spectra) at two temperatures. Correlations of these spectra with other macromolecular properties will be reported elsewhere.

Conclusions

1. Procedures for the preparation of dinitroxide spin labels have been elaborated.

2. A qualitative correspondence has been established between the conformations and the esr spectra of flexible dinitroxides in various solvent systems (Table IV).

3. The intramolecular exchange interaction in the nitroxides described here is of the *direct* type.[11,21] It is effective only when the biradical molecules flex until the interacting groups are separated by a distance shorter than 6 Å.

4. The dipolar interaction introduces splitting of each line in the esr spectra of frozen samples and the

dipolar splittings permit the measurement of the separation distance *d* between the subgroups of the biradicals. The spectra appropriate for this analysis (which should be made by comparison with computer-simulated spectra) are described in entry G, Table IV (also Figure 5). The appearance of H-type spectra (Table IV) upon freezing indicates that the biradical is coiled so that its nitroxide subunits are less than 6 Å apart.

5. None of the biradicals described here is suitable for strain gauge applications because there is no unique correspondence between the strains on the functional groups and the separation distance between the nitroxide subunits. The strain gauge would be realized by restricting the number of internal degrees of freedom.

6. Design considerations for a workable biradical strain gauge are outlined.

The Decomposition of Bis(α-naphthoyl) and α-Naphthoyl Benzoyl Peroxides

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Abstract: The thermal decomposition of bis(α-naphthoyl) peroxide in benzene and carbon tetrachloride at 60° is a mixed spontaneous and induced radical reaction. Experiments with scavengers indicate a large amount of cage recombination, the major part of which is proposed to give an α-lactone (IV) as an intermediate. IV can either react with α-naphthoyl hypoiodite (formed in the presence of iodine) to give bis(1,4-naphthoyloxy)naphthalene or rearrange to give 4-(α-naphthoyloxy)-1-naphthoic acid. α-Naphthoyl benzoyl peroxide behaves similarly, giving 4-benzoyloxy-1-naphthoic acid. The photolysis of bis(α-naphthoyl) peroxide in CCl₄ does not give 4-naphthoyloxynaphthoic acid, but does give naphthyl naphthoate, which is also one of the cage products of the thermal reaction.

The products of the decomposition of bis(α-naphthoyl) peroxide have been reported by Kharasch and Dannley[1a] and its behavior as an initiator of styrene polymerization has been described by Cooper[1b] and by Takebayashi, *et al.*[1c] The decomposition rate as measured by iodometric analysis of the peroxide in styrene is about four times that estimated from the polymerization rate,[1b,c] suggesting an unusually low efficiency in the production of free radicals. Furthermore, the rate of decomposition of bis(α-naphthoyl) peroxide appears to be almost two orders of magnitude greater than that of benzoyl peroxide[2] even after allowing for induced decomposition. The usual acceleration by *nonparticipating ortho* substituents is less than one order of magnitude, the factor of 6.5 for *o*-methyl being typical.[3a] The range of effects for *meta* and *para* substituents on the rate of decomposition of benzoyl peroxides is about a factor of 6 or 7.[3a,b]

(1) (a) M. S. Kharasch and R. L. Dannley, *J. Org. Chem.*, 10, 406 (1945); (b) W. Cooper, *J. Chem. Soc.*, 3106 (1951); (c) M. Takebayashi, T. Shingaki, and H. Matsui, *Bull. Chem. Soc. Japan*, 27, 371 (1954).

(2) (a) K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, 68, 1686 (1946); (b) D. F. DeTar, *ibid.*, 89, 4058 (1967); (c) D. F. DeTar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *ibid.*, 89, 4051 (1967).

(3) (a) A. T. Blomquist and A. J. Buselli, *ibid.*, 73, 3883 (1951); (b) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, 72, 5426 (1950).

Kinetics

The participation of radical-induced reactions in the decomposition of peroxides is usually indicated by an increased first-order rate constant at higher initial concentrations as well as by a lower rate constant in the presence of scavengers. For oversimplified models in which there is only one chain-carrying and one chain-breaking step the order *n* of the induced decomposition term in eq 1 varies from $1/2$ to 2 in steps of $1/2$.[3b] The observed first-order rate constant is expressed by eq 2.

$$-\frac{dp}{dt} = k_1 P + k_i P^n \quad (1)$$

$$k \equiv k_1 + k_i P^{(n-1)} \quad (2)$$

For certain of these models $n = 1$ and the first-order term of eq 1 may contain a contribution from induced decomposition as well as from the spontaneous reaction. It should also be noted that because of the much greater complexity[2b] of actual chain reactions as compared with the models from which eq 1 is derived, the use of eq 1 for extrapolation to give the rate constant at infinite dilution may not be justified even though it gives an adequate fit to the rates in the range of concentrations in which the rates can actually be measured. Some

