CHEMISTRY OF FREE RADICALS CONTAINING OXYGEN

PART 3.—THERMOCHEMISTRY AND REACTIVITY OF THE HIGHER ALKOXYL RADICALS RO·

By Peter Gray and A. Williams
School of Chemistry, University of Leeds

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The self-consistent thermochemistry derived in part 1 for the lower alkoxy radicals RO· (R ranging from methyl to butyl), has been extended to the higher aliphatic, alicyclic and aralkyl derivatives.

The correlations between stability and thermochemistry previously considered in outline for the lower radicals have been explored and extended to the more complex radicals. When a radical can decompose by different paths the series,

$$H < \text{aryl groups} < \text{alkyl groups} < \text{ring fission},$$

is obtained for increasing ease (from left to right) of reaction. This is also the order of diminishing energy requirements.

Bond energies are derived for some ethers, epoxides, cyclic ethers, esters, formals and carbonates.

1. Introduction

Attention has been drawn recently [1] to two important areas in free-radical chemistry especially in need of development: measurements of bond dissociation and clarification of processes involving oxygen and oxygen-containing free radicals. The first part of this series [2] described the derivation of a self-consistent thermochemistry for the lower alkoxyl radicals. Subsequent developments [3-6] have confirmed the thermochemical data and conclusions of part 1 and they will be used here without further comment.

In this paper, the thermochemistry is extended to more complex radicals of the same general formula RO·. They are the higher aliphatic derivatives ($C_nH_{2n+1}O$· with $n > 4$), the alicyclic derivatives ($C_nH_{2n-1}O$· such as cyclohexoxyl) and the aryl-substituted alkoxyl radicals of which the simplest member is $C_6H_5CH_2O$·, benzoxyl. Mention is also made of alkoxyl radicals which contain an ether linkage (including O-heterocyclic derivatives). Phenolic radicals such as PhO· which are not members of this family are not discussed in this paper.

2. Alternative routes to enthalpies of formation of free alkoxyl radicals

Three principal paths lead towards the enthalpies of formation of the free alkoxyl radicals. The first proceeds by the union of thermodynamic and kinetic data [7, 8] and combines heats of formation determined calorimetrically with activation energies derived from kinetic measurements and identified with dissociation energies of particular bonds. The assumptions and approximations of this approach are discussed elsewhere.[2, 7, 8]

The second path makes use of the constancy [2] of oxygen-hydrogen bond dissociation energy $D(\text{RO—H})$ in the alcohols, which has been found [2] always to lie near to 102 kcal mole^{-1}. This offers a reliable guide to alkoxyl radical heat of formation ΔH_{RO} when the heat of formation of the gaseous alcohol ROH is known.

The third path makes more systematic use of existing thermochemical data and employs the group energy term $\Delta H_f(\text{—O}\cdot)$. The heat of formation $\Delta H_f(\text{M})$ of a molecule may be expressed as the sum of a set of terms each characteristic of a constituent group in the molecule, and recently the same approach has been extended [9] successfully to free radical heats of formation.

In principle, the route proceeding via activation energies and heats of formation, with its firm basis in experiment and the possibility it offers of making several independent estimates of the enthalpies of formation of each alkoxyl radical, is the best. However, 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 heat of formation ΔH_{RO} to be derived. Secondly, because of the high molecular weights of the parent compounds ROX (they may, e.g., be peroxides with twenty carbon atoms) failure to determine combustion heats 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.

3. ENTHALPIES OF FORMATION DERIVED FROM ACTIVATION ENERGIES

Peroxides, hydroperoxides, nitrate, nitrite, hyponitrite and hypochlorite esters, all of general formula ROX, satisfy the critical requirement that, in appropriate circumstances, their decomposition is controlled by the fission of the bond RO—X, and 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 reaction,

$$\text{RO—X} \xrightarrow{E} \text{RO} + \text{X}, \quad \Delta H = E.$$

So that if the enthalpies of formations of the gaseous species involved are ΔH_{ROX}, ΔH_{X} and ΔH_{RO} we have

$$\Delta H_{\text{RO}} = \Delta H_{\text{ROX}} - \Delta H_{\text{X}} + E.$$

ACTIVATION ENERGIES

Activation energies of first-order decomposition have been reported for some peroxides and hydroperoxides. As stressed in part 1, hydroperoxide decompositions are frequently less simple than peroxide decompositions and correspondingly greater care has to be exercised in identifying E values with bond dissociation energies. In general, the values of E for hydroperoxides decompositions in solution are lower limits for E and for gas phase calculations $E = 38$ to 39 is adopted. The values listed are in kcal mole^{-1}.

ALIPHATIC.—Di-*tert*.-amyl peroxide, 37·0 (gas phase [11]); *n*-octyl hydroperoxide, 26·9 (solution [12]); 2 : 2 : 4-tri-methylpentyl-4-hydroperoxide, 26·9 (solution [12]).

ALICYCLIC.—Cyclo-hexyl hydroperoxide, 34·0 (solution [12]); decalyl-9-hydroperoxide, 32·1 (solution [12]).

ARYL-SUBSTITUTED.—Cumyl hydroperoxide, 29·0 (solution [12]); tetralyl-1-hydroperoxide, 29·0 (solution [12]).

STANDARD ENTHALPIES OF FORMATION (IN THE GASEOUS STATE) OF ROX

In general all experimental values reported for the higher peroxides come from bomb-calorimetry and are based [13] on $\Delta H^\circ_f(\text{CO}_2, g) = 94{\cdot}05$ kcal mole^{-1} and $\Delta H^\circ_f(\text{H}_2\text{O}, l) = 68{\cdot}32$ 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 vapour pressure data or from the application of empirical guides. Useful rules for estimating L_v have been given by Klages.[14] Values for L_v may also be derived by application of Clapeyron's equation to vapour pressure data such as those tabulated by Stull.[15] Values are expressed in kcal mole^{-1} in the list which follows. Enthalpies of formation refer to the condensed state (*l*, liquid, *s*, solid). Latent heats (indirect values italicized) are in parentheses.

