Enthalpies of formation and O—O and C—O bond strengths in polyoxides RO_xR' and $RO_x^{\cdot}$

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Bond strengths in RO—OOR′, ROO—OH, and ROO—OOR′ (R, R′ = H, Me, Et, and Bu^t) molecules, calculated by the semiempirical quantum-chemical methods, were used to determine the enthalpies of formation of polyoxides RO_xR' (x = 3, 4) and related radicals and the bond strengths (D/kcal mol^{-1}) in these molecules: D(ROOO—OR′) = 33.2±0.9, D(ROOO—OH) = 37.5±0.7, D(R—O$_x$R′) = 76.0±1.2, D(H—OOO$^{\cdot}$) = 58.6, D(R′—OOO$^{\cdot}$) = 42.8±0.8. A new value of Benson's polyoxide thermochemical increment, Δ_fH°[O—(O)$_2$] = 11.1±1.0 kcal mol^{-1}, was suggested.

Key words: polyoxides, enthalpy of formation, bond strengths, quantum-chemical calculations; thermochemistry.

There are no experimental data on the enthalpy of formation (Δ_fH°) of the highest RO_xR' polyoxides and $RO_x^{\cdot}$ radicals (x = 3, 4; R, R′ = H, Alk) in the literature. For these molecules, the Δ_fH° values are usually calculated by the method of the additivity of thermochemical increments.[1] A key parameter of these calculations is the increment for [O—(O)$_2$], which is the thermochemical contribution of the O atom bonded to two other oxygen atoms to the enthalpy of formation of the molecule. This increment has been previously determined (see Refs. 2—7), but the results obtained differ widely. This circumstance makes the thermochemical analysis of reactions of higher polyoxides difficult.

Quantum-chemical methods can be used to calculate the Δ_fH° values of molecules and radicals. However, in our opinion, the direct estimation of Δ_fH° of polyoxides[6] is quite rough because of significant errors in the calculation.[8] For calculating the bond strengths (D) of organic compounds, semiempirical quantum-chemical methods are promising.[9] Applying this approach to polyoxides gives satisfactory results in the calculations of hydropolyoxide O—H bond strengths (AM1 method),[10] and ROO—OOR (MNDO method),[11] RO—OOR, RO—OOH and ROO—OH (AM1 and MNDO)[11,12] bond strengths.

This work is a continuation of the study of the thermochemistry of higher polyoxides by semiempirical quantum-chemical methods.

Results and Discussions

The enthalpies of formation of higher polyoxides were calculated by the equation

$$\Delta_fH^\circ(RO_xOOR') = \Delta_fH^\circ(RO_x^{\cdot}) + \Delta_fH^\circ(R'OO^{\cdot}) - D(RO_x{-}OOR'), \qquad (1)$$

where x = 1, 2; R, R′ = H, Me, Et, and Bu^t.

The best Δ_fH° values for alkoxyl and peroxyl radicals were chosen based on a critical analysis of the experimental values (Table 1). The O—O bond strengths were estimated by the semiempirical MNDO and AM1 methods according to an approach described earlier.[9] The D(O—O) values obtained are presented in Table 2.

Table 1. Enthalpies of formation of radicals

R	Δ_fH°/kcal mol^{-1}		
	R$^{\cdot}$	RO$^{\cdot}$	ROO$^{\cdot}$
H	52.1[13]	9.4[13]	3.5[14—16]
Me	34.9[17]	4.1[18]	4.5*
Et	27.8[19]	−4.1[20]	−3.9*
Bu^t	9.5[19,21]	−22.8[4,22]	−25.2[16]

* Calculated from the D(ROO—H),[10] Δ_fH°(H$^{\cdot}$), and Δ_fH°(ROOH) values.

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Table 2. Results of quantum-chemical calculations of O—O bond strengths of RO—OOR′ polyoxides

R	R′	D(O—O)/kcal mol^{-1}	
		MNDO	AM1
H	H	25.0	25.2
H	Me	26.6	25.4
H	Et	26.1	24.3
H	Bu^t	24.9	22.4
H	OH	28.6	27.6
H	OMe	27.9	26.9
H	OEt	27.9	27.4
H	OBu^t	27.8	27.7
Me	H	20.7	18.8
Me	Me	22.2	19.0
Me	Et	21.8	18.0
Me	Bu^t	20.5	16.0
Me	OH	24.4	21.3
Me	OMe	23.8	20.2
Me	OEt	23.8	21.1
Me	OBu^t	23.6	21.4
Et	H	21.7	21.0
Et	Me	23.0	21.2
Et	Et	22.7	20.1
Et	Bu^t	21.4	18.1
Et	OH	25.4	23.6
Et	OMe	24.8	23.0
Et	OEt	24.8	23.3
Et	OBu^t	24.6	23.7
Bu^t	H	19.3	22.1
Bu^t	Me	20.8	22.2
Bu^t	Et	20.3	21.1
Bu^t	Bu^t	18.4	19.1
Bu^t	OH	23.1	24.6
Bu^t	OMe	22.5	24.0
Bu^t	OEt	22.5	24.5
Bu^t	OBu^t	22.2	24.7
OH	H	7.1	5.9
OH	Me	8.7	6.8
OH	Et	8.6	5.7
OH	Bu^t	7.3	4.0
OMe	Me	10.4	8.2
OMe	Et	10.1	6.3
OMe	Bu^t	8.9	4.7
OEt	Et	9.8	5.4
OEt	Bu^t	8.6	3.5
OBu^t	Bu^t	7.4	1.7

