Quantum-chemical calculations of O—O bond strengths in organic hydrotrioxides

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The O—O bond strengths in ten organic hydrotrioxides have been calculated by semiempirical MNDO and AM1 methods. The RO—OOH bond strength is independent of the nature of substituent R and is equal to 20.4±1.0 kcal mol^{-1} (MNDO) or 20.8±1.1 kcal mol^{-1} (AM1). The influence of the inductive effect of substituent R on the value of D(ROO—OH) has been established.

Key words: polyoxides, bond strength, quantum-chemical calculations.

Organic hydrotrioxides are promising sources of singlet oxygen[1,2] and efficient oxidants, which make it possible to perform oxidative transformations of organic compounds of various classes under mild conditions.[2—5] It is known[6] that hydrotrioxides decompose to form free radicals. Therefore, the decomposition of ROOOH by homolysis of the O—O bonds seems highly probable. Unfortunately, published data on these bond strengths are very scarce. Despite the fact that more than twenty values of activation energies (E_a) of thermal decomposition of ROOOH are determined, the real bond strength (D) can strongly differ from the E_a value, because hydrotrioxides tend to induced decomposition and self-association in solutions[7—9] followed by the formation of intra- and intermolecular hydrogen bonds.

This work presents the results of quantum-chemical calculations of the RO—OOH and ROO—OH bond strengths obtained by the semiempirical MNDO and AM1 methods. The applicability of these methods for such estimations has been shown previously,[10,11] and the calculation procedure is described in the literature.[12] We also attempted to use the PM3 method, but it gave unsatisfactory results.

The geometry of all ten hydrotrioxides was completely optimized. According to the published data,[13,14] the optimum conformation of ROOOH is the *anti*-form, in which the H atom and substituent R are localized at different sides of the plane formed by the oxygen atoms. The results of the calculations are presented in Table 1. The RO—OOH bond strength is independent of the structure of R, and the D(RO—OOH) values calculated by different semiempirical methods agree.

MNDO: D(RO—OOH) = 20.4±1.0 kcal mol^{-1};

AM1: D(RO—OOH) = 20.8±1.1 kcal mol^{-1}.

The value D(RO—OOH) = 23 kcal mol^{-1} obtained on the basis of measurement of the gas release rate upon thermal decomposition of di-*tert*-butyltrioxide was recommended[15] for thermochemical calculations. Since the gas release rate was registered only at two temperatures, the E_a value of thermal decomposition is an estimated one (see Ref. 16).

The kinetics of overall decomposition of propan-2-ol hydrotrioxide is studied[17] in various solvents. The linear dependence of the activation energy on the logarithm of pre-exponential factor (compensation effect) is determined (Eq. (1)).

Table 1. Calculated O—O bond strengths (D/kcal mol^{-1}) in hydrotrioxides

ROOOH	D(RO—OOH)		D(ROO—OH)	
	MNDO	AM1	MNDO	AM1
HOOOH	25.0	25.2	25.0	25.2
MeOOOH	20.7	18.8	26.6	25.4
EtOOOH	21.7	21.0	26.1	24.3
$Me_2CHOOOH$	21.0	22.0	25.6	23.7
Me_3COOOH	18.9	22.1	24.6	22.4
$HOCH_2OOOH$	21.4	21.3	25.9	24.8
$MeOCH_2OOOH$	21.1	19.5	25.9	24.6
$ClCH_2OOOH$	18.9	19.7	27.5	25.5
$Cl_2CHOOOH$	20.3	21.3	29.6	26.9
Cl_3COOOH	20.0	21.3	30.8	27.0

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$$E = (1.71\pm0.51) + (1.42\pm0.07)\log A \qquad (1)$$

Estimation of the activation energy of decomposition of propan-2-ol hydrotrioxide in the gas phase ($\log A = 13$) by Eq. (1) gives $E_a = D(\text{RO—OOH}) = 20.2$ kcal mol^{-1}, which agrees with the results of quantum-chemical calculations.