ALIPHATIC:[16] *n*-hexyl-1-hydroperoxide (*l*), − 71·64 (*13*); *n*-hexyl-2-hydroperoxide (*l*), − 74·14 (*13*); *n*-hexyl-3-hydroperoxide (*l*), − 72·94 (*13*); *n*-heptyl-1-hydroperoxide (*l*), − 82·0 (*16*); *n*-heptyl-2-hydroperoxide (*l*), − 82·8 (*16*); *n*-heptyl-3-hydroperoxide (*l*), − 82·9 (*16*); *n*-heptyl-4-hydroperoxide (*l*), − 79·8 (*16*).

ALICYCLIC:[16, 17] cyclo-hexyl hydroperoxide (*l*) − 65·3 (*13*); 1-methyl-cyclohexyl hydroperoxide (*l*), − 79·0 (*16*); decalyl-9-hydroperoxide, (*s*) − 83·2 (*17*).

ARYL-SUBSTITUTED: tetralyl-1-hydroperoxide (*s*) − 44·6 and − 44·3 (*20*).

4. 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(RO—H) of the oxygen hydrogen bond is 102 kcal mole^{-1}, we have

$$\mathrm{ROH} \rightarrow \mathrm{RO} + \mathrm{H}, \quad \Delta H = 102 \text{ kcal mole}^{-1};$$

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

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. In the list which follows, enthalpies of formation (kcal mole^{-1}) refer to the standard state (*l*, liquid; *s*, solid) at 25°C. Latent heats (indirect values in italics) are in parentheses.

ALIPHATIC ALCOHOLS.—*iso*-Propanol[18] (*l*), − 76·18 (10·62); *n*-butanol[19] (*l*), − 79·7 (11·80); *n*-pentan-1-ol[19] (*l*), − 85·9 (12·45); *n*-hexan-1-ol[19] (*l*), − 92·0 (13·05); *n*-heptan-1-ol[19] (*l*), − 97·9 (13·55); *n*-octan-1-ol[19], − 103·7 (14·00); *n* nonan-1-ol[19] (*l*), − 109·45 (14·40).

ALICYCLIC ALCOHOLS.—Cyclo-pentanol[20, 21] (*l*), − 71·8 (11·7); cyclo-hexanol[20, 21] (*l*), − 83·5 (11·7); cyclo-heptanol[23] (*l*), − 94·0 (*13*); decalin-9-ol,[17] (*l*), − 106 (*18*).

ARYL-SUBSTITUTED ALCOHOLS.—Benzyl alcohol[24, 16] (*l*), − 38·49 (16·1); di-phenyl carbinol[24] (*s*), − 25·16 (*18*); triphenyl carbinol (*s*), 0·80 (*20*); tetralin-1-ol[17] (*l*) − 68 (*20*).

5. ENTHALPIES OF FORMATION DERIVED FROM GROUP-ENERGY-TERMS

The principle may be expressed by the equation,

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

where $\Delta H(g_i)$ is that part of the enthalpy of formation assigned to the *i*th group. When the concept is extended[9] to free radicals the heat of formation of a free radical R• is expressed as

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

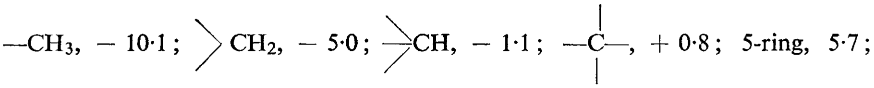
where the term $\Delta H(g)$ represents the contribution of that atom or group to which the unpaired electron is formally assigned, e.g. in the alkoxyl radicals it is the oxygen atom. The data of part 1 lead to the group energy term $\Delta H\,(-\,O\cdot) = 6{\cdot}5$ kcal mole^{-1} and thus

$$\Delta H_f(RO\cdot)\ \text{kcal mole}^{-1} = 6{\cdot}5 + \sum_i \Delta H(g_i).$$

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 been tabulated. This procedure is adequate for those radicals which are derived from aryl-substituted methanols; they possess the resonance energy of the parent molecule for which this procedure allows. *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 benzoxyl radical $C_6H_5CH_2O\cdot$ than in the β-phenyl ethyl radical, $C_6H_5CH_2CH_2\cdot$.

NUMERICAL VALUES OF GROUP ENERGY TERMS USED

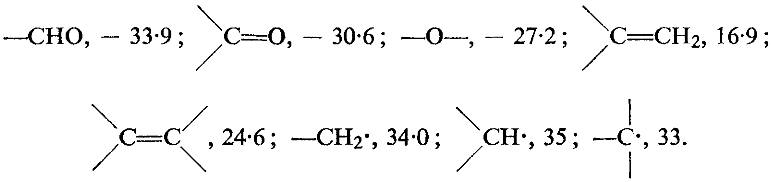
Values (kcal mole^{-1}) employed in this paper for the contributions of various groups in the enthalpy of formation in the gaseous state are as follows:



$-CH_3$, − 10·1; $>CH_2$, − 5·0; $>CH-$, − 1·1; $-\overset{|}{\underset{|}{C}}-$, + 0·8; 5-ring, 5·7;

6-ring, − 0·5; —OH, primary − 41·9, secondary 5·7, tertiary 49·2.

