THE THERMOCHEMISTRY AND REACTIVITY OF ALKOXYL RADICALS

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Received January 30, 1959

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[1] On leave of absence (1958–59) from University of Leeds.

I. INTRODUCTION

Alkoxyl is the generic name for the free radicals, $RO\cdot$, derived from the parent alcohol, ROH, by loss of the hydroxylic hydrogen atom. The higher members may contain straight and branched aliphatic chains, alicyclic and aryl groups, and hetero-atoms. Correspondingly, dialkoxyls are diradicals derived from the glycols. Basically, all are substituted methoxyl radicals and $CH_3O\cdot$ is the simplest member of the series. Since the methylene radical (CH_2) and the oxygen atom (O) are isoelectronic, the methoxyl radical is the oxygen analog of free ethyl, $C_2H_5\cdot$; the oxygen analog of free methyl is, of course, the hydroxyl group. In this sense hydroxyl is the zeroth member of the alkoxyl series.

The unpaired electron formally associated with the oxygen atom is essentially localized there in all the alkoxyl radicals considered. Delocalization occurs in conjugated systems such as the aromatic oxy-radicals (phenoxyl, $C_6H_5O\cdot$, and its derivatives) and the unsaturated radicals (vinyloxyl, $CH_2{=}CHO\cdot$, and its derivatives); these two classes lie outside the scope of this review.

Alkoxyl radicals participate in many important reactions (see table 1). They are intermediates in the pyrolysis and photolysis of numerous organic peroxides and esters (of organic and inorganic acids) and in the decomposition of explosives. They take part in the controlled oxidations of organic chemistry. They initiate polymerization. They are the intermediates through which autoxidations, combustion, and degradative nitrations proceed. The technical importance of the last group widens the interest of studies of alkoxyl radicals.

The need thus exists for a comprehensive development of the chemistry of alkoxyl radicals and for work on a scale similar to that being done on free alkyl

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The need thus exists for a comprehensive development of the chemistry of alkoxyl radicals and for work on a scale similar to that being done on free alkyl decomposition reactions in which the alkoxyl radical is the important intermediate.

Finally a list of methods available for the controlled generation of alkoxyl radicals is given.

A. EVIDENCE FOR THE PARTICIPATION OF FREE ALKOXYL RADICALS

Evidence for the existence of alkoxyl radicals in reactions has been discussed in a number of papers and reviews (22, 57, 104, 135, 153, 285, 290). The main problem is that alkoxyl radicals cannot be isolated and most evidence is indirect. Because it is important to understand the nature of the evidence available, a summary of the salient features is presented here. The available evidence may be classified as follows: (*1*) direct evidence: mass-spectrometry; (*2*) indirect evidence: analytical, kinetic, thermochemical, and optical.

From the evidence available it will be shown that the interpretation of reaction systems based on alkoxyl radical intermediates gives a consistent scheme which explains all known facts.

1. Mass-spectroscopic evidence

It has been reported (57) that alkoxyl radicals generated in the pyrolysis of ether have been detected by the mass-spectrometer. At 1000°C. methoxyl radicals were not detected in the pyrolysis of dimethyl ether (162), although phenoxyl radicals have been shown to be present in the pyrolysis of anisole (128). This method, which can be applied to any system, however complex, has not been extensively exploited so far.

2. Optical evidence

The fluorescence spectra of certain molecules containing alkoxyl groups have been studied (265). Methyl nitrite, methyl nitrate, and methyl chloroformate all show the same band system (3300–3500 A.) (which is not emitted by CHO or CH_2O), and the emitter is probably the methoxyl group. Also, ethyl nitrate and diethyl peroxide emit a band which is characteristic of the ethoxyl group. This method of providing evidence for the participation of alkoxyl radicals in chemical reactions has not yet been applied diagnostically.

3. Chemical evidence

Chemical evidence, which is applicable to any system, consists of the recognition of stable reaction products which can have come only from alkoxyl radicals. For example, in the presence of a molecule with a weakly attached hydrogen atom the hydrogen is abstracted by the alkoxyl radical and the corresponding alcohol produced.

$$RO\cdot + H{-}X \rightarrow ROH + X\cdot$$

$$2X\cdot \rightarrow \text{dimer}$$

If the alkoxyl radical is optically active, then this activity is retained (146). In the presence of unsaturated compounds, addition to the double bond may occur, resulting in the formation of an ether containing the RO• group. Association with an alkyl radical, nitric oxide, or nitrogen dioxide to give the ether, nitrite, or nitrate, respectively, is another example of a reaction in which the structure of the RO group is retained. Since the decomposition of alkoxyl radicals produces free alkyl radicals together with aldehydes or ketones, these products are also characteristic.

4. Kinetic evidence

If the thermal decomposition of a molecule ROX is controlled by the homogeneous initial fission $ROX \rightarrow RO\cdot + X$, and if there is no significant attack by $RO\cdot$ or X on the parent molecule, then the reaction will be first order (second order at low pressures), the preëxponential factor will have a value greater than or equal to 10^{13}, and the activation energy will be approximately equal to the bond-dissociation energy and roughly constant for all members of the series.

Although such kinetic evidence alone might be explained by an intramolecular reaction, taken together with other evidence for the presence of $RO\cdot$ and X it is very convincing.

5. Thermochemical evidence

If the thermochemical quantities of the reaction

$$ROX \rightarrow RO\cdot + X\cdot$$

are known, then the enthalpy of formation of the alkoxyl radical may be calculated (see Section III,B).

If the same value for $\Delta H_{RO\cdot}$ is derived in this way from more than one parent ROX, e.g., RONO or ROOR, then the presumption that the reaction proceeds by fission is very strong.

6. Chemiluminescence

Under certain conditions, reactions involving alkoxyl radicals are accompanied by blue chemiluminescence. This has been observed for the following systems: $\underline{CH_3ONO_2}$ (107, 108), $\underline{CH_3ONO_2 + O_2}$ (94), $CH_3ONO_2 + NO$ (109), $\underline{CH_3ONO_2 + NO_2}$ (109); $C_2H_5ONO_2$ (107, 108), $\underline{C_2H_5ONO_2 + O_2}$ (94); $C_3H_7ONO_2$ (95), CH_3ONO (90, 93, 94), $CH_3ONO + O_2$ (94); $CH_3ONO + NO_2$ (90); C_2H_5ONO (90), iso-C_3H_7ONO (90); $C_2H_5OOC_2H_5$ (112, 188), iso-$C_3H_7OOC_3H_7$-iso (113), $\underline{CH_3OCH_3 + O_2}$ (254). Some of these reactions (underscored above) have been examined by spectroscopy; they give the spectrum of excited formaldehyde. The formation of excited formaldehyde in decomposition (also see Section VII,A) is associated with the presence of the $CH_3O\cdot$ radical. Where this radical is absent (e.g., in isomeric CH_3NO_2), this type of chemiluminescence is not found.

B. DECOMPOSITIONS INVOLVING ALKOXYL RADICALS

1. Peroxide family

The peroxide family consists of the dialkyl peroxides (ROOR), the hydroperoxides (ROOH), and the peroxy esters. Of these, the dialkyl peroxides and the hydroperoxides have been studied most extensively. Decomposition of

TABLE 2

Activation energies in the decomposition reactions of nitrites, nitrates, and peroxides

Compound	Activation Energies of Decomposition		
	Values reported	References	Value adopted
	kcal. mole^{-1}		*kcal. mole*$^{-1}$
Nitrites:			
CH_3ONO	36.4	(258)	36.4
C_2H_5ONO	34.3 ± 3.37 ± 1	(225, 258)	37.7
n-C_3H_7ONO	37.65; 34.7	(258)	37.7
sec-C_3H_7ONO	37.0	(258)	37.0
n-C_4H_9ONO	37.0	(258)	37.0
Nitrates:			
CH_3ONO_2	39.5	(7)	38.4
$C_2H_5ONO_2$	32 ± 5; 34.6	(202, 271)	36.4
	36.6 to 41.2	(157)	
	38.8; 39.5	(1, 64)	
n-$C_3H_7ONO_2$	38.9	(202)	37.6
Peroxides:			
CH_3OOCH_3	35.3; 36.9	(111a, 270)	36
$C_2H_5OOC_2H_5$	29.9; 31.3; 31.6; 31.7	(111a, 113, 221, 265)	34
tert-$C_4H_9OOC_2H_5$	36.0	(265)	36.0
$C_3H_7OOC_3H_7$	36.5	(112)	36.5
tert-$C_4H_9OOC_4H_9$-*tert*	34 ± 2 and 36 ± 1; 38	(180, 23)	
	36 to 40; 37; 38	(163, 32, 130)	37.0
	38.6; 39.5	(214, 217)	
tert-$C_5H_{11}OOC_5H_{11}$-*tert*	39.1	(217)	37.0
$C_6H_5(CH_3)_2COOC(CH_3)_2C_6H_5$	34.5 ± 0.5	(12)	34.5
Hydroperoxides:			
tert-$C_5H_{11}OOH$	39.1	(22)	39.1
n-$C_8H_{17}OOH$	26.9	(272)	39
2,4,4-Trimethylpentyl-2 hydroperoxide	26.9	(272)	39
cyclo-$C_6H_{11}OOH$	34.0	(66)	39
$C_6H_5(CH_3)_2COOH$	29.0, 30.4	(272, 69)	39
Tetralyl hydroperoxide	29.0	(272)	39
Decalyl hydroperoxide	32.1	(272)	39
sec-Decalyl hydroperoxide	31.7	(272)	39
Cumene hydroperoxide	−30.4	(69)	39

peroxides may be achieved by any of three methods: pyrolysis, photolysis, and catalysis by redox mechanisms. All three classes have been studied kinetically and by product analysis. In all cases there is no doubt that oxygen–oxygen bond fission occurs, resulting in the formation of alkoxyl radicals.

Kinetic data are available for many peroxides. Table 2 gives activation energies for peroxides, and it is seen that within any class the activation energy is constant within experimental error. This, together with constant preëxponential factors, indicates that the rate-determining step is oxygen–oxygen bond fission, yielding alkoxyl radicals.

Decomposition products of dialkyl peroxides are readily interpreted in terms of the reactions of alkoxyl radical intermediates; in the case of hydroperoxides and peroxy esters other reactive intermediates are also involved. The following list gives some typical examples of peroxide decompositions which are readily interpreted in terms of alkoxyl radical formation; other examples are given in Section IV.

Dialkyl peroxides: ethyl (15, 112), isopropyl (113), *tert*-butyl (60, 217, 218), triphenylmethoxyl (293).

Hydroperoxides: methyl (168), ethyl (113), isopropyl (113), *tert*-butyl (165, 171), *tert*-amyl (173), cyclohexyl (66), triphenylmethoxyl (295).

Peroxy carbonates: methyl, ethyl, isopropyl, isobutyl, *n*-butyl (181).

In many instances when the peroxide has been decomposed in the presence of a hydrogen donor the alcohol has been isolated in large quantities. These reactions are considered in Section IV,B.

2. The nitrite and nitrate families

It is well established that the first and rate-determining step in the thermal decomposition of both nitrite and nitrate esters is the fission of the oxygen–oxygen bond, generating a free alkoxyl radical.

Within either the nitrite or the nitrate series the activation energy is fairly constant (see table 2), thus indicating that the bond-breaking step occurs in each. The reactions are homogeneous and the preëxponential factors approximately equal to 10^{13}. Further evidence is provided for oxygen–nitrogen bond fission when the decompositions of nitrites and nitrates are inhibited by nitric oxide or nitrogen dioxide and by the exchange reactions occurring during the decomposition of nitrates in the presence of nitric oxide, which results in some nitrite being formed, and during the decomposition of nitrites in the presence of nitrogen dioxide, which results in nitrate being formed. This is explained by the following reactions:

Nitrites: $\mathrm{RONO} \rightarrow \mathrm{RO}\cdot + \mathrm{NO}$

$\mathrm{RO}\cdot + \text{(added) } \mathrm{NO} \rightarrow \mathrm{RONO}$ inhibition

$\mathrm{RO}\cdot + \text{(added) } \mathrm{NO_2} \rightarrow \mathrm{RONO_2}$ nitrate formation

This has been found for methyl nitrite (106), ethyl nitrite (206, 207) [but not inhibition (157)], isopropyl nitrite (157), and *tert*-butyl nitrite (158).

Nitrates: $\mathrm{RONO_2} \rightarrow \mathrm{RO}\cdot + \mathrm{NO_2}$

$\mathrm{RO}\cdot + \text{(added) } \mathrm{NO_2} \rightarrow \mathrm{RONO_2}$ inhibition

$\mathrm{RO}\cdot + \text{(added) } \mathrm{NO} \rightarrow \mathrm{RONO}$ nitrite formation

This has been studied in ethyl nitrate (155, 156, 202, 203, 206, 208) and *n*-propyl nitrate (160).

The chemical evidence that alkoxyl radicals play the role of intermediates in the decomposition of nitrites and nitrates is quite extensive. The more stable alkoxyl radicals generated in the decomposition of lower or phenyl-substituted nitrites retain their RO structure. Alcohol formation has been reported for the following nitrites decomposed in the presence of hydrogen donors: methyl nitrite (106), ethyl nitrite (106), *tert*-butyl nitrite (306), cyclohexyl nitrite (105), and benzyl nitrite (100).

The decomposition products of nitrates are more difficult to interpret, because the $\mathrm{NO_2}$ species accompanying the alkoxyl radical is extremely reactive and extensive and secondary reactions occur. However, nitrate esters have been studied (23) in pressed pellets of potassium bromide and the reaction followed by infrared methods. The evidence indicates that the initial step is nitrogen–oxygen bond fission. At high temperatures and especially with unstable radicals decomposition occurs and alkyl radicals are produced. Thus in the decomposition of nitrites, nitroso compounds characterize the formation of intermediate alkoxyl radicals. In the case of the nitrates, nitro compounds are produced.

A chemiluminescent mode of decomposition is characteristic of both the nitrites and the nitrates. Gray (89) has shown that the two equimolecular mixtures of [nitrite + NO_2] and [nitrate + NO] have the same critical-pressure limits of both chemiluminescence and explosion. That is, the two mixtures behave at high temperatures as if they were identical, an equivalence which can readily be explained by the production of alkoxyl radicals in each.

3. Hypochlorites

The kinetics of the decomposition of alkyl hypochlorites have not been studied, but extensive analysis has been made of the decomposition products. The following have been studied: methyl hypochlorite (44), ethyl hypochlorite (44), *tert*-butyl hypochlorite (305). The products include ketones, aldehydes, alkyl chloride, and hydrochloric acid. These products are in accord with the formation of an alkoxyl radical and its subsequent further reaction.

$$\mathrm{ROCl} \rightarrow \mathrm{RO}\cdot + \mathrm{Cl}\cdot$$

From 1-methyl cyclopentyl hypochlorite (36a) the ketone $CH_3CO(CH_2)_3Cl$ is formed.

4. Hyponitrites

Decomposition of hyponitrites results in the formation of alkoxyl radicals:

$$\mathrm{RCH_2ON{=}NOCH_2R} \rightarrow \mathrm{2RCH_2O}\cdot + \mathrm{N_2}$$

This is analogous to the formation of alkyl radicals from azo compounds. The decomposition products of hyponitrites are readily interpreted if the above mode of decomposition occurs. Hyponitrites that have been studied are ethyl, *n*-propyl, *n*-butyl, and benzyl (200). The decomposition of benzyl hyponitrite has been shown to initiate polymerization (114), presumably owing to the formation of alkoxyl radicals:

5. Esters of organic acids

Esters may decompose to give alkoxyl radicals:

$$\mathrm{RCOOR} \rightarrow \mathrm{RCO}\cdot + \mathrm{RO}\cdot$$

This reaction occurs in the photochemical decomposition of esters in the gas phase, providing a clear-cut way of generating alkoxyl radicals at any required temperature. Evidence for this reaction is based on kinetic studies and extensive analysis of the products. Esters that have been studied in this way are: methyl acetate (298), methyl-d_3 acetate (299, 300), and *n*-propyl and isopropyl propionates (301).

Esters also decompose to give alkoxyl radicals when irradiated by high-energy sources (47).

A source of alkoxyl radicals that has not yet been used is the photolysis of the carbonate esters; the hydrocarbon analog is of course the generation of alkyl radicals by the photolysis of ketones.

6. Ethers

Decomposition of ethers may proceed through an alkoxyl intermediate:

$$\mathrm{ROR'} \rightarrow \mathrm{R} + \mathrm{OR'}$$

This reaction occurs only at high temperatures and the alkoxyl radical rapidly decomposes. At 1000°C. no methoxyl radicals can be detected in the pyrolysis of dimethyl ether (162). At lower temperatures alkoxyl radicals are generated, but the reaction is complicated by an intramolecular reaction (72, 73).

7. Alcohols

Decomposition of alcohols occurs by an intramolecular mechanism. The mercury-photosensitized decomposition results in the loss of an α-hydrogen atom in the case of methanol (205) and alkoxyl radicals are not generated.

C. GENERATION OF FREE ALKOXYL RADICALS

In order to generate an alkoxyl radical so that its behavior may be studied, compounds of the general formula ROX, which decompose by fission of the RO—X bond, are required. Such molecules are given in table 1.

If the radical is to be generated thermally, the RO—X bond should be weak, so that the radical is readily liberated and its reactions may be followed. This consideration excludes some familiar derivatives of ROX such as the alcohols, metal alkoxides, ethers, acetals, and simple organic esters, because the temperatures needed for their decomposition bring too many other reactions into play for the role of the alkoxyl radical to be readily disentangled. There remain (*1*) the esters of inorganic oxyacids, i.e., hypochlorites, hyponitrites, nitrites, and nitrates, and (*2*) the peroxide family, i.e., dialkyl peroxides, hydroperoxides, esters of peroxides, and peroxycarbamates.

If the alkoxyl radical is to be generated by photolysis the condition that the RO—X bond should be weak is no longer necessary. Moreover, since light which is conveniently strongly absorbed has much more energy than the minimum necessary to break weak RO—X bonds, photolytic methods are more successful in systems such as organic esters, ethers, and acetals with stronger RO—X bonds which are also less susceptible to thermal study. The methods available for different classes of compounds are given in table 1, together with comments on their applicability and experimental difficulties.

III. THERMOCHEMISTRY OF FREE ALKOXYL RADICALS

Consistent thermal data comprising heats of reaction and enthalpies of formation of alkoxyl radicals must form the basis of any attempt to systematize their chemistry. Such data are of the greatest value in making choices between plausible kinetic schemes offering alternative interpretations of complex reactions.

The key to thermochemistry is the knowledge of the enthalpy of formation of the alkoxyl radical. This section deals with the alternative routes leading to enthalpies of formation. Their merits and the validity of the primary data which they employ are assessed. Bond-dissociation energies in oxygenated compounds such as ethers are derived, and the thermochemistry of the principal classes of the reactions of alkoxyl radicals is outlined.

Because of their instability, free radicals cannot usually be examined directly. Their enthalpies of formation must be derived indirectly by measurements on reactions in which they take part. Because of the complexities involved neither spectroscopic methods nor electron-impact methods (see Appendix II) have been applied successfully. Thus great reliance must be placed on other methods which provide the necessary data.

A. ALTERNATIVE ROUTES TO THE ENTHALPIES OF FORMATION OF FREE ALKOXYL RADICALS

Three principal paths lead towards the enthalpies of formation of free alkoxyl radicals. The first proceeds by the union of thermodynamic and kinetic data and combines heats of formation determined calorimetrically with activation energies derived from kinetic measurements and identified with dissociation energies of particular bonds.

The second path makes use of the constancy (91) of the oxygen–hydrogen bond-dissociation energy $D(\mathrm{RO—H})$ in the alcohols, which has been found always to be near 102 kcal. mole^{-1}. This offers a reliable guide to the heat of formation, $\Delta H_{\mathrm{RO}\cdot}$, of the alkoxyl radical when the heat of formation of the gaseous alcohol ROH is known. This path is most valuable for complex alkoxyl radicals for which the heats of formation of the parent alcohols have often been determined.

The third path makes more systematic use of existing thermochemical data and employs the group-energy term $\Delta H(\text{—O}\cdot)$. Study (70) of arithmetical relations between experimental values of, for example, the heats of combustion of organic compounds shows that the heat of formation, $\Delta H_f(\mathrm{M})$, of a molecule may be expressed as the sum of a set of terms each characteristic of a constituent group in the molecule; recently the same approach has been extended (70) successfully to heats of formation of free radicals.

In principle the first path, proceeding via activation energies and heats of formation, with its firm basis in experiment and the possibility that it offers of making several independent estimates of the enthalpies of formation of each alkoxyl radical, is the best. However, in assessing merit, two further aspects peculiar to the higher members of the alkoxyl series must be considered. First, that it is rare for there to be sufficient experimental data for more than one independent value of the heat of formation, $\Delta H_{\mathrm{RO}\cdot}$, to be derived. Second, because of the high molecular weights of the parent compounds ROX, failure to determine heats of combustion with great precision leads to considerable errors in the numerically smaller heats of formation. These are the reasons which contribute to the relative importance of the two other paths to the heats of formation.

B. ENTHALPIES OF FORMATION DERIVED FROM ACTIVATION ENERGIES

Peroxides, hydroperoxides, nitrate esters, nitrite esters, hyponitrite esters, and hypochlorite esters, all of the general formula ROX, satisfy the critical requirement that, under appropriate circumstances, their decomposition is controlled by the fission of the bond RO—X. This offers a means of relating the heat of formation of the radical RO• to measurable quantities, by identifying the enthalpy increase ΔH and the activation energy E. In the reversible reaction

$$\mathrm{RO{-}X} \underset{E_2}{\overset{E_1}{\rightleftharpoons}} \mathrm{RO}\bullet + \mathrm{X}\bullet \qquad \Delta H$$

if the enthalpies of formation of the gaseous species involved are ΔH_{ROX}, ΔH_{X}, and $\Delta H_{\mathrm{RO}\cdot}$, we have:

$$\Delta H_{\mathrm{RO}\cdot} = \Delta H_{\mathrm{ROX}} - \Delta H_{\mathrm{X}} + \Delta H \tag{1}$$

If the various quantities on the right-hand side of equation 1 can be measured, $\Delta H_{\mathrm{RO}\cdot}$ may be found. This relation is the basis of the kinetic method of determining bond-dissociation energies developed by Szwarc (266). He sets $\Delta H = E_1 - E_2$, the difference between the two experimental activation energies of forward and reverse reactions. When X is itself a free radical, there is considerable support for setting $E_2 = 0$ and writing

$$\Delta H_{\mathrm{RO}\cdot} = \Delta H_{\mathrm{ROX}} - \Delta H_{\mathrm{X}} + E_1 \tag{2}$$

thus reducing the number of unknowns from four to three. Discussion of the assumptions of this method are given elsewhere (53, 267).

This method is particularly suitable for nitrates, peroxides, and hydroperoxides. In the case of peroxides, where fission leads to the formation of two alkoxyl radicals, equation 2 reduces to:

$$\Delta H_{\mathrm{RO}\cdot} = \tfrac{1}{2}(E_1 + \Delta H_{\mathrm{ROOR}}) \tag{3}$$

1. *Activation energies of decomposition*

The principal compounds that have been studied are the nitrites, nitrates, peroxides, and hydroperoxides. Activation energies of their first-order decomposition are listed in table 2. The hydroperoxide decompositions are frequently less simple than peroxide decomposition and correspondingly greater care has to be exercised in identifying E values with bond-dissociation energies. In general, the experimental values of E for hydroperoxide decompositions in solution are lower limits for bond energy, and for gas-phase calculations $E = 39$ kcal. mole^{-1} is adopted.

2. *Standard enthalpies of formation (in the gaseous state) of* ROX

Values of standard enthalpies of formation of the molecules ROX in the gaseous state at 25°C. are needed to complete the experimental data. The values reported

TABLE 3

Enthalpies of formation of molecules* ROX *in their standard state and the heats of vaporization*

Molecule (state)	Enthalpy of Formation in Standard State		Heat of Vaporization†	
	kcal. mole⁻¹		*kcal. mole⁻¹*	
Nitrites:				
Methyl	−20.33	(*14*)‡	5.4	(*14*)‡
Ethyl	−30.50	(*14*)	6.3	(*14*)
n-Propyl	−38.01	(*14*)	6.75	
Nitrates:				
Methyl	−37.2	(*102*, 296)	8.15	(*184*)
Ethyl	−45.51	(*96*)	8.67	(*96*, 98, 121)
n-Propyl	−51.27	(*96*)	9.70	(*96*)
Isopropyl	−54.92	(*96*)	9.27	(*96*)
Peroxides:				
Diethyl	−54.6	(*307*)	7.3	(*27*)
Di-*tert*-butyl	−94.3	(*217*)	9.6	(*217*)
Hydroperoxides:				
tert-Butyl	−52.3(g)	(*21*)		(*61*)
n-Hexyl-1-	−71.64	(*215*)	*13*	
n-Hexyl-2-	−74.14	(*215*)	*13*	
n-Hexyl-3-	−72.94	(*215*)	*13*	
n-Heptyl-1-	−82.0	(*215*)	*16*	
n-Heptyl-2-	−82.8	(*215*)	*16*	
n-Heptyl-3-	−82.9	(*215*)	*16*	
n-Heptyl-4-	−79.8	(*215*)	*16*	
Cyclohexyl	−65.3	(30)	*13*	
1-Methylcyclohexyl	−79.0	(30)	*16*	
Decalyl-9- (s)	−83.2	(30)	*17*	
Tetralyl-1- (s)	−44.6	(*30*, 215)	20	

* The values are taken from the italicized references.

† Italicized heats of vaporization are estimated values (106).

‡ References are given in parentheses.

for most peroxides come from bomb calorimetry and are based (186) on $\Delta H_f(\text{CO}_2, \text{g}) = 94.05$ kcal. mole⁻¹ and $\Delta H_f(\text{H}_2\text{O}, \text{liq}) = 68.32$ kcal. mole⁻¹. They refer to the liquid state and require latent heat data for conversion to heats of formation in the gaseous state. Direct calorimetric measurements of latent heats are the exception, and usually values are derived via the Clapeyron equation from vapor pressure data or by the application of empirical rules (142). Stull (264) has made a useful compilation of vapor pressure data. In table 3 the enthalpies of formation in the standard state (l, liquid; s, solid) are given, together with latent heats of vaporization (indirect values in parentheses).

C. ENTHALPIES OF FORMATION DERIVED FROM THE PARENT ALCOHOLS

If the enthalpy of formation of the parent alcohol ΔH_{ROH} is known and the dissociation energy $D(\text{RO—H})$ of the oxygen–hydrogen bond is 102 kcal. mole⁻¹, we have:

$$\text{ROH} \longrightarrow \text{RO} + \text{H} \qquad \Delta H = 102 \text{ kcal. mole}^{-1}$$

$$\Delta H_{\text{RO}\cdot}(\text{kcal. mole}^{-1}) = \Delta H_{\text{ROH}} - \Delta H_{\text{H}} + 102 = \Delta H_{\text{ROH}} + 50$$

The equations above show the essential similarity of this calculation to that used when the first path (Section III,A) is followed.

TABLE 4

Enthalpies of formation of molecules ROH *in their standard state and the heats of vaporization*

Alcohol (state)	Enthalpy of Formation in Standard State		Heat of Vaporization*	
	kcal. mole^{-1}		*kcal. mole^{-1}*	
Aliphatic alcohols:				
Methyl	−57.02	(236)†	8.94	(236)†
Ethyl	−66.36	(236)	10.11	(236)
n-Propyl	−73.25	(236)	11.05	(236)
sec-Propyl	−76.18	(198)	10.62	(195)
n-Butyl	−79.7	(236)	11.8	(236)
Isobutyl	−80.2	(91)	10.8	
sec-Butyl	−82.0	(91)	10.5	
tert-Butyl	−87.9	(217)	10.89	(195)
1-Pentanol	−85.9	(236)	12.43	(236)
1-Hexanol	−92	(236)	13.05	(236)
1-Heptanol	−97.9	(236)	13.55	(236)
1-Octanol	−103.7	(236)	14.00	(236)
1-Nonanol	−109.45	(236)	14.4	(236)
Alicyclic alcohols:				
Cyclopentanol	−71.8	(190)	11.7	(226)
Cyclohexanol	−83.5	(190)	11.7	(226)
cis-2-Methylcyclohexanol	−96.1	(249	*12*	(106)
Cycloheptanol	−94	(250)	*13*	(106)
Decalin-9-ol	−106	(30)	*18*	(106)
Aryl alcohols:				
Benzyl (l)	−38.49	(197, 215)	16.1	(264)
Diphenylcarbinol (l)	−25.16	(197)	*18*	(106)
Triphenylcarbinol (s)	+0.80	(197)	*20*	(106)
Tetralin-1-ol (l)	−68	(30)	*20*	(106)

* Estimated values are italicized.

