AM1 calculations of O—H bond dissociation energies in polyoxides

S. L. Khursan[a] and V. V. Shereshovets[b]*

[a]*Bashkortostan State University,*
32 ul. Frunze, 450074 Ufa, Russian Federation.
Fax: +7 (347 2) 331 677
[b]*Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,*
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 356 066

Energies of homolytic cleavage of O—H bonds in 33 compounds of the general formula RO_nH (n = 2, 3, and 4) were calculated by the AM1 method. For hydrotrioxides and hydrotetroxides, the bond dissociation energies are virtually independent of the nature of the substituent R: $D(RO_n{-}H) = 92.3 \pm 0.8$ kcal mol^{-1} (n = 3 and 4).

Key words: polyoxides; quantum-chemical calculations; bond dissociation energy.

The data on the O—H bond dissociation energies in polyoxides RO_nH (n = 2, 3, and 4) provide valuable information on the reactivities and thermochemical properties of these compounds. Because of a low thermal stability of higher (n = 3 and 4) polyoxides, these data are difficult to obtain experimentally; therefore, we used the semiempirical quantum-chemical AM1 method[1] for determining O—H bond dissociation energies in molecules of polyoxides. Previously,[2] it was demonstrated that the C—H bond dissociation energy in alkanes can be calculated with a high degree of accuracy with the use of the analogous MNDO approximation.

With the aim of examining the possibility of the use of the AM1 method, we calculated the O—H bond dissociation energies in hydroperoxides (Table 1). The procedure for calculation of the bond dissociation energy D was reported previously.[2] The data in the literature correlate well with the calculated values of D(O—H) except for those of perchloroethyl hydroperoxide C_2Cl_5OOH and peracetic acid MeC(O)OOH. Whereas the cause of a substantial deviation of the calculated value of $D(C_2Cl_5OO{-}H)$ from the experimental value is still unclear, the D(MeC(O)OO—H) value (88.4 kcal mol^{-1}) was, in our opinion, underestimated.

Actually, according to the data given in Table 1, D(ROO—H) linearly depends on the Taft's induction constant of the substituent R:

$$D(\mathrm{ROO{-}H}) = (87.3 \pm 1.2) + (4.01 \pm 0.85) \cdot \sigma^*(\mathrm{R}) \qquad (1)$$

(6 points; r = 0.99; 95 % confidence interval). Only the point for R = MeCO does not fit this dependence; according to Eq. (1), D(MeC(O)OO—H) = 93.9 kcal mol^{-1}, which is in satisfactory agreement with the results of calculations by the AM1 method (see Table 1). Therefore, the data obtained indicate that the AM1 method can be used for calculations of D(O—H) for peroxides and, apparently, for related polyxides RO_nH (n = 3 and 4).

The calculated bond dissociation energies D(O—H) and effective charges on the H atoms are given in Table 2. It is evident that the O—H bond in hydrotrioxides becomes slightly stronger as the induction capability of the R substituent enhances. For 17 compounds, it was found that

$$D(\mathrm{ROOO{-}H}) = (92.04 \pm 0.22) + (0.87 \pm 0.32) \cdot \sigma^*(\mathrm{R}), \qquad (2)$$

the values of D that do not fit this correlation are marked in Table 2. Dependence (2) is accurate with a moderate correlation coefficient (0.83) because the range of the change of D is ~3 kcal mol^{-1}, whereas we estimated the error in calculations of the O—H bond dissociation energy by the AM1 method as 1—2 kcal mol^{-1}.