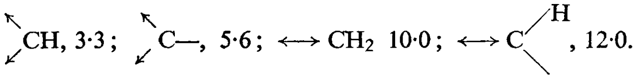
In later parts of the paper group energy terms are again utilized in discussing the thermochemistry of alkoxyl radical reactions. There, group energy terms for ketones, double bonds, etc., are also employed. The appropriate values are:



$-CHO$, − 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.

Group energy terms for aromatic or conjugated molecules are :



$\nwarrow\!\!\!\swarrow CH$, 3·3; $\nwarrow\!\!\!\swarrow C-$, 5·6; $\longleftrightarrow CH_2$ 10·0; $\longleftrightarrow C\!\!<^{H}$, 12·0.

6. ENTHALPIES OF FORMATION OF THE ALKOXYL RADICALS

The standard heats of formation (ΔH_{RO}) in the gaseous state at 25°C derived in the preceding sections are listed together in table 1.

The consistency of the various methods is greatest where there is duplication of data and the possibility of a check on, e.g., heats of formation. Errors of several kcal mole^{-1} are to be expected in the absolute values of ΔH_{RO} for the higher members primarily because of the errors in measurements of heats of combustion of higher hydroperoxides and alcohols. The values derived from group energy terms may be absolutely in error, but their relative errors are not likely to be serious. Table 1 includes for comparison entries for hydroxyl and four lower alkoxyl radicals.

TABLE 1.—ENTHALPIES OF FORMATION OF THE ALKOXYL RADICALS

Values (kcal mole^{-1}) 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	
HYDROXYL				9·0
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	−15·0
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	−31·0		−29·7	−30
n-C_6H_{13}-3-O	−30·0		−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		−35·0	−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-$C_6H_{11}O$	−22·0	−22·8	−19·5	−21
cyclo-$C_7H_{13}O$		−31·0	−24·5	−27
1-methyl-cyclo-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
$C_6H_5CHCH_3O\cdot$			17·5	17
$C_6H_5C(CH_3)_2O\cdot$			9·2	9
$(C_6H_5)_2CHO$		43	49·6	46
$(C_6H_5)_3CO$		71	69·7	70
tetralyl-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

7. BOND DISSOCIATION ENERGIES IN OXYGEN COMPOUNDS

In part 1 values of the dissociation energies of the hydrogen-oxygen bond in the alcohols and of the carbon-oxygen bond in the ethers were derived from the enthalpies of formation of the alkloxyl radicals found there. These data are now extended to esters and orthoesters, higher aliphatic ethers, aromatic ethers and cyclic ethers (O-heterocyclic derivatives). Mean values of oxygen bond dissociation energies in some acetals and formals are also reported.

The auxiliary thermcchemical data used are listed together in an appendix.

7.1. CARBON-OXYGEN BONDS IN THE ALIPHATIC AND AROMATIC ETHERS

Thermochemical data for the parent ethers are very limited. Recently, di*iso*propyl ether [18] has been added to the list of aliphatic ethers of known thermochemistry: among the unsaturated and aromatic ethers, methyl allyl ether, methyl phenyl ether (anisole), ethyl phenyl ether and diphenyl ether have known heats of formation (see appendix).

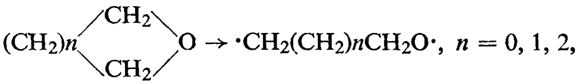
ether	C_3H_7—OC_3H_7	C_3H_5—OCH_3	C_6H_5—OCH_3	C_6H_5—OC_2H_5	$(C_6H_5)_2O$
B.D.E.	78·4	53	85·9	85·3	$\overline{D} = 95$

It will be seen that the carbon-oxygen bond in di*iso*propyl ether has essentially the same energy, *ca.* 77 kcal mole^{-1}, as it has in dimethyl and diethyl ethers and in methyl ethyl ether.[2] When the radical R is stabilized by resonance, as in allyl methyl ether, the bond energy D(R—OR′) is expected to drop abruptly, and this fall is unmistakable though its magnitude may be in some error as it depends on an old value [25] for the combustion heat of the ether.

In the alkyl-aryl ethers, the oxygen bond to the aromatic ring is stronger: 87 or 84 kcal mole^{-1}, according to the value adopted for $\Delta H_f^\circ(C_6H_5)$. In the diaryl ethers, such as diphenyl ether, only a mean bond dissociation energy can be derived until $\Delta H_f^\circ(C_6H_5O\cdot)$ is known: it is about 95 kcal mole^{-1}.

7.2. 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:



$$(CH_2)_n\left\langle\begin{matrix} CH_2 \\ CH_2 \end{matrix}\right\rangle O \rightarrow \cdot CH_2(CH_2)_nCH_2O\cdot,\quad n = 0, 1, 2, \qquad (4)$$

cyclic molecule diradical

In this process it is to be expected that the enthalpy requirements will be least when the ring is small and breaking it relieves strain and to increase with increasing ring size up to 6 to the normal value found for D(C—O) in the ethers. The figures below for D(C—O) confirm this expectation. The enthalpies of formation on which they are based are taken from recent experimental data (see appendix) for the molecules and from group-energy-term calculations for the diradicals.

parent cyclic ether	ΔH_f° kcal mole^{-1}	diradical formed	ΔH_f° kcal mole^{-1}	bond dissociation energy	number of atoms in ring
tetrahydropyran	− 50·7	$\cdot CH_2(CH_2)_4O\cdot$	20·5	71·2	6
tetrahydrofuran	− 43·08	$\cdot CH_2(CH_2)_3O\cdot$	25·5	68·6	5
trimethylene oxide		$\cdot CH_2(CH_2)_2O\cdot$			4
ethylene oxide	− 12·19	$\cdot CH_2CH_2O\cdot$	35·5	47·7	3
propylene oxide	− 22·02	$\cdot CH_2CH(O\cdot)CH_3$	29·5	51·5	3
		$\cdot OCH_2\dot{C}HCH_3$	~28·5	50·5	

7.3. CARBON-OXYGEN BONDS IN THE ORGANIC ESTERS

For the process

$$R'CO—OR \rightarrow R'CO + RO$$

$$\text{molecule} \rightarrow \text{acyl radical} + \text{alkoxyl radical},$$

recent values for the heats of formation of the formyl, acetyl and benzoyl radicals enable D(R′CO—OR) to be estimated for the esters of formic, acetic and benzoic acids. Data used in compiling the summarizing table below are listed in the appendix.