† References are given in parentheses.

The necessary data are the standard enthalpies of formation of the gaseous alcohols, and in nearly every case these are derived from the heats of combustion of the liquids combined with latent heats of vaporization. Enthalpies of formation are given in table 4.

D. ENTHALPIES OF FORMATION DERIVED FROM GROUP-ENERGY TERMS

The principle may be expressed by the equation:

$$\Delta H_f(\mathrm{M}) = \Sigma_i \, \Delta H(g_i)$$

where $\Delta H(g_i)$ is that part of the enthalpy of formation assigned to the i^{th} group.

When the concept is extended (71) to free radicals the heat of formation of a free radical R• is expressed as:

$$\Delta H_f(\mathrm{R}\bullet) = \Sigma_i \, \Delta H(g_i) + \Delta H(g)$$

where the term $\Delta H(g)$ represents the contribution of that atom or group to which the unpaired electron is formally assigned; in the alkoxyl radicals it is the oxygen atom. The value for the group-energy term $\Delta H(\text{—O}\bullet)$ has been found (91) to be 6.5 kcal. mole^{-1}, and this value may be used in conjunction with values appropriate to the other groups in the radical to obtain the enthalpies of formation required.

$$\Delta H_f(\mathrm{RO}\bullet) \text{ (kcal. mole}^{-1}\text{)} = 6.5 + \Sigma \, \Delta H(g_i)$$

For conjugated molecules, ions, or radicals another term (ϵ, the resonance energy) is added to the right-hand side of the equation. Values of ϵ appropriate to various groups (such as the C_6 aromatic ring) have also been tabulated. They are adequate for the radicals derived from aryl-substituted methanols. *Extra* delocalization energy, due to interaction of the free electron of the terminal atom with the "aromatic" electrons of the ring, is expected to be no larger in, e.g., the benzyloxyl radical, $C_6H_5CH_2O\cdot$, than in the α-phenylethyl radical, $C_6H_5CH_2CH_2\cdot$. This is of course not true of the radicals derived from phenol or vinyl alcohol (not considered here), which should show the stability associated with the benzyl or allyl radicals. The numerical values of the group-energy terms for the contribution of various groups to the enthalpy of formation in the gaseous state are as follows:

$$-CH_3,\ -10.1;\ >CH_2,\ -5.0;\ -\overset{|}{\underset{|}{C}}H,\ -1.1;\ -\overset{|}{\underset{|}{C}}-,\ +0.8;\ \text{five-membered ring, } 5.7;$$

$$\text{six-membered ring, } -0.5;\ -OH\ \text{(primary)},\ -41.9;\ -OH\ \text{(secondary)},\ 45.7;\ -OH\ \text{(tertiary)},\ 49.2$$

In later parts of this section group-energy terms are again utilized in discussing the thermochemistry of the reactions of alkoxyl radicals; there, group-energy terms for ketones, double bonds, etc. are employed. The appropriate values are:

$$-CHO,\ -33.9;\ >C{=}O,\ -30.6;\ -O-,\ -27.2;\ >C{=}CH_2,\ 16.9;$$

$$>C{=}C<,\ 24.6;\ -CH_2\cdot,\ 34.0;\ >CH\cdot,\ 35;\ -\overset{|}{\underset{|}{C}}\cdot,\ 33.0$$

Group-energy terms for aromatic or conjugated molecules are:

$$\overset{\searrow}{\underset{\swarrow}{}}CH,\ 3.3;\ \overset{\searrow}{\underset{\swarrow}{}}C-,\ 5.6;\ \leftrightarrow CH_2,\ 10.0;\ \leftrightarrow C\overset{/H}{\underset{\backslash}{}},\ 12.0$$

E. ENTHALPIES OF FORMATION OF THE ALKOXYL RADICALS

The standard heats of formation ($\Delta H_{RO\cdot}$) in the gaseous state at 25°C. derived in the preceding sections are listed in table 5, which sets out the results of the different methods of obtaining $\Delta H_{RO\cdot}$. For comparison, table 5 includes the enthalpy of formation of the hydroxyl radical, the zeroth member of the series. The approximations inherent in the methods, together with experimental errors in the values of activation energies and enthalpies of formation, limit the accuracy of $\Delta H_{RO\cdot}$ values in the first half of the table to $\pm$ 2 kcal. mole^{-1}; the relative errors may be smaller. The reliability of the various methods is greatest where there is duplication of data, e.g., heats of formation. Errors of several kilocalories per mole are to be expected in the absolute values of $\Delta H_{RO\cdot}$ for the higher members, primarily because of errors in measurements of heats of combustion of higher hydroperoxides and alcohols. However, although the values

TABLE 5

Enthalpies of formation of the alkoxyl radicals

Values refer to gaseous state at 25°C.

Radical and Class	Source of Data used for ΔH_{RO}.			Adopted Value
	Activation energies	Alcohol	Group-energy term	
	kcal. mole^{-1}	*kcal. mole*$^{-1}$	*kcal. mole*$^{-1}$	*kcal. mole*$^{-1}$
Hydroxyl:				
HO•	—	—	—	9
Lower aliphatic radicals:				
CH_3O•	−0.5	2.0	−3.6	−0.5
C_2H_5O•	−8.5	−6.3	−8.6	−8.5
n-C_3H_7O•	−13	−12.2	−13.6	−13.0
sec-C_3H_7O•	−15	−15.9	−14.7	−15
n-C_4H_9O•	−17	−17.9	−18.6	−17
iso-C_4H_9O•	−18	−19.4	−19.8	−18
sec-C_4H_9O•	−20	−21.5	−19.8	−20
tert-C_4H_9O•	−25	−27.0	−24.9	−25
Higher aliphatic radicals:				
n-C_5H_{11}-1-O•	—	−23.4	−23.5	−23.5
tert-$C_5H_{11}O$•	−30.0	—	−28.0	−29.0
n-C_6H_{13}-1-O•	−29.0	−28.9	−28.1	−29.0
n-C_6H_{13}-2-O•	−31	—	−29.7	−30
n-C_6H_{13}-3-O•	−30	—	−34.0	−32
n-C_7H_{15}-1-O•	−36.0	—	−34.0	−35
n-C_7H_{15}-2-O•	−37.0	—	—	−37
n-C_7H_{15}-3-O•	−37.0	—	−35	−36
n-C_7H_{15}-4-O•	−34.0	—	—	−34
n-C_8H_{17}-1-O•	—	−39.7	−38.5	−38
n-C_9H_{19}-1-O•	—	−45.0	−43.5	−44
Alicyclic radicals:				
cyclo-C_5H_9O•	—	−10.8	−8.4	−10
cyclo-$C_6H_{11}O$•	−22	−22.8	−19.5	−21
cyclo-$C_7H_{13}O$•	—	−31.0	−24.5	−27
1-Methylcyclo-C_6H_{11}-1-O•	−33.0	—	−28.0	−30
Decalyl-9-O•	−33.0	−38.0	−34.0	−34
Aryl-substituted radicals:				
$C_6H_5CH_2O$•	—	27.5	23.7	25
$C_6H_5CHCH_3O$•	—	—	17.5	17
$C_6H_5C(CH_3)_2O$•	—	—	9.2	9
$(C_6H_5)_2CHO$•	—	43	49.6	46
$(C_6H_5)_3CO$•	—	71	69.7	70
Tetral-1-O•	6.0	2.0	14.6	8
Radicals containing a hetero atom:				
Tetrahydropyran-1-O•	—	—	−41.7	−42
$CH_3OCH_2CH_2O$•	—	—	−40.7	−41

derived for the higher members from group-energy terms may be absolutely in error, their relative errors are not likely to be serious.

F. BOND-DISSOCIATION ENERGIES IN OXYGEN COMPOUNDS

The enthalpies of formation of the alkoxyl radicals may be used to give values for the dissociation energies of the hydrogen–oxygen bond in the alcohols and of the carbon–oxygen bond in the alkoxyl radicals themselves and in the aliphatic, aromatic, and cyclic ethers. Mean values of oxygen bond-dissociation energies in some acetals and formals are also reported.

In recent years, values for the heats of formation of the lower acyl radicals

TABLE 6

Bond-dissociation energies in alcohols and alkoxyl radicals

R	H	CH_3	C_2H_5	n-C_3H_7	*sec*-C_3H_7	n-C_4H_9	iso-C_4H_9	*sec*-C_4H_9	*tert*-C_4H_9
D(RO—H).......	120	100	99	101	100	103	103	103	104
D(R—O•)........	101	91	92	94	94	95			89

(R′CO, where R′ = C_nH_{2n+1} with $n = 0, 1, 2$) have been derived, and these are here combined with heats of formation of alkoxyl radicals (RO•) to determine the carbon–oxygen bond-dissociation energies D(R′CO—OR) in the esters. The carbon–oxygen bond-dissociation energies in the carboxylic acids D(RCO—OH) are determined in a similar manner. The auxiliary thermochemical data used are listed in Appendix I.

1. Hydrogen–oxygen bond in the alcohols D(RO—H)

The equation ROH → RO• + H• has the form molecule → radical + atom. Thus

$$D(\text{RO—H}) = \Delta H_f(\text{RO}\cdot) + \Delta H_f(\text{H}\cdot) - \Delta H_f(\text{ROH})$$

enabling estimates of the dissociation energy to be made. The values obtained are given in table 6. The hydrogen–oxygen bond strength does not appear to vary significantly from one alcohol to another but lies close to 102 kcal. mole^{-1}. The hydrogen–carbon bond strength is probably somewhat less, since when methanol undergoes mercury-photosensitized reaction (205), ethylene glycol is formed:

$$CH_3OH \xrightarrow[h\nu]{Hg} \cdot CH_2OH$$

$$2(\cdot CH_2OH) \longrightarrow HOCH_2CH_2OH$$

2. The carbon–oxygen links in the alcohols D(R—OH) *and in the alkoxyl radicals D*(RO•)

The two bond dissociations have similar equations:

$$ROH \rightarrow R\cdot + \cdot OH \quad \text{and} \quad RO\cdot \rightarrow R\cdot + \cdot O\cdot$$

molecule → radical + radical radical → radical + atom

and require comparable amounts of energy, about 90 and 95 kcal. mole^{-1}, respectively. The bond strengths are given in table 6.

3. The carbon–oxygen link in the ethers D(RO—R′)

The bond dissociation is:

$$ROR' \rightarrow R\cdot + \cdot OR'$$

molecule radical + radical

TABLE 7

The carbon–oxygen bond-dissociation energy in the ethers

Ether	Radicals Formed	Bond-dissociation Energy	Ether	Radicals Formed	Bond-dissociation Energy
		kcal. mole^{-1}			*kcal. mole*$^{-1}$
Aliphatic ethers:			*Cyclic ethers:*		
CH_3OCH_3	$CH_3\bullet + CH_3O\bullet$	77	Propylene oxide	$\bullet OCH_2\bullet CHCH_3$	50.5
$C_2H_5OC_2H_5$	$C_2H_5\bullet + C_2H_5O\bullet$	77		$\bullet CH_2CH(O\bullet)CH_3$	51.5
$C_3H_7OC_3H_7$	$C_3H_7\bullet + C_3H_7O\bullet$	78.4	Ethylene oxide	$\bullet CH_2CH_2O\bullet$	47.7
$C_3H_5OCH_3$	$C_3H_5\bullet + CH_3O\bullet$	53	Trimethylene oxide	$\bullet CH_2(CH_2)_2O\bullet$	—
Aryl ethers:			Tetrahydrofuran	$\bullet CH_2(CH_2)_3O\bullet$	68.6
$C_6H_5OCH_3$	$C_6H_5\bullet + CH_3O\bullet$	85.9	Tetrahydropyran	$\bullet CH_2(CH_2)_4O\bullet$	71.2
$C_6H_5OC_2H_3$	$C_6H_5\bullet + C_2H_5O\bullet$	85.3			
$C_6H_5OC_6H_5$	$C_6H_5\bullet + C_6H_5O\bullet$	$\bar{D} = 90$			

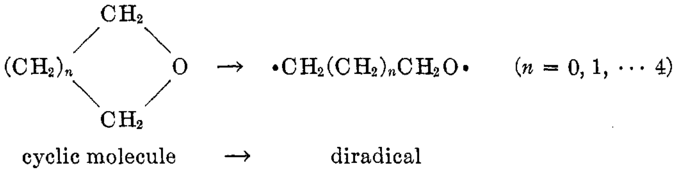
Although heats of formation of a number of alkyl and aryl radicals are now known (see Appendix I), thermochemical data for the parent ethers are very limited. Bond-dissociation energies have been derived for four aliphatic ethers: methyl allyl ether, methyl phenyl ether (anisole), ethyl phenyl ether, and diphenyl ether. Values obtained are given in table 7.

The bond-dissociation energies for the aliphatic ethers are close to 77 kcal. mole^{-1}. When the radical R is stabilized by resonance the bond energy is expected to drop abruptly; in allyl methyl ether this fall is unmistakable, though its magnitude may be in some error as it depends on an old value for the heat of combustion of the ether. A similar pattern is to be expected in benzyl methyl ether, for which the heat of formation is not yet known.

In the aryl alkyl ethers the oxygen bond to the aromatic ring is stronger, 87 or 84 kcal. mole^{-1}, according to the value (40, 51, 266) adopted for $\Delta H(C_6H_5\bullet)$. In the diaryl ethers such as diphenyl ether only a *mean* bond-dissociation energy, $\bar{D}$, can be derived until $\Delta H(C_6H_5O\bullet)$ is known; $\bar{D}$ is 97 (or 94) kcal. mole^{-1}.

4. Carbon–oxygen bonds in the cyclic ethers and epoxides

When the oxygen atom attached to the bond to be broken is part of a ring, bond fission yields a diradical. For a typical polymethylene oxide the process may be represented thus:



It is to be expected that the enthalpy requirements will be least when the ring is small and breaking it relieves strain but will increase with increasing ring size to the normal value found for $D(C—O)$ in the ethers. The values for $D(C—O)$ in table 7 confirm this expectation. The enthalpies of formation on which they are based are taken from recent experimental data (see Appendix I) for the molecules and from group-energy term calculations for the diradicals.

TABLE 8

The carbon–oxygen bond-dissociation energy in the organic esters

Ester	$D(\mathrm{RCO—OR'})$	Ester	$D(\mathrm{RCO—OR'})$	Ester	$D(\mathrm{RCO—OR'})$
	kcal. mole⁻¹		*kcal. mole⁻¹*		*kcal. mole⁻¹*
Methyl acetate......	87.7	Isopropyl acetate....	86.9	Methyl formate......	82.7
Ethyl acetate.......	87.1	*n*-Butyl acetate......	90.9	Methyl benzoate....	86
n-Propyl acetate....	88.8	Isobutyl acetate.....	92.1	Ethyl benzoate......	85.6

5. *Carbon–oxygen bonds in the organic esters*

The equation is

$$\begin{array}{ccccc} \mathrm{R'CO—OR} & \rightarrow & \mathrm{R'CO\cdot} & + & \mathrm{RO\cdot} \\ \text{molecule} & \rightarrow & \text{acyl radical} & + & \text{alkyl radical} \end{array}$$

and until recently insufficient data were available for enthalpy changes in the above reaction to be calculated. Values for the heats of formation of the formyl, acetyl, and benzoyl radicals are now available from a number of sources, and it is possible to evaluate $D(\mathrm{RCO—OR})$ for the esters of formic, acetic, and benzoic acids. Values obtained are given in table 8. Data used in compiling the table are listed in Appendix I. It is found that in the acetates $D(\mathrm{CH_3CO—OR})$ lies always near the same mean value of 88.9 kcal. mole^{-1}, and the value found in the two benzoates is not significantly different. This value is markedly greater than in the ethers, and though this bond is broken in ester photolysis, it is sufficiently strong for thermal decomposition to proceed by intramolecular elimination rather than bond fission. Inconsistencies and errors of the order of 2 kcal. mole^{-1} have been detected (106) in some of the thermal data (142, 241) for esters, and these limit the accuracy of the bond-dissociation energies.

6. *Carbon–oxygen bonds in formals, acetals, and ortho esters*

A group of oxygenated compounds not previously considered comprises dimethyl ether, methylal, methyl orthoformate, and methyl orthocarbonate; these belong to the series $\mathrm{CH_{4-n}(OCH_3)_n}$ with n varying from 1 to 4. Closely related are the members of the series $\mathrm{(CH_3)_{4-n}C(OCH_3)_n}$ with n varying from 1 to 4; viz., methyl *tert*-butyl ether, 2,2-dimethoxypropane (the ketal of methanol and acetone), methyl orthoacetate, and methyl orthocarbonate. Mean values, $\bar{D}(\mathrm{C—O})$, can be obtained for the members of the series with known enthalpies of formation. The values found are: in methylal, $\mathrm{CH_2(OCH_3)_2}$, $\bar{D} = 87$ kcal. mole^{-1}; in methyl orthoformate, $\mathrm{CH(OCH_3)_3}$, $\bar{D} = 86$ kcal. mole^{-1}. In the cyclic formal 1,3-dioxane ("trimethylene formal"), $\bar{D}$ is ca. 90 kcal. mole^{-1}.

In the "normal" carbonates $\mathrm{(CH_3O)_2CO}$ and $\mathrm{(C_2H_5O)_2CO}$ the lower values of the mean bond-dissociation energies reflect the stability of the carbon monoxide produced simultaneously:

$$\mathrm{(RO)_2CO \rightarrow 2RO\cdot + CO} \qquad \Delta H = 2\bar{D}$$

For R = $\mathrm{CH_3}$, $\bar{D}$ is 55 kcal. mole^{-1}; for R = $\mathrm{C_2H_5}$, $\bar{D}$ is 57 kcal. mole^{-1}.

G. THERMOCHEMISTRY OF REACTIONS OF ALKOXYL RADICALS

The reactions undergone by alkoxyl radicals may be assigned to six principal groups: (*1*) association with other radicals, (*2*) addition to unsaturated compounds, (*3*) hydrogen abstraction, (*4*) disproportionation, (*5*) rearrangement, and (*6*) decomposition. In classes 1 to 4 the essential structure of the alkoxyl radical is preserved, while in classes 5 and 6 it is lost. In this section the thermochemistry of the different classes of reaction is outlined, and in Section VI the contribution of thermochemistry to reactivity is discussed.

1. Association with other radicals

Association with other radicals occurs with the liberation of the dissociation energy of the bond formed:

$$\begin{array}{ccccccc} RO\cdot & + & X\cdot & \rightarrow & ROX & & \Delta H = -D(RO-X) \\ \text{radical} & + & \text{radical} & \rightarrow & \text{molecule} & & \end{array}$$

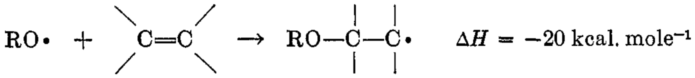
Dimerization to form the symmetrical parent peroxide is an interesting special case:

$$RO\cdot + RO\cdot \rightarrow ROOR \qquad \Delta H = D(RO-OR)$$

In the list which follows average values of $D(RO-X)$ are indicated for classes of compounds and not for particular molecules. Bond-dissociation energies, $D(RO-X)$, in kcal. mole^{-1}: alcohols (RO—H), 102; ethers (RO—R), 75 to 80; organic esters (RCO—OR), 85 to 90; nitrites and nitrates (RO—NO and RO—NO_2), 35 to 40; peroxides (RO—OR), 35 to 40; hydroperoxides (RO—OH), 35 to 40.

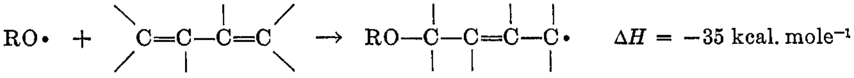
2. Addition to unsaturated compounds

Addition of an alkoxyl radical to an ethylenic double bond is exothermic. For methoxyl radicals adding to ethylene or propylene, ΔH is -15 or -20 kcal. mole^{-1}; opening the double bond is more than compensated by forming the new oxygen–carbon link.



$$RO\cdot + \rangle C{=}C\langle \rightarrow RO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \qquad \Delta H = -20\ \text{kcal. mole}^{-1}$$

Addition to a conjugated diene is considerably more exothermic because the delocalization energy in the allyl-like radical produced is considerably greater than in the parent diene:



$$RO\cdot + \rangle C{=}\overset{|}{C}-\underset{|}{C}{=}C\langle \rightarrow RO-\overset{|}{\underset{|}{C}}-\underset{|}{C}{=}\overset{|}{C}-\overset{|}{\underset{|}{C}}\cdot \qquad \Delta H = -35\ \text{kcal. mole}^{-1}$$

When methoxyl radicals add to butadiene, $-\Delta H$ is about 35 kcal. mole^{-1}. The best authenticated examples are afforded by those additions to conjugated systems which, followed by dimerization, yield the unsaturated diether as product:

$$C_6H_5(CH_3)_2CO\cdot + CH_2{=}CHCH{=}CH_2 \xrightarrow[\text{(2) dimerization}]{\text{(1) addition}} [C_6H_5(CH_3)_2COCH_2CH{=}CHCH_2-]_2$$

3. Hydrogen abstraction

Hydrogen abstraction is a characteristic mode of reaction; by its means the alkoxyl radical, satisfying its free valency at the expense of another molecule, forms the alcohol. In the gas phase, the exothermicity is the amount by which the strength of the hydrogen–oxygen bond formed exceeds that of the bond which is broken. In a solvent, this difference requires correction for the (usually small) heats of solution involved:

$$RO\cdot + XH \rightarrow ROH + X\cdot \qquad -\Delta H = D(RO—H) - D(X—H)$$

For any given hydrogen donor XH, the near-constancy of 102 kcal. mole^{-1} for D(RO—H) implies nearly equal exothermicity for hydrogen abstraction by a variety of alkoxyl radicals. For any particular alkoxyl radical, hydrogen abstraction will be most exothermic from those donors which have the weakest X—H bonds and the pattern of donor reactivity already familiar in alkyl radical reactions may be expected to occur. Typical values of enthalpy changes on hydrogen abstraction in the gas phase are listed in table 9; they are based on D(RO—H) = 102 kcal. mole^{-1} and on values of D(X—H) derived from thermal data in Appendix I.

Internal hydrogen abstraction, e.g., from a distant methylene group in a long-chain alkoxyl radical, is discussed in Section III,5 with other examples of rearrangement.

4. Disproportionation

Alkoxyl radicals from primary or secondary alcohols may react in pairs to form the alcohol and the corresponding carbonyl derivative:

$$\underset{\text{radical + radical}}{2RR'CHO\cdot} \rightarrow \underset{\text{molecule}}{RR'CHOH} + \underset{\text{molecule}}{RR'CO} \qquad \Delta H = -87.5\ \text{kcal. mole}^{-1}$$

TABLE 9

Enthalpy changes in hydrogen-abstraction reactions based on D(RO—H) = ca. 102 kcal.mole^{-1}

$$RO\cdot + XH \rightarrow ROH + X\cdot \qquad \Delta H$$

Class of C—H Bond in Donor XH	Example	D(X—H)	Exothermicity $-\Delta H$
			kcal. mole^{-1}
Aliphatic, saturated:			
Primary	Methane	101	1
	Ethane	96	6
Secondary	Propane	94	8
Tertiary	Isobutane	89	13
Unsaturated molecules:			
Primary	Propylene	77	25
	Toluene	77	25
Secondary	Cyclohexene	73	27
Tertiary	Cumene	74	26
Aldehydic bonds:			
Aliphatic	Acetaldehyde	80	22
Aromatic	Benzaldehyde	78	24

The reaction is very exothermic because a strong oxygen–hydrogen bond is formed and the breaking of the weak carbon–hydrogen bond is accompanied by the change from C—O to C═O.

Enthalpies of reaction derived from the heats of formation of alkoxyl radicals and of the appropriate alcohols and carbonyl compounds (Appendix I) are listed for some typical alkoxyl radicals. They lie near the value of 84 to 87 kcal. mole^{-1} derived solely from group-energy terms:

	Aliphatic		Alicyclic	Aryl-substituted
Radical.............	*sec*-$C_3H_7O\bullet$	*n*-C_5H_{11}-1-$O\bullet$	cyclo-$C_6H_{11}O\bullet$	$C_6H_5CH_2O\bullet$
Enthalpy change....	−83	−90	−85.4	−83.6

Closely allied to disproportionation is the loss of an α-hydrogen atom to any attacking radical, not necessarily another alkoxyl radical:

$$RR'CHO\bullet + R''\bullet \rightarrow RR'CO + R''H$$

This hydrogen abstraction is a competitor of radical–radical association (see Section III,G,1) and is favored by the weakness of the bond joining the α-hydrogen atom to carbon (see Section III,G,6), which is so much more pronounced in the alkoxyl radical than in its parent molecule RR'CHOX.

5. *Rearrangement (isomerization)*

Rearrangement, replacing an oxygen radical by a carbon radical, involves a basic change in structure:

$$\underset{\text{O-radical}}{RR'R''CO\bullet} \rightarrow \underset{\text{C-radical}}{RR'\dot{C}OR''} \qquad \Delta H = D(R\text{—}C) - D(R\text{—}O)$$

The enthalpy change is the difference in C—R and O—R bond-dissociation energies, and the electronegativities of oxygen and carbon suggest that the rearrangement should be exothermic and may be expected to occur readily. In fact, rearrangements in thermal reactions appear to be confined to the triply aryl-substituted alkoxyl radicals (of which triphenylmethoxyl, $(C_6H_5)_3CO\bullet$, is the simplest example); these rearranged radicals yield the pinacol ethers by dimerization.

$$\underset{\text{Triphenylmethoxyl}}{(C_6H_5)_3CO\bullet} \rightarrow (C_6H_5)_2\dot{C}OC_6H_5 \rightarrow \underset{\substack{\text{Diphenyl ether of}\\ \text{benzophenone pinacol}}}{[(C_6H_5)_2\overset{|}{C}OC_6H_5]_2}$$

Instead of an alkyl group, a hydrogen atom may move from the α-carbon atom to the oxygen and produce an exactly parallel change to the examples above, e.g.:

$$CH_3O\bullet \rightarrow \bullet CH_2OH \rightarrow (\text{—}CH_2OH)_2$$

TABLE 10

Thermochemistry of rearrangement of alkoxyl radicals

$$RR'R''CO\cdot \rightarrow RR'\cdot COR'' \qquad \Delta H = D(R''—C) - D(R''—O)$$

Type of Rearrangement	Parent O-radical	Resulting C-radical	ΔH
			kcal. mole⁻¹
Hydrogen-atom migration from α-carbon atom.....	$CH_3O\cdot$	$\cdot CH_2OH$	−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-$C_6H_{10}OH$	−14
Hydrogen-atom migration from distant CH_2 group.	$RCH_2(CH_2)_nO\cdot$	$RCHCH_2OH$	−8.5
Alkyl-group migration...........................	$CH_3CH_2O\cdot$	$\cdot CH_2OCH_3$	5
	$(CH_3)_2CHO\cdot$	$\cdot CH(CH_3)OCH_3$	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 expansion....................................	cyclo-$C_6H_{11}O\cdot$		4
Aryl-group migration.............................	$(C_6H_5)_3CO\cdot$	$\cdot C(C_6H_5)_2OC_6H_5$	*−1.5**
	$C_6H_5(CH_3)_2CO\cdot$	$\cdot C(CH_3)_2OC_6H_5$	−1.5

* Figures in italics are derived from group-energy terms.

If the hydrogen atom migrates to the —O• of the radical from a position other than the α-carbon atom, the change may be regarded as an internal hydrogen abstraction. Such rearrangements are expected from longer-chain derivatives:

$$RCH_2(CH_2)_nCH_2O\cdot \rightarrow RCH(CH_2)_nCH_2OH \qquad \Delta H = -8.5 \text{ kcal. mole}^{-1}$$

Similarly, an analog of disproportionation may occur when the alkoxyl radical is a diradical; then, for example, a terminal $\cdot CH_2—$ group may abstract the hydrogen of a primary or secondary alkoxyl group.

$$\cdot CH_2(CH_2)_nCH_2O\cdot \rightarrow CH_3(CH_2)_nCHO \qquad \Delta H = -79 \text{ kcal. mole}^{-1}$$

Enthalpies of formation of "carbinyl" (i.e., 1-hydroxyalkyl and its derivatives) radicals have been derived both from electron-impact data (59) and by calculation (71); from these figures (see Appendix II) it is possible to calculate the heats of rearrangement given in table 10.

