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**THEORETICAL STUDY OF THE REACTIVITY OF HYDROCARBON  
AND OXYGENATED ALKOXY RADICALS: COMPARISON OF THE  
ISOMERIZATION AND THE  $\beta$ -C—H BOND DISSOCIATION  
PATHWAYS**

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**Abstract**

We show the presence of an ether group in alkoxy radicals significantly lowers the activation energy of the  $\beta$ -C-H dissociation and only slightly increases the isomerization barrier. Moreover, a 1-6 isomerization mechanism involving a 7-membered transition state may compete with the usual 1-5 isomerization.

*Keywords:* Alkoxy, isomerization,  $\beta$ -C-H dissociation, *ab initio*

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**INTRODUCTION**

The alkoxy radicals are important intermediate species during the oxidation of VOC (Volatile Organic Compounds) in atmospheric chemistry [1]. The most common reactions [1,2] of alkoxy radicals are reaction with O<sub>2</sub> (if an  $\alpha$ -H is present), isomerization *via* 1,5 H-shift through a 6-membered transition state (TS) and decomposition by  $\beta$ -C-C or C-O (if an ether oxygen atom is present). Because of the increasing use as industrial solvents and fuel additives of oxygenated

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compounds such as ethers, their tropospheric oxidation has received significant attention. Dimethyl ether (DME)  $\text{CH}_3\text{OCH}_3$ , and dimethoxymethane (DMM)  $\text{CH}_3\text{OCH}_2\text{OCH}_3$ , have been proposed as possible alternative diesel fuels. Atmospheric degradation of these compounds produces the corresponding oxygenated alkoxy radicals:  $\text{CH}_3\text{OCH}_2\text{O}^\bullet$  and  $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^\bullet$ . We have recently shown that the presence of an ether oxygen atom in alkoxy radicals appears to lower the  $\beta$ -C-H dissociation activation energy making this channel competitive with the other loss processes [3].

Numerous studies have been devoted to the reactivity of the hydrocarbon alkoxy radicals (see references [1,2,4-11] for example) compared to few studies concerning the oxygenated alkoxy radicals [3,12-17]. Our previous calculations [3] on some oxygenated alkoxy radicals have revealed that, in addition to the  $\beta$ -C-H bond scission and the reaction with  $\text{O}_2$ , a possible competing loss process for  $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^\bullet$  radical is the 1,6 isomerization through a seven-membered transition state. This is a very unusual case, since typically only the 1,5 isomerization is habitually considered, which however does not exist for this oxygenated radical.

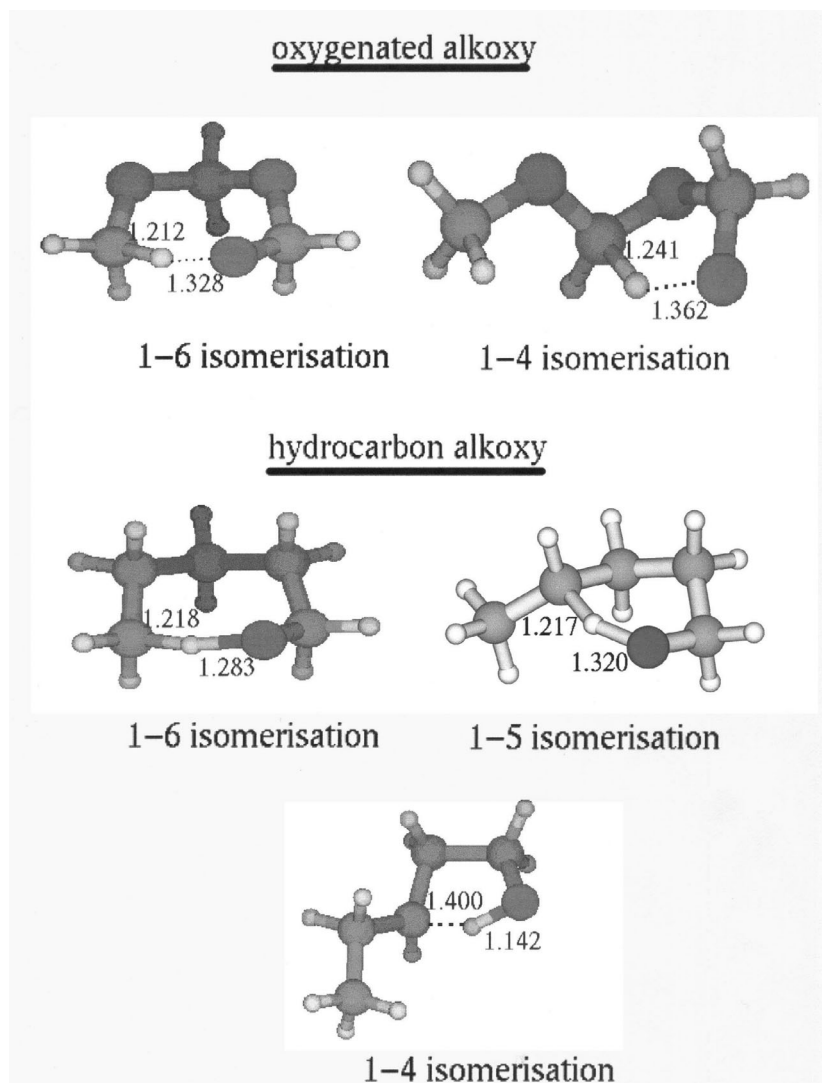
From these results, it was interesting to compare the isomerization processes and the  $\beta$ -C-H bond scission for two types of alkoxy radicals: those issued from the ethers degradation ( $\text{HOCH}_2\text{O}$ ,  $\text{CH}_3\text{OCH}_2\text{O}$  and  $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}$ ) and those issued from the analogous hydrocarbon compounds degradation ( $\text{CH}_3\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$  and  $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{O}$ ).