Table 1. Inductive constants of the substituents and O—H bond dissociation energies (kcal mol^{-1}) in hydroperoxides

Hydroperoxide ROOH	$\sigma^*(\mathrm{R})$[6]	D(O—H)	
		Data from the literature[3—5]	AM1
Me_3COOH	−0.30	85.7	86.1
Me_2CHOOH	−0.19	87.1[a]	86.7
EtOOH	−0.10	87.4	87.5
HOOH	0.49	88.2	88.8
MeC(O)OOH	1.65	88.4	94.8
$C_6H_5C(O)OOH$	2.20	97.1	95.3
C_2Cl_5OOH	2.65[b]	97.3	90.7

[a] For *sec*-alkyl ROOH. [b] Under the assumption that $\sigma^*(C_2Cl_5) = \sigma^*(CCl_3)$ based on the close values of $\sigma^*(C_2F_5)$ and $\sigma^*(CF_3)$.[6]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 327—329, February, 1996.

Table 2. Effective charges on the H atom (q(H), e) and O—H bond dissociation energies (kcal mol^{-1}) in polyoxides calculated by the AM1 method

Polyoxide	q(H)	D(O—H)	Polyoxide	q(H)	D(O—H)
HOOH	0.210	88.8	$HOCH_2OOOH$	0.214	92.7
MeOOH	0.196	88.5	HOCHMeOOOH	0.214	92.2
EtOOH	0.193	87.5	$HOCMe_2OOOH$	0.211	92.8
Me_2CHOOH	0.190	86.7	$MeOCH_2OOOH$	0.215	92.5
Me_3COOH	0.189	86.1	MeOCHMeOOOH	0.213	92.8
MeC(O)OOH	0.212	94.8	$MeOCMe_2OOOH$	0.212	92.9
HOOOH	0.213	91.9	MeCOCHMeOOOH	0.212	92.3
MeOOOH	0.209	91.3	$MeCOCH(C_3H_7)OOOH$	0.212	92.3
EtOOOH	0.209	91.6	$(MeO)_2CMeOOOH$	0.217	93.7*
$Me_2CHOOOH$	0.208	91.9	$(EtO)_2CMeOOOH$	0.217	93.7*
Me_3COOOH	0.207	92.0	HC(O)OOOH	0.223	93.6
CFH_2OOOH	0.217	93.1	MeC(O)OOOH	0.207	90.1*
CF_2HOOOH	0.213	91.5*	HOOOOH	0.211	91.8
$CClH_2OOOH$	0.217	92.8	MeOOOOH	0.209	92.0
CCl_2HOOOH	0.214	91.7*	EtOOOOH	0.208	91.8
CCl_3OOOH	0.219	92.9*	$Me_3COOOOH$	0.206	91.3
CF_3CH_2OOOH	0.220	92.8			

* Not included in correlation Eq. (2).

The energies of homolytic cleavage of the O—H bonds in hydroperoxides is 5±2 kcal mol^{-1} lower than those in ROOOH and ROOOOH. This is contradictory to the conclusion[7] based on the comparison of the O—H bond orders in MeOOH and MeOOOH (*ab initio* calculations by the MP2/6-31G** method).

However, a comparison of acidic properties of hydroperoxides and hydrotrioxides is indicative of the fact that the H atom is more "acidic" in ROOOH. First, this is evidenced by the results of Ref. 7, where it was demonstrated that MeOOOH is a stronger acid than MeOOH. Second, the results listed in Table 2 point to the fact that in going from hydroperoxides to hydrotrioxides, the ionic character of the O—H bond increases. Finally, according to the results of potentiometric titration, the values of pK_a in water for hydroperoxides with different structures are in the range 11.1—12.8 [8] (for HOOH, pK_a = 11.6), whereas for HOOOH, $pK_a \simeq 9 \div 10$.[9] Peracids are stronger than ROOOH; for peracids, $pK_a = 7.1 \div 8.2$ [8] (for MeC(O)OOH, pK_a = 8.2 and for $C_6H_5C(O)OOH$, pK_a = 7.78).

