The Bimolecular Self-reactions of Secondary Peroxy Radicals. Product Studies[1]

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The principal products formed from 1-ethoxyethyl hydroperoxide and 1,2-diphenylethyl hydroperoxide on oxidation with reagents that are presumed to generate the corresponding *sec*-alkylperoxy radicals (Ce(IV), *tert*-butoxy, and Ag_2O) have been identified. The products formed when the corresponding alkoxy radicals are generated in pairs have also been identified. It is concluded that the Russell (1) concerted cyclic mechanism in which tetroxide decomposed to molecular products is not the exclusive route for the bimolecular self-reaction of *sec*-alkylperoxy radicals. It is suggested that there is also a second tetroxide decomposition process which yields radical products. The second process may yield "free" alkoxy radicals or it may, perhaps, yield the products of β-scission of the alkoxy radicals in a step concerted with O—O homolysis of the tetroxide. The relative importance of tetroxide decomposition to molecular and to radical products will depend on the structure of the alkyl groups, the temperature and, perhaps, the solvent.

Les principaux produits formés dans l'oxydation de l'éthoxy-1 éthylhydroperoxyde et diphémyl-1,2 éthyl hydroperoxyde par des réactifs susceptibles d'engendrer les radicaux *sec*-alkylperoxy correspondants (Ce(IV), *ter*-butoxy, et Ag_2O) ont été identifiés. Les produits issus des radicaux alkoxy correspondants, lorsque ceux ci étaient formés par pairs, ont été également identifiés. Le mécanisme cyclique concerté de Russell (1) selon lequel le tétroxyde se décompose en produits moléculaires, n'est donc pas la voie exclusive dans l'autoréaction bimoléculaire des radicaux *sec*-alkylperoxy. Une seconde voie pour la décomposition du tétroxyde en produits radicalaires a été proposée. Ce second processus peut conduire aux radicaux alkoxy libres, ou aux produits de scission β des radicaux alkoxy selon une étape concertée avec homolyse O—O du tétroxyde. L'importance relative de la décomposition du tétroxyde en produits moléculaires ou radicalaires dépendra de la structure des groupes alkyles, de la température et peut être du solvant.

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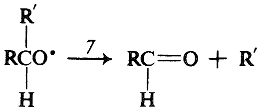
In 1957 Russell (1) suggested that the bimolecular self-reaction of secondary alkylperoxy radicals involved the concerted decomposition (reaction *2*) of an initially formed tetroxide (see Scheme 1).

The most frequently postulated alternative mechanism involves decomposition of the tetroxide to give two alkoxy radicals and oxygen (reaction *3*). According to the Russell mechanism the ketone, RR′CO, and the alcohol, RR′CHOH, will be formed in equimolar quantities. The same will be true of the non-concerted mechanism provided that all the alkoxy radicals that escape the cage (reaction *5*) undergo β-scission,



$$\underset{\mathrm{H}}{\overset{\mathrm{R'}}{\mathrm{RCO^{\bullet}}}} \xrightarrow{7} \underset{\mathrm{H}}{\mathrm{RC{=}O}} + \mathrm{R'}$$

If, however, the free alkoxy radicals abstract a hydrogen atom there will be a preponderance of alcohol.

The Russell, or concerted, mechanism is supported by a considerable body of experimental evidence (2–5), most of which has been obtained at ambient temperatures (20–60°). The non-concerted decomposition will be favored at higher temperatures because it will have a higher activation energy than the concerted process. For example, it has been estimated (6) that with *s*-butylperoxy radicals k_3/k_2 is ~0.04 at 30° and ~0.3 at 100°.

Two experimental observations have prevented the unreserved acceptance of the Russell mechanism as the dominant process at ambient temperatures and below. Firstly, thermochemical calculations suggest that if the overall reaction proceeded by the concerted route it should have a negative activation energy of several kilocalories per mole (7). However, experimental measurements in the temperature range -16 to $-90°$ indicate a positive activation energy of ~3 kcal/mol for a number of *sec*-alkylperoxy radicals (8, 9). Secondly, Diaper (10) has reported that 1-methoxy (**1***a*) and 1-*tert*-butoxynonane-1-hydroperoxide (**1***b*) were smoothly oxidized to di-(1-alkoxyalkyl)peroxides by 1 equiv of

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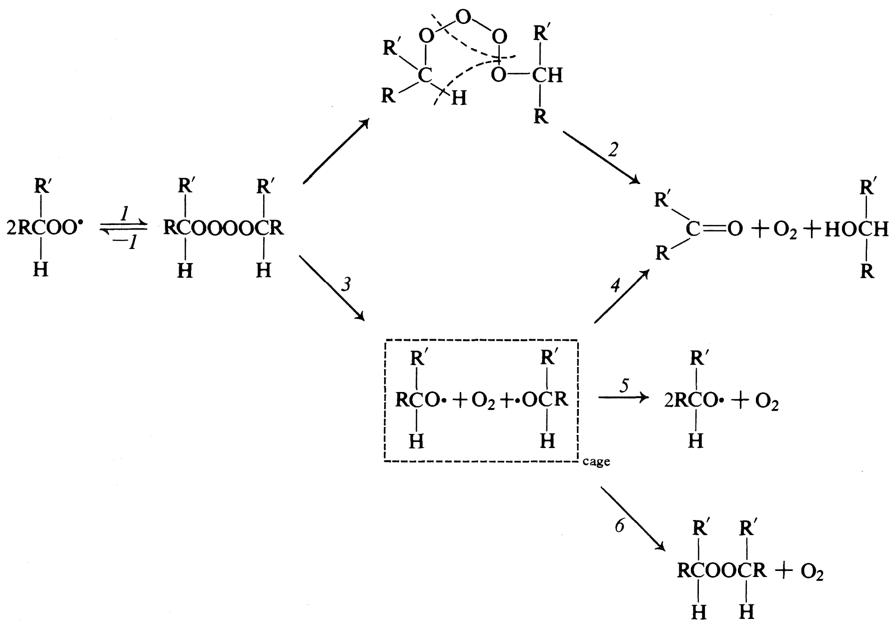
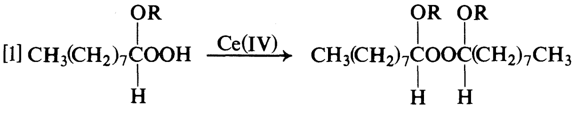