The temperature dependences of the rate constants of radical decomposition of cumene hydrotrioxide (3.58 *M* solution of cumene in acetone-d_6)[6] and propan-2-ol have been studied previously.[18] The E_a values obtained (23.9 and 25.2 kcal mol^{-1}, respectively) are the sums of the RO—OOH bond strength and activation energy of viscous flow of the solvent. The latter value estimated from the temperature dependences of viscosity of acetone, cumene, and propan-2-ol[19,20] are 2.0 kcal mol^{-1} for a cumene solution in $(CD_3)_2CO$ and 5.0 kcal mol^{-1} for propan-2-ol*. It follows from the data presented that $D(\text{RO—OOH}) = 21.9$ kcal mol^{-1} ($R = PhMe_2C$) and 20.2 kcal mol^{-1} ($R = HOMe_2C$). These values are in good agreement with those calculated by semiempirical methods (see Table 1).

The ROO—OH bond strength is somewhat higher and depends on the nature of substituent R. This dependence is satisfactorily described by the Hammett equation, using the Taft scale for characterization of the inductive effect of R.[21]

$$\text{MNDO: } D(\text{ROO—OH}) = (25.5\pm0.6) + (1.97\pm0.49)\sigma^*,\ r = 0.97;$$

$$\text{AM1: } D(\text{ROO—OH}) = (23.8\pm0.6) + (1.38\pm0.49)\sigma^*,\ r = 0.94.$$

In both cases, HOOOH and MeOOH are excluded from the dependence.

The difference in the O—O bond strengths testifies to the higher probability of the decomposition of ROOOH to alkoxyl and hydroperoxyl radicals, which agrees with the previous conclusions.[15] Absolute values of strengths do not also contradict the experimental facts. For example, the correlation between D(RO—OOH) and D(ROO—OH) can be easily determined from thermochemical equations (2) and (3).

$$D(\text{RO—OOH}) = \Delta_f H^\circ(\text{RO}^\cdot) + \Delta_f H^\circ(\text{HOO}^\cdot) - \Delta_f H^\circ(\text{ROOOH}), \qquad (2)$$

$$D(\text{ROO—OH}) = \Delta_f H^\circ(\text{ROO}^\cdot) + \Delta_f H^\circ(\text{HO}^\cdot) - \Delta_f H^\circ(\text{ROOOH}) \qquad (3)$$

Accepting $\Delta_f H^\circ(\text{HO}^\cdot) = 9.4$ kcal mol^{-1}, $\Delta_f H^\circ(\text{HOO}^\cdot) = 3.5$ kcal mol^{-1} (see Ref. 18) and excluding the enthalpy of formation of hydrotrioxide, we obtain

$$D(\text{ROO—OH}) - D(\text{RO—OOH}) = \Delta_f H^\circ(\text{ROO}^\cdot) - \Delta_f H^\circ(\text{RO}^\cdot) + 5.9. \qquad (4)$$

For example, for $R = CMe_3$: $\Delta_f H^\circ(\text{ROO}^\cdot) = -25.2$ kcal mol^{-1},[22] $\Delta_f H^\circ(\text{RO}^\cdot) = -22.8$ kcal mol^{-1},[23] from where $\Delta D = 3.5$ kcal mol^{-1}. For R = Me, $\Delta_f H^\circ(\text{ROO}^\cdot) = 4.5$ kcal mol^{-1} (from the O—H bond strength in MeOOH[11] and $\Delta_f H^\circ(\text{ROOH}) = -31.3$ kcal mol^{-1})[23], $\Delta_f H^\circ(\text{RO}^\cdot) = 4.1$ kcal mol^{-1},[24] from where $\Delta D = 6.3$ kcal mol^{-1}. The calculation of ΔD from the data of Table 1 gives 3.0 and 6.2 kcal mol^{-1} for R = Bu^t and Me, respectively.

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* Since the activation energy of viscous flow somewhat changes as the temperature changes, E_a is calculated for the temperature range, in which rate constants of the homolytic decomposition of ROOOH were measured.

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