A decrease in pK_a in the order ROOH > ROOOH > RC(O)OOH is determined by an increase in the ionic character of the O—H bond (see Table 2), which leads to an increase in the energy of its homolytic cleavage. Apparently, the above-mentioned dependence is general; this dependence for hydroperoxides and acids is shown in Fig. 1; in this figure, the region of the values of pK_a and D(O—H) is indicated by the dashed line. The above-mentioned experimental data agree with an increase in the O—H bond dissociation energy, which we found in going from hydroperoxides to hydrotrioxides; these results cast some doubt on the conclusion made previously,[7] that hydrotrioxides undergo induced homolysis more readily than hydroperoxides.

A weak effect of the R substituent on the O—H bond dissociation energy in hydropolyxides (n = 3 and 4) allows the recommendation that the average value of D(RO$_n$—H), which is independent of the structure of R, be used in practical thermochemical calculations. For 27

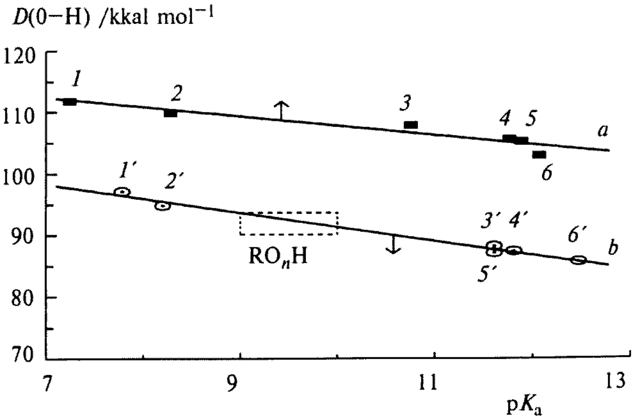


Fig. 1. Relationships between the O—H bond dissociation energies in (*a*) acids and (*b*) hydroperoxides and pK_a. The values of pK_a for peroxides were taken from Ref. 8; the values of pK_a for acids were taken from Ref. 10; D(ROO—H) values are given in Table 1 (for MeC(O)OOH, D = 94.8 was used, which was obtained by the AM1 method), D(RC(O)O—H) values were taken from Ref. 11: *1*, $CF_3C(O)OH$; *2*, $(C(O)OH)_2$; *3*, HC(O)OH; *4*, MeC(O)OH; *5*, EtC(O)OH; *6*, $Me_3CC(O)OH$; *1′*, $C_6F_5C(O)OOH$; *2′*, MeC(O)OOH; *3′*, HOOH; *4′*, EtOOH; *5′*, $(Me)_2CHOOH$; *6′*, Me_3COOH. The region of the values of pK_a and D(OH) typical of higher polyoxides is indicated by the dashed line.

compounds (see Table 2), the following equality is valid:

$$D(\mathrm{RO}_n\text{—H}) = 92.3\pm0.8 \text{ kcal mol}^{-1}.$$

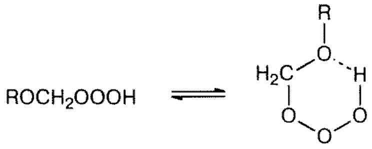
Because ROOOH derivatives may be formally considered as rOOH (r = RO), a weak effect of the R substituent on D(O—H) is attributable to the fact that the induction properties of RO depend only slightly on the nature of the R substituent. The $\sigma^*(\mathrm{RO}) = 1.68$ value is commonly accepted.[6] The use of Eq. (1) leads to D(ROOO—H) = 94.0 kcal mol^{-1}, which agrees satisfactorily with the average value of D.

