

A DFT study on the decomposition of semiperacetals

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Abstract

The decomposition of symmetric semiperacetals obtained from aldehydes and hydrogen peroxide leading to carboxylic acids and dihydrogen is reinvestigated by means of DFT calculations.

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1. Introduction

Hydrogen peroxide is one of the most versatile oxidizing agents used in technical processes. This is due to the fact that chemists have learned to control and direct the reactivity of H₂O₂ by employing a whole variety of catalysts. In addition, the price of hydrogen peroxide has decreased during the years due to the implementation of new processes for H₂O₂ generation [1,2] and by building up larger and larger capacities all over the world.

In general, hydrogen peroxide shows four different types of reactivity:

- homolytic cleavage of the O–O bond resulting in the formation of highly reactive hydroxyl radicals,
- deprotonation giving the strongly nucleophilic hydroperoxide anion, which, e.g. can be employed in aliphatic substitution reactions,
- protonation of H₂O₂ generating an excellent leaving group (H₂O) and thus perform the hydroxonium cation (HO⁺), a potent electrophile and oxidizing agent; the activation of organo peroxides by η² coordination to Lewis acidic transition metal centres can be understood in a similar way [3,4],
- in contrast to the reactivities discussed above, disproportionation of the metastable H₂O₂, often catalyzed by redox active transition metal ions, is frequently found as an unproductive side reaction, which generates dioxygen following the equation H₂O₂(l) → H₂O(l) + 1/2O₂(g); ΔH° = –98.2 kJ mol^{–1}, ΔG° = –119.2 kJ mol^{–1} [5].

However, more than 100 years ago it was reported for the first time, that mixtures of hydrogen peroxide and certain aldehydes (esp. formaldehyde) evolve dihydrogen! From a safety point of view, this fact should really not be ignored at all, since dihydrogen gives highly explosive mixtures with air and even with hydrogen peroxide itself. Since the original publication of Blank and Finkenbeiner in 1898 [6] this puzzling type of reactivity of an oxidizing agent was reinvestigated and thus reported several times in the literature [7–11]. In 1923 Wieland and Wingler proposed that for this reaction, which is dominant in solutions wherein the concentration of H₂O₂ is (much) lower than the concentration of formaldehyde, the symmetric semiperacetal di(hydroxymethyl)peroxide HOCH₂–OO–CH₂OH (**1b**) should be the crucial intermediate (Scheme 1).

A few years later, Rieche, one of the pioneers in organo peroxide chemistry, could prove that alkyl substituted derivatives HOCRH–OO–CRHOH show an enhanced stability compared to **1b** [12–14]. From these investigations and from the work of Mosher and others in the mid-1960s it became obvious that hydrogen evolution requires at least one hydrogen atom at the carbonyl carbon atom and it was proposed that the reaction should follow a concerted pathway. A radical type mechanism was ruled out [15–19].

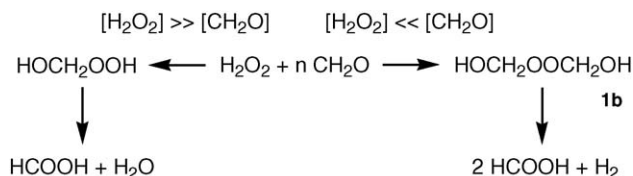
To finally clarify the mechanism of the hydrogen evolution, we have carried out DFT calculations, which will be discussed below.

2. Results and discussion

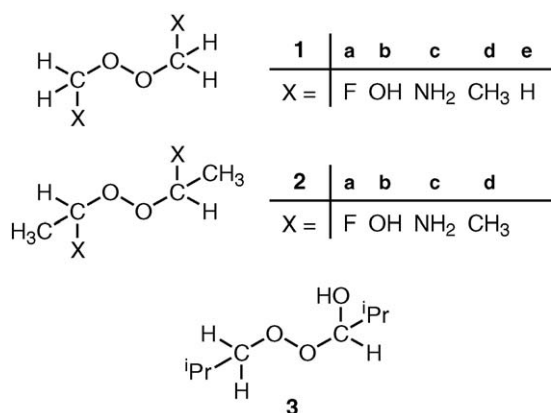
For a deeper insight into the electronic requirements of the H₂ formation from semiperacetals, the substituents at the central carbon atom were varied: we thus included the organo peroxides

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Scheme 1.



