot} \quad (13)$$

Whatever the source of benzoyloxy radicals, it is certainly just a minor reaction pathway, judging from the minute amounts of biphenyl and phenyl benzoate that are observed. Thus, a minor product such as **6** or products derived from it might easily escape detection.

The observation of molecular nitrogen (N_2) as one of the products suggests that at least part of the sulfenimidyl radicals disappear via radical coupling (eq 10). There is a report in the literature[35] that the dibenzenesulfenimidyl radical quantitatively decomposes to nitrogen (N_2) and diphenyl disulfide; the initial step in this process was proposed to be dimerization to the hydrazine derivative **4** (eq 10), followed by loss of N_2 (eq 11). Thus, eq 10 and 11 probably account for about 40% of the disappearance of the hydrazine intermediate **4**.

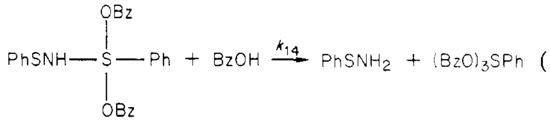
The remaining hydrazine intermediate **4** may react with benzoyl peroxide to give sulfur-oxidized species such as **5** (eq 12). This is, of course, an oxidative addition analogous to eq 8.

Table IV. Individual Rate Constants and Isotope Effects for the Reaction of Dibenzenesulfenimide and Benzoyl Peroxide at 35 °C[a]

	$(PhS)_2NH$	$(PhS)_2ND$	k_H/k_D
k_8	0.0319 ± 0.0009	0.029 ± 0.003	1.1 ± 0.1
k_{-8}	0.27 ± 0.02	0.39 ± 0.06	0.7 ± 0.1
k_9	15.1[b]	15.1[b]	1.0[b]
k_{14}	100 ± 5	c	

[a] Units for the rate constants are $M^{-1}\ s^{-1}$. [b] No error limits could be determined for these values. See text and ref 23. [c] The effect of benzoic acid was not determined for the reaction involving deuterated sulfenimide.

The results with benzoic acid added to the initial reaction mixture require that the acid retard the appearance of the sulfenimidyl radical by reaction with a steady-state intermediate, and, as we suggested above, **3** is a likely structure for this intermediate. One possible reaction between benzoic acid and **3** is a substitution of the PhSNH group by the benzoate ligand as shown in eq 14.



$$PhSNH{-}\overset{OBz}{\underset{OBz}{S}}{-}Ph + BzOH \xrightarrow{k_{14}} PhSNH_2 + (BzO)_3SPh \quad (14)$$

3

Kinetic Treatment. A steady-state treatment of eq 8, 9, and 14 gives the expression shown in eq 15 for the rate

$$\frac{-d[BzOOBz]}{dt} = \frac{1}{2}\frac{d[(PhS)_2N\cdot]}{dt} = \frac{k_8k_9[(PhS)_2NH]^2[BzOOBz]}{k_{-8} + k_9[(PhS)_2NH] + k_{14}[BzOH]} \quad (15)$$

of appearance of the sulfenimidyl radical. This relationship has the same form as the empirical equation (eq 4) found by analysis of the rate–concentration data. By comparison of the two equations, the relationships in eq 16–19 are obtained. The constants k, k', and k'' (and, thus,

$$k_8 = k/k' \quad (16)$$

$$k_{-8} = k'' \quad (17)$$

$$k_9 = k' \quad (18)$$

$$k_{14} = k''' \quad (19)$$

also k_8, k_{-8}, and k_9) were evaluated by the curve-fitting procedure as described in the Results section. The remaining constant, k''' ($=k_{14}$), can be evaluated from the plot of rate^{-1} vs. [BzOH]. The slope of this line, which according to eq 15 should be equal to $k_{14}/k_8k_9 \cdot [(PhS)_2NH]^2[BzOOBz]$, is $4.6 \pm 0.2 \times 10^7\ M^{-2}$ s. Thus, all the rate constants were determined from these relationships and are summarized in Table IV.

Electron Transfer or Nucleophilic Substitution? Neither eq 8 nor eq 9 has been written as an elementary process. Thus, the problem remains to establish, if possible, the detailed mechanisms of these reactions.