### Computational details

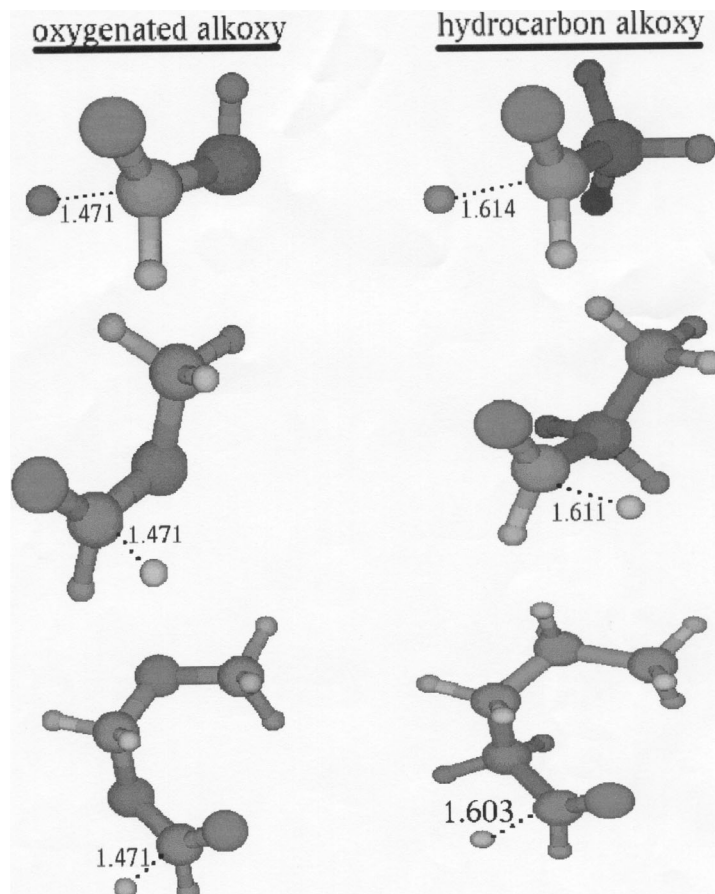
*Ab initio* computations were carried out using the Gaussian98 software package [18]. All optimized geometries and associated harmonic vibrational frequencies (and ZPE corrections) were obtained at two levels of theory: HF-DFT(B3LYP)/6-31G\*\* and UMP2(Frozen Core)/cc-pVDZ. Energy calculations were performed at two levels of theory: HF-DFT(B3LYP)/6-31G\*\* and CCSD(T)/cc-pVDZ//MP2/cc-pVDZ. The TS have been characterized by one imaginary frequency (first order saddle points on the potential energy surface (PES)). Intrinsic reaction coordinate analyses (IRC) were performed at both HF-DFT(B3LYP) and UMP2 levels of theory in order to confirm that a specific transition state connects the designated local minima.

### RESULTS AND DISCUSSION

The optimized transition state structures for the isomerization processes and the  $\beta$ -C-H bond scissions are presented in Fig. 1 and Fig. 2, respectively.



**Fig. 1.** Transition state optimized geometries obtained at the MP2/cc-pVDZ level of theory for isomerization processes of  $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{O}$  and  $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}^\bullet$  (distances in Angström)



**Fig. 2.** Transition state optimized geometries obtained at the MP2/cc-pVDZ level of theory for  $\beta$ -C-H bond dissociations (distances in Angström)

Generally speaking, we can note that the presence of the ether functional group in alkoxy radicals leads to more reactant-like transition states. Actually, in the isomerization TS structures the forming O-H bond length is longer for the oxygenated alkoxy. Similarly, for the  $\beta$ -C-H bond dissociation, the breaking C-H bond length is shorter for the TS containing an ether oxygen atom. The larger exothermicity for the processes involving the oxygenated radicals, predicted at the CCSD(T)/MP2 level of theory, can explain this geometrical result (see the enthalpies of reaction  $\Delta_r H(0\text{ K})$  reported in Tables 1 and 2). This corroborates the well known Hammond postulate that assumes the more exothermic the reaction the more closely will its transition structure resemble the reactants.