SCHEME 1



$$[1]\quad \mathrm{CH_3(CH_2)_7\overset{OR}{\underset{H}{C}}OOH} \xrightarrow{\mathrm{Ce(IV)}} \mathrm{CH_3(CH_2)_7\overset{OR}{\underset{H}{C}}OO\overset{OR}{\underset{H}{C}}(CH_2)_7CH_3}$$

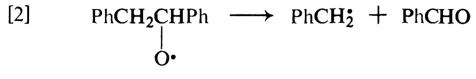
1

a $R = CH_3$

b $R = (CH_3)_3C$

Ce(IV) in methanol at 0° (eq. 1). Since Ce(IV) oxidizes alkyl hydroperoxides to the corresponding peroxy radicals in high yield (11, 12) it seems not unreasonable to suppose that 1-alkoxyalkylperoxy radicals react by the radical pathway and that the caged alkoxy radicals combine (reaction *6*, Scheme 1) rather than disproportionate.

Diaper's products contrast sharply with the products normally found in processes which are presumed to involve the bimolecular self-reaction of secondary alkylperoxy radicals. Numerous studies (1, 4, 6, 9, 13–16) attest to the fact that such products are the appropriate alcohol and ketone and that these are formed in high yield and in *approximately* equimolar amounts. Diaper's results prompted us, therefore, to investigate the products formed from an analogous peroxy radical, 1-ethoxyethylperoxy. Although little or no di-(1-ethoxyethyl)peroxide was formed, the other products suggested that alkoxy radicals played a significant role in the reaction. Our product studies were, therefore, extended to the 1,2-diphenylethylperoxy radical which was chosen because any free alkoxy radical should undergo a relatively rapid β-scission to yield benzaldehyde which could be easily detected in the reaction mixture (eq. 2). Attempts were also made to study the behavior of caged pairs of 1-ethoxyethoxy and 1,2-diphenylethoxy radicals in order to avoid some of the assumptions otherwise necessary in interpreting the results of the peroxy radical studies (*cf.* refs. 3 and 4).



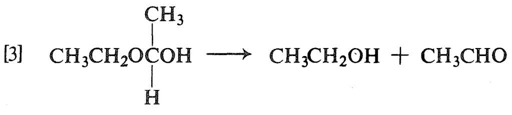
$$[2]\quad \mathrm{PhCH_2\underset{O\bullet}{C}HPh} \longrightarrow \mathrm{PhCH_2^{\bullet}} + \mathrm{PhCHO}$$

Results and Discussion

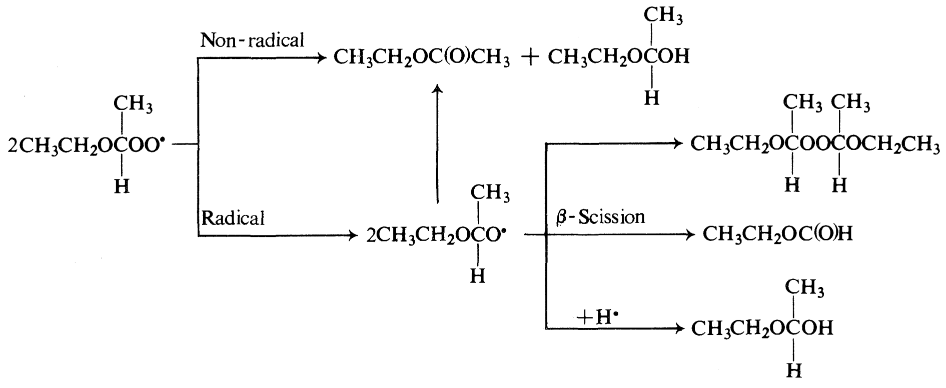
1-Ethoxyethylperoxy Radicals

These peroxy radicals were most conveniently prepared by oxidation of 1-ethoxyethyl hydroperoxide either by ceric ammonium nitrate, *tert*-butoxy radicals, or silver oxide. The principal reaction products expected from their self-reaction are shown in Scheme 2 while the yields of the products actually found are listed in Tables 1 and 2.

Ethanol was presumably formed by decomposition of the hemiacetal (eq. 3). The acetalde-



$$[3]\quad \mathrm{CH_3CH_2O\overset{CH_3}{\underset{H}{C}}OH} \longrightarrow \mathrm{CH_3CH_2OH} + \mathrm{CH_3CHO}$$



SCHEME 2

TABLE 1. Products from the Ce(IV) oxidation of 1-ethoxyethyl hydroperoxide in methanol at 0° (yields are mol/mol of hydroperoxide)

Initial hydroperoxide concentration (M)	Methyl formate	Ethyl formate	Ethyl acetate	Ethanol	1,1-Dimethoxy-ethane	Oxygen
0.18	0.09	0.17	0.47	0.58	0.4	0.4
0.25[a]	[b]	0.03	0.3	[c]	0.2[d]	[e]
0.33	0.05	0.06	0.06	0.25	0.08	[e]
0.45	0.09	0.10	0.3	0.53	0.22	0.4
0.83	0.08	0.16	0.4	0.5	0.22	0.4

[a] In ethanol.
[b] Not present.
[c] Solvent.
[d] 1,1-Diethoxyethane.
[e] Not measured.

hyde formed in this process appeared as the appropriate dialkoxyethane in alcoholic solvents (eq. 4). The presence of methyl formate in

[4] $CH_3CHO + 2ROH \rightarrow CH_3CH(OR)_2 + H_2O$

methanol but not in ethanol, CCl_4 or benzene was probably the result of a *trans*-esterification of ethyl formate (eq. 5).