Table I. Constants for Equation 1

Peroxide	Solvent	T, °C	n	$10^4 \times k_1$, sec^{-1}	$10^4 \times k_i$, M^{-1} or $M^{-1/2}$ sec^{-1}
Bis(α-naphthoyl)	C_6H_6	60.0	2	1.80	15.3[a]
	C_6H_6	60.0	3/2	1.24	8.46[b]
	CCl$_4$	59.6	3/2	0.42	2.90[c]
α-Naphthoyl benzoyl	C_6H_6	60.0	3/2	0.21	0.52[c]
Dibenzoyl	C_6H_6	60.0	3/2	0.0194	0.050[d]
	C_6H_6	80.0	3/2	0.328	0.428[d]

[a] From the slope of the line in Figure 1. [b] Average of the values obtained by the method of ref 2a. [c] By the method of ref 2a. Agreement with the value obtained from the initial rates is good. [d] From ref 2a.

Table II. Effect of Scavengers

Peroxide	Scavenger	$10^3 \times$ initial concn, M Peroxide	Scavenger	T, °C	$10^4 \times k$,[a] sec^{-1}	k/k_1[b]	Apparent radical yield[c]
α-N[d]	G•	1.07	1.18	59.9	1.86[f]	1.03 (1.50)	0.71
		0.716	1.18	54.6	1.02		0.72
		1.07	1.18	54.6	1.01		0.64
		0.716	1.18	64.5	2.92		0.84
		1.07	1.18	64.5	3.09		0.77
BEN[g]	G	0.586	1.09	79.8	0.345	1.05	1.71
		1.76	1.09	79.8	0.351	1.07	
α-N	S[h]	55.0	200	60.0	1.79	0.99	
α-N	I$_2$/CCl$_4$	23.8	98	59.9	0.37[i]	0.87	0.85[j]

[a] First-order rate constant obtained from decrease in absorbance of the scavenger except where otherwise noted. [b] Ratio of apparent first-order rate constant to k_1 of Table I, value in parentheses is for $n = {}^3/_2$. [c] Yield of radical estimated from scavenger bleaching per mole of peroxide. The experiments with benzoyl peroxide suggest that the yields obtained with galvinoxyl may be too low, since the radical efficiency with this peroxide should approach 2.0. [d] Bis(α-naphthoyl) peroxide. [e] Galvinoxyl (see ref 5). [f] The Arrhenius plot at the other two temperatures gives 1.84×10^{-4}. [g] Dibenzoyl peroxide. [h] trans-Stilbene. [i] In CCl$_4$, from the intensity of the carbonyl absorption at 1768 cm^{-1}. [j] From I$_2$ uptake measured from the visible absorption at about 33% peroxide decomposition. Beyond this point iodine is reliberated. giving a final radical yield of only 0.38.

constants for use with eq 1 have been collected in Table I.

In the case of benzoyl peroxide or of bis(α-naphthoyl) peroxide in CCl$_4$, the best half-integral value of n for the empirical representation of the rates is ${}^3/_2$. However, for bis(α-naphthoyl) peroxide in benzene the titrimetric rates are fitted as well or better by the use of $n = 2$. The major difficulty with the choice of $n = {}^3/_2$ is that the rates predicted at very low peroxide concentrations are too low in comparison with actual rates as measured by means of galvinoxyl[4] using the excess scavenger method[5,6] (Table II).

Reaction Products

The reaction products are summarized in Tables III–V.

Benzene Solution. The products of the decomposition of bis(α-naphthoyl) peroxide in benzene at 60°, $P_0 = 0.029\ M$, are compared in Table III with those from the decomposition of benzoyl peroxide in benzene at 80° at the same initial concentration.[2b,c] This concentration is, coincidentally, near that at which the amounts of induced decomposition in the two systems are estimated to be the same. As is clear from the

(4) P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962).

(5) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **87**, 3928 (1965); (b) R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).

(6) If a scavenger fails to trap all of the radicals, induced decomposition of the peroxide may cause the yield of scavengable radicals to increase during a run and the rate constant as measured by the scavenger will be too high. An indication that scavenging by galvinoxyl may not be complete is the slightly higher radical yields obtained in runs of lower initial peroxide concentration, but the effect is probably too small to explain the discrepancy with eq 1, $n = {}^3/_2$. Koelsch's radical, bisbiphenylenephenylallyl, was unusable as a scavenger. It appeared to react directly both with α-naphthoyl peroxide at 60° and with benzoyl peroxide at 80°, both in benzene.

radical yields in Table II, there is a great deal more cage reaction, or reaction not leading to scavengable radicals, in the decomposition of bis(α-naphthoyl) peroxide than in the decomposition of benzoyl peroxide and this aspect of the reaction will be discussed in a later section. The induced decomposition of bis(α-naphthoyl) peroxide should be responsible for about 20% of the products in benzene (assuming $n = 2$ and no first-order induced decomposition).