6. Decomposition by hydrogen-atom elimination

By loss of an α-hydrogen atom, alkoxyl radicals derived from primary or secondary alcohols yield aldehydes or ketones, respectively:

	ΔH
	kcal. mole⁻¹
$RCH_2O\cdot \rightarrow RCHO + H$	17
$RR'CHO\cdot \rightarrow RR'CO + H$	16
radical $\rightarrow$ molecule + atom	

Some of the energy needed to sever the hydrogen–carbon link is supplied by the simultaneous formation of the carbonyl double bond. Enthalpies of reaction listed here are derived from thermochemical data for the carbonyl compounds (see Appendix I) and from the radical thermochemistry established here.

Enthalpy requirements of hydrogen-atom elimination

Primary Alkoxyls	kcal. mole^{-1}	Secondary Alkoxyls	kcal. mole^{-1}
$CH_3O\cdot$	25	$(CH_3)_2CHO\cdot$	18
$C_2H_5O\cdot$	21	$(C_6H_5)_2CHO\cdot$	19.7
n-$C_3H_7O\cdot$	19	cyclo-$C_6H_{11}O\cdot$	16
n-$C_4H_9O\cdot$	23	Tetralyl-1-$O\cdot$	16
$C_6H_5CH_2O\cdot$	15.9	$RR'CHO\cdot$ in general	16
$RCH_2O\cdot$ in general	16.7		

Methoxyl occupies a special place among primary alkoxyl groups, and hydrogen abstraction from it requires 25 kcal. mole^{-1}. From other primary radicals, hydrogen abstraction requires 16.7 kcal. mole^{-1}, and from the secondary radicals, 16.0 kcal. mole^{-1}. These figures show the increasing ease of loss of a hydrogen atom in the progression methoxyl, primary alkoxyl, secondary alkoxyl. Cyclic alkoxyl radicals and aryl-substituted radicals appear to take their place in the appropriate general families.

7. Decomposition by carbon-radical elimination

A more profound change in structure occurs when an alkoxyl radical yields a carbonyl compound by loss of an alkyl or aryl radical. Decomposition of primary alkoxyl radicals by this mode can occur in only one way, but alternative paths may be available for secondary and tertiary radicals. If R, R′, and R″ are alkyl or aryl radicals we have:

$$\begin{array}{llcccl} \text{Primary} & RCH_2O\cdot & \rightarrow & R\cdot & + & CH_2O \\ \text{Secondary} & RR'CHO\cdot & \rightarrow & R\cdot & + & R'CHO \text{ or } R'\cdot + RCHO \\ \text{Tertiary} & RR'R''CO\cdot & \rightarrow & R\cdot & + & R'R''CO, \text{etc.} \\ & \text{radical} & \rightarrow & \text{radical} & + & \text{molecule} \end{array}$$

When the alkoxyl radical is derived from an alicyclic alcohol, carbon–carbon bond fission in the ring may occur and lead not to two separate free radicals but to a single radical according to path 2 below:

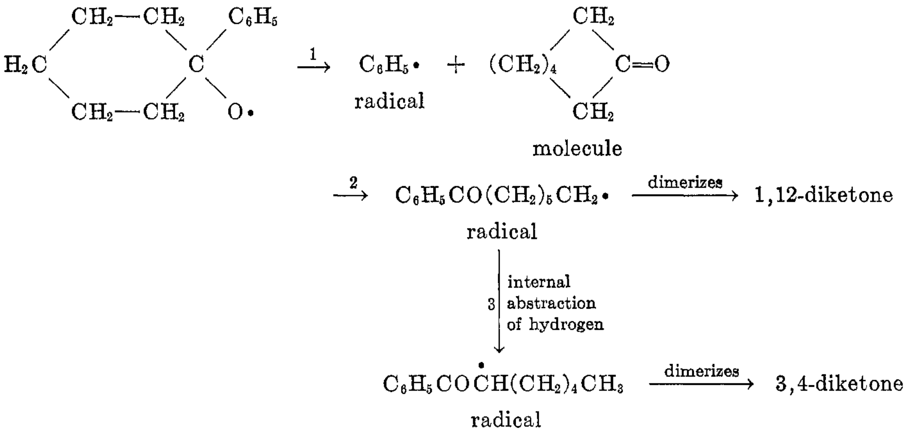


TABLE 11

Enthalpy requirements of alkoxyl decomposition via carbon–carbon bond fission

Alkoxyl radical → alkyl radical + carbonyl compound ΔH

Parent Alkoxyl	Alkyl Radical	Carbonyl Compound	ΔH
			kcal. mole^{-1}
Primary derivatives:			
Ethoxyl	CH_3	CH_2O	13
n-Propoxyl	C_2H_5	CH_2O	10
n-Butoxyl	*n*-C_3H_7	CH_2O	11
n-Amoxyl	*n*-C_4H_9	CH_2O	14.8
tert-Butylmethoxyl	*tert*-C_4H_9	CH_2O	4.8
Benzyloxyl	C_6H_5	CH_2O	16.3
Secondary derivatives:			
Isopropoxyl	CH_3	CH_3CHO	6.4
sec-Butoxyl	CH_3	C_2H_5CHO	5.1
	C_2H_5	CH_3CHO	4.4
n-Pent-3-oxyl	C_2H_5	C_2H_5CHO	3.1
2-Methoxybut-3-oxyl	CH_3	*sec*-C_3H_7CHO	3.4
	C_3H_7	CH_3CHO	3
n-Hex-3-oxyl	C_2H_3	C_3H_7CHO	3.5
	C_3H_7	C_2H_5CHO	6
α-Phenylethoxyl	CH_3	C_6H_5CHO	6.8
	C_6H_5	CH_3CHO	11.7
Diphenylmethoxyl	C_6H_5	C_6H_5CHO	12.2
Tertiary derivatives:			
tert-Butoxyl	CH_3	$(CH_3)_2CO$	4.7
tert-Amoxyl	CH_3	$CH_3COC_2H_5$	1.1
	C_2H_5	$(CH_3)_2CO$	0.7
3-Methyl-*n*-pent-3-oxyl	CH_3	$(C_2H_5)_2CO$	0.5
	C_2H_5	$CH_3COC_2H_5$	−0.5
3-Ethyl-*n*-pent-3-oxyl(triethylmethoxyl)	C_2H_5	$(C_2H_5)_2CO$	−2.5
Diphenylethoxyl	CH_3	$(C_6H_5)_2CO$	2
	C_6H_5	$C_6H_5COCH_3$	7
Triphenylmethoxyl	C_6H_5	$(C_6H_5)_2CO$	7.9
Cyclic derivatives:			
Cyclohexoxyl	Ring fission	$\bullet CH_2(CH_2)_4CHO$	1.1
1-Methylcyclohexoxyl	Ring fission	$\bullet CH_2(CH_2)_4COCH_3$	1.4
	CH_3	Cyclohexanone	2.9
1-Phenylcyclohexoxyl	C_6H_5	Cyclohexanone	9
	Ring fission	$\bullet CH_2(CH_2)_4COC_6H_5$	5.5
Decalyl-9-oxyl	1,9-Bond fission		−0.7
	9,10-Bond fission		0.2

This mode of reaction (path 2), though strictly a rearrangement, is more conveniently dealt with here. A subsequent rearrangement (path 3) to an *n*-alkyl ketone is considered with the disproportionation reactions which it closely resembles.

Enthalpy requirements of carbon–carbon bond fission are again partly met by electronic rearrangements accompanying the formation of a carbonyl (double) bond. The thermochemistry of these reactions is set out in table 11, which is arranged according to the class of radical involved and which deals with primary, secondary, and tertiary families successively, treating wholly aliphatic radicals before aryl-substituted and alicyclic ones.

IV. THE REACTIONS OF FREE ALKOXYL RADICALS

In this section the known reactions of the simpler alkoxyl radicals are assembled and described. The arrangement is basically the same as that used in the survey (Section III,G) of the thermochemistry of alkoxyl radicals: association (including dimerization), hydrogen abstraction, addition, rearrangement, decomposition by carbon–hydrogen or by carbon–carbon bond fission, disproportionation, and metathesis. Within each of these eight classes, reactions are discussed radical by radical. Where they do not introduce novel features (for example, hydrogen abstractions by aryl-substituted radicals) the reactions of complex radicals are included here. This arrangement permits easy reference to the reaction thermochemistry and ready comparison with analogous alkyl radicals. Thermochemistry, analogy, and this systematic study of the simple radicals in isolation, together with a reaction-kinetics analysis of the classes of reaction, form the foundation of Section V, where the principles governing the relative importance of different modes of reaction are established and of Section VII where these principles are applied.

In the same manner this section prepares the ground for the interpretation of complex alkoxyl radicals. Identical principles apply and the same classification is possible for convenience and conciseness; however, complex radicals are grouped together in Section VI.

A. ASSOCIATION WITH RADICALS, INCLUDING DIMERIZATION

Alkoxyl radicals may associate with free atoms or radicals to form molecules. The reaction is:

$$\begin{array}{ccccccc} \mathrm{RO}\cdot & + & \cdot\mathrm{X} & \rightarrow & \mathrm{ROX} & & \Delta H = -D(\mathrm{RO{-}X}) \\ \text{radical} & + & \text{radical} & \rightarrow & \text{molecule} & & \end{array}$$

This reaction is analogous to that of free alkyl radicals:

$$RCH_2\cdot + \cdot CH_3 \rightarrow RCH_2CH_3$$

An amount of energy $D(\mathrm{RO{-}X})$ in kilocalories per mole must be removed to stabilize the nascent molecule, and in this type of reaction the presence of a third body is of great importance. At low pressures a fall-off in the rate of association is expected.

The best opportunities for this reaction to occur are provided when the species $X\cdot$ does not dimerize readily itself and is present in considerable excess. For this reason, nitric oxide and nitrogen dioxide, which behave as free radicals and may easily be maintained in excess, are the most readily investigated; association with other radicals has also been observed.

When an alkoxyl radical collides with another radical there are two possibilities. One is association, the subject of this section; the other is disproportionation, which will be treated later (Section IV,G). The dimerization of alkoxyl radicals is a particular type of association. Few instances are known, the reason being that temperatures are often too high for the oxygen–oxygen bond to be formed.

1. Methoxyl radicals

Methoxyl radicals associate with free alkyl radicals. In the thermal decomposition of methyl *tert*-amyl peroxide at 195°C. (216), the free radicals produced include methoxyl and ethyl and association to methyl ethyl ether occurs. Dimerization of the ethyl radicals occurs to a greater extent than association with methoxyl.

$$CH_3O\cdot + C_2H_5\cdot \rightarrow CH_3OC_2H_5$$

Association of $CH_3O\cdot$ with nitric oxide occurs, producing methyl nitrite. Pyrolysis of dimethyl peroxide in the presence of nitric oxide gives a 100 per cent yield of methyl nitrite (204) by the reaction:

$$CH_3O\cdot + NO \rightarrow CH_3ONO$$

The same reaction has been suggested to account for the production of methyl nitrite in the oxidation of acetaldehyde by nitrogen dioxide (34) and to explain (106) some kinetic features of the decomposition of methyl nitrite. In the pyrolysis of methyl nitrite, the first-order rate constant falls off below 50 mm. of mercury. This is the reverse of association and thus third-body requirements of the association may be expected to make themselves felt at this pressure (243).

A similar association reaction with nitrogen dioxide also occurs in the oxidation of acetaldehyde by nitrogen dioxide, resulting in the formation of methyl nitrate (34).

$$CH_3O\cdot + NO_2 \rightarrow CH_3ONO_2$$

2. Trideuteromethoxyl radicals

Trideuteromethoxyl radicals have been shown to associate with methyl and trideuteromethyl radicals (297, 298, 299, 300). The radicals were produced by the photochemical decomposition of methyl and deutero-substituted acetates at relatively low temperatures (≃60°C.). The reactions are 1 and 3 below:

$$CH_3\cdot + CD_3O\cdot \xrightarrow{k_1} CH_3OCD_3 \quad (1)$$

$$\xrightarrow{k_2} CH_3D + CD_2O \quad (2)$$

$$CD_3\cdot + CD_3O\cdot \xrightarrow{k_3} CD_3OCD_3 \quad (3)$$

$$\xrightarrow{k_4} CD_4 + CD_2O \quad (4)$$

A study of competition between the reactions yields that the ratios are independent of temperature. This suggests that the difference in activation energies is zero; probably the individual activation energies are also zero.

3. Ethoxyl radicals

Methyl ethyl ether has been detected by a mass-spectrometer as a product of pyrolysis of ethyl *tert*-butyl peroxide at 195°C. (239). This peroxide acts as a source of ethoxyl and methyl radicals, which undergo association. Ethoxyl radicals have also been shown (297) to react with ethyl radicals in the low-temperature photolysis of ethyl propionate, where the products include diethyl ether (297).

Ethoxyl radicals react with nitric oxide. Decomposition of diethyl peroxide by photolysis (131, 177) or by pyrolysis (156) in the presence of nitric oxide yields ethyl nitrite. The association reaction is:

$$C_2H_5O\cdot + NO \rightarrow C_2H_5ONO$$

Association with nitrogen dioxide also occurs. This is the reverse of the initial step in the decomposition of ethyl nitrite (201, 202), and evidence for it comes from the retardation of decomposition by added nitrogen dioxide (203, 207, 208). In addition, ethyl nitrate is produced when ethyl nitrite is pyrolyzed in the presence of nitric oxide, because association with nitrogen dioxide competes with that with nitric oxide. Association with nitrogen dioxide is said to be more rapid than with nitric oxide (206).

4. *n-Propoxyl radicals*

The thermal decomposition of *n*-propyl nitrate at 181°C. in the gas phase results in the formation of some *n*-propyl nitrite by association of *n*-propoxyl radicals with nitric oxide. The yield is increased by added nitric oxide (157, 159).

5. *tert-Butoxyl radicals*

Photolysis of *tert*-butyl peroxide (185) produces *tert*-butoxyl radicals and methyl radicals, which associate to give the *tert*-butyl methyl ether.

The association reaction with nitric oxide has been shown to occur. In the decomposition of di-*tert*-butyl peroxide at 160°C. in the presence of nitric oxide *tert*-butyl nitrite is formed (26, 217). The rate of association relative to the decomposition of alkoxyl radicals has been measured (26).

$$(CH_3)_3CO\cdot \xrightarrow{k_1} (CH_3)_2CO + CH_3\cdot$$

$$(CH_3)_3CO\cdot + NO \xrightarrow{k_2} (CH_3)_3CONO$$

It was found that the relationship between the activation energies of both reactions is $E_{(\text{fission})} = 13.2 \pm 2.4 - E_{(\text{association})}$ kcal. mole^{-1}. If $E_{(\text{association})} = 0$, then $E_{(\text{fission})} = 13.2 \pm 2.4$ kcal. mole^{-1}. Other reactions of *tert*-butoxyl radicals have been studied (see Section IV,F) and the best value for $E_{(\text{fission})}$ is 13 kcal. mole^{-1}.

Additional evidence for this reaction comes from a study of the retardation of the pyrolysis of *tert*-butyl nitrite by nitric oxide (157) and the formation of *tert*-butyl nitrite in the pyrolysis of *tert*-butyl nitrate (159).

6. *Cyclohexoxyl radicals*

In the nitration of cyclohexane with nitrogen dioxide at 100°C. both cyclohexoxyl and cyclohexyl radicals are produced, and association to give dicyclohexyl ether occurs (277).

7. *Tetrahydropyranoxyl radicals*

Pyrolysis of *tert*-butyl-2-tetrahydropyran peroxide at 230°C. generates both tetrahydropyranoxyl radicals and free methyl radicals, and association of these radicals occurs (171).

8. α-Cumyloxyl radicals

Decomposition of cumene hydroperoxide at 100°C. in certain solvents or alone gives high yields of the dimer (161). This is the only known example of the dimerization of alkoxyl radicals.

$$2C_6H_5(CH_3)_2CO\cdot \rightarrow C_6H_5(CH_3)_2COOC(CH_3)_2C_6H_5$$

B. ABSTRACTION OF HYDROGEN BY ALKOXYL RADICALS

When alkoxyl radicals are generated in the presence of a molecule containing a weakly bonded hydrogen atom, then this hydrogen may be abstracted. The enthalpy decrease of this reaction is the difference in the RO—X and X—H bond-dissociation energies. The reaction is:

$$\begin{array}{ccccccccc} RO\cdot & + & HX & \rightarrow & ROH & + & X\cdot & \xrightarrow{\text{dimerizes}} & X—X \\ \text{radical} & + & \text{molecule} & \rightarrow & \text{molecule} & + & \text{radical} & & \end{array}$$

It has been suggested (181) that three factors contribute to the *P* and *E* parameters of the velocity constant:

(*1*) *Energy factor:* This is dependent on the strengths of the X—H bond to be broken and of the RO—H bond to be formed; the quantity is (roughly) constant for all alkoxyl radicals.

(*2*) *Steric factor:* The accessibility of the hydrogen atom in the donor molecule may make some contribution to the activation energy.

(*3*) *Repulsion factor:* Substituents in the donor molecule may repel approaching alkoxyl radicals, and this will influence the rate of reaction.

Hydrogen-abstraction reactions reflect the stability of the alkoxyl radical. For instance, the methoxyl radical gives high yields of the alcohol in both gas- and liquid-phase reactions and even at quite high temperatures. In direct contrast to this is the *tert*-butoxyl radical, which decomposes readily above room temperature.

Hydrogen-abstraction reactions of alkoxyl radicals are very similar to those of alkyl radicals. The analogous reaction is:

$$RCH_2\cdot + HX \rightarrow RCH_2—H + X\cdot$$

When a hydrogen atom is abstracted from a molecule the most weakly attached hydrogen atom is removed. The order of ease of removal is tertiary hydrogen > secondary hydrogen > primary hydrogen. If the hydrogen atom is activated by a double bond, a phenyl group, or a carbonyl group, it is removed even more easily. For methyl radicals the relative rate of hydrogen abstraction is given below.

Velocity constants [$10^{-6}k$ *per hydrogen atom at 182°C.* (*mole*$^{-1}$ *cc. sec.*$^{-1}$)] *for the reactions of methyl radicals with various classes of compounds*

Class of compound	Alkane	Alkene	Alkyne	Ether	Alcohol
Type of hydrogen atom:					
Primary	0.3	5	7	1.5	2
Secondary	2.1	17	38	—	10
Tertiary	15	53	—	19	31

The same relative ease of hydrogen abstraction may be expected to hold true for alkoxyl radicals, and from the limited evidence available this is found to be so.

Hydrogen abstraction by aryl-substituted alkoxyl radicals presents further complications. Decomposition or rearrangement of the radical occurs in preference to the hydrogen-abstraction reaction. This suggests that aryloxyl free radicals are less stable, but in addition they may also be less effective at hydrogen abstraction than simpler alkoxyl radicals. This is analogous to the aryl-substituted alkyl radicals, which are known to have low preëxponential factors for hydrogen-abstraction reactions.

1. Methoxyl radical

This relatively stable alkoxyl radical will in the presence of a good hydrogen donor give high yields of methanol. Hydrogen abstraction from many donors has been investigated. In the gas phase methoxyl radicals generated in the pyrolysis at 200°C. of *tert*-butyl methyl peroxide have been shown (22, 239) to abstract hydrogen atoms from cyclohexene. Hydrogen abstraction from cyclohexene (204) and isopropylbenzene (106) has been observed for methoxyl radicals generated in the pyrolysis of methyl nitrite. Numerous hydrocarbons have been used in the liquid phase (181). From diphenylmethane there is 70 per cent hydrogen abstraction at 118°C. and greater than 80 per cent from diphenylethane at 115°C.; from *p*-cymene there is 73.3 per cent abstraction at 110°C. and 68.4 per cent at 155°C.; from toluene there is 100 per cent abstraction at 110°C. Hydrogen abstraction from other substrates has also been suggested. In the photolysis (298) of methyl acetate there is hydrogen abstraction from the parent acetate; for this process the activation energy is 5 to 6 kcal. mole^{-1}. Hydrogen abstraction from dimethyl ether occurs during its pyrolysis; a suggested (224) activation energy is 15 to 20 kcal. mole^{-1}. Methoxyl radicals generated in the pyrolysis of dimethyl peroxide (269) abstract hydrogen atoms from methanol and formaldehyde; the difference in activation energies for the two reactions is 3 kcal. mole^{-1}.

2. Ethoxyl radical

The stability of this radical is only slightly less than that of the methoxyl radical, but decomposition occurs readily at high temperatures. Hydrogen abstraction from many donors has been studied. Cyclohexene has been used in the gas phase (22, 239) and a 65 per cent yield of ethanol obtained; this is a lower yield than for the methoxyl radical under identical conditions and reflects the lower stability of this radical.

Ethoxyl radicals abstract hydrogen atoms from ethyl acetate in the gas phase (297). The activation energy for this reaction was obtained in terms of the activation energy for decomposition of the ethoxyl radical by carbon–carbon bond fission; the value of $E_{(\text{fission})} - E_{(\text{abstraction})}$ is 7 to 8 kcal. mole^{-1}. If $E_{(\text{fission})} =$ 21 kcal. mole^{-1} (see Section IV,F) then $E_{(\text{abstraction})} =$ 13 to 14 kcal. mole^{-1}. This value is high and a lower value of 8 to 12 kcal. mole^{-1} has been suggested (247).

Hydrogen abstraction from ethyl nitrite may occur at moderately high temperatures. It has been estimated (225) that $E_{(\text{abstraction})} - E_{(\text{fission})} = 16$ kcal. mole^{-1}; if $E_{(\text{fission})} = 21$ kcal. mole^{-1}, then $E_{(\text{abstraction})} = 37$ kcal. mole^{-1}. This value is improbably high despite the fact that ethoxyl radicals generated from diethyl peroxide do not abstract hydrogen atoms from ethyl nitrite at 181°C. (156).

In the liquid phase many reactions have been studied. One source of ethoxyl radicals that has been used is ethyl peroxydicarbonate (181). Hydrogen abstraction from isopropylbenzene occurs, giving a 78 per cent yield of the alcohol at 125°C., whereas there is only 3 per cent hydrogen abstraction from trimethylacetic acid because it has no weakly attached hydrogen atoms. Ethoxyl radicals generated in the pyrolysis of nitrite have been shown to abstract hydrogen atoms from liquid isopropylbenzene, giving a 70–100 per cent yield of the alcohol (106).

Hydrogen abstractions by ethoxyl radicals are more affected by the steric effects of nearby groups in the donor molecule than are abstractions by methyl radicals (182); one such group that hinders hydrogen abstraction is the carbomethoxyl group.

3. α-Chloroethoxyl radical

These radicals have been generated in the liquid phase by decomposition of the dialkyl peroxycarbonate (181); they abstract a hydrogen atom from isopropylbenzene to the same extent as ethoxyl radicals do under identical conditions.

4. n-Propoxyl radical

Thermal decomposition of gaseous *n*-propyl nitrite (157) and di-*n*-propyl peroxide (112) leads to the formation of small quantities of the alcohol. This may be due to hydrogen abstraction from the parent molecule, but there is no direct evidence for it. *n*-Propoxyl radicals have been shown to abstract a hydrogen atom from liquid isopropylbenzene to give a 60 per cent yield of alcohol (181).

5. Isopropoxyl radical

The thermal decomposition of isopropyl nitrite at 181°C. in the gas phase yields 2-propanol as a minor product. It has been suggested (160) that the isopropoxyl radical abstracts a hydrogen atom from one of the other species present —acetone, acetaldehyde, or NOH—but it may also arise from disproportionation. Hydrogen abstraction from cyclohexene occurs in the gas phase at 195°C., the products including 19 per cent of the alcohol (22, 239). In the liquid phase isopropoxyl radicals abstract hydrogen from isopropylbenzene, giving a 50 per cent yield at 143°C.; from pivalic acid, which contains no weakly attached hydrogen atom, there is only 6 per cent abstraction at 140°C. (181).

6. n-Butoxyl radical

This radical abstracts a hydrogen atom from cyclohexene at 195°C. in the gas phase; the products include 30 per cent of 1-butanol (22, 239). In the liquid phase at 130°C. abstraction from isopropylbenzene occurs, giving yields of the alcohol greater than 60 per cent (181).

7. *Isobutoxyl radical*

This radical abstracts a hydrogen atom from cyclohexene at 195°C. in the gas phase, giving a 6 per cent yield of the alcohol (22, 239). From isopropylbenzene in the liquid phase at 130°C. an 83 per cent yield of alcohol is obtained (181).

8. *tert-Butoxyl radical*

The most convenient source of this radical is di-*tert*-butylperoxide. At temperatures required to break the oxygen–oxygen bond, the butoxyl radical is also unstable in the gaseous state and its own decomposition occurs. Thus, hydrogen-abstraction reactions only occur to any large extent when the radical is generated at low temperatures in the liquid phase.

Hydrocarbons: Hydrogen abstraction from hydrocarbons gives *tert*-butyl alcohol and a free alkyl radical, which dimerizes. In many cases both the alcohol and the dimer have been isolated, providing conclusive proof that this reaction occurs. Dimers have been isolated (67) among the products of hydrogen-abstraction reactions from toluene, ethylbenzene, isopropylbenzene, and cyclohexane.

The rate of hydrogen abstraction relative to the rate of decomposition has been measured (302). Hydrogen abstraction from methyl hydrocarbon groups is the most difficult. If the relative rate of 1.0 is given to the hydrogen-abstraction reaction from *tert*-butylbenzene, then the rate for toluene and for mesitylene is 12.2 and for 1-methylnaphthalene it is 17. Activation energies of abstraction and decomposition have been compared; if the value for decomposition of the *tert*-butoxyl radical is 15 kcal. mole^{-1} (see Section IV,A), then activation energies of abstraction from *tert*-butylbenzene are 1 to 7 kcal. mole^{-1} (218) and from toluene, 3.7 kcal. mole^{-1} (33).

Secondary hydrogen atoms are abstracted more easily than are primary groups. In the liquid phase *n*-hexadecane has a relative rate of 7 (to *tert*-butylbenzene). If the hydrogen atom is activated by a cyclohexyl or benzyl group the rate is increased; in cyclohexane the relative rate is 20, while in tetralin it is 76. The activation energy for abstraction of a hydrogen atom from tetralin is 4 kcal. mole^{-1} (33).

The α-methylene groups in nonvinylic olefins are extremely reactive and hydrogen abstraction readily occurs. Typical are cyclohexene, 2,6-dimethyl-2,6-octadiene, digeranyl, and rubber (67).

Hydrogen atoms are lost most easily from tertiary groups. The relative rates (*tert*-butylbenzene = 1) are high for such compounds. For example, 2,3-dimethylpentane has a value of 28, and if the hydrogen is activated it is even more reactive as in the case of isopropylbenzene (relative rate = 51). The activation energy for abstraction from isopropylbenzene is small (218), about 0 to 1 kcal. mole^{-1}. Values of $E_{(\text{abstraction})}$ for other hydrocarbons containing a tertiary group are larger; known values (33) are: 8 kcal. mole^{-1} for 2,3-dimethylbutane, 7 for 2,5-dimethylhexane, and 7.5 for methylcyclohexane.

Ketones and aldehydes: Hydrogen abstraction from ketones occurs quite readily, since the α-methylene group is activated by the carbonyl group. Both *tert*-butyl alcohol and the keto dimer have been isolated from methyl ethyl ketone and cyclohexane (176).

From aldehydes the aldehydic hydrogen is removed and the radical produced dimerizes or decomposes. This reaction has been observed with acetaldehyde (283), benzaldehyde (238), and acrolein (283).

Other donors: The hydrogen-abstraction reaction from ethylenimine has been studied in the gas phase at 130–154°C. (32). The products are *tert*-butyl alcohol, ethylene, and nitrogen, consistent with the reaction:

$$tert\text{-}C_4H_9O\cdot + (CH_2)_2NH \rightarrow tert\text{-}C_4H_9OH + (CH_2)_2N\cdot$$

The activation energy for the reaction has been obtained in terms of that for decomposition; if $E_{(\text{fission})} = 15$ kcal. mole^{-1}, then the activation energy for abstraction is 3 ± 2 kcal. mole^{-1}.

