347. *Alkoxy-radicals. Part I. The Kinetics of Thermal Decomposition of Dibenzyl Hyponitrite in Solution.*

By S. K. Ho and J. B. de Sousa.

The rate of decomposition of dibenzyl hyponitrite in various organic solvents is decreased by radical inhibitors, indicating the presence of induced decomposition. At a sufficiently high concentration of inhibitor, such as *p*-benzoquinone or styrene, the rate is of the first order and independent of inhibitor concentration.

At maximum inhibition the rate is relatively insensitive to the nature of the solvent, indicating that the decomposition is by a non-ionic mechanism. An average value of 24·94 ± 0·24 kcal. mole^{-1} was obtained for the activation energy of decomposition, and the frequency factor, *ca.* 10^{13} sec.$^{-1}$, falls within the range for unimolecular reactions.

Besides nitrogen, products found in various solvents were benzaldehyde and benzyl alcohol. The constancy of the yield of benzaldehyde at high dilutions indicates a " cage " disproportionation of benzyloxy-radicals formed in pairs.

Evidence for the recombination of benzyloxy-radicals is considered, and a preliminary study of the effect of dibenzyl hyponitrite on the polymerisation of methyl methacrylate reported.

Studies have been made on alkoxy-radicals derived from the pyrolysis and/or photolysis of alkyl nitrites and nitrates, dialkyl peroxides, and carboxylic acid esters.[1] The present work concerns the reactions of alkoxy-radicals formed in the decomposition of dialkyl and diaralkyl hyponitrites.

The lower dialkyl hyponitrites were first prepared by Zorn,[2] and the dibenzyl ester by Hantzsch and Kaufmann.[3] Partington and Shah [4] found several such esters to decompose according to the scheme (A) initially proposed by Zorn.

$$\mathrm{R\cdot CH_2\cdot O{-}N{=}N{-}O\cdot CH_2R \longrightarrow N_2 + R\cdot CHO + R\cdot CH_2\cdot OH} \quad . \ . \ . \ . \ . \quad (A)$$

In 1956, the thermal decomposition of diethyl hyponitrite, studied mass-spectrometrically,[5] was found to occur at a lower temperature than that of di-t-butyl peroxide, suggesting a lower energy of activation for the decomposition of the former. The products above 250° were nitrogen, formaldehyde, and the methyl radical, which are accounted for by reactions (1) and (2) (R = Me):

$$\mathrm{R\cdot CH_2\cdot O\cdot N{=}N\cdot O\cdot CH_2R \longrightarrow 2R\cdot CH_2O\cdot + N_2} \quad (1)$$

$$\mathrm{R\cdot CH_2\cdot O\cdot \longrightarrow R\cdot + CH_2O} \quad (2)$$

$$\mathrm{Ph\cdot CH_2\cdot O\cdot \longrightarrow Ph\cdot CHO + H\cdot} \quad (3)$$

$$\mathrm{2Ph\cdot CH_2\cdot O\cdot \longrightarrow Ph\cdot CH_2\cdot OH + Ph\cdot CHO} \quad (4)$$

$$\mathrm{2Ph\cdot CH_2\cdot O\cdot \longrightarrow Ph\cdot CH_2\cdot O\cdot O\cdot CH_2Ph} \quad (5)$$

$$\mathrm{R\cdot + Ph\cdot CH_2\cdot O\cdot N{=}N\cdot O\cdot CH_2Ph \longrightarrow Ph\cdot \dot{C}H\cdot O\cdot N{=}N\cdot O\cdot CH_2Ph + RH} \quad (6)$$

$$\mathrm{Ph\cdot \dot{C}H\cdot O\cdot N{=}N\cdot O\cdot CH_2Ph \longrightarrow Ph\cdot CHO + N_2 + Ph\cdot CH_2\cdot O\cdot} \quad (7)$$

$$\mathrm{Ph\cdot CH_2\cdot O\cdot + HS \longrightarrow Ph\cdot CH_2\cdot OH + S\cdot} \quad (8)$$

[R· = Ph·CH₂·O· or S· (solvent radical).]

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[1] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954, Vol. I, p. 232; Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88, 1336; Bell, Rust, and Vaughan, *ibid.*, 1950, **72**, 337, 338; Seubold, Rust, and Vaughan, *ibid.*, 1951, **73**, 18; Gray and Williams, *Trans. Faraday Soc.*, 1959, **55**, 760; *Chem. Rev.*, 1959, **59**, 239; Luft, *Z. Elektrochem.*, 1956, **60**, 94; Wijnen, *J. Chem. Phys.*, 1958, **28**, 271.

[2] Zorn, *Ber.*, 1878, **11**, 1306.

[3] Hantzsch and Kaufmann, *Annalen*, 1896, **292**, 317.

[4] Partington and Shah, *J.*, 1932, 2593.

[5] Lossing and de Sousa, unpublished work, Ottawa, 1956.

