J. Phys. Chem. A **2003,** *107,* 4531−4546 **4531**

Structures, Intramolecular Rotation Barriers, and Thermochemical Properties of Methyl Ethyl, Methyl Isopropyl, and Methyl *tert*-Butyl Ethers and the Corresponding Radicals

Chiung-Chu Chen and Joseph W. Bozzelli*

Department of Chemistry and Environmental Science,
New Jersey Institute of Technology, Newark, New Jersey 07102

Received: September 24, 2002; In Final Form: February 28, 2003

Structures and thermochemical properties, ΔH°_{f298}, $S^\circ(T)$, and $C_p(T)$ ($50 \leq T/\mathrm{K} \leq 5000$) of three ethers and the corresponding radicals were determined by ab initio and density functional calculations. Molecular structures and vibration frequencies were determined at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels, with single point calculations for the energy at the B3LYP/6-311+G(3df,2p) and MP2/6-311+G(2df,2p) levels, respectively, and with composite methods CBSQ and G3(MP2) with B3LYP/6-31G(d,p) and MP2/6-31G(d,p) optimized geometries. Enthalpies of formation (ΔH°_{f298}) were determined at each calculation level using the group balance isodesmic reactions. Standard entropy, $S^\circ(T)$, and heat capacity, $C_p(T)$, from vibrational, translational, and external rotational contributions were calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional study. Potential barriers for internal rotation were calculated at the B3LYP/6-31G(d) level, and hindered internal rotational contributions to entropy and heat capacity were calculated by summation over the energy levels obtained by direct diagonalization of the Hamiltonian matrix of hindered internal rotations. Evaluations of data from the isodesmic reactions at each calculation level results in the enthalpy of formation being −52.22 ± 0.84, −60.13 ± 0.94, and −67.78 ± 1.44 kcal/mol for methyl ethyl ether (CCOC), methyl isopropyl ether (C2COC), and methyl *tert*-butyl ether (C3COC), respectively. Standard enthalpies are −1.67 ± 0.98, −9.31 ± 2.18, and −7.93 ± 1.81 kcal/mol for methyl ethyl ether radicals, $C^{\bullet}H_2CH_2OCH_3$ ($C^{\bullet}COC$), $CH_3C^{\bullet}HOCH_3$ ($CC^{\bullet}OC$), and $CH_3CH_2OC^{\bullet}H_2$ ($CCOC^{\bullet}$), respectively. Standard enthalpies are −10.06 ± 0.85, −17.33 ± 2.38, and −16.75 ± 1.71 kcal/mol for methyl isopropyl ether radicals, $C^{\bullet}H_2CH(CH_3)OCH_3$ ($C2^{\bullet}COC$), $(CH_3)_2C^{\bullet}OCH_3$ ($C2C^{\bullet}OC$), and $(CH_3)_2CHOC^{\bullet}H_2$ ($C2COC^{\bullet}$), respectively. Methyl *tert*-butyl ether radicals have enthalpies of −17.74 ± 1.13 and −24.54 ± 1.97 kcal/mol for $C^{\bullet}H_2(CH_3)_2COCH_3$ ($C3^{\bullet}COC$) and $(CH_3)_3COC^{\bullet}H_2$ ($C3COC^{\bullet}$), respectively. Bond strengths on the ethers are in order C−H bond > C−C bond > central C−O bond > terminal C−O bond, with one exception of C−C bond energy for C2COC being slightly lower than that of the C−O bond (C2C−OC) by 0.5 kcal/mol. Thermodynamic properties of the O/C2 group and the ether gauche interaction term were determined for group additivity application. The hydrogen bond increment group values for ROCJ, RJCOC, and RCJOC were also derived.

Introduction

Thermochemical parameters are important in evaluating reaction paths and kinetic processes in the atmosphere and in combustion environments. These values also provide a base for estimation of equilibria and energies for simple dissociation reactions. Several experimental and theoretical studies have been reported on related properties of three title ethers. Pilcher et al.[1] used a frame calorimeter to determine ΔH°_{f298} (methyl ethyl ether, CCOC) = −51.73 ± 0.16 and ΔH°_{f298} (methyl isopropyl ether, C2COC) = −60.24 ± 0.23 kcal/mol. Fenwick et al.[2] and Smutny et al.[3] derived ΔH°_{f298} (methyl *tert*-butyl ether, C3COC) = −67.78 ± 1.44 and −70.0 ± 1.2 kcal/mol, respectively, from the measured enthalpy of combustion and enthalpy of vaporization. Cox et al.[4] reanalyzed the value from Smutny[3] and reported ΔH°_{f298} (C3COC) = −67.45 ± 0.45 kcal/mol. Pedley[5] evaluated values of −51.72 ± 0.17, −60.23 ± 0.24, and −67.76 ± 0.26 kcal/mol for enthalpies of formation on CCOC, C2COC, and C3COC, respectively. Cohen[6] reported −51.89, −60.21, and −68.81 kcal/mol, by means of Benson's group additivity method, for ΔH°_{f298} of CCOC, C2COC, and C3COC, respectively. Verevkin[7] reevaluated the Benson's group additivity values and reported ΔH°_{f298} (CCOC) = −51.94, ΔH°_{f298} (C2COC) = −60.23 and ΔH°_{f298} (C3COC) = −67.81 kcal/mol.

Detar[8] compared the performances of a set of basis set/electron correction methods (BSECMs) in calculating absolute and relative enthalpies of 21 alcohols and ethers. He reported that the best of the BSECMs are with MP2/6-31+G(d,p)//6-31G(d,p) and with MP2/6-311+G(2df,2p)//6-31G(d,p), which give standard deviations of about 0.5 kcal/mol. The estimated standard deviation of the experimental ΔH°_{f298} of these same compounds is about 0.4 kcal/mol. This study calculated ΔH°_{f298} are −60.79 and −67.96 kcal/mol for C2COC and C3COC at the MP2/6-311+G(2df,2p)//6-31G(d,p) level.

We have found only limited values for the heat capacity and entropies. Chao et al.[9] calculated the heat capacity of CCOC from the statistical mechanical method by employing spectroscopic constants. Andon et al.[10] calculated the entropies of C2COC and C3COC from the measurement of the heat capacity

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* Author for correspondence. E-mail: bozzelli@njit.edu. Phone: (973)-596-3459. Fax: (973)-642-7170.

10.1021/jp022131n CCC: $25.00

and enthalpy of fusion in the crystal and liquid states at 12−350 K. Stull et al.[11] employed a $-CH_2-$ increment from the parent hydrocarbon method to estimate the entropy and heat capacity for three title ethers. Guthrie[12] reported entropy value of C2COC at B3LYP/6-31G(d,p) calculation.

The dimethyl ether radical (COC$^{\bullet}$) has been widely studied. Mayer et al.[13] reported ΔH°_{f298}(COC$^{\bullet}$) = −0.48 kcal/mol derived from the G2 energies by the atomization method. Good and Francisco[14] reported ΔH°_{f298}(COC$^{\bullet}$) as 0.9 kcal/mol using G2 and isodesmic reactions that do not incorporate group balance. Yamada et al.[15] reported a value of 0.1 kcal/mol using G2 and CBSQ with the group balance isodesmic reaction. Loucks et al.[16] determined the experimental value of −5.0 kcal/mol by measuring the activation energy for the decomposition of 1,2-dimethoxyethane. Holmes and Lossing[17] also reported an experimental value of −1.3 ± 2.0 kcal/mol using mass spectral techniques.