The process shown in eq 8 is an oxidative addition of the peroxide to one of the sulfurs of the sulfenimide. As shown in Figure 6, this type of addition could occur by either an initial electron transfer or a nucleophilic substitution.

The mechanism suggested for eq 9 is shown in Figure 7. Reaction a, the elimination of benzoic acid, should be particularly favorable due to the stability of the ylide **7**. Ylide **7** could then react either by nucleophilic displacement (eq b and c) or by electron transfer (eq d and e) to form the ultimately observed products.

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[31] The empirical rate expression (eq 3) also argues against the benzoyloxy radical as an intermediate. Equation 3 tells us that whatever the intermediate leading to the formation of the sulfenimidyl radical is, it must be a "free" species that is capable of reverting back to the sulfenimide and peroxide reactants. It is highly unlikely that the benzoyloxy radical, once it escapes from the solvent cage, could do so.

[32] (a) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2341 (1971); (b) L. J. Kaplan and J. C. Martin, *ibid.*, **95**, 793 (1973).

[33] Y. Okamoto, K. L. Chellappa, and R. Homsany, *J. Org. Chem.*, **38**, 3172 (1973).

[34] D. F. DeTar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *J. Am. Chem. Soc.*, **89**, 4051 (1967).

[35] D. H. R. Barton, I. A. Blair, P. D. Magnus, and R. K. Norris, *J. Chem. Soc., Perkin Trans. 1*, 1031 (1973).

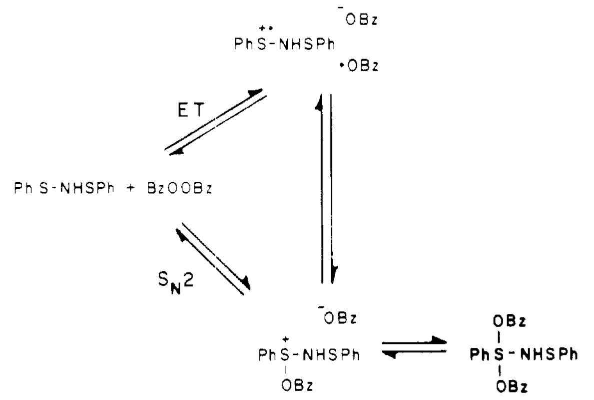

Figure 6. Reaction scheme for eq 8 showing both the electron-transfer and the nucleophilic-substitution pathways. Note the electron is shown as being donated from one of the sulfur atoms, not from the imide nitrogen.[40]

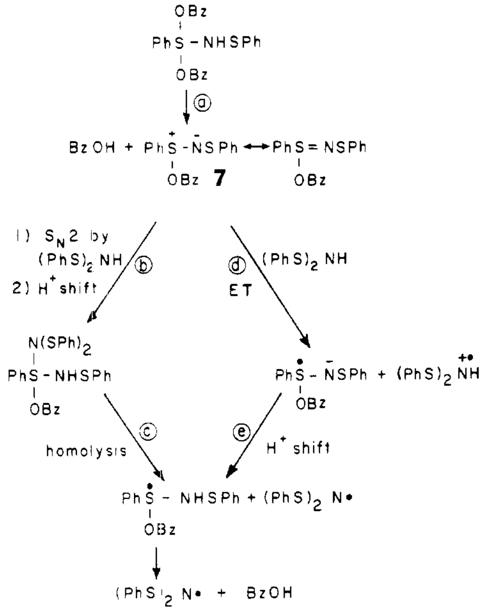

Figure 7. Reaction scheme for eq 9 showing both the electron-transfer and the nucleophilic-substitution pathways.

The situation here is similar to that encountered in previous studies of nucleophile/peroxide systems (see below). Both the nucleophilic-substitution and the electron-transfer pathways can rationalize the final products, and neither the kinetics nor the products provide a basis for choice between the S_N2 and electron-transfer mechanisms.[1c]

There are, however, several types of inferential evidence that suggest an initial electron-transfer process.

(1) The ease of oxidation and relatively low nucleophilicity of dibenzenesulfenimide should favor its reaction as a one-electron donor in both eq 8 and 9.