[5] $CH_3OH + CH_3CH_2OCHO \rightarrow CH_3CH_2OH + CH_3OCHO$

Diaper (10) obtained di-(1-*tert*-butoxynonyl)-peroxide in 45% yield by the oxidation of **1***b* with Ce(IV). In contrast, we could detect no di-(1-ethoxyethyl)peroxide among the products from the Ce(IV) oxidation of 1-ethoxyethyl hydroperoxide under similar experimental conditions. Although the product balances were not too good the sum of [formate] + [acetate] + $\frac{1}{2}$([ethanol] + [dimethoxyethane]) for the Ce(IV) experiments with initial hydroperoxide concentrations of 0.18, 0.45, and 0.83 M were such that less than 10% of the hydroperoxide could have been converted to peroxide. This difference in products is surprising but is not necessarily inconsistent with the radical reaction playing an important role in the bimolecular self-reactions of these peroxy radicals. That is, high molecular weight alkoxy radicals will diffuse from the cage more slowly than low molecular weight radicals and so they will yield more peroxide if reaction *6* of Scheme 1 is the principal cage process. The cage lifetime may also be increased by hydrophobic bonding between the 1-*tert*-butoxynonoxy radical pair. That is, methanol is a hydrophilic solvent and as such will rather poorly solvate such large alkoxy radicals and so they will tend to remain in the cage for longer than the small, readily solvated, 1-ethoxyethoxy radicals. While the different peroxide yields can be rationalized in this way, it is by no means certain that the metal ion does not play a role in peroxide formation, the extent of this role depending on the hydroperoxide. An example of

TABLE 2. Products from the *tert*-butyl hyponitrite induced decomposition of 1-ethoxyethyl hydroperoxide at 40° (yields are mol/mol of hydroperoxide)

Initial hydroperoxide concentration (*M*)	Solvent	Methyl formate	Ethyl formate	Ethyl acetate	Ethanol	Acetaldehyde	1,1-Dimethoxyethane
0.1	Methanol	[a]	[a]	[b]	1.0	[c]	0.3
0.25	Methanol	[a]	[a]	[b]	0.92	[c]	0.24
0.33	Methanol	0.14	0.18	0.18	0.76	[c]	0.25
0.4	Methanol	0.03	[a]	0.38	0.6	[c]	~1.0
0.25	Ethanol	[c]	0.12	1.0	[d]	[c]	0.76[e]
0.1	CCl_4	[c]	0.06	0.5	0.21	0.2	[c]
0.2	CCl_4	[c]	0.05	0.38	0.14	0.3	[c]
0.4	CCl_4	[c]	0.05	0.41	0.18	0.13	[c]
0.4	Benzene	[c]	0.04	0.54	0.05	0.08	[c]
Oxidation with silver oxide at 23°[f]							
0.05	Benzene	[c]	0.12	0.12	0.52	0.36	[c]

[a] Not detected.
[b] Obscured by other v.p.c. peaks.
[c] Not present.
[d] Solvent.
[e] 1,1-Diethoxyethane.
[f] Hydroperoxide destroyed in 2 days. In the absence of Ag_2O the hydroperoxide is stable for this length of time.

the difficulties involved in interpreting products is provided by the observation that 3% di-*sec*-butyl peroxide is formed in the Co(II)-catalyzed decomposition of *sec*-butyl hydroperoxide (17) but none is produced in the *tert*-butoxy radical induced decomposition (4).

The yields of the products formed by the oxidation of 1-ethoxyethyl hydroperoxide in methanol by Ce(IV) and by *tert*-butoxy were quite similar. The average yields for the Ce(IV) oxidation of 0.18, 0.45, and 0.83 M hydroperoxide and the yield for the *tert*-butoxy oxidation of 0.33 M hydroperoxide (which gave a good product balance) are, respectively, methyl formate, 0.09 and 0.14; ethyl formate, 0.14 and 0.18; ethyl acetate, 0.39 and 0.18; ethanol, 0.54 and 0.76; dimethoxy ethane, 0.28 and 0.25. This similarity implies that both reactions involve similar intermediates, *i.e.* peroxy radicals (eqs. 6 and 7). Irrespective of the mechanism of the subsequent reactions of the peroxy radicals the fact that the yield of ethanol was two or three times that of dimethoxyethane can only be accounted for if the latter compound was unstable under the reaction conditions. In separate experiments it was shown that dimethoxyethane was stable to Ce(IV) but was oxidized by *tert*-butoxy to form methyl acetate (among other products). Methyl acetate was one of the minor products identified in the *tert*-butoxy oxidations of the hydroperoxide (eq. 8). In the Ce(IV) reactions the dimethoxyethane may be oxidized by the radicals formed in this reaction.

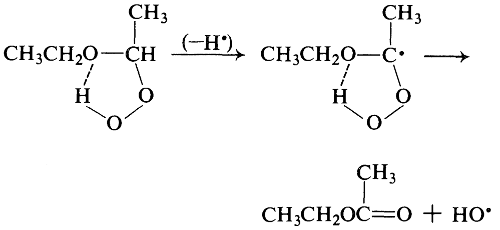
$$[6]\quad \mathrm{ROOH + Ce(IV) \rightarrow ROO\cdot + Ce(III) + H^+}$$

$$[7]\quad \mathrm{ROOH} + t\text{-}\mathrm{BuO\cdot \rightarrow ROO\cdot} + t\text{-}\mathrm{BuOH}$$

$$[8]\quad \mathrm{(CH_3O)_2CHCH_3 \xrightarrow{(-H^\cdot)} (CH_3O)_2\dot{C}CH_3 \longrightarrow CH_3OC(O)CH_3 + CH_3^\cdot}$$

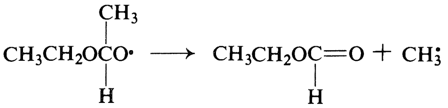
The yields of ethanol and acetaldehyde were more nearly equal in CCl_4 and in benzene (both t-butoxy and Ag_2O oxidations). However, there is no obvious reason why [acetate] was so much less than $\frac{1}{2}$([ethanol] + [acetaldehyde(dimethoxy ethane)]) for the Ag_2O oxidation and for t-butoxy oxidation in methanol, whereas the reverse was the case for t-butoxy oxidation in CCl_4 and in benzene. For the Ce(IV) oxidation these quantities were equivalent as we would expect if they arose from tetroxide by way of reactions *2* or *3* + *4* of Scheme 1. Excess ethyl acetate might arise from abstraction of the tertiary hydrogen of the hydroperoxide (eq. 9), but a deficiency is difficult to account for.