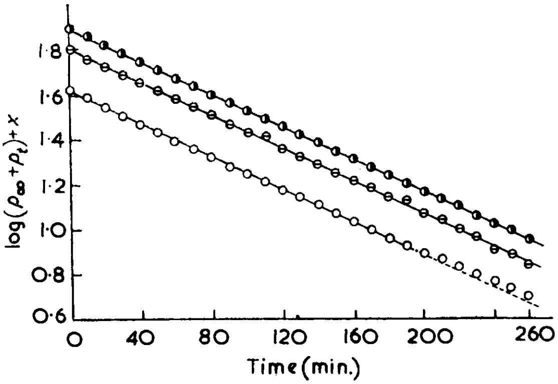
Reaction (2), suggested by Walsh,[6] has been confirmed by Lossing and de Sousa[7] who decomposed various n-alkyl nitrites in a flow system and found that the alkoxy-radicals formed decompose giving mainly formaldehyde and an alkyl radical. Dibenzyl hyponitrite had been used as a radical catalyst in the polymerisation of methyl methacrylate[8] and in the Wohl–Ziegler bromination reaction.[9] It thus appears that, in solution as well as in the gas phase, decomposition of hyponitrite esters follows a radical path.

In the present work the dibenzyl ester has been selected for study as it is a crystallisable solid whereas the dialkyl esters are liquids difficult to purify.

RESULTS

In earlier studies[2,4] decomposition was carried out in absence of solvent, or in water or aqueous alcohol where solvolytic reactions may well occur. It is then of importance to identify the products in other solvents and it is now found that benzaldehyde, benzyl alcohol, and nitrogen are formed in a variety of aromatic solvents and in cyclohexane. A quantitative yield of nitrogen, estimated volumetrically, was reported by Partington and Shah.[4] In our hands fresh solutions, prepared at room temperature, immediately begin to evolve nitrogen which was obtained in yields of *ca.* 95%. Some loss of nitrogen occurred during vacuum-degassing in the manometer vessel before measurement. The nitrogen was free from formaldehyde which might possibly arise by reaction (2) (R = Ph). A further complication due to the formation of hydrogen atoms in step (3) is considered unlikely on thermochemical grounds. Gray and Williams[1] cite for aryl-substituted alkoxy-radicals a value of 3—4 kcal. mole^{-1} for [D(C–H)–D(C–Ar)] where Ar is an aryl group, and consequently, the benzyloxy-radical should preferentially decompose by reaction (2). Since the absence of reaction (2) has been established experimentally in the range of our working temperatures, it appears unlikely that reaction (3) will occur to a significant extent.

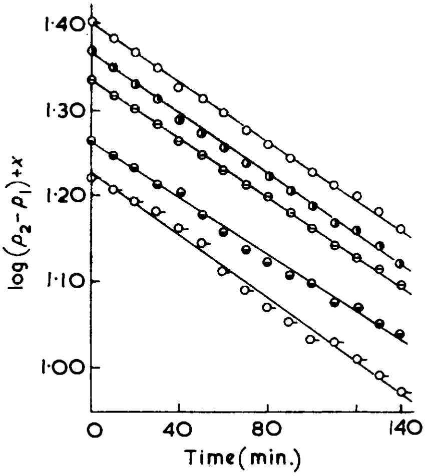
FIG. 1. *Decomposition of dibenzyl hyponitrite* (0·05M) *in chlorobenzene at* 45° *with and without inhibitor* (*infinity reading plot*).



○ Without inhibitor (x = 0). ⊖ With 0·03M-styrene (x = 0·3). ◑ With 0·8M-p-benzoquinone (x = 0·3).

(x is an arbitrary displacement, for clarity.)

FIG. 2. *Decomposition of dibenzyl hyponitrite* (*various concentrations in nitrobenzene at* 34·95° *in the absence of inhibitor* (*Guggenheim plot*).



○ 0·075M (x = 0·5). ◑ 0·050M (x = 0). ⊖ 0·30M (x = 0). ◒ 0·010M (x = 0). ○– 0·0075M (x = 0).

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[6] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269.

[7] Lossing and de Sousa, *J. Amer. Chem. Soc.*, 1959, **81**, 281.

[8] Harris, Marshall, and Jarrett, *Nature*, 1947, **159**, 843.

[9] Hasbruck, Spielman, and Hamlin, U.S.P. 2,727,906/1955.

Kinetic measurements were made by following the rate of evolution of nitrogen by a manometric method similar to those employed by others.[10] The method involved vacuum-degassing, and rate measurements were limited to solvents which could be frozen in carbon dioxide–acetone, liquid air not being available. The solvents used were cyclohexane, benzene, chlorobenzene, bromobenzene, nitrobenzene, *o*-nitrotoluene, styrene, *p*-xylene, and carbon tetrachloride. First-order plots of the rate of evolution of nitrogen in all the solvents mentioned (with the exception of carbon tetrachloride) are linear to at least 75% of complete decomposition and thereafter begin to curve very gradually as shown in Fig. 1. Values of the first-order rate constant k obtained from the linear portion of the plot are reproducible within 3%.

The values of k at 40° are shown in Table 1. The highest are for the halogenated benzenes and the lowest for the nitro-compounds, which is consistent with their behaviour as retarders of radical-chain reactions. Styrene, which has been used by Swain *et al.*[11] as an inhibitor in the decomposition of dibenzoyl peroxide in solution, shows an intermediate value at this temperature. The rate constant for the decomposition of dibenzyl hyponitrite in styrene was obtained by Guggenheim's method as the styrene became highly viscous during the later stages of decomposition and an accurate value of the final pressure of nitrogen could not be obtained.

