Hydrogen Evolution from Peroxides − a Concerted Reaction

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DFT calculations provide strong evidence that the evolution of hydrogen from mixtures of aldehydes and hydrogen peroxide proceeds by a concerted mechanism. The electronic influence of a series of substituents is correlated with the enthalpies of activation and reaction, and the calculated isotope effect of the reaction is compared with experimentally obtained data.

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Introduction

Discovered in 1818 by Thénard,[1] hydrogen peroxide has had an astonishing career. For about 80 years, it remained something of an unstable curiosity in academic laboratories. This changed at the beginning of the 20th century, when a new process, the anodic oxidation of sulfuric acid, was established, making more highly concentrated hydrogen peroxide solutions with increased purity and stability accessible.[2] Nowadays hydrogen peroxide is mainly synthesised by the anthraquinone process,[3] which allows the production of ultrapure and highly concentrated solutions of this versatile oxidising agent. This stimulated investigations in the chemistry of inorganic and organic peroxides and their reactivities and resulted in a multitude of new applications of "active oxygen" compounds.[4,5]

Disproportionation is a typical reaction for metastable compounds in intermediate oxidation states. In the case of hydrogen peroxide, water and dioxygen are formed [$H_2O_2(l) \rightarrow H_2O(l) + {}^1/_2\, O_2(g)$; $\Delta H^\circ = -98.2\ \mathrm{kJ{\cdot}mol^{-1}}$, $\Delta G^\circ = -119.2\ \mathrm{kJ{\cdot}mol^{-1}}$],[6] in a reaction that is slow at room temperature but strongly accelerated by catalytically active compounds such as MnO_2 or certain enzymes (catalases). The generation of explosive mixtures of dioxygen and volatile organics therefore has to be included in safety considerations when working with hydrogen peroxide. On the other side, organic peroxides, widely used as initiators in radical polymerisations, are known to decompose by homolytic O−O bond cleavage at elevated temperatures.

However, there is still another critical reaction relating to the use of hydrogen peroxide and organic peroxides: mixtures with aldehydes (especially formaldehyde) can release dihydrogen! This has been known for about a hundred years and has been reported several times, but the fact that a reagent considered to be of strongly oxidising nature can evolve a reducing molecule such as dihydrogen is still puzzling. In this paper a quantum chemical study on this phenomenon is reported. First, though, a short overview on antecedent investigations is given.

In 1898 Blank and Finkenbeiner treated formaldehyde with hydrogen peroxide in the presence of a base and for the first time observed the evolution of dihydrogen from such mixtures.[7] A few years later, it was shown that working at acidic or neutral pH gives the same results.[8,9] From mechanistic investigations, Wieland and Wingler postulated bis(hydroxymethyl) peroxide $HOCH_2{-}OO{-}CH_2OH$ (**1b**) as the reactive intermediate.[10] This work was further improved upon by Fry and Payne, who found that the evolution of hydrogen is concentration-dependent (Scheme 1), with the symmetric semi-peracetal **1b** being formed at low concentrations of hydrogen peroxide and the asymmetric semi-peracetal $HOCH_2{-}OOH$ at high concentrations.[11,12]

for $[H_2O_2] \ll [CH_2O]$:

$$H_2O_2 + 2\,CH_2O \longrightarrow HOCH_2OOCH_2OH \quad \textbf{(1b)}$$
$$HOCH_2OOCH_2OH \longrightarrow 2\,HCOOH + H_2$$

for $[H_2O_2] \gg [CH_2O]$:

$$H_2O_2 + CH_2O \longrightarrow HOCH_2OOH$$
$$HOCH_2OOH \longrightarrow HCOOH + H_2O$$

Scheme 1

At the same time, Rieche synthesised some higher symmetric semi-peracetals $HOCRH{-}OO{-}CRHOH$, which turned out to be more stable than the mother compound **1b**.[13−15] Later it was proposed that **1b** decomposes to dihydrogen and formic acid in a concerted reaction, a radical

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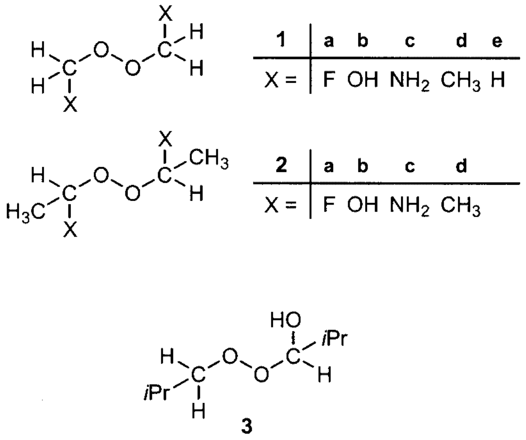
type pathway being ruled out.[16−19] These findings were expanded by Ingold, who verified the evolution of hydrogen during the decomposition of a whole series of organic peroxides with α CH units.[20]

Results and Discussion

With this in mind, a quantum chemical investigation of the evolution of dihydrogen from the organic peroxides **1a−e**, **2a−d** and **3**, as shown in Scheme 2, was started (for details see Exp. Section).



