335. L. Jambon, Bull. Soc. chim. France, [3], 23, 825 (1900).
336. H. J. Lucas and A. R. Kemp, J. Amer. Chem. Soc., 43, 1663 (1921).
337. German P. 164 666 (1905); Chem. Zentr., II, 1702 (1905).
338. R. Forcrand, Compt. rend., 114, 1370, 1434 (1892); Chem. Zentr., II, 148, 200 (1892); Ann. Chim. (France), [6], 30, 66 (1893).
339. W. S. Hinegardner and T. B. Jonson, J. Amer. Chem. Soc., 51, 1507 (1929).
340. R. Forcrand, Compt. rend., 115, 46 (1892); Chem. Zentr., II, 348 (1892).
341. R. Forcrand, Compt. rend., 116, 192, 437 (1893); Chem. Zentr., I, 562, 643 (1893).
342. R. Schmidt, J. prakt. Chem., 31, 405 (1885).
343. Kh. Kimura and T. Takueti, Chem. Eng. (Japan), 27, 2 (1963); Ref. Zhur. Khim., 20B, 388 (1963).
344. C. Schall, J. prakt. Chem., 48, 241 (1893).
345. A. A. Morton and R. L. Letsinger, J. Amer. Chem. Soc., 67, 1537 (1945).
346. H. Niederhäusern, Ber., 15, 1119 (1882).
347. C. Böttinger, Chem.-Ztg., 19, 23 (1895).
348. H. Pauly, K. Schübel, and K. Lockemann, Annalen, 383, 288 (1911).
349. B. Elsner, Monatsh., 40, 361 (1919).
350. A. Purgotti, Gazzetta, 16, 527 (1886); Chem. Zentr., I, 335 (1887).

Lomonosov Moscow University

U.D.C. 541.515

CHEMISTRY OF UNSTABLE OXYGEN--CONTAINING RADICALS

L. M. Terman

INTRODUCTION

In recent years there has been particular interest in unstable free radicals having an unpaired electron on an oxygen atom. A recent review [1] described the production, thermochemistry, and reactions of a large group of alkoxy--radicals, but the four years since its publication have seen a considerable increase of work on these radicals, and this has persuaded us to write the present article.

We shall consider the gas- and liquid-phase reactions most typical of RO· radicals, but not those of stable oxygen-containing radicals such as the substituted phenoxy--radicals, nor heterogeneous reactions involving hydroperoxides.

REACTIONS OF RO· RADICALS

Oxygen-containing radicals with an unpaired electron on the oxygen atom are produced as unstable intermediates in many chemical processes. We indicate below only the main ones; a detailed list was given in the above review [1].

RO· radicals are produced in the light- and heat-induced decomposition of alkyl and aralkyl

nitrites: $RONO \rightarrow RO^{\cdot} + NO$,

nitrates: $RONO_2 \rightarrow RO^{\cdot} + NO_2$,

hyponitrites: $RONNOR \rightarrow 2RO^{\cdot} + N_2$,

hypochlorites: $ROCl \rightarrow RO^{\cdot} + Cl$,

and peroxides: $ROOR \rightarrow 2RO^{\cdot}$,

and in the decomposition, in solution, of dialkyl and diaralkyl peroxodicarbonates:

$$ROCOOCOR \rightarrow 2ROCO^{\cdot} \rightarrow 2RO^{\cdot} + 2CO_2,$$

dialkyl diperoxocarbonates:

$$ROOCOOR \rightarrow ROOCO^{\cdot} + RO^{\cdot} \rightarrow ROO^{\cdot} + CO_2 + RO^{\cdot},$$

and dialkyl monoperoxocarbonates:

$$ROCOOR \rightarrow ROC^{\cdot} + RO^{\cdot}.$$

The formation of RO· radicals in the photolysis of organic esters and ethers has been described.

The RO· radicals are usually identified by indirect kinetic and analytical methods. Direct mass-spectrometric determination of free RO· radicals has been described only for the phenoxy-radicals produced in the pyrolysis of anisole [2] and the methoxy-radicals produced in the decomposition of methanol and dimethyl ether light-sensitised by mercury [3]. The RO· radicals produced by thermal or photo-decomposition undergo various reactions, the main ones being decomposition, hydrogen abstraction, and disproportionation, depending on the structure of the radicals and the chemical and physical properties of the medium. Moreover, the RO· radicals may isomerise or react with other active particles or radicals present, or with compounds containing double bonds.

Below we list the main reactions of RO· radicals in the gaseous and liquid phases. Since liquid-phase reactions have attracted most attention in recent years, we shall give them more attention here also.

1. Decomposition of RO· radicals. Alkoxy--radicals can decompose by two reactions: with the elimination of a hydrogen atom:

$$RCH_2O^{\cdot} \rightarrow H^{\cdot} + RC\!\!<\!\!\begin{matrix}O\\H\end{matrix},$$

or the alkyl radical:

$$RCH_2O^{\cdot} \rightarrow R^{\cdot} + CH_2O.$$

Of these two the second is more favourable thermodynamically [4] (see Table 1), and experimental observations support this.

The decomposition of methoxy-radicals has been observed in the photolysis of methyl nitrate [6]:

$$CH_3O^{\cdot} \rightarrow CH_2O + H^{\cdot},$$

and decomposition of ethoxy-radicals at a carbon–hydrogen bond in the pyrolysis [7] and photolysis [8] of ethyl nitrate.

TABLE 1. Enthalpy required for decomposition of radicals.

Radical	Required enthalpy, kcal mole^{-1}	
	for elimination of an H-atom	for elimination of an R-radical
$CH_3O^{\cdot}$	25	—
$C_2H_5O^{\cdot}$	21	13
n-$C_3H_7O^{\cdot}$	19	11
n-$C_4H_9O^{\cdot}$	23	11
$(CH_3)_2CHO^{\cdot}$	18	6.4
cyclo-$C_6H_{11}O^{\cdot}$	16	1.1 * (ring opening)

* A different value has more recently been given [5].

Decomposition of the ethoxy-radical at the carbon–carbon bond with formation of formaldehyde and a methyl radical is much more frequently met with, for example, in the pyrolysis of ethyl nitrite [9,10] or nitrate [11,12]:

$$C_2H_5ONO \rightarrow C_2H_5O^{\cdot} + NO,$$
$$C_2H_5O^{\cdot} \rightarrow CH_3^{\cdot} + CH_2O.$$

Ethane and methane have been found in the decomposition of diethyl peroxide [13–15], ethyl hydroperoxide [14], and ethyl t-butyl peroxide [16], showing that the ethoxy-radicals decompose with the formation of methyl radicals.

The n-propoxy-radicals obtained from di-n-propyl peroxide [14], n-propyl nitrate [17], and n-propyl nitrite [10,18] decompose in this way:

$$CH_3CH_2CH_2O^{\cdot} \rightarrow C_2H_5^{\cdot} + CH_2O.$$

The isopropoxy-radical [10,19] is less stable; even in the presence of cyclohexene, which readily loses an α-hydrogen atom, the isopropoxy-radicals are 48% decomposed [16]:

$$\text{iso-}C_3H_7O^{\cdot} \rightarrow CH_3^{\cdot} + CH_3CHO.$$

Under the same conditions, n-butoxy-radicals are 29% decomposed with the formation of formaldehyde and n-propyl radicals:

$$CH_3CH_2CH_2CH_2O^{\cdot} \rightarrow CH_2O + CH_3CH_2CH_2^{\cdot},$$

and in the presence of cyclohexene isobutoxy-radicals are 67% decomposed by the reaction [16]:

$$(CH_3)_2CHCH_2O^{\cdot} \rightarrow (CH_3)_2CH^{\cdot} + CH_2O.$$

The decomposition products of isobutyl nitrite contained formaldehyde and 2-nitrosopropane [10,18].