The values of k over a ten-fold range of concentrations for several solvents are given in Table 2. There appears to be a trend towards lower rate constants with decreasing concentration, though the variations are within the margin of experimental error. The values marked with an asterisk are for the highest dilutions where the plots are slightly wavy (Fig. 2). At these low pressures of nitrogen the method appears to be not so reliable, possibly owing to inadequate stirring (see Experimental section).

TABLE 1. *Rates of decomposition of dibenzyl hyponitrite in different solvents.*

(Temperatures in °C are enclosed in parentheses)

	k, in absence of *p*-benzoquinone (10^{-4} sec.$^{-1}$)	k_d, in presence of 0·8M-*p*-benzoquinone (10^{-4} sec.$^{-1}$)		k, in absence of *p*-benzoquinone (10^{-4} sec.$^{-1}$)	k_d, in presence of 0·8M-*p*-benzoquinone (10^{-4} sec.$^{-1}$)
Chlorobenzene	1·62 (39·95)	1·42 (40·00)	Cyclohexane ...	1·63 (39·95)	—
Bromobenzene	1·62 (39·90)	1·43 (40·00)	Nitrobenzene ...	1·28 (39·90)	1·26 (40·00)
Benzene	1·47 (40·00)	1·38 (40·00)	*o*-Nitrotoluene	1·29 (39·90)	1·28 (39·95)
p-Xylene	1·48 (40·00)	1·38 (40·00)	Styrene	1·52 (40·00)	—

TABLE 2. *Effect of initial concentration of dibenzyl hyponitrite on rate of decomposition.*

In chlorobenzene at 34·95° ± 0·05°.

Concn. of ester (M)	0·075	0·050	0·030	0·0098 *
Rate, 10^4k (sec.$^{-1}$)	0·85	0·82	0·80	0·84 *

In nitrobenzene at 34·95° ± 0·05°.

Concn. of ester (M)	0·075	0·050	0·030	0·010 *	0·0075 *
Rate, 10^4k (sec.$^{-1}$)	0·66	0·67	0·66	0·63 *	0·70 *

In cyclohexane at 34·90° ± 0·05°.

Concn. of ester (M)...............	0·074	0·050	0·030	0·0098 *	0·0074 *
Rate, 10^4k (sec.$^{-1}$)	0·86	0·85	0·82	0·84 *	0·64 *

TABLE 3. *Effect of concentration of* p-*benzoquinone on rates of decomposition of dibenzyl hyponitrite in chlorobenzene at* 34·95° ± 0·05°.

(0·05M-Dibenzyl hyponitrite throughout.)

p-Benzoquinone (M)	0	0·10	0·16	0·25	0·34	0·38	0·42	0·50	0·55
Half-life, $t_{\frac{1}{2}}$ (hr.)......	2·32	2·39	2·45	2·52	2·52	2·62	2·65	2·64	2·68
p-Benzoquinone (M)	0·62	0·68	0·75	0·80	0·88	1·00	1·12	1·25	1·50
Half-life, $t_{\frac{1}{2}}$ (hr.)......	2·70	2·67	2·77	2·71	2·79	2·75	2·80	2·75	2·76

The possible presence of an induced chain reaction indicated by the lower rates in retarding solvents such as nitrobenzene and *o*-nitrotoluene is further supported by inhibitory effects in presence of styrene, chloranil, and *p*-benzoquinone. In all solvents the effect of inhibitors

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[10] DeTar, *J. Amer. Chem. Soc.*, 1955, **77**, 2013; 1956, **78**, 3911; Bartlett and Jones, *ibid.*, 1957, **79**, 2153; Tobolsky and Van Hook, *ibid.*, 1958, **80**, 779.

[11] Swain, Stockmayer, and Clark, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

was to decrease the rate of nitrogen evolution and to increase the half-life. Table 1 shows the effect of 0·8M-*p*-benzoquinone on the rate constant in various solvents: its inhibitory effect varied, being greatest with the halogenobenzenes and very slight in nitrobenzene and *o*-nitrotoluene. The decomposition thus shows features in common with that of dibenzoyl peroxide in solution although, as will appear, the amount of induced decomposition in the case of dibenzyl hyponitrite is less.

To measure the rate of the spontaneous decomposition the use of inhibitors to suppress the induced reaction has been adopted and solutions of styrene and quinones were used, following the work of others.[11,12] The rates of decomposition of dibenzyl hyponitrite in solution at maximum inhibition by both styrene or *p*-benzoquinone are close. Thus the values for k at 40° in chlorobenzene is $1{\cdot}42 \times 10^{-4}$ sec.$^{-1}$ with *p*-benzoquinone and $1{\cdot}40 \times 10^{-4}$ sec.$^{-1}$ with styrene as inhibitors. Styrene was, however, more difficult to handle and *p*-benzoquinone was used for more detailed studies. The use of chloranil and phenanthraquinone was also abandoned as they did not have the required range of solubility.