It can be noticed that the DFT method produces  $\beta$ -C-H bond dissociation enthalpies with a large deviation of 31-51 kJ/mol when compared with the CCSD(T) values. This behaviour is also observed for  $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$  at the G2 and B3P86/6-31G\*\* levels (52.4 and 89.7 kJ/mol respectively). Generally, the CCSD(T) predictions are definitely more accurate, but the discrepancy in these values is unusually large. Indeed, it has been recently found [19] that B3LYP, CCSD(T) and experimental values for the C-H dissociation energy of nine hydrocarbon molecules are relatively close with a maximum deviation of 5 kcal/mol, in contrast with our results for radicals dissociation.

In addition, Table 1 shows the activation parameters ( $\Delta H^\ddagger(0\text{K})$ ,  $\Delta G^\ddagger(298\text{K})$ ) for the various isomerization pathways. As expected for the hydrocarbon alkoxy  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  the smallest activation enthalpy corresponds to the isomerization which involves the six-membered TS (1-5 isomerization). But, our calculations show surprisingly that the 1-6 isomerization involving a seven-membered TS (never considered in usual kinetic models) could be a competitive way (activation enthalpy and free energy higher by about 8 kJ/mol only). Concerning the corresponding oxygenated alkoxy,  $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}$ , the 1-6 H-shift is clearly more favoured than the 1-4 H-shift.

**Table 1**

Enthalpy of reaction, activation enthalpy and free energies (kJ/mol) for various isomerization processes computed at the CCSD(T)/cc-pVDZ//MP2(Frozen Core)/cc-pVDZ level (results in brackets are the HF-DFT(B3LYP)/6-31G\*\* values)

	Isomerization	$\Delta_r H(0\text{K})$	$\Delta H^\ddagger(0\text{K})$	$\Delta G^\ddagger(298\text{K})$
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{O}$	1-6	-7.1 (0.8)	36.8 (25.9)	38.5 (31.4)
	1-5	-24.7 (-22.2)	28.4 (16.3)	31.4 (20.1)
	1-4	-22.6 (-20.1)	70.6 (59.8)	71.9 (61.9)
$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}$	1-6	-20.1 (-10.9)	44.7 (32.6)	50.6 (38.9)
	1-4	-26.3 (-15.9)	86.1 (69.0)	88.2 (69.8)

The presence of an ether oxygen atom in the alkoxy radical increases the isomerization barrier height by a few kJ/mol (*e.g.* from 36.8 to 44.7 kJ/mol for the 1-6 H-shift). In contrast, for the  $\beta$ -C-H bond scission (see Table 2), the activation barrier is lowered by about 20-40 kJ/mol when the alkoxy radical contains an ether functional group. It is interesting to note that the computed activation enthalpy set for the  $\beta$ -C-H dissociation tends to follow the same

trend as the corresponding set of the enthalpies of reaction. That fits in with what the Bell-Evans-Polanyi principle suggests, namely a linear relationship between the activation energy and the heat of reaction is sometimes observed within a series of closely related reactions.

**Table 2**

Enthalpy of reaction, activation enthalpy and free energies (kJ/mol) for  $\beta$ -C-H bond fission processes computed at the CCSD(T)/cc-pVDZ//MP2(Frozen Core)/cc-pVDZ level (results in brackets are the HF-DFT(B3LYP)/6-31G\*\* values)

	$\Delta_r H(0\text{ K})$	$\Delta H^\ddagger(0\text{ K})$	$\Delta G^\ddagger(298\text{ K})$
CH <sub>3</sub> CH <sub>2</sub> O	44.3 (75.7)	88.6 (94.0)	88.2 (93.2)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O	30.1 (81.5)	73.2 (99.9)	72.7 (98.6)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> O	48.9 (82.3)	94.5 (103.7)	95.3 (104.1)
HOCH <sub>2</sub> O	-10.9 (26.8)	50.6 (58.1)	51.0 (59.4)
CH <sub>3</sub> OCH <sub>2</sub> O	-7.9 (25.5)	52.2 (55.6)	52.7 (56.0)
CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>2</sub> O	-4.2 (29.3)	56.4 (61.0)	57.3 (60.2)

Let us now compare the rate of the two loss processes for the two analogous radicals, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>O and CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>2</sub>O, by using the activation free energies. From Tables 1 and 2 it is clear that the  $\beta$ -C-H bond scission and the isomerization are competitive when ether groups are present. If not, the  $\beta$ -C-H dissociation is very unlikely to occur.

Further calculations are needed to confirm our conclusions about the isomerization processes. More precisely, it would be interesting to examine the possibility of isomerization reactions involving n-membered TS (with n>6) for larger alkoxy radicals. This may be interesting for atmospheric modelling since isomerization leads to products different from those generated by the  $\beta$ -C-H bond scission and reaction with O<sub>2</sub>.

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