The s-butoxy-radical decomposes to form acetaldehyde and the ethyl radical [10,18]:

$$CH_3CH_2CH(CH_3)O^{\cdot} \rightarrow CH_3CH_2^{\cdot} + CH_3CHO.$$

Decomposition of the t-butoxy-radical to acetone and the methyl radical has been observed in the pyrolysis of di-t-butyl peroxide [7,20–29], t-butyl nitrite [24,31,32], and t-butyl hydroperoxide [7,30]:

$$(CH_3)_3CO^{\cdot} \rightarrow CH_3^{\cdot} + CH_3COCH_3.$$

The activation energy for the decomposition of the t-butoxy-radical is 11–13 kcal mole^{-1}. [33–38] Other t-alkoxy-radicals decompose similarly. At 250°, triethylmethoxyl radicals are 61% decomposed into butane and diethyl ketone [39]:

$$(C_2H_5)_3CO^{\cdot} \rightarrow C_2H_5^{\cdot} + (C_2H_5)_2CO.$$

In the decomposition of mixed t-alkoxy-radicals it is the largest hydrocarbon radical which is the more likely to be produced; for example, the decomposition of the t-pentyloxy-radical is 87–88% by the mechanism producing acetone with elimination of the ethyl radical [22]:

$$CH_3CH_2C(CH_3)_2O^{\cdot} \rightarrow CH_3CH_2^{\cdot} + (CH_3)_2CO.$$

Data obtained in the decomposition of a series of unsymmetrical alkoxy t-butyl peroxides in the presence of cyclohexene have been used to establish the following order of stability for simple alkoxy-radicals [40]:

$$CH_3O^{\cdot} > CH_3CH_2O^{\cdot} > CH_3CH_2CH_2CH_2O^{\cdot} > CH_3CH(CH_3)O^{\cdot} > (CH_3)_2CHCH_2O^{\cdot} > (CH_3)_3CO^{\cdot}.$$

This experimental order is in good agreement with thermochemical data: the alkoxy-radicals which decompose more readily have a lower enthalpy requirement for decomposition [4]. The elimination of a radical with formation of a carbonyl compound in a series of alicyclic oxy-radicals $C_5H_{10}\rangle C\langle^{R}_{O^{\cdot}}$ is thermochemically favourable only with certain substituents, for example, when R is t-butyl, benzyl, or 2-allyl; in most cases the oxy-radical decomposes with ring rupture, which in the case of cyclohexyloxy-radicals requires less energy than loss of a radical [5] (Table 2).

In fact, in the decomposition of cyclohexyl nitrite at 80–225° approximately 40% of the cyclohexyloxy-radicals decompose by ring opening with formation of a new radical. It is probably because of this radical that adipic acid is obtained in the presence of oxygen.

In the liquid phase the decomposition reactions are less characteristic of RO$^{\cdot}$ radicals. The isopropoxy- and cyclohexyloxy-radicals remain undecomposed at 40–70° in certain solvents [41,42], and methoxy-, ethoxy-, n-propoxy-, isopropoxy-, and n-butoxy-radicals generated in various solvents have not decomposed even at 120–155°. [43–45] Tertiary RO$^{\cdot}$ radicals decompose in solvents in which hydrogen abstraction is difficult; the relative yields of products from decomposition of t-butoxy-radicals in more than 30 hydrocarbons have been investigated [18,46], and Table 3 gives the relative rates of reaction of hydrocarbons with t-butoxy-radicals at 135° for 25 h. Decomposition of the t-butoxy-radicals is greatest in benzene and t-butylbenzene, in which hydrogen abstraction is difficult (Table 3).

TABLE 2. Enthalpy required for decomposition of substituted cyclohexyloxy-radicals.

Aloxy	Group lost	Carbonyl compound	ΔH required, kcal mole^{-1}
Cyclohexyloxy	H	cyclohexanone	16
	ring opening	$\cdot CH_2(CH_2)_4CHO$	0
1-Methylcyclohexyloxy	CH_3	cyclohexanone	4
	ring opening	$\cdot CH_2(CH_2)_4COMe$	2
1-Phenylcyclohexyloxy	C_6H_5	cyclohexanone	9
	ring opening	$\cdot CH_2(CH_2)_4COC_6H_5$	2
1-Butylcyclohexyloxy	C_4H_9	cyclohexanone	−5
	ring opening	$\cdot CH_2(CH_2)_4COC_4H_9$	+1.2
Decalyl-9-oxy	1–9 ring opening	monocyclic radical	−1
	9–10 ring opening	ditto	0
1-Hydroxycyclohexyloxy	OH	cyclohexanone	20
	ring opening	$\cdot CH_2(CH_2)CH{=}CHCHO$	1
Tetrahydropyranyl-1-oxy	H	1-hydroxytetrahydropyran	16
	ring opening	$\cdot CH_2(CH_2)_3OCHO$	0
1-Ethylcyclohexyl hydroperoxide	H	cyclohex-1-enol	−3
	ring opening	$\cdot CH_2(CH_2)_2CH{=}CHCHO$	1

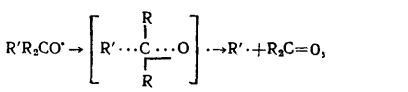
TABLE 3. Relative rates of reaction of t-butoxy-radicals with hydrocarbons.

Hydrocarbon	Butanol / acetone	Hydrocarbon	Butanol / acetone
Benzene	0.015	Cyclohexane	18
t-Butylbenzene	0.48	Ethylbenzene	4.5
Mesitylene	7.4	Tetralin	24
1-Methylnaphthalene	3.2	2,3-Dimethylpentane	4.6
2-Methylnaphthalene	1.8	Decalin	18
n-Hexadecane	5.8	Isopropylbenzene	3.4

It has recently been shown that the isotope effect is fairly large in the decomposition of the t-butoxy-radical[47]; when ^{14}C is introduced the rate of decomposition of the radical $(CH_3)_3{}^{14}CO^{\cdot}$ decreases by 7%.

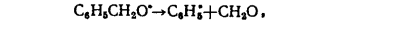
In the decomposition of tertiary alkoxy-radicals the rate of loss of n-alkyl is ten times that for methyl, and the rate for secondary alkyl is 20 times that for ethyl[48].

An important factor in the decomposition of alkoxy--radicals is the nature of the alkyl radical generated, and especially its stability[49]. It is thought that the decomposition includes a transition state, the free energy of activation of which decreases with increasing stability of the radical which is produced:



and in fact the stable benzyl radical is very readily eliminated from the $\alpha\alpha$-dimethylphenethoxy-radical; dimethylbenzylmethanol, produced by abstraction of hydrogen from the solvent by the undecomposed radical, is only formed in small amounts (less than 5%).

Aralkyloxy-radicals show the same features as the simple oxygen-containing radicals. The first member of this series, the benzyloxy-radical, is exceptionally stable[50-52]. In reactions of benzyl nitrite, dibenzyl hyponitrite, or *p*-nitrobenzyl nitrite in solution, no formaldehyde or phenol derivatives, such as would be formed in decomposition of the benzyloxy-radical:

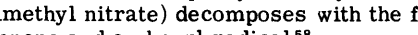


are observed. The benzyloxy-radicals produced in the thermal decomposition of dibenzyl peroxodicarbonate in benzene, carbon tetrachloride, chloroform, or isopropyl alcohol[41,42,53,54] at 40–70° also do not decompose.

The α-phenylethoxy-radical does not decompose at temperatures up to 132°.[55]

The α-methylbenzyloxy-radical is somewhat less stable[16]. The phenylmethoxy-radical — from bis(diphenylmethyl) peroxide — decomposes in bromobenzene, isopropylbenzene, or nitrobenzene with the formation of benzophenone. At 210° a phenyl radical is also eliminated (0.03 mole per mole of peroxide)[56,57]. The triphenylmethoxy-radical (from triphenylmethyl nitrate) decomposes with the formation of benzophenone and a phenyl radical[58].

The cumyloxy-radical also decomposes readily[59]:

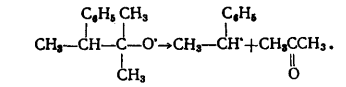


but no elimination of a phenyl radical is observed. At approximately 160° decomposition of the radical completely suppresses the abstraction of hydrogen from the solvent[60].

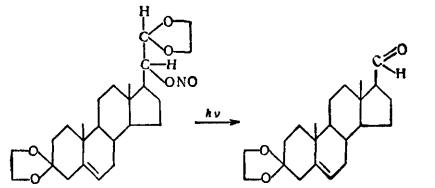
The ease of intramolecular fragmentation in $C_6H_5R_2CO^{\cdot}$ radicals thus decreases in the series $CH_3 > C_6H_5 > H$.

The following order of stability of aralkyloxy-radicals in the liquid phase has been suggested, based on experimental results and thermochemical calculations[50] (Table 4).

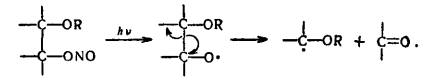
Decomposition of the *L*-(+)-2-methyl-3-phenylbutoxy--radical has been observed in the thermal decomposition of *L*-(+)-2-methyl-3-phenyl-2-butyl hypochlorite[61] in anhydrous solvents:



An interesting example of decomposition of an alkoxy--radical has been observed in the photolysis of steroidal nitrites[62]. The main photolysis products are carbonyl compounds and acids produced by the scission of oxygen--containing groups adjacent to the active centre, for example:



or[63]



2. Hydrogen abstraction. In all their reactions, particularly in the gas phase, RO$^{\cdot}$ radicals decompose into a carbonyl compound and an alkyl radical, so that in the presence of reagents with an easily broken carbon–hydrogen bond, the hydrogen may be abstracted either by the RO$^{\cdot}$ radical with the formation of an alcohol, or by the R$^{\cdot}$ radical with the formation of the corresponding hydrocarbon RH. We shall consider only reactions involving direct abstraction of hydrogen by RO$^{\cdot}$ radicals.