Table 3 shows that an increase in the concentration of *p*-benzoquinone decreases the half-life of dibenzyl hyponitrite in 0·05M-solution in chlorobenzene until about 0·7M-concentration, thereafter being without effect; the k_d values obtained by using the " final " pressure and by the Guggenheim method agreed within 3%. The first-order plot is linear throughout the range of accurate observation (90% of total decomposition). Over a ten-fold variation of concentration in dibenzyl hyponitrite in presence of 0·8M-*p*-benzoquinone the rates show no concentration-dependence below a 0·05M-concentration of dibenzyl hyponitrite (Table 4).

Values of the spontaneous rates of decomposition in various solvents were therefore evaluated at 0·8M- and 0·05M-concentration in *p*-benzoquinone and dibenzyl hyponitrite respectively (Tables 1, 5). Specimen first-order plots for five temperatures are detailed in Fig. 3.

TABLE 4. *Decomposition of dibenzyl hyponitrite in presence of* 0·8M-p-*benzoquinone at* 34·95° ± 0·05°.

In chlorobenzene		In nitrobenzene	
Ester (M)	10^4k_d (sec.$^{-1}$)	Ester (M)	10^4k_d (sec.$^{-1}$)
0·074	0·72	0·0098	0·68
0·050	0·71	0·0073	0·77
0·030	0·75		
In nitrobenzene			
Ester (M)	10^4k_d (sec.$^{-1}$)	Ester (M)	10^4k_d (sec.$^{-1}$)
0·075	0·66	0·010	0·60
0·050	0·62	0·0074	0·62
0·030	0·61		

TABLE 5. *Rates of decomposition of dibenzyl hyponitrite in different solvents.*

Solvent	10^4k_d (sec.$^{-1}$)	10^4k_d (sec.$^{-1}$)
Chlorobenzene	0·18 (25·00)	0·71 (35·00)
Bromobenzene	0·18 (25·00)	0·76 (34·95)
Benzene	0·20 (25·00)	0·70 (34·95)
p-Xylene	0·21 (24·95)	0·72 (35·00)
Cyclohexane	0·24 (24·95) *	0·78 (34·90) †
	0·18 (24·95) †	— —
Nitrobenzene	0·17 (24·95)	0·65 (34·95)
o-Nitrotoluene	0·18 (24·95)	0·67 (35·00)
Styrene	0·20 (24·90) *	0·81 (35·00) *

A typical plot of the energy of activation is shown in Fig. 4 and a complete summary is given in Table 6. The frequency factors in all solvents range from 10^{13} to 10^{14} sec.$^{-1}$, typical of unimolecular reactions. The low activation energy of *ca.* 25 kcal. mole^{-1} is in conformity with the concerted rupture of the two O–N bonds yielding the stable nitrogen molecule. The scheme in which two bonds are broken simultaneously with the formation of the N–N triple bond as a source of compensating energy is similarly considered to operate in the decomposition of azoalkanes [13] and in the α-phenylated azoalkanes.[14] In the present study it was confirmed

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[12] Bartlett, Hammond, and Kwart, *J. Amer. Chem. Soc.*, 1958, **80**, 5313.

[13] Semenov, " Some Problems of Chemical Kinetics and Reactivity," Pergamon Press, London, 1958, Vol. I, p. 270.

[14] Cohen and Wang, *J. Amer. Chem. Soc.*, 1955, **77**, 4510.

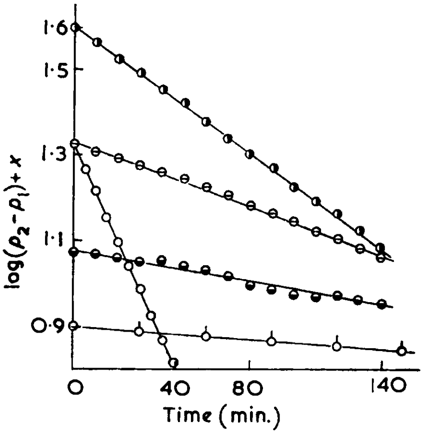
that polymerisation of methyl methacrylate as well as styrene was catalysed by dibenzyl hyponitrite. The effect of quinones, nitro-compounds, and styrene on the rate of decomposition of dibenzyl hyponitrite in solution indicates that, at least in part, the decomposition proceeds by spontaneous decomposition into radicals which may induce chains in absence of inhibitors. In addition, the relative insensitivity of the spontaneous rates in various solvents from non-polar cyclohexane and benzene through the increasingly polar solvents bromobenzene, chlorobenzene, nitrobenzene, and *o*-nitrotoluene is that to be expected of a non-ionic reaction. In fact, the most highly polar solvents, nitrobenzene and *o*-nitrotoluene, show the lowest rate. This is in contrast to the thermal decomposition of azobisisobutyronitrile at 62·5° where nitrobenzene shows the highest rate, values of $10^5 k_d$ in benzene, nitrobenzene, and chlorobenzene being 1·18, 1·79, and 1·54 sec.$^{-1}$, respectively.