Bach et al.[18] estimated the C−H bond energy of CCOC−H as 96.20 kcal/mol from G2 energy. Adopting ΔH°_{f298}(CCOC) = −51.73 kcal/mol[1] and ΔH°_{f298}(H) = −52.1 kcal/mol, ΔH°_{f298}(CCOC$^{\bullet}$) is calculated to be −7.63 kcal/mol. Atadinc et al.[19] reported the rate constants for H-abstraction reaction from C3COC by OH radical at MP2/6-31G(d,p) and PMP2/6-31G(d,p) level. Use of their forward and reverse rate constant expressions leads to calculation for ΔH°_{f298} (C3$^{\bullet}$COC) and ΔH°_{f298} (C3COC$^{\bullet}$) as −14.58 and −20.60 kcal/mol, using ΔH°_{f298} (C3COC) = −67.78 kcal/mol, ΔH°_{f298} (OH) = 8.96 kcal/mol, and ΔH°_{f298} (H_2O) = −57.80 kcal/mol. To our knowledge, there are no other estimates of thermochemical properties for the corresponding alkoxymethyl radicals and methoxyalkyl radicals, which result from loss of a hydrogen from the title ethers.

In this study we use ab initio and density functional calculations with isodesmic reactions that retain group balance to estimate thermochemical properties for methyl ethyl ether (CCOC), methyl isopropyl ether (C2COC), methyl *tert*-butyl ether (C3COC), and the corresponding alkoxymethyl radicals (CCOC$^{\bullet}$, C2COC$^{\bullet}$, and C3COC$^{\bullet}$) and methoxyalkyl radicals (C$^{\bullet}$COC, CC$^{\bullet}$OC, C2$^{\bullet}$COC, C2C$^{\bullet}$OC, and C3$^{\bullet}$COC) derived from H atom loss.

Calculation Methods

All of the density functional and ab initio calculations were performed using the Gaussian94 and Gaussian98 program suites.[20,21] The geometry optimization, harmonic vibration frequencies, and zero-point vibrational energies (ZPVE) were computed with the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels of theory. The optimized geometry parameters were used to obtain total electronic energies at the MP2/6-311+G(2df,2p)//MP2/6-31G(d,p) and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) single point levels of calculation. Complete basis set (CBSQ)[22−24] model chemistry based on MP2/6-31G(d,p) and B3LYP/6-31G(d,p) geometries were also calculated. The G3(MP2)[25] method was also modified to use MP2/6-31G(d,p) and B3LYP/6-31G(d,p) geometries and zero-point energies.

B3LYP/6-31G(d,p) was chosen because it is commonly used and is reported to yield accurate geometries and reasonable energies.[26−29] B3LYP/6-311+G(3df,2p) was chosen to see if this large basis set results in an improvement to the above commonly used density functional calculation method. Detar[8] reported that MP2/6-311+G(2df,2p)//6-31G(d,p) provides high quality enthalpies of formation for 21 alcohols and ethers using basis set/electron correction methods (BSECMs).

The CBSQ method has been discussed in detail in refs 22−24. CBSQ requires the UMP2/6-311+G(3d2f,2df,2p) energy, MP4(SDQ)/6-31+G(d(f),p) energy, QCISD(T)/6-31+G′ energy, and CBS extrapolation. The 6-31G′ basis is a modification of the 6-31G(d) basis obtained by combining the 6-31G sp functions with the 6-311G(d,p) polarization exponents. The total CBSQ energy is calculated from

$$E(\mathrm{CBSQ}) = E(\mathrm{UMP2}) + \Delta E(\mathrm{CBS}) + \Delta E(\mathrm{MP4}) + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{ZPE}) + \Delta E(\mathrm{emp}) + \Delta E(\mathrm{spin})$$

where ΔE(CBS) is obtained from the CBS extrapolation,[30,31]

$$\Delta E(\mathrm{MP4}) = E[\mathrm{MP4(SDQ)/6\text{-}31{+}G(d(f),p)}] - E[\mathrm{MP2/6\text{-}31{+}G(d(f),p)}]$$

$$\Delta E(\mathrm{QCI}) = E[\mathrm{QCISD(T)/6\text{-}31{+}G'}] - E[\mathrm{MP4(SDQ)/6\text{-}31{+}G'}]$$

The empirical term, ΔE(emp), is

$$\Delta E(\mathrm{emp}) = -0.00533\sum_{i}\Big(\sum_{\mu=1}^{N_{ii}} C_{\mu ii}\Big)^2 |S|_{ii}^{\,2}$$

where $(\sum C_{\mu ii})^2$ is the interference factor and $|S|_{ii}$ is the absolute overlap integral.[32]

The spin contamination correction term, ΔE(spin), is

$$\Delta E(\mathrm{spin}) = -0.0092\Delta\langle S^2\rangle$$

which adds a correction proportional to the error in the UHF $\langle S^2\rangle$.

We made two modifications in the present study. First, the geometries are obtained at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels instead of MP2(FC)/6-31G′. Second, the zero-point energies are obtained at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels and scaled by 0.9806 and 0.9608, respectively, as recommended by Scott et al.[33] These calculations are referred to as CBSQ// B3LYP/6-31G(d,p) and CBSQ// MP2/6-31G(d,p).

We also modified G3(MP2)[25] theory using the geometries and the zero-point energies obtained at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels. These calculations are referred to as G3(MP2)//B3LYP/6-31G(d,p) and G3(MP2)//MP2/6-31G(d,p). Two single point energy calculations are carried out at the QCISD(T)/6-31G(d) and MP2/G3MP2large levels. The total G3MP2 energy is calculated from

$$E(\mathrm{G3MP2}) = \mathrm{QCISD(T)/6\text{-}31G(d)} + \Delta E(\mathrm{MP2}) + E(\mathrm{HLC}) + \Delta E(\mathrm{ZPE})$$

where the correction at the second-order Møller−Plesset level (MP2) is given by

$$\Delta E(\mathrm{MP2}) = E[\mathrm{MP2/G3MP2large}] - E[\mathrm{MP2/6\text{-}31G(d)}]$$

Higher level correction, E(HLC), is

$$E(\mathrm{HLC}) = -An_{\alpha} - Bn_{\beta} \qquad \text{for molecule}$$

$$E(\mathrm{HLC}) = -Cn_{\alpha} - Dn_{\beta} \qquad \text{for atom}$$

where n_{α} and n_{β} are the number of α and β valence electrons, respectively, with $n_{\alpha} \geq n_{\beta}$. For G3(MP2)//B3LYP/6-31G(d,p) calculation, $A = 0.005046$, $B = 0.004995$, $C = 0.007865$, and $D = 0.002323$. For G3(MP2)//MP2/6-31G(d,p) calculation, $A = 0.004808$, $B = 0.004471$, $C = 0.007324$, and $D = 0.002021$.