Gray has estimated the exothermicity of hydrogen abstraction from various hydrocarbons (Table 5).[4] It is seen that hydrogen abstraction should take place least readily from saturated hydrocarbons and most readily from the α-methylene group of unsaturated hydrocarbons, and in fact with cyclohexene hydrogen abstraction completely suppresses addition of RO$^{\cdot}$ radicals to the double bond[64].

TABLE 4. Order of stability of aralkyloxy--radicals.

Radical	Atom or radical lost	Residual carbonyl compound	Increase in enthalpy, kcal mole^{-1}	Stability, decreasing from most (1) to least (6)
$C_6H_5CH_2O^{\cdot}$	$C_6H_5^{\cdot}$	CH_2O	16.3	1
	$H^{\cdot}$	C_6H_5CHO	19.9	
$(C_6H_5)_2CHO^{\cdot}$	$C_6H_5^{\cdot}$	C_6H_5CHO	15.8	2
	$H^{\cdot}$	$(C_6H_5)_2CO$	19.4	
$(C_6H_5)_3CO^{\cdot}$	$C_6H_5^{\cdot}$	$(C_6H_5)_2CO$	11.5	3
$C_6H_5CH(CH_3)O^{\cdot}$	$CH_3^{\cdot}$	C_6H_5CHO	6.8	4
	$C_6H_5^{\cdot}$	CH_3CHO	10.7	
$(C_6H_5)_2CH_3CO^{\cdot}$	$H^{\cdot}$	$C_6H_5COCH_3$	9.6	
	$CH_3^{\cdot}$	$(C_6H_5)_2CO$	2.4	5
	$C_6H_5^{\cdot}$	$C_6H_5COCH_3$	5.6	
	$CH_3^{\cdot}$	$C_6H_5COCH_3$	0.3	6
$C_6H_5C(CH_3)_2O^{\cdot}$	$C_6H_5^{\cdot}$	$(CH_3)_2CO$	8.0	

TABLE 5. Enthalpy change for hydrogen abstraction: $RO^{\cdot} + XH \rightarrow ROH + X^{\cdot}$, assuming $D_{(RO-H)} = 102$ kcal mole^{-1}.

XH	Compound	D_{X-H}	Exothermicity, $-\Delta H$, kcal mole^{-1}
Aliphatic compounds	methane	101	1
Primary	ethane	96	6
Secondary	propane	94	8
Tertiary	isobutane	89	13
Unsaturated			
Primary	propene	77	25
	toluene	77	25
Secondary	cyclohexene	73	27
Tertiary	cumene	74	26
Aldehydes			
Aliphatic	acetaldehyde	80	22
Aromatic	benzaldehyde	78	24

In the gas phase hydrogen abstraction depends to a large extent on the stability of the RO$^{\cdot}$ radicals[40]; in the presence of the same hydrocarbon the relative yields of hydrogen abstraction and radical decomposition products differ according to the structure of the radicals.

Methoxy-radicals are the most stable, and in the gas phase they remove hydrogen from cyclohexene [16,40] to produce methanol (76% yield). In the photolysis of methyl acetate[65] the methoxy-radicals abstract hydrogen from acetate molecules; the energy of activation for the abstraction of hydrogen from the acetate by the methoxy-radical (5 kcal mole^{-1}) is one-half the energy of activation for hydrogen abstraction by the methyl radical (10 kcal × × mole^{-1}) [66,67]. The $CH_3O^{\cdot}$ radicals produced by the thermal decomposition of dimethyl peroxide[68] disproportionate to give methanol and formaldehyde, and the latter then loses hydrogen by reaction with further $CH_3O^{\cdot}$ radicals, so that the final reaction products are methanol and carbon monoxide only. On the other hand, in the decomposition of dimethyl peroxide in methanol[69], the methoxy-radicals abstract hydrogen from the alcohol, and the resulting $^{\cdot}CH_2OH$ radical dimerises to produce ethylene glycol.

The methoxy-radicals produced in the decomposition of dimethyl peroxide[70] and methyl nitrite[70,71] abstract hydrogen from ethane, propane, n-butane, isobutane, neopentane, and cyclopropane.

The ethoxy-radical is somewhat less stable, so that the yield of ethanol by reaction with cyclohexene [16,40] is lower (65%) than the yield of methanol in the corresponding reaction of methoxy-radicals.

In the gas phase the ethoxy-radicals produced in the photolysis of ethyl propionate[71] abstract hydrogen from the parent ester molecule; the energy of activation for this process (5.5 kcal mole^{-1}) is in good agreement with the value previously obtained for the methoxy-radical [65-67].

The pyrolysis of ethyl nitrite or nitrate would also be expected to show reaction of ethoxy-radicals with unreacted molecules of the starting material [11,19], but addition of diethyl peroxide to the pyrolysis zone has shown [72,73] that the ethoxy-radicals derived from the peroxide do not abstract hydrogen from ethyl nitrite or nitrate.

The extent of hydrogen abstraction from cyclohexene at 195° by propoxy- and butoxy-radicals [16,40] is shown in Table 6.

TABLE 6. Yield of products from the abstraction of hydrogen from cyclohexene at 195° in the gas phase by RO$^{\cdot}$ radicals obtained by the decomposition of unsymmetrical alkyl t-butyl peroxides.

RO$^{\cdot}$	ROH, %	RO$^{\cdot}$	ROH, %
n-$C_4H_9O^{\cdot}$	30	$(CH_3)_3CO^{\cdot}$	8
iso-$C_3H_7O^{\cdot}$	19		
$(CH_3)_2CHCH_2O^{\cdot}$	6		

t-Butoxy-radicals are unstable and only rarely abstract hydrogen in gas-phase reactions. Their reaction with aziridine at 129-154° is known [33], and photolysis of di-t-butyl peroxide at 30° has produced a small quantity of t-butyl alcohol [22].

t-Butyl alcohol has been identified in reactions with aldehydes [26,74]. The energy of activation for abstraction of hydrogen from isobutane by t-butoxy-radicals is ~ 4 kcal × × mole^{-1}. [38]

Hydrogen abstraction is more typical of RO$^{\cdot}$ radicals in the liquid phase.

In the same solvent under the same temperature conditions, hydrogen abstraction from the solvent by alkyloxy-radicals decreases in the series [43,44]:

$$^{\cdot}OCH_3 > {}^{\cdot}OC_2H_5 > {}^{\cdot}OC_3H_7 > {}^{\cdot}OC_4H_9 > {}^{\cdot}OCH(CH_3)_2.$$

The methoxy-radical abstracts hydrogen from toluene at 155° to give a 100% yield of methanol; the yield of methanol is somewhat lower (70-80%) in diphenylmethane or diphenylethane. The yields of the corresponding alcohols in the reaction of ethoxy- and chloroethoxy-radicals with isopropylbenzene at 125° are of the same order, while n-propoxy- and n-butoxy-radicals give a 60% yield of alcohol and isopropoxy-radicals give only a 50% yield.

Hydrogen abstraction by t-butoxy-radicals has been the most investigated reaction, including abstraction from saturated and alkyl-aromatic hydrocarbons [35,46].

Table 7 shows the relative velocity constants for hydrogen abstraction from various hydrocarbons by $CH_3^{\cdot}$, $CCl_3^{\cdot}$, t-$C_4H_9O^{\cdot}$, and ROO$^{\cdot}$ radicals [75], the rate of abstraction of hydrogen from the methyl group of toluene being taken as the unit.

The decomposition of di-t-butyl peroxide in cyclohexene has produced almost 100% butanol [64]:

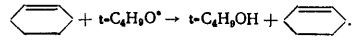


TABLE 7. Relative rates of hydrogen abstraction by radicals.

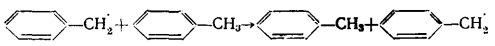
Substance	ROO$^{\cdot}$	$^{\cdot}CCl_3$	Polystyryl	t-Butoxy	$CH_3^{\cdot}$	
	90°	91.5%	100°	135°	80°	65°
Toluene	1.0	1.0	1.0	1.0	1.0	1.0
o-Xylene	—	—	—	1.2	—	0.99
m-Xylene	1.15	1.0	—	1.25	—	1.0
p-Xylene	1.6	1.13	—	1.52	—	1.19
Mesitylene	1.9	1.0	—	1.22	—	0.94
Ethylbenzene	7.75	4.6	3.7	3.2	3.5	4.14
Cumene	13.3	12.5	9.0	5.1	10	12.9
Indane	37	7.1	—	—	—	8.3
Tetralin	134	25.6	—	15.2	—	2.3
Diphenylmethane	16	11.9	9.5	—	—	—

The dimers and trimers of the radicals from the solvent, which are obtained in high yield, retain the initial unsaturation.