ACETATES	$D(\mathrm{CH_3CO{—}OR})$	FORMATES	$D(\mathrm{HCO{—}OR})$
methyl	87·7	methyl	82·7
ethyl	87·1		
n-propyl	88·8	BENZOATES	$D(\mathrm{C_6H_5CO{—}OR})$
*iso*propyl	86·9	methyl	86
n-butyl	90·9	ethyl	85·6
*iso*butyl	92·1		

It is found that in the acetates $D(\mathrm{CH_3CO{—}OR})$ lies always near to the 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 that 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.

7.4. 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 $\mathrm{CH_{4-\mathit{n}}(OCH_3)_\mathit{n}}$ with n varying from 1 to 4. Closely related are the members of the series $\mathrm{(CH_3)_{4-\mathit{n}}C(OCH_3)_\mathit{n}}$ with n varying from 1 to 4, viz., methyl *tert.*-butyl ether, 2 : 2-dimethoxy propane (the ketal of methanol and acetone), methyl orthoacetate and methyl orthocarbonate. Mean values, $\bar{D}(\mathrm{C{—}O})$, 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 dioxan (" 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:

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

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

8. Thermochemistry of alkoxyl radical reactions

The reactions undergone by alkoxyl radicals [27] 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 clases 1 to 4 the essential structure of the alkoxyl radical is preserved, while in (5) and (6) it is lost.[27, 28] In this section the thermochemistry of the different classes of reaction is outlined and in § 10 the contribution of thermochemistry to reactivity is discussed.

8.1. Association with other radicals

Association with other radicals occurs with the liberation of the dissociation energy of the bond formed: dimerization to form the symmetrical parent peroxide is an interesting special case:

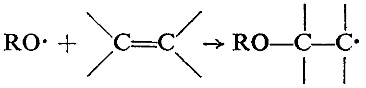
$$\mathrm{RO\cdot + X \rightarrow ROX}, \qquad \Delta H = -\,D(\mathrm{RO{—}X}),$$
$$\mathrm{RO\cdot + RO\cdot \rightarrow ROOR}, \qquad \Delta H = -\,D(\mathrm{RO{—}OR}).$$

Numerous instances are known and quoted elsewhere.[27] In the list which follows, average values of $D(\mathrm{RO{—}X})$ are indicated for classes of compounds and not for particular cases.

Bond dissociation energies, $D(\mathrm{RO{—}X})$, 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.

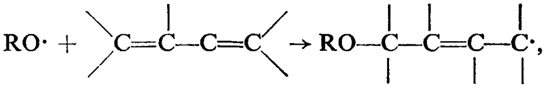
8.2. Addition to unsaturated compounds

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:



$\Delta H \simeq -20$ 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:



$\Delta H \simeq -35$ kcal $mole^{-1}$.

When methoxyl radicals add to butadiene, − ΔH is about 35 kcal $mole^{-1}$. The best authenticated examples[29] are afforded by those additions to conjugated systems which, followed by dimerization, yield the unsaturated di-ether as a product: e.g.,

$$PhMe_2CO\cdot + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{(2) dimerization}]{\text{(1) addition}} (PhMe_2CCOCH_2CH{=}CHCH_2{-})_2.$$

8.3. Hydrogen abstraction

Hydrogen abstraction is a characteristic mode of reaction; many references to its occurrence are listed in tables 4 and 5 of ref. (27). In the gas phase, the exothermicity is the amount by which the strength of the HO 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:

$$RO\cdot + XH \rightarrow ROH + X, \qquad -\Delta H = D(RO{-}H) - D(X{-}H).$$

Table 2.—Enthalpy changes in hydrogen abstraction reactions based on D(RO—H) *ca.* 102 kcal $mole^{-1}$

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

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	*iso*butane	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

For any given hydrogen donor XH, the near-constancy of 102 kcal mole^{-1} for D(RO—H) implies nearly equal exothermicity for 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.

Internal hydrogen abstraction, e.g. from a distant methylene group in a long-chain alkoxyl radical, is discussed in § 8.5 with other examples of rearrangement.

Typical values of enthalpy changes on hydrogen abstraction in the gas phase are listed in table 2: they are based on D(RO—H) = 102 kcal mole^{-1} and on values of D(X—H) derived from thermal data in the appendix.

8.4. Disproportionation

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

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

$$2R_1R_2CHO\cdot \rightarrow R_1R_2CHOH + R_1R_2CO$$

$$\text{radical} + \text{radical} \rightarrow \text{molecule} + \text{molecule.}$$

Reaction is very exothermic because a strong O—H bond is formed and the breaking of the weak C—H 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) 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*-$C_3H_7O\cdot$	*n*-C_5H_{11}-1-$O\cdot$	cyclo-$C_6H_{11}O$	$C_6H_5CH_2O$
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:

$$R_1R_2CHO\cdot + R\cdot \rightarrow R_1R_2CO + RH.$$

This H-abstraction, which is a competitor of radical-radical association (see § 8.1), is favoured by the weakness of the bond joining α-H to carbon (see § 8.6) which is so much more pronounced in the alkoxyl radical than in its parent molecule R_1R_2CHOX.