1. Enthalpies of Formation (ΔH°_{f298}). The isodesmic reaction 1 with group balance is selected to determine ΔH°_{f298} of methyl ethyl ether (CCOC), methyl isopropyl ether (C2COC), and methyl *tert*-butyl ether (C3COC). ΔH°_{f298} values of corresponding alkoxymethyl radicals (CCOC$^\bullet$, C2COC$^\bullet$, and C3COC$^\bullet$) and methoxyalkyl radicals (C$^\bullet$COC, CC$^\bullet$OC, C2$^\bullet$COC, C2C$^\bullet$OC, and C3$^\bullet$COC) are derived from the group isodesmic reactions 2−4 and bond dissociation enthalpies of ΔH°_{298}(CH$_3$CH$_2$−H) (101.1 kcal/mol) and ΔH°_{298}(CH$_3$OCH$_2$−H) (96.4 kcal/mol).

$$(CH_3)_xCH_{3-x}OCH_3 + CH_3OH \leftrightarrow (CH_3)_xCH_{3-x}OH + CH_3OCH_3 \qquad x = 1-3 \quad (1)$$

$$(CH_3)_xCH_{3-x}OC^\bullet H_2 + CH_3CH_3 \leftrightarrow (CH_3)_xCH_{3-x}OCH_3 + CH_3OC^\bullet H_2 \qquad x = 1-3 \quad (2)$$

$$C^\bullet H_2C(CH_3)_{x-1}CH_{3-x}OCH_3 + CH_3CH_3 \leftrightarrow (CH_3)_xCH_{3-x}OCH_3 + CH_3C^\bullet H_2 \qquad x = 1-3 \quad (3)$$

$$C^\bullet(CH_3)_xH_{2-x}OCH_3 + CH_3OCH_3 \leftrightarrow (CH_3)_xCH_{3-x}OCH_3 + CH_3OC^\bullet H_2 \qquad x = 1, 2 \quad (4)$$

The basic requirement of an isodesmic reaction is bond conservation, where the number of each bond type is conserved in the reaction. An isodesmic reaction will lead to more accurate results if groups are also conserved in the reaction, because next nearest neighbor interactions are also conserved. Accuracy to near 1 kcal/mol using this method of enthalpy estimation is illustrated in several previous studies.[34−37]

Density functional and ab initio calculations at MP2/6-311+G(2df,2p)//MP2/6-31G(d,p), B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p), CBSQ//MP2/6-31G(d,p), CBSQ//B3LYP/6-31G(d,p), G3MP2//MP2/6-31G(d,p), and G3MP2//B3LYP/6-31G(d,p) levels of theory were performed on the most stable conformer of each compound.

2. Entropies ($S^\circ(T)$'s) and Heat Capacities ($C_p(T)$'s) ($50 \le T/\mathrm{K} \le 5000$). Entropies and heat capacities in the temperature range 50−5000 K were calculated using the rigid-rotor-harmonic-oscillator approximation based on scaled vibrational frequencies, molecular mass, and moments of inertia of the optimized BLY3/6-31G(d,p) and MP2/6-31G(d,p) structures. The ROTATOR program calculates the $S^\circ(T)$'s and $C_p(T)$'s from hindered rotor contributions by direct integration over energy levels resulting from the structure and the calculated intramolecular rotation potential energy curves.[38,39] This includes contributions from the conformers of each internal rotation. The program includes these contributions to S and C_p at all temperatures. The number of optical isomers and spin degeneracy of unpaired electrons were also incorporated for calculation of $S^\circ(T)$'s and $C_p(T)$'s.

Potential barriers of internal rotations about central and terminal C−O, C−C, C$^\bullet$−C, and C$^\bullet$−O bonds were calculated at the B3LYP/6-31G(d) level. The geometries and harmonic vibrational frequencies were also calculated for all rotational conformers at the same level. A Fourier series was used to represent the potential calculated at discrete torsional angles:

$$V(\Phi) = a_0 + a_i \cos(i\Phi) + b_i \sin(i\Phi) \qquad i = 1, 2, 3, ... \quad (F1)$$

where values of the coefficients are calculated to provide the true minima and maxima of the torsional potentials with allowance of a shift of the theoretical extrema of angular positions. Further descriptions of this method to calculate contributions from the internal rotors are reported by Lay et al.[38,39]

Results and Discussion

1. Geometries and Vibrational Frequencies. The geometries of all species were optimized at B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels. The optimized geometry for the minimum energy structures and the numerical values of the structural parameters including carbon−carbon and carbon−oxygen bond distances along with applicable bond angles are listed in Table 1. The full parameters of optimized structures are given as Supporting Information (Table S1).

The C$_1$−C$_2$ bonds in MP2/6-31G(d,p) geometries are slightly longer than those in B3LYP/6-31G(d,p), whereas the terminal C$_4$−O$_3$ bond lengths in MP2/6-31G(d,p) geometries are slightly shorter than those in B3LYP/6-31G(d,p). The differences are less than 0.013 Å. The C−C and C−O bond lengths increase with the increased methyl substitution. Differences of bond angles and dihedral angles are within 1.9° and 10.7° between B3LYP/6-31G(d,p) and MP2/6-31G(d,p) geometries.

The vibration frequencies and moments of inertia for all species are listed in Table 2, the calculated vibration frequencies were scaled by the factors 0.9614 and 0.9370 for B3LYP/6-31G(d,p) and MP2/6-31G(d,p) theoretical frequencies, respectively. Torsion frequencies are not included in Table 2. Vibrational frequencies are within ±6% between MP2/6-31G(d,p) and B3LYP/6-31G(d,p) calculations, with the exception of four frequencies of CC$^\bullet$OC(ν_3), CCOC$^\bullet$ (ν_3), C2COC$^\bullet$ (ν_5), and C3COC$^\bullet$ (ν_7).

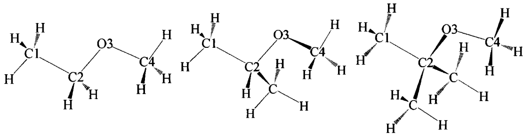
2. Rotational Barriers. Potential barriers for internal rotations of the three title ethers and the corresponding radicals were calculated at the B3LYP/6-31G(d) level. The potential energy was calculated as a function of the dihedral angle by varying the torsion angle in 30° intervals and allowing other parameters to be optimized. (One exception is calculation of the rotation barrier of the methyl radical group, −C$^\bullet$H$_2$. The dihedral angle of two hydrogens on methyl radical was fixed in the angle of the most stable conformer and an interval of 15° was used). The minima and maxima on the torsional potential were optimized. The geometries and harmonic vibrational frequencies were calculated for all rotational conformers and transition states at B3LYP/6-31G(d) level. The barriers for internal rotations were calculated from the differences between the total energy of each conformation and that of the most stable conformer, where the zero point vibrational energy (ZPVE) and thermal correction to 298 K were also included. The calculated rotation barriers about C−O, C−C, C$^\bullet$−O, and C$^\bullet$−C bonds are listed in Table 3.

Rotation about Central C−O Bonds. Potential diagrams for internal rotation barriers about central C−O bonds are shown in Figures 1−3 for the three title ethers (CC−OC, C2C−OC, and C3C−OC), methoxyalkyl radicals (C$^\bullet$C−OC, C2$^\bullet$C−OC, and C3$^\bullet$C−OC) and alkoxymethyl radicals (CC−OC$^\bullet$, C2C−OC$^\bullet$ and C3C−OC$^\bullet$), respectively. Points are calculated values at the B3LYP/6-31G(d) level. Lines are results of Fourier expansions (eq F1). Coefficients of the Fourier expansion components, a_i and b_i in eq F1 are presented in the Supporting Information (Table S2).