Scheme 2.

1a–e, **2a–d** and **3** (Scheme 2) into our calculations, although some of these molecules will never be synthesized at all. The unsymmetric derivative **3** was used by Mosher et al. in a series of investigations on the thermodynamic parameters of this reaction [16] and therefore can be considered to build a bridge between theory and experiment. Detailed information on the calculation method and the basis set can be found in Section 4.

Additionally to the enthalpies of reaction and activation of the H₂ evolution from the organo peroxides **1a–e**, **2a–d** and **3**, the competing homolytic cleavage (RXHC–O–O–CHXR → RXHCO•) was calculated for comparison. For all cases, a six membered transition state for the H₂ evolution could be found (Fig. 1).

As depicted in Fig. 1, the geometries of the transition states strongly depend on the substituents attached to the central carbon atoms of the peroxides: Strongly π donating substituents

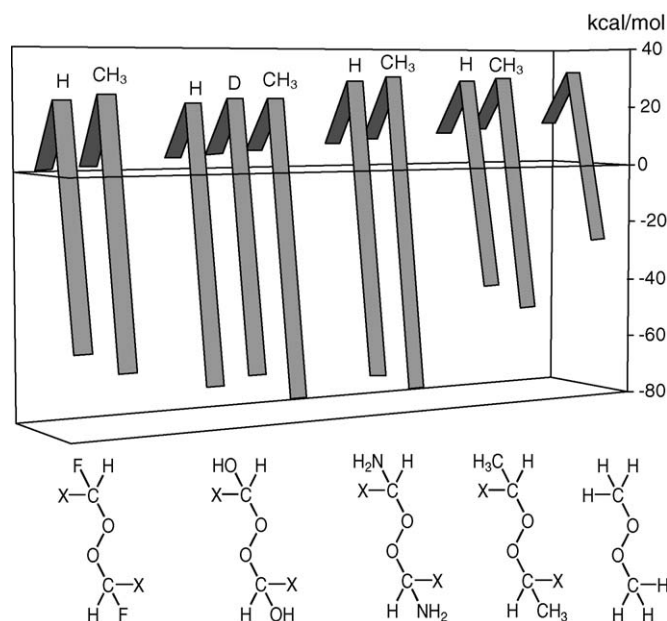


Fig. 2. Plot of the enthalpies of reaction and activation of the hydrogen evolution from semiperacetals following a concerted reaction via a six membered transition state (substituents X depicted in the graphic).

(e.g. NH₂) give rise to “early” transition states with long H–H distances, short O–O distances, and a higher degree of “pyramidalisation” (sum of angles: ∠(R₁CR₂) + ∠(OCR₁) + ∠(OCR₂)) of the ring carbon atoms. These transition states exhibit twisted or chair conformations. Substituents without π donation lead to planar “late” transition states.

The results of the calculations concerning the thermodynamics of these transformations are summarized in Table 1, the corresponding enthalpies (ΔH_R and ΔH[‡]) are plotted in Fig. 2.