Hydrogen abstraction from alcohols, esters, and ethers by *tert*-butoxyl radicals has been also studied. Those examined are ethanol, 2-propanol, 1-butanol (282), benzyl benzoate (219), and benzyl ether (125). In all instances an activated hydrogen atom is removed, that is, an atom in the α-position to the activating group.

9. n-Octoxyl radical

When *n*-octyl nitrite is refluxed at its normal boiling point, *n*-octoxyl radicals are generated. In the presence of a hydrogen donor 1-octanol is produced (110) and the hydrocarbon radical formed reacts with radical catchers (2-cyano-2-propyl) generated from the α,α′-azoisobutyronitrile. Large yields of alcohol are formed from diphenylmethane and 1-methylnaphthalene as solvents. In toluene 57 per cent and in ethylbenzene 70 per cent of the octyloxyl radicals are converted.

10. Cyclohexoxyl radical

This radical has been generated by the pyrolysis of the nitrite in the liquid phase. Hydrogen abstraction from isopropylbenzene occurs readily, and large yields of cyclohexanol have been obtained (100).

11. Benzyloxyl radical

The benzyloxyl radical, $C_6H_5CH_2O\cdot$, has been generated by pyrolysis of the nitrite in both the gas and the liquid phase. Hydrogen abstraction from isopropylbenzene occurs at 100°C. in the liquid phase, giving large yields of benzyl alcohol (100).

12. α-Phenylethoxyl radical

This radical has been generated by the thermal decomposition of *tert*-butyl α-phenylethyl peroxide (146). The radical abstracts a hydrogen atom from thiophenol without rearrangement, and the optical configuration in the peroxide is preserved in the alcohol.

$$C_6H_5CH(CH_3)O\cdot + C_6H_5SH \rightarrow C_6H_5CH(CH_3)OH + C_6H_5S\cdot$$

$$2C_6H_5S\cdot \rightarrow C_6H_5SSC_6H_5$$

At 125°C. in the liquid phase, yields of pure α-phenylethanol greater than 55 per cent and of diphenyl disulfide greater than 60 per cent have been obtained. The thiophenol is a particularly good donor, for at 130°C. hydrogen abstraction from isopropylbenzene does not occur; instead, the free radical decomposes.

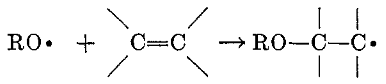
13. α-Cumyloxyl radical

The decomposition of di-α-cumyl peroxide yields α-cumyloxyl radicals. In the presence of hydrogen donors such as isopropylbenzene (12, 140), *tert*-butylbenzene (140), diisopropylcarbinol (140), and dodecane (140) the hydrogen-abstraction reaction occurs, giving the alcohol, phenylmethylcarbinol.

Kinetic studies (12) of the reaction with isopropylbenzene give a value of the activation energy of abstraction in terms of the decomposition reaction; it was found that $E_{(\text{fission})} - E_{(\text{abstraction})} = 7.3$ kcal. mole^{-1} (see Section IV,F,13).

C. ADDITION TO DOUBLE BONDS

Alkoxyl radicals may add onto double bonds. The reaction is:



$$RO\cdot + {>}C{=}C{<} \rightarrow RO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot$$

radical + molecule → radical

The reaction is second order and bimolecular. Not many activation energies have been measured, but probably the steric factor is much less than unity. The bimolecular competing reaction is hydrogen abstraction. If a molecule has a hydrogen in an α-methylene position so that D(C—H) is small, this hydrogen is abstracted in preference to addition of the alkoxyl radical to the double bond.

The addition of alkoxyl radicals is analogous to the propagating steps of vinyl polymerization, and there is more information about these alkyl systems than there is about alkoxyl addition. For example, the addition of methyl radicals to different double bonds has been studied (222), and the steric factors are found to be in the region of 10^{-4}; activation energies (gaseous phase) for addition of the methyl radical are: C_2H_4, 7.0 kcal. mole^{-1}; C_3H_6, 6.0; C_2H_2, 5.5; butadiene, 2.5 (278). The relative rates of addition of methyl radicals to liquid aromatic compounds are: benzene, 1; biphenyl, 5; naphthalene, 22; anthracene, 820. Although, strictly speaking, the methyl radical is the analog of the hydroxyl radical, the same increase in reactivity with increasing conjugation towards the alkoxyl radicals is expected.

1. Methoxyl radical

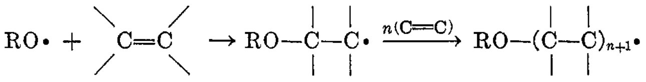
Addition of methoxyl radicals to propylene has been observed (279) during the pyrolysis of methyl nitrite in the presence of propylene.

2. tert-Butoxyl radical

Evidence for the addition of *tert*-butoxyl radicals to double bonds comes from several sources. These radicals, generated from *tert*-butyl hydroperoxide by a one-electron transfer reaction with Fe(II), add to isoprene, chloroprene, and butadiene, and the dimers have been isolated (139). This provides an elegant proof that addition occurs.

$$tert\text{-}C_4H_9O\cdot + CH_2{=}CHCH{=}CH_2 \longrightarrow tert\text{-}C_4H_9OCH_2CH{=}CHCH_2\cdot \longrightarrow \text{dimer}$$

Additive polymerization of vinylic unsaturated compounds, such as styrene or methyl methacrylate (139) in which transfer reactions are difficult, is initiated by *tert*-butoxyl radicals.



$$RO\cdot + \;\rangle C{=}C\langle \;\rightarrow RO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot \xrightarrow{n(C=C)} RO{-}(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_{n+1}\cdot$$

By contrast there is negligible addition to compounds such as cyclohexene (67, 204). Here activation energies of addition are expected to be higher, and also dehydrogenation can occur easily. This is in agreement with comparisons made with the addition of methyl radicals. In the case of acrolein, hydrogen abstraction leads to decomposition of the molecule (283). With benzene, hydrogen abstraction occurs in preference to addition.

An intermediate case is provided by 1-heptene (67). This vinylic compound possesses a dual reactive capacity and may undergo additive polymerization or dehydrogenation. Evidence for the addition of *tert*-butoxyl radicals comes from infrared analysis of the products.

The rate of addition to butadiene of *tert*-butoxyl radicals generated photochemically has been compared (284) with the rate of decomposition. Their relationship is $E_{(\text{addition})} = E_{(\text{fission})} - 5.8$ kcal. mole^{-1}. If $E_{(\text{fission})} = 15$ kcal. mole^{-1} (see Section IV,A), then $E_{(\text{addition})} = 9.2$ kcal. mole^{-1}. This activation energy is greater than the value for methyl radicals, which is 2.5 kcal. mole^{-1}.

3. Cyclohexoxyl radical

The decomposition of cyclohexyl hydroperoxide in benzene solution at 70°C. will initiate the polymerization of styrene (65). This initiation is caused by both the alkoxyl and the hydroxyl radicals generated.

4. Benzyloxyl radical

The polymerization of methyl methacrylate has been initiated by benzyloxyl radicals generated from the hyponitrite (114) at temperatures up to 30°C.

5. α-Cumyloxyl radical

This radical has been generated in aqueous solution by a one-electron transfer of the hydroperoxide (69) or the dialkyl peroxide (139). In the latter case addition to unsaturated compounds such as isoprene, chloroprene, and butadiene readily occurs and the di-ether is formed:

$$C_6H_5(CH_3)_2CO\cdot + CH_2{=}CHCH{=}CH_2 \rightarrow C_6H_5(CH_3)_2COCH{=}CHCH{=}CH_2\cdot$$

$$C_6H_5(CH_3)_2COCHCHCH{=}CH_2\cdot \rightarrow \text{dimer}$$

D. REARRANGEMENT (ISOMERIZATION)

Alkoxyl radicals may rearrange to the isomeric form thus:

$$R_3CO\cdot \rightarrow R_2\dot{C}OR$$

where R may be an alkyl group or a hydrogen atom. This reaction is favored thermodynamically (see Section III,G). Rearrangement is favored by the vacancy in one of the orbitals of the oxygen atom; in the alkoxonium ion, RO^+, where an orbital is completely vacant, rearrangement is the predominant reaction (see Section VIII).

There is clear chemical evidence for this reaction only in the completely aryl-substituted alkoxyl radicals, e.g., $(C_6H_5)_3CO\cdot$. With other alkoxyl radicals, it is possible that the radicals do isomerize to a small extent and that this reaction is immediately followed by a decomposition which will give the same products as the alkoxyl radical (148); under electron-impact conditions the rearranged alkoxyl radicals may be formed (59). The behavior of alkoxyl radicals is in contrast to that of alkyl radicals, which may isomerize even when not completely substituted; for example, neophyl (281).

1. Methoxyl radical

Although the rearrangement reaction of methoxyl radicals is exothermic, there is no evidence that this reaction occurs to any appreciable extent, since the dimer, ethylene glycol, has not been detected.

$$CH_3O\cdot \rightarrow \cdot CH_2OH;\ \ 2\cdot CH_2OH \rightarrow HOCH_2CH_2OH$$

2. Triphenylmethoxyl radical

This radical has been generated in xylene solution by the decomposition of triphenylmethyl peroxide (293); the radical rearranges and a 70 per cent yield of the dimer, benzopinacol, has been isolated. The rearrangement reaction is:

$$(C_6H_5)_3CO\cdot \rightarrow (C_6H_5)_2\dot{C}OC_6H_5 \xrightarrow{\text{dimerizes}} \text{benzopinacol}$$

This reaction has also been studied (141) in cumene solution at 120–140°C., the source of the radicals being *tert*-butyl triphenylmethyl peroxide. Under these conditions the rearranged radical associates with a free α-cumyl radical.

$$(C_6H_5)_3CO\cdot \rightarrow (C_6H_5)_2\dot{C}OC_6H_5 \xrightarrow{C_6H_5(CH_3)_2C\cdot} (C_6H_5)_2(C_6H_5O)CC(CH_3)_2C_6H_5$$

3. p-Tolyldiphenylmethoxyl radical

This radical may rearrange by migration of the phenyl or the *p*-tolyl group. The reactions are:

$$p\text{-}CH_3C_6H_4(C_6H_5)_2CO\cdot \longrightarrow (C_6H_5)_2\dot{C}O(C_6H_4CH_3\text{-}p) \text{ or } p\text{-}CH_3C_6H_4(C_6H_5)\dot{C}OC_6H_5$$

The radical has been generated (141) in cumene solution by the decomposition of *tert*-butyl *p*-tolyldiphenylmethyl peroxide. The relative rates of migration of the phenyl and the *p*-tolyl groups were compared and found to be the same.

4. α-Naphthyldiphenylmethoxyl radical

In this radical rearrangement may occur by migration either of the α-naphthyl group or of a phenyl group. The radical has been generated in cumene solution by decomposition of the *tert*-butyl peroxide. It was found (141) that the α-naphthyl group migrates six times more readily than the phenyl group. The reactions are:

$$\alpha\text{-}C_{10}H_7(C_6H_5)_2CO\cdot \longrightarrow \alpha\text{-}C_{10}H_7(C_6H_5)\dot{C}OC_6H_5 \text{ or } (C_6H_5)_2\dot{C}OC_{10}H_7\text{-}\alpha$$

5. p-Diphenylyldiphenylmethoxyl radical

This radical has been generated in cumene solution by the decomposition of *tert*-butyl *p*-diphenylyldiphenylmethyl peroxide. Rearrangement occurs (141), the *p*-diphenyl group migrating six times more readily than the phenyl group in this radical.

$$p\text{-}C_6H_5C_6H_4(C_6H_5)_2CO\cdot \longrightarrow p\text{-}C_6H_5C_6H_4(C_6H_5)\dot{C}OC_6H_5 \longrightarrow (C_6H_5)_2\dot{C}OC_6H_4C_6H_5\text{-}p$$

6. Mononitrotriphenylmethoxyl radical

This radical has been generated (18) by the decomposition of mononitrotriphenylmethyl peroxide in benzene solution at 115–128°C. Rearrangement occurs mainly by migration of the nitrophenyl group, and *p*-nitrobenzophenone is found in the products.

$$p\text{-}O_2NC_6H_4(C_6H_5)_2CO\cdot \longrightarrow (C_6H_5)_2\dot{C}OC_6H_4NO_2\text{-}p \longrightarrow C_6H_5COC_6H_4NO_2\text{-}p + C_6H_5\cdot$$

E. DECOMPOSITION BY CARBON–HYDROGEN BOND FISSION

The decomposition of the alkoxyl radical $RCH_2O\cdot$ is analogous to that of the alkyl radical $RCH_2CH_2\cdot$; the carbonyl compound RCHO and the olefin $RCHCH_2$ are isoelectronic.

$$RCH_2O\cdot \longrightarrow RCH{=}O + H\cdot$$

$$RCH_2CH_2\cdot \longrightarrow RCH{=}CH_2 + H\cdot$$

In normal molecules the carbon–hydrogen bond is stronger than the carbon–carbon bond and the same relation is true for radicals. In alkyl radicals the activation energy for carbon–hydrogen bond fission is about 20–40 kcal. mole^{-1} compared with a value of 15–25 kcal. mole^{-1} for carbon–carbon bond fission.

Similar values are expected for alkoxyl radicals, and thus carbon–hydrogen bond fission is expected to play only a minor role in the decomposition of alkoxyl radicals. The only alkoxyl radicals in which carbon–hydrogen bond fission occurs to any extent are methoxyl and ethoxyl.

1. Methoxyl radical

This reaction is the only thermochemically possible unimolecular mode of decomposition of the methoxyl radical.

$$CH_3O\cdot \rightarrow H\cdot + CH_2O \qquad \Delta H = 25 \text{ kcal. mole}^{-1}$$

It has been suggested that this reaction occurs in the photolysis of methyl nitrite (87) and in the pyrolysis of dimethyl ether at high temperatures (224).

2. Ethoxyl radical

The decomposition reaction by carbon–hydrogen bond fission is:

$$C_2H_5O\cdot \rightarrow H\cdot + CH_3CHO \qquad \Delta H = 13 \text{ kcal. mole}^{-1}$$

Decomposition by carbon–carbon bond fission is a competitor and will predominate at lower temperatures because it has a lower activation energy. At high temperatures fission of the carbon–hydrogen bond may be relatively more important. A study of the relative amount of decomposition by both modes has been made in the photolysis of ethyl nitrate (88). At low temperatures about 47 per cent decomposition occurs by carbon–hydrogen bond fission. The activation energy for decomposition was estimated to be 21 kcal. mole^{-1}.

F. DECOMPOSITION BY CARBON–CARBON BOND FISSION

This reaction is analogous to the decomposition of alkyl radicals by carbon–carbon bond fission. It takes precedence over decomposition by fission of the carbon–hydrogen bond (see Section IV,E).

1. Ethoxyl radical

The decomposition reaction is:

$$CH_3CH_2O\cdot \rightarrow CH_3\cdot + CH_2O$$

Evidence for it comes from a number of systems in which ethoxyl radicals are known to be present. Breakdown to methyl radicals results in the formation of ethane by the dimerization of methyl radicals, of methane by hydrogen abstraction, and of nitrosomethane and nitromethane when nitric oxide or nitrogen dioxide is present.

The most detailed analytical data come from work on the pyrolysis of ethyl *tert*-butyl peroxide at about 190°C. (22, 239) and on the slow and explosive decompositions of diethyl peroxide (112, 113, 222) and ethyl hydroperoxide (112). In all these systems the products include formaldehyde, ethane, and methane. Decomposition of ethyl *tert*-butyl peroxide in the gas phase at 195°C. with nitrogen as a carrier results in 82.5 per cent decomposition of the alkoxyl radicals generated. In the presence of cyclohexene as a carrier hydrogen abstraction occurs and competitive decomposition is reduced to 18 per cent.

The pyrolysis of ethyl nitrite has been shown (225) to yield methyl radicals (by their removal of metallic radicals), formaldehyde (2, 86), and nitrosomethane (86). The products of the pyrolysis of ethyl nitrate contain formaldehyde and nitromethane (155).

Ethoxyl radicals have been postulated (224) to occur in the first step of the pyrolysis of diethyl ether, and there is some new evidence for this derived from the decomposition of ethers in the presence of nitrous oxide (137).

Two estimates have been made of the activation energy of decomposition of ethoxyl radicals. The kinetics (224) of the pyrolysis of ether lead to a value of $E_{(\text{fission})}$ = 28 to 34 kcal. mole^{-1}; the photolysis of ethyl nitrite (88) indicates a value of $E_{(\text{fission})}$ = 21 kcal. mole^{-1}. The enthalpy of decomposition is 12 kcal. mole^{-1}.

2. n-Propoxyl radical

The decomposition reaction is:

$$CH_3CH_2CH_2O\cdot \rightarrow C_2H_5\cdot + CH_2O$$

Explosive decomposition of di-*n*-propyl peroxide (at temperatures near 200°C. and pressures near 68 mm.) produces formaldehyde and *n*-butane, the latter arising from the dimerization of ethyl radicals (112). Pyrolysis of *n*-propyl nitrite at 320°C. in the gas phase at low pressures and at atmospheric pressures yields formaldehyde (2, 86) and ethane (86). Similarly, the decomposition of *n*-propyl nitrate at 151°C. in the gas phase yields formaldehyde and nitroethane (159). The yield of nitroethane from propyl nitrate is greater than that of nitromethane in the corresponding decomposition of ethyl nitrate (155), because the propoxyl radical is less stable than the ethoxyl radical and more decomposition occurs.

3. Isopropoxyl radical

The thermal decomposition of *tert*-butyl isopropyl peroxide at 195°C. in the gas phase yields isopropoxyl radicals. Even in the presence of cyclohexene their decomposition occurs, analysis of the products indicating 48 per cent radical decomposition (22).

The thermal decomposition products of isopropyl nitrite at 181°C. in the gas phase include acetaldehyde and nitrosomethane (2, 86). These result from the fission of the isopropoxyl radicals and the subsequent association of methyl with nitric oxide.

$$(CH_3)_2CHO\cdot \rightarrow CH_3\cdot + CH_3CHO$$

4. n-Butoxyl radical

The decomposition of *n*-butyl *tert*-butyl peroxide in the presence of cyclohexene at 195°C. in the gas phase produces *n*-butoxyl radicals (22). Decomposition of these radicals occurs simultaneously with hydrogen abstraction, the products indicating that 29 per cent radical decomposition occurs. The reaction is:

$$CH_3CH_2CH_2CH_2O\cdot \rightarrow CH_3CH_2CH_2\cdot + CH_2O$$

Pyrolysis products from *n*-butyl nitrite (2, 86) include formaldehyde and 1-nitrosopropane resulting from radical decomposition and the subsequent association of *n*-propyl with nitrogen dioxide.

5. Isobutoxyl radical

Pyrolysis of *tert*-butyl isobutyl peroxide at 195°C. in the gas phase yields isobutoxyl radicals. Even in the presence of cyclohexene 67 per cent radical decomposition occurs (22). The reaction is:

$$(CH_3)_2CHCH_2O\cdot \rightarrow (CH_3)_2CH\cdot + CH_2O$$

The products of the pyrolysis of isobutyl nitrite include formaldehyde (2, 86) and 2-nitrosopropane.

6. sec-Butoxyl radical

The pyrolysis of *sec*-butyl nitrite at 32°C. in the gas phase yields nitroethane and acetaldehyde (2, 86). These products arise from the decomposition of *sec*-butoxyl radicals:

$$(CH_3CH_2)CH_3CHO\cdot \rightarrow CH_3CH_2\cdot + CH_3CHO$$

7. tert-Butoxyl radical

The decomposition of *tert*-butoxyl yields acetone and free methyl:

$$(CH_3)_3CO\cdot \rightarrow CH_3\cdot + (CH_3)_2CO\cdot$$

This decomposition reaction has been observed in the pyrolysis of numerous *tert*-butoxyl derivatives: di-*tert*-butyl peroxide (60, 172, 180, 185), *tert*-butyl hydroperoxide (165, 172), *tert*-butyl nitrite (48), *tert*-butyl nitrate (159), and *tert*-butyl hypochlorite (305). More work on *tert*-butoxyl radicals has been carried out than on all the other alkoxyl radicals combined, because of their application in the synthetic polymer industry. Commercial use is made of di-*tert*-butyl peroxide as a source of *tert*-butoxyl radicals; their decomposition by carbon–carbon bond fission gives methyl radicals, which then initiate polymerization (135, 278).

Concentrations of methyl radicals have been determined mass-spectrometrically at different temperatures. In one investigation (163) the following results were obtained:

Temperature	Peroxide	Pressure of Products		
		C_2H_6	CH_4	CH_3
°K.		*microns*	*microns*	*microns*
453	2.29	1.42	0.142	1.37
506	2.25	1.25	0.162	1.51

Knowledge of the activation energy for decomposition (E_f) comes from three comparisons with other reactions.

E_f from competition with association: By comparison of the rate of decomposi-

tion of *tert*-butoxyl radicals with that of association to give *tert*-butyl nitrite it has been found (26) that $E_f - E_{(\text{association})} = 13.2 \pm 2.4$ kcal. mole^{-1}. The activation energy for association will be close to zero, so that $E_f = 13.2 \pm 2.4$ kcal. mole^{-1}. If it is further assumed that this association reaction has similar rate constants to the association of methyl radicals and nitric oxide, it may be deduced that the logarithm of the preëxponential factor in liter-mole^{-1} sec.$^{-1}$ units is 9.7 ± 1.2. Comparison of decomposition with the two association reactions of methyl with itself and with *tert*-butoxyl leads (167a) to $E_{(\text{fission})} \simeq 9$ kcal. mole^{-1}.

E_f from competition with addition to a monomer: The rate of association to butadiene has been compared with the rate of decomposition of *tert*-butoxyl radicals (284). The value obtained in terms of these is $E_f - E_{(\text{addition})} = 5.8$ kcal. mole^{-1}. If the value for $E_{(\text{addition})}$ is assumed to be the same as for methyl radicals, a value of 11.2 ± 2 kcal. mole^{-1} is obtained for E_f.

E_f from competition with hydrogen abstraction: Comparisons have been made of the rates of decomposition of *tert*-butoxyl radicals with the rate of abstraction of a hydrogen atom from various substrates. The values (kcal. mole^{-1}) obtained for $E_{(\text{fission})} - E_{(\text{abstraction})}$ are: *tert*-butyl benzene, 11.0 (218); toluene, 11.3 (33); tetralin, 11.0 (33); isopropylbenzene, 16 ± 4 (218); 2,3-dimethylbutane, 7.0 (33); 2,5-dimethylhexane, 8 (33); methylcyclohexane, 7.5 (33); ethylenimine, 12 ± 2 (32); di-*tert*-butyl peroxide, 3 (167a). The best value for $E_{(\text{fission})}$ from all these determinations is 13 ± 2 kcal. mole^{-1}.

8. tert-Amoxyl radical

Decomposition of the radical is predominantly to acetone and ethyl radicals:

$$CH_3CH_2(CH_3)_2CO\cdot \xrightarrow{1} CH_3CH_2\cdot + (CH_3)_2CO$$

A secondary reaction may also occur in which the smaller group breaks off:

$$CH_3CH_2(CH_3)_2CO\cdot \xrightarrow{2} CH_3\cdot + CH_3CH_2COCH_3$$

Pyrolysis of di-*tert*-amyl peroxide at 235–250°C. in the gas phase has been used as a source of these radicals (173). The decomposition products are mainly *n*-butane and acetone (87–88 per cent), products which are consistent with decomposition of the radical by fission of the carbon–ethyl bond (path 1). Smaller quantities (4–5 per cent) of ethane and methyl ethyl ketone, consistent with fission of the carbon–methyl bond (path 2), are also present.

9. sec-Hexoxyl radical

Decomposition of this radical may occur by two paths:

$$n\text{-}C_4H_9(CH_3)CHO\cdot \xrightarrow{1} n\text{-}C_4H_9\cdot + CH_3CHO$$

$$n\text{-}C_4H_9(CH_3)CHO\cdot \xrightarrow{2} CH_3 + n\text{-}C_4H_9CHO$$

The pyrolysis products of *sec*-hexyl nitrite at 320°C. in the gas phase include acetaldehyde and nitrosobutane (86), products which are consistent with decomposition by path 1. No products have been isolated which would indicate that the second decomposition is also occurring.

10. Triethylmethoxyl radical

The decomposition reaction is:

$$(C_2H_5)_3CO\cdot \rightarrow C_2H_5\cdot + (C_2H_5)_2CO$$

Pyrolysis of the dialkyl peroxide results in the formation of this radical (170). At 250°C. about 61 per cent decomposition of the radical occurs, resulting in the formation of diethyl ketone and of ethyl radicals which dimerize to yield *n*-butane.

11. Pentamethylethoxyl radical

This radical has been generated by the pyrolysis of *tert*-butyl pentamethylethyl peroxide (170). The predominant decomposition is the one in which the largest alkyl group is lost.

$$(CH_3)_3CC(CH_3)_2O\cdot \rightarrow (CH_3)_3C\cdot + (CH_3)_3CO\cdot$$

12. Triphenylmethoxyl radical

The decomposition products of triphenylmethyl nitrate (53) contain benzophenone and picric acid; triphenylmethyl hydroperoxide yields benzophenone and phenol (295) and ditriphenylmethyl peroxide gives benzophenone and biphenyl (293). These products are consistent with the formation of triphenylmethoxyl radicals and their subsequent decomposition by the following reaction:

$$(C_6H_5)_3CO\cdot \rightarrow C_6H_5\cdot + (C_6H_5)_2CO$$

13. α-Cumyloxyl radical

Decomposition of this radical usually occurs by fission of a carbon–methyl bond.

$$C_6H_5(CH_3)_2CO\cdot \rightarrow CH_3\cdot + C_6H_5COCH_3$$

Decomposition products of the dialkyl peroxide (13, 140) in cumene solution at 111–150°C. include acetophenone and methane. The amount of decomposition by fission increases with the temperature by comparison with the hydrogen-abstraction reaction; with cumene, the activation energy for decomposition is found in terms of that for hydrogen abstraction. The value is $E_f - E_{(\text{abstraction})} =$ 7.3 kcal. mole^{-1}. If $E_{(\text{abstraction})}$ is the same as for the *tert*-butoxyl radical, then $E_f = 7$ to 9 kcal. mole^{-1}. This is less than the corresponding value for carbon–methyl bond fission in *tert*-butoxyl radicals and may be attributed to weakening of the bond by the phenyl group.

The photochemical decomposition of the dialkyl peroxide and of the hydroperoxide has been studied (192). In carbon tetrachloride solution, when irradiated by light of wavelength 3130 A., decomposition by fission of the carbon–methyl bond occurs. When irradiated by light of wavelength 2537 A., fission of the carbon–phenyl bond occurs, giving phenyl radicals.

G. DISPROPORTIONATION

When two radicals collide they may either associate or undergo disproportionation. The disproportionation reaction is a special case of hydrogen abstraction, the hydrogen being transferred from one radical to another. When the two radicals are alkoxyl radicals, the reaction is:

$$2RCH_2O\cdot \rightarrow RCH_2OH + RCHO$$

The reaction is analogous to the disproportionation of alkyl radicals, where there is clear evidence (129) that it occurs.

$$2RCH_2CH_2\cdot \rightarrow RCH_2CH_2H + RCH{=}CH_2$$

Disproportionation of alkoxyl radicals is considerably more exothermic ($\Delta H = -70$ to 90 kcal. mole^{-1}) than hydrogen abstraction ($\Delta H = 0$ to 20 kcal. mole^{-1}), because of the formation of a double bond. Consequently, disproportionation is expected to have a low activation energy.

Many of the reactions studied so far are difficult to interpret; it is impossible to distinguish by product analysis the disproportionation reaction from the reaction in which the alkoxyl radical abstracts a hydrogen atom from the parent molecule, because identical products are obtained. With nitrites, there is some evidence (154) that attack on the parent molecule does not occur and that the disproportionation reaction occurs in an analogous way to the alkyl radicals.

Disproportionation has not been observed in halogenated compounds (16), owing to the strength of the carbon–halogen bond.