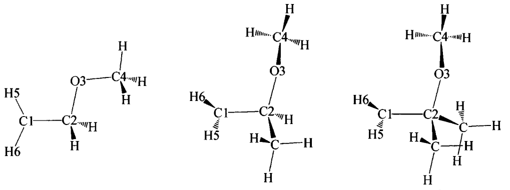
Calculations of rotation barrier about the central C−O bond in C3COC (Figure 1) yields a 3-fold symmetrical potential where the maxima occur when a methyl group eclipses one of the three −CH$_3$ groups on the quaternary C atom at a barrier of 2.9 kcal/mol. Durig et al.[40] reported the barrier of 3.57 kcal/mol from the analysis of far-infrared spectra in the gas phase. This 0.7 kcal/mol difference for the barrier results in an error of 0.3 and 0.03 cal/(mol K) at 298 K for the entropy and heat capacity contribution from internal rotation, respectively.

The maxima barrier for rotation about the central C−O bond in C2COC is 4.98 kcal/mol, corresponding to the −CH$_3$ group

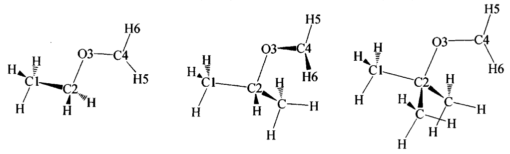
TABLE 1: Selected Geometric Parameters[a] for Methyl Ethyl Ether, Methyl Isopropyl Ether, and Methyl *tert*-Butyl Ether and the Corresponding Radicals



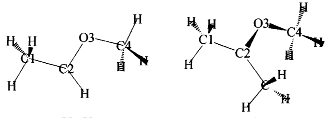
	$CH_3CH_2OCH_3$		$(CH_3)_2CHOCH_3$		$(CH_3)_3COCH_3$	
	X=Y=H		X=H, Y=CH_3		X=Y=CH_3	
Parameter	B3LYP[b]	MP2[b]	B3LYP	MP2	B3LYP	MP2
r (C_1-C_2)	1.5193	1.5120	1.5250	1.5161	1.5326	1.5265
r (C_2-O_3)	1.4170	1.4191	1.4289	1.4295	1.4422	1.4412
r (O_3-C_4)	1.4102	1.4147	1.4114	1.4165	1.4131	1.4179
r (C_2-X)	1.1040	1.0980	1.5319	1.5225	1.5374	1.5265
r (C_2-Y)	1.1040	1.0980	1.1043	1.0997	1.5374	1.5265
∠(O_3-C_2-C_1)	108.49	107.85	106.20	105.71	103.2	103.0
∠(C_4-O_3-C_2)	112.78	111.45	114.80	113.47	117.91	116.48
∠(X-C_2-C_1)	110.53	110.80	112.12	112.02	110.2	111.0
∠(Y-C_2-C_1)	110.53	110.80	109.01	109.37	110.2	111.0
∠(C_4-O_3-C_2-C_1)	-179.96	-179.99	162.12	164.58	180.0	180.0
∠(X-C_2-C_1-O_3)	-120.96	-120.59	-122.39	-121.87	-118.6	-118.5
∠(Y-C_2-C_1-O_3)	120.95	120.59	116.97	116.94	118.6	118.5



	$C^{\bullet}H_2CH_2OCH_3$		$C^{\bullet}H_2(CH_3)CHOCH_3$		$C^{\bullet}H_2(CH_3)_2COCH_3$	
	X=Y=H		X=H, Y=CH_3		X=Y=CH_3	
Parameter	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
r (C_1-C_2)	1.4827	1.4829	1.4953	1.4928	1.5008	1.4968
r (C_2-O_3)	1.4163	1.4190	1.4282	1.4282	1.4435	1.4407
r (O_2-C_4)	1.4107	1.4148	1.4141	1.4185	1.4152	1.4202
r (C_2-X)	1.1076	1.0998	1.1054	1.1002	1.5394	1.5282
r (C_2-Y)	1.1126	1.1042	1.5362	1.5251	1.5421	1.5294
r (H_5-C_1)	1.0833	1.0771	1.0849	1.0793	1.0855	1.0798
r (H_6-C_1)	1.0837	1.0778	1.0857	1.0798	1.0860	1.0799
∠(O_3-C_2-C_1)	109.56	108.59	112.0	111.4	110.6	110.2
∠(C_4-O_3-C_2)	112.66	111.27	113.73	112.34	116.46	114.93
∠(X-C_2-C_1)	110.65	110.76	109.2	109.2	111.34	111.35
∠(Y-C_2-C_1)	110.80	111.13	105.83	105.58	103.1	103.1
∠(H_5-C_1-C_2)	120.23	120.08	121.12	120.59	121.57	120.52
∠(H_6-C_1-C_2)	119.62	118.93	119.21	118.46	119.19	118.61
∠(C_4-O_3-C_2-C_1)	-177.54	-178.27	-69.1	-68.8	-61.8	-64.1
∠(X-C_2-C_1-O_3)	122.40	121.60	121.0	120.7	123.2	123.4
∠(Y-C_2-C_1-O_3)	-121.18	-120.67	-118.9	-118.3	-113.3	-113.2
∠(H_5-C_1-C_2-O_3)	22.77	29.29	154.0	160.0	149.0	159.7
∠(H_6-C_1-C_2-O_3)	-166.88	-166.18	-38.1	-38.3	-41.9	-38.8



	$CH_3CH_2OC^{\bullet}H_2$		$(CH_3)_2CHOC^{\bullet}H_2$		$(CH_3)_3COC^{\bullet}H_2$	
	X=Y=H		X=H, Y=CH_3		X=Y=CH_3	
Parameter	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
r (C_1-C_2)	1.5175	1.5107	1.5229	1.5146	1.5306	1.5202
r (C_2-O_3)	1.4291	1.4308	1.4396	1.4392	1.4543	1.4517
r (O_3-C_4)	1.3591	1.3645	1.3598	1.3652	1.3603	1.3658
r (C_2-X)	1.1007	1.0951	1.1016	1.0971	1.5343	1.5236
r (C_2-Y)	1.0988	1.0931	1.5277	1.5189	1.5353	1.5249
r (H_5-C_4)	1.0836	1.0781	1.0838	1.0783	1.0840	1.0785
r (H_6-C_4)	1.0893	1.0841	1.0901	1.0847	1.0871	1.0819
∠(O_3-C_2-C_1)	108.37	107.61	106.48	105.99	103.5	103.2
∠(C_4-O_3-C_2)	115.30	113.75	116.02	114.48	118.92	117.34
∠(X-C_2-C_1)	111.01	111.18	109.48	109.75	110.0	110.1
∠(Y-C_2-C_1)	111.15	111.30	113.14	112.95	110.1	110.2
∠(H_5-C_4-O_3)	113.18	112.54	113.09	112.46	112.50	111.79
∠(H_6-C_4-O_3)	118.10	117.39	117.85	117.19	119.35	118.72
∠(C_4-O_3-C_2-C_1)	-177.16	-177.53	160.84	162.80	-175.1	-176.1
∠(X-C_2-C_1-O_3)	120.18	119.93	116.42	116.48	117.9	117.7
∠(Y-C_2-C_1-O_3)	-120.02	-119.66	-121.31	-120.79	-117.9	-117.9
∠(H_5-C_4-O_3-C_2)	176.43	176.12	-178.18	-176.74	-177.12	-175.87
∠(H_6-C_4-O_3-C_2)	28.10	31.19	-30.78	-32.33	-29.26	-31.23