The total yields of recovered product are about the same in the two systems, 67% of the naphthyl groups vs. 70% of the phenyl groups and 86% of the CO$_2$ groups vs. 92% for benzoyl peroxide. Our yield of 1-phenylnaphthalene has been compared with the yield of biphenyl from benzoyl peroxide.[2c] The products from benzoyl peroxide also included dihydrobiphenyl (0.10) and tetrahydroquaterphenyl (0.40) which tend to decompose to biphenyl in the injection port of the glpc apparatus.[2c] There is clearly less decarboxylation of aroyloxy radicals in the case of α-naphthoyl peroxide than in the case of benzoyl peroxide. Taken with the high reaction rate, this suggests some anichimeric reaction[7] giving cyclic radicals such as I and II, the latter leading to the formation of 8-hydroxy-1-naphthoic lactone.

I   II
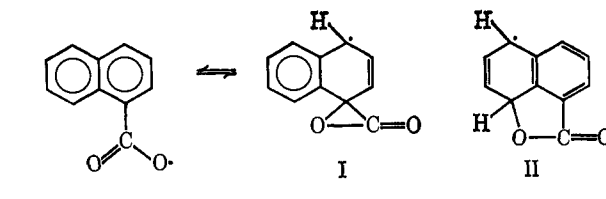
(7) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964).

Table III. Decomposition Products from Bis(α-naphthoyl) Peroxide[b] (α-N) and α-Naphthoyl Benzoyl Peroxide (α-NB) at 60° [a]

| Product | Yield, mol/mol of peroxide | | | | Product | Yield, mol/mol | |
	α-N in C_6H_6	α-N in cumene	α-N in CCl_4	α-NB in CCl_4		α-N CCl_4	α-NB CCl_4
4-(α-Naphthoyloxy)-1-naphthoic acid	0.163	0.128	0.118	0.000	4-Benzoyloxy-1-naphthoic acid		0.033
Naphthyl naphthoate	0.101 (0.032)[c]	0.061	0.032		Unidentified naphthoates	0.034	0.034
1-Phenylnaphthalene	0.347 (0.37)[c]				$CHCl_3$	0.072	0.083
Naphthoic acid	0.297 (0.16)	0.673	0.104		4-Trichloromethyl-1-naphthoic acid[e]	0.208	0.367
8-Hydroxy-1-naphtholactone	0.046	0.010	0.054		Naphthoyl chloride precursor[f]	0.12	
Phenyl naphthoate	0.014 (0.032)[c]				Chlorobenzene		0.893
Naphthalene	0.140	0.322	Trace	Trace	1-Chloronaphthalene	0.79	0.32
SS[d]	0.023	0.130	0.108	0.202			
CO_2	0.98 (1.65)						

[a] Initial concentrations 0.024–0.029 M in degassed solvent or under argon. [b] Besides the tabulated products for this peroxide in benzene there was also a trace of 1,1'-binaphthyl and 5.6 wt % of unidentified acid. [c] The numbers in parentheses are the yields of corresponding product from benzoyl peroxide. See ref 2c. [d] Biphenyl, bicumyl, or hexachloroethane. [e] Isolated as the dicarboxylic acid after hydrolysis. [f] Determined as the anilide after pyrolysis.

Table IV. Effects of Reaction Conditions on Yields of Cage Products from Bis(α-naphthoyl) Peroxide at 60°

| Initial peroxide concn, M | Conditions[c] | Yield, mol/mol of peroxide | | Initial peroxide concn, M | Conditions[c] | Yield, mol/mol of peroxide | |
		NNA[a]	NNt[b]			NNA[a]	NNt[b]
0.0037	Degassed C_6H_6[c]	0.256	0.078	0.0036	0.0072 M G[d]	0.255	
0.029		0.162	0.101	0.029	Cumene solvent	0.128	0.061
0.058		0.147	0.108	0.058	0.2 M t-S[e]	0.239	0.086

[a] 4-(1-Naphthoyloxy)-1-naphthoic acid. [b] 1-Naphthyl 1-naphthoate. [c] Solvent is degassed C_6H_6 unless otherwise noted. [d] Galvinoxyl. [e] trans-Stilbene.

Table V. Products from the Decomposition of Bis(α-naphthoyl) Peroxide[a]

| Product iodine concn, M | Yield, mol/mol of peroxide | | | |
	0.000	0.032	0.11	0.11 (wet)[b]
4-(1-Naphthoyloxy)-1-naphthoic acid[c] (NNA)	0.118	0.016	0.0085	0.054
1-Naphthoic acid[c]	0.104	0.623[e]	0.57 (0.71)[d]	1.100
1,4-Bis(1-naphthoyloxy)-naphthalene[f] (NNN)		0.187	0.208	0.154
1-Naphthyl-1-naphthoate (NNt)	0.032		0.043	
1-Iodonaphthalene		0.206	0.299	0.052
1-Chloronaphthalene	0.79	0.082	0.015	0.003
Hexachloroethane	0.108	0.0025	Trace	0.002

[a] In CCl_4 plus I_2 at 60°, P_0 = 0.025 – 0.026 M. [b] Water saturated. [c] Acids determined by extraction, then glpc analysis as methyl esters. [d] Reaction mixture treated directly with CH_2N_2, then acid isolated as methyl ester. [e] Also shown to be present by infrared before work-up. [f] A reaction between silver 1-naphthoate and iodine in the presence of 1-naphthoyl 1-naphthoate gave no NNN, so this substance is not formed via reaction of naphthoyl hypoiodite with naphthyl naphthoate.