O—O bond strengths in trioxides. The RO—OOH, ROO—OH and RO—OOR bond strengths have been calculated previously.[11,12] The D(O—O) values have been demonstrated[12] to be in a good agreement with the few experimental data available. The D(RO—OOH) and D(RO—OOR) values are practically independent of the character of R and the method of calculation, and varied from 18.8 to 22 kcal mol^{-1}. The D(ROO—OH) bond strength is 4—8 kcal mol^{-1} higher on the average. In Table 2, the previously published data[11,12] were added to the D(RO—OOR′) values of the nonsymmetrical trioxides.

ROO—OOR′ bond strengths. The central O—O bond is the weakest one in tetraoxides. Tetraoxides are in equilibrium with peroxyl radicals at $T < -100$ °C. The variation in the enthalpy of the equilibrium formation of ROOOOR is 8—9 kcal mol^{-1} (R = *tert*- or *sec*-Alk). The D(ROO—OOR′) values calculated by the MNDO method are in good agreement with this magnitude, but the AM1 results are less reasonable (see Table 2).

Substitution of the D(RO—OOR′), D(ROO—OH) and D(ROO—OOR′) values in Eq. (1) allows the enthalpies of formation of all polyoxides under consideration to be determined. The D(ROO—OOR′) values obtained by the AM1 method were not used to calculate $\Delta_f H°$. The results of calculations according to Eq. (1) presented in Table 3 are in good agreement as a whole. For example, the enthalpy of formation of *tert*-butylhydrotrioxide can be calculated from the data of Table 1 and 2 in two ways that produce close results:

(1) R = Bu^t, R′ = H, $x = 1$, $\Delta_f H° = -40.0$ kcal mol^{-1};

(2) R = H, R′ = Bu^t, $x = 1$, $\Delta_f H° = -39.5$ kcal mol^{-1}.

The enthalpies of formation of polyoxides have been used from here on to estimate the D(RO—OOOR′) values and the C—O (H—O) bond strengths of polyoxide molecules and radicals.

ROOO—OR′ bond strengths. The D(RO—OOOR′) values are close to the D(RO—OOR′) values (see Table 2). This fact is quite logical. However, it is easy to show that the data on the central and non-central O—O bond strengths of the tetraoxides are not self-consistent. Indeed, from the combination of the thermochemical Eqs. (2)—(4)

$$\Delta_f H°(\mathrm{ROOOOR}) = \Delta_f H°(\mathrm{RO}^{\cdot}) + \Delta_f H°(\mathrm{ROOO}^{\cdot}) - D(\mathrm{RO{-}OOOR}), \quad (2)$$

$$\Delta_f H°(\mathrm{ROOOOR}) = 2\Delta_f H°(\mathrm{ROO}^{\cdot}) - D(\mathrm{ROO{-}OOR}), \quad (3)$$

$$\Delta_f H°(\mathrm{ROOOH}) = \Delta_f H°(\mathrm{H}^{\cdot}) + \Delta_f H°(\mathrm{ROOO}^{\cdot}) - D(\mathrm{ROOO{-}H}) \quad (4)$$

it follows, that

$$D(\mathrm{ROO{-}OOR}) = 2\Delta_f H°(\mathrm{ROO}^{\cdot}) + \Delta_f H°(\mathrm{H}^{\cdot}) - \Delta_f H°(\mathrm{RO}^{\cdot}) - \Delta_f H°(\mathrm{ROOOH}) + D(\mathrm{RO{-}OOOR}) - D(\mathrm{ROOO{-}H}).$$

It has been previously shown[10] that the AM1 method can be used to estimate the RO$_x$—H bond strengths, when $x = 2$ to 4. When R = Bu^t the use of published[10] data and the $\Delta_f H°$ and D values from Table 3 results in D(ROO—OOR) = −4.3 kcal mol^{-1}, which disagrees with the experimental data.[26—29] Therefore, the MNDO and AM1 methods are unsuitable for estimating the non-central O—O bond strengths of tetraoxides. The