	$CH_3C^{\bullet}HOCH_3$		$(CH_3)_2C^{\bullet}OCH_3$	
	X=H		X=CH_3	
Parameter	B3LYP	MP2	B3LYP	MP2
r (C_1-C_2)	1.4878	1.4866	1.4946	1.4921
r (C_2-O_3)	1.3683	1.3720	1.3806	1.3837
r (O_2-C_4)	1.4189	1.4232	1.4184	1.4232
r (C_2-X)	1.0923	1.0881	1.4993	1.4979
∠(O_3-C_2-C_1)	114.46	113.20	111.0	110.0
∠(C_4-O_3-C_2)	114.92	113.40	117.82	115.96
∠(X-C_2-C_1)	120.83	120.08	119.46	118.33
∠(C_4-O_3-C_2-C_1)	177.60	177.18	-175.0	-175.9
∠(X-C_2-C_1-O_3)	146.30	142.20	146.4	141.7

[a] Distances in angstroms and angles in degrees. [b] Geometrical parameters optimized at the B3LYP/6-31g(d,p) and MP2(full)/6-31g(d,p) level of theory.

eclipsing one of two $-CH_3$ groups on the tertiary C atom (∠C−C−O−C = 3.3° and 122.3°). Two minima occur at C−C−O−C dihedral angles of 197.8° and 284.7° (anti conformers), and the methyl group twists 18° away from 180° (away from CH_3 group toward the H atom) due to the repulsion of the methyl group on tertiary C atom.

Rotation about the $-OCH_3$ group in CCOC has a global minima at the C−C−O−C dihedral angle of 180° and two symmetrical minima at ∼±75° with an energy 1.42 kcal/mol above the global minimum. Three maxima occur when a $-CH_3$ group eclipses the $-CH_3$ group or the two H atoms on the secondary C atom with energies of 6.67, 2.61, and 2.61 kcal/mol above the global minimum, respectively.

The rotation potential about the central C−O bond in C3COC$^{\bullet}$ (Figure 2) yields a 3-fold symmetrical potential with a barrier of 2.07 kcal/mol; this barrier is lower by 0.83 kcal/mol than that of C3COC.

Two minima occur when the $-C^{\bullet}H_2$ group is anti to one of the two $-CH_3$ groups on the quaternary C atom (∠C−C−O−C dihedral angles = 284° and 207°) in rotation of the central C−O bond on the C2COC$^{\bullet}$ radical. One of these two conformers (∠C−C−O−C = 207°) has a slightly higher energy, 0.5 kcal/mol, which results from the H in the $-C^{\bullet}H_2$ group oriented toward the H atom in the methyl group.

The highest barriers for rotation of the central C−O bond in CCOC$^{\bullet}$ and C2CO$^{\bullet}$C radicals are 4.58 and 4.23 kcal/mol, respectively; these are lower than barriers in parent molecules CCOC and C2COC by 2.09 and 0.75 kcal/mol.

The potential energy for rotation of the $-OCH_3$ group in the C3$^{\bullet}$COC radical (Figure 3) shows two symmetry-related minima at ∼±60° and a third minimum at a C−C−O−C dihedral angle of 180°, which is 1.63 kcal/mol higher in energy. The $-CH_3$ group eclipsing two $-CH_3$ groups on the quaternary C corresponds to the highest barrier of 4.22 kcal/mol.

For rotation about the central C−O bond on C2$^{\bullet}$COC, the energy of the anti conformer of two $-CH_3$ groups is lower than the energies of both the conformer with the $-CH_3$ group anti to $-C^{\bullet}H_2$ and the conformer with $-CH_3$ gauche to $-C^{\bullet}H_2$ and $-CH_3$ groups, by 1.07 and 1.91 kcal/mol, respectively. The energy of $-CH_3$ eclipsed with $-CH_3$ is slightly higher (0.75 kcal/mol) than that of $-CH_3$ eclipsed with $-C^{\bullet}H_2$. In C$^{\bullet}$C−OC, the energy of the conformer of $-CH_3$ gauche with $-C^{\bullet}H_2$ is slightly higher (0.21 kcal/mol) than that of the anti conformer and there is a 5 kcal/mol barrier to reach the eclipsed structure.

TABLE 2: Vibration Frequencies and Moments of Inertia for Model Stable (Parent) Molecules and Model Free Radicals

molecule	frequencies (cm^{-1})[a]	moments of inertia (amu bohr^2)
$CH_3CH_2OCH_3$	278, 449, 796, 839, 995, 1078, 1122, 1126, 1161, 1194, 1253, 1353, 1384, 1435, 1440, 1441, 1456, 1462, 1489, 2842, 2862, 2868, 2902, 2936, 3004, 3008, 3013	64.04, 436.26, 466.23
	276, 446, 793, 838, 999, 1076, 1119, 1122, 1158, 1188, 1248, 1347, 1385, 1430, 1448, 1451,1463, 1470, 1493, 2864, 2882, 2907, 2943, 2947, 3034, 3034, 3044[b]	*64.55, 431.16, 461.64*[b]
$(CH_3)_2CHOCH_3$	291, 346, 429, 482, 777, 884, 896, 912, 1079, 1101, 1116, 1137, 1158, 1193, 1322, 1333, 1360, 1373, 1431, 1436, 1442, 1445, 1456, 1464, 1470, 2845, 2867, 2915, 2928, 2934, 2997, 3000, 3002, 3006, 3013	239.55, 478.83, 644.92
	290, 347, 427, 479, 779, 893, 896, 917, 1072, 1100, 1122, 1131, 1165, 1188, 1324, 1326, 1364, 1374, 1426, 1443, 1448, 1451, 1461, 1472, 1475, 2865, 2888, 2932, 2936, 2960, 3021, 3027, 3029, 3031, 3037	*236.68, 472.60, 636.42*
$(CH_3)_3COCH_3$	274, 325, 349, 395, 440, 488, 699, 828, 878, 887, 923, 1001, 1007, 1083, 1137, 1164, 1191, 1212, 1242, 1352, 1354, 1378, 1427, 1429, 1442, 1444, 1447, 1457, 1461, 1467, 1478, 2882, 2925, 2930, 2934, 2937, 2996, 2996, 3001, 3004, 3005, 3010, 3011	414.61, 665.67, 666.44
	285, 328, 353, 393, 437, 483, 703, 841, 889, 900, 921, 1004, 1007, 1077, 1129, 1155, 1202, 1228, 1253, 1351, 1354, 1376, 1424, 1434, 1445, 1448, 1454, 1460, 1469, 1474, 1481, 2902, 2927, 2930, 2934, 2975, 3017, 3020, 3025, 3025, 3028, 3030, 3032	*409.48, 656.45, 657.80*