In Cumene Solution. The products of the decomposition of bis(α-naphthoyl) peroxide in cumene are like those in benzene except that abstraction of hydrogen from the solvent replaces addition of radicals to the solvent. Although the recovery of naphthyl groups is 69% there is a large deficit of identifiable hydrogen sources to balance the yields of naphthalene and α-naphthoic acid.

In CCl_4. The noncage products from the decomposition of bis(α-naphthoyl) peroxide (p_0 = 0.024 M) in CCl_4 are largely 1-chloronaphthalene and 4-trichloromethyl-1-naphthoic acid, a product of the induced decomposition. Structure III is similar to those proposed by Walling for intermediates in the induced

$$Cl_3C \cdot + (C_{10}H_7COO)_2 \longrightarrow \text{III} + C_{10}H_7COO \cdot \quad (3)$$

III
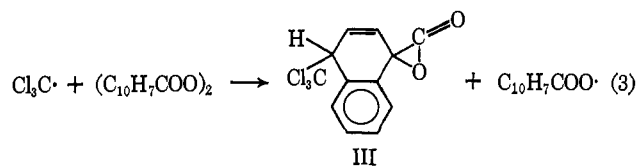
decomposition of benzoyl peroxides.[8] The decomposition products from α-naphthoyl benzoyl peroxide in CCl_4 include 4-trichloromethyl-1-naphthoic acid but no 4-trichloromethylbenzoic acid. This is to be expected in view of the known relative reactivities of

(8) (a) C. Walling and E. S. Savas, J. Amer. Chem. Soc., 82, 1738 (1960); (b) C. Walling and Z. Ćeković, ibid., 89, 6681 (1967).

Figure 1. First-order rate constants for bis(α-naphthoyl) peroxide in C_6H_6 at 60°.

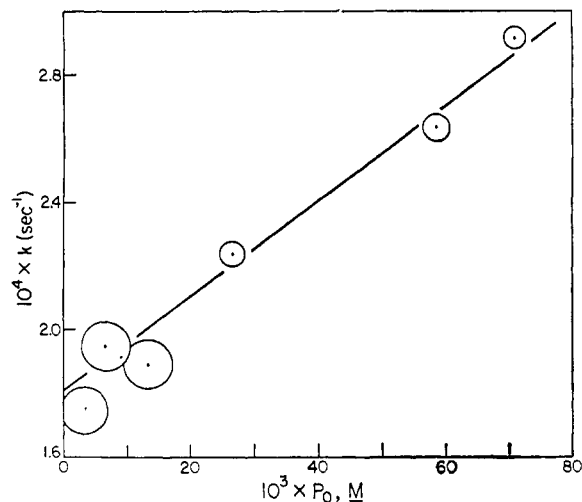Figure 2. First-order plots of decomposition of bis(α-naphthoyl) peroxide at 60° in benzene: A, 0.00679 M; B, 0.0708 M.

naphthalene and benzene ring systems.[9] The yield of 4-trichloromethyl-1-napthoic acid from the decomposition of bis(α-naphthoyl) peroxide is only about half that expected on the basis of the kinetics, but the intermediate lactone might reasonably be quite sensitive to further reaction with naphthoyloxy radicals.

Some chlorine atom sources are missing, and this may be connected with the presence of a precursor of naphthoyl chloride in the product.[10]

The Cage Reaction

The yields of scavengable radicals in Table II and the polymerization efficiencies[1b,c] put an upper limit of 65% on that part of the reaction not leading to separated free radicals. 4-Naphthoyloxy-1-naphthoic acid (NNA) is obviously the product of such a reaction as can be seen from the effects of solvent, initial peroxide concentration, and the presence of scavengers reported in Table IV. The case of naphthyl naphthoate (NNt) is less clear but it is probable that the yield in dilute solution, at least, represents cage product. The sum of these yields is only 50% of the upper limit of 65% of possible cage product as compared with a total naphthyl group recovery, from all types of reaction, of about 70%.

We suggest that compound IV, a hypothetical precursor of NNA, is diverted in part to other products.[11] The hypothesis of an intermediate such as IV is supported by the effects of iodine or iodine plus water in Table V. Iodine in CCl_4 is known to intercept acyloxy radicals as acyl hypoiodites.[12] The known

(9) (a) R. L. Dannley and M. J. Gippin, *J. Amer. Chem. Soc.*, **74**, 332 (1952); (b) E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953); (c) D. I. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 562 (1961).