Table 3. Enthalpies of formation of polyoxides

R	R′	$\Delta_f H^\circ$/kcal mol^{-1}			$\Delta(\Delta_f H^\circ)$*/kcal mol^{-1}	
		RO_2R'	RO_3R'	RO_4R'	$RO_3R'-RO_2R'$	$RO_4R'-RO_3R'$
H	H	−32.5[23]	−12.2	−0.1	20.3	12.1
Me	H	−31.3[24]	−12.1	−0.7	19.2	11.4
Et	H	−39.0**	−20.8	−9.0	18.2	11.8
Bu^t	H	−58.8[25]	−39.7	−29.0	19.1	10.7
Me	Me	−30.0[25]	−12.0	−1.4	18.0	10.6
Et	Me	−37.4**	−20.7	−9.5	16.7	11.2
Bu^t	Me	−55.3**	−39.3	−29.6	16.0	9.7
Et	Et	−46.1[25]	−29.4	−17.6	16.7	11.8
Bu^t	Et	−63.5**	−48.0	−37.7	15.5	10.3
Bu^t	Bu^t	−83.4[25]	−66.8	−57.8	16.6	9.0
H	—	3.5	27.6	39.6	24.1	12.0
Me	—	4.5	27.1	39.2	22.6	12.1
Et	—	−3.9	18.7	30.7	22.6	12.0
Bu^t	—	−25.2	0.2	10.2	25.4	10.0

* Calculated as $\Delta_f H^\circ$(ROOOR′) − $\Delta_f H^\circ$(ROOR′) and $\Delta_f H^\circ$(ROOOOR′) − $\Delta_f H^\circ$(ROOOR′), respectively.

** Calculated by Benson's addition principle.[1]

D(RO—OOOR′) values may be calculated from Eqs. (2) and (4) as follows:

$$D(\mathrm{RO{-}OOOR'}) = \Delta_f H^\circ(\mathrm{RO^{\cdot}}) + \Delta_f H^\circ(\mathrm{R'OOOH}) - \Delta_f H^\circ(\mathrm{H^{\cdot}}) - \Delta_f H^\circ(\mathrm{ROOOOR'}) + D(\mathrm{R'OOO{-}H}). \quad (6)$$

The non-central O—O bond strength was found to be practically independent of the character of the substituent R:

$$D(\mathrm{ROOO{-}OH}) = 37.5\pm0.7 \text{ kcal mol}^{-1} \ (n = 4),$$

$$D(\mathrm{ROOO{-}OR'}) = 33.2\pm0.9 \text{ kcal mol}^{-1} \ (n = 12), \quad \mathrm{R'} \neq \mathrm{H}$$

(*n* is the number of independent determinations of the bond strengths).

C—O (H—O) bond strengths in polyoxides. Combining the literature data[10] and the $\Delta_f H^\circ$ values of hydropolyoxides allows the enthalpies of formation of polyoxide radicals $RO_x^{\cdot}$ to be calculated when $x = 3$ and 4 (see Table 3). In turn, based on the $\Delta_f H^\circ$ values of alkyl (see Table 1) and polyoxide radicals, the C—O (H—O) bond strengths in polyoxides, including *D*(R—OOO$^{\cdot}$), may be estimated when $\Delta_f H^\circ(O_3)$ = 34.1 kcal mol^{-1} (see Ref. 14):

Polyoxide	*D* /kcal mol^{-1}	*n*	Peroxide	*D* /kcal mol^{-1}	*n*
H—OOO$^{\cdot}$	58.6	1	H—OO$^{\cdot}$	48.6	1
R′—OOO$^{\cdot}$	42.8±0.8	3	R′—OO$^{\cdot}$	32.3±2.2	3
R′—O$_x$R (x = 3, 4)	76.0±1.2	24	R′—OOR	68.9±1.9	12

Determination of the $\Delta_f H^\circ$[O—(O)$_2$] values. The values presented in Table 3 enables Benson's polyoxide increment of [O—(O)$_2$] to be calculated. According to the literature data,[1]

$$\Delta_f H^\circ[\mathrm{O{-}(O)_2}] = \Delta_f H^\circ(\mathrm{ROOOR}) - \Delta_f H^\circ(\mathrm{ROOR}) = \Delta_f H^\circ(\mathrm{ROOOOR}) - \Delta_f H^\circ(\mathrm{ROOOR}).$$

However, the difference between the enthalpies of formation of trioxide and peroxide significantly exceeds the corresponding $\Delta(\Delta_f H^\circ)$ values of tetraoxide and peroxide. The reason for this phenomenon has been previously discussed in detail.[30] The reason is that the peroxide molecule is stabilized by the dipole interaction between the oxyl fragments, which is lacking in tri- and tetraoxides. Thus the difference between $\Delta_f H^\circ$(ROOOOR) and $\Delta_f H^\circ$(ROOOR), practically independent of the character of R (see Table 3), is the thermochemical increment: $\Delta_f H^\circ$[O—(O)$_2$] = 11.1±1.0 kcal mol^{-1}.