1. Methoxyl radical

The disproportionation reaction is

$$CH_3O\cdot + CH_3O\cdot \rightarrow CH_3OH + CH_2O$$

Some evidence for this comes from the decomposition of nitrites and peroxides. The gas-phase decomposition of methyl nitrite results in the formation of methanol and formaldehyde (41, 106, 258). The existing kinetic evidence suggests that they are produced by a disproportionation reaction (106). These products are also obtained in the photolysis (269) and pyrolysis (111a, 270) of dimethyl peroxide. Trideuteromethoxyl radicals, produced in the photolysis of methyl formate, undergo disproportionation in the same manner (299):

$$2CD_3O\cdot \rightarrow CD_2O + CD_3OD$$

2. Ethoxyl radical

The reaction is:

$$C_2H_5O\cdot + C_2H_5O\cdot \rightarrow C_2H_5OH + CH_3CHO$$

The pyrolysis of ethyl nitrite (260), ethyl nitrate (1), and ethyl peroxide (112) at 140–250°C. gives products—ethanol and acetaldehyde—which may be produced by this reaction. At higher temperatures decomposition of the radicals occurs. The chemiluminescent mode of decomposition of diethyl peroxide also gives large yields of the alcohol and the aldehyde.

The thermal decomposition of *tert*-butyl ethyl peroxide (22) at 195°C. in the gas phase gives acetaldehyde and ethanol in small yields; these probably result from disproportionation. In the presence of cyclohexene (22), a good hydrogen donor, the products contain acetaldehyde despite the competing reactions.

The products of the pyrolysis of ethyl nitrite contain acetaldehyde and ethanol. If it is correct (154) that ethoxyl radicals (generated by the pyrolysis of diethyl peroxide) do not abstract hydrogen atoms from ethyl nitrite, these products from the pyrolysis of ethyl nitrite must result from a disproportionation reaction.

3. n-Propoxyl radical

The thermal decomposition of di-*n*-propyl peroxide (113) at 180°C. and of *n*-propyl nitrite (157) at 170–210°C. yields propionaldehyde and *n*-propyl alcohol (113), probably by disproportionation; explosive decomposition of the peroxide (113) results mainly in butane and formaldehyde from the decomposition of the alkoxyl radical.

4. Isopropoxyl radical

The pyrolysis of isopropyl nitrite (157) results in the formation of isopropyl alcohol, acetone, and nitric oxide. The alcohol and the ketone are probably produced by disproportionation:

$$2(CH_3)_2CHO\bullet \rightarrow (CH_3)_2CHOH + (CH_3)_2CO$$

5. d-2-Octoxyl radical

The thermal decomposition (145) of optically active *d*-2-octyl nitrite in the liquid phase at 100°C. results in the formation of the theoretical yield of optically pure *d*-2-octanol and 80 per cent of the theoretical yield of octanone. These products must arise via the alkoxyl radicals and most probably by disproportionation.

$$2d\text{-}C_6H_{12}CH(CH_3)O\bullet \rightarrow C_6H_{13}COCH_3 + d\text{-}C_6H_{13}CH(CH_3)OH$$

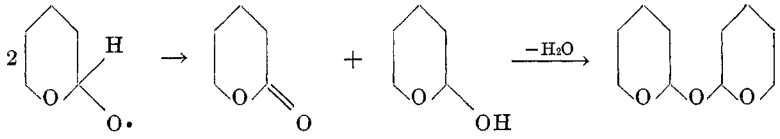
6. Cyclohexoxyl radical

The thermal decomposition of liquid cyclohexyl nitrite gives a 40 per cent yield of cyclohexanol (100), together with other products that may be formed in the reaction of cyclohexanone with nitric oxide. The cyclohexanol and the cyclohexanone may be produced in a disproportionation reaction.

$$\text{cyclo-}C_6H_{11}O\bullet \rightarrow \text{cyclo-}C_6H_{11}OH + \text{cyclo-}C_6H_{10}O$$

7. Tetrahydropyran

The thermal decomposition (171) of *tert*-butyl tetrahydropyran 2-peroxide at 250°C. produces δ-valerolactone and di-2-tetrahydropyran ether (which is known to be formed by the dehydration of 2-hydroxytetrahydropyran). The reaction is:



8. Benzyloxyl

This radical has been generated by the thermal decomposition of the nitrite and the hyponitrite. The pyrolysis of benzyl nitrite (100) at 100–200°C. gives high yields of benzaldehyde and benzyl alcohol, presumably from the disproportionation reaction:

$$2C_6H_5CH_2O\cdot \rightarrow C_6H_5CHO + C_6H_5CH_2OH$$

Similarly, the decomposition of benzyl hyponitrite at 50°C. gives the same products from the same reaction (114).

H. DECOMPOSITION BY RADICAL ATTACK

This is a special type of disproportionation, and all known instances involve transfer of a hydrogen atom from the alkoxyl radical to the attacking species. The attacking species may be a free radical or an odd-electron molecule. This reaction occurs extensively only when a large excess of the attacking species is present.

1. Methoxyl radical

In the photolysis of methyl-d_3 acetate (299) both methoxyl and methyl free radicals are generated. These may associate (see Section IV,A) or undergo disproportionation to formaldehyde and methane:

$$CH_3O\cdot + CH_3\cdot \rightarrow CH_2O + CH_4$$

Attack on methoxyl by molecular oxygen has been suggested (111a) to occur during the oxidation of methyl radicals:

$$CH_3O\cdot + O_2 \rightarrow CH_2O + HO_2\cdot$$

Nitrous oxide is found in the product of the pyrolysis (8, 41, 99, 106, 204) and the photolysis (87) of methyl nitrite. This has been ascribed to the abstraction of a hydrogen atom from methoxyl radicals by nitric oxide.

$$CH_3O\cdot + NO \rightarrow CH_2O + HNO$$

$$2HNO \rightarrow H_2O + N_2O$$

2. Ethoxyl radical

Nitrous oxide is produced in the pyrolysis of ethyl nitrite (158); it may result from the reaction of nitric oxide with ethoxyl radicals.

$$C_2H_5O\cdot + NO \rightarrow CH_3CHO + HNO$$

$$2HNO \rightarrow H_2O + N_2O$$

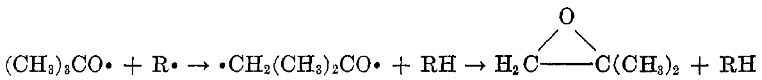
The decomposition of ethoxyl radicals by oxygen molecules has been suggested (133) in the photoöxidation of diethyl ketone.

$$C_2H_5O\cdot + O_2 \rightarrow CH_3CHO + HO_2\cdot$$

Since $HO_2\cdot$ radicals may be the important chain-carrying entities in the explosive decomposition of hydrocarbon–oxygen mixtures, this reaction may partially account for the facilitation of "knock" (280) when alkoxyl radical-producing substances are added to engine fuels.

3. *tert-Butoxyl radical*

In the gas- (185) and liquid- (290) phase decomposition of di-*tert*-butyl peroxide isobutylene oxide is produced. This may result from the attack of free radicals on *tert*-butoxyl radicals:



where R = *tert*-$C_4H_9O\cdot$ or $CH_3\cdot$.

4. *Allyloxyl radical*

This radical has an extremely reactive α-hydrogen atom which is readily lost to an attacking radical. In the pyrolysis of *tert*-butyl allyl peroxide, allyloxyl and *tert*-butoxyl radicals are generated (39), the latter abstracting a hydrogen from the allyloxyl radical.

$$CH_2{=}CHCH_2O\cdot \quad + \quad tert\text{-}C_4H_9O\cdot \xrightarrow{60°C.} CH_2{=}CHCHO \quad + \quad tert\text{-}C_4H_9OH$$

5. *Cyclohexenoxyl radical*

This radical, generated from *tert*-butyl cyclohexene peroxide, yields cyclohexenoxyl and *tert*-butoxyl radicals, the latter abstracting a hydrogen atom from the alkoxyl radical.

V. FACTORS AFFECTING DOMINANCE OF DIFFERENT MODES OF REACTION

In Section IV the various types of reaction which alkoxyl radicals may undergo were dealt with separately. Experimentally it is, of course, impossible to study the radicals in isolation; more than one reaction occurs simultaneously and competitively. The relative importance assumed by the different reactions depends not only on the nature of the particular alkoxyl radical but also on its concentration, on the physical conditions, and on its chemical environment. The factors which govern the relative importance of the different classes of reaction will be considered in this section and will serve as a basis for the discussion in Sections VI and VII of the chemistry of complex alkoxyl radicals and of alkoxyl radicals in complex systems.

The problem is one of reaction kinetics and is most suitably analyzed in kinetic terms. First, the kinetic order is made the basis of an alternative classification of the reactions of alkoxyl radicals. Next, differences *within* each of the three kinetic classes are discussed. When this is possible in terms of the parameters A and E of the Arrhenius equation, transition-state theory is found to be a valuable guide to assigning values of A and thermochemistry to interpreting values of E. Particular attention is paid to the thermochemistry of decomposition reactions. When known, the behavior of the corresponding alkyl radicals also serves as a useful parallel. Finally, a brief outline is given of competition between reactions of different classes.

TABLE 12

Kinetic classification of reactions of alkoxyl radicals

Rate Equation, Kinetic Order, and Half-life	Reaction	Exothermicity $-\Delta H$	E
		kcal. mole^{-1}	*kcal. mole*$^{-1}$
$k_2[RO\bullet]\,[M]$	Association with radicals	30 to 100	0
Second order (overall)	Addition to unsaturated molecules	15 to 40	5 to 10
$\frac{\ln 2}{k_2[M_0]}$	Loss of hydrogen atom to radicals	0 to 80	10
(M in excess)	Hydrogen abstraction	2 to 30	5 to 10
$k_2[RO\bullet]^2$ Second order	Dimerization	35 to 40	0
$\frac{1}{k_2[RO\bullet]}$	Disproportionation	75 to 85	0
$k_1[RO\bullet]$	Rearrangement by radical migration	0 to 5	Unknown
First order	Rearrangement by hydrogen-atom migration; internal hydrogen abstraction	0 to 5	Unknown
$\frac{\ln 2}{k_1}$	Decomposition by radical elimination	0 to 15	10 to 30
	Decomposition by hydrogen-atom elimination	10 to 25	15 to 40
(Second-order regime not attained)	Decomposition by ring fission	0 to 5	Unknown

A. KINETIC CLASSIFICATION OF REACTIONS OF ALKOXYL RADICALS

Before the interrelations of thermochemistry and reactivity can be examined a kinetic classification of the reactions is necessary. This classification, which cuts across the previous grouping (e.g., by separating dimerization from all other radical–radical associations), is based on the molecularity and on the kinetic order of reaction. It is presented in table 12, which shows how "chemically" distinct types of reaction are divided among three groups, with velocities depending on $[RO\bullet]$, $[RO\bullet][M]$, and $[RO\bullet]^2$, respectively. The importance of this classification is that, if two reactions belong to different groups, it is possible to control their relative importance by variations in concentration alone; if two reactions belong to the same kinetic group, their relative importance may be discussed without ambiguity.

B. SECOND-ORDER REACTIONS BETWEEN ALKOXYL RADICALS AND OTHER SPECIES

The reactions with other radicals, with unsaturated molecules, and with hydrogen donors are in many respects the easiest to study because, although they all respond identically to variations in $RO\bullet$ and are all enhanced at the expense of other classes of reaction by increase in substrate concentration M, they may be separated by choosing different substrates. The only limitation on this occurs when the substrate M has a dual function. For example, alkoxyl radicals remove α-hydrogen from 1-heptene as well as adding to its double bond; similarly, other radicals may either associate with alkoxyl radicals or abstract a hydrogen atom from them.

Association with other radicals leads to liberation of energy and the nascent molecule needs to be stabilized by handing on this energy in collisions. Evidence of third-body effects has so far been obtained only for association with the diatomic odd-electron molecule nitric oxide, where they make themselves felt at pressures near 50 mm. (methoxyl), 10 mm. (ethoxyl), and 0.5 mm. (propoxyl), respectively. The need to dissipate this energy and the nature of reaction imply that association is not favored by an increase in temperature; near-zero values of E find support from work on *tert*-butoxyl. The steric influences are restrictive. Translation and rotational modes are converted on association to internal modes of motion, and steric factors (P) are expected to lie in the range 10^{-2} to 10^{-4}.

The competitive reaction of loss of α-hydrogen by the alkoxyl radical to the attacking radical is also exothermic, but it does not require any third-body stabilization. It may be expected therefore to be favored at low pressures and to be most prominent when the M—H bond formed by the radical M• is strongest.

Hydrogen abstraction by the alkoxyl radical occurs even when only slightly exothermic; no endothermic abstractions have been observed. As the strength of the donor X—H bond weakens, so abstraction of hydrogen from it is increasingly exothermic and the velocity constant for hydrogen abstraction increases. The expected correlation between E and ΔH, though so far based on very few experimental Arrhenius parameters, is found. Extensive references are given in tables 4 and 5 of reference 104.

Addition to unsaturated systems has most frequently been observed in reaction with conjugated dienes or activated double bonds. Addition then leads to a relatively stable, substituted allyl radical; it is strongly exothermic ($\Delta H = -35$ kcal. mole^{-1}) and activation energies of 8 to 10 kcal. mole^{-1} have been reported. Addition to simple olefins, although exothermic by 15 to 20 kcal. mole^{-1}, has rarely been observed; addition of *tert*-butoxyl to 1-heptene is exceptional. The reason is only partly due to absence of conjugation; unless the olefin contains no α-methylene or aldehydic hydrogen, competition from hydrogen abstraction is severe and occurs almost exclusively from donors such as cyclohexene or acraldehyde. In these instances, thermochemistry tells us that addition and abstraction are about equally energetic and reported activation energies are similar; an explanation is to be sought in the steric requirements of the two—association and metathetical reactions, respectively.

C. SECOND-ORDER REACTIONS BETWEEN PAIRS OF ALKOXYL RADICALS

These are the reactions of dimerization and disproportionation; they have as their analogs in the previous class association with another radical. Both are favored relatively to other classes by high RO• concentration.

Dimerization is the reverse of the initial step in peroxide pyrolysis. It has rarely been observed in thermal reactions, partly because it has not been seriously sought for and partly because the peroxide formed by it has low thermal stability and can reach only a small stationary concentration. The energy released is the dissociation energy of the oxygen–oxygen bond, and this energy has to be dissipated in third-body collisions. Dimerization is thus aided by low temperatures and by deënergizing collisions; the best authenticated instances occur in solutions.

$$2C_6H_5C(CH_3)_2O\cdot \rightarrow [C_6H_5C(CH_3)_2O—]_2$$

2-Phenyl-2-propanoxyl Di-α-cumyl peroxide

There is no evidence available yet to suggest that dimerization requires any activation energy. Although dipole–dipole repulsion is involved, the relation between bond strengths and activation energies shows no clear evidence in favor of the suggestion.

Disproportionation is strongly exothermic, liberating some 80 kcal. per alkoxyl radical pair compared with the 35 to 40 kcal. released in dimerization. Furthermore, as it is a metathesis, no deactivating collisions are necessary to take away this energy. However, the correlation between ΔH and ΔE observed in general hydrogen abstractions suggests that disproportionation may have a near-zero activation energy and that changing temperature will not separate it from dimerization. Disproportionation, which appears best established in the pyrolysis of peroxides, is probably a component reaction of the decomposition of nitrite esters; Wijnen's recent work on the deuterated methyl acetates establishes it firmly for methoxyl. Analogy with the isoelectronic ethyl radicals suggests that, for methoxyl, disproportionation and dimerization should have nearly equal steric requirements and near-zero activation energy, and should be equally frequent under ordinary conditions.

D. UNIMOLECULAR DECOMPOSITIONS AND REARRANGEMENTS

The half-lives of decomposition and rearrangement reactions are independent of concentration (so long as the first-order regime is maintained), and these modes are favored equally relative to others by low concentrations of RO• and the absence of all but inert substrates.

Rearrangement by migration of an α-hydrogen atom or an α-alkyl group or by internal hydrogen abstraction has not in fact been demonstrated, though all these are exothermic reactions (91, 104) without any obviously stringent orientational restrictions. The exothermicities of the rearrangements which do occur are very imprecise and their activation energies unknown, though the ease of migration of Ar in the substituted methoxyl family, $Ar(C_6H_5)_2CO\cdot$, has been established. Relative to phenyl, these figures (18, 141) are: 1-naphthyl and 4-diphenylyl = 6; phenyl and *p*-tolyl = 1; *p*-nitrophenyl = zero.

Decomposition may take several forms and all are distinguished from the kinetically similar rearrangement reactions by their energy and entropy requirements. Whereas rearrangement is exothermic or thermoneutral and its entropy change is small, bond fission in decomposition is always accompanied by increases in enthalpy and entropy; vibrational modes of motion are replaced either by new translational or rotational modes and, in many decompositions, by both. The frequency with which decomposition reactions occur is in further contrast with the rarity of rearrangement, and the different types of decomposition merit closer study.

The salient experimental data requiring to be interpreted may be outlined. First, decomposition by carbon–hydrogen bond fission never occurs if there is an alternative path available. In methoxyl, where there is no alternative, relatively high temperatures are required to bring about decomposition; the activation energy lies near 40 kcal. mole^{-1}. Secondly, when as in mixed alkoxyl radicals more than one mode of decomposition is possible, both modes occur, though ethyl, *n*-butyl, and *tert*-butyl radicals are eliminated more readily than methyl. Thirdly, in cyclic derivatives the ring is broken in preference to elimination of an attached group; this is true whether the exocyclic group is a hydrogen atom, an alkyl radical, or an aryl radical. It thus appears that normally the largest alkyl group comes out most readily, though when a ring is present it is broken preferentially. It is essential to realize that these conclusions represent predominant trends and not completely exclusive modes. Finally, in aryl-substituted systems, phenyl groups are eliminated less readily than alkyl groups and hydrogen atoms are lost only in disproportionation. Taking all the facts together, it is probably safe to set as the order of *increasing* ease of fission in a single, mixed radical the series: $H < C_6H_5 < CH_3 < C_2H_5 < (CH_3)_2CH < (CH_3)_3C <$ ring fission.

The previous paragraphs dealt with single alkoxyl radicals which could follow alternative paths of decomposition. Different radicals may be compared with one another without ambiguity only when more detailed kinetic data are available. At present the relative stability towards decomposition of different alkoxyl radicals has to be inferred from experiments in which decomposition competes with other modes of reaction. Vaughan and his collaborators (22) measured, for a series of alkoxyl reactions, the relative rates of decomposition and hydrogen abstraction from the same donor (cyclohexene). They concluded that the lower alkoxyl radicals, arranged in order of diminishing stability, formed the series: $CH_3O\cdot > C_2H_5O\cdot > n\text{-}C_4H_9O\cdot > sec\text{-}C_3H_7O\cdot >$ iso-$C_4H_9O\cdot > tert\text{-}C_4H_9O\cdot > tert\text{-}C_5H_{11}O\cdot$. The thermochemical aspects of these decompositions will now be considered in a little more detail.

E. COMPARATIVE THERMOCHEMISTRY OF DECOMPOSITION REACTIONS

So far as the difficulties of decomposition by elimination of hydrogen atoms are concerned the data of Section IV,G,6 are clear; elimination of hydrogen requires from 16 to 25 kcal. mole^{-1} and its activation energy will be considerably higher—for methoxyl, some 40 kcal. mole^{-1}.

Alkyl-radical elimination needs smaller energies—from a maximum of 16 kcal. mole^{-1} to a minimum of about 3. Wherever alternative paths are open to a radical, the difference in energy requirements, $D(\text{C—H}) - D(\text{C—alkyl})$, is always some 8 to 12 kcal. mole^{-1} in favor of alkyl elimination. Within the group of alkyl-radical eliminations, differences between different alkyl eliminations from the same parent are small; individually they may be insignificant, but taken as a whole they indicate that a bulky group, e.g., a tertiary alkyl group, is more readily lost than a methyl or some other small radical.

Ring fission requires the least energy of all, only 1 to 2 kcal. mole^{-1}. If the dissociation energies of the alternative routes, alkyl elimination *versus* ring fission, are compared for 1-R-cyclohexyl-1-oxyl radicals, it is found that ring fission requires far less energy than the loss of a hydrogen atom (R = H) and requires less energy than radical elimination for R = CH_3 or C_2H_5, but suggests that if R is *tert*-butyl, radical loss should be thermochemically favored. Though Hey, Stirling, and Williams (120) ascribe preferential ring fission in phenyl-substituted cyclohexoxyl to "resonance energy arising from the conjugation of the carbonyl group with the aromatic nucleus," the ready occurrence (44) of the same fission with the methyl-substituted radical suggests that it is essentially a property of the ring rather than of the substituent.

The aryl-substituted radicals form an interesting class. Energy requirements for the elimination of a phenyl group are always more than for the elimination of an alkyl group from mixed radicals, and more than for ring opening. In radicals where either a carbon–alkyl or a carbon–aryl bond may be broken, the mean difference $D(\text{C—Ar}) - D(\text{C—R})$ is about 5 kcal. mole^{-1}. Elimination of phenyl groups does not, however, need as much energy as elimination of hydrogen atoms; the mean value (105) for the difference $D(\text{C—H}) - D(\text{C—Ar})$ is 3 to 4 kcal. mole^{-1}. It should be noted that uncertainties in the heat of formation of the parent alkoxyl radical have no effect on these *differences*, which depend solely on the heats of formation of the products; in fact, it is not even necessary to know the heat of formation of the parent radical to make valid comparisons of this type.

The parallels between reactivity and thermochemistry are further emphasized when Vaughan's series (22) for the stability of alkoxyl radicals is examined in the light of thermochemistry. In table 13 this series is placed alongside that obtained when the radicals are arranged in order of diminishing *minimum* enthalpy requirements of decomposition. The correlation is striking; the alkoxyl radicals which decompose at the fastest rate are also thermochemically least stable.

TABLE 13

Thermochemistry and stability of alkoxyl radicals

Thermochemical data in kcal. mole^{-1}; in the last column 1 = most stable, 6 = least stable

Radical	Minimum Enthalpy Requirements for Decomposition	Activation Energy of Decomposition	Order of Stability
	kcal. mole^{-1}	*kcal. mole^{-1}*	
$CH_3O\bullet$	25	25–40	1
$C_2H_5O\bullet$	13	15–20	2
n-$C_4H_9O\bullet$	11		3
iso-$C_3H_7O\bullet$	10		4
n-$C_3H_7O\bullet$	10		—
iso-$C_4H_9O\bullet$	7		5
sec-$C_4H_9O\bullet$	5		—
tert-$C_4H_9O\bullet$	5	13	6
$C_6H_5(CH_3)_2CO\bullet$	—	10	—
cyclo-$C_6H_{11}O\bullet$	1	—	—

F. COMPETITION BETWEEN REACTIONS OF DIFFERENT CLASSES

From Section IV and the discussion in B, C, and D above, it is clear that, while reactions of dimerization and rearrangement are rare and reactions of addition and association are readily suppressed by removal of unsaturated molecules and free radicals, the reactions of decomposition, hydrogen abstraction, and to a less extent disproportionation are normally always present. Their activation energies diminish in the order written and their relative importance depends principally on (*1*) the alkoxyl radical (RO•) concerned, (*2*) its concentration, (*3*) the temperature T, and (*4*) the concentration of the parent molecule [ROX] and of other species [XH] from which hydrogen may be abstracted.

By lowering the concentrations of RO•, disproportionation can be reduced in importance relative to the other processes, despite its favorably low activation energy. Similarly, by reducing [XH], the partner in hydrogen abstraction, this reaction can be partially suppressed until decomposition is the only significant reaction. This state is still more readily attained at elevated temperatures because, owing to the greater activation energy, the rate of decomposition increases more rapidly with temperature than does the rate of hydrogen abstraction. Thus, decomposing a nitrite or peroxide at a low partial pressure and a high temperature in a stream of inert gas will produce almost exclusively the decomposition products of the appropriate alkoxyl radical.

In order that hydrogen abstraction from a particular donor XH should preponderate, it is necessary to increase the donor concentration. A practical limit is reached if reaction is carried out in the dissolved state when the frequency of collisions between XH and RO• can not be increased at any given temperature; this represents the maximum extent of competition, and hydrogen abstraction can then be favored relative to decomposition only by reducing the rates of both by lowering the temperature.

For disproportionation to be preëminent at any given temperature, a high concentration of alkoxyl radicals and the absence of hydrogen donors (other than the parent molecule necessary as the source of RO•) are essential. The presence of the parent ROX of course prevents the complete suppression of hydrogen abstraction. When other substances are absent, the yield can be increased only by lowering the temperature to leave the rate of disproportionation nearly the same and to lower the rates of its competitors.

VI. REACTIONS OF COMPLEX ALKOXYL RADICALS

Complex alkoxyl radicals are those which have substituents that influence their reactivity and those which are structurally complex. These radicals have basically similar reactions to those of the more simple alkyl- or aryl-substituted radicals; thus their reactions may be recognized and their mechanisms readily interpreted. The position of the substituent plays an important part. If it is in a position adjacent to the oxygen (—O•), it may make a significant contribution to the reaction; elsewhere in the molecule its influence is usually negligible.

In this section reactions of alkoxyl radicals which are complicated by the effects of substituents or structure are considered; the uncomplicated reactions,

TABLE 14

Reactions of aryl-substituted alkoxyl radicals that have been observed

Radical	Reaction	References
$C_6H_5CH_2O\bullet$	Association	(100)
	Hydrogen abstraction	(100)
	Disproportionation	(100)
	Decomposition by radical attack	(100)
	Addition to double bond	(114)
$(C_6H_5)_3CO\bullet$	Rearrangement	(141)
	Decomposition	(53, 293, 295)
$C_6H_5(CH_3)CHO\bullet$	Hydrogen abstraction	(146)
$C_6H_5(CH_3)_2CO\bullet$	Hydrogen abstraction	(12, 140)
	Addition to double bonds	(69, 139)
	Decomposition	(13, 140, 192)
	Dimerization	(161)
$(C_6H_5C_6H_4)(C_6H_5)_2CO\bullet$	Rearrangement	(141)
α-$C_{10}H_7(C_6H_5)_2CO\bullet$	Rearrangement	(141)
(p-$NO_2C_6H_4)(C_6H_5)_2CO\bullet$	Rearrangement	(18)
	Decomposition	
α-Tetraloxyl	Disproportionation	(291)
	Decomposition by radical attack	(291)

such as disproportionation or association, have already been considered in their appropriate sections.

The substituted radicals discussed are the aryl, the halogenated, the nitrite-substituted, and the hydroxyl-substituted alkoxyl radicals. Also considered are the dialkoxyl radicals, whose reactions depend upon the relative positions of the two —O• groups, and the cyclic alkoxyl radicals with the —O• on the ring, in which fission of the ring occurs. Alkoxyl radicals containing double bonds are not discussed separately here; alkoxyl radicals containing triple bonds have not been extensively investigated, because the parent peroxides are too explosive (169); however, experiments have been begun on them (170a).

A. ARYL-SUBSTITUTED ALKOXYL RADICALS

The reactions of a number of aryl-substituted alkoxyl radicals have been examined. In the great majority of cases the reactions, summarized in table 14, fall in one of the classes that have been considered in Section IV.

In this section, reactions will be considered that are exclusive to the aryl-substituted alkoxyl radicals. The first is dimerization. When two alkoxyl radicals collide they may undergo association or disproportionation. With simple alkoxyl radicals only the competing disproportionation reaction is found, but certain aryl-substituted alkoxyl radicals, in which disproportionation is not possible, are found to undergo association if the temperature is low enough for the oxygen–oxygen bond formed not to undergo fission again. An example of this is found in the decomposition of α-cumyl hydroperoxide (153), when the α-cumyloxyl radicals generated undergo dimerization.

$$2C_6H_5C(CH_3)_2O\bullet \rightarrow C_6H_5C(CH_3)_2O\text{—}OC(CH_3)_2C_6H_5$$

Rearrangement is another reaction only found in completely aryl-substituted alkoxyl radicals; for example, the triphenylmethoxyl radical or its derivatives (see Section IV,D). This is the main reaction of such radicals and is accompanied by only little decomposition; disproportionation and hydrogen abstraction are not found. A substituent in one of the benzene rings may change its migrating power. For example, the electron-attracting *p*-nitrophenyl group migrates more readily than a phenyl group in the *p*-nitrotriphenylmethoxyl radical (18).

Apart from these two reactions, dimerization and rearrangement, the behavior of the aryl-substituted alkoxyl radicals is the same as that of the simple alkoxyl radicals.