radical	frequencies	moments of inertia (amu bohr^2)
$C^{\bullet}H_2CH_2OCH_3$	282, 404, 463, 807, 926, 1022, 1068, 1126, 1137, 1181, 1198, 1354, 1405, 1428, 1440, 1448, 1471, 2750, 2813, 2861, 2903, 3008, 3053, 3162	58.29, 414.12, 448.51
	281, 408, 464, 811, 939, 1022, 1080, 1123, 1131, 1177, 1196, 1355, 1420, 1431, 1451, 1462, 1478, 2809, 2869, 2882, 2947, 3036, 3068, 3185	*58.76, 410.09, 444.61*
$CH_3C^{\bullet}HOCH_3$	275, 452, 583, 857, 992, 1035, 1089, 1131, 1155, 1237, 1336, 1380, 1422, 1435, 1441, 1453, 1458, 2855, 2889, 2946, 2948, 2984, 3003, 3021	52.83, 435.33, 464.12
	275, 452, 655, 856, 1013, 1032, 1090, 1127, 1150, 1224, 1333, 1384, 1432, 1435, 1453, 1459, 1469, 2904, 2908, 2988, 2990, 2991, 3034, 3049	*53.44 430.03, 459.27*
$CH_3CH_2OC^{\bullet}H_2$	286, 457, 623, 790, 833, 1006, 1074, 1139, 1177, 1236, 1251, 1352, 1383, 1436, 1441, 1456, 1476, 2882, 2922, 2938, 2986, 3010, 3016, 3132	58.73, 414.53, 448.93
	289, 454, 735, 789, 836, 1013, 1076, 1141, 1174, 1217, 1248, 1347, 1386, 1441, 1448, 1463, 1484, 2900, 2944, 2956, 2999, 3036, 3046, 3151	*59.08, 409.45, 444.13*
$C^{\bullet}H_2CH(CH_3)OCH_3$	272, 318, 442, 452, 540, 788, 881, 904, 1007, 1091, 1102, 1106, 1138, 1188, 1286, 1327, 1352, 1404, 1429, 1439, 1440, 1453, 1465, 2832, 2868, 2920, 2933, 3005, 3010, 3015, 3033, 3139	224.58, 468.47, 622.16
	273, 317, 443, 452, 548, 790, 887, 911, 1024, 1091, 1107, 1116, 1131, 1185, 1294, 1323, 1355, 1416, 1426, 1447, 1450, 1459, 1473, 2858, 2889, 2937, 2962, 3034, 3034, 3039, 3047, 3161	*222.39, 462.97, 614.37*
$(CH_3)_2C^{\bullet}OCH_3$	286, 325, 361, 477, 740, 914, 922, 939, 1045, 1082, 1128, 1156, 1249, 1264, 1360, 1374, 1420, 1431, 1434, 1436, 1446, 1457, 1462, 2828, 2845, 2894, 2951, 2953, 2955, 2998, 3003, 3014	231.54, 459.39, 650.39
	289, 344, 367, 469, 749, 914, 919, 942, 1060, 1081, 1124, 1149, 1251, 1260, 1365, 1374, 1425, 1434, 1443, 1447, 1456, 1464, 1473, 2881, 2892, 2911, 2985, 2987, 2992, 3028, 3034, 3043	*229.02, 454.21, 641.17*
$(CH_3)_2COC^{\bullet}H_2$	299, 339, 440, 491, 641, 776, 889, 900, 915, 1092, 1108, 1149, 1182, 1224, 1321, 1332, 1359, 1376, 1431, 1436, 1444, 1448, 1465, 2877, 2929, 2936, 2979, 3001, 3009, 3011, 3014, 3127	234.36, 456.96, 618.54
	302, 338, 440, 489, 739, 783, 899, 903, 921, 1090, 1119, 1153, 1184, 1208, 1323, 1327, 1364, 1376, 1437, 1443, 1449, 1455, 1470, 2893, 2933, 2938, 2993, 3025, 3032, 3036, 3038, 3146	*231.73, 451.16, 610.43*
$C^{\bullet}H_2C(CH_3)_2OCH_3$	268, 309, 344, 389, 436, 465, 553, 715, 824, 879, 898, 952, 988, 1071, 1134, 1135, 1159, 1201, 1217, 1347, 1362, 1405, 1423, 1432, 1439, 1445, 1451, 1466, 1468, 2882, 2928, 2931, 2935, 2999, 3001, 3005, 3011, 3017, 3033, 3138	399.74, 643.08, 658.74
	289, 308, 344, 386, 432, 471, 565, 718, 840, 889, 904, 964, 989, 1067, 1129, 1144, 1169, 1212, 1234, 1345, 1362, 1413, 1420, 1440, 1445, 1455, 1457, 1471, 1477, 2900, 2930, 2933, 2973, 3022, 3027, 3029, 3032, 3036, 3043, 3157	*394.66, 634.83, 649.22*
$(CH_3)_3COC^{\bullet}H_2$	262, 333, 355, 393, 444, 495, 621, 697, 823, 885, 893, 929, 1008, 1011, 1144, 1179, 1216, 1221, 1243, 1357, 1359, 1382, 1426, 1430, 1440, 1442, 1452, 1460, 1473, 2933, 2934, 2940, 3001, 3004, 3006, 3010, 3013, 3014, 3016, 3132	408.97, 637.95, 642.75
	270, 334, 358, 390, 443, 489, 699, 733, 843, 894, 903, 926, 1010, 1012, 1142, 1184, 1208, 1233, 1255, 1355, 1357, 1379, 1432, 1437, 1444, 1446, 1458, 1465, 1476, 2932, 2932, 2936, 3014, 3022, 3024, 3030, 3032, 3034, 3035, 3151	*403.94, 629.32, 634.30*

[a] Frequencies are scaled by the factors 0.9614 and 0.9370 for B3LYP/6-31G(d,p) and MP2/6-31G(d,p) theoretical frequencies. Torsion frequencies are not included. [b] Italic: calculated at MP2/6-31G(d,p).

TABLE 3: Relative Energies[a] (Δ*E*, kcal/mol) for the Torsional Potential Energy of the Three Title Ether Molecules, Alkylmethoxy Radicals, and Methoxyalkyl Radicals