The formation of chlorine-substituted alkenes in the reaction of various alkenes with t-butyl hypochlorite demonstrates that the reaction occurs by hydrogen abstraction from the alkene, and not by addition of a t-butoxy-radical to the double bond[57]; in the light-induced reaction of but-2-ene with t-butyl hypochlorite at 40° the double-bond addition product makes up only 3–4% of the total, 96 ± 3% being chlorobutene isomers.

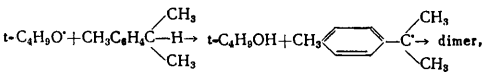
t-Butoxy-radicals react with substituted cycloalkanes by hydrogen abstraction from a side-chain, without affecting the ring[76], and the reaction with ethylene and propene oxides proceeds analogously: with t-butyl hypochlorite, the corresponding chlorocyclopropanes or chloro-epoxides are produced in high yield. On the other hand, the liquid-phase chlorination of these compounds with chlorine gives large amounts of acyclic chlorinated products. The selectivity of hydrogen abstraction by RO· radicals in this case has provided a convenient preparative procedure.

In alkyl-aromatic solvents t-butoxy-radicals abstract hydrogen from the α-carbon atom, producing a stabilised benzyl-type radical, which then dimerises. The hydrogen transfer reaction



does not occur in these reactions[77]. The reaction with isopropylbenzene produces 2,3-dimethyl-2,3-diphenylbutane[20]. Hydrogen abstraction from cumene by t-butoxy-radicals is also observed in the decomposition of di-t-butyl diperoxycarbonate[78], and analogous products are found with ethylbenzene and toluene[64]. t-Butoxy-radicals only abstract hydrogen from the side-chains of alkylbenzenes, unlike the radicals obtained in the decomposition of acetyl or benzoyl peroxide, which can also react with the aromatic nucleus[79].

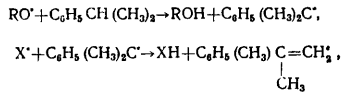
The reaction of RO· radicals with p-chlorotoluene has given 1,2-di-(p-chlorophenyl)ethane[80], and dehydro-dimers are obtained in the reaction of di-t-butyl peroxide with diphenylmethane; 4-methylbiphenyl; o-, m-, and p-chloro-, p-bromo-, and p-iodo-toluene; β- and γ-picolines; and p-methylanisole[81,82]. The hydrogen atom of tertiary groups is readily abstracted[36]; in p-methylcumene hydrogen is abstracted from the isopropyl-group, and only one dimer is obtained:



no 1,2-di-(p-isopropylphenyl)ethane, the dimerisation product of radicals which might be obtained by hydrogen abstraction from the p-methyl-group, being found[81,82]. When the peroxide is decomposed in anisole, the dimer, as expected, is not formed.

The reactivity of these alkylbenzenes towards t-butoxy-radicals, measured by the relative rate of formation of the dimer, depends on the substituent groups, and the influence of these is not due solely to their stabilising effect on the benzyl radicals produced by hydrogen abstraction, but also by their polar character, since the results obtained in the decomposition of di-t-butyl peroxide in a series of alkyl-aromatic solvents with various substituents are in accordance with the Hammett σ and ρ parameters[83]. For the reaction of t-butoxy-radicals with alkyl-aromatic solvents the value $\sigma = -0.5$ was found.

In some cases the abstraction of hydrogen from alkyl-aromatic solvents is not accompanied by formation of the corresponding dimers[5]. It is thought that the solvent radicals react with oxy-radicals, giving up hydrogen to them, or combine with other active particles in the system, for example, nitric oxide if the reaction occurs by decomposition of nitrites:



where X· = NO or RO·.

Hydrogen abstraction from benzaldehyde by t-butoxy-radicals produces t-butyl alcohol in 100% yield[84]; the radicals from the solvent give complex association products. Tertiary benzylamines $C_6H_5CH_2NRR'$ are dehydrogenated by t-butoxy-radicals to $C_6H_5\dot{C}HNRR'$ radicals, which then dimerise or disproportionate, depending on R and R'.[85] Analogous reactions are observed with benzyl ethers $C_6H_5CH_2OH$.[86,87]

In dimethylformamide[88] the products of the thermal decomposition of di-t-butyl peroxide are t-butyl alcohol and a mixture which indicates that hydrogen is abstracted both from a methyl and the formyl group of the solvent.

At 140° t-butoxy-radicals abstract an α-hydrogen atom from primary and secondary alcohols, forming RR'C·–OH radicals, which then dimerise to a glycol. A mixture of alcohols produces mixed glycols[89].

In the decomposition of di-t-butyl peroxide in n-butyric acid at 116° hydrogen is abstracted by the t-butoxy-radicals from the α-carbon atom, and the resulting radical dimerises. In the decomposition of the peroxide in ethyl butyrate, hydrogen abstraction from the acid residue of the ester is six times as rapid as from the alcoholic residue, and is ten times as rapid in the α-position as in the β-position[90].

In the decomposition of cyclohexyl or 1-methylcyclohexyl nitrite in cumene[5] the yield of the corresponding alcohol is 0.90–0.97 mole per mole of initial nitrite. In chlorobenzene, as in pyrolysis of the pure nitrites, the yield of alcohol does not exceed 0.6 mole.

The benzyloxy-radical abstracts hydrogen from cumene[91], and the α-methylbenzyloxy-radical abstracts hydrogen from benzenethiol, producing 1-phenylethanol in 55% yield[92]; this alcohol is formed in 20–26% yield in the thermal decomposition of phenethyl nitrite[55].

In cumene, the diphenylmethoxy-radical produces 15–24% of 2,2-diphenylethanol[56]. Hydrogen abstraction by the cumenyloxy-radical from cumene decreases rapidly as the temperature is raised from 110° to 160°.[93]

Isopropoxy-, cyclohexyloxy-, and benzyloxy-radicals abstract hydrogen from isopropyl alcohol, dehydrogenating it to acetone[53,94].

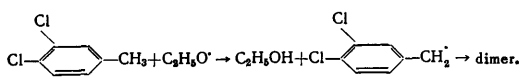
The reactions of R· and RO· radicals can be compared by investigating the decomposition of dialkyl peroxodicarbonates and acetyl peroxide in various solvents[43–45]. In solvents whose molecules contain a labile readily removed hydrogen atom, this is abstracted by R· and RO· radicals at approximately the same rate. In solvents without such hydrogen atoms, RO· radicals undergo disproportionation more than they participate in hydrogen abstraction (Table 8).

TABLE 8. Comparison of the reactions of free alkyl and alkoxy--radicals.

Free radical		Solvent: isopropylbenzene (A) hydrogen abstraction from solvent, %	isopropylbenzene (A) disproportionation, %	p-isopropylmethylbenzene (A') hydrogen abstraction from solvent, %	p-isopropylmethylbenzene (A') disproportionation, %	trimethylacetic acid (B) hydrogen abstraction from solvent, %	trimethylacetic acid (B) disproportionation, %
$\cdot CH_3$	(125°) A' (125°) A (125°) B (110°) A	100 61	0 0	100 73.3	0 0	71.0 28.9	0 68.1
$\cdot OCH_3$	(130°) B (110°) A						
$\cdot OC_2H_5$	(130°) A' (110°) A (140°) B	70.4	18.8	58.7	13.7	5.3	95
$\cdot C_3H_7$	(125°) A (135°) B	78	22			0—3	20.0 (50% dimerisation)
$\cdot OC_3H_7$	(145°) A (140°) B	51.7	33.3			5.6	92.5
$\cdot O(CH_3)_3$	(135°) A	0	84.0				
$\cdot OC_4H_9$-iso	(130°) A	83.5	9.5				
$\cdot OC_4H_9$	(135°) A	61.8	3.7				

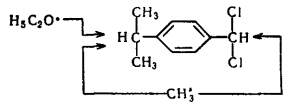
In some cases intramolecular hydrogen abstraction is observed; for example, in the decomposition of bis-(1-methylperoxocarbonatocyclohexyl) peroxide [95] the main products are methanol and the saturated $CH_2(CH_2)_4C(=O)O$ and unsaturated $CH_2(CH_2)_2CH=CHC(=O)O$ lactones, the latter being formed when hydrogen abstraction by the RO· radicals from the solvent is difficult. In isopropyl alcohol the yield of unsaturated lactone is 13 mole %, and in cyclohexane and benzene 39–46 mole %, of the total amount of lactones. At the same time there is almost complete absence of reaction between methoxy-radicals and the solvents, which shows that the formation of methanol in solvents with a difficultly removable hydrogen atom proceeds by an intramolecular reaction, the dehydrogenation product being the unsaturated lactone.