B. HALOGEN-SUBSTITUTED ALKOXYL RADICALS

Substitution of a hydrogen atom in an alkoxyl radical by a more electronegative halogen atom X will result in a change of reactivity. There are two reasons for this. The first is that the C—X bond strength differs from the C—H bond strength, and secondly the electronegative substituent, if extremely electronegative, will affect the strength of the adjacent carbon–carbon bond. Other changes in bond strength are subordinate to these.

The reactions which are most affected are (*i*) decomposition by C—X bond fission, (*ii*) disproportionation by C—X bond fission and O—X bond formation, (*iii*) rearrangement by internal C—X bond fission and O—X bond formation, (*iv*) decomposition by C—C bond fission. Other reactions such as hydrogen abstraction are largely unaffected.

1. *Trichloromethoxyl radical*

This radical is produced in the thermal decomposition of chloropicrin at 138–170°C. and 6–20 cm. of mercury. The reaction products are carbonyl chloride, nitrosyl chloride, and, in quantities greater than the equilibrium proportion, a mixture of nitric oxide and chlorine (253). The reaction is homogeneous and first order, so a possible mechanism is:

Initial fission: $CCl_3NO_2 \rightarrow CCl_3\cdot + NO_2$

Formation of alkoxyl radical: $\begin{cases} CCl_3\cdot + NO_2 \rightarrow CCl_3ONO \\ CCl_3ONO \rightarrow CCl_3O\cdot + NO \end{cases}$

$$CCl_3O\cdot \rightarrow COCl_2 + Cl\cdot$$

Further reactions lead to the observed production of nitrosyl chloride and molecular chlorine:

$$Cl\cdot + NO + M \rightarrow ClNO + M$$

$$Cl\cdot + ClNO \rightarrow Cl_2 + NO$$

$$Cl\cdot + Cl\cdot + M \rightarrow Cl_2 + M$$

2. *Trifluoromethoxyl radical*

This radical has been generated by the thermal decomposition of the dialkyl peroxide CF_3OOCF_3 (209). At temperatures of about 225°C. to 325°C. the radical reacts, producing carbonyl fluoride. This may be due to decomposition:

$$CF_3O\cdot \rightarrow CF_2O + F\cdot$$

or to disproportionation:

$$2CF_3O\cdot \rightarrow CF_2O + (CF_3OF)$$

3. Pentafluoroethoxyl radical

There is some evidence that this radical is formed in the oxidative degradation of fluorine compounds (see Section VII,C) by nitrogen dioxide. The predominant reaction at 100°C. and low pressures (10 mm.) is one of decomposition. The reaction is rather similar to the decomposition of the simpler alkoxyl radicals in that the alkyl group attached to the α-carbon atom is lost.

$$CF_3CF_2O\cdot \rightarrow CF_3\cdot + CF_2O$$

4. Dibromoisopropoxyl radical

The decomposition of the dialkyl peroxide in solution has been studied (28) at low temperatures (about 90°C.) and although intramolecular decomposition occurs, some free alkoxyl radicals also are probably generated. The products include dibromoacetone, which may result from disproportionation of the alkoxyl radicals:

$$2(BrCH_2)_2CHO\cdot \rightarrow (BrCH_2)_2CO + (BrCH_2)_2CHOH$$

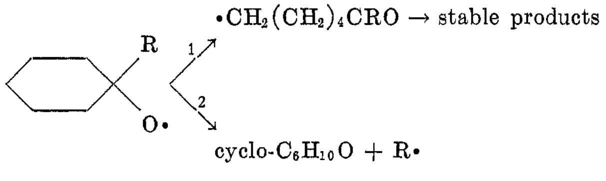
5. α-Chloroperfluoropropoxyl radical

This radical has been generated in the degradative nitration of perfluoro iodides in the presence of chlorine (16, 17). The α-chlorine atom is expelled in preference to decomposition of the radical by carbon–carbon bond fission.

$$CF_3CF_2CFClO\cdot \rightarrow CF_3CF_2CFO + Cl\cdot$$

C. CYCLIC ALKOXYL RADICALS

The cyclic derivatives which are most different from aliphatic alkoxyl radicals are those in which the —O• group is attached to the ring. Essential differences are expected to be confined to the decomposition reaction, which may take either of two paths:



In all radical decompositions that have been examined path 1 is exclusive and the formation of the diketone (and, if nitric oxide is present, the nitroso compound as well) is typical of this mode. Formation of the cyclic ketone and a free radical R• is as yet unknown but is thermodynamically possible.

The thermochemistry of these reactions has been considered in Section III,G. In reactions other than decomposition, cyclic derivatives behave like other secondary alkoxyl radicals, and these reactions have been considered in their appropriate sections.

1. 1-Methylcyclopentoxyl radical

Decomposition of the dialkyl peroxide in benzene at 300°C. in a nitrogen atmosphere results in the formation of the alkoxyl radical (234). This decomposes to give the keto radical, which dimerizes to the diketone.

$$\text{cyclo-}C_5H_8(CH_3)O\cdot \rightarrow \cdot CH_2(CH_2)_2COCH_3 \rightarrow \text{2,11-dodecanedione}$$

2. 1-Methoxycyclopentoxyl radical

The thermal decomposition of this radical, generated from the dialkyl peroxide at 200°C. in benzene solvent (234), yields the keto radical, which dimerizes to yield dimethyl sebacate.

$$\text{cyclo-}C_5H_8(OCH_3)O\cdot \rightarrow \cdot CH_2(CH_2)_3COOCH_3 \rightarrow \text{dimethyl sebacate}$$

3. 1-Hydroxycyclopentoxyl radical

This radical has been generated from the dialkyl peroxide (234). Ring fission occurs giving the alkyl radical, which dimerizes to give the dimer.

$$\text{cyclo-}C_5H_8(OH)O\cdot \rightarrow \cdot CH_2(CH_2)_3COOH \rightarrow \text{sebacic acid}$$

4. Cyclohexoxyl radical

This radical has been generated by pyrolysis of the nitrite (106). In chlorobenzene solvent, at about 90°C., the radical decomposes by ring fission and the alkyl radical is produced, which combines with a nitric oxide molecule to give the nitroso compound.

$$\text{cyclo-}C_6H_{11}O\cdot \rightarrow \cdot CH_2(CH_2)_4CHO \xrightarrow{NO} NOCH_2(CH_2)_4CHO$$

Although the ring strain is less in this radical than in the cyclopentoxyl compounds, ring fission still occurs.

5. 1-Methylcyclohexoxyl radical

This radical has been generated from the dialkyl peroxide (234), the *tert*-butyl peroxide (170), and the hydroperoxide (118, 119). Whether the radical is generated in the gas phase or in solution, the predominant reaction is that of ring fission and occurs readily at low temperatures (200–300°C.).

$$\text{cyclo-}C_6H_{10}(CH_3)O\cdot \rightarrow \cdot CH_2(CH_2)_4COCH_3 \rightarrow \text{dimer}$$

$$\cdot CH_2(CH_2)_4COCH_3 \rightarrow CH_3(CH_2)_3\dot{C}HCOCH_3 \rightarrow \text{dimer}$$

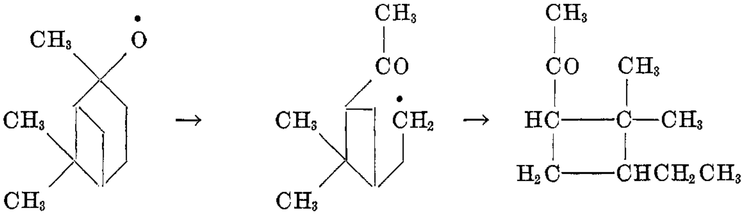
6. 1-Hydroxycyclohexoxyl radical

This radical has been generated from the dialkyl peroxide (234) under conditions similar to those used for 1-hydroxycyclopentyl peroxide. Ring fission again occurs, giving the alkyl radical.

$$\text{cyclo-}C_6H_{10}(OH)O\cdot \rightarrow \cdot CH_2(CH_2)_4COOH \rightarrow \text{dimer}$$

7. *Pinanoxyl radical*

This radical has been generated from the hydroperoxide (242). Here ring fission may occur in one of three ways; two involve ring splitting, and one involves loss of a free methyl radical. Ring fission is found to occur in the following manner:



8. *1-Phenylcyclohexoxyl radical*

This radical has been generated from the dialkyl peroxide (120). It undergoes decomposition by ring fission and yields the dimer. The reaction in which the bulky phenyl group is lost has not been detected.

$$\text{cyclo-}C_6H_{10}(C_6H_5)O\cdot \rightarrow C_6H_5CO(CH_2)_4CH_2\cdot$$

$$2C_6H_5CO(CH_2)_4CH_2\cdot \rightarrow \text{dimer (1,12-diketone)}$$

$$\xrightarrow[\text{hydrogen abstraction}]{\text{internal}} C_6H_5COCH(CH_2)_3OH \rightarrow \text{dimer}$$

9. *Pyran-1-oxyl radical*

This radical has been generated (171) from *tert*-butyl pyran peroxide by pyrolysis in the gas phase at about 250°C. It does not decompose readily by ring fission and disproportionation occurs (see Section IV,G).

D. DIALKOXYL RADICALS

The dialkoxyl radicals have two —O• groups and their reactions are determined by the positions of these groups relative to each other. The diradical, which has two terminal —O• groups, is analogous to the carbon diradicals $\cdot CH_2(CH_2)_nCH_2\cdot$, which have been postulated (237) in the polymerization of olefins.

In the decomposition of bridged peroxides or peroxide polymers there is no doubt that these dialkoxyl radicals play an important role. In the decomposition of the dinitrites and dinitrates the first step, fission of one of the oxygen–nitrogen bonds, may be followed by fission of the second oxygen–nitrogen bond; if it is, then a dialkoxyl radical is formed. Alternatively, after fission of the first oxygen–nitrogen bond the radical may decompose by fission of a carbon–carbon bond within the molecule, followed by fission of the second oxygen–nitrogen bond. In this case, the final products are still the same as if dialkoxyl radicals were the intermediate produced.

The important structural feature of these compounds is the relative positions of the —O• groups. With 1,2 and 1,4 compounds the reactions are simple decompositions and may be interpreted in terms of dialkoxyl radicals. With 1,3 or 1,5 compounds the reactions may be more complex; first one —O• group is formed by fission of one oxygen–nitrogen bond, and then the other nitrite group may be split off as a whole as nitrogen dioxide. These compounds are considered later in Section E.

1. 1,2-Dialkoxyl radicals

The best authenticated examples of the formation of dialkoxyl radicals are the decompositions of bridged peroxides and peroxide polymers. Examples of such peroxides are given in table 15, together with the dialkoxyl intermediates and the products. In each case the dialkoxyl radical decomposes. Systems in which there is opportunity for hydrogen-abstraction reactions to occur have not yet been studied.

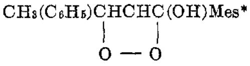
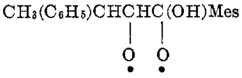
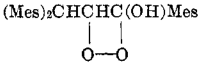
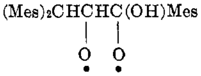
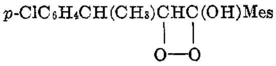
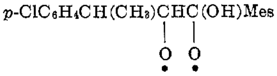
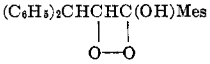
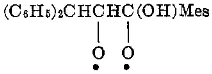
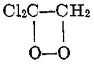
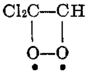
The decomposition of 1,2-dinitrites and dinitrates may be interpreted by assuming that dialkoxyl radical intermediates are formed. The decomposition of such compounds has been studied; known examples have been collected in table 16. In all cases, the experimental conditions are such that the predominant reaction of the dialkoxyl intermediate is decomposition.

Decomposition in the liquid phase would be expected to result in disproportionation. The liquid-phase decomposition (147) of butane 2,3-dinitrite at 120°C. produces the dialkoxyl radical, and this radical undergoes disproportionation; in addition some decomposition occurs. The reactions are:

$$\mathrm{ONOCH(CH_3)CH(CH_3)ONO \rightarrow \bullet O{-}CH(CH_3)CH(CH_3){-}O\bullet}$$

TABLE 15

1,2-Dialkoxyl radicals formed from bridged peroxides and peroxide polymers

Bridged Peroxide	Dialkoxyl Radical	Products	Reference
 $\begin{array}{l}\mathrm{CH_3(C_6H_5)CHCHC(OH)Mes^{*}}\\ \qquad\qquad\;\;\mathrm{|\quad\;|}\\ \qquad\qquad\;\;\mathrm{O—O}\end{array}$	 $\begin{array}{l}\mathrm{CH_3(C_6H_5)CHCHC(OH)Mes}\\ \qquad\qquad\quad\;\;\mathrm{|\quad|}\\ \qquad\qquad\quad\;\;\mathrm{O\quad O}\\ \qquad\qquad\quad\;\;\bullet\quad\;\bullet\end{array}$	$\mathrm{CH_3(C_6H_5)C{=}CHOOH}$ $\mathrm{MesCOOH}$	(76)
 $\begin{array}{l}\mathrm{(Mes)_2CHCHC(OH)Mes}\\ \qquad\;\;\mathrm{|\;\;|}\\ \qquad\;\;\mathrm{O—O}\end{array}$	 $\begin{array}{l}\mathrm{(Mes)_2CHCHC(OH)Mes}\\ \qquad\;\;\mathrm{|\quad|}\\ \qquad\;\;\mathrm{O\quad O}\\ \qquad\;\;\bullet\quad\;\bullet\end{array}$	$\mathrm{MesCOOH}$ $\mathrm{Mes_2C{=}CHOH}$	(76)
 $\begin{array}{l}p\text{-}\mathrm{ClC_6H_4CH(CH_3)CHC(OH)Mes}\\ \qquad\qquad\qquad\;\;\mathrm{|\;\;|}\\ \qquad\qquad\qquad\;\;\mathrm{O—O}\end{array}$	 $\begin{array}{l}p\text{-}\mathrm{ClC_6H_4CH(CH_3)CHC(OH)Mes}\\ \qquad\qquad\qquad\quad\mathrm{|\quad|}\\ \qquad\qquad\qquad\quad\mathrm{O\quad O}\\ \qquad\qquad\qquad\quad\bullet\quad\;\bullet\end{array}$	$p\text{-}\mathrm{ClC_6H_4C(CH_3){=}CHOH}$ $\mathrm{MesCOOH}$	(76)
 $\begin{array}{l}\mathrm{(C_6H_5)_2CHCHC(OH)Mes}\\ \qquad\quad\;\;\mathrm{|\;\;|}\\ \qquad\quad\;\;\mathrm{O—O}\end{array}$	 $\begin{array}{l}\mathrm{(C_6H_5)_2CHCHC(OH)Mes}\\ \qquad\qquad\mathrm{|\quad|}\\ \qquad\qquad\mathrm{O\quad O}\\ \qquad\qquad\bullet\quad\;\bullet\end{array}$	$\mathrm{(C_6H_5)_2CHCHO}$ $\mathrm{MesCOOH}$	(134)
 $\begin{array}{l}\mathrm{Cl_2C—CH_2}\\ \;\;\;\mathrm{|\quad|}\\ \;\;\;\mathrm{O—O}\end{array}$	 $\begin{array}{l}\mathrm{Cl_2C—CH_2}\\ \;\;\;\mathrm{|\quad|}\\ \;\;\;\mathrm{O—O}\\ \;\;\;\bullet\quad\;\bullet\end{array}$	$\mathrm{CCl_2O,\ CH_2O}$	(167)
$\mathrm{[—OC(C_6H_5)_2CH_2O—]_n}$	$\mathrm{\bullet OC(C_6H_5)_2CH_2O\bullet}$	$\mathrm{(C_6H_5)_2CO,\ CH_2O}$	(257)

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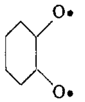
* Mes = mesityl, i.e., 2,4,6-$\mathrm{(CH_3)_3C_6H_2}$.

TABLE 16

Decomposition of 1,2- and 1,4-dialkoxyl radicals

Source of Alkoxyl Radical	Alkoxyl Radical	Products	Reference
Glycol dinitrite Glycol dinitrate	$\cdot OCH_2CH_2O\cdot$	$2CH_2O$	(211) (263)
Propane 1,2-dinitrite	$\cdot OCH_2(CH_3)CH_2O\cdot$	CH_3CHO, CH_2O	(147)
Butane 2,3-dinitrite Butane 2,3-dinitrate	$\cdot OCH(CH_3)(CH_3)CHO\cdot$	$2CH_3CHO$	(147) (213)
cis-Cyclohexane 1,2-dinitrite		$CHO(CH_2)_4CHO$	(147)
trans-Cyclohexane 1,2-dinitrite			(147)
1,4-Butanediol dinitrate	$\cdot OCH_2(CH_2)_2CH_2O\cdot$	$2CH_2O$ $CH_2{=}CH_2$	(213)
2,5-Dimethyl-3-hexyn-2,5 dihydroperoxide	$\cdot O(CH_3)_2CC{\equiv}CC(CH_3)_2O\cdot$	$2CH_3COCH_3$, C_2H_2	(170a)

(*a*) *Disproportionation:*

$$2\cdot O{-}CH(CH_3)CH(CH_3){-}O\cdot \rightarrow CH_3COCOCH_3 + CH_3CH(OH)CH(CH_3)OH$$

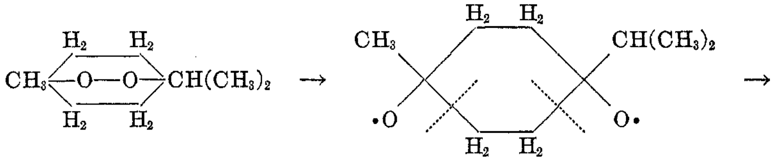
$$\rightarrow 2CH_3COCH(CH_3)OH$$

(*b*) *Fission:*

$$\rightarrow 2CH_3CHO$$

2. 1,4-Dialkoxyl radicals

These radicals are produced in the decomposition of cyclic compounds containing a bridged peroxide group. An example is provided by the thermal decomposition of dihydroascaridole (175). At 240°C. in the liquid phase the products are 6-methyl-2,5-heptanedione, a gas (presumably ethylene), and some polymer. If the decomposition proceeds by means of a 1,4-dialkoxyl radical, the reactions are:



$$CH_3CO(CH_2)_2COCH(CH_3)_2 + C_2H_4$$

As has been shown in Section VI,C, the carbon–carbon bonds in the ring undergo fission in preference to the carbon–methyl or the carbon–isopropyl bonds.

The decomposition of 1,4-dinitrites and 1,4-dinitrates has been studied, and the reactions may be interpreted by assuming a dialkoxyl radical intermediate. These reactions are summarized in table 16.

In the decomposition of butane 1,4-dinitrite at low temperatures two reactions of the dialkoxyl radical occur; the main one is internal hydrogen transfer and this is accompanied by 10 per cent decomposition.

$$\mathrm{ONOCH_2CH_2CH_2CH_2ONO \rightarrow \cdot OCH_2CH_2CH_2CH_2O\cdot + 2NO}$$

$$\text{hydrogen transfer:}\quad \mathrm{\cdot OCH_2CH_2CH_2CH_2O\cdot \rightarrow HOCH_2CH_2CH_2CHO}$$

$$\text{decomposition:}\quad \mathrm{\cdot OCH_2CH_2CH_2CH_2O\cdot \rightarrow 2CH_2O + CH_2{=}CH_2}$$

Decomposition of butane 1,4-dinitrate at higher temperatures ($\simeq$ 300°C.) also produces the dialkoxyl radical, but under these conditions complete decomposition is found to occur (213).

Decomposition of the 1,4-dialkoxyl radical may also occur at low temperatures if the hydrogen-transfer reaction is prevented by substitution of methyl groups in the α-carbon atom.

$$\mathrm{ONOC(CH_3)_2CH_2CH_2C(CH_3)_2ONO \rightarrow \cdot OC(CH_3)_2CH_2CH_2C(CH_3)_2O\cdot + 2NO}$$

$$\mathrm{\cdot OC(CH_3)_2CH_2CH_2C(CH_3)_2O\cdot \rightarrow 2(CH_3)_2CO + CH_2{=}CH_2}$$

If the α-carbon atoms are only partially substituted by methyl groups, some hydrogen transfer may occur. For example:

$$\mathrm{ONOCH(CH_3)CH_2CH_2CH_2ONO \rightarrow \cdot OCH(CH_3)CH_2CH_2CH_2O\cdot}$$

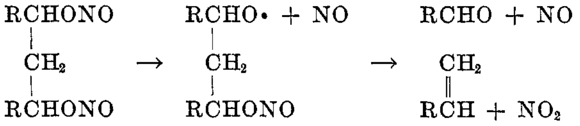
$$\begin{aligned}\mathrm{\cdot OCH(CH_3)CH_2CH_2CH_2O\cdot} &\rightarrow \mathrm{HOCH(CH_3)CH_2CH_2CHO}\quad (20\%)\\ &\rightarrow \mathrm{2CH_3CHO + CH_2{=}CH_2}\quad (80\%)\end{aligned}$$

A striking example of the ready fission of a 2,5-dialkoxyl radical is provided by recent work (170a) on the acetylenic peroxide 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide:

$$\mathrm{\cdot O(CH_3)_2CC{\equiv}CC(CH_3)_2O\cdot \rightarrow 2CH_3COCH_3 + C_2H_2}$$

E. ALKOXYL RADICALS CONTAINING A NITRITE GROUP

The 1,3-dinitrites are quite different from the 1,2- or 2,4-dinitrites. These 1,3-compounds do not form a dialkoxyl radical on decomposition, nor can their reactions be based on such an intermediate. They have an unusual reaction in that after formation of the first —O• group by fission of an oxygen–nitrogen bond, the second nitrite group is split out as nitrogen dioxide.



$$\begin{array}{c} \mathrm{RCHONO} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{RCHONO} \end{array} \rightarrow \begin{array}{c} \mathrm{RCHO\cdot + NO} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{RCHONO} \end{array} \rightarrow \begin{array}{c} \mathrm{RCHO + NO} \\ \\ \mathrm{CH_2} \\ \| \\ \mathrm{RCH + NO_2} \end{array}$$

Table 17 gives known examples of this reaction; in each case the products include nitrogen dioxide and an olefin.

In the presence of a suitable hydrogen donor, the intermediate alkoxyl radical abstracts a hydrogen, giving the alcohol. This stabilizes the radical and the second nitrite group decomposes normally by oxygen–nitrogen bond fission, resulting in the formation of an alkoxyl radical. For example, decomposition of propane 1,3-dinitrite in the presence of paraffin oil at 125°C. gives a 60 per cent yield of

TABLE 17

Decomposition of alkoxyl radicals containing a nitrite group (149)

Dinitrite Source	Alkoxyl Radical Produced	Products from Alkoxyl Radical
Propane 1,3-dinitrite	$ONOCH_2CH_2CH_2O\bullet$	NO_2, $CH_2{=}CH_2$, CH_2O
Butane 1,3-dinitrite	$ONOCH_2CH_2CH(CH_3)O\bullet$	NO_2, $CH_2{=}CH_2$, CH_3CHO
	$ONOCH(CH_3)CH_2CH_2O\bullet$	NO_2, $CH_3CH{=}CH_2$, CH_2O
Pentane 2,3-dinitrite	$ONOCH(CH_3)CH_2CH(CH_3)O\bullet$	NO_2, $CH_3CH{=}CH_2$, CH_3CHO

1,3-propanediol (149). The reaction may be accounted for by the following mechanism:

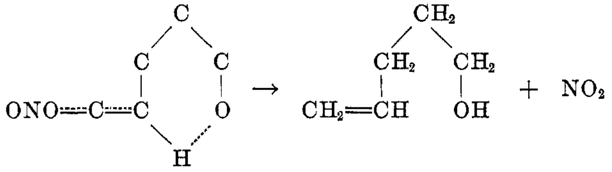
$$ONOCH_2CH_2CH_2ONO \rightarrow ONOCH_2CH_2CH_2O\bullet \xrightarrow{RH} ONOCH_2CH_2CH_2OH$$

$$ONOCH_2CH_2CH_2OH \rightarrow \bullet OCH_2CH_2CH_2OH \xrightarrow{RH} HOCH_2CH_2CH_2OH$$

The gas-phase decomposition of 1,5- and 1,6-dinitrites proceeds via a nitrite-substituted alkoxyl radical. For example, the decomposition of pentamethylene dinitrite proceeds by the following reaction route:

$$ONOCH_2CH_2(CH_2)_3ONO \rightarrow ONOCH_2CH_2(CH_2)_3O\bullet + NO \rightarrow$$
$$NO_2 + CH_2{=}CH(CH_2)_3OH + NO$$

The intermediate stage may involve a six-membered-ring transition state in which internal hydrogen abstraction occurs.



In the gas-phase decomposition of a 1,6-dinitrite (for example, hexamethylene 1,6-dinitrite) the transition state probably involves a seven-membered ring in which internal hydrogen transfer occurs.

VII. The Role of Alkoxyl Radicals in Complex Systems

In Section IV the reactions of alkoxyl radicals in simple systems which are readily interpreted have been considered. But in many systems, reaction conditions may be such that the intermediate products decompose or may be involved in competitive, consecutive reactions. In other systems, more than one species of alkoxyl radical may be present. However, the reaction mechanisms in such systems can frequently be interpreted by applying our knowledge of the reactions and reactivity of the simple alkoxyl radicals involved.

In this section the interpretation of certain complex reaction systems will be discussed. In each, the role which the alkoxyl radical plays will be stressed and a survey of the complete mechanism will not be attempted.

A. THERMAL OXIDATION OF HYDROCARBONS BY MOLECULAR OXYGEN

Alkoxyl radicals are among the important oxygenated free-radical intermediates in the thermal oxidation of hydrocarbons at low temperatures. Evidence for their participation is twofold. Firstly, alcohols are produced and usually their only possible precursors are alkoxyl radicals. The oxidation of propane provides an example of this, since relatively large yields of methanol are found (240). Secondly, formaldehyde is produced from each carbon atom in the carbon skeleton of the molecule. This has been demonstrated by the oxidation of labelled molecules (75, 189). The only simple mechanism by which this can occur is by the degradation of alkoxyl radicals:

$$\mathrm{RCH_2O\cdot \rightarrow R\cdot + CH_2O}$$

Further evidence comes from a study of the oxidation of isobutane (19). Acetone is the product; with excess hydrocarbon methane is formed when nearly all the oxygen is consumed.

$$\mathrm{(CH_3)_3CO\cdot \rightarrow (CH_3)_2CO + CH_3\cdot}$$

$$\mathrm{CH_3\cdot + RH \rightarrow CH_4 + R\cdot}$$

The first oxygenated free radical produced from the fuel molecule and oxygen is the peroxyl radical, and it is subsequent reactions of this that lead to the formation of the alkoxyl radical. The peroxyl radicals are probably formed (20) by the following mechanism:

$$\mathrm{R{-}H + X \rightarrow R\cdot + HX}$$

$$\mathrm{R\cdot + O_2 \rightarrow RO_2\cdot}$$

where X may be oxygen, an atom, or a radical.

The point at which the oxygen attacks the hydrocarbon has been investigated (36, 286), and the order of reactivity of the carbon–hydrogen bond is found to be tertiary > secondary > tertiary. Thus the structure of the peroxyl radical produced is known and also that of the alkoxyl radical produced from it.

Alkoxyl radicals are produced from alkyl peroxyl radicals in a number of ways. The most important proceeds by the formation of a hydroperoxide intermediate. The reactions are:

$$\mathrm{RO_2\cdot + R'H \rightarrow ROOH + R'\cdot}$$

$$\mathrm{ROOH \rightarrow RO\cdot + \cdot OH}$$

Many oxidation processes have been interpreted in terms of this mechanism (20, 45, 245, 286), and often hydroperoxides have been detected in the oxidation products (14, 77, 78, 245). This mechanism is most likely when the decomposition of peroxyl radicals to an aldehyde and a hydroxyl radical is minimized, i.e., at low temperatures and with secondary or tertiary peroxyl radicals, because the parent molecules (R′H) provide a ready source of easily abstracted hydrogen. Moreover, secondary peroxyl radicals are less likely to decompose by elimination of a hydroxyl radical; in tertiary radicals it is not possible at all. For example, the oxidation of methane at high temperatures may not involve alkoxyl radical intermediates (127), but the oxidation at low temperatures of secondary and tertiary hydrocarbons does (see Section X,A,1,2).

