Hydrogen Bonding in Hydroxy-Alkylperoxy and Hydroxy-Alkoxy Radicals: A Theoretical *ab initio* Study

A contribution to subproject CMD

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Introduction

β-hydroxy-alkylperoxy and β-hydroxy-alkoxy radicals are key intermediates in the OH-initiated tropospheric oxidation of (poly-)alkenes, the simplest representative of which is ethene :

$$C_2H_4 + \dot{O}H \xrightarrow{O_2} HOCH_2CH_2O\dot{O} \qquad (1)$$

$$HOCH_2CH_2O\dot{O} + NO \longrightarrow HOCH_2CH_2\dot{O}^* + NO_2 \qquad (2)$$

$$HOCH_2CH_2\dot{O} \xrightarrow{\text{prompt/thermal}} \dot{C}H_2OH + CH_2O \qquad (3)$$

$$HOCH_2CH_2\dot{O} + O_2 \longrightarrow HOCH_2CHO + H\dot{O}_2 \qquad (4)$$

After the attack of OH and the subsequent addition of O_2, the resulting peroxy radical can combine with NO, quickly dissociating to NO_2 and an ethoxy radical. This $HOCH_2CH_2O$ radical is vibrationally hot, and will either decompose promptly, or lose the excess energy in collisions with the bath gas. The relaxed ethoxy radicals then either decompose thermally or react with oxygen molecules (Orlando *et al.*, submitted ; Barnes *et al.*, 1993).

Some of the rotamers of the peroxy and oxy radicals in this mechanism can be stabilised by an intramolecular hydrogen bond between the hydrogen of the hydroxy group and an oxygen of the (per)oxy radicalar site.

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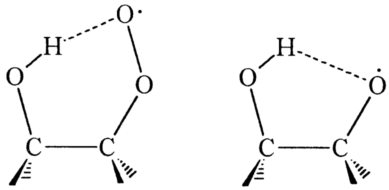


The aims of this work were to identify and characterise the intramolecular H bonding using *ab initio* methods, and to evaluate some of its effects on the peroxy and oxy reaction kinetics.

Ab initio characterisation of the radicals

The geometries, vibrational frequenties and relative energies (inc. ZPE) for all β-hydroxy-ethylperoxy and β-hydroxy-ethoxy radical equilibrium structures, and for the saddle points for decomposition of the oxy radical to $HOCH_2$ + CH_2O, were obtained using B3LYP-DFT quantum chemical methods (Becke's 3-parameter nonlocal-exchange functional with the nonlocal correlation functional of Lee, Yang, and Parr). Single point Coupled Cluster CCSD(T) calculations were then performed on the B3LYP-DFT geometries. The very small difference found between the DFT and CC relative energies (average : ± 0.2 kcal/mol) confirms that B3LYP-DFT reliably describes the rotamerism.

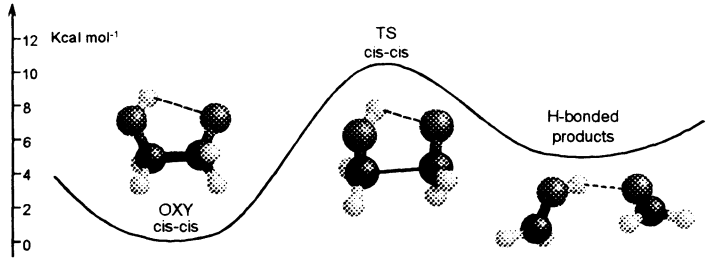
The $HOCH_2CH_2OO$ peroxy radical was found to have thirteen structurally and energetically different rotamers, all but one with two enantiomers. Most of the rotamers have the hydroxyl HO- function in "*trans*" with respect to the peroxy OO function. Two rotamers, with the hydroxy-H directed towards the peroxy function, are stabilised by an intramolecular H-bond, lowering their relative energy by 2.7 kcal/mol on average. At 290 K, these two stabilised structures should account for 95 % of the equilibrium population.

Five rotamers were identified for the $HOCH_2CH_2O$ ethoxy radical, most with two enantiomers. Of these, one rotamer has the HO- function in "*cis-cis*" geometry with respect to the -O radical function, allowing for an intramolecular H-bond. The ZPE-corrected relative energy for this structure is on average 2.5 kcal/mol lower than the other structures. This stabilisation is comparable to that for the H-bonded peroxy radicals. Again, the equilibrium population for the ethoxy radicals at 290K consists mainly (95 %) of hydrogen-bonded rotamers.

Decomposition kinetics of the hydroxy-alkoxy radicals

Under atmospheric conditions (1 atm., 298 K), 80 % of the oxy radicals formed in reaction 2 decompose to CH_2OH + CH_2O. The experimental energy barrier for this dissociation is only $E_b \approx 10\text{-}11$ kcal/mol (Orlando *et al.*, submitted). Given that the hydroxy-ethoxy radical is stabilised by hydrogen bonding, this barrier is surprisingly low.