Alkoxy-radicals show an interesting selectivity in hydrogen abstraction from the solvent [44,45]: in chloro-substituted aralkyls the position of the chlorine with respect to the supposed point of attack by the alkoxy-radicals has a substantial influence on the course of the reaction. Thus in the reaction of $C_2H_5O\cdot$ radicals with 3,4-dichlorotoluene the dimer 1,2-bis-(3,4-dichlorophenyl)ethane is formed in 61% yield, the disproportionation of the $C_2H_5O\cdot$ radicals in this solvent occurring to no more than 11%:

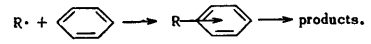


In 2,6-dichlorotoluene the corresponding dimer, produced from the radicals of the solvent by hydrogen abstraction from the α-position, is formed in only 21% yield, disproportionation of the ethoxy-radicals in this solvent occurring to the extent of 27%; and in benzal chloride there is no attack at the α-position at all, practically no tetrachlorotolane being formed [tolane is diphenylacetylene (Ed. of Translation)].

These results are explained by the so-called "repulsion effect", which is suffered by the approaching alkoxy-radical if chlorine atoms or methoxycarbonyl groups are close to the most probable point of attack. In some cases this effect causes a change in the point of attack. In their reaction with p-isopropylbenzylidene dichloride $(CH_3)_2CHC_6H_4CHCl_2$, ethoxy-radicals abstract only the α-hydrogen of the isopropyl group, giving a symmetrical dimer, while methyl radicals react equally with both α-hydrogen atoms, giving a mixture of isomers of the dimer:



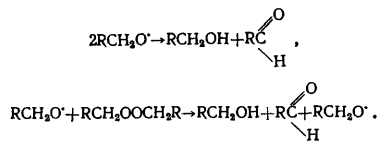
The absence of reaction products of RO· radicals with benzene can apparently be explained in an analogous manner [41,54]. The free electron on the electronegative oxygen atom hinders the formation of the transitional π complex, the existence of which has been clearly demonstrated in the reaction of R· radicals with aromatic compounds:



The selectivity of hydrogen abstraction by the t-butoxy--radical is due to its polar properties, which are equal to those of the chlorine atom [96], but unlike chlorine, t-butoxy--radicals are considerably more sensitive to the strength of the carbon–hydrogen bond; their reactivity towards primary, secondary, and tertiary hydrogen atoms is in the proportion 1 : 8 : 44, as against 1 : 3 : 4.5 for chlorine.

3. Disproportionation. The disproportionation of alkoxy-radicals is considerably more exothermic than hydrogen abstraction. According to Gray [1,4] ΔH for disproportionation is -70 (-90) kcal mole^{-1}.

In many cases it is difficult to distinguish between disproportionation and reaction of the radical with the starting material, since the products are the same:



Clearly, this matter can only be resolved kinetically, by showing the presence or absence of the initiated decomposition.

Such special investigations have not been carried out (with certain exceptions [51,53]), so that by the term "disproportionation" is generally understood both reaction between two RO· radicals, and reaction between an RO· radical and the starting material.

Disproportionation in the gas phase is uncommon. For methyl radicals produced in the pyrolysis of dimethyl peroxide [68] disproportionation is observed at 113–143°. The methoxy- and ethoxy-radicals formed in the photolysis of methyl acetate [65] and ethyl propionate [97] and the $CD_3O\cdot$ radicals produced in the photolysis of [D_3]methyl acetate [66,67] also disproportionate.

The reaction products obtained in the slow decomposition of di-n-propyl peroxide [14] in the gas phase at 146–175° contain propionaldehyde and propanol, which may be formed by disproportionation of $CH_3CH_2CH_2O\cdot$ radicals; however, initiated decomposition of the peroxide is more probable in this case:

$$CH_3CH_2CH_2O\cdot+(CH_3CH_2CH_2O)_2\rightarrow CH_3CH_2CH_2OH+$$
$$+CH_3CH_2CHO+CH_3CH_2CH_2O\cdot.$$

Disproportionation of $CH_3O^{\bullet}$, $C_2H_5O^{\bullet}$, $n\text{-}C_3H_7O^{\bullet}$, $iso\text{-}C_3H_7O^{\bullet}$, and $n\text{-}C_4H_9O^{\bullet}$ radicals in the liquid phase is observed when they are formed in solvents in which hydrogen abstraction is difficult, for example, in trimethylacetic acid or methyl trimethylacetate [43]. 100% disproportionation of the ethoxy-radicals takes place in dimethyl succinate or dimethyl malonate [44], or 2,6-dichlorotoluene or benzaldehyde [45]. Isopropyloxy-radical disproportionation products have been found in the pyrolysis of diisopropyl peroxocarbonates [98]. With t-butoxy-radicals the reaction is observed to a slight degree, and produces acetone and the t-butyl methyl ether [99]:

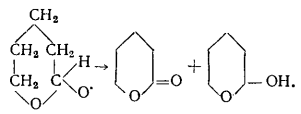
$$2\,(CH_3)_3CO^{\bullet} \rightarrow (CH_3)_2C{=}O + CH_3OC\,(CH_3)_3.$$

Disproportionation of benzyloxy- and cyclohexyloxy-radicals occurs in the decomposition of dibenzyl and dicyclohexyl peroxodicarbonates in benzene, carbon tetrachloride, or acetic acid [41,42]. The rate of decomposition of these peroxocarbonates in benzene and carbon tetrachloride is not affected by the presence of 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazino-radicals [53], which shows the absence of initiated decomposition of the peroxides, so that the formation of the corresponding alcohol and ketone in the reaction of the RO• radicals must be due exclusively to their disproportionation.

Disproportionation is also observed when peroxodicarbonates are decomposed in the presence of various metals. Here direct attack of the RO• radicals on the metal with formation of the corresponding alkoxides does not occur [100]. The formation of octanone and (+)-octan-2-ol in the thermal decomposition of optically active (+)-oct-2-yl nitrite [101] is due to disproportionation:

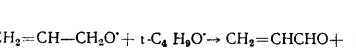
$$2(+)\text{-}C_6H_{13}CH\,(CH_3)\,O^{\bullet} \rightarrow C_6H_{13}COCH_3 + (+)\text{-}C_6H_{13}CH\,(CH_3)\,OH,$$

and similarly for 2-hydroxytetrahydropyran and δ-valerolactone in the thermal decomposition of t-butyl tetrahydropyran-2-yl peroxide [102]:



Disproportionation between two different RO• radicals has been observed in the pyrolysis of allyl t-butyl and t-butyl cyclohexyl peroxides [103]:

$$CH_2{=}CH{-}CH_2O^{\bullet} + t\text{-}C_4H_9O^{\bullet} \rightarrow CH_2{=}CHCHO + t\text{-}C_4H_9OH,$$



The benzyloxy-radicals produced in the decomposition of benzyl nitrite [50] and benzyl hyponitrite [51,104] undergo disproportionation. In the latter case the disproportionation occurs in a "cage" of solvent, since dilution of the hyponitrite solution from 0.1 M to 0.0001 M had practically no effect on the yield of benzaldehyde [104]. The possibility is not excluded of a mechanism whereby two radicals formed in the solvent "cage" first dimerise to dibenzyl peroxide, and then are re-formed by its decomposition and disproportionate. However, dimerisation of two alkoxy-radicals, as will be shown below, is a rare event, and is only found with cumenyloxy-radicals [1]:

$$2C_6H_5C\,(CH_3)_2O^{\bullet} \rightarrow [C_6H_5C\,(CH_3)_2O]_2.$$

Disproportionation has been invoked to explain the formation of 1-phenylethanol in the thermal decomposition of pure 1-phenylethyl nitrite [55].

It is seen from the above that disproportionation is one of the most typical reactions of RO• radicals in the liquid phase. Even in solvents which readily give up hydrogen, in many cases there is parallel formation of disproportionation products [41]. In this connection it is an interesting fact that isopropyloxy-*C* radicals $(CH_3)_2CHOH$ do not disproportionate [53].

4. Reactions with other radicals. RO• radicals can interact with other radicals present in the system.

The methoxy-radicals produced in the thermal decomposition of methyl t-pentyl peroxide combine with methyl radicals to give a considerable quantity of dimethyl ether [105].

In the photolysis of methyl acetate [106] and [D_3]methyl acetate [66,67] the $CH_3O^{\bullet}$ and $CH_3^{\bullet}$ radicals are found to disproportionate and also to recombine, the ratio of the two rates of reaction K_{dis}/K_{recom} being 1.4 and independent of the temperature, indicating the zero energy of activation for the disproportionation.