In contrast to the decomposition via homolysis [20], the decomposition of the organo peroxides via evolution of hydrogen is obviously exothermic (see Table 1). To access the degree of competition between the two mechanisms of decomposition requires a detailed evaluation of the corresponding transition states. Qualitatively, our institution tells us that the looyse variational transition state of the homolysis still should be favoured

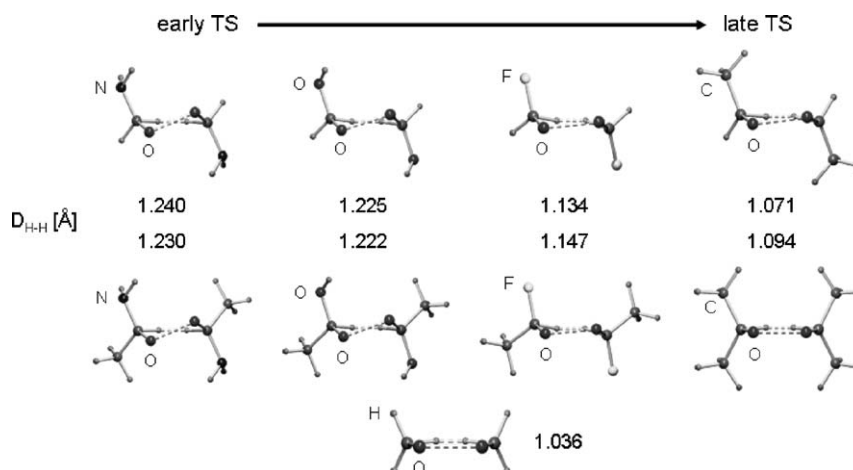


Fig. 1. Calculated transition states for the H₂ evolution from symmetric semiperacetals including the H–H distances.

Table 1
Calculated enthalpies and free energies^a for the decomposition reactions of the organo peroxides **1a–e**, **2a–d**, **3–H** and **3–D**

Comp.	Substituents at C	HR ₁ R ₂ COOCR ₁ R ₂ H → TS → H ₂ ^b + 2 R ₁ R ₂ C=O		HR ₁ R ₂ CO•
		Transition state ^c ΔH [‡] (ΔG [‡]) (kcal/mol)	Products ^d ΔH _R (ΔG _R) (kcal/mol)	
1a	H, H, F	23.35 (24.10)	−54.46 (−59.56)	19.85 (7.32), 4.30 × 10 ^{−6}
2a	H, CH ₃ , F	25.05 (25.92)	−60.97 (−82.07)	21.98 (9.31), 1.50 × 10 ^{−7}
1b–H	H, H, OH	21.94 (21.89)	−67.49 (−87.92)	22.88 (9.01), 2.48 × 10 ^{−7}
1b–D	D, D, OH	23.26 (23.22)	−64.83 (−86.12)	23.82 (9.81), 6.43 × 10 ^{−8}
2b	H, CH ₃ , OH	23.55 (23.88)	−73.53 (−95.80)	23.82 (10.13), 3.75 × 10 ^{−8}
1c	H, H, NH ₂	29.00 (29.77)	−68.18 (−88.57)	27.31 (14.69), 1.70 × 10 ^{−11}
2c	H, CH ₃ , NH ₂	30.54 (31.33)	−73.21 (−93.59)	29.17 (15.97), 1.96 × 10 ^{−12}
1d	H, H, CH ₃	28.83 (29.74)	−40.37 (−60.63)	24.98 (11.85), 2.09 × 10 ^{−9}
2d	H, CH ₃ , CH ₃	30.11 (30.29)	−48.65 (−68.09)	27.95 (15.57), 3.85 × 10 ^{−12}
1e	H, H, H	32.24 (33.14)	−26.23 (−45.56)	27.01 (15.15), 7.83 × 10 ^{−12}
3–H	H, H, iPr/H, OH, iPr	22.78 (22.56)	−57.97 (−80.48)	21.60 (7.61), 2.64 × 10 ^{−6}
3–D	D, D, iPr, D, OH, iPr	24.11 (23.87)	−55.41 (−78.76)	22.18 (8.07), 1.21 × 10 ^{−6}

^a Electronic and thermal enthalpies and free energies (in parentheses) at 298.150 K and 1.00000 atm.