1	a	b	c	d	e
X =	F	OH	NH_2	CH_3	H

2	a	b	c	d
X =	F	OH	NH_2	CH_3

Scheme 2

Although some of these compounds are far from being synthesised in reality, they were calculated in order to provide an impression on the influence of certain substituents on the energetics of the decomposition. The results are presented in Table 1.

Obviously, the decomposition of the organoperoxides by evolution of hydrogen is an exothermic reaction, unlike the decomposition through homolysis. The energies of activation of the homolysis reactions could not be determined, since the corresponding transition states could not be found in the calculations. This is consistent with computational results obtained by Bach et al., who investigated the homolysis of a series of organoperoxides at a high level of theory.[21] However, these values can be estimated as at most a few kcal/mol higher than the corresponding reaction enthalpies, which are in some cases slightly lower and in other cases slightly higher than the enthalpies of activation of the hydrogen evolution reactions. This gives a hint that hydrogen evolution from organoperoxides bearing at least one hydrogen atom at each α-carbon atom is not just thermodynamically but also kinetically achievable. For a real competition between hydrogen evolution and homolytic cleavage, the structures of the transition states have to be evaluated. Although the transition state structures for the homolysis could not be found, chemical intuition tells us that they should be entropically favoured over the geometrically constricted six-membered ring structures of transition states of the decomposition reactions. This becomes clear if the free energies of the homolyses are compared with the free energies of activation from the hydrogen evolution, which differ by a factor of 2−3. On the other hand, the dominant reaction of two radicals $HR^1R^2C-O\cdot$ in a solvent cage will be the back reaction to the organoperoxides $HR^1R^2C-O-O-CR^2R^1H$ (equilibrium constants given in Table 1).

The enthalpies of activation for the hydrogen evolution correlate roughly with the inductive constants σ(I) of the Hammett equation,[22] implying stabilisation of the transition state by electron-withdrawing groups. A slight destabilisation by the presence of an additional methyl group

Table 1. Calculated enthalpies and free energies (electronic and thermal enthalpies and free energies, the latter in parentheses, at 298.150 K and 1.00000 atm) for the decomposition reactions of the organoperoxides **1a−1e**, **2a−2d**, **3-H** and **3-D**

		$HR^1R^2COOCR^1R^2H \rightarrow TS \rightarrow H_2$ [a] $+$ **2** $R^1R^2C{=}O$		$HR^1R^2CO\cdot$
	Substituents at C	Transition state[b] $\Delta H^\ddagger$ ($\Delta G^\ddagger$) [kcal/mol]	Products[c] ΔH_R (ΔG_R) [kcal/mol]	Homolysis[d] ΔH_R (ΔG_R)[kcal/mol], in italics: $K \times 10^3$ [e]
1a	H, H, F	23.35 (24.10)	−54.46 (−59.56)	19.85 (7.32) *52.2*
2a	H, CH_3, F	25.05 (25.92)	−60.97 (−82.07)	21.98 (9.31) *23.4*
1b-H	H, H, OH	21.94 (21.89)	−67.49 (−87.92)	22.88 (9.01) *26.4*
1b-D	D, D, OH	23.26 (23.22)	−64.83 (−86.12)	23.82 (9.81) *19.1*
2b	H, CH_3, OH	23.55 (23.88)	−73.53 (−95.80)	23.82 (10.13) *16.8*
1c	H, H, NH_2	29.00 (29.77)	−68.18 (−88.57)	27.31 (14.69) *2.7*
2c	H, CH_3, NH_2	30.54 (31.33)	−73.21 (−93.59)	29.17 (15.97) *1.6*
1d	H, H, CH_3	28.83 (29.74)	−40.37 (−60.63)	24.98 (11.85) *8.4*
2d	H, CH_3, CH_3	30.11 (30.29)	−48.65 (−68.09)	27.95 (15.57) *1.9*
1e	H, H, H	32.24 (33.14)	−26.23 (−45.56)	27.01 (15.15) *2.2*
3-H	H, H, *i*Pr/H, OH, *i*Pr	22.78 (22.56)	−57.97 (−80.48)	21.60 (7.61) *46.4*
3-D	D, D, *i*Pr D, OH, *i*Pr	24.11 (23.87)	−55.41 (−78.76)	22.18 (8.07) *38.6*