TABLE 6. *Activation energy (E_a in kcal. mole^{-1}) of decomposition of dibenzyl hyponitrite in different solvents in presence of* 0·8M-p-*benzoquinone.*

Solvent	E_a	Average E_a	Solvent	E_a	Average E_a
Chlorobenzene	24·97	25·11	Cyclohexane †	25·69 †	25·33 †
	25·44			24·96 †	
	24·61		Nitrobenzene	24·52	24·56
	25·43			24·60	
Bromobenzene	25·05	25·13	*o*-Nitrotoluene	24·58	24·00
	25·22			23·41	
Benzene	24·59	24·96	Syrene *	24·57 *	24·90 *
	25·33			25·22 *	
p-Xylene	25·35	25·40			
	25·45				

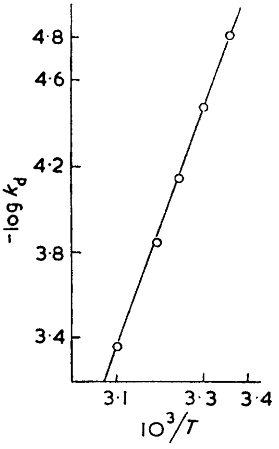
* Without any *p*-benzoquinone. † In presence of 0·025M-*p*-benzoquinone only.

FIG. 3. *Decomposition of dibenzyl hyponitrite* (0·05M) *in chlorobenzene in presence of* 0·8M-p-*benzoquinone at different temperatures (Guggenheim plot).*



○ 49·45° (x = 0). ◑ 40·0° (x = 0·15). ⊖ 35·0° (x = 0). ◒ 30·0° (x = 0). ♁ 25° (x = 0).

FIG. 4. *Decomposition of dibenzyl hyponitrite* (0·05M) *in chlorobenzene in presence of* 0·8M-p-*benzoquinone at different temperatures (determination of activation energy).*



The amount of induced reaction appears to be less than in the case of dibenzoyl peroxide. Thus at 35° the half-life of a 0·05M-solution of dibenzyl hyponitrite is increased from 2·32 hr. in absence of inhibitor to 2·75 hr. at maximum inhibitor, an increase of 18·5%. For dibenzoyl peroxide at 80° the half-life is increased from 1·08 hr. to 1·75 hr., an increase of 62%.[11] Comparison with azobisbutyronitrile [15] and dibenzoyl peroxide [16] shows a narrower range of variation

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[15] Hammond, Sen, and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3244.

[16] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686.

for k_d values for dibenzyl hyponitrite in several solvents: compare the data in Table 1 with those in the preceeding paragraph and the following values of 10^5k_d for the thermal decomposition of dibenzoyl peroxide at 80° in benzene, cyclohexane, and nitrobenzene, which are 3·28, 6·36, and 3·28 sec.$^{-1}$, respectively.

DISCUSSION

The details of the reaction must be viewed from the quantitative and qualitative aspects of the products and in terms of the processes (1)—(8). Although the evidence indicates a radical chain, it is possible that the reaction, at least in part, proceeds through a molecular mechanism. In the decomposition of azobisisobutyronitrile where the azo-group is also eliminated in the form of molecular nitrogen, a possible transition state has been considered which is similar to a *cis*-azo-compound and the mechanism then is assumed to involve a *trans*- to *cis*-transformation. Hammond *et al.*[15] consider such a mechanism unlikely as the efficiency of radical production in solution appears to vary more with the nature of the solvent than does the rate of decomposition.

Evidence for a *trans*-configuration of the hyponitrite ion has been adduced on the basis of Raman and infrared spectra.[17] Hunter and Partington [18] assigned a *trans*-configuration to dibenzyl hyponitrite on the basis of dipole-moment measurements. Known energies of activation for conversion of *cis*- into *trans*-isomers for aromatic azo-compounds [19] are of the order of 25 kcal. mole^{-1}. In these compounds as well as in ethylenic compounds the energy of the transition state is lowered by possibilities of conjugation with the phenyl group: thus, Wheland and Chen [20] calculated a value of 33 kcal. mole^{-1} for the conversion of *cis*- into *trans*-di-imide (H–N=N–H). Dibenzyl hyponitrite has a non-conjugated azo-linkage and the energy of activation for *cis*- into *trans*-conversion should therefore be higher than for conjugated azo-compounds. Further, the activation energy for the *trans*- to *cis*-change must include the enthalpy difference between the two isomers in the ground state. For the azobenzenes [21] this is of the order of 10 kcal. mole^{-1}. Thus it appears that such a mechanism of decomposition for dibenzyl hyponitrite would involve energies in excess of the energy for decomposition of 25 kcal. mole^{-1}. The existing evidence appears not to support a molecular mechanism occurring to any significant extent and it may be envisaged that decomposition occurs by a concerted rupture of the two O–N bonds in a *trans*-configuration, with the elimination of nitrogen and the formation of two benzyloxy-radicals in a solvent cage.[22]

The products, benzaldehyde and benzyl alcohol, have been accounted for by Gray and Williams [1] as resulting from the disproportionation of benzyloxy-radicals which may be derived from the same (cage disproportionation [22]) or from different parent molecules. In addition, benzyl alcohol may arise by hydrogen-abstraction from solvent, reaction (8), and from the parent hyponitrite, reactions (1 + 4), which gives a radical which may decompose into the benzyloxy-radical, nitrogen, and benzaldehyde. This is analogous to the decomposition of radicals formed by hydrogen abstraction from dibenzyl ethers studied by Huang and Si-Hoe: [23]

$$\mathrm{Ph{\cdot}\dot{C}H{\cdot}O{\cdot}CH_2Ph \longrightarrow Ph{\cdot}CHO + Ph{\cdot}CH_2{\cdot}}$$