^b H is replaced by D for compounds **1b–D** and **3–D**.

^c ΔH[‡] and ΔG[‡] for HR₁R₂COOCR₁R₂H → TS.

^d ΔH_R and ΔG_R for HR₁R₂COOCR₁R₂H → H₂ + 2R₁R₂C=O.

^e ΔH_R and ΔG_R for HR₁R₂COOCR₁R₂H → 2HR₁R₂C–O.

^f Equilibrium constant for the homolytic cleavage of the organoperoxides.

by entropy due to the constricted six membered ring structures of the transition states of the H₂ evolution mechanism. This becomes clear, when the free energies of the homolyses are compared with the free energies of activation of the hydrogen evolution, which differ by a factor of 2–3.

Although the homolytic dissociation is expected to be faster, it will not be an effective sink for the peroxide, since an important fraction of the HR₁R₂C–O• radicals will recombine rather than diffusing out of their solvent cage. Complete negligence of the diffusion (only in cage recombination) out of the solvent cage will result in the hypothetical equilibrium constants given in Table 1. However on comparing the calculated enthalpies of activation of the H₂ evolution with the endothermic reaction enthalpies of the homolysis, it becomes clear, that at least for the compounds **1b–H**, **1b–D**, and **2b**, H₂ evolution can compete with the homolysis (Fig. 3).

The substituent effects calculated for the H₂ evolution were correlated with different parameters of the Hammett series [21]: as shown in Fig. 4, the computational reaction enthalpies strongly depend on the π donation capability (stabilization of the product) of the substituents X and thus correlate excellently with the Hammett constants σ(*R*), a fact which is also reflected by the transition state geometries (see Fig. 1). However, the enthalpies of activation could be correlated roughly with the inductive constants σ(*I*), implying a stabilisation of the transition state by electron withdrawing groups, which is proved additionally by the fact that additional methyl group (in the series **2a–d**) slightly destabilise the transition states.

Since C–H bond cleavage and H–H bond formation simultaneously take place during the H₂ evolution, the kinetic isotope effect of this transformation was already investigated by Durham and Mosher [17] with compound **3** (see Scheme 2). Computational investigations on **3** showed a transition state which exhibits the substituent depending features discussed above: the

OH substituted site exhibits a geometry typical for an early TS, the C substituted site is observed in a late TS geometry (Fig. 5).

From the differences in the free energies of activation of **3–H** and its perdeuterated congener **3–D** a kinetic isotope effect of 9.13 was calculated based on an Arrhenius type model, which is about a factor of 2.5–3.0 times higher than the data published in the literature [17]. This is in agreement with the results of the calculation on **1b–H** and **1b–D** (IE_{kin}: 9.39). At the moment, we can only speculate about the reasons for

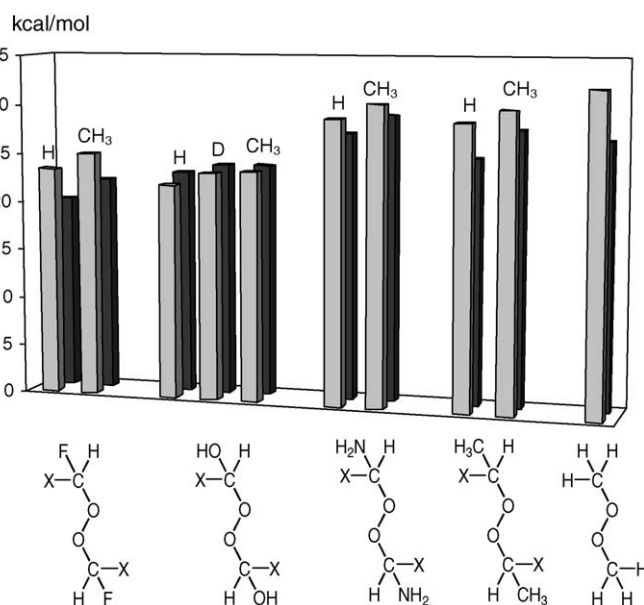


Fig. 3. Comparison of the calculated enthalpies of activation of H₂ evolution (front row, light grey) and the reaction enthalpies of O–O bond homolysis (rear row, dark grey) of the semiperacetals (substituents X depicted in the graphic).