torsion angle	Δ*E*[a]	rrelative fraction	av $\Delta H^{\circ}_{\mathrm{f298}}$[b]	$\Delta H^{\circ}_{\mathrm{f298}}$[c]	torsion angle	Δ*E*	relative fraction	av $\Delta H^{\circ}_{\mathrm{f298}}$	$\Delta H^{\circ}_{\mathrm{f298}}$	torsion angle	Δ*E*	relative fraction	av $\Delta H^{\circ}_{\mathrm{f298}}$	$\Delta H^{\circ}_{\mathrm{f298}}$
CCOC			−52.27	**−52.22**	**C2COC**			−60.14	**−60.13**	**C3COC**			−67.78	**−67.78**
C−COC					C2−COC					C3−COC				
0	3.22				2.2	3.16				6	3.22			
59.9	0.00				61.2	0.00				68.3	0.00			
CC−OC					C2C−OC					C3C−OC				
0.0	6.67				3.3	4.98				0	2.90			
75.3	1.42	0.0175			64.3	2.12	0.0035			62	0.00			
118.5	2.62				122.3	4.98								
180.0	0.00	0.9649[d]			197.8	0.00	0.8720[e]							
241.5	2.62				241.5	1.15								
284.7	1.42	0.0175			284.7	0.00	0.1246							
CCO−C					C2CO−C					C3CO−C				
0.1	2.63				4.5	1.88				0	1.58			
60.7	0.00				66.5	0.00				61.7	0.00			
C$^{\bullet}$COC			−1.72	**−1.67**	**C2$^{\bullet}$COC**			−10.14	**−10.06**	**C3$^{\bullet}$COC**			−17.77	**−17.74**
C$^{\bullet}$−COC					C2$^{\bullet}$−COC					C3$^{\bullet}$−COC				
0	0.14				0	0.85				0	1.13			
22.9	0				67.5	1.6				41.4	1.73			
96	1.45				153.8	0				149.7	0			
166.8	0				225	1.59				225	1.91			
276.5	0.9				315	0.46	0.0812			315	0.26	0.0740		
C$^{\bullet}$C−OC					C2$^{\bullet}$C−OC					C3$^{\bullet}$C−OC				
0.5	5.20				2.8	4.76				0.0	2.75			
70.8	0.21	0.1298			64.3	1.91	0.0070			61.8	0.00	0.1148		
118.8	2.26				125.4	5.95				124.2	4.22			
177.6	0.00	0.7404[f]			200.4	1.07	0.0290			180.0	1.63	0.0073		
241.2	2.26				241.7	2.09				235.8	4.22			
289.0	0.21	0.1298			290.9	0.00	0.8828[d]			298.2	0.00	0.8038[e]		
C$^{\bullet}$CO−C					C2$^{\bullet}$CO−C					C3$^{\bullet}$CO−C				
0.8	2.69				1.3	2.15				−4.6	1.53			
61.4	0.00				61.6	0.00				61.9	0.00			
CCOC$^{\bullet}$			−8.01	**−7.93**	**C2COC$^{\bullet}$**			−16.83	**−16.75**	**C3COC$^{\bullet}$**			−24.54	**−24.54**
C−COC$^{\bullet}$					C2−COC$^{\bullet}$					C3−COC$^{\bullet}$				
0.1	3.19				1.9	3.12				1.6	3.23			
60.0	0.00				160.8	0				59.5	0			
CC−OC$^{\bullet}$					C2C−OC$^{\bullet}$					C3C−OC$^{\bullet}$				
−2.3	4.58				−0.3	4.19				−2.3	2.07			
84.9	0.85	0.0499			67.9	2.19	0.0043			59.5	0.00			
118.2	1.32				121.7	4.23								
183.0	0.00	0.8380[f]			207.3	0.50	0.0739							
236.4	1.31				238.5	0.95								
282.6	0.37	0.1122			283.9	0.00	0.8595[d]							
CCO−C$^{\bullet}$					C2CO−C$^{\bullet}$					C3CO−C$^{\bullet}$				
0	0.79				0	1.11				0	0.96			
29.3	0				30	0.6	0.0624			30.4	0			
96.5	5.67				96.6	5.7				100.1	4.13			
183.6	0				182.2	0				183.1	0			
274.4	5.67				285	6.63				285	5.5			
CC$^{\bullet}$OC			−9.32	**−9.31**	**C2C$^{\bullet}$OC**			−17.33	**−17.33**					
C−C$^{\bullet}$OC					C2−C$^{\bullet}$OC									
−7.4	1.25				6.18	1.82								
52.4	0				65.8	0								
CC$^{\bullet}$-OC					C2C$^{\bullet}$-OC									
0.0	0.74				0.0	1.13								
30.30	0.00				38.3	0.00								
105.76	4.90	0.9943[d]			104.63	2.49								
176.20	2.10	0.0057			174.96	0.00								
269.92	4.95				279.38	2.94								
CC$^{\bullet}$O−C					C2C$^{\bullet}$O−C									
1.6	1.57				−8.7	2.01								
62.9	0.00				54.7	0.00								

[a] Relative energies were calculated as the difference in total energies + scaled (0.9806) zero-point vibrational energies + thermal correction to 298 K, where the corresponding torsional frequencies are excluded in the calculation of ZPVE and thermal correction. Base on B3LYP/6-31G(d) level of theory. [b] The average values at six levels (MP2/6-311+G(2df,2p)//6-31G(d,p), B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p), CBSQ//B3LYP/6-31G(d,p), CBSQ//MP2/6-31G(d,p), G3MP2//MP2/6-31G(d,p), and G3MP2//B3LYP/6-31G(d,p)). [c] The statistical distribution of rotational conformers is included. [d] Also includes 4 isomers from rotation about 2 $-CH_3$ groups. [e] Also includes 6 isomers from rotation about 3 $-CH_3$ groups. [f] Also includes 2 isomers from rotation about a $-CH_3$ group and 1 isomer from rotation about a $-C^{\bullet}H_2$ group.

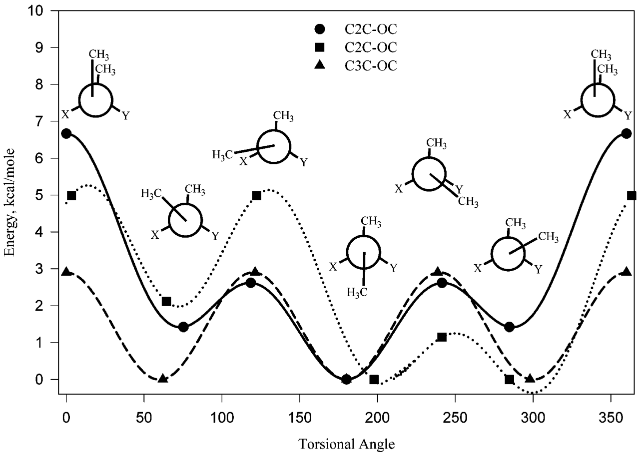


Figure 1. Potential barriers for internal rotations about the central C−O bond in methyl ethyl ether (CCOC), methyl isopropyl ether (C2COC), and methyl *tert*-butyl ether (C3COC). Points are calculated values at the B3LYP/6-31G(d) level of theory for CC−OC, C2C−OC, and C3C−OC, in circles, squares, and triangles, respectively. Lines are results of the Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S2).

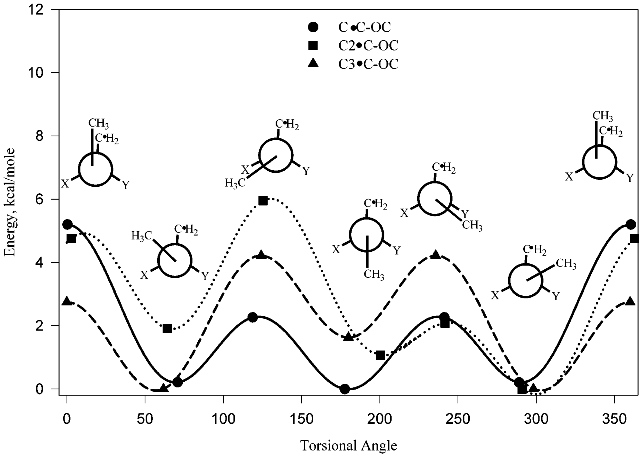


Figure 2. Potential barriers for internal rotations about the central C−O bond in alkyl methoxyl radicals ($C^\bullet C$−OC, $C2^\bullet C$−OC, and $C3^\bullet C$−OC bonds). Points are calculated values at the B3LYP/6-31G(d) level of theory for $C^\bullet C$−OC, $C2^\bullet C$−OC, and $C3^\bullet C$−OC, in circles, squares, and triangles, respectively. Lines are results of the Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S2).