[9]



With regard to the mechanism of the peroxy radical self-reaction, the most significant product is formate. In methanol it is conceivable that this could be formed by way of an oxidation of the solvent to formic acid. However, formate was also formed in CCl_4 and in benzene. It seems most likely that it was produced principally by β-scission of 1-ethoxyethoxy radicals (eq. 10). If this is correct, it implies that alkoxy radicals were present in these systems and hence that at least some tetroxide probably decomposed by reaction *3* of Scheme 1, with some of the alkoxy radicals escaping from the cage (reaction *5*). The relative importance of reactions *2* and *3* cannot be estimated without some knowledge of the behavior of caged ethoxyethoxy radical pairs (reactions *4*, *5*, and *6*).

[10]



$$\mathrm{CH_3CH_2O\underset{H}{\overset{CH_3}{C}}O\cdot \longrightarrow CH_3CH_2O\underset{H}{C}{=}O + CH_3^\cdot}$$

Decomposition of Di-(1-ethoxyethyl)-peroxide

The principal products formed by thermal decomposition of di-(1-ethoxyethyl)peroxide in cumene at 130° are listed in Table 3. The production of hydrogen can probably be best explained by a non-radical concerted decomposition of the peroxide (eq. 11) (3, 18). This process accounts for about one quarter of the peroxide, *i.e.* ~0.25 mol H_2 and ~0.5 mol ethyl acetate. The remaining ethyl acetate and the

[11]

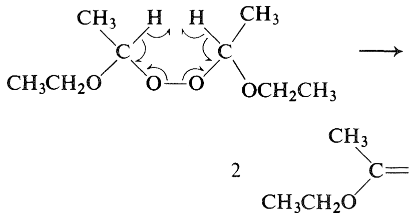


TABLE 3. Products from the thermal decomposition of di-(1-ethoxyethyl)peroxide in cumene at 130° (yields are mol/mol of peroxide)

Initial peroxide concentration (*M*)	Ethyl formate	Ethyl acetate	Ethanol	Acetaldehyde	Hydrogen	Methane	Dicumyl
0.46	0.45	1.1	0.5	0.45	[a]	[a]	0.14
0.20	0.50	1.05	[b]	[b]	0.24	0.47	[a]
0.10	0.45	1.05	[b]	[b]	0.25	0.37	0.18
0.05	0.37	0.95	[b]	[b]	0.27	0.40	0.16

[a] Not measured.
[b] Not detected.

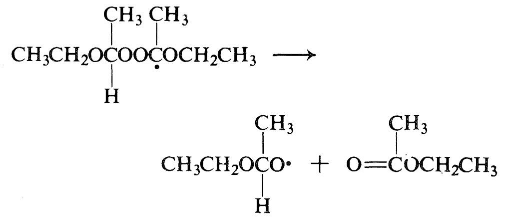
other products are presumed to arise by processes involving free radicals.

The data can be interpreted in two extreme ways depending on the importance assigned to alkoxy radical disproportionation in the cage (reaction *4*, Scheme 1). If it is assumed that there is no cage disproportionation[3] then the approximately equal concentrations of ethanol and acetaldehyde (at the highest initial concentration of peroxide[4]) can be explained by hydrogen abstraction by free alkoxy radicals (eq. 12),

$$[12] \quad CH_3CH_2OCH(CH_3)O^{\bullet} + SH \longrightarrow S^{\bullet} + [CH_3CH_2OCH(CH_3)OH] \downarrow CH_3CH_2OH + CH_3CHO$$

where SH is either cumene (hence the bicumyl) or peroxide (hence the remaining ethyl acetate[5]).

[13]



$$CH_3CH_2O\overset{CH_3}{\underset{H}{C}}OO\overset{CH_3}{C}OCH_2CH_3 \longrightarrow CH_3CH_2O\overset{CH_3}{\underset{H}{C}}O^{\bullet} + O{=}\overset{CH_3}{C}OCH_2CH_3$$

On the alternative assumption that cage disproportionation is very important, the ethanol, acetaldehyde, and remaining ethyl acetate are assumed to be formed in the cage (eq. 14).

$$[14] \quad \boxed{2CH_3CH_2OCH(CH_3)O^{\bullet}}_{\text{cage}} \longrightarrow CH_3CH_2OH + CH_3CHO + CH_3CH_2OC(O)CH_3$$

Attempts to distinguish between these alternative mechanisms were unsuccessful.[6,7]

Ethyl formate and methane were formed in approximately equal amounts and constitute about one third of the products formed from alkoxy radical precursors. This presumes that these products arose by β-scission of free alkoxy radicals, the expelled methyl being converted to methane by solvent or peroxide (eq. 15). In

$$[15] \quad CH_3^{\cdot} + SH \rightarrow CH_4 + S^{\cdot}$$

the hydroperoxide oxidations at 0–40°, formate constituted a rather similar fraction of the products (say 20 ± 10% for those experiments in which the product balance was reasonable). On the basis of the first assumption (*i.e.* all alkoxy radical pairs escape the cage with one third undergoing β-scission and two thirds abstracting H at 130°) it is difficult to predict what fraction of the product from a caged pair of alkoxy radicals would be formate at temperatures 100° lower. For *sec*-alkoxy radicals β-scission would