8.5. Rearrangement (isomerization)

Rearrangement, replacing an O-radical by a C-radical, involves a basic change in structure:

$$R_1R_2R_3CO\cdot \rightarrow R_1R_2\dot{C}OR_3, \qquad \Delta H = D(\text{R—C}) - D(\text{R—O}),$$

$$\text{O-radical} \rightarrow \text{C-radical.}$$

The enthalpy change is the difference in C—R and O—R bond dissociation energies and the electronegativities of O and C suggest that rearrangement should be exothermic and should occur readily. In fact, rearrangements in thermal reactions [30] appear to be confined to the triply aryl-substituted alkoxyl radicals (of which triphenylmethoxyl, $Ph_3CO\cdot$, is the simplest example); these rearranged radicals yield the pinacol ethers by dimerization:

$$Ph_3CO\cdot \rightarrow Ph_2\dot{C}OPh \rightarrow (Ph_2\overset{|}{C}OPh)_2$$

triphenyl methoxyl — diphenyl-phenoxy-methyl — diphenyl ether of benzophenone pinacol

Instead of an alkyl group, a hydrogen atom may move to the oxygen. Migration from the α-carbon atom has not been established in thermal reactions though it is suspected in mass spectrometric work.[31, 32] If the hydrogen atom migrates to the $—O\cdot$ 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:

$$RCH_2(CH_2)_nCH_2O\cdot \rightarrow R\dot{C}H(CH_2)_nCH_2OH, \qquad \Delta H \simeq -8{\cdot}5 \text{ kcal mole}^{-1}.$$

Similarly, an analogue of disproportionation may occur when the alkoxyl radical is a diradical: then, e.g., a terminal $\cdot CH_2–$ group may abstract the α-H of a primary or secondary alkoxyl.

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

Franklin has derived enthalpies of formation of " carbinyl " (i.e. 1-hydroxy alkyl and its derivative) radicals both from D'Or and Collin's electron impact data [31] and by calculation: from his figures [32] (see appendix) it is possible to calculate the heats of rearrangement listed in table 3.

TABLE 3.—THERMOCHEMISTRY OF POSSIBLE REARRANGEMENT REACTIONS (ISOMERIZATIONS) OF ALKOXYL RADICALS

$$R_1R_2R_3CO\cdot \rightarrow R_1R_2\dot{C}OR_3, \qquad \Delta H = D(R_3 — C) - D(R_3 - O)$$

type of rearrangement	parent O-radical	resulting C-radical	ΔH kcal mole^{-1}
H-atom migration from from α-carbon	$CH_3O\cdot$	$\cdot CH_2OH$	− 7·5
	$C_2H_5O\cdot$	$\cdot CH(CH_3)OH$	− 9·5
	$(CH_3)_2CHO\cdot$	$\cdot CH(CH_3)_2OH$	− 12
	$C_6H_5CH_2O\cdot$	$\cdot CH(C_6H_5)OH$	− 11
	cyclo-$C_6H_{11}O\cdot$	cyclo-$C_6H_{10}OH$	− 14
H-atom migration from distant CH_2 group	$RCH_2(CH_2)_nO\cdot$	$RCH(CH_2)_nOH$	− *8·5*
alkyl group migration	$CH_3CH_2O\cdot$	$\cdot CH_2OCH_3$	5
	$(CH_3)_2CHO\cdot$	$\cdot CHCH_3OCH_3$	0·5
	$(CH_3)_3CO\cdot$	$\cdot C(CH_3)_2OCH_3$	0·5
	$C_6H_5C(CH_3)_2O\cdot$	$—C\cdot CH_3C_6H_5(OCH_3)$	− *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 derived from group energy terms.

8.6. DECOMPOSITION I: H-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})
$R_1CH_2O\cdot \rightarrow R_1CHO + H,$	17
$R_1R_2CHO\cdot \rightarrow R_1R_2CO + H,$	16
radical 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) and from the radical thermochemistry established here. Figures in italics are derived from group-energy terms.

ENTHALPY REQUIREMENTS (kcal mole^{-1}) OF H-ATOM ELIMINATION.—Methoxyl, 25; *Primary alkoxyls*: C_2H_5O, 21; *n*-C_3H_7O, 19; *n*-C_4H_9O, 23; *iso*C_4H_9O and RCH_2O in general, 16·7; $C_6H_5CH_2O$, 15·9. *Secondary alkoxyls*: $(CH_3)_2CHO$, 18; $(C_6H_5)_2CHO$, 19·7; cyclo-$C_6H_{11}O\cdot$, tetralyl-1-O· and R_1R_2CHO in general, *16*.

These figures, which show the increasing ease of H-atom loss in the progression 1°-methoxy 2°-alkoxyl alkoxyl are in agreement with those derived from group-energy terms[9] which yield the values of ΔH written against the two general equations above. Cyclic alkoxyl radicals and aryl-substituted radicals appear to take their place in the appropriate general families.