Three structurally and energetically different transition states were characterised for the decomposition of the hydroxy-ethoxy radical to CH_2OH + CH_2O, using B3LYP-DFT. One of the transition states (*cis-cis* TS) has the intramolecular hydrogen bond still intact. This H-bond is possible - despite the lengthening of the C-C bond - thanks to the two CH_2O moieties being almost planar in the TS. As a result, this *cis-cis* TS is located only 10 kcal/mol (B3LYP-DFT energy) above the H-bond-stabilised *cis-cis* ethoxy radical. The two transition states without an internal hydrogen bond have relative energies 1.9 and 3.3 kcal/mol above the *cis-cis* TS. These higher lying transition states are hardly accessible in the thermal dissociation, and are of limited importance even in the prompt decomposition of the energised ethoxy radicals, as discussed below. As such, the H-bond stabilised transition state is of key importance in the competition between dissociation of the ethoxy radical and its reaction with O_2.



B3LYP-DFT relative energies (+ ZPE) for the dissociation of H-bonded hydroxy-ethoxy radicals

Prompt dissociation of hot $HOCH_2CH_2O^*$ *radicals*

The energetics of the RO_2 + NO reaction (2) is not influenced by the hydrogen bonding. Adopting a ΔE_{react} of −11 kcal/mol, the same as for the $C_2H_5O_2$ case, the (RRKM) lifetime of the intermediate $HOCH_2CH_2OONO^*$ is 5×10^{-12} sec., which ensures ergodicity. Hence, the nascent vibrational energy distribution $P(E_{\text{vibr}})$ for the $HOCH_2CH_2O^*$ radicals formed in reaction 2 can be calculated

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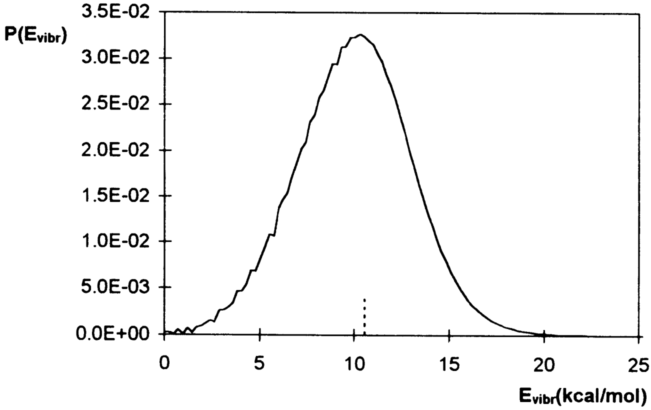
using Seperate Statistical Ensemble Theory (Wittig *et al.*, 1985), where the vibrational states of all ethoxy-radical rotamers are considered. As shown in the figure below, a large fraction of the ethoxy radicals is formed with $E_{vibr} > E_b$. By Master Equation analysis (Vereecken *et al.*, 1997), taking the lowest TS at 10.5 kcal/mol (the experimental E_b) above the *cis-cis* ethoxy radical, we predict that 30 % of the oxy radicals dissociate promptly at 298 K and 1 atm. Recent experiments performed at NCAR (Orlando *et al.*, submitted) found 25 % prompt dissociation. The theoretically expected prompt dissociation using only non-H-bond-stabilised transition states is 10 %.



Nascent vibrational energy distribution of oxy radicals formed in reaction (2)

Thermal dissociation of $HOCH_2CH_2O$ *radicals*

Using the B3LYP vibrational and geometric data, the TST high-pressure pre-exponential factor A_{inf} for dissociation through the *cis-cis* transition state at 298 K is 1.1×10^{13} s^{-1}. The high pressure rate constant, assuming the B3LYP-DFT barrier of E_b = 10 kcal/mol, is then $_{kinf} = 5\times10^5$ s^{-1}. Based on Troe's low-pressure theory and fall-off formalism (Troe, 1977, 1979), we find that the rate constant is a factor of 2.5 below the high-pressure limit at 1 atm., resulting in a thermal decomposition rate constant of $k_{therm} = 2\times10^5$ s^{-1}, in agreement with the experimental value obtained at NCAR : $k_{exp} \approx 1.3\times10^5$ s^{-1} (Orlando *et al.*, submitted). A transition state without H-bonding would be approximately 2 kcal/mol higher in energy, resulting in a thermal dissociation 15 times slower. It would then be outrun by the reaction with O_2, resulting in a significantly lower yield of $CH_2OH + CH_2O$. At 298 K, approximately 93 % of the calculated thermal dissociation flux is through the H-bonded *cis-cis* TS.

Conclusions

Intramolecular hydrogen bonds in β-hydroxy-alkylperoxy- and β-hydroxy-alkoxy radicals have been characterised for the first time. B3LYP-DFT relative energies were confirmed by single-point CCSD(T) calculations. The stabilisation energies are of the order of 2.5 kcal/mol, which are typical values for such hydrogen bonds.

In atmospheric conditions, both types of radicals are present dominantly as the H-bonded rotamers. In some laboratory experiments, other rotamers may dominate. The persistence of the hydrogen bond during the $HOCH_2$–CH_2O dissociation entails a low energy barrier and a high reaction rate. Hydrogen bonds can also occur in peroxy and oxy radicals from (biogenic) alk(adi)enes, such as isoprene, and play an important role in their dissociation rates.

Acknowledgements

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