Benzaldehyde may be produced by means of a cage or non-cage disproportionation and by the induced reaction. The induced reaction and the non-cage disproportionation are second-order reactions and their importance would depend on the initial concentration of dibenzyl hyponitrite, whereas the cage disproportionation has a probability independent of the concentration of dibenzyl hyponitrite. In solution in cyclohexane, yields of benzaldehyde can be determined by spectrophotometry. Solutions of dibenzyl hyponitrite of

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[17] Kuhn and Lippincott, *J. Amer. Chem. Soc.*, 1956, **78**, 1820.
[18] Hunter and Partington, *J.*, 1933, 309.
[19] Le Fèvre and de Sousa, *J.*, 1955, 3154.
[20] Wheland and Chen, *J. Chem. Phys.*, 1956, **24**, 67.
[21] Corruccini and Gilbert, *J. Amer. Chem. Soc.*, 1939, **61**, 2925.
[22] Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120.
[23] Huang and Si-Hoe, *Proc. Chem. Soc.*, 1957, 354.

various concentrations were sealed in degassed ampoules and decomposed at 30°, 35°, and 40° in thermostats until no further yield of nitrogen was observable and for a minimum period of at least 15 half-lives. Analyses for benzaldehyde were carried out by using its ultraviolet absorption maximum at 285·5 mμ. At this wavelength benzaldehyde absorbs strongly (ε 1000) whereas absorption by benzyl alcohol (ε 2) is negligible. The yields of benzaldehyde over a thousand-fold range of concentration are given in Table 7. At 40° the yield drops from 65% at 0·1M to 50% at 0·001M and remains stationary thereafter to at least 0·0001M. The high and constant yield of benzaldehyde at high dilutions strongly supports a cage disproportionation. For the decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride over a 600-fold range in concentration, DeTar and Weis [24] found that at 55° cage processes accounted for 55% of the reaction. As cage-radical reactions are not regarded as susceptible to inhibition, the yield of benzaldehyde is being checked in presence of radical inhibitors. The efficiency of radical production is being examined with the aid of inhibitors such as quinones, diphenylpicrylhydrazyl, and iodine concurrently with studies of efficiencies in the polymerisation of monomers. The yield of benzaldehyde is independent of temperature at high dilutions in the range 30—40° within the range of experimental error, there being here no significant difference between the activation energies for diffusion out of a cage and disproportionation in a cage, both of which should be small.

TABLE 7. *Percentage yield of benzaldehyde in the decomposition of dibenzyl hyponitrite in cyclohexane.* [Percentage yield = 100 × concn. of Ph·CHO found/concn. of $(CH_2Ph)_2N_2O_2$.]

Concn. (M) of soln.	Ph·CHO (%) 40·0°	35·0°	30·0°
0·1000	65·34		
0·0500	65·58		
0·0100	57·38		
0·00748	55·80		
0·00500	53·15		
0·00453	53·47	55·44	55·44
0·00399	53·50		
0·00351	52·91	53·48	53·21
0·00301	53·95	52·46	53·27
0·00198	53·02	50·77	53·02
0·00149	51·29	50·08	51·56
0·00100	50·55	49·95	49·74
	50·89		
0·000762		49·60	50·12
0·000500	50·29		
0·000492			49·60
0·000103	50·29		51·05

No example of dimerisation of alkoxy-radicals is available, except for the cases of the cumyloxy-radical cited by Gray and Williams [1] which cannot undergo disproportionation by transfer of a hydrogen atom (as in the benzyloxy-radical) so that it may dimerise. Solutions of dibenzyl hyponitrite decomposed at low temperatures did not give tests for peroxide, and only benzaldehyde and benzyl alcohol were isolated. Quantitative spectroscopical studies indicated erratic yields of benzyl alcohol and the total yield of benzaldehyde and the alcohol exceeds the theoretical: the reaction may proceed by dimerisation and then a reversible fission of the dibenzyl peroxide. An approximate estimate of the contribution of the reverse of reaction (5) to the rate of formation of benzaldehyde could be made if the rate of decomposition of dibenzyl peroxide were available. This does not appear to have been studied, though the related di-α-cumyl peroxide decomposes [25] in cumene by a first-order non-chain mechanism according to the rate equation $k = 4{\cdot}31 \times 10^{14} \exp(-34{,}500/\boldsymbol{R}T)$ sec.$^{-1}$.

TABLE 8. *Determination of benzaldehyde (in duplicate) for* 0·00076M-*solutions of dibenzyl hyponitrite in cyclohexane after decomposition.*

	Optical density Sample A	Sample B	Average	Ph·CHO (%)
96 hr. at 35°	0·378	0·374	0·376	49·01
96 + 65 hr. at 35°	0·379	0·373	0·376	49·01
96 hr. at 35° + 65 hr. at 100°	0·419	0·420	0·420	54·74

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[24] DeTar and Weis, *J. Amer. Chem. Soc.*, 1956, **78**, 1820.

[25] Bailey and Godin, *Trans. Faraday Soc.*, 1956, **52**, 68.