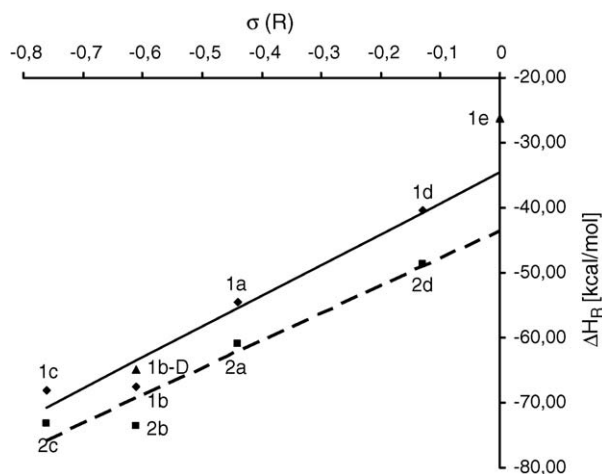


Fig. 4. Correlation of the reaction enthalpies with the Hammett factors $\sigma(R)$; (\blacklozenge) and (—) **1a–d** (Pearson coef.: 0.9776), (\blacksquare) and (---) Pearson coef.: 0.9700.

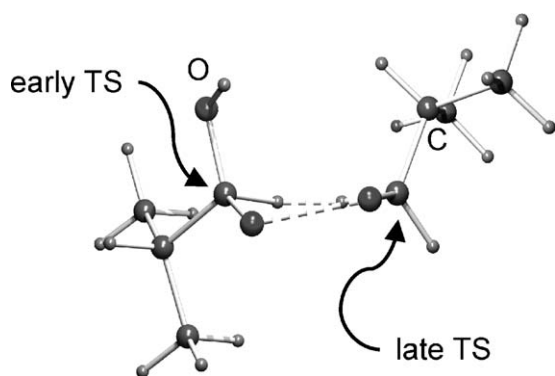


Fig. 5. Calculated transition state for the H_2 evolution from **3**.

these findings: our model for the calculation of the isotope effects employs the same preexponential factors for the protonated and the deuterated species, which is only an approximation. Additionally, solvent effects have not been included in the calculations and experimental temperature was about 100 K higher than the temperature set for the calculations. We exclude some intrinsic problems of the quantum chemical method applied since the calculated enthalpies of activation are in excellent agreement with experimental data from the literature (1-hydroxyisobutyl-1-isobutyl-1,1-peroxide (**3-H**): $\Delta H^\ddagger(\text{exp.}) = 20.8$ kcal/mol, $\Delta H^\ddagger(\text{calcd.}) = 22.78$ kcal/mol) [17].

3. Conclusion

With the DFT calculations presented in this paper it could be shown, that semiperacetals bearing at least one proton on each α -carbon atom can decompose via a cyclic six membered transition state resulting in dihydrogen evolution. This has to be taken into account in terms of safety considerations when working with hydrogen peroxide in the presence of aldehydes because it may give rise to the formation of explosive mixtures of hydrogen/hydrogen peroxide or hydrogen/oxygen.

4. Experimental section

All quantum chemical calculations were performed with the program Gaussian98W [22] using the B3LYP gradient corrected exchange-correlation functional [23,24] in combination with the 6-311 + G** basis set [25–27]. Full geometry optimizations were carried out in C_1 symmetry using analytical gradient techniques and the resulting structures were confirmed to be true minima by diagonalization of the analytical Hessian Matrix. Only the heterochiral diastereomers of **2a–c** were calculated.

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