In the photolysis of ethyl propionate [97] the ratio K_{dis}/K_{recom} for the ethoxy- and ethyl radicals is 2.3. Ethyl methyl ether has been found in the decomposition of t-butyl ethyl peroxide [73].

The formation of 1,2-epoxy-2-methylpropane in the decomposition of di-t-butyl peroxide may be due to the reaction [60]:

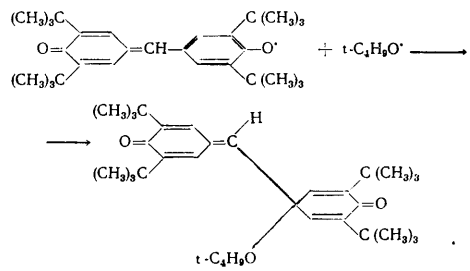
$$(CH_3)_3CO^{\bullet} + R^{\bullet} \rightarrow RH + CH_2{-}C\,(CH_3)_2.$$

The reaction between RO• radicals and nitrogen monoxide or dioxide is of this type. Methoxy-radicals can combine with nitrogen monoxide to give methyl nitrite [38], or disproportionation may occur [107]:

$$CH_3O^{\bullet} + NO \rightarrow CH_2O + HNO, \qquad 2HNO \rightarrow H_2O + N_2O.$$

An analogous reaction is known for ethoxy-radicals [31,108]. Such reactions are less characteristic of t-butoxy-radicals. At 160° the rate of combination of nitrogen monoxide with $(CH_3)_3CO^{\bullet}$ is ~0.7 that of decomposition of the radical [34].

The combination of t-butoxy-radicals with the stable galvinoxyl† free radical has been described [109]:



No dimerisation with the formation of oxygen–oxygen bonds occurs, and in general this dimerisation is not a characteristic of RO• radicals; according to approximate calculations [109] the activation barrier for this reaction is fairly high: 5 kcal. Investigation of the thermal decomposition of di-t-butyl monoperoxocarbonate [110] has also shown that there is no recombination of RO• radicals in the solvent "cage".

The products of the reaction of RO• radicals with another stable free radical, the 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazino-radical, have not been described,

† See Ref.109 for a derivation of this name (Ed. of Translation)].

but it is known that the (2,4,6-trinitrophenyl)hydrazino--radical is an active acceptor of RO· radicals, and may be used to study the kinetics of their formation in solution [111].

5. Isomerisation. Gray and Williams [1,4] found that the isomerisation of RO· radicals is thermodynamically favourable (Table 9).

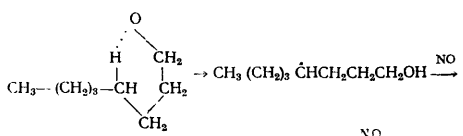
Isomerisation of alkoxy-radicals has been observed in the light-induced reaction of a number of tertiary alkyl hypochlorites [112], a free-radical chain reaction producing the corresponding chlorohydrins:

$$RCH_2(CH_2)_nC(CH_3)_2O \rightarrow \dot{R}CH(CH_2)_nC(CH_3)_2OH \xrightarrow{\text{hypochlorite}}$$
$$\xrightarrow{\text{hypochlorite}} RCHCl(CH_2)_nC(CH_3)_2OH + RCH_2(CH_2)_nC(CH_3)_2O\cdot, \text{ etc.}$$

The yield of the isomerisation product increases with the number of carbon atoms in the t-alkoxy-radical. The intramolecular nature of the hydrogen abstraction step in the rearrangement is demonstrated by the constant yield of isomerisation product as the concentration of hypochlorite in the solution is increased from 1.7 to 6.7 M. No isomerisation of primary or secondary alkoxy-radicals was detected [112], but it was later shown that intramolecular hydrogen abstraction occurs in the light-induced and thermal decomposition of n-butyl hypochlorite, with subsequent formation of the chlorohydrin [113].

The isomerisation of the alkoxy-radical in the light--induced decomposition of an alkyl nitrite leads to formation of nitroso-alcohol dimers [114]; the isomerisation passes through an intermediate six-membered ring, so that the yield of nitroso-dimer is directly dependent on the structure of the alkoxy-radical.

In the decomposition of n-octyl nitrite the main reaction product is the dimer of 4-nitrosooctan-1-ol:

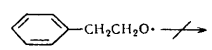


$$\xrightarrow{NO} CH_3(CH_2)_3CHCH_2CH_2CH_2OH \rightarrow \text{dimer},$$
$$NO$$

but with alkyl nitrites having less than five carbon atoms no intermediate six-membered ring compound can be formed, and the yield of nitroso-dimers is very much less. The same effect is observed with substituted alkylaromatic [115] and cyclohexyloxy-radicals [116]. Cyclohexyl nitrite itself gives a very low yield (4%) of nitroso-dimer, while 2-cyclohexylcyclohexyl nitrite gives a 30% yield of the dimer [116].

No dimer has been detected in the photolysis of benzyl nitrite, but 4-phenylbutyl and 5-phenylpentyl nitrites give up to 35% yields of nitroso-dimer.

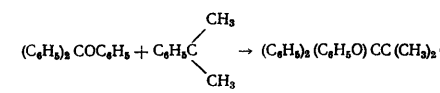
There is no evidence for the migration of hydrogen from the benzene nucleus [115]:



Other cases are known of the isomerisation of aryl-substituted alkoxy-radicals. Triphenylmethoxy isomerises into the phenyl ether [117]:

$$(C_6H_5)_3CO\cdot \rightarrow (C_6H_5)_2\dot{C}OC_6H_5 \rightarrow \text{dimer}.$$

In solution in cumene at 120–140° the isomerised triphenylmethoxy-radical combines with the α-cumenyl-radical [91]:



The diphenyl-*p*-tolylmethoxy-radical can isomerise in two ways, with migration of either the *p*-tolyl or a phenyl group [91]:

$$p\text{-}CH_3C_6H_4(C_6H_5)_2CO\cdot \rightarrow (C_6H_5)_2COC_6H_4CH_3 \text{ or } p\text{-}CH_3C_6H_4(C_6H_5)COC_6H_5.$$

The 1-naphthyldiphenylmethoxy- and biphenylylmethoxy--radicals can also isomerise in two ways in solution in cumene, but the rate of migration of the 1-naphthyl or biphenylyl group is six times that of the phenyl [91].

The *p*-nitrophenyldiphenylmethoxy-radical isomerises by migration of the *p*-nitrophenyl group; the resulting radical then decomposes [118]:

$$p\text{-}NO_2C_6H_4(C_6H_5)_2CO \rightarrow (C_6H_5)_2COC_6H_4NO_2 \rightarrow C_6H_5\cdot + C_6H_5COC_6H_4NO_2.$$

The use of optically active compounds has shown that the 1-phenylethoxy-radical does not isomerise in solution [92], and the absence of isomerisation has been demonstrated for gas-phase reactions of $CH_3O\cdot$ radicals [3] and for reactions of $(CH_3)_2CHO\cdot$ radicals in solvents [94].

6. Addition to a double bond. The addition of RO· radicals to a double bond has been demonstrated in the reaction of di-t-butyl or di-α-cumenyl peroxide with butadiene, isoprene, and chloroprene [119,120]:

$$t\text{-}C_4H_9O\cdot + CH_2{=}CH{-}CH{=}CH_2 \rightarrow t\text{-}C_4H_9OCH_2{-}CH{=}CH{-}CH_2 \rightarrow \text{dimer}.$$

An oxygen-containing polymer is obtained in the decomposition of di-t-butyl peroxide in hex-1-ene, which shows the addition of the RO· radicals to the double bond of the hexene [113]. Benzyloxy-radicals initiate the polymerisation of methyl methacrylate [29].

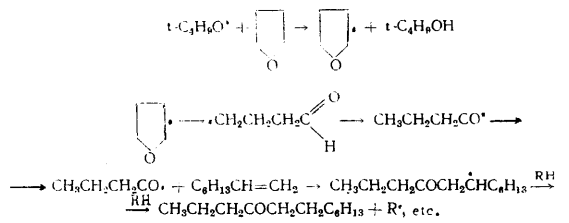
^{14}C-labelled di-t-butyl peroxide has been used to demonstrate that in the polymerisation of styrene the initiation is caused mainly by t-butoxy-radicals [47]. At low concentrations of styrene in the solution and at high temperatures the polymerisation is initiated by the methyl radicals produced in the decomposition of the t-butoxy-radicals.

The complex light-induced decomposition of steroidal nitrites has been explained by the intramolecular reaction of the resulting alkoxy-radical with a double bond [121].

TABLE 9. Thermochemistry of isomerisation of alkoxy--radicals.