(2) Dibenzenesulfenimide is one of the most effective species at inducing the decomposition of benzoyl peroxide of any nucleophile yet studied, as can be seen from the data in Table V. The data presented in this table suggest the interesting and potentially useful generalization that in a series of analogous reactions, those involving one-electron transfer tend to occur faster than do reactions proceeding via nucleophilic substitution. It is not unreasonable that ET reactions might respond more sensitively to a decreasing ionization potential in a series of donors than does the S_N2 process.

(3) The order of reactivity of dibenzenesulfenimide with various peroxidic compounds tends to parallel the reduction potentials of these compounds (Table I). This tendency for activation energies to follow reduction potentials of reactants has previously been cited as evidence in favor of an electron-transfer process.[36,37] It must be noted, however, that the ionization potential of a nucleophile can also be correlated with its nucleophilicity;[38,39] thus, although the correlation observed here is suggestive, it does not require an electron-transfer mechanism.

Table V. Rate Constants for the Decomposition of Benzoyl Peroxide by Nucleophiles at 35 °C

nucleophile	solvent	k^a	mechanism
$(PhS)_2NH^b$	PhH	6.3×10^{-2}	ET
Ph_2NOH^c	PhH	7.6×10^{-2}	ET
Ph_2NH^d	PhH	3.4×10^{-2}	?
Me_2S^e	CCl_4	1.0×10^{-2}	S_N2
Et_2NH^d	PhH	8.0×10^{-3}	S_N2
$PhNMe_2^f$	$PhCH_3$	1.1×10^{-3}	?

[a] Biomolecular rate constant (in $M^{-1}s^{-1}$) for the reaction of the nucleophile with benzoyl peroxide. In some cases, the reproducibility of these rate constants is poor. [b] This work. [c] G. R. Chalfont and M. J. Perkins, *J. Chem. Soc. B*, 245 (1971). [d] S. Kashino, Y. Mugino, and S. Hasegawa, *Bull. Chem. Soc. Jpn.*, 40, 2004 (1967). [e] Temperature was 41 °C. W. A. Pryor and H. T. Brickley, *J. Org. Chem.*, 37, 2885 (1972). [f] D. M. Graham and R. B. Mesrobian, *Can. J. Chem.*, 41, 2938 (1963).

(4) Kinetic isotope effects (KIE) produced by β deuteration of the nucleophile have been shown to distinguish between electron-transfer and nucleophilic-displacement mechanisms for certain nucleophile/peroxide reactions.[1c] We have proposed (see above) that benzoyl peroxide reacts at a sulfur of the sulfenimide;[40] the deuteration at nitrogen is, therefore, β to the reactive site. Thus, the KIE should have the same interpretation[1c] as before; i.e., the KIE should be greater than unity if the initial reaction is a one-electron transfer from the sulfenimide to the peroxide but less than unity if the initial reaction is a nucleophilic displacement. The data in Table IV *suggest* that k_H/k_D is greater than unity, and, therefore, *suggest* that the initial reaction is a one-electron transfer. However, the large error limits preclude a firm conclusion based on the KIE in this case.

Conclusion

It has been extremely difficult to assign an unambiguous mechanism to nucleophile/peroxide reactions; generally, electron-transfer and nucleophilic-substitution pathways cannot be distinguished on the basis of products or kinetics. In this respect, the dibenzenesulfenimide/benzoyl peroxide system is very similar to systems that have been studied previously.

As an illustration of this similarity, consider the thoroughly studied reaction of *N,N*-dimethylaniline (DMA) and benzoyl peroxide. This reaction clearly produces scavengable free radicals, since it initiates the polymerization of styrene in the dark at low temperatures.[9,11] In addition, "radical-type" products (such as (*p*-benzoyl-

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[36] M. F. Margaritova and K. A. Rusakova, *Uysokomol. Soyed. A*, **11**, 2741 (1969); *Chem. Abstr.* **72**, 66080 (1970).

[37] L. G. Melik-Organdzhanyou, O. A. Chalrykyau, and N. M. Beileryou, *Uch. Zap., Erevan. Gos. Univ.*, 122 (1971); *Chem. Abstr.*, **78**, 71085 (1973).