8.7. DECOMPOSITION II: C-RADICAL ELIMINATION

A more profound change in structure[28] 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[27, 33] are available for secondary and tertiary radicals. If R_1, R_2, R_3 represent H atoms or alkyl or aryl radicals we have:

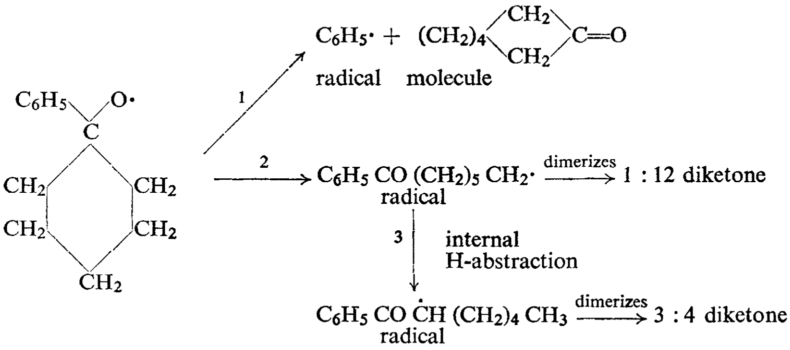
primary $R_1CH_2O\cdot \rightarrow R\cdot + CH_2O$,

secondary $R_1R_2CHO\cdot \rightarrow R_1\cdot + R_2CHO$ *or* $R_2\cdot + R_1CHO$,

tertiary $R_1R_2R_3CO\cdot \rightarrow R_1\cdot + R_2R_3CO$ etc.,

radical → radical + molecule.

When the alkoxyl radical is derived from an alicyclic alcohol, carbon-carbon bond fission in the ring may occur[34, 35] and lead not to two separate free radicals but to a single radical according to path 2 below:



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

Enthalpy requirements of C—C bond fission are again partly met by electronic rearrangements accompanying carbonyl (double) bond formation. Table 4 lists thermochemistry of these reactions (arranged according to the class of radical involved) dealing with primary, secondary and tertiary families successively and treating wholly aliphatic radicals before aryl-substituted and alicyclic ones.

TABLE 4.—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
*iso*butoxyl	*iso*C_3H_7	CH_2O	9
n-amyloxyl	*n*-C_4H_9	CH_2O	14·8
t-butyl methoxyl	*tert.*-C_4H_9	CH_2O	4·8
benzyloxyl	C_6H_5	CH_2O	16·3
SECONDARY DERIVATIVES			
*iso*propoxyl	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-methyl-but-3-oxyl	CH_3	*sec.*-C_3H_7CHO	3·4
	C_3H_7	CH_3CHO	3
n-hex-3-oxyl	C_2H_5	C_3H_7CHO	3·5
	C_3H_7	C_2H_5CHO	6
n-hept-3-oxyl	C_2H_5	C_4H_9CHO	3·5
	C_4H_9	C_2H_5CHO	9
α-phenyl ethoxyl	CH_3	C_6H_5CHO	6·8
	C_6H_5	CH_3CHO	11·7
diphenyl methoxyl	C_6H_5	C_6H_5CHO	12·2
TERTIARY DERIVATIVES			
tert.-butoxyl	CH_3	$(CH_3)_2CO$	4·7
tert.-amyloxyl	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 (triethyl methoxyl)	C_2H_5	$(C_2H_5)_2CO$	−2·5
α-cumyl-oxyl	CH_3	$C_6H_5COCH_3$	1·8
	C_6H_5	$(CH_3)_2CO$	8
1 : 1-diphenyl ethoxyl	CH_3	$(C_6H_5)_2CO$	2
	C_6H_5	$C_6H_5COCH_3$	7
triphenyl methoxyl	C_6H_5	$(C_6H_5)_2CO$	7·9
CYCLIC DERIVATIVES			
cyclo-hexyloxyl	—	$\cdot CH_2(CH_2)_4CHO$	1·1
α-methyl-cyclo-hexyloxyl	—	$\cdot CH_2(CH_2)_4COCH_3$	1·4
	CH_3	cyclohexanone	2·9
α-phenyl-cyclohexyloxyl	C_6H_5	cyclohexanone	9
	—	$\cdot CH_2(CH_2)_4COC_6H_5$	5·5
decalyl-9-oxyl	1-9 bond fission		−0·7
	9-10 bond fission		0·2

9. KINETIC CLASSIFICATION OF ALKOXYL RADICAL REACTIONS

It is, of course, experimentally impossible to study alkoxyl radicals in isolation and the relative importance of the different modes of reaction depends not only on the nature of the particular alkoxyl radical but also on its concentration, on the physical conditions and its chemical environment. Before the interrelations of thermochemistry and reactivity can be examined, a kinetic classification of the reactions is necessary. This classification,[27] which cuts across the previous grouping (e.g. by separating dimerization from all other radical-radical associations), is based on the molecularity and the kinetic order of reaction. It is outlined in table 5, which shows how " chemically " distinct types of reaction are divided among three groups, with velocities depending on [RO·], [RO·][M] and $[RO·]^2$ respectively. The importance of this grouping is that, if two reactions belong to different groups, it is possible to control their relative importance by variations of concentration alone: if two reactions belong to the same kinetic group their relative importance may be discussed in thermochemical terms.

TABLE 5.—KINETIC CLASSIFICATION OF ALKOXYL RADICAL REACTIONS

rate equation, kinetic order and half-life	reaction (section)	exothermicity $-\Delta H$ kcal mole^{-1}	Arrhenius parameters	
			P or $10^{-13}A$ (estimated)	E kcal mole^{-1}
k_2[RO·][M]	association with radicals (8·1)	30-100	10^{-1}-10^{-4}	0
second-order (overall)	addition to unsaturated molecules (8·2)	15-40	10^{-2}-10^{-4}	10
$\frac{\ln 2}{k_2[M]_0}$ (M in excess)	H-atom loss to radicals (8·4)	0-80	10^{-2}-10^{-4}	10
	H-abstraction (8·3)	2-30	10^{-2}-10^{-4}	5-10
$k_2[RO·]^2$ second-order	dimerization (8·1)	35-40	10^{-2}-10^{-5}	0
$\frac{1}{k_2[RO·]_0}$	disproportionation (8·4)	75--85	10^{-2}-10^{-5}	0
k_1[RO·]	rearrangement by radical migration (8·5)	0-5	1-10^{-2}	unknown
first-order	rearrangement by H-atom migration (8·5); internal H-abstraction (8·5)	0-5	1-10^{-2}	unknown
$\frac{\ln 2}{k_1}$	decomposition by radical elimination (8·7)	0·15	10-10^4	10-30
	decomposition by H-atom elimination (8·6)	10-25	10-10^3	1540
	decomposition by ring fission (8·7)	0-5	1-10^2	unknown