(10) Attempted distillation of the decomposed reaction mixture from bis(α-naphthoyl) peroxide gives 0.12 mol/mol of naphthoyl chloride, a product not present before the distillation. The acid chloride does not, as previously proposed,[1a] come from trichloromethyl ester, since this would have given phosgene as well [see A. Senning, *Chem. Rev.*, 385 (1965)]. On the other hand, abstraction of Cl from the lactone III or from trichloromethylnaphthalene should give naphthyldichloromethyl radicals. Naphthyldichloromethyl naphthoate should pyrolyze to 2 mol of naphthoyl chloride and no phosgene.

(11) Part of the naphthyl naphthoate may come from such a process via loss of CO_2 to give a carbene or loss of H and CO_2 to give aroyloxy-naphthyl radical. We did not test this hypothesis by the appropriate labeling experiment.
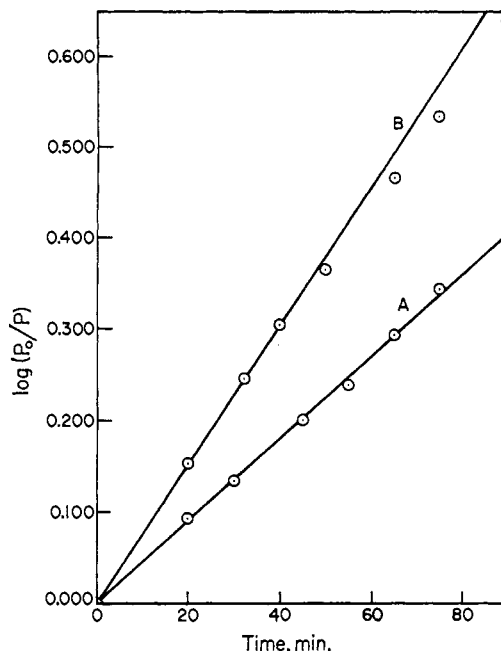
reactions of the hypoiodites[13] include decomposition to the corresponding iodide (the iodonaphthalene in Table V), hydrolysis to the carboxylic acid,[12b] and addition to

peroxide $\longrightarrow$

IV, Ar = naphthyl
or phenyl

$$Ar—\overset{\overset{\displaystyle O}{\|}}{C}—O—\text{[naphthalene]}—\overset{\overset{\displaystyle O}{\|}}{C}—OH \quad (4)$$

Ar = naphthyl (NNA)
or phenyl (BNA)
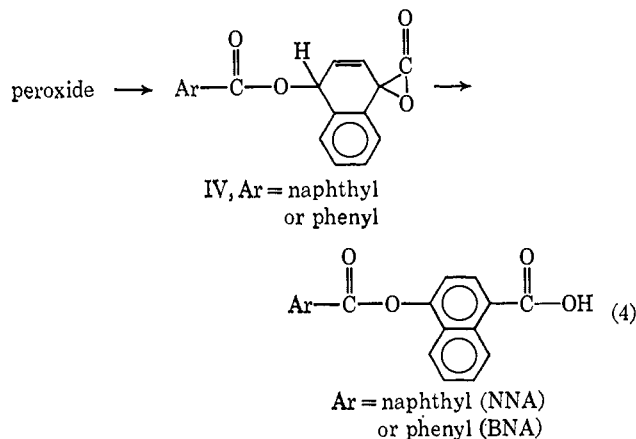
alkenes. The maximum in I_2 uptake part way through the reaction (Table II) supports a temporary storage of iodine is the form of hypoiodite.

Iodine in CCl_4 drastically reduces the yield of NNA while slightly increasing the yield of NNt. The lowered yield of NNA is more than compensated by the appearance of a new product, 1,4-bis(1-naphthoyloxy)-naphthalene (NNN). A change in product without increase in reaction rate usually means the diversion of an intermediate, and we propose that IV is converted to NNN by reaction with naphthoyl hypoiodite. Water diverts part of the naphthoyl hypoiodite from reacting by eq 5 and consequently reduces the yield of NNN while restoring an equivalent amount of the NNA yield.

(12) (a) G. S. Hammond, *J. Amer. Chem. Soc.*, **72**, 3737 (1950); (b) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950); (c) D. F. De-Tar and R. C. Lamb, *ibid*, **81**, 122 (1959).

(13) (a) A. Perret and A. Perrot, *Helv. Chim. Acta*, **28**, 558 (1945); (b) J. E. Leffler, W. J. M. Mitchell, and B. C. Menon, *J. Org. Chem.*, **31**, 1153 (1966); (c) J. E. Leffler and L. J. Story, *J. Amer. Chem. Soc.*, **89**, 2333 (1967).