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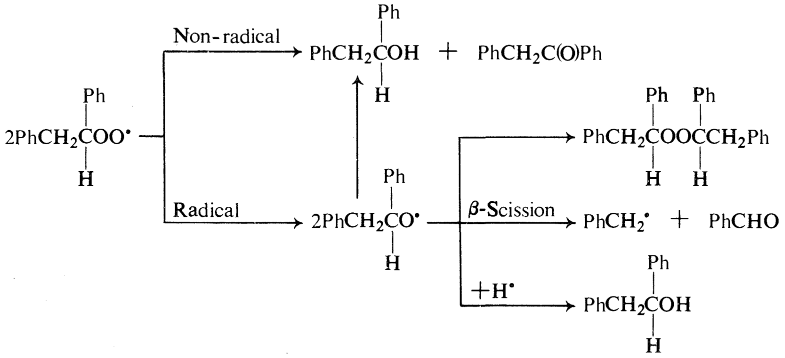
[3] Under similar conditions it has been reported both that "there is very little, if any, disproportionation of two *sec*-butoxy radicals in the solvent cage" (3), and that there is a significant amount of cage disproportionation of the *sec*-butoxy radicals (19).

[4] It is uncertain whether our failure to detect either of these compounds at lower peroxide concentrations was due to their further reaction under the experimental conditions or to poor resolution on the v.p.c.

[5] In this connection, it is worth noting that di-*sec*-butyl peroxide is not subject to induced decomposition under similar conditions (3). However, di-(1-ethoxyethyl)-peroxide should be a much better H donor than di-*sec*-butyl peroxide.

[6] Although the yield of acetate decreased with decreasing peroxide concentration (which argues in favor of an induced decomposition) the yield of formate also decreased rather than increasing as it should if the peroxide was the principal H donor to the alkoxy radicals.

[7] The product yield with 0.10 *M* peroxide initially was unaffected by the addition of 0.2 *M* 2,6-di-*tert*-butyl-4-methylphenol. This does not rule out induced decomposition of the peroxide since a sufficiently rapid attack of the alkoxy radicals on the solvent would prevent their interception by the phenol. If this is true, it must be cumyl radicals that induce decomposition of the peroxide.



SCHEME 3

decrease in importance relative to hydrogen abstraction as the temperature was lowered. *If* this is also the case for *sec*-α-alkoxyalkoxy radicals then the high yields of formate in the hydroperoxide oxidations imply that most (say $\geq 80\%$) of the bimolecular self-reactions of the peroxy radicals yield alkoxy radicals and that the concerted process is relatively unimportant. On the other hand, if β-scission predominates over hydrogen abstraction as the temperature is decreased, then approximately 20% of the peroxy radicals react to give alkoxy radicals. On the basis of the second assumption (*i.e.* that one third of the alkoxy radical pairs escape the cage while two thirds disproportionate in the cage) one would predict that most peroxy radical pairs yield alkoxy radicals. This is because the ratio of alkoxy diffusion from the cage to disproportionation in the cage is not expected to be very dependent on the temperature.

The production of formate in the hydroperoxide oxidations argues in favor of some of the peroxy–peroxy reactions yielding free alkoxy radicals. Although far from definitive, the peroxide decomposition experiments suggest that the majority of such reactions yield alkoxy radicals and that the non-radical process is relatively unimportant (probably $\leq 20\%$ of the total reaction).

1,2-Diphenylethylperoxy Radicals

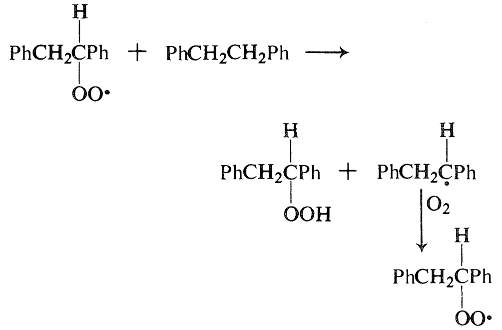
The possible self-reactions of these peroxy radicals are shown in Scheme 3. 1,2-Diphenylethylperoxy radicals were conveniently produced for product studies either by oxidation of 1,2-diphenylethyl hydroperoxide or by autoxidation of bibenzyl.

Oxidation of 1,2-Diphenylethyl Hydroperoxide

The products formed by the oxidation of this hydroperoxide with *tert*-butoxy radicals, with Ce(IV), and with silver oxide, are listed in Table 4. In the Ce(IV) oxidations the yield of 1,2-diphenylethanol was reduced and the yield of benzaldehyde enhanced by the facile and quantitative oxidation of this alcohol to the aldehyde (20). If some allowance is made for this side-reaction, then the yields of the four oxygen-containing compounds were reasonably similar in the different experiments. These products are, therefore, presumed to arise from 1,2-diphenylethylperoxy radicals.

Autoxidation of Bibenzyl

The major product formed during the autoxidation of bibenzyl was of course, 1,2-diphenylethyl hydroperoxide (eq. 16). Benzaldehyde and benzoin were minor products (see Table 4) and were probably formed in the chain terminating step. It is uncertain whether or not 1,2-diphenylethanol was formed in termination since our analytical procedure (v.p.c.) required the rather large amount of hydroperoxide to be reduced to the alcohol (with Ph_3P) before the actual analysis. The error in the estimation of "termination" alcohol from the total yield of alcohol and the iodiometrically measured yield of hydroperoxide would be of similar magnitude to the

[16]


$$\mathrm{PhCH_2C(H)(OO^\bullet)Ph} + \mathrm{PhCH_2CH_2Ph} \longrightarrow \mathrm{PhCH_2C(H)(OOH)Ph} + \mathrm{PhCH_2\dot{C}(H)Ph} \xrightarrow{O_2} \mathrm{PhCH_2C(H)(OO^\bullet)Ph}$$