10. THERMOCHEMISTRY AND REACTIVITY

A quantitative investigation of differences in reactivity is most suitably carried out in terms of the parameters A and E of the Arrhenius equation. Transition-state theory is a helpful guide to probable magnitude of A or the related entropy of reaction; in a similar sense, thermochemistry underlies the value of the energy of activation. In the sections which follow the three kinetically distinct groups are discussed first and " internal " differences examined. Finally thermochemical aspects of decomposition are considered.

10.1. 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·] 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 *n*-hept-1-ene as well as adding to its double bond; similarly, other radicals may either associate with alkoxyl radicals or abstract hydrogen atoms from them.

Association with other radicals [27] 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 to 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 favoured by an increase in temperature: near-zero values of E find support from work on *tert.*-butoxyl.[37] The steric influences are restrictive. Translational 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 α-hydrogen loss 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 favoured at low pressures and to be most prominent when the M—H bond formed by the radical 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 H-abstraction 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 ref. (27).

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 ($\Delta H \simeq -35$ 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 *n*-hept-1-ene is exceptional.[38] 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 olefins such as cyclohexene or acraldehyde.

10.2. SECOND-ORDER REACTIONS BETWEEN PAIRS OF ALKOXYL RADICALS

These are dimerization and disproportionation; they are both favoured relatively to other classes by high RO· concentration.

Dimerization is the reverse of the initial step in peroxide pyrolysis. The energy released is the dissociation energy of the O—O bond and this energy has to be dissipated in third-body collisions. There is no evidence that dimerization requires any activation energy and it is thus aided by low temperatures and by de-energizing collisions: the best authenticated instances [39] do occur in solution:

$$\underset{\text{2-phenyl propan-2-oxyl}}{2C_6H_5CMe_2O\cdot} \rightarrow \underset{\text{di-}\alpha\text{-cumyl peroxide}}{(C_6H_5CMe_2O-)_2}$$

Disproportionation is strongly exothermic, liberating some 80 kcal per alkoxyl radical pair compared with the 35-40 kcal released in dimerization; the correlation [27, 42] between ΔH and E suggests that disproportionation should have a near-zero activation energy; furthermore, no deactivating collisions are needed. Disproportionation, which appears best established in the pyrolyses of peroxides,[2, 40] is probably a component reaction of nitrite ester decompositions [33, 41] also. Wijnen's [26] recent work on the deuterated methyl acetates establishes it for methoxyl. Analogy with the isoelectronic ethyl radicals [1] suggests that for methoxyl, disproportionation and dimerization should have nearly equal steric requirements and near-zero activation energy.

10.3. 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 favoured equally relative to other classes by low concentrations of RO· and the absence of all but inert substrates.

Rearrangement by migration of an α-hydrogen atom, an α-alkyl group, or by internal hydrogen abstraction has not been established, though all these examples are exothermic reactions [32] without any obviously stringent orientational restrictions. The exothermicities (table 3) of the rearrangements which do occur are very imprecise and the activation energies are unknown, though the ease of migration of Ar in the substituted methoxyl family, $ArPh_2CO\cdot$, has been established; relative to phenyl, these figures [30] are: 1-naphthyl ≈ 4-diphenyl = 6; phenyl ≈ *p*-tolyl = 1; and *p*-nitrophenyl = zero.

Whereas rearrangement is exothermic or thermoneutral and its entropy change is small, 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. Decomposition is thus favoured by increase of temperature; even at 100°, decomposition is frequent while rearrangement is rare. The various types of decomposition are discussed in § 10.4 and § 10.5.

10.4. Comparative thermochemistry of decomposition reactions

Modes of decomposition of a single radical.—The salient experimental data requiring to be interpreted [42] may be outlined. First, decomposition by C—H 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 decomposition about; the activation energy [3*d*] lies near to 40 kcal mole^{-1}. Secondly, when in higher alkoxyl radicals more than one mode of reaction is possible, both occur. Though ethyl, *n*-butyl and *tert.*-butyl radicals are eliminated more readily [43] than methyl, it is essential to realize that this represents a predominant trend and not a completely exclusive mode. Thirdly, in cyclic derivatives [34, 44] the ring is broken in preference to elimination of an attached " exocyclic " group: this is true whether the exocyclic group is an H atom, an alkyl or an aryl radical. Taking these facts together we may generalize that normally the largest alkyl group comes out most readily, though when a ring is present it is broken preferentially. Finally, in aryl-substituted systems, phenyl groups are eliminated less readily [45] than alkyl groups: H-atoms are lost, but only in disproportionation.[46] It is probably safe to set as the order of *increasing* ease of fission in a mixed radical the series:

$$H < C_6H_5 < CH_3 < C_2H_5 < (CH_3)_2CH < (CH_3)_3C < \text{ring fission.}$$

The thermochemical aspects of these experimental results will now be considered. So far as the difficulties of decomposition by H-atom elimination are concerned, the data of § 8.6 and § 8.7 (table 4) are clear: H-elimination 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 then the difference in energy requirements, D(C—H) − D(C—alkyl) is always some 8 to 12 kcal mole^{-1} in favour of alkyl elimination. Within the group of alkyl radical eliminations, differences between different alkyl eliminations from the parent are small: individually they may be insignificant but taken together with the data of part 1, they indicate that a bulky group, e.g. *tertiary* alkyl, is more readily lost than a methyl or other small radical.