IV ⇌ [chemical structure: naphthalene with H, O—C—C₁₀H₇ at top, + charge, and C=O / O⁻ at bottom] I—O—$\overset{O}{\overset{\|}{C}}$—$C_{10}H_7$ →

[chemical structure with H, O—C—C₁₀H₇ groups] $\xrightarrow[-\text{HI}]{-CO_2}$ [chemical structure: naphthalene with O—C—C₁₀H₇ groups]   (5)

NNN

$HI + I$—O—$\overset{O}{\overset{\|}{C}}$—$C_{10}H_7 \xrightarrow{fast} I_2 + HO$—$\overset{O}{\overset{\|}{C}}$—$C_{10}H_7$
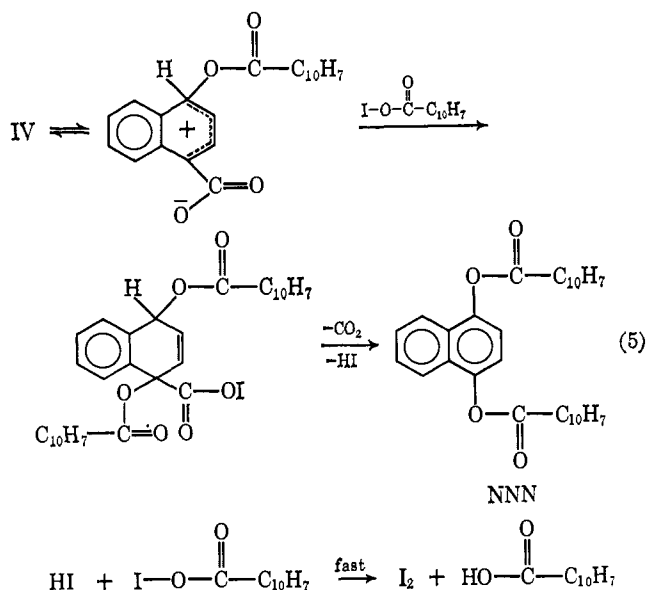
Although the amount of geminate recombination and the nature of the product might suggest that IV is formed by an ionic process analogous to the carboxy-inversion reaction,[14] all of our results can be explained equally well on the basis of a single mechanism, homolysis with cage recombination. Recombination of geminate radicals at remote bonding positions that must require considerable rotation of one of the partners is not unusual. For example, t-butyltriphenyl peracetate gives about a 16% yield of p-t-butoxytriphenylmethane in cumene, chlorobenzene, and styrene and a 10% yield in vinyl acetate.[15] Azocumene[16] and phenyl-azotriphenylmethane[17] behave analogously. The amount of geminate recombination from bis(α-naphthoyl) peroxide is about the same, or not much greater, than the 55% of cage products found in the decomposition of Δ-phenylvaleryl peroxide.[18]

Photolysis. A preliminary study of the photolysis of bis(α-naphthoyl) peroxide in CCl₄, using a 3500-Å light source through Pyrex, gave 1-chloronaphthalene (0.745 mol/mol vs. 0.79 for the thermal decomposition), hexachloroethane (0.178 mol/mol vs. 0.108), and naphthyl naphthoate (0.054 mol/mol vs. 0.032). NNA, the major cage product of the thermal reaction, was not formed. If the formation of IV and NNA depends on an anchimerically assisted process in the thermal decomposition, their absence in the photochemical decomposition is to be expected.

Experimental Section[19]

Bis(α-naphthoyl) Peroxide. Caution: sometimes explodes when scratched. This compound was prepared from H₂O₂ by the general method of Greene and Kazan[20] in 88% yield (crude), and twice recrystallized by adding CH₃OH to a CHCl₃ solution. The pure material has an absorption tail extending into the visible region,

(14) J. E. Leffler, *J. Amer. Chem. Soc.*, **72**, 67 (1950).
(15) J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).
(16) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 137 (1966).
(17) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967).
(18) D. F. Detar and C. Weis, *ibid.*, **79**, 3041 (1957).
(19) R. G. Zepp, Dissertation, The Florida State University, 1969.
(20) F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

which gives it a very pale yellow color. When heated in a melting point apparatus initially at 90° it explodes at 98°.

Per-α-naphthoic Acid.[19] The peracid was made from Li₂O₂ and the acid chloride in aqueous dimethoxyethane. After precipitation by the addition of cold 20% H₂SO₄, it was washed in ether solution with cold aqueous sodium acetate to remove α-naphthoic acid. After drying the ether solution over Na₂SO₄ at 2°, solvent was removed at 10° to give the peracid as colorless crystals, 86% yield. This compound decomposes in C₆H₆ or in CCl₄ with the development of a violet color.

α-Naphthoyl Benzoyl Peroxide. The general procedure of Greene and Kazan[20] was used starting with perbenzoic acid and α-naphthoic acid, giving the peroxide in 71% yield. It was recrystallized twice by adding methanol to a chloroform solution, cooling to −10°, and seeding. The iodometric assay after two crystallizations was 99.7%. A kinetic study established the absence of the two symmetrical peroxides.