[38] J. O. Edwards, *J. Am. Chem. Soc.*, **87**, 3010 (1965).

[39] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[40] Electron donation from the sulfur (not the imide nitrogen) in dibenzenesulfenimide is supported by a simple ab initio (STO-3G) calculation. With $PhSNH_2$ as a model, the highest occupied MO is found to be mainly localized on sulfur. Thus, the relative site in either an ET or SN process by sulfenimide is an electron pair localized on sulfur.

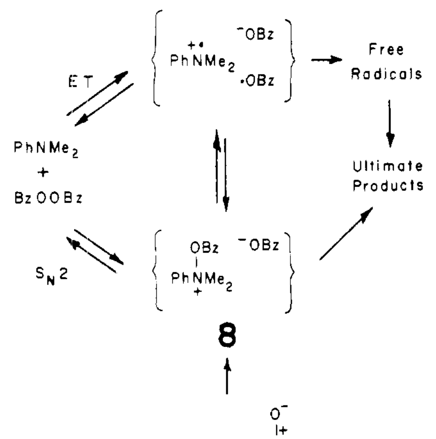

Figure 8. Scheme showing the reaction of dimethylaniline (DMA) and benzoyl peroxide.

oxy)dimethylaniline from homolytic attack on DMA by benzoyloxy radicals) have been identified. These observations led Horner[11] to propose a mechanism in which the initial reaction is the donation of an electron by DMA to benzoyl peroxide. (See Figure 8, ET pathway.) In contrast, Walling later proposed that the initial reaction involves nucleophilic displacement at a peroxide oxygen by the amine (Figure 8, S_N2 pathway).[9] Walling based his conclusion on the lack of solvent effects on the reaction and on the low efficiency of radical production; however, neither of these observations conclusively discriminate between an S_N2 and an electron-transfer mechanism.[1c] Even the direct observation of the amine cation radical[12] does not distinguish one mechanism from the other, as seen in Figure 8; either pathway could lead to any one of these observations. As Figures 6, 7, and 8 show, the potential for crossing from one mechanism to the other at several points makes a distinction based on products and/or kinetics extremely difficult, if not impossible.

For the DMA–benzoyl peroxide system, the most conclusive experiment involves the independent synthesis of intermediate 8 in situ from benzoic acid anhydride (Bz_2O) and dimethylaniline *N*-oxide (DMAO) (see Figure 8). When radical production from authentic 8 was compared to radical production from the DMA/BzOOBz reaction, it was found that the DMA/BzOOBz reaction produces significantly more radicals[9] than does 8 synthesized from DMAO and Bz_2O.[14] This rules out a mechanism that is solely S_N2, since if radicals arise entirely via 8, the radical yields from the two pathways would agree. On the other hand, this experiment does *not* explicitly prove that *all* of the observed radicals arise exclusively from an initial electron transfer. For example, the reaction could occur by both pathways.

The situation with the sulfenimide/peroxide reaction is quite similar. The products do not discriminate between radical production mechanisms, and the kinetics, while considerably more complex than those in the DMA/Bz_2O_2 example, shed no light on the initial sulfenimide–peroxide interaction. Preparation of 3 by an independent pathway might clarify the problem if a suitable procedure were available.[1b,14] At this time, we prefer the electron-transfer mechanism based on the indirect and inferential evidence cited above.

Experimental Section

Chemicals. Reagent benzene was distilled before use. Commercial benzoyl peroxide was crystallized by dissolving it in a minimum amount of chloroform, adding this to methanol, and chilling the mixture. Reagent styrene was washed with aqueous KOH, dried, and distilled under reduced pressure.