Ring fission requires least energy of all, only 1 to 2 kcal mole. If the dissociation energies of the alternative routes, alkyl elimination against ring fission, are compared for 1-R-cyclo-hexyl-1-oxyl radicals it is found that ring fission requires far less energy than H-atom loss (R = H), and slightly less energy than radical elimination for R=CH_3 or C_5H_5 ; however, if R is *tert.*-butyl, radical loss should be thermochemically favoured. Though Hey *et al.*[35] 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 this special explanation is not necessary.

The aryl-substituted radicals form an interesting class. Energy requirements for phenyl elimination are always more than for alkyl elimination from mixed radicals, and more than for ring-opening. In radicals where either a carbon-alkyl or carbon-aryl bond may be broken the mean difference D(C—Ar) − D(C—R) is about 5 kcal mole^{-1}. Elimination of phenyl groups does not, however, need as much energy as H-atom elimination: the mean value [27, 42] for the difference D(C—H) − D(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*: it is not necessary to know the heat of formation of the parent radical to make valid comparisons of this type.

COMPARISONS BETWEEN DIFFERENT RADICALS.—At present, different radicals may be compared with one another most readily by experiments in which decomposition competes with other modes of reaction. Vaughan and his collaborators [28] measured the relative rates of decomposition and hydrogen abstraction from the same hydrogen donor, cyclohexene, for a series of alkoxyl radicals and they concluded that the radicals could be arranged in order of *diminishing* stability as:

$$CH_3O > C_2H_5O > n\text{-}C_4H_9\text{-1-}O > sec.\text{-}C_3H_7O > iso C_4H_9O > tert.\text{-}C_4H_9O.$$

The parallelisms between reactivity and thermochemistry are further emphasized when this series [28] for alkoxyl radical stability is examined in the light of thermochemistry. In table 6 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 6.—THERMOCHEMISTRY AND STABILITY OF ALKOXYL RADICALS

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

radical	minimum enthalpy requirement for decomposition	activation energy in decomposition	order of stability Vaughan,[28]
CH_3O	25	25-40	1
C_2H_5O	13	15-20	2
n-C_4H_9O	11	—	3
isoC_3H_7O	10	—	4
n-C_3H_7O	10	—	—
isoC_4H_4O	7	—	5
sec-C_4H_9O	5	—	—
tert.-C_4H_9O	5	10-15	6
$C_6H_5(CH_3)_2CO\cdot$	—	10	—
cyclo-$C_6H_{11}O\cdot$	1	—	—

APPENDIX

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 list following of ΔH_f° (*g*, 25°C, 1 atm) in kcal mole^{-1} have been selected from recent determinations: the list is a continuation of that provided for the lower alkoxyl radicals in part 1. Entries to which no further reference is given here may be sought there and in part 2.[61]

ATOMS

Hydrogen,[13] 52·1; carbon,[13] 170·4; oxygen,[13] 59·2.

RADICALS

Hydroxyl,[61] 8·9; methyl, 31·5; methylene, 95; methyne[13] (CH), 142·1; ethyl, 24·5; *n*-propyl, 22; *iso*propyl, 17; *tert.*-butyl, 4·5; *n*-butyl, 19; allyl, 30; phenyl, 69; benzyl, 43; formyl,[36] $\sim$0; acetyl,[49] — 11; benzoyl,[50] 15·2. Values for hydrocarbon radicals in this list are taken from Szwarc's compilations.[7]

MOLECULES

WATER AND THE LOWER ALCOHOLS, see part 1. HIGHER ALCOHOLS, see §4 of this paper.

ETHERS: Di*iso*propyl ether,[15, 18] — 76·4; methyl allyl ether,[25] — 22·3; methyl phenyl ether [51,52] (anisole), — 16·9; ethyl phenyl ether,[51,52] — 29·8; diphenyl ether,[52,53] 6·1; for lower ethers see part 1. CYCLIC ETHERS: tetrahydropyran,[53] — 50·7; tetrahydrofuran,[53] — 43·08; ethylene oxide,[13] — 12·19; propylene oxide,[54] — 22·02. ACETALS, KETALS, etc.: methylal,[25] — 79·35; 1:3 dioxan,[55] — 90·84; trimethyl orthoformate,[25] — 118·6. ESTERS: methyl formate,[13] — 83·6; methyl, ethyl, *n*- and *sec.*-propyl, *n*- and *iso*butyl acetates,[56] — 99·2, — 106·58, — 112·8, — 115·85, — 118·9 and — 121·1 respectively; methyl benzoate,[14] — 71·7; ethyl benzoate,[14] — 79·1; dimethyl carbonate,[25] — 137·1; diethyl carbonate,[25] — 156·9.

OLEFINS:[57] Ethylene, 12·50; propylene, 4·88; cyclohexene, — 1·7; 1:3-butadiene, 26·33 ALDEHYDES: formaldehyde, — 27·7; acetaldehyde, — 39·8; propionaldehyde, — 46 1. benzaldehyde,[58] — 7·2. KETONES: acetone, — 51·8; methyl ethyl ketone, — 58·4; cyclohexanone,[48] — 59; cyclopentanone,[48] — 61; acetophenone,[58, 59] — 16·9; ethyl phenyl ketone,[59] — 299·8; benzophenone,[20, 58-60] 12·3.

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