1,4-Bis(1-naphthoyloxy)naphthalene. This compound was made from naphthoyl chloride and 1,4-dihydroxynaphthalene by heating the stoichiometric mixture at 80° with exclusion of moisture. The reaction mixture was then dissolved in 2:1 ether-dichloromethane, washed with 10% aqueous NaOH, then with saturated NaCl, and finally dried over MgSO₄. The crude product melted at 174–175° after three recrystallizations from acetone.

Anal. Calcd for C₃₂H₂₀O₄: C, 82.04; H, 4.30. Found: C, 82.24; H, 4.48.

Products of the Decomposition. Volatile products from the decomposition in benzene were analyzed by means of a 7 ft × ⅛ in. liquid-vapor chromatographic column of 10% FFAP on Chromosorb W-AW-DMCS (acid washed, dimethyldichlorosilane treated), an 8 ft × ⅛ in. column containing 10% SE51 on the same Chromosorb, and a 17 in. × ⅛ in. column containing 6% SE30. Volatile products and methylated acids from the decompositions in CCl₄ were analyzed on a 10 ft × ¼ in. column containing 15% SE51 on Chromosorb W-AW-DMCS and a 4 ft × ¼ in. column containing 8% Carbowax 20M terminated with terephthalic acid on Chromosorb W-AW-DMCS. The volatile products were identified by retention times and comparison of the collected peaks with known compounds by means of their ir spectra. Quantitative analysis was done with a flame ionization detector and suitable external standards, averaging the results from three known and three unknown mixtures.

4-(1-Naphthoyloxy)-1-naphthoic acid crystallizes on cooling the solutions of decomposition products. It was identified by conversion to the methyl ester, mp 129.5–132°. The ir spectrum of the crude ester showed that methyl 2-(1-naphthoyloxy)-1-naphthoate and methyl 8-(1-naphthoyloxy)-1-naphthoate were absent, or present only in very small amounts. The purified ester, mp 135–136.5°, had an ir spectrum identical with that of a synthetic sample and did not depress its melting point.

Anal. Calcd for C₂₃H₁₆O₄: C, 77.51; H, 4.53. Found: C, 77.33; H, 4.51.

Naphthoyl Chloride Precursor. The filtrate after removing naphthoyloxynaphthoic acid from a concentrated solution of the products of decomposition of bis(α-naphthoyl) peroxide in CCl₄ was distilled *in vacuo* in an apparatus having two liquid N₂-cooled traps, one containing cyclohexylamine. The first fraction (120–122° (12 mm)) was a mixture of 1-chloronaphthalene and C₂Cl₆. When the pot temperature was raised above 150° the contents rapidly darkened and became more viscous. The second fraction did not distil until the pot reached 240–250°, then came over as a yellow oil, 108–110° (0.4 mm). This fraction was identified as a mixture of 1-chloronaphthalene, 1-naphthoyl chloride, and 8-hydroxy-1-naphtholactone. The naphthoyl chloride was identified by several characteristic bands in the second fraction and by isolation of the anilide. Fraction 3 came over after the pot had reached 300–325° and contained further amounts of naphthoyl chloride and the lactone. No acid chloride was present (infrared) in the solution of decomposition products before pyrolysis.

After collecting fraction 3, the trap containing cyclohexylamine at liquid N₂ temperature was thawed, whereupon an exothermic reaction occurred giving a colorless solid identical with cyclohexylamine hydrochloride. No dicyclohexylurea was present and hence no COCl₂ was formed in the pyrolysis. Similar results were obtained using a trap containing aniline in ether solution.

1,4-Naphthalenedicarboxylic Acid. This substance was isolated and identified as its methyl ester after hydrolysis of the CCl₄ reaction mixture, mp (ester) 63–64°, neutralization equiv 109.

1,4-Bis(1-naphthoyloxy)naphthalene. On concentration of the neutral products from the decomposition in CCl₄-I₂, this product

precipitated from solution, mp after recrystallization from acetone, 170–172°. It was identified by ir, mass spectrum, hydrolysis products, and comparison with the synthetic sample.

Anal. Calcd for $C_{32}H_{20}O_4$: C, 82.04; H, 4.30. Found: C, 81.85; H, 4.30.

Kinetics and Mechanism of the Sulfoxide–Silane Reaction

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Abstract: The kinetics of the reaction between aromatic sulfoxides and trichlorosilane have been examined. The reaction follows the rate equation, rate = k [sulfoxide] [trichlorosilane]. The solvent and the substitution effect have been investigated. An isotope effect of k_H/k_D = 2.0–2.4 is observed. The activation parameters are $\Delta H^{\ddagger}$ = 7.1 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = −31 ± 1.4 eu. Based on these observations, a mechanism involving a four-center transition state is proposed.