TABLE 4. Products from the oxidation of 1,2-diphenylethyl hydroperoxide and from the autoxidation of bibenzyl

	Hydroperoxide oxidation[a]				
Products	t-BuO· in benzene at 56°[b]	Ce(IV) in methanol at 0°[c]	Ce(IV) in methanol at 0°[d]	Ag_2O in benzene at 60°[e]	Bibenzyl autoxidation at 56°[f]
PhCHO	0.27	0.41	0.75	0.27	0.24
$PhCH_2OH$	0.09	0.1	0.21	trace	[g]
$PhCH_2CH(OH)Ph$	0.30	0.15	(~1.0)[h]	0.41	(~2.1)[i]
$PhCH_2C(O)Ph$	0.30	0.34	0.37	0.30	0.65
$PhCH_2CH_2Ph$	trace	trace	trace	trace	[j]

[a] Yields are mol/mol of hydroperoxide.
[b] [t-$BuON_2OBu$-t]/[hydroperoxide] = 0.1 *M*/0.18 *M*
[c] [Hydroperoxide]/[Ce(IV)] = 0.1 *M*/0.1 *M*
[d] [Hydroperoxide]/[Ce(IV)] = 0.2 *M*/0.1 *M*
[e] [Ag_2O]/[hydroperoxide] = 0.25 *M*/0.25 *M*
[f] Yields are mol/mol of initiating (or terminating) radicals.
[g] Not detected.
[h] Excess hydroperoxide (~1.0) was reduced quantitatively to diphenylethanol with triphenylphosphine. The yield of diphenylethanol formed in the Ce(IV) oxidation was therefore ~0. It was presumed that the alcohol was formed and was oxidized to benzaldehyde (see text).
[i] Hydroperoxide (~2.0) formed in the autoxidation chain was reduced with Ph_3P. Because of the large amount of diphenylethanol produced in this way, it was not possible to estimate how much was formed in chain termination (see text).
[j] Substrate.

TABLE 5. Products formed from thermal decomposition of bis-(1,2-diphenylethyl)hyponitrite (yields are mol/mol of hyponitrite[a])[b]

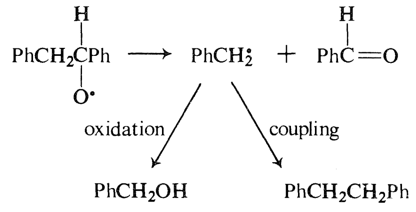
Solvent	Temperature (°C)	PhCHO	$PhCH_2$ PhCHOH	$PhCH_2$ PhC=O	$PhCH_2$ $PhCH_2$
CCl_4	78[c]	1.5	0	0.1	0.3
Cyclohexane	81	1.2	0.4	0.1	0.4
V.p.c.	260	1.7	0.04	0.2	0.5

[a] Based on the assumption that B (as defined in the Experimental) was bis-(1,2-diphenylethyl)-hyponitrite.
[b] Mean yields based on a number of experiments with different batches of hyponitrite and at initial hyponitrite concentrations in the range 0.03–0.12 *M*.
[c] Almost identical product yields were obtained in a decomposition at 30°.

amount of alcohol expected to be formed in termination.

It seems likely that the bimolecular self-reactions of 1,2-diphenylethylperoxy radicals yield benzaldehyde, benzyl alcohol, 1,2-diphenylethanol, and benzoin. The last two compounds may be formed either by the non-radical or radical reactions.

The benzaldehyde and the benzyl alcohol and bibenzyl detected in the hydroperoxide oxidations were presumably formed via free 1,2-diphenylethoxy radicals (Scheme 4).



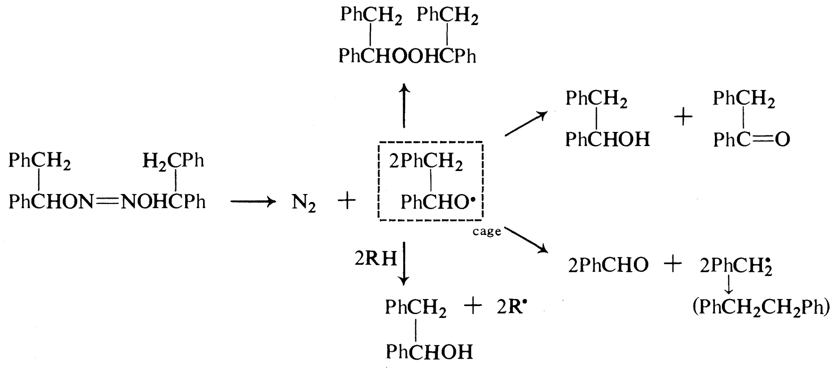
SCHEME 4

Bis-(1,2-diphenylethyl)hyponitrite

An attempt was made to study the chemistry of caged pairs of 1,2-diphenylethoxy radicals by the preparation and decomposition of bis-(1,2-diphenylethyl)hyponitrite. Unfortunately this hyponitrite could not be prepared with a purity better than 30% (see experimental). However, we feel confident that the four products listed in Table 5 resulted from the thermal decomposition of this hyponitrite according to Scheme 5.

The sum of the yields of benzaldehyde, diphenylethanol, and benzoin was 1.94 in the decomposition at 260° which is in good agreement with the expected value of 2.0. Product balances were less satisfactory for the decompositions in CCl_4 or cyclohexane.

The principal fate of 1,2-diphenylethoxy radical pairs is diffusion from the cage, followed in



SCHEME 5

CCl_4 by β-scission, while in cyclohexane, at 80°, β-scission predominates but hydrogen abstraction from the solvent plays a significant role. Since there was relatively little benzoin or (in CCl_4) diphenylethanol, disproportionation in the cage cannot be important. However, carbonyl yields determined by i.r. spectroscopy were generally about 10–20% less than the yields of benzaldehyde and benzoin[8] measured by v.p.c. and recorded in Table 5. This suggests that some of the benzaldehyde found by v.p.c. arose from decomposition (in the injection port) of bis-(1,2-diphenylethyl)peroxide. In summary, the majority of the alkoxy radicals escape the cage and undergo β-scission or, in a suitable donor, abstract a hydrogen. About 10–20% of the caged pairs probably combine to yield peroxide but less than 10% of the pairs disproportionate in the cage. Hiatt's results (3, 4) suggest that caged *sec*-butoxy radical pairs behave rather similarly.