Alkoxyl radicals are also formed by the decomposition of secondary or tertiary peroxyl radicals (20, 245, 276). For example, the products of the slow combustion of propane may be explained (240) by such a mechanism.

$$(CH_3)_2CHOO\cdot \rightarrow CH_3CHO + CH_3O\cdot$$

The reaction of two peroxyl radicals (20) may also produce alkoxyl radicals:

$$RO_2\cdot + RO_2\cdot \rightarrow 2RO\cdot + O_2$$

It has also been suggested (244) that peroxyl radicals react with oxygen to give an alkoxyl radical and ozone, and that this latter entity may be the active intermediate responsible for chain branching during the slow combustion of hydrocarbons in oxygen:

$$RO_2\cdot + O_2 \rightarrow RO\cdot + O_3$$

Many oxidation products produced by the rearrangement of peroxyl radicals (20) do not involve alkoxyl radical intermediates. The oxidations of some hydrocarbons that proceed predominantly through alkoxyl radical intermediates will now be considered; the examples have been chosen for their diversity and to emphasize the role of the alkoxyl intermediate.

1. *The combustion of isoöctane*

The oxidation of isoöctane may be explained (285) by the following mechanism. The single tertiary carbon–hydrogen bond is attacked by oxygen, producing a free alkyl radical which combines with oxygen to give a peroxyl radical. The hydroperoxide is formed by hydrogen abstraction and this decomposes to give an alkoxyl radical.

$$(CH_3)_3CCH_2CH(CH_3)_2 \rightarrow (CH_3)_3CCH_2\dot{C}(CH_3)_2 \xrightarrow[\text{(2) hydrogen abstraction}]{\text{(1) } O_2} (CH_3)_3CCH_2C(CH_3)_2OOH$$

$$(CH_3)_3CCH_2C(CH_3)_2OOH \rightarrow (CH_3)_3CCH_2C(CH_3)_2O\cdot + \cdot OH$$

$$(CH_3)_3CCH_2C(CH_3)_2O\cdot \rightarrow (CH_3)_3CCH_2\cdot + (CH_3)_2CO$$

The alkyl radicals produced react with oxygen, forming a hydroperoxide which decomposes to an alkoxyl radical.

$$(CH_3)_3CCH_2\cdot \rightarrow (CH_3)_3CCH_2OO\cdot \rightarrow (CH_3)_3CCH_2OOH$$

$$(CH_3)_3CCH_2OOH \rightarrow (CH_3)_3CCH_2O\cdot + \cdot OH$$

$$(CH_3)_3CCH_2O\cdot \rightarrow (CH_3)_3C\cdot + CH_2O$$

This degradative process is repeated.

$$(CH_3)_3C\cdot + O_2 \rightarrow (CH_3)_3COO\cdot \rightarrow (CH_3)_3COOH$$

$$(CH_3)_3COOH \rightarrow (CH_3)_3CO\cdot + \cdot OH$$

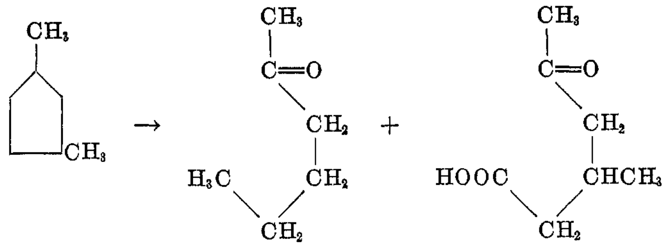
$$(CH_3)_3CO\cdot \rightarrow CH_3\cdot + (CH_3)_2CO$$

Thus the degradative oxidation of isoöctane may be explained by the formation and subsequent decomposition of alkoxyl radicals.

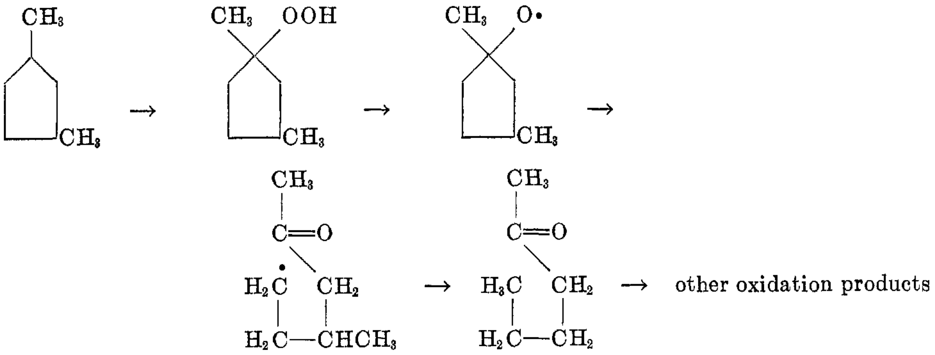
2. Slow oxidation of cyclic hydrocarbons

The slow oxidation of cyclic compounds such as 1,3-dimethylcyclopentane and 1,3-dimethylcyclohexane has been studied (45). The reactions occur in the liquid phase in the presence of excess oxygen at 80°C. and under these conditions hydroperoxides are readily formed.

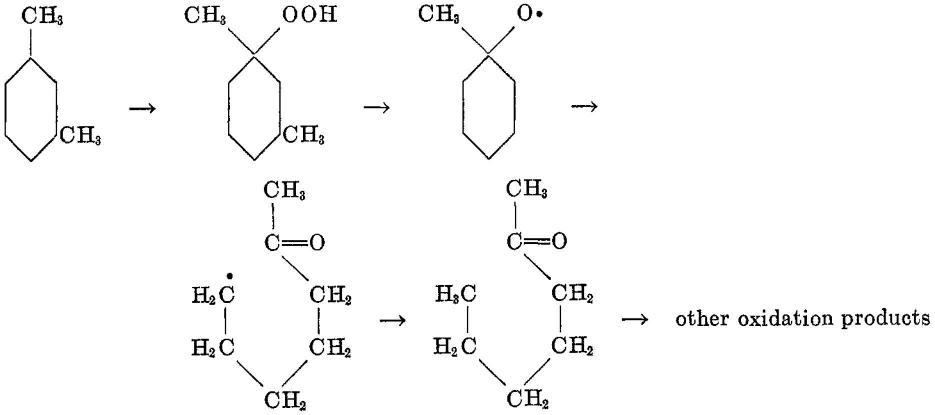
The oxidation of dimethylpentane gives the following products:



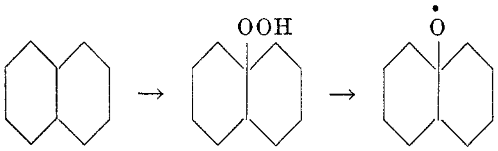
This has been interpreted (83) by the following mechanism:



Similarly, with dimethylcyclohexane:

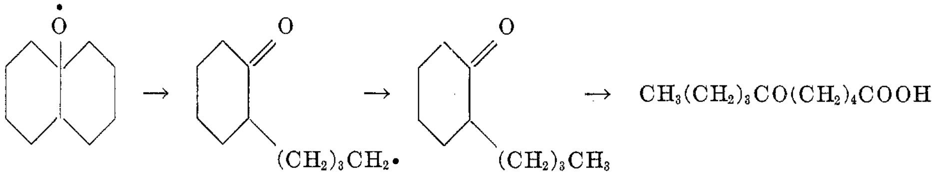


Oxidation of decahydronaphthalene in the vapor or liquid phase results in the formation of acidic degradation products. The mechanism of this oxidation has been shown to involve alkoxyl radicals (123). The initial stages are:

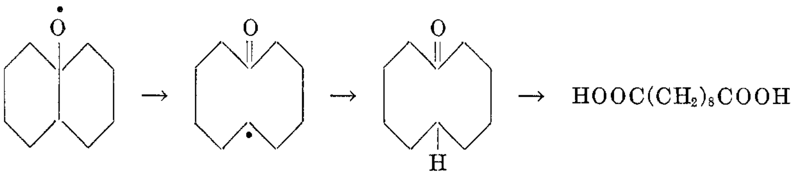


and this reaction is followed by degradation of the alkoxyl radical by one of two paths.

Path 1:

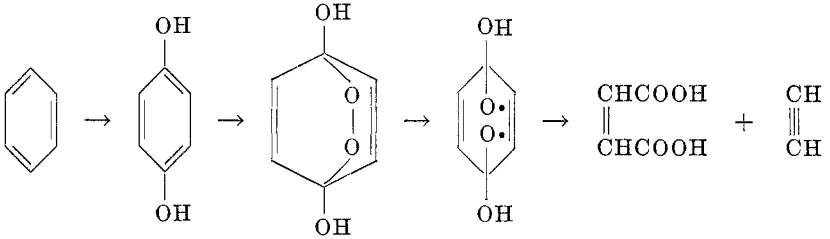


Path 2:



3. The oxidation of benzene

It has been suggested (193) that the gas-phase oxidation of benzene proceeds by means of a dialkoxyl radical intermediate. The initial reactions result in the formation of a 1,4-peroxide in which the oxygen–oxygen bond undergoes fission, giving the dialkoxyl radical. This radical subsequently decomposes, yielding maleic acid and acetylene.



4. Oxidation of amines

Alkoxyl radicals may play an intermediate role in the gas-phase oxidative degradation of amines. The following reactions have been suggested (54) to account for the formation of diethylamine:

$$(C_2H_5)_3N \rightarrow CH_3CH(OOH)N(C_2H_5)_2 \rightarrow CH_3CHO + {\cdot}OH + (C_2H_5)_2N{\cdot}$$

$$(C_2H_5)_2N{\cdot} + XH \rightarrow (C_2H_5)_2NH$$

B. OXIDATION BY NITROUS OXIDE

Alkoxyl radicals play an important role as the reactive intermediate in the oxidation of hydrocarbons by nitrous oxide. At temperatures less than 600–

700°C. the nitrous oxide undergoes little decomposition but the hydrocarbon decomposes, yielding free alkyl radicals. The radicals are oxidized by nitrous oxide to give alkoxyl radicals, which at these temperatures decompose:

$$RCH_2\cdot + N_2O \rightarrow RCH_2O\cdot + N_2$$

The oxidation of ethane (136, 137) and of the hydrocarbon propane to nonane (251) by nitrous oxide have been interpreted in this way, which explains the kinetics followed and the products found. In the oxidation of ethane in the gas phase, alkyl radicals are initially generated and the following reactions occur:

$$C_2H_5\cdot + N_2O \rightarrow C_2H_5O\cdot + N_2 \qquad E_{act} = 16 \text{ to } 32 \text{ kcal. mole}^{-1}$$

$$C_2H_5O\cdot \rightarrow \cdot CH_3 + CH_2O$$

$$2C_2H_5O\cdot \rightarrow C_2H_5OH + CH_3CHO$$

C. PHOTOÖXIDATION

The photoöxidation of saturated hydrocarbons is similar in many respects to the thermal oxidation. Peroxyl radicals are formed, and these may decompose (aldehydic mechanism) or form a hydroperoxide (peroxidic mechanism). Whether the parent molecule is a normal, a secondary, or a tertiary hydrocarbon determines which mechanism is followed (35); the temperature at which the oxidation occurs is also important. High yields of hydroperoxides have been isolated in many cases (20), and this mechanism, which results in the formation and subsequent reaction of alkoxyl radicals, is extremely important under photochemical conditions (246, 276, 293).

The photoöxidation of halogenated compounds has been studied. In the photooxidation of perfluoroiodoalkanes (117) alkoxyl radicals play a leading role in the oxidative degradation of the parent molecule. The oxidation of iodoperfluoropropane may be explained by the following mechanism:

$$C_3F_7I \xrightarrow{h\nu} C_3F_7\cdot \xrightarrow{O_2} C_3F_7O_2$$

$$C_3F_7O_2 \xrightarrow{C_3H_7I} C_3F_7OOI \rightarrow C_3F_7O\cdot + \cdot OI$$

$$C_3F_7O\cdot \rightarrow C_2F_5\cdot + COF_2$$

$$C_2F_5\cdot \xrightarrow{O_2} C_2F_5O_2\cdot \rightarrow C_2F_5OOI \rightarrow C_2F_5O\cdot$$

$$C_2F_5O\cdot \rightarrow CF_3\cdot + COF_2$$

$$CF_3\cdot \xrightarrow{O_2} CF_3O_2\cdot \rightarrow CF_3O\cdot \rightarrow COF_2 + F\cdot$$

D. DEGRADATIVE NITRATION OF HYDROCARBONS

The reaction between alkyl radicals and nitrogen dioxide may take three different courses: association to a nitroparaffin or to an alkyl nitrite or oxidation to an alkoxyl radical (90).

$$R\cdot + NO_2 \rightarrow RNO_2 \tag{1}$$

$$R\cdot + NO_2 \rightarrow RONO \tag{2}$$

$$R\cdot + NO_2 \rightarrow RO\cdot + NO \qquad \Delta H = -20 \text{ kcal. mole}^{-1} \tag{3}$$

Except under special conditions, reaction 2 cannot occur, because the molecule formed is not stable, the nitrite almost immediately decomposing to an alkoxyl radical and a molecule of nitric oxide (reaction 3).

The alkoxyl radical may react by any of the reactions discussed in Section IV. Nitration is usually conducted at high temperature; consequently the predominant reaction is decomposition of the alkoxyl radical. This results in loss of formaldehyde to form a lower alkyl radical; the lower alkyl radical then undergoes a pattern of changes similar to that of its precursor.

The nitration agents frequently used are nitric acid or a chlorine–nitrogen dioxide mixture, nitration being carried out in the gas phase. The initial stage is abstraction of a weakly attached hydrogen atom from the parent. The ease of hydrogen abstraction is in the order tertiary > secondary > primary hydrogen, and so the alkoxyl radical generated initially may be inferred and the whole pattern of reactions interpreted. Three examples of degradative nitration will now be discussed.

1. Degradative nitration of propane

At 400–700°C. the nitration of propane by nitrogen dioxide has been studied (9, 10, 115). The first step is the formation of *n*- and *sec*-propyl radicals by hydrogen abstraction from the parent hydrocarbon. The alkyl radicals combine with nitrogen dioxide to give two products: the nitroalkane, which is isolated, and the nitrite, which decomposes to give the alkoxyl radical. Decomposition of alkoxyl produces an alkyl radical and the chain is repeated. The reactions are:

(*a*) *n-Propyl radical:*

Association: $CH_3CH_2CH_2\cdot + NO_2 \rightarrow CH_3CH_2CH_2NO_2$

$\rightarrow CH_3CH_2CH_2ONO$

Degradation: $CH_3CH_2CH_2ONO \rightarrow CH_3CH_2CH_2O\cdot + NO$

$CH_3CH_2CH_2O\cdot \rightarrow CH_3CH_2\cdot + CH_2O$

Propagation: $CH_3CH_2\cdot + NO_2 \rightarrow CH_3CH_2ONO$

$\rightarrow CH_3CH_2NO_2$

$CH_3CH_2ONO \rightarrow CH_3CH_2O\cdot + NO$

$CH_3CH_2O\cdot \rightarrow CH_3\cdot + CH_2O$

$CH_3\cdot + NO_2 \rightarrow CH_3NO_2$

(*b*) *sec-Propyl radical:*

$$(CH_3)_2CH\cdot + NO_2 \rightarrow (CH_3)_2CHNO_2$$

$$\rightarrow (CH_3)_2CHONO$$

Degradation and propagation occur in similar ways to that of the *n*-propyl radical.

By adjusting the conditions the amount of degradation (i.e., the amount of breakdown by fission of alkoxyl radicals) may be altered (10). This can be achieved in two ways: Firstly, the number of alkoxyl radicals may be increased by adding oxygen to the system. The following additional reactions occur:

$$R\bullet + O_2 \rightarrow RO_2\bullet$$

$$RO_2\bullet + XH \rightarrow ROOH \rightarrow RO\bullet + OH$$

$$RO\bullet \rightarrow \text{degradation products}$$

Secondly, degradation may be facilitated by increasing the temperature. Under these more severe conditions decomposition of the radical occurs to a much greater extent.

2. Degradative nitration of perfluoroalkanes

The degradative nitration of perfluoroalkanes has also been studied (16). When heptafluoroiodopropane is photolyzed in the presence of nitric oxide, heptafluoronitrosoalkane is produced. In the absence of mercury, which would remove from the reaction zone the nitrogen dioxide produced by the photolysis of nitric oxide, the formation of heptafluoronitrosopropane is accompanied by extensive breakdown of the perfluoroalkyl chain to give carbonyl fluoride, 2–5 per cent pentafluoronitrosoethane, trifluoronitrosomethane, and smaller amounts of the corresponding nitro compounds. These products may be explained by the mechanism:

$$C_3F_7I \xrightarrow{h\nu} C_3F_7\bullet + I$$

$$C_3F_7\bullet + NO \rightarrow C_3F_7NO$$

$$\begin{aligned} C_3F_7\bullet + NO_2 &\rightarrow C_3F_7NO_2 \\ &\rightarrow C_3F_7ONO \end{aligned}$$

accompanied by degradation via the perfluoroalkoxyl radical:

$$C_3F_7ONO \xrightarrow{h\nu} C_3F_7O\bullet + NO$$

$$C_3F_7O\bullet \rightarrow C_2F_5\bullet + COF_2$$

$$C_2F_5\bullet + NO \rightarrow C_2F_5NO$$

$$C_2F_5\bullet \xrightarrow{NO_2} C_2F_5ONO \xrightarrow{h\nu} C_2F_5O\bullet$$

$$C_2F_5O\bullet \rightarrow COF_2 + CF_3\bullet$$

$$CF_3\bullet \xrightarrow{NO} CF_3NO$$

$$CF_3\bullet \xrightarrow{NO_2} CF_3ONO \rightarrow CF_3O\bullet$$

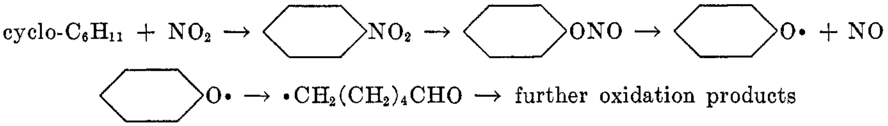
$$CF_3O\bullet \xrightarrow{SiO_2} COF_2 + SiF_4$$

3. Degradative nitration of cyclohexane

Degradative nitration of cyclohexane by nitric acid occurs by the following mechanism in hydrocarbon solution (277):

$$HNO_3 \rightarrow HO\cdot + NO_2$$

$$C_6H_{12} + \cdot OH \rightarrow H_2O + C_6H_{11}$$



E. REACTIONS OF ALKOXYL RADICALS IN FLAMES

The types of flame considered here are the near-uniform inflammations of heated substances (spontaneous ignition), the propagation of a flame after ignition through a combustible mixture (premixed flames), and the flame formed at the boundary between a fuel and an oxidant (diffusion flames).

1. Spontaneous ignition

When a mixture of combustible gases, such as a hydrocarbon with oxygen or a peroxide alone, is admitted suddenly to a hot vessel, exothermic reaction occurs and explosion may ensue. The reactions which take place before explosion (preflame region) are those of decomposition and oxidation and in general differ only slightly from those of isothermal systems. When the isothermal reactions involve alkoxyl radicals, as is commonly the case, then so do the preflame reactions. The subsequent reactions which occur as the reactant inflames are rather those of premixed flames (Section VI,E). Spontaneous ignitions are often complex, a succession of inflammations occurring in a particular mixture (81). The temperature reached in the early stages, which may be quite low, has earned for one very common group the title "cool flames," to distinguish them from the subsequent more violent, very hot flames in which combustion is completed. Cool flames are found in a wide variety of combustions supported by oxygen. The blue light which they emit is chemiluminescent, not thermal, radiation, corresponding to excited formaldehyde falling to its ground state. Long associated with the formation and reaction of organic peroxides, the cool flame and its luminescence have recently been suggested (90) to arise always in systems containing alkoxyl radicals and the reaction

$$CH_3O\cdot + \cdot OH \rightarrow CH_2O^* + H_2O \qquad \Delta H = -94 \text{ kcal. mole}^{-1}$$

is an alternative to other disproportionation type reactions, for example:

$$CH_3O\cdot + CH_3O\cdot \rightarrow CH_2O^* + CH_3OH$$

$$CH_3O\cdot + CH_3\cdot \rightarrow CH_2O^* + CH_4$$

The spontaneous ignition of explosive vapors which contain the oxygen for their own combustion has also been interpreted in terms of alkoxyl radicals. Typical members of these classes are the alkyl peroxides (113) and hydroperoxides (112), the nitrate esters (7, 107, 108), and the nitrite esters (89). The inflammations of these substances, all known to involve alkoxyl radicals, strikingly parallel normal oxidations in showing the same, distinct modes—slow reactions, chemiluminescent "cool" flames, explosion (hot flames), and detonation. Information obtained about them is also valuable for the light it throws on oxidation. In particular, the identification of the chemiluminescence of the decomposition of methyl nitrate as formaldehyde emission (93, 94) supports the view that the presence of alkoxyl radicals is normally a necessary and always a sufficient condition for the production of cool flames.

The role of peroxides in promoting knock in petrol engines (287, 288) is also to be associated with the participation of alkoxyl radicals, an interpretation foreshadowed by Ubbelohde's early work (280), which showed ethyl nitrite but not the isomeric nitroethane to be a proknock, and by the German practice in the 1939–45 war of using methyl nitrate to vary the properties of petrol (gasoline) and paraffin (kerosene).

2. Stationary flames in premixed gases and in monofuels

In premixed gases, fuel and oxidant form a homogeneous mixture through which exothermic reaction is propagated. It is always important to distinguish preflame reactions from those occurring in the light-emitting zone of the flame and frequently necessary to recognize the complexity of the flame itself. For example, the chief heat-releasing zone may be preceded by a cool or a blue flame and succeeded by an afterglow. These features are most marked at low pressures, when the reaction zones may often be separated even though they were completely coalesced at atmospheric pressure (78, 81, 93, 94, 111).

Like the reactions preceding spontaneous ignition, preflame reactions are expected to have more affinity with isothermal systems than with the subsequent changes in the hot flame itself. Analytical work confirms this resemblance to gas-phase slow combustion (276) with the characteristic build up of peroxide and aldehyde intermediates. Cool flames in premixed gases are intermediate in character. They are preceded by the production of organic peroxides, and these may be only partially consumed in the cool flame itself. Alkoxyl radicals enter as the first product of peroxide pyrolysis; by their decomposition carbonyl compounds arise and degradation of the fuel is advanced. Cool flames in combustion reactions are most satisfactorily examined in flow systems which permit them to be held stationary. Recent papers (14, 79, 80, 144) describe some of their properties and give many useful references to earlier work.

The hot zones of flames, in which the principal heat-releasing reactions occur, are thought not to involve alkoxyl radicals directly but rather as precursors of the simpler fragments: e.g., CH, CN, HO, NH, C_2.

Complementary to the oxidation flames of premixed gases are the decomposition flames of substances such as alkyl peroxides and nitrate explosives, which contain the oxygen for their own combustion. These are known to involve alkoxyl radicals, and their study (89, 93, 94, 107, 108, 113) has implications for cool and hot flames.

Flames of nitrate esters are discussed later (Section VI,F). Recently methyl nitrite has been shown to be capable of maintaining a decomposition flame (93, 99). This flame depends for its existence on the normally difficult reduction of nitric oxide; the present evidence (94, 99) supports the view that this is achieved by participation of methoxyl radicals rather than by reaction with stabler products such as methanol or formaldehyde (8).

3. Stationary diffusion flames

When a flame is maintained at the boundary between a fuel and an oxidant flowing parallel to one another, steep temperature and concentration gradients are established in the steady state. Fresh fuel and oxidant diffuse in towards the heat-releasing zone; products diffuse outwards and are simultaneously borne away by the (longitudinal) flow. Visually distinct zones of flame are frequently established, the innermost being the hottest. Analytical study by chemical and spectroscopic means has shown that before the visible reaction zones are reached decomposition is invariably extensive on both fuel and oxidant sides if these are complex molecules, for example, hydrocarbon–nitric acid. Once again alkoxyl radicals may not survive to enter the hottest zones, but they are certainly involved in the outer zones and in the preflame regions on the fuel side, where alkyl radicals from the pyrolysis of the hydrocarbon meet oxygen and hydroxyl carried to them by diffusion.

4. Detonation

Detonation, the most violent and rapid of flame propagations, has few of its chemical reactions exactly assigned. The application of shock tubes to the study of simple systems (e.g., peroxides, nitrates, and hydrocarbon–oxygen mixtures) has begun, however, and is likely to supply further information. Lack of knowledge of the spectroscopy of alkoxyl radicals may make progress slow at first.

F. THE DECOMPOSITION OF NITRATE EXPLOSIVES

In Section II,6,2 the evidence was presented for the formation of alkoxyl radicals as the primary step in the decomposition of nitrate esters; greatest assurance can be placed in this interpretation for the simplest esters—methyl, ethyl, *n*-propyl, isopropyl, and *tert*-butyl nitrates. Although isopropyl nitrate has found technical application as a monofuel, methyl nitrate–methanol (myrol) mixtures have been discarded and the most important nitrate explosives are all polyesters, of which the chief are nitroglycerin, pentaerythritol tetranitrate, the nitrocelluloses, and cordite.

All these explosives contain the oxygen for their own exothermic combustion, and their decomposition shows many similarities to the oxidation of a fuel. In general, the initial step is fission of the O—NO_2 bond:

$$RO{-}NO_2 \rightarrow RO\cdot + NO_2$$

The alkoxyl radical then performs the same function as it does in mediating combustion; it offers a path by which degradation to simpler (alkyl) radicals occurs. Carbonyl compounds—formaldehyde, aldehydes, and ketones—are formed simultaneously and they, together with the alkyl radicals, are oxidized by the nitrogen dioxide. As with the flames described in Section VI,E, alkoxyl

TABLE 18

References to participation of alkoxyl radicals in the decomposition of nitrate explosives by various modes

Nitrate Explosive	References	
	Slow decomposition	Flame and explosion
Methyl nitrate	(6, 89)	(6, 25, 89, 93, 94, 107, 108, 220)
Ethyl nitrate	(1, 155, 156, 206, 203)	
n-Propyl nitrate	(156, 202)	(95, 213)
Isopropyl nitrate		(95, 212, 261)
tert-Butyl nitrate	(159)	
1,2-Ethanediol dinitrate	(201, 202)	(261, 262)
2,3-Butanediol dinitrate		(213)
1,3-Propanediol dinitrate	(202)	
1,3-Butanediol dinitrate	(202)	
1,4-Butanediol dinitrate		(213)
Nitroglycerin	(201, 202, 232, 235)	(230, 235)
1,2,4-Butanetriol trinitrate	(202)	
Methyltrimethylolmethane trinitrate		(121, 122)
Ethyltrimethylolmethane trinitrate	(202)	
Pentaerythritol tetranitrate	(202)	(230)
Trimethylolnitromethane trinitrate	(202)	
Cellulose nitrate	(303a)	

radicals are most readily recognized and most influential in the earliest stages of reaction; when the flame itself is reached, they have split into simpler fragments.

Table 18 lists some recent references to nitrate explosives, simple and complex; these are not intended to be exhaustive but to indicate present-day trends. Some representative examples are discussed briefly below.

1. Alkoxyl radicals in mononitrate ester flames: methyl, ethyl, n-propyl, and isopropyl nitrates

The nitrates listed above, with *tert*-butyl nitrate, are also those that have been most carefully examined in isothermal decomposition. All authors agree on initial oxygen–nitrogen bond fission both in thermal decomposition and in flames. Once again, the alkoxyl radicals, by their own fission to alkyl radicals, provide a degradation path leading to the end product of combustion. Spectroscopic work (93, 94, 303), detailed chemical analysis (155, 156, 187, 212, 261), and isotopic substitution experiments (261) all serve to clarify the general picture. A typical set of equations for the main paths in the *n*-propyl nitrate flame is:

$$n\text{-}C_3H_7ONO_2 \rightarrow n\text{-}C_3H_7O\cdot + NO_2$$

$$n\text{-}C_3H_7O\cdot \rightarrow C_2H_5\cdot + CH_2O$$

$$C_2H_5\cdot + NO_2 \rightarrow (C_2H_5O\cdot + NO) \text{ and some } C_2H_5NO_2$$

$$C_2H_5O\cdot \rightarrow CH_3\cdot + CH_2O$$

$$CH_3\cdot + NO_2 \rightarrow \text{etc.}$$

$$n\text{-}C_3H_7O\cdot + NO \rightarrow n\text{-}C_3H_7ONO$$

This particular example and the role of subsidiary reactions are discussed in reference 212.