Dibenzenesulfenimide. Dibenzenesulfenimide was prepared by a modification of the procedure of Lecher et al.[41] Benzenesulfenyl chloride (prepared from benzenethiol and sulfuryl chloride) in dry ethyl ether was slowly added to a three- to fivefold excess of ammonia (by liquid volume) in sufficient ether to dissolve all of the ammonia. The temperature of the reaction vessel was maintained at −78 °C. When addition was complete, the solution was allowed to warm to room temperature. The ammonium chloride was then filtered off, and the solvent was removed under reduced pressure. The residue was then taken up in a minimum amount of benzene at room temperature and stirred for several minutes with activated charcoal. This mixture was then filtered into 4 or 5 volumes of hexane or petroleum ether. The sulfenimide readily crystallized out of this solvent system when it was well chilled. Several recrystallizations resulted in very pure dibenzenesulfenimide, mp 128–130 °C (lit.[41] mp 126.5–128 °C). Yields were on the order of 25% of the pure material: NMR δ 7.1–7.4 (m, 10 H), 4.6 (s, 1 H); the latter proton readily exchanged with deuterium when the sample was shaken with D_2O; mass spectrum, parent peak at m/e 233. Anal. Calcd: C, 61.77; H, 4.75; N, 6.00. Found: C, 62.24; H, 4.85; N, 5.87.

Dibenzenesulfenimide-*N*-*d*. Dibenzenesulfenimide (0.50 g, 2.15 mmol) in tetrahydrofuran was slowly added to a 10-mol excess of *n*-butyllithium in THF at −78 °C. After the addition was completed, the reaction mixture was stirred for another hour at −78 °C. Then, 4 mL of deuterium oxide (99% isotopic purity) was added, and the mixture was allowed to warm to room temperature. After the mixture was filtered and the solvent evaporated, the crude deuterated material was crystallized as above from benzene/petroleum ether. The yield of deuterated material was 60% with an isotopic purity (by mass spectrum) of 90%.

Product Studies. Chromatography. Elution of a dibenzenesulfenimide (0.993 g, 4.25 mmol)/benzoyl peroxide (0.998 g, 4.11 mmol) reaction mixture on a silica gel column allowed the isolation of 1.09 g (8.93 mmol) of benzoic acid (109%) and 0.42 g (1.93 mmol) of diphenyl disulfide (45%). In confirmation of these results, direct injection of a reaction mixture onto a 6-ft, 10% DEGS on Chromosorb W column (Varian 1400 gas chromatograph, Spectra-Physics Autolab System I integrator) gave the following compounds and yields: benzoic acid (100%), diphenyl disulfide (50%), phenyl benzoate (1.4%), biphenyl (0.2%). These compounds were identified by comparing their retention times with those of authentic samples. The yield of diphenyl disulfide may be high in the GLC analysis, since it is known that S–N compounds thermally decompose to diphenyl disulfide.

Determination of Nitrogen. Dibenzenesulfenimide and benzoyl peroxide in benzene were allowed to react in a thoroughly degassed, sealed ampule. After reaction was complete, the ampule was attached to a vacuum line of known volume through a Toepler pump. The noncondensable gas produced by the reaction was transferred into the known volume. Measurement of the final temperature and pressure gave the amount of nitrogen produced. (We have assumed that nitrogen is the only noncondensable gas present. There could, of course, be some hydrogen. However, that would mean that we are missing a considerable amount of the nitrogen. Also, it is not likely that much H_2 would be formed in the presence of an oxidizing agent such as benzoyl peroxide.)

Analysis of the Nonvolatile Tar. Dibenzenesulfenimide and benzoyl peroxide in benzene were allowed to react in an ampule. The ampule was then attached to a high-vacuum line, and all volatile materials were drawn off. The volatile materials included the solvent, benzoic acid, diphenyl disulfide, and nitrogen. The tarry material remaining was subjected to elemental analysis. The following elemental yields were found: C, 57.8%; H, 4.6%; N, 5.8%; S, 31.8% (by difference).

Kinetics. Solutions of dibenzenesulfenimide and benzoyl peroxide were prepared separately and equilibrated at the desired temperature in a water bath. Aliquots (1 mL) from each solution were mixed in a cuvette in the thermostated cell compartment of a UV–vis instrument (Beckman DU optics with a Gilford Model 22 detection system). The absorbance at 535 nm was monitored as a function of time. For consistency, rates were determined over

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[41] H. Lecher, F. Holschneider, K. Koberle, W. Speer, and P. Stocklin, *Chem. Ber.*, 58, 409 (1925).

the time period of 60–180 s of reaction time.

Acknowledgment. This work was supported in part by grants from the National Science Foundation and from the National Institutes of Health.