With regard to the bimolecular self-reactions of peroxy radicals, the data in Table 4 indicate that 1,2-diphenylethylperoxy radicals react together to give *approximately* equal quantities of benzaldehyde, diphenylethanol, and benzoin. The benzaldehyde is presumably formed from diphenylethoxy radicals. According to the data in Table 5 the other two compounds must be formed by a process *not* involving diphenylethoxy radicals. This latter process is, presumably, the concerted decomposition of the tetroxide. That is, approximately one third of the 1,2-diphenylethylperoxy radical pairs react via reactions *3* and *5* of Scheme 1 and two thirds via reaction *2*.

Conclusion

The present results provide evidence that not all secondary alkylperoxy radicals undergo their bimolecular self-reactions entirely by the concerted cyclic mechanism at ambient temperatures. A significant fraction of the overall reaction can apparently yield free alkoxy radicals. However, it is far from clear why, at similar temperatures, 1-ethoxyethylperoxy pairs yield alkoxy radicals in (probably) ≥80% yield, while 1,2-diphenylethylperoxy pairs yield alkoxy radicals in ~33% yield, and *sec*-butylperoxy pairs yield *sec*-butoxy radicals in only ~4% yield (4, 6). Possibly dialkyl tetroxides that can yield alkoxy radicals, that are very subject to β-scission, decompose by multiple bond scission, *i.e.* by a concerted but non-cyclic mechanism. Thus, although di-*tert*-butyl tetroxide probably undergoes one-bond scission (eq. 17) (21, 22), most

$$[17] \quad \mathrm{Me_3COOOOCMe_3} \xrightarrow{\text{slow}} \mathrm{Me_3CO^\bullet} + (\mathrm{^\bullet OOOCMe_3}) \xrightarrow{\text{fast}} \mathrm{O_2} + \mathrm{^\bullet OCMe_3}$$

other di-*tert*-alkyl tetroxides are less stable than the *tert*-butyl compound (21–23) and their stability decreases as the derived alkoxy radicals become more unstable with respect to β-scission. This suggests that β-scission may be synchronized with (and therefore assist) O—O scission of the tetroxide. Suitably substituted tetroxides (both di-*tert*-alkyl and di-*sec*-alkyl) may therefore, perhaps, decompose by two-bond (or more) scission, *e.g.* as in eq. 18.

If this explanation of our analytical data is

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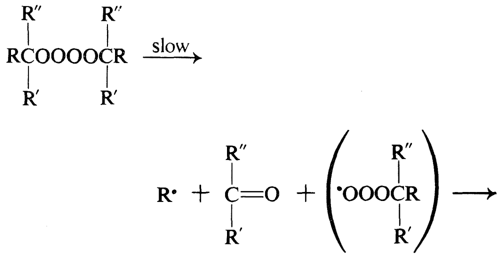
[8] I.r. spectroscopy only gives the sum of benzaldehyde and benzoin since the C=O fundamental stretching bands for these two compounds occur at almost the same frequency.

[18]



$$\mathrm{R\overset{R''}{\underset{R'}{C}}OOOO\overset{R''}{\underset{R'}{C}}R} \xrightarrow{\text{slow}} \mathrm{R^{\bullet}} + \overset{\mathrm{R''}}{\underset{\mathrm{R'}}{\mathrm{C}}}{=}\mathrm{O} + \left(\mathrm{{}^{\bullet}OOO\overset{R''}{\underset{R'}{C}}R}\right) \longrightarrow$$

correct, it suggests that structural factors may have a profound effect not only on the rates of the bimolecular self-reactions of *sec*-alkylperoxy radicals, but also on their mechanism of reaction. Thus, for example, diphenylmethylperoxy radicals (24) should decompose principally by the concerted cyclic mechanism since neither phenyl nor hydrogen are readily cleaved from alkoxy radicals and since the hydrogen that must be transferred in the cyclic process will be quite labile. Evidence favoring the Russell mechanism for this peroxy radical has been presented previously (24). In contrast, peroxy radicals such as $(PhCH_2)_2CHOO^{\bullet}$ or $(Ph_3C)_2CHOO^{\bullet}$ are expected to react principally by the concerted non-cyclic route since they would yield unstable alkoxy radicals and since the central hydrogen is not particularly labile. It is expected that these two peroxy radicals would react more rapidly than, for example, $(CH_3CH_2)_2CHOO^{\bullet}$. For this radical the concerted non-cyclic process would be less favored so that reaction would be more likely to occur by the concerted cyclic process. Evidence favoring the cyclic process for $CH_3CH_2(CH_3)CHOO^{\bullet}$ has been obtained (25).

In conclusion, *sec*-alkylperoxy radicals can react both by the concerted cyclic (Russell) mechanism and by a process which yields either "free" alkoxy radicals or the products of β-scission of the alkoxy radicals in a step concerted with O—O homolysis of the tetroxide. The relative importance of these two processes will depend on the nature of the alkyl groups, the temperature and, perhaps, the solvent.

Experimental

Materials

1-Ethoxyethyl hydroperoxide was prepared from H_2O_2 and ethyl vinyl ether by the method of Milas *et al.* (26). Iodiometric titration indicated that the product was >90% pure. Reduction with a slight excess of triphenyl phosphine gave only acetaldehyde and ethanol. Ethyl formate was not formed in this reduction, nor was it present in the hydroperoxide.

Di-(1-ethoxyethyl)peroxide was prepared from H_2O_2 and ethyl vinyl ether in the presence of a small amount of thionyl chloride by the method of Lederer and Weissermel (27). Titration for peroxide indicated that the product was >90% pure.