Type of isomerisation	Initial radical	Radical obtained	ΔH, kcal × × mole^{-1}
Migration of a hydrogen atom from carbon	$CH_3O\cdot$	$\cdot CH_2OH$	−7.5
	$C_2H_5O\cdot$	$\cdot CH(CH_3)OH$	−9.5
	$(CH_3)_2CHO\cdot$	$\cdot CH(CH_3)_2OH$	−12
	$C_6H_5CH_2O\cdot$	$\cdot CH(C_6H_5)OH$	−11
	cyclo-$C_6H_{11}O\cdot$	cyclo-$\cdot C_6H_{10}OH$	−14
Migration of hydrogen atoms from distant CH_2--groups	$RCH_2(CH_2)_nO\cdot$	$RCHCH_2OH$	−8.5
	$CH_3CH_2O\cdot$	$\cdot CH_2OCH_3$	5
Migration of a methyl group	$(CH_3)_2CHO\cdot$	$\cdot CH(CH_3)OCH_3$	0.5
	$(CH_3)_3CO\cdot$	$\cdot C(CH_3)_2OCH_3$	0.5
	$C_6H_5C(CH_3)_2O\cdot$	$\cdot CCH_3C_6H_5(OCH_3)$	−1.5
Ring opening	cyclo-$C_6H_{11}O\cdot$	—	4
Migration of an aryl group	$(C_6H_5)_3CO\cdot$	$\cdot C(C_6H_5)_2OC_6H_5$	−1.5
	$C_6H_5(CH_3)_2CO\cdot$	$\cdot C(CH_3)_2OC_6H_5$	−1.5

The products obtained from di-t-butyl peroxide and tetrahydrofuran in the presence of oct-1-ene indicate the following reactions to occur [122]:



In other cases there is no direct evidence of addition of RO· radicals to double bonds. For example, in the polymerisation of styrene in the presence of cyclohexyl hydroperoxide the initiators may be other radicals present in the system [123].

The infrared spectra of the polymer obtained from ethylene in the presence of diethyl peroxodicarbonate exhibit the characteristic carbonate group absorption bands [124], and hence the initiation is due mainly to ROC(=O)O· radicals [125-127]. The polymerisation of other monomers in the presence of peroxocarbonates presumably proceeds analogously.

C-radicals and O-oxyradicals behave differently towards double bonds. By ^{14}C-labelling, investigation of the decomposition of diisopropyl peroxodicarbonate in isopropyl alcohol in the presence of maleic acid has shown that the isopropyloxy O-radical $(CH_3)_2CHO\cdot$ does not add to the double bond of maleic acid, while the isomeric C-radical $(CH_3)_2C(OH)\cdot$ adds to the maleic acid to give a high yield of terebic acid [94,128] [3-carboxy-4-methylpentan--4-olide (Ed. of Translation)].

The t-butoxy-radical may react with alkenes not by addition at the double bond, but by abstraction of α-hydrogen [26,57,129].

1. P.Gray and A.Williams, Chem.Rev., 59, 239 (1959).
2. K.U.Ingold and F.P.Lossing, Canad.J.Chem., 31, 30(1953).
3. R.F.Pottie, A.G.Harrison, and E.P.Lossing, Canad.J. Chem., 39, 102 (1961).
4. P.Gray and A.Williams, Trans.Faraday Soc., 55, 760(1959)
5. P.Gray, P.Rathbone, and A.Williams, J.Chem.Soc., 2620 (1961).
6. J.A.Gray and D.W.G.Style, Trans.Faraday Soc., 48, 1137 (1952).
7. N.A.Milas and D.M.Surgenor, J.Amer.Chem.Soc., 68, 205 (1946).
8. J.A.Gray and D.W.G.Style, Trans.Faraday Soc., 49, 52 (1953).
9. F.O.Rice and J.Rodowskas, J.Amer.Chem.Soc., 57, 350 (1935).
10. B.G.Govenlock and J.Trotman, J.Chem.Soc., 1670 (1956).
11. J.B.Levy, J.Amer.Chem.Soc., 76, 3254 (1954).
12. H.Theile, Angew.Chem., 60A, 65 (1948).
13. E.J.Harris and A.C.Egerton, Proc.Roy.Soc., 168A, 1 (1938).
14. E.J.Harris and B.E.Englund, J.Org.Chem., 21, 140(1956).
15. R.E.Rebbert and V.J.Laidler, J.Chem.Phys., 20, 574 (1952).
16. E.K.Bell, J.H.Raley, F.F.Rust, F.H.Seubold, and W.T.Vaughan, Discuss.Faraday Soc., 10, 242 (1959).
17. J.B.Levy and F.J.Adrian, J.Amer.Chem.Soc., 77, 2015 (1955).
18. D.G.Adler, M.W.T.Pratt, and P.Gray, Chem.and Ind., 1517 (1955).
19. E.H.Pollard, H.S.B.Marschall, and A.E.Pedler, Trans. Faraday Soc., 52, 59 (1956).
20. J.H.Raley, F.F.Rust, and W.E.Vaughan, J.Amer.Chem. Soc., 70, 88 (1948).
21. J.Murawski, J.S.Roberts, and M.Szwarc, J.Chem.Phys., 19, 698 (1951).
22. L.M.Dorfman and Z.W.Salsburg, J.Amer.Chem.Soc., 73, 255 (1951).
23. G.McMillan and M.J.H.Wijnen, Canad.J.Chem., 36, 1227 (1958).
24. A.D.Joffe, Research, 7, 44 (1954).
25. F.F.Rust, F.H.Seubold, and W.E.Vaughan, J.Amer.Chem. Soc., 70, 95 (1948).
26. D.H.Volman and R.K.Brinton, J.Chem.Phys., 20, 1764 (1952).
27. F.P.Lossing, K.U.Ingold, and A.W.Tickner, Discuss.Faraday Soc., 14, 34 (1953).
28. L.Herk and M.Szwarc, J.Amer.Chem.Soc., 82, 3558 (1960).
29. I.Harris, I.Marshall, and K.B.Jarrett, Nature, 159, 843 (1947).
30. J.T.Martin and R.G.W.Norrish, Proc.Roy.Soc., 220A, 322 (1953).
31. J.B.Levy, Ind.Eng.Chem., 48, 762 (1956).
32. P.Gray, Chem.and Ind., 120 (1960).
33. R.V.Brinton and D.H.Volman, J.Chem.Phys., 20, 25(1952).
34. F.W.Birss, C.J.Dauby, and C.Hinshelwood, Proc.Roy.Soc., 239A, 154 (1957).
35. J.H.T.Brook, Trans.Faraday Soc., 53, 327 (1957).
36. A.Raley, F.F.Rust, and W.E.Vaughan, J.Amer.Chem.Soc., 70, 1336 (1948).
37. M.T.Jagniss, J.S.Roberts, and M.Szwarc, J.Amer.Chem. Soc., 74, 6005 (1952).
38. G.R.McMillan, J.Amer.Chem.Soc., 82, 2422 (1960).
39. N.A.Milas and L.A.Perry, J.Amer.Chem.Soc., 68, 1938 (1946).
40. F.F.Rust, R.H.Seubold, and W.E.Vaughan, J.Amer.Chem. Soc., 72, 338 (1950).
41. G.A.Razuvaev and L.M.Terman, Zhur.Obshch.Khim., 30, 2387 (1960).
42. G.A.Razuvaev and L.M.Terman, Sbornik Nauch.Rabot Inst. Fiz.-Org.Khim., Akad.Nauk Beloruss.SSR, 51 (1960).
43. H.C.McBay and O.Tucker, J.Org.Chem., 19, 869 (1954).
44. H.C.McBay, O.Tucker, and A.Milligan, J.Org.Chem., 19, 1003 (1954).
45. H.C.McBay, O.Tucker, and P.T.Graves, J.Org.Chem., 24, 536 (1959).
46. A.L.Williams, E.A.Oberright, and J.W.Brooks, J.Amer. Chem.Soc., 78, 1190 (1956).
47. J.K.Allen and P.G.Bevington, Proc.Roy.Soc., 262, 271 (1961).
48. E.D.Green, M.L.Savitz, H.H.Lau, D.Osterholtz, and W.W.Smith, J.Amer.Chem.Soc., 83, 2196 (1961).
49. J.K.Kochi, J.Amer.Chem.Soc., 84, 1193 (1962).
50. P.Gray, P.Rathbone, and A.Williams, J.Chem.Soc., 3932 (1960).
51. J.B.DeSousa and S.K.Ho, Nature, 186, 776 (1960).