[a] H is replaced by D for compounds **1b-D** and **3-D**. [b] $\Delta H^\ddagger$ and $\Delta G^\ddagger$ for $HR^1R^2COOCR^1R^2H \rightarrow TS$. [c] ΔH_R and ΔG_R for $HR^1R^2COOCR^1R^2H \rightarrow H_2 + 2\ R^1R^2C{=}O$. [d] ΔH_R and ΔG_R for $HR^1R^2COOCR^1R^2H \rightarrow 2\ HR^1R^2C-O\cdot$. [e] Equilibrium constant for the homolytic cleavage of the organoperoxides.

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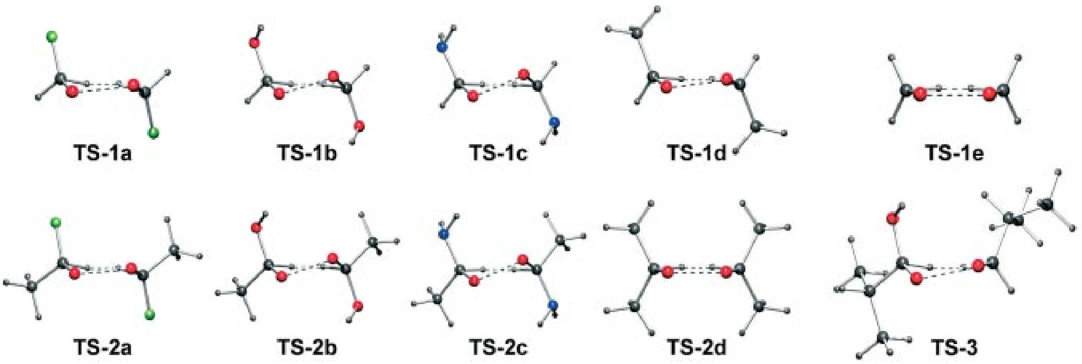


Figure 1. Calculated transition state structures for the decomposition reactions of organoperoxides **1a**−**1e**, **2a**−**2d**, and **3**

Table 2. Parameters of transition state geometries for the decomposition reactions of organoperoxides **1a**−**1e**, **2a**−**2d**, and **3**

Compound	Subst. at C	*d*(H−H) (Å)	*d*(O−O) (Å)	*d*(C−O) (Å)[a]	Σ∠ at C (°)[a] [b]	Imag. freq. [cm^{-1}]
1a	H, H, F	1.134	1.989	1.254	343.58	−1023.80
2a	H, CH_3, F	1.147	1.991	1.259	342.76	−736.98
1b-H	H, H, OH	1.225	1.959	1.288	341.98	−845.09
1b-D	D, D, OH	1.225	1.959	1.288	341.98	−690.46
2b	H, CH_3, OH	1.222	1.970	1.293	341.75	−599.25
1c	H, H, NH_2	1.240	1.949	1.301	340.49	−833.83
2c	H, CH_3, NH_2	1.230	1.956	1.306	340.52	−629.98
1d	H, H, CH_3	1.071	1.987	1.291	348.12	−1043.69
2d	H, CH_3, CH_3	1.094	1.973	1.303	346.22	−769.10
1e	H, H, H	1.036	2.003	1.283	349.91	−1090.08
3	H, H, *i*Pr	1.127	1.991	1.305	346.23	−853.72
	H, OH, *i*Pr			1.283	344.48	−733.31

[a] Mean value (not for **3**). [b] Sum of angles: R^1CR^2 + OCR^1 + OCR^2

(in the series **2a**−**2d**) can be interpreted by similar electronic considerations. On the other hand, the reaction enthalpies correlate excellently with the Hammett constants σ(R), which can easily be understood as stabilisation of the product through π donation by the substituents. This corroborates the transition state geometries (Figure 1, Table 2).