In solution, di-α-cumyl peroxide would have a half-life of 1·26 × 10^6 hr. at 35° (by extrapolation),[25] whereas the half-life of dibenzyl hyponitrite at 35° in cyclohexane is 2·46 hr. Thus it appears that at 35° benzaldehyde should be formed directly by disproportionation of benzyloxy-radicals generated by the parent hyponitrite.

A study of the rate of appearance of benzaldehyde at 35° in cyclohexane solutions in the absence of oxygen using the 285·5 mμ maximum was attempted. The optical density increased rapidly, though the kinetics were not strictly of the first-order. This may be due to the fact that dibenzyl hyponitrite has a small but finite absorption at 285·5 mμ (ε = 20). Half the final yield of benzaldehyde is formed in 2·75 hr. This compares with 2·46 hr. for the half-life of dibenzyl hyponitrite in cyclohexane at 35°. After several half-lives at 35° the yield of benzaldehyde remains constant (Table 8). The yield after 96 and 161 hr. at 35° is the same (49%), indicating that dibenzyl peroxide if present does not give benzaldehyde in this period of time. However, subjecting solutions which had undergone decomposition for 96 hr. at 35° to a further 65 hr. at 100° (at which the calculated half-life of dibenzyl peroxide is 55 hr.) increased the yield of benzaldehyde by 5%. The reverse of reaction (5) followed by disproportionation (4) is indicated. It appears that benzyloxy-radicals undergo disproportionation and dimerisation in a cage, and this is being further studied.

TABLE 9. *Rate of polymerisation of methyl methacrylate compared with concentration of dibenzyl hyponitrite.*

Initiator concn. M (M)	$\sqrt{M}$	10^4R_p (mole $l.^{-1}$ sec.$^{-1}$)	$10^4R_p/\sqrt{M}$	Initiator concn. M (M)	$\sqrt{M}$	10^4R_p (mole $l.^{-1}$ sec.$^{-1}$)	$10^4R_p/\sqrt{M}$
0·01	0·1	1·76	17·6	0·0060	0·078	1·30	16·6
0·0089	0·094	1·59	17·0	0·0052	0·071	1·31	18·7
0·0075	0·086	1·51	17·5				

Polymerisation.—Both styrene and methyl methacrylate were polymerised by dibenzyl hyponitrite. Quantitative studies were made on the bulk polymerisation of methyl methacrylate, the rate being followed by the weight of polymer formed. The plot of percentage polymerisation against time gives a straight line passing through the origin, showing no inhibition period. The rate of polymerisation R_p is proportional to the square of the initiator concentration (Table 9). Further studies on this and other monomers are being undertaken.

EXPERIMENTAL

Materials.—Benzene and toluene. B.D.H. sulphur-free grades were stirred several times with concentrated sulphuric acid until the acid layer was only slightly coloured. The hydrocarbon layer was then separated from the acid and washed successively with water, 20% sodium carbonate solution, and water. Fractional distillation, after drying ($CaCl_2$), gave benzene, b. p. 80—80·5°, and toluene, b. p. 110—110·5°.

Chlorobenzene, bromobenzene, and p-*xylene.* B.D.H. reagents were dried ($CaCl_2$) and fractionally distilled: chlorobenzene, b. p. 132°; bromobenzene, b. p. 150°; *p*-xylene, b. p. 138°.

Nitrobenzene and o-*nitrotoluene.* "AnalaR" reagents (B.D.H.) were washed successively with 10% sodium hydrogen carbonate solution and water then dried ($MgSO_4$) and fractionally distilled: nitrobenzene, b. p. 210—211°; *o*-nitrotoluene, b. p. 220—221°. Freshly purified and distilled samples were used for kinetic studies, as aged samples give variable results.

Cyclohexane. Cyclohexane (B.D.H.) was shaken mechanically with 10% sulphuric acid and 1% oleum for 24 hr., then washed with water, 2N-sodium hydroxide solution, 10% potassium permanganate solution, and water. It was dried ($CaCl_2$) and fractionally distilled; b. p. 80·5°.

Carbon tetrachloride. "AnalaR" carbon tetrachloride, dried ($CaCl_2$) and fractionally distilled, had b. p. 76·5°.

Styrene and methyl methacrylate. The monomers (Light & Co.) were shaken thrice with 4% ice-cold sodium hydroxide solution and ice-water. After drying ($MgSO_4$) in a refrigerator they were fractionally distilled in a stream of argon immediately before use, giving styrene, b. p. 35°/10 mm., and methyl methacrylate, b. p. 100—101°.

p-Benzoquinone. A B.D.H. sample was steam-distilled, dried, recrystallised from light petroleum (b. p. 80—100°), and dried over silica gel and paraffin wax; it had m. p. 115° (sublimes).

Chloranil. This was used as supplied by B.D.H.

Benzaldehyde. Crude benzaldehyde was shaken several times with cold 5% sodium carbonate solution. The benzaldehyde layer was then dried ($CaCl_2$) and distilled (b. p. 179—180°) in a current of argon immediately before use in spectroscopic analysis.

Benzyl alcohol. Benzyl alcohol was washed with sodium hydrogen sulphite solution and saturated brine. After being dried ($MgSO_4$) it was fractionally distilled in a stream of argon and used immediately for spectroscopic work, then having b. p. 204—205°.