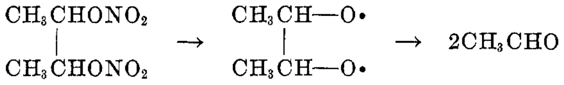
2. Alkoxyl radicals in dinitrate flames: glycol dinitrate and 2,3-butanediol dinitrate

When the alkoxyl radical from a mononitrate decomposes, it advances the degradative sequence by forming a carbonyl compound and an extremely active alkyl radical, which is in turn immediately attacked by the nitrogen dioxide:

$$C_2H_5ONO_2 \rightarrow C_2H_5O\cdot + NO_2$$

$$C_2H_5O\cdot \rightarrow CH_3\cdot + CH_2O$$

The 1,2-diol dinitrates, however, give no such alkyl radical. Instead, carbonyl compounds only are formed. If the reaction is represented for simplicity as a single step, we have:



$$\begin{array}{c} CH_3CHONO_2 \\ | \\ CH_3CHONO_2 \end{array} \rightarrow \begin{array}{c} CH_3CH—O\cdot \\ | \\ CH_3CH—O\cdot \end{array} \rightarrow 2CH_3CHO$$

The dialkoxyl radical splits to yield two *molecules* (see Section V,E) of acetaldehyde. The difference is that although the nitrogen dioxide is attacked and reduced, the process is slower than the radical reactions above and a measurable concentration of nitrogen dioxide may arise (212, 303). The dinitrates and the premixed aldehyde–nitrogen dioxide mixtures are better models of complex polynitrates than are the simple nitrate esters.

3. Alkoxyl radicals in polynitrate explosives

To date, the detailed mechanism is largely conjectural and relies considerably on extrapolation from the properties of the above-mentioned systems. Leading references are to be found in table 15; much of the pioneering work has been done by Phillips (202, 203). It may be recorded as a curiosity that nitroglycerin vapor decomposes with chemiluminescence under conditions similar to those required for more volatile nitrates (107, 108).

VIII. THE ALKOXONIUM (RO^+) CATION

The chemistry of alkoxonium cations differs from that of the alkoxyl radicals because the reactions are often typically ionic, and also because vacant-orbital rearrangement reactions of the ion occur more readily than those of the radical.

Both nitrogen and carbon analogs are known: RCH_2^+, RNH^+, RO^+. Much work has been done on the chemistry of carbonium ions, and this frequently enables useful comparisons of reactions and reactivity to be made. The chemistry of RO^+ is outlined here for comparison with the reactions of the free radical.

A. GENERATION OF RO^+ IN SOLUTION

Alkoxonium ions are best generated in solution by heterolytic fission of the RO—X bond in compounds of that type to give an alkoxonium cation and the anion X^- (278). In principle, fission may vary from slight polarization of the O—X bond, through formation of ion-pairs, to dissociation into free ions:

$$\underset{\text{(covalent)}}{RO—X} \rightleftharpoons \underset{\text{(polarized)}}{RO^{\delta+}X^{\delta-}} \rightleftharpoons \underset{\text{(ion-pair)}}{(RO^+)(X^-)} \rightleftharpoons \underset{\text{(separate ions)}}{RO^+ + X^-}$$

Equations are written here (Section VIII,A,B,C) in terms of the free ion RO^+. This oversimplified picture is discussed in Section VIII,D. Alkoxonium-ion formation from molecules of the type RO—X is facilitated by the removal of X^- by an acceptor molecule or positive ion. This is demonstrated by the peroxide family:

$$ROOH + H^+ \rightleftharpoons (ROOH_2)^+ \rightleftharpoons RO^+ + H_2O$$

$$ROOR' + H^+ \rightleftharpoons (ROOR'H)^+ \rightleftharpoons RO^+ + R'OH$$

Similar reactions are possible with the hypohalites:

$$ROBr + AlBr_3 \rightleftharpoons (ROAlBr_4) \rightleftharpoons RO^+ + AlBr_4^-$$

$$ROF \ + BF_3 \rightleftharpoons (ROBF_4) \rightleftharpoons RO^+ + BF_4^-$$

These methods of generating alkoxonium ions are closely analogous to some of those available for the production of carbonium ions. Thus the isoelectronic molecules RCH_2X undergo reactions with strong acids. Examples are:

$$RCH_2OH + H^+ \rightleftharpoons (RCH_2OH_2)^+ \rightleftharpoons RCH_2^+ + H_2O$$

$$RCH_2OH + BF_3 \rightleftharpoons (RCH_2OHBF_3) \rightleftharpoons RO^+ + (BF_3OH)^-$$

B. GENERATION OF RO^+ IN THE GAS PHASE

Alkoxonium ions are generated during the combustion of hydrocarbons at high temperatures and have been shown by a mass-spectrometer (143) to be present in flames. The methoxonium ion, CH_3O^+, has been detected in methane and acetylene flames, but no alkoxonium ion has been found in ethylene and ethane flames.

C. REACTIONS OF RO^+ (OR ITS SOLVATED FORMS)

Evidence that alkoxonium ions are intermediates in many reactions comes from the nature of the products, the significant influences of solvent polarity, and enhanced migration aptitudes characteristic of a positive ion. In some cases the same peroxide may decompose by free-radical or polar mechanisms, thus yielding different products. Examples of such dual mechanisms are to be found with hydroperoxides, diacyl peroxides, and per esters (154).

Some typical reactions of RO^+ are discussed below; they are similar to those of the carbon and nitrogen analogs.

1. *Combination with a negative ion*

This demonstrates the acidic (Lewis acid) property of this ion; the reaction is in effect neutralization.

$$RO^+ + Cl^- \rightleftharpoons ROCl$$

$$RO^+ + OH^- \rightleftharpoons ROOH$$

Similar reactions of carbonium ions are well known. For instance, the diazotization of *n*-butylamine results in the formation of a butyl carbonium ion. These ions combine with chloride or nitrate ions to give the alkyl chloride or the alkyl nitrate (126).

2. Displacement

This reaction occurs when the alkoxonium ion replaces a group in a molecule and a charged ion is expelled. The reaction is of the type:

$$RO^+ + XH \rightleftharpoons ROX + H^+$$

3. Rearrangement (isomerization)

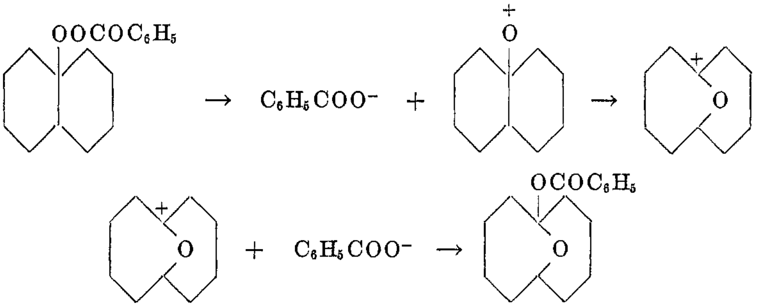
Examples of rearrangement are quite numerous, since it occurs much more readily than in the free alkoxyl radical. The reasons for this have been discussed in Section V,D. Since rearrangement is essentially an electrophilic displacement by a positively charged atom attacking the migrating group, the important electronic consideration is the degree to which the migrating group is able to accept and stabilize a positive charge in the transition state.

An example of this reaction is found in the acid-catalyzed decomposition of (*p*-nitrophenyl)diphenylmethyl hydroperoxide (18). Its decomposition in ether in the presence of sulfuric acid generates the positive ion which rearranges.

$$p\text{-}O_2NC_6H_4C(C_6H_5)_2OOH \xrightarrow{H^+} p\text{-}O_2NC_6H_4C(C_6H_5)O^+ \longrightarrow p\text{-}O_2NC_6H_5\overset{+}{C}(C_6H_5)OC_6H_5$$

The phenyl group migrates in preference to the electron-attracting *p*-nitrophenyl group. This behavior is opposite to that of the free radical (see Section IV,D).

The decomposition of 9-decalyl perbenzoate also proceeds by means of alkoxonium intermediates which undergo rearrangement (17, 58). The reactions are:



The 9-decaloxonium ion undergoes rearrangement, and it is neutralized by the negative ion present.

Many other examples of this reaction (see 153, 285) are known to occur in the acid-catalyzed decomposition of peroxides.

D. THE NATURE OF RO^+

For simplicity the foregoing reactions have been written as if RO^+ existed as a stable, independent ion. However, even carbonium ions are not formed without a strongly acidic medium and the greater electronegativity of oxygen is more in accord with an "ionization" of ROX that does not proceed far beyond $RO^{\delta+}—X^{\delta-}$, at least in solution. The extreme view is that RO^+ is never formed but that all reactions involving it are concerted changes in which neither offspring (RO^+ or X^-) of the particular progenitor ROX ever becomes completely free. Support for this view comes from the study (58) of isotopically (^{18}O) labelled 9-decalyl perbenzoate. This molecule isomerizes with complete (98 per cent) retention of identity by the two benzoate oxygens. Thus, free benzoate ion is not formed; nor, therefore, is free "decaloxonium."

On the other hand, the hydrated form $RO_2H_2^+$ probably does exist if only at a stationary state concentration; the speed of its rearrangement may prevent it from reaching the ionic equilibrium.

IX. THE ALKOXIDE ANION (RO^-)

Solid alkoxides of electropositive metals (such as potassium and sodium) contain alkoxide ions and so do their solutions in the parent alcohol. This is exactly parallel to the solution of hydroxides in water. The alkoxides of less electropositive metals, such as zinc and cadmium, and the coördination compounds, such as $Na[Zn(OC_2H_5)_4]$, contain alkoxyl–metal covalent bonds and do not ionize to alkoxide ions in solution.

Just as hydrogen ions are formed in pure water, so are alkoxide ions formed in alcohols, though to an even smaller extent. Values of the equilibrium constant for the ionization

$$ROH \rightleftharpoons RO^- + H^+$$

have been measured (56, 183). Expressed as their negative logarithms (pK values) they are: CH_3OH, 18; C_2H_5OH, 18; iso-C_3H_7OH, 18; *tert*-C_4H_9OH, 19; *tert*-$C_5H_{11}OH$, 19:

A few values exist of the equilibrium constant, K_h, for the reaction

$$OH^- + ROH \rightleftharpoons RO^- + H_2O$$

For ethyl alcohol (37) $K_h = 0.79$. The numerical values make it clear that the common reagent alcoholic potash contains very little hydroxide ion; it is essentially all K^+ and $OC_2H_5^-$ ions.

A. REACTIONS

The reactions of the alkoxide ion are intermediate between those of the isoelectronic carbanion RCH_2^- and the hydroxide ion. It possesses nucleophilic and basic properties. Basic properties are shown by the reaction with cations and with water:

$$RO^- + H_3O^+ \rightleftharpoons ROH + H_2O$$

$$RO^- + NO^+ \rightleftharpoons RONO$$

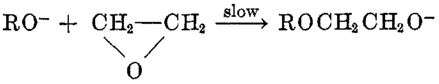
$$RO^- + H_2O \rightleftharpoons ROH + OH^-$$

With alkyl halides, both nucleophilic substitution and olefin elimination occur, depending upon the conditions (84). Nucleophilic substitution occurs by the following mechanisms:

$$RO^- + Alk—X \rightarrow RO^-\cdots Alk\cdots X \rightarrow ROAlk + X^-$$

The rate at which this reaction occurs depends upon the nucleophilic nature of the substituting alkoxide. The hydroxide ion is the most powerful, and ethoxide ion is intermediate between it and the weakly nucleophilic phenoxide ion (153).

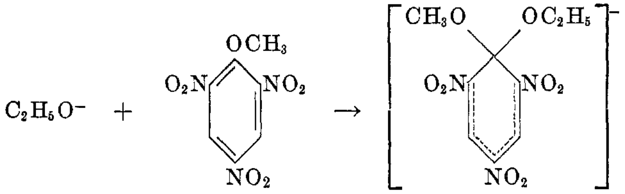
Another nucleophilic reaction of alkoxides is the opening of epoxide rings (126), this taking place in the solvent alcohol:



$$RO^- + \underset{O}{CH_2{-}CH_2} \xrightarrow{\text{slow}} ROCH_2CH_2O^-$$

$$ROH + ROCH_2CH_2O^- \xrightarrow{\text{fast}} ROCH_2CH_2OH + RO^-$$

Alkoxide ions may also react with substituted aromatic molecules to produce addition compounds or molecular complexes (3). An example of this is the reaction of trinitroanisole with ethoxide radicals:



This is followed by further reactions to give a complex.

Electrode reactions: Electrolysis of solutions containing ethoxide ions results in the alkoxide ion losing an electron at the electrode and reverting to a free radical. An example of this is found in the electrolysis of ethanol under basic conditions (4). The reactions are:

$$C_2H_5OH + OH^- \rightarrow C_2H_5O^- + H_2O$$

$$C_2H_5O^- \xrightarrow{\text{electrode}} C_2H_5O\bullet + e$$

$$C_2H_5O\bullet \rightarrow CH_3CHO + H\bullet$$

$$\rightarrow CH_2O + \bullet CH_3$$

The alkoxyl radical that is formed at the electrode decomposes in the usual manner.

B. ANALOGIES WITH THE CARBANIONS

Although quite similar in many respects the alkoxide ion is very much more stable than the carbanion. This is shown by the ease of formation of alkoxide ions and by the fact that they exist as stable entities in solution. This behavior reflects the greater electronegativity of oxygen. In contrast to this, carbanions are difficult to form and particular reactions often cannot be attributed to discrete carbanions. The main similarity is in their electronic structure which is such that there are no vacant orbitals. As a result of this, rearrangement reactions are not possible; this is characteristic of both carbanions and alkoxide ions and quite different from the behavior of carbonium and alkoxonium ions.

X. Related Systems and Some General Aspects of the Chemistry of Alkoxyl Radicals

Attention has already been drawn to some of the general principles underlying the reactivity of alkoxyl radicals. In particular, use has been made of the isoelectronic principle in finding analogs among the relatively well-investigated alkyl radicals, of thermochemistry in revealing the energy requirements of different types of reaction, and of transition-state theory in interpreting kinetic properties.

In this section these aspects are very briefly summarized and general references are given to work on some closely related radicals. Attention is called to some of the gaps in our knowledge of alkoxyl chemistry and to a family of nitrogen radicals whose chemistry seems particularly ready for development.

A. OTHER OXYGENATED RADICALS

1. Aryloxyl radicals and semiquinone radical ions

The aryloxyl radicals, derived from phenols by oxygen–hydrogen bond fission, have $C_6H_5O\cdot$ as their simplest member. Like the alkoxyl radicals they are formed in the pyrolysis of ethers (258) and in the photolysis of phenyl esters (297). They show, similarly, the reactions of association, addition, and hydrogen abstraction. Differences also are expected and found. The diaryl peroxides are less stable than the alkyl ones. Secondly, the free electron is delocalized from the neighborhood of the oxygen atom in the phenoxyl radical just as it is from the CH_2 group in benzyl. Finally, the structure of the aromatic ring is such that neither rearrangement, nor decomposition, nor even disproportionation can occur by the paths possible for the alkoxyls.

All these factors contribute to the superior stability of the aryloxyl radicals. This stability finds striking expression in the heavily substituted phenoxyl radicals (179), which are readily prepared and quite stable under ordinary conditions.

The paramagnetic semiquinone anions (285) are among the best known free-radical ions. Recently electron spin resonance studies have contributed to a revival of interest in these radicals by giving more detailed information on the interaction of the odd electron with the hydrogen nuclei and other substituents.

2. Alkyl peroxyl radicals

These radicals, of the general formula $RO_2\cdot$ (where $R =$ alkyl), and the hydroperoxyl radical, $HO_2\cdot$, are of the greatest importance in autoxidations (20, 276). Their best known reactions are their formation by the association of an alkyl group with molecular oxygen and the chain-propagating reaction of hydrogen abstraction:

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot$$

Recent reviews (20, 276) of oxidation processes give many leading references to them. Of especial interest in the alkoxyl field is their decomposition by combination in pairs with the elimination of molecular oxygen:

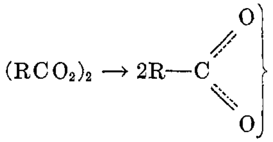
$$2RO_2\cdot \rightarrow 2RO\cdot + O_2$$

Compare this with the familiar reaction:

$$2NO_2 \rightarrow 2NO + O_2$$

3. *Acyloxyl radicals,* $RCO_2\cdot$, *and acyl radicals,* $RCO\cdot$

The acyloxyl radicals, $RCO_2\cdot$ and $ArCO_2\cdot$, which are derived from the organic acids by hydrogen–oxygen bond fission, are intermediates in the Kolbe electrolysis of aqueous organic acids. They are most conveniently generated by pyrolysis of the diacyl peroxides:



The two oxygen atoms of the radical are equivalent and the electron is not confined to either. Though this delocalization confers some stability on the radical, decomposition to the even stabler carbon dioxide molecule and an alkyl radical is exothermic (268). This mode of decomposition is the normal fate of $RCO_2\cdot$ and, e.g., acetyl or benzoyl peroxides are excellent thermal sources of methyl or phenyl radicals. In solution, in the presence of a hydrogen donor, formation of the parent acid competes at low temperatures:

$$RCO_2\cdot \rightarrow R\cdot + CO_2$$

$$RCO_2\cdot + XH \rightarrow RCOOH + X$$

Acetic acid, which regenerates $CH_3CO_2\cdot$ radicals by this reaction, prolongs their existence when used as solvent medium.

Among the other known reactions of these radicals are association and addition (285, 289a). Kharasch and his school (285) and recently Szwarc (268) have made major contributions to free-radical chemistry by their studies of these radicals.

The acyl radicals $R\dot{C}O$ and $Ar\dot{C}O$ (289a) have the odd electron associated not with oxygen but with carbon and lie outside this field, though by their ready decomposition to $R\cdot$ and CO they show similarities to $RCO_2\cdot$.

B. SULFUR ANALOGS

The thiols, RSH, and the thiophenols, ArSH, contain the relatively weak sulfur–hydrogen bond, whose fission produces the sulfur analogs of alkoxyl. These $RS\cdot$ radicals are thought (289a) to play important roles in biological processes. They associate with other radicals, abstract hydrogen atoms, and add to olefinic bonds (289a). In addition, they dimerize readily (289a) to form disulfides; the strength of the sulfur–sulfur link has been estimated (51) as 63 kcal. $mole^{-1}$. Though the other reactions are common to $RS\cdot$ and $RO\cdot$, the stability of this dimer and the readiness of its formation afford a sharp contrast.

C. ISOELECTRONIC ANALOGS

There are two types of isoelectronic analogs to $RO\cdot$: those in which oxygen is replaced by F^+, N^-, or C^{--}, and those in which oxygen is replaced by NH or CH_2. The chemistry of RF^+ and RN^- is still unknown and the latter analogies are employed here.

1. Bond strengths in analogs to the peroxides

The bond-dissociation energies (kcal. mole^{-1}) in this series may be tabulated thus (see also references 51 and 251a):

F—F	HO—OH	$H_2N—NH_2$	$H_3C—CH_3$
37	50	60	86
	RO—OR	RNH—NHR	$RCH_2—CH_2R$
	37	74	79

The entries for the alkyl derivatives of course depend somewhat on the nature of R, and the values here correspond to diethyl peroxide and butane. The entry for 1,2-dimethylhydrazine is an estimate from appearance potential measurements (58b).

2. Isoelectronic analogs of the alkoxyl radicals

The analogs of hydroxyl and alkoxyl are:

F·	HO·	$H_2N·$	$H_3C·$
	RO·	RHN·	$RH_2C·$

The methyl radical is thought (285) to be planar or very nearly so and the odd electron to occupy the *p*-orbit perpendicular to this plane. The orientation in HO· and $·NH_2$ of the hydrogen atoms and the electron-pair orbits are probably intermediate between this and a symmetrical tetrahedral distribution. Similar principles apply to RO· and $RCH_2·$.

There are the most striking parallels between the reactivity of $RCH_2·$ and RO·. All the reactions of association, addition, hydrogen abstraction, rearrangement, and disproportionation are known, with the olefinic $>C{=}CH_2$ replacing the carbonyl compounds $>C{=}O$ and so on. Activation energies of hydrogen abstraction are lower when the attacking radical is RO· than for alkyl, and secondary differences such as these arise from the greater electronegativity of oxygen.

3. Isoelectronic analogs of charged species

The representative members of the two series of anions and cations are RO^-, RNH^-, RCH_2^- and RO^+, RNH^+, and RCH_2^+, respectively. Because of the electronegativity differences mentioned above, the carbonium cations, RCH_2^+, and the alkoxide (alcoholate) antions, RO^-, are the most stable and best investigated members of the two series. For this reason, although interpretation of RO^+ chemistry is assisted by the established properties of RCH_2^+, little additional information about RO^- comes from its analogs.

D. REACTIVITY, KINETICS, AND THERMOCHEMISTRY

Reactivities reflect reaction velocities, and the existing data on the elementary reactions considered here are adequately represented by the Arrhenius parameters *A* and *E*.

Transition-state theory is the best guide to unknown values of A, especially if data are available for comparable reactions. In general terms, A values are expected to lie in one of the four ranges corresponding to (*1*) associations, (*2*) internal rearrangements, (*3*) metatheses, and (*4*) decompositions.

Thermochemistry, especially in the form of bond-dissociation energies, has proved useful as a guide to activation energies. The correlations presented here have had a modest success, especially vis-à-vis decomposition reactions. A change of E by 2 kcal. mole^{-1} corresponds to more than a tenfold change of reaction rate, so sensitive correlation with changes in ΔH are not unexpected. But the limitations must be emphasized; the absence of many thermochemically favored rearrangement reactions is a reminder of them.

E. FUTURE DEVELOPMENTS

Two areas of the chemistry of alkoxyl radicals especially call for development. First is the chemistry of radicals more complex than *tert*-butoxyl (which has received the lion's share of attention to date). Of especial interest are the cyclic and aryl-substituted radicals, for which a pattern can already be discerned in general terms. The oxygen-substituted radicals and diradicals no less require investigation; only the simplest are understood. The second area is that of kinetics. It is to the wealth of kinetic data for simple radicals (especially methyl) that the chemistry of alkyl radicals owes its preëminence. The techniques are well established (258, 285), and the accurate determination of kinetic parameters for the elementary reactions of alkoxyl radicals is within easy reach. The recent work of Wijnen (297–301) on ester photolyses as a route to alkoxyl kinetics is especially noteworthy. It seems likely that the hyponitrites, the carbonates, and the peroxydicarbonates will prove as valuable in alkoxyl chemistry as the azoalkanes, the ketones, and the acyl peroxides have proved to the alkyl series:

$CH_3N{=}NCH_3$	Azomethane	$CH_3ON{=}NOCH_3$	Methyl hyponitrite
CH_3COCH_3	Acetone	$CH_3OCOOCH_3$	Methyl carbonate
$(CH_3CO_2)_2$	Acetyl peroxide	$(CH_3OCO_2)_2$	Methyl peroxydicarbonate

F. CHEMISTRY OF THE ALKYLAMINO (RNH•) RADICALS

Intermediate between the isoelectronic RO• and RCH_2• radicals are the alkylaminos, RNH•, so far not investigated systematically, but expected to share many of their neighbors' properties. Differences there are: experimental problems will not be the same as those met and overcome in the RCH_2• field, but they are unlikely to be harder than those presented by RO•; the thermochemical background to nitrogen compounds is much less familiar than the thermochemistry of compounds of carbon, hydrogen and oxygen; the strength of the bond in molecular nitrogen may introduce novel reactions. However, it seems clear that with the general reactions of the alkoxyl and alkyl families so firmly established, development of the chemistry of RNH• well deserves attention and could now be very rapid.

The authors are grateful to Dr. D. R. Stull of the Dow Chemical Corporation, Midland, Michigan, and to Dr. M. J. Wijnen of the Celanese Corporation of

America, Texas, for permitting them to refer to their experimental data. They also thank Dr. J. L. Franklin of the Humble Oil and Refining Company, Texas, Dr. Ross Stewart of the University of British Columbia, and Dr. J. Powling and Dr. L. Phillips of E.R.D.E., Waltham Abbey, England, for helpful discussions.

XI. APPENDICES

APPENDIX I

Thermochemical data

Bond energies: The bond-dissociation energy convention used here is based on enthalpy changes in reactions carried out in the gaseous phase at 25°C. and, unless specifically distinguished, enthalpies of formation, etc. quoted refer to this standard state.

Standard enthalpies of formation in the gaseous state: The entries in the following table of ΔH_f° (g; 25°C.; 1 atm.) have been selected from recent determinations, where possible. It is not a critical compilation.

Substances	ΔH_f°	References
	kcal. mole^{-1}	
Atoms:		
Hydrogen	52.1	(186)
Carbon	170.4	(186)
Oxygen	59.2	(186)
Radicals:		
Hydroxyl	8.9	(92)
Nitric oxide	21.6	(186)
Nitrogen dioxide	8.0	(186)
Methyl	31.5	(267)
Ethyl	24.5	(267)
n-Propyl	22	(267)
sec-Propyl	17	(267)
n-Butyl	19	(267)
tert-Butyl	4.5	(267)
Methylene	95	(186)
Methyne	142.1	(186)
Allyl	30	(267)
Phenyl	69	(258)
Benzyl	43	(258)
Formyl	0	(258)
Acetyl	−11	(38, 268)
Benzoyl	15.2	(40)
Molecules:		
H_2O	−57.80	(186)
CO_2	−94.05	(186)
Acetals, ketals, etc.:		
Methylal	−79.35	(273)
1,3-Dioxane	−90.84	(68)
Esters:		
Trimethyl orthoformate	−118.6	(273)
Methyl formate	−83.6	(186)
Methyl acetate	−99.2	(241)
Ethyl acetate	−106.58	(241)
n-Propyl acetate	−112.8	(241)
sec-Propyl acetate	−115.85	(241)
n-Butyl acetate	−118.9	(241)
Molecules—continued		
Isobutyl acetate	−121.1	(241)
Methyl benzoate	−71.7	(138)
Ethyl benzoate	−79.1	(138)
Dimethyl carbonate	−137.1	(273)
Diethyl carbonate	−156.9	(273)
Olefins:		
Ethylene	12.50	(5)
Propylene	4.88	(5)
Cyclohexene	−1.7	(5)
1,3-Butadiene	26.33	(5)
Aldehydes:		
Formaldehyde	−27.7	(186)
Acetaldehyde	−39.8	(186)
Propionaldehyde	−46.1	(186)
Benzaldehyde	−7.2	(142)
Ethers:		
Dimethyl ether	−45.3	(186)
Methyl ethyl ether	−53.2	(186)
Diisopropyl ether	−76.4	(196, 264)
Methyl allyl ether	−22.3	(273)
Methyl phenyl ether	−16.9	(116, 166)
Ethyl phenyl ether	−29.8	(11, 166)
Diphenyl ether	6.1	(11, 42)
Tetrahydropyran	−50.7	(42)
Tetrahydrofuran	−43.08	(42)
Ethylene oxide	−12.19	(186)
Propylene oxide	−22.02	(247)
Ketones:		
Acetone	−51.8	(174)
Methyl ethyl ketone	−58.4	(198)
Cyclohexanone	−59.1	(50)
Cyclopentanone	−50.8	(50)
Acetophenone	−22	(49, 142)
Ethyl phenyl ketone	−29	(49)
Benzophenone	12.3	(198)

APPENDIX II

Electron impact on alkyl nitrites

Thermal dissociation takes place as a result of the collisional excitation of higher vibrational levels. Electronic collisions may also be used for determining dissociation energies. If the dissociation energy $D(\mathrm{RO} - \mathrm{X})$ is measured, then the enthalpy of the alkoxyl radical may be determined, as shown in Section III,E.

This method has been used for the aliphatic nitrites. D'Or and Collin (59) measured the appearance potential of NO^+ from a number of aliphatic nitrites. The ionization potential of NO is known and it is possible to calculate $D(\mathrm{RO{—}NO})$. Using values of $D(\mathrm{RO{—}NO})$ obtained in this way the enthalpies of formation of alkoxyl radicals were considerably less than the values obtained by thermochemical measurements.

It has been suggested (71) that the radicals rearrange to give the hydroxy radical (or carbinyl; see Section IV,D), and the values of $\Delta H_f(\mathrm{R\dot{C}HOH})$ obtained from electron-impact methods agree with calculated values of $\Delta H_f(\mathrm{R\dot{C}HOH})$.

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