Strongly π-donating substituents (e.g. NH_2) give rise to "early" transition states with long H−H distances, short O−O distances and higher degrees of "pyramidalisation" [sum of angles: $\angle(R^1CR^2) + \angle(OCR^1) + \angle(OCR^2)$] of the ring carbon atoms. These transition states exhibit twisted or chair conformations. Substituents without π donation

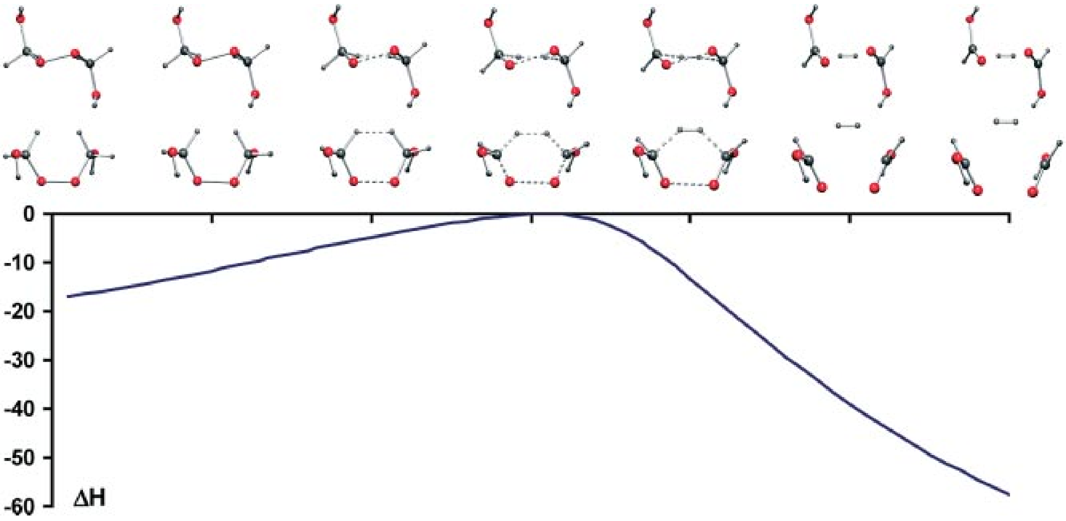
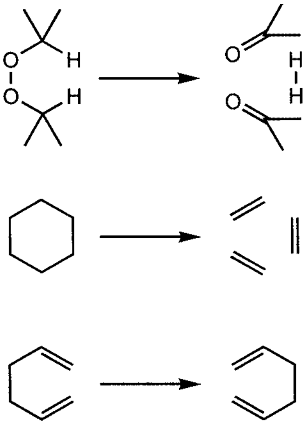


Figure 2. Structures and enthalpies obtained by an IRC calculation starting with the transition state structure of compound **1b** (data relative to the enthalpy of activation)

lead to planar "late transition states". Following the internal reaction coordinate (IRC, calculated for compound **1b**) clearly establishes the concerted nature of the reaction. Figure 2 shows the simultaneous bond-cleavage and -formation during the reaction.

From a mechanistic point of view and from the conformations of the transition states, these reactions are related to retro [2+2+2] cycloadditions or to [3+3] sigmatropic rearrangements.[23−25] As depicted in Scheme 3, the net changes in bond orders are similar in both cases.



Scheme 3

Since C−H bond cleavage and H−H bond formation take place during the transformation, quite a large kinetic isotope effect should be expected. Therefore, in addition to compound **1b**, its perdeuterated congener **1b-D** was also included in the calculations (see Table 1). A kinetic isotope effect of 9.39 can be calculated from the differences in the free energies of activation, and this is about a factor of 2.5−3 times higher than the data published in the literature,[17] where a kinetic isotope effect of 3−4 was determined experimentally for the unsymmetrical peroxide **3**. An analogous calculation of the isotope effect of the hydrogen evolution from **3** resulted in a value of 9.13, which excellently corroborates the isotope effect calculated first. A precise interpretation of the differences between experimentally determined and calculated isotope effects is hard to give at the moment. Solvent effects have not been included in the calculations, and the experimental temperature was about 100 K higher than the temperature set for the calculations. Some intrinsic problems of the quantum chemical method applied could also play a role. However, the calculated enthalpies of activation are in excellent agreement with experimentally determined data from the literature [1-hydroxyisobutyl-1-isobutyl 1,1-peroxide (**3-H**: $\Delta H^{\ddagger}$(exp.) = 20.8 kcal/mol, $\Delta H^{\ddagger}$(calcd.) = 22.78 kcal/mol].[17]

Conclusion

It has been demonstrated by DFT calculations that the evolution of dihydrogen from organoperoxides bearing at least one proton on each α-carbon atom is a concerted reaction proceeding through cyclic six-membered transition states. This not generally known reaction may in some cases even be energetically favoured over the homolytic cleavage of the O−O bond. It especially 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.

Experimental Section

All quantum chemical calculations were performed with the program Gaussian98W,[26] with use of the B3LYP gradient corrected exchange-correlation functional[27,28] in combination with the 6−311+G** basis set.[29−31] Full geometry optimizations were carried out in C_1 symmetry by use of 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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