The physicochemical cause of a slight change in D(O—H) in a series of higher polyxides is determined by specific properties of O atoms of the polyoxide chain, which hinder the inductive effect of the R substituent on the O—H bond. As a result, the coefficient ρ in Eq. (2) is substantially smaller than that in Eq. (1). An analogous regularity is observed when acidic properties of alcohols and hydroperoxides are compared.[8] For a 40 % MeOH aqueous solution, a satisfactory correlation between the values of $\mathrm{p}K_\mathrm{a}$ for hydroperoxides and the σ* constants for the R substituents is observed, which is characterized by $\rho = -0.51$. Under the same conditions, acidic properties of alcohols $\mathrm{RCH_2OH}$ are described by the following equation:

$$\mathrm{p}K_\mathrm{a} = -1.42\cdot\sigma^* + \text{const.}$$

The ratio between the ρ constants reflects the value of the transmission coefficient of the inductive effect of the R substituent on the ability of the proton to split out from the O—H group when the $\mathrm{CH_2}$ fragment is replaced with the oxygen atom.[8] An attachment of one more O atom should diminish the dependence between acidic properties of hydrotrioxides and the structure of R. Therefore, it can be proposed that the values of $\mathrm{p}K_\mathrm{a}$ for ROOOH with different structures are in the range 9—10.

It is known[7] that hydrotrioxides are capable of forming hydrogen bonds. The splitting of the signal in the ^{1}H NMR spectra of a number of hydrotrioxides[12—15] is attributable to their dimerization as well as to the presence of an intramolecular hydrogen bond:



(1)

The energy of homolysis of the ROOO—H bond increases due to formation of the hydrogen bond.

According to *ab initio* calculations,[7] dimerization of MeOOOH is thermodynamically more favorable by 8.6—15.1 kcal mol^{-1}, *i.e.*, formation of one O...H hydrogen bond is attended with a decrease in the total energy by 4—8 kcal mol^{-1}. Therefore, when hydrogen bonds occur in hydrotrioxides, the ROOO—H bond dissociation energy is 95—100 kcal mol^{-1}.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-05231).

References

1. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
2. S. L. Khursan, *React. Kinet. Catal. Lett.*, 1993, **51**, 95.
3. J. L. Holmes, F. P. Lossing, and P. M. Mayer, *J. Am. Chem. Soc.*, 1991, **103**, 9723.
4. E. T. Denisov and T. G. Denisova, *Kinet. Katal.*, 1993, **34**, 199 [*Kinet. Catal.*, 1993, **34** (Engl. Transl.)].
5. E. T. Denisov and T. G. Denisova, *Kinet. Katal.*, 1993, **34**, 986 [*Kinet. Catal.*, 1993, **34** (Engl. Transl.)].
6. A. N. Vereshchagin, *Induktivnyi effekt. Konstanty zamestitelei dlya korrelyatsionnogo analiza* [*Inductive Effect: Constants of Substituents for Correlation Analysis*], Nauka, Moscow, 1988 (in Russian).
7. J. Koller, M. Hodoscek, and B. Plesnicar, *J. Am. Chem. Soc.*, 1990, **112**, 2124.
8. V. L. Antonovskii and M. M. Buzlanova, *Analiticheskaya khimiya organicheskikh peroksidnykh soedinenii* [*Analytical Chemistry of Organic Peroxide Compounds*], Khimiya, Moscow, 1978 (in Russian).
9. G. Czapski and B. H. J. Bielski, *J. Phys. Chem.*, 1963, **67**, 2180.
10. *Spravochnik khimika* [*Chemist's Handbook*], Ed. B. P. Nikol'skii, Khimiya, Moscow—Leningrad, 1964 (in Russian).
11. V. V. Takhistov, *Organicheskaya mass-spektrometriya* [*Organic Mass Spectrometry*], Nauka, Leningrad, 1990 (in Russian).
12. F. E. Stary, D. E. Emge, and R. W. Murray, *J. Am. Chem. Soc.*, 1974, **96**, 5671.
13. N. Ya. Shafikov, R. A. Sadykov, V. V. Shereshovets, A. A. Panasenko, and V. D. Komissarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1923 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **40**, 1588 (Engl. Transl.)].
14. B. Plesnicar, F. Kovac, and M. Schara, *J. Am. Chem. Soc.*, 1988, **110**, 214.
15. V. V. Shereshovets, D. Sci. (Chem.) Thesis, Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences, Ufa, 1992 (in Russian).

Received June 8, 1995