1,2-Diphenylethyl hydroperoxide was prepared from H_2O_2 and 1,2-diphenylethanol (Aldrich, recrystallized from benzene:hexane, 1:20) by the method of Davies *et al.* (28). This hydroperoxide is a white crystalline material, m.p. 55°, purity >90% by iodiometric titration. Reduction of the hydroperoxide with Ph_3P gave only 1,2-diphenylethanol. Benzaldehyde was not formed in this reduction, nor was it present in the hydroperoxide. The hydroperoxide is stable at 56° yielding no benzaldehyde even after 8 days at this temperature.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.33; H, 6.64.

Bis-(1,2-diphenylethyl)hyponitrite was probably prepared in about 30% yield by reaction of 1,2-diphenylethyl bromide with silver hyponitrite according to the procedure of Partington and Shah (29). The bromide was prepared in 86% yield by reaction of 1,2-diphenylethanol with anhydrous HBr in benzene at its freezing point (30). The bromide was purified by dry column chromatography on silica using trichloroethylene as the solvent. The purified bromide, $n_D{}^{20}$ 1.6019 (lit. (30) $n_D{}^{20}$ 1.6019), showed no OH or C=O absorption bands in the i.r. V.p.c. confirmed that it contained no benzaldehyde, 1,2-diphenylethanol, benzoin, or bibenzyl.

The bromide (2.1 g) was dissolved in 20 ml of purified ether and cooled to −10°. Silver hyponitrite (2.2 g, 100% excess) was added in small portions with continuous stirring, the ether being kept under a blanket of dry argon. At the end of the addition all organic bromide was gone (copper wire test). The silver bromide and excess silver hyponitrite were removed by filtration. Removal of the ether in an air stream at 0° (or under vacuum) resulted in a vigorous evolution of nitrogen and the separation of oily white crystals. At this stage, the i.r. spectrum (mull) showed a large, hydrogen-bonded, OH band but little or no C=O band. On warming the crystalline mass, nitrogen evolution began again and became rapid at ~50°. The crystals remaining were *trans*-stilbene. The oily contaminant and/or some of the crystalline material is believed to be bis-(1,2-diphenylethyl)hyponitrite. Nitrogen evolution experiments indicated that the compound decomposing rapidly at 0° (compound A) was formed in ~10% yield based on starting bromide while that decomposing rapidly at 50° (the hyponitrite, compound B) was formed in ~30% yield. The balance of the material (~60%) was stilbene. All attempts to separate B from stilbene by fractional crystallization or by trituration from the stilbene crystals were frustrated by its low yield (relative to stilbene) and by its instability. However, we believe that B is the desired dialkyl hyponitrite and that compound A may be the mono-alkyl hyponitrite or, perhaps, hyponitrous acid. The raw product gave an intense i.r. absorption at 980 cm^{-1} which appears to be a characteristic of hyponitrites (31, 32). This band disappeared as B decomposed and the decomposition products and their yields were consistent with B being bis-(1,2-diphenylethyl)hyponitrite. Various modifications of the preparation described above such as changing the solvent, did not increase the yield of B.

The half-life for decomposition of B was ~6 h at 30°. This may be compared with half-lives of ~40 h at this temperature for di-*tert*-butyl hyponitrite (31) and ~4 h for dibenzyl hyponitrite (33) and for dicumyl hyponitrite (34).

tert-Butylhyponitrite was prepared by the method of Kiefer and Traylor (31). All other compounds were commercial materials that were purified by standard procedures before use.

Hydroperoxide Decompositions

Ceric ammonium nitrate (1.0 M) in methanol was added slowly with stirring to a 0.2 M solution of the hydroperoxide in methanol at 0°. Addition was continued until the color of the added ceric solution was not completely destroyed. The solution was stirred for a further 15 min at 0° and the reaction products were then analyzed by v.p.c. The products formed in the hydroperoxide oxidation were treated similarly. Only 1,2-diphenylethanol reacted, and that only slightly, under these conditions.

tert-Butyl hyponitrite (0.1 M) in benzene was heated with the hydroperoxide (0.18 M) in benzene, under vacuum, for ten half-lives of the hyponitrite before the samples were analyzed.

Silver oxide (freshly prepared) was reacted with the hydroperoxide (0.18 M) in benzene under vacuum until the hydroperoxide had been destroyed.

Peroxide Decomposition

Di-(1-ethoxyethyl)peroxide was decomposed for 8 h in undiluted cumene under vacuum at 130°.

Autoxidation of Bibenzyl

Bibenzyl (5.3 M) containing α,α'-azo-bis-isobutyronitrile (0.19 M) was shaken under 1 atm of oxygen at 56°. The oxygen absorption rate was $\sim 3 \times 10^{-6}\ M\,\mathrm{s}^{-1}$, corresponding to a chain length of ~2. After 67 h the bibenzyl had absorbed 0.7 M of oxygen. The accumulated hydroperoxide was reduced with a slight excess of Ph_3P before v.p.c. analysis of the products.

Hyponitrite Decomposition

These experiments were carried out on the raw product obtained by reacting 1,2-diphenylethyl bromide with silver hyponitrite. After the preparation of each batch of hyponitrite the solvent was evaporated under reduced pressure and the raw product was divided into portions which were dissolved in CCl_4 or cyclohexane. I.r. spectra were recorded after the samples had stood at room temperature for 15–30 min (in order to destroy compound A). Only very small amounts of carbonyl- and hydroxyl-containing compounds were present at this time. One sample of B was decomposed at 50° in a system that allowed the nitrogen yield, and hence the purity of the hyponitrite, to be measured. A second sample was injected directly into the v.p.c. to determine the products of rapid thermal cracking (at 260°). The remaining samples were decomposed in refluxing CCl_4 or cyclohexane or at 30°, under a blanket of argon, and were analyzed by i.r. spectroscopy (for $C{=}O$) and by v.p.c.

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