Autoxidation Resistant Cyclopentyl Methyl Ether

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The bond dissociation energy of the C–H bond at the α-position of an ether oxygen in cyclopentyl methyl ether (CPME) has been evaluated theoretically to be 393.3 kJ/mol by using an isodesmic reaction method. Essential factors accounting for this rather higher bond dissociation energy in CPME comparable to secondary C–H bond have been investigated on the basis of the structures and their thermodynamic data such as heats of formation (ΔH_f°) of CPME radical and relevant ether radicals evaluated by the theoretical approach.

Cyclopentyl methyl ether (CPME: CAS No. 5614-37-9) is used widely now because it is as stable as *tert*-butyl methyl ether (*t*-BuOMe) against autoxidation leading to lower peroxide production. The extent of peroxide production in CPME from 30 day exposure to air without stabilizing agent is below 20 ppm as shown in Figure 1.[1] Why is CPME so resistant against autoxidation though it has a *tert*-hydrogen at the α-position of the ether oxygen? In this paper, we have evaluated the structures and the heats of formations (ΔH_f°) of the CPME radical (CPME*) and related ether radicals by using a theoretical approach and investigated factors accounting for the higher resistibility of CPME against autoxidation. In addition, the MM3 force field[2] has been extended to deal with ether radicals in order to carry out the molecular design of functional ethers efficiently.

First of all, the data for the heat of formation (ΔH_f°) of CPME* is requisite to evaluate the bond dissociation energy (ΔBH°) of CPME. As there are no available accurate data from experiments, a theoretical method via an isodesmic reaction (1) to evaluate the heat of formation of CPME radical (CPME*) has been adopted.

$$\mathrm{CPME^* + CH_3OCH_3 \rightarrow CPME + CH_3OCH_2^*} \quad (1)$$

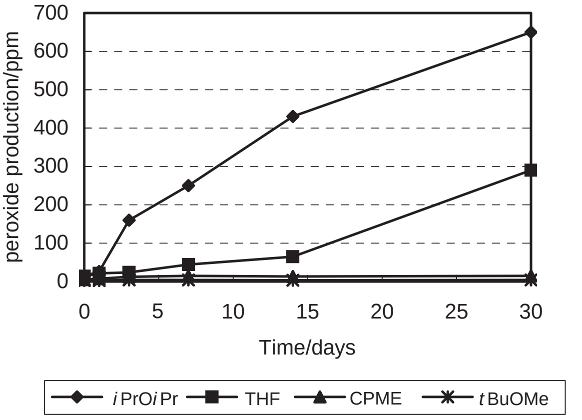
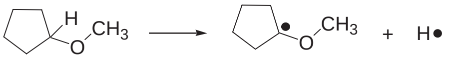


Figure 1. Experimentally determined peroxide production profiles of ethers by exposing to air. Generated peroxides were analyzed by using $Na_2S_2O_3$.

The reaction enthalpy for the above isodesmic reaction (ΔH°_{rec}) was derived by ab initio (CBS-Q//MP2/6-31+G*) calculation including zero-point energy correction (vibrational analysis) with Gaussian 03.[3] As ΔH°_{rec} is expressed as eq 2, the heat of formation of CPME* at 298 K can be evaluated by putting the necessary heats of formation energy data for CPME, CH_3OCH_2*, and CH_3OCH_3 molecules into eq 2.

$$\Delta H^\circ_{rec} = \Delta H^\circ_{f298}(\mathrm{CPME}) + \Delta H^\circ_{f298}(\mathrm{CH_3OCH_2^*}) - \Delta H^\circ_{f298}(\mathrm{CPME^*}) - \Delta H^\circ_{f298}(\mathrm{CH_3OCH_3}) \quad (2)$$

We calculated ΔH°_{f298}(CPME*) to be −47.9 kJ/mol by using the reported heats of formation energy data[4] in Table 1. As the bond-dissociation reaction of the C–H bond at the α-position of ether oxygen is expressed as shown typically as in eq 3, the bond-dissociation energy of the C–H bond (ΔBH°) can be predicted by adding the heat of formation of the hydrogen radical H* ($\Delta H^\circ_{f298}(\mathrm{H^*}) = 218$ kJ/mol)[5] to the energy difference of the heats of formation ($\delta\Delta H_f^\circ$) of the ether radical and parent ether as expressed in eq 4.



(3)

$$\Delta BH^\circ_{298}(\text{C–H:ether}) = \Delta H^\circ_{f298}(\text{ether radical}) - \Delta H^\circ_{f298}(\text{parent ether}) + \Delta H^\circ_{f298}(\mathrm{H^*}) \quad (4)$$

By putting the determined value of ΔH°_{f298}(CPME*) into eq 4, the bond-dissociation energy for the C–H bond at the α-position of the ether oxygen in CPME (ΔBH°_{298}(C–H$_\alpha$:CPME)) was evaluated to be 393.3 kJ/mol. In Table 2, the literature data for the bond-dissociation energy (ΔBH°) of relevant ethers are compiled together with the heats of formation (ΔH_f°) of the ether radicals and parent ethers. It should be noticed that the theoretically evaluated bond-dissociation energy for the C–H bond of CPME is larger by 2–3 kJ/mol than those of diisopropyl ether (*i*PrO*i*Pr) and THF which are liable to produce peroxides as by-products.