52. N.Kornblum and V.M.Weaver, J.Org.Chem., 23, 1213 (1958).
53. G.A.Razuvaev, L.M.Terman, and G.G.Petukhov, Dokl. Akad.Nauk SSSR, 136, 628 (1960).
54. L.M.Terman, Candidate's Dissertation, Institute of Organo-elemental Compounds, Academy of Sciences of the USSR, 1962.
55. P.Gray, M.J.Pearson, and P.Rathbone, J.Chem.Soc., 4006 (1961).
56. J.I.G.Cadogan, D.H.Hey, and W.A.Sanderson, J.Chem. Soc., 4498 (1958).
57. C.Walling and W.Thaler, J.Amer.Chem.Soc., 83, 3877 (1961).
58. S.J.Cristol and J.E.Leffler, J.Amer.Chem.Soc., 76, 4468 (1954).
59. M.S.Kharasch, A.Fono, and N.Nudenberg, J.Org.Chem., 16, 105 (1951).
60. H.A.Bent and B.Crawford, J.Amer.Chem.Soc., 79, 1793 (1957).
61. F.D.Green, J.Amer.Chem.Soc., 81, 2688 (1959).
62. A.L.Nussbaum, C.H.Robinson, E.P.Oliveto, and D.H.R.Barton, J.Amer.Chem.Soc., 83, 2400 (1961).
63. A.L.Nussbaum, E.P.Juan, C.H.Robinson, A.Mitchell, E.P.Oliveto, J.M.Beaton, and D.H.Barton, J.Org.Chem., 27, 20 (1962).
64. E.H.Farmer and C.G.Moore, J.Chem.Soc., 131 (1951).
65. M.H.J.Wijnen, J.Chem.Phys., 27, 710 (1957).
66. M.H.J.Wijnen, J.Chem.Phys., 28, 271 (1958).
67. M.H.J.Wijnen, J.Chem.Phys., 28, 939 (1959).
68. P.L.Hanst and J.G.Calvert, J.Phys.Chem., 63, 104 (1959).
69. J.Takezaki and C.Takeuchi, J.Chem.Phys., 22, 1527(1954).
70. R.Shaw and A.F.Trotman-Dickenson, J.Chem.Soc., 3210 (1960).
71. R.Shaw and A.F.Trotman-Dickenson, Proc.Chem.Soc., 61 (1959).
72. J.B.Levy, J.Amer.Chem.Soc., 76, 3790 (1954).
73. J.B.Levy, J.Amer.Chem.Soc., 75, 1801 (1953).
74. R.K.Brinton and D.H.Volman, J.Chem.Phys., 20, 1053 (1952).
75. J.A.Meyer, V.Stannett, and M.Szwarc, J.Amer.Chem.Soc., 83, 25 (1961).
76. C.Walling and P.S.Fredricks, J.Amer.Chem.Soc., 84, 3326 (1962).
77. J.H.T.Brook and R.W.Glazebrook, Trans.Faraday Soc., 56, 1014 (1960).
78. M.M.Martin, J.Amer.Chem.Soc., 83, 2869 (1961).
79. H.Pines and C.N.Pillai, J.Amer.Chem.Soc., 82, 2921 (1960).
80. A.L.J.Beckwith and W.A.Waters, J.Chem.Soc., 1001 (1957).
81. K.M.Johnston and G.H.Williams, Chem.and Ind., 328 (1958).
82. K.M.Johnston and G.H.Williams, J.Chem.Soc., 1168 (1960).
83. K.M.Johnston and G.H.Williams, J.Chem.Soc., 1446(1960).
84. F.F.Rust, F.H.Seubold, and W.E.Vaughan, J.Amer. Chem.Soc., 70, 3258 (1948).
85. R.L.Huang, J.Chem.Soc., 1816 (1959).
86. R.L.Huang and S.S.Hoe, Proc.Chem.Soc., 12, 354 (1957).
87. R.L.Huang and Geo Oon-Keong, J.Chem.Soc., 3190 (1959).
88. K.Schwetlick, Angew.Chem., 72, 208 (1960).
89. K.Schwetlick, W.Geyer, and H.Hartmann, Angew.Chem., 72, 779 (1960).
90. A.L.J.Beckwith, Austral.J.Chem., 13, 244 (1960).
91. M.S.Kharasch, A.C.Pochkus, A.Fono, and N.Nudenberg, J.Org.Chem., 16, 1458 (1951).
92. N.Kornblum and H.E.de la Mare, J.Amer.Chem.Soc., 74, 3049 (1959).
93. H.C.Bailey and G.W.Godin, Trans.Faraday Soc., 52, 68 (1956).
94. L.M.Terman, G.A.Razuvaev, and G.G.Petukhov, Dokl. Akad.Nauk SSSR, 136, 1349 (1960).
95. G.A.Razuvaev, A.I.Kirillov, and V.S.Etlis, Zhur.Obshch. Khim., 33, 131 (1963).
96. C.Walling and B.B.Jacknow, J.Amer.Chem.Soc., 82, 6108, 6113 (1960).
97. M.H.J.Wijnen, J.Amer.Chem.Soc., 82, 3034 (1960).
98. S.G.Cohen and D.B.Sparrow, J.Amer.Chem.Soc., 72, 611 (1950).
99. D.A.Aleksandrova, Huang Yü-li, A.N.Pravednikov, and S.S.Medvedev, Dokl.Akad.Nauk SSSR, 123, 1029 (1958).
100. L.M.Terman and G.A.Razuvaev, Zhur.Obshch.Khim., 31, 3132 (1961).
101. N.Kornblum and E.Oliveto, J.Amer.Chem.Soc., 71, 226 (1949).
102. N.A.Milas, R.L.Peeler, and O.L.Mageli, J.Amer.Chem. Soc., 76, 2322 (1954).
103. T.W.Campbell and G.M.Coppinger, J.Amer.Chem.Soc., 73, 1788 (1951).
104. S.K.Ho and J.B.Sousa, J.Chem.Soc., 1788 (1961).
105. J.H.Raley and D.O.Colammer, J.Amer.Chem.Soc., 74, 1606 (1952).
106. A.D.Jenkins and D.W.G.Style, Nature, 170, 706 (1952).
107. J.A.Gray and D.W.G.Style, Trans.Faraday Soc., 49, 52 (1953).
108. J.B.Levy, J.Amer.Chem.Soc., 78, 1780 (1956).
109. P.D.Bartlett and Toshio Funahashi, J.Amer.Chem.Soc., 84, 2596 (1962).
110. P.D.Bartlett and H.Sakurai, J.Amer.Chem.Soc., 84, 3269 (1962).
111. J.C.McGowan and T.Powell, J.Appl.Chem., 9, 93 (1959).
112. C.Walling and A.Padwa, J.Amer.Chem.Soc., 83, 2207 (1961).
113. E.L.Jenner, J.Org.Chem., 27, 1031 (1962).
114. P.Kabasakalian and E.P.Tawnley, J.Amer.Chem.Soc., 84, 2711 (1962).
115. P.Kabasakalian and E.P.Tawnley, J.Amer.Chem.Soc., 84, 2716 (1962).
116. P.Kabasakalian and E.P.Tawnley, J.Amer.Chem.Soc., 84, 2724 (1962).
117. H.Wieland, Ber., 44, 2550 (1911).
118. P.D.Bartlett and J.D.Cotman, J.Amer.Chem.Soc., 72, 3095 (1950).
119. M.S.Kharasch, D.Schwartz, and N.Nudenberg, J.Org. Chem., 18, 337 (1953).
120. D.H.Volman and V.M.Graven, J.Amer.Chem.Soc., 75, 3111 (1953).
121. A.L.Nussbaum, R.Wayne, E.Juan, O.Zagnetko, and E.P.Oliveto, J.Amer.Chem.Soc., 84, 1070 (1962).
122. T.J.Wallace and R.J.Gritter, J.Org.Chem., 26, 5256 (1961).
123. D.M.Fairbrother, H.A.Skinner, and E.W.Ewans, Trans. Faraday Soc., 53, 779 (1957).
124. H.N.Friedlander, J.Polymer Sci., 58, 455 (1962).
125. G.H.Weisemann, U.S.P. 2 728 755 (1955); Chem.Abs., 50, 6093c (1956); W.C.Gerveny, D.E.Burney, and G.H.Weisemann, U.S.P. 2 685 577 (1954); Chem.Abs., 49, 666h (1955).
126. D.Seed, U.S.P. 2 865 903 (1958); Chem.Abs., 53, 6688f (1959); B.P. 812 602 (1959); Chem.Abs., 53, 15 644b (1959).
127. Chem.Eng.News, 37, 50 (7th September 1959).
128. J.N.Pitts, R.L.Letsinger, R.P.Taylor, J.M.Patterson, G.Recktenwald, and R.Martin, J.Amer.Chem.Soc., 81, 1068 (1959).
129. C.R.Parks and O.Lorenz, J.Polymer Sci., 50, 287 (1961).