Appendix

The following method was used to estimate the rate of appearance of the sulfenimidyl radical when styrene was included in the reaction mixture. The observed rate of radical appearance, R_{obsd}, is equal to the total rate of radical appearance, R_T, from the reaction of the sulfenimide and peroxide (eq 9) less the rate of radical disappearance, R_D, due to addition of the radical to styrene (eq 6). (See eq 20.)

$$R_{\text{obsd}} = R_T - R_D \qquad (20)$$

Since we are dealing with short reaction times and initial rates, these rates can be replaced with the appropriate radical concentration (eq 21).

$$[(\text{PhS})_2\text{N}\cdot]_{\text{obsd}} = [(\text{PhS})_2\text{N}\cdot]_T - [(\text{PhS})_2\text{N}\cdot]_D \qquad (21)$$

The rate of sulfenimidyl radical disappearance via addition to styrene, R_D, is given by eq 22.

$$R_D = k_6[(\text{PhS})_2\text{N}\cdot]_{\text{obsd}}[\text{styrene}] \qquad (22)$$

At short times t, that portion of the sulfenimidyl radical concentration which has disappeared by way of addition to styrene is given by eq 23.

$$[(\text{PhS})_2\text{N}\cdot]_D = k_6(t)[(\text{PhS})_2\text{N}\cdot]_{\text{obsd}}[\text{styrene}] \qquad (23)$$

Combining eq 21 and 23 gives eq 24, where the radical concentration at time t that has appeared as a result of the sulfenimide/peroxide reaction is expressed in terms of the observed radical concentration at time t.

$$[(\text{PhS})_2\text{N}]_T = (1 + k_6(t)[\text{styrene}])[(\text{PhS})_2\text{N}]_{\text{obsd}} \qquad (24)$$

These corrected radical concentrations are then used to determine the corrected rates of radical appearance that are given in parentheses in Table III.

Registry No. 1, 24364-84-9; benzoyl peroxide, 94-36-0; benzenesulfenyl chloride, 931-59-9; dibenzenesulfenimide-*N-d*, 73680-07-6; benzoic acid, 65-85-0; diphenyl disulfide, 882-33-7.

Cyclopropanones. Formation of Vinylcyclopropanols and Their Rearrangement to Cyclobutanones

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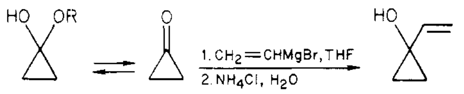
Received February 25, 1980

Vinylcyclopropanols, formed by the addition of vinylmagnesium bromide to the ethyl hemiketal of cyclopropanone, may be converted to cyclobutanone derivatives on reaction with various electrophiles. The ring enlargement of 1-vinyl-2-methylcyclopropanol takes place by preferential migration of the more highly substituted carbon atom.

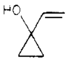
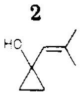
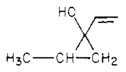
Cyclopropanones, among the most reactive carbonyl compounds in organic chemistry, have previously found limited use in synthesis partly because of difficulties in the preparation and handling of such energetic systems.[2] However, when trapped in the form of addition products which can yield the three-membered ketone in situ, cyclopropanone can be a participant in a number of useful chemical transformations including cyclobutanone and β-lactam formation.[2]

Among the cyclopropanone precursors has been the ethyl hemiketal (**1a**), which can be formed on addition of ethyl alcohol to solutions of cyclopropanone resulting from the addition of ketene to diazomethane.



1a, R = Et
b, R = Me
c, R = Ph

Table I. Vinylcyclopropanols from Cyclopropanones[a]

cyclopropanol	yield, %
 **2**	65
 **3**	65
 **4**	68

[a] All cyclopropanols were further characterized as the corresponding acetates, formed by treatment of the alcohol with 1 equiv of ethylmagnesium bromide followed by acetyl chloride.

In previous work[3] we have found that such alcohol addition products (**1**) are in equilibrium with the free ketone in solution and undergo nucleophilic attack by carbanionic reagents. For example, reduction of **1a** to cyclopropanol takes place with lithium aluminum hydride, and reactions of **1a** with Grignard reagents lead to 1-substituted cyclopropanol derivatives.[4-6]

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