Why is the ΔBH° of the C–H bond of CPME so strong and resistive to autoxidation though it is a *tert*-hydrogen? Investigating the optimized structures of CPME* by MP2/6-31+G* calculation, it was found that bond angle strain at the radical carbon atom in CPME* was noticeable in the structural change from

Table 1. The reported heats of formation[4] and calculated energies to estimate ΔH°_{rec} for the isodesmic reaction

Species	ΔH_f°/kJ mol^{-1}	Energy (298 K)/hartree CBS-Q//MP2/6-31+G*
CPME	−223.2	−310.464550
CPME*		−309.816714
CH_3OCH_3	−184.1	−154.744492
CH_3OCH_2*	1.3	−154.092823

Table 2. Heats of formation of ether radicals and the bond-dissociation energies for the C–H bond at the α-position of the ether oxygen at 298 K

	Literature values[4]				MM3 calculations		
	ΔH_f°/kJ mol^{-1}		$\delta\Delta H_f^\circ$	Bond-dissociation energy (ΔBH°)/kJ mol^{-1}	ΔH_f°/kJ mol^{-1}		$\delta\Delta H_f^\circ$
	ether	radical			ether	radical	
MeOMe*	−184.1	1.3	185.4	403.4	−183.9	1.5	185.4
tBuOMe*	−283.6	−102.7	180.9	398.9	−283.8	−103.1	180.7
THF*	−184.1	−10.5	173.6	391.6	−186.7	−11.4	175.3
EtOEt*	−251.5	−70.0	181.5	399.5	−250.5	−71.8	178.8
iPrOiPr*	−318.8	−146.0	172.8	390.8	−317.3	−144.1	173.2
CPME*	−223.2	−47.9	175.3	393.3	−223.3	−45.9	177.4

CPME to CPME*. Though the α-carbon atom of ether oxygen in CPME takes sp^3 hybridization, the radical carbon (C*) in CPME* has to take a planar structure and its related bond angles are trigonal nature (ca. 120°). However, it is rather difficult for the radical carbon atom in CPME* to possess a 120° bond angle owing to the cyclic five-membered ring structure. Therefore, this bond angle strain of the CPME* leads to more instability relative to parent CPME, i.e., to larger energy difference of the heat of formation ($\delta\Delta H_f^\circ$) between the ether radical and parent ether.

As accurate structural and thermodynamic data of CPME* have been obtained by MP2/6-31+G* calculation, it is possible to make the MM3 force field[2] for the ether radicals on the basis of those data. Though ab initio method is certainly trustworthy to estimate complicated physical properties such as bond-dissociation energies and heats of formation of the radicals, molecular mechanics approach provides easier and more convenient tool for organic chemists to predict such properties in much faster time when the MM3 force field can be properly extended. As the fundamental MM3 force field parameters for the alkyl radicals[6] such as van der Waals parameter for the radical carbon (C*: atom type 29) and the related bond stretching parameters have been already settled, the other necessary parameters are those concerning the C*–O bond found in ether radicals. Therefore, the bond stretching, angle bending, and relevant torsional (dihedral angles) parameters with regard to the C*–O bond have been determined on the basis of the fundamental structural and energy data of the model ether radical compounds **1**–**4** shown in Figure 2. The optimized structures for the model compounds were calculated by UMP2/6-31+G* calculations. The heats of formation (ΔH_f°)[7] can be evaluated from the steric energy (*SE*) derived from the MM3 calculations by using eq 5 if the bond energy term (*BE*) for C*–O (29–6) bond is determined appropriately.

$$\Delta H_f^\circ = 4RT + BE + SE \qquad (5)$$

The bond energy term (*BE*) for C*–O (29–6) has been determined to reproduce the reported reliable heats of formation[4] on ether radicals. The determined MM3 force field parameters for the ether radicals were compiled in Supporting Information.[8]

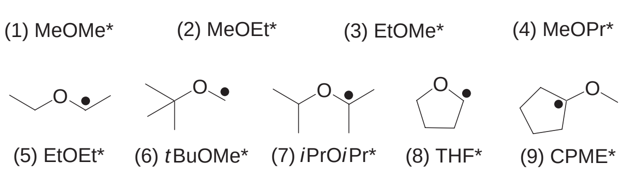

(1) MeOMe* (2) MeOEt* (3) EtOMe* (4) MeOPr*
(5) EtOEt* (6) tBuOMe* (7) iPrOiPr* (8) THF* (9) CPME*

Figure 2. Ether radical compounds.

By using thus determined MM3 force field, structures and the heats of formation of the CPME* and the related ether radicals shown in Figure 2 have been calculated. The calculated MM3 structures of those ether radicals are accurate enough to reproduce the structures determined by more sophisticated quantum mechanical (QM) calculations. In addition, the estimated heats of formation (ΔH_f°) of the ether radicals by MM3 calculations are linearly correlated well with the reported values in the literature (correlation coefficient $r = 0.91$).

It was found that any structural characteristics inherent to the parent ethers leading to more instability of the ether radicals can contribute significantly to higher bond dissociation energy (ΔBH°) of ether molecules, and this guideline may be useful to design functional ethers with less peroxides production.

References and Notes

1 It is very difficult to keep track of the peroxide production profile of diethyl ether precisely by experiments because of its higher volatility. No experimental data is available in the literature.

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8 See the all MM3 parameters in the Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/jounals/chem-lett/. The details how to determine the MM3 parameters will be reported soon in *Bull. Chem. Soc. Jpn.*

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