Dibenzyl hyponitrite. The ester was prepared from silver hyponitrite and benzyl iodide according to Partington and Shah.[4] When freed from benzyl iodide by repeated precipitation from ether with light petroleum (b. p. 60—80°), it had m. p. 47—48° (decomp.). When heated rapidly the solid ester decomposed with a puff but not violently. The ester was stored in a desiccator kept in a refrigerator. Under these conditions deterioration is slow.

Products of Decomposition.—Solutions (0·5M) of freshly prepared dibenzyl hyponitrite in benzene and in cyclohexane were sealed under vacuum in vessels and allowed to decompose at 40°. After 5 days the ampoules were cooled and opened, and the solvent was removed under reduced pressure at room temperature in a stream of argon (to prevent oxidation of benzaldehyde). The residue was shaken in ether with a concentrated solution of sodium hydrogen sulphite. The addition compound was collected, washed with ether, and decomposed with sodium carbonate solution, and the liberated aldehyde was taken up in ether. The ether layer was then washed with sodium carbonate solution and evaporated in a stream of argon. The residue on treatment with 2,4-dinitrophenylhydrazine reagent gave large amounts of benzaldehyde 2,4-dinitrophenylhydrazone; after recrystallisation it had m. p. and mixed m. p. 235°. The dimedone had m. p. and mixed m. p. 198—200°. The ether solution which had been extracted with sodium hydrogen sulphite was dried and evaporated. The residue gave high yields of benzyl 3,5-dinitrobenzoate, m. p. and mixed m. p. 113°.

The highly dilute solutions left over from kinetic measurements gave tests for benzaldehyde only after storage, though after evaporation in the case of volatile solvents the odour of benzaldehyde was noticeable in the residual liquid which gave derivatives immediately.

Polymerisation Rates.—Equal volumes (5 ml.) of a solution of freshly prepared dibenzyl hyponitrite in freshly distilled methyl methacrylate were sealed in degassed ampoules. The ampoules were then simultaneously immersed in a thermostat (25°). At regular intervals the ampoules were removed from the bath and opened, and the contents completely transferred with the minimum quantity of benzene into methanol (100 ml.) containing quinol. The polymer was centrifuged off, washed with more methanol, and redissolved in the minimum amount of benzene at room temperature. After re-precipitation the polymer was collected on a sintered-glass crucible and dried *in vacuo* at 56° to constant weight.

Apparatus.—All thermostats were controlled to within 0·05°. Spectroscopic work was performed with an S.P. 500 Unicam spectrophotometer and fused-silica 1 cm. cells with ground-glass stoppers.

Vessels for manometric measurements were constructed from 1·5 cm. Pyrex tubing of varying lengths (depending on the volumes of nitrogen expected) up to 8 cm. and capacity 15 c.c. The bottom was sealed and rounded off, and there was attached to the top a standard-taper joint for connection to the vacuum-system. Magnetic stirring was provided. A capillary side-arm near the top of the vessel was fused to a vertical capillary tube 80 cm. long and of 0·05 mm. internal diameter, the bottom of which was immersed in a large pool of mercury. The vertical manometer tubing was mounted against a metre rule graduated in mm. The whole apparatus was of a single-fused construction and was tested for leaks before use. Careful cleaning with chromic acid and distilled water was followed by drying and degassing on a vacuum-line. Solutions were delivered into the main vessel through capillary tubes below the construction made to facilitate sealing-off between the main vessel and the standard-taper joint for attachment to the vacuum-system. After admission of the solution, the vessel was attached to the vacuum-system by the standard-taper joint and frozen in carbon dioxide–acetone. Evacuation then followed, through a tap which permitted communication to a vacuum-system (10^{-3} mm.). The tap was then closed and the solid allowed to thaw to dispel any entrapped gas. The cycle of freezing, evacuation, and thawing was repeated twice, the solution then frozen again, and sealing carried out at the prepared constriction. After melting of the contents the main vessel was completely immersed in the appropriate thermostat. Pressure readings were taken at suitable intervals and corrected for the existing barometric pressure.

Agitation within the vessel was effected by a horse-shoe magnet (varnished to prevent rusting) mounted below the vessel on a shaft driven by a motor. Efficient agitation was necessary in order to avoid supersaturation and sudden jumps in pressure. In the case of very dilute solutions, when the volume of solution was large relative to the size of the vessel, stirring appeared to be insufficient and plots were slightly wavy.

Detection of Formaldehyde.—A 0·0456M-solution of dibenzyl hyponitrite in chlorobenzene (2·8 ml.) was sealed in a break-seal vessel under the same conditions as for the kinetic runs. The break-seal was then immersed in a thermostat at 40°, and after decomposition it was attached to the vacuum-system and the freshly evolved gases were transferred and absorbed in chromotropic acid. Analysis for formaldehyde was carried out according to the directions of Lee.[26] The absorption in the range 560—600 mμ was determined. No increase in absorption was found though 1 μmole of formaldehyde in the volume of solution used for analysis should show an optical density of 0·660 at 580 mμ.

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[26] Lee, *Analyt. Chem.*, 1956, **28**, 1621.