Because of the probable polarization of the Si–H bond into $Si^{\delta+}$–$H^{\delta-}$, silicon hydrides reduce a number of organic functional groups.[1] Their use as synthetic reagents has, however, been superseded by aluminum hydrides and borohydrides. Recently, Fritzche, *et al.*,[2] observed that silanes are superior to lithium aluminum hydride (LAH) in the reduction of phosphine oxides to phosphines even though LAH is a stronger reducing agent. The reason for this can be readily understood if one examines reaction 1. It is

$$R_3P{=}O + HSiCl_3 \longrightarrow R_3P + HOSiCl_3 \qquad (1)$$
$$\downarrow HSiCl_3$$
$$H_2 + Cl_3SiOSiCl_3$$

essentially an oxygen-transfer reaction.[3] The reaction is favorable because of the high bond energy of the Si–O bond and the reaction is pushed to completion by the subsequent step to give a high yield of phosphine. We have examined[5] the corresponding reaction between sulfoxides and trichlorosilane and found that there is a dichotomy of behavior toward trichlorosilane between aromatic and aliphatic sulfoxides. Aromatic sulfoxides are reduced to the sulfides quantitatively whereas aliphatic sulfoxides are converted to the mercaptals and sulfides (reactions 2 and 3).

$$Ar_2S{=}O + HSiCl_3 \longrightarrow Ar_2S + HOSiCl_3 \qquad (2)$$

$$RCH_2{-}\underset{\underset{O}{\|}}{S}{-}CH_2R + HSiCl_3 \longrightarrow$$

$$RCH(SCH_2R)_2 + RCH_2SCH_2R \quad (3)$$

Amine oxides were found to be converted by chlorosilanes[4] to the corresponding amines (reaction 4).

Thus, deoxygenation by silane appears to be a general reaction and assumes increasing significance in the synthesis of phosphorus[6] and sulfur compounds.

There is still lacking however a mechanistic description of the intimate details involved in this type of oxygen-transfer reaction. We have undertaken therefore an investigation of the kinetics of reaction 2.

$$R_3N{\rightarrow}O + Cl_3SiSiCl_3 \longrightarrow R_3N + Cl_3SiOSiCl_3 \qquad (4)$$

Experimental Section

Materials. Diphenyl, di-*p*-chlorodiphenyl, and di-*p*-tolyl sulfoxide were commercially available (Aldrich) and were purified by recrystallization. Di-*p*-methoxydiphenyl sulfoxide was prepared by the method of Smiles and LeRossignol.[7] Trichlorosilane was obtained from Alfa Inorganics and was purified by distillation, bp 31.5° (760 mm), before use. Trichlorosilane-*d*, obtained from Merck Sharp and Dohme of Canada Ltd., was shown by nmr and mass spectrometry to be greater than 99% pure. Solvents used were purified by distillation from recommended drying agents.

Procedures. On a preparative scale the following procedure was used for reducing aromatic sulfoxides to the sulfides. To a solution of the sulfoxide (10 g) in dry ether (100 ml) in a three-necked flask fitted with a condenser protected by a drying tube ($CaCl_2$) and an addition funnel, a twofold excess of trichlorosilane in 50 ml of ether was added slowly. The solution was stirred for 1 hr. The excess silane was hydrolyzed with water and the ether was allowed to evaporate. The residue was taken up in boiling ethanol and filtered. The ethanol solution on cooling yielded the crystalline sulfide.

Kinetics. Using the fact that the ultraviolet spectra of sulfoxides and the corresponding sulfides are quite different (Table I), the kinetics of the reaction were studied photometrically. A Beckman DB spectrophotometer was used at constant wavelength to monitor the disappearance of sulfoxide or apearance of sulfide. The solutions of sulfoxides and silane used were equilibrated for a half-hour at the given temperature before each run. The temperature of the temperature-controlled cell holders was found to vary within ±0.1°.

Pseudo-first-order conditions were used for the reactions with an excess of (at least hundredfold stoichiometrically) silane. All runs were repeated at least once. The values of the pseudo-first-order rate constant (k') were calculated from plots of ln ($A_0 - A_\infty$)/($A_0 - A_t$) *vs.* time (t) by the method of least squares. The rate constants were calculated from the initial portion of the reaction for which first-order kinetics were seen to be valid, and for all com-

(1) For a review of some aspects of silicon hydride reactions in organic chemistry, see R. Calas, *Pure Appl. Chem.*, **11**, 61 (1966).

(2) H. Fritsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964); *ibid.*, **98**, 176 (1965).

(3) That reaction I is more of a deoxygenation was dramatically demonstrated by Mislow, *et al.*,[4] who found that phosphine oxide was converted to phosphine by perchloropolysilane Si_nCl_{2n+2}.

(4) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788, 7012 (1969).

(5) T. H. Chan, A. Melnyk, and D. N. Harpp, *Tetrahedron Lett.*, 201 (1969).

(6) See, for example, G. Maïkl and R. Potthast, *ibid.*, 1755 (1968), for the synthesis of 1-phenylphosphol.

(7) S. Smiles and R. Le Rossignol, *Proc. Chem. Soc., London*, 745 (1908).