This value is in good agreement with the estimation $\Delta_f H^\circ$[O—(O)$_2$] = 11.6±1.4 kcal mol^{-1}, obtained on the basis of an analysis of the conformational potential energy surfaces of hydrogen polyoxides,[30] but differs from the other literature data[6,7] and the value recommended in one of the works by Benson *et al.*[5] The approach suggested in this work was based on the consideration of the set of equations (a)—(c)

$$\mathrm{Bu^tOOOOBu^t} \rightleftharpoons 2\ \mathrm{Bu^tOO^{\cdot}} \quad \text{(a)}$$

$$\mathrm{Bu^tOOOBu^t} \rightleftharpoons \mathrm{Bu^tO^{\cdot}} + \mathrm{Bu^tOO^{\cdot}} \quad \text{(b)}$$

$$\mathrm{Bu^tOOBu^t} \rightleftharpoons 2\ \mathrm{Bu^tO^{\cdot}} \quad \text{(c)}$$

with the known heat effects ΔH°_a = 9.0 kcal mol^{-1} and ΔH°_c = 38.0 kcal mol^{-1}, and also applies the addition principle $\Delta H^\circ_b = 0.5(\Delta H^\circ_a + \Delta H^\circ_c)$.[4] By splitting the molecules into thermochemical groups, it is easy to obtain

$$\Delta H^\circ_c - \Delta H^\circ_b = \Delta H^\circ_b - \Delta H^\circ_a = \Delta_f H^\circ(\mathrm{RO^{\cdot}}) - \Delta_f H^\circ(\mathrm{ROO^{\cdot}}) + \Delta_f H^\circ[\mathrm{O{-}(O)_2}].$$

It follows that $\Delta_f H^\circ[O{-}(O)_2]$ is equal to 14.8 kcal mol^{-1} (see Ref. 5). The addition principle gives ΔH°_b = 23.5 kcal mol^{-1}, which is a quite rough approximation. Earlier[11] it was found to be ΔH°_b = 20.3 kcal mol^{-1}, and therefore, the value obtained by this method[5] is overestimated by more than 3 kcal mol^{-1}.

The thermochemical characteristics obtained in this work can be useful in analyzing the mechanisms of oxidative processes. For example, according to our data, the enthalpy of formation of the $HOOO^\cdot$ radical (27.6 kcal mol^{-1}) is larger than the sum of the $\Delta_f H^\circ$ of the products of its dissociation, $HO^\cdot$ and O_2, by 18.2 kcal mol^{-1}. This fact indicates that the hydrotrioxyl radical is highly labile and makes its role in the processes of oxidation of saturated organic compounds by ozone negligible. Consequently, the interaction of O_3 with C—H bond occurs either according to the ionic mechanism:

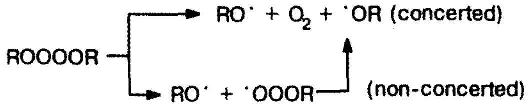
$$R{-}H + O_3 \rightarrow [R^+ + HOOO^-] \rightarrow ROOOH,$$

when R—H is ethers, alcohols, acetals, alkylaromatic compounds (effectively stabilizing a positive charge), or involves radicals:

$$R{-}H + O_3 \rightarrow R^\cdot + O_2 + {}^\cdot OH.$$

In this case, ROOOH formation is impossible. The radical mechanism is more probable for alkanes. It is possible that this is the reason for the lack of data on the formation of hydrotrioxides of aliphatic hydrocarbons. Increasing in the temperature favors the radical process of ozonative oxidation. Indeed, in the reaction of ozone with 1,1-diethoxyethane, the yield of ROOOH decreases as the temperature increases.[31]

Another example is the irreversible dissociation of *tert*-tetraoxides. Two mechanisms of this reaction have been discussed:[32,33]



According to our data, the ΔH° value for the concerted process is 11.2 kcal mol^{-1}, and for the non-concerted process the D(O—O) bond strength is 35.2 kcal mol^{-1} (R = Bu^t). Since the energy of the irreversible dissociation of ROOOOR is estimated as *ca.* 17 kcal mol^{-1}, the decomposition occurs *via* concerted fragmentation into two $RO^\cdot$ radicals and an O_2 molecule.

Thus, a knowledge of the energetics of reactions of polyoxide molecules, and of the favorable channels by which they form and decompose are important for understanding and effectively carrying out oxidative processes.

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