The maxima barriers about rotation of the central C−O bond in CC−OC, C2C−OC, and C3C−OC are higher than those of the alkoxymethyl and methoxyalkyl radicals. These barriers decrease with an increase in methyl substitution on ether carbon.

Methyl Rotations about the CH_3−O Bonds. Potential curves for rotations of the CH_3 group on the oxygen atom show 3-fold symmetrical potentials with barriers of 2.63, 1.88, and 1.58 kcal/mol for CCO−C, C2CO−C, and C3CO−C, respectively. The CH_3−O barriers are slightly increased when there is a radical across the ether link on the alkyl chain, with barriers heights of 2.69, 2.15, and 1.53 kcal/mol for ($C^\bullet CO$−C, $C2^\bullet CO$−C, and $C3^\bullet CO$−C). The barriers decrease with an increase in methyl substitution. Rotation of the terminal C−O bond on the $C2C^\bullet OC$ radical has higher a barrier than that of $CC^\bullet OC$, by 0.44 kcal/mol.

Rotation about C−C Bonds. The rotation barrier of C−C bond in the three title ethers and the alkoxymethyl radicals is about 3.2 kcal/mol and this is not significantly changed by methyl substitution.

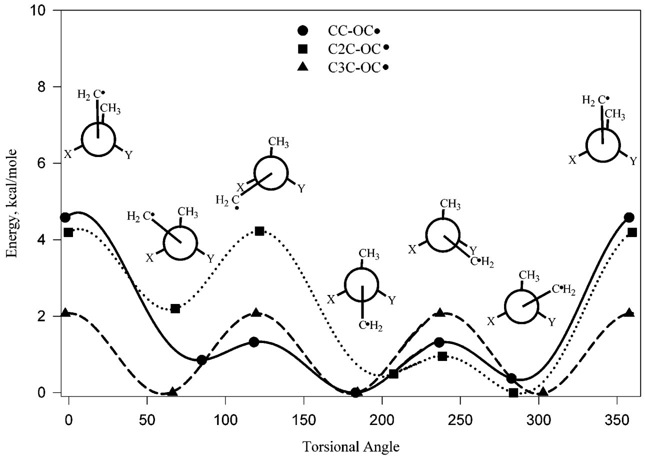


Figure 3. Potential barriers for internal rotations about the central C−O bond in methoxyalkyl radicals ($CC−OC^\bullet$, $C2C−OC^\bullet$, and $C3C−OC^\bullet$ bonds). Points are calculated values at the B3LYP/6-31G(d) level of theory for $CC−OC^\bullet$, $C2C−OC^\bullet$, and $C3C−OC^\bullet$, in circles, squares, and triangles, respectively. Lines are results of the Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S2).

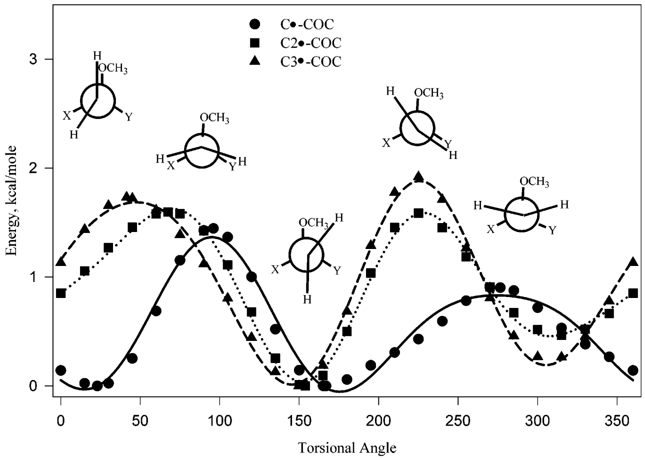


Figure 4. Calculated potential curve of the rotation of the $−C^\bullet H_2$ group in alkyl methoxyl radicals ($C^\bullet$−COC, $C2^\bullet$−COC, and $C3^\bullet$−COC bonds). Points are calculated values at the B3LYP/6-31G(d) level of theory for $C^\bullet$−COC, $C2^\bullet$−COC, and $C3^\bullet$−COC, in circles, squares, and triangles, respectively. Lines are results of the Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S2).

Rotation about $−C^\bullet H_2$ in Methoxyalkyl Radicals ($C^\bullet COC$, $C2C^\bullet OC$, and $C3^\bullet COC$). Figure 4 shows the calculated potential curve for rotation of the $−C^\bullet H_2$ group in the methoxyalkyl radicals ($C^\bullet$−COC, $C2^\bullet$−COC, and $C3^\bullet$−COC bonds). The $−C^\bullet H_2$ torsions are approximated by 2-fold rotation potential.

In $C^\bullet COC$, two minima are located at H−C−C−O dihedral angles of 23° and 167°, where one H atom of the $−C^\bullet H_2$ group is near anti to the CH_3 group. The maxima occur when the unpaired electron orbital of the $−C^\bullet H_2$ group is near the eclipsed position (H−C−C−O dihedral angles of 96°) and anti (H−C−C−O dihedral angles of 276°) with the $−CH_3$ group. The eclipse structure has a 0.47 kcal/mol higher energy than that of the anti structure.

For $−C^\bullet H_2$ rotation in $C2^\bullet COC$ and $C3^\bullet COC$, there is no minimum located at the H−C−C−O dihedral angles of ∼30°, due to repulsion of the $−CH_3$ group on the oxygen (C−O−C−C dihedral angle = 180° in $C^\bullet COC$, but ∼−60° in $C2^\bullet COC$ and $C3^\bullet COC$). Two maxima occur when a H atom of the -$C^\bullet H_2$ group is eclipsed to the methyl group. The maximum barrier

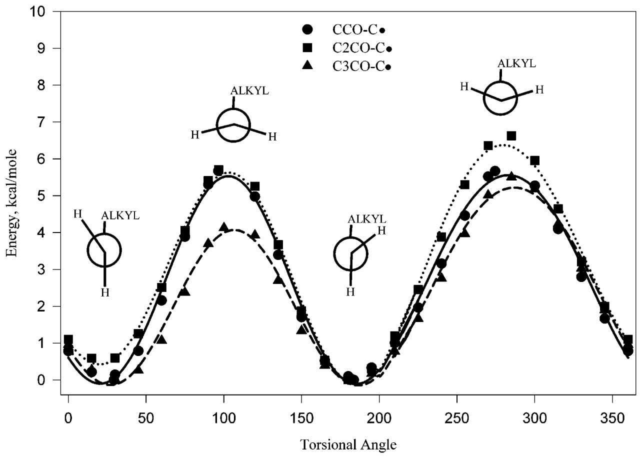


Figure 5. Calculated potential curve of the rotation of the $-C^{\bullet}H_2$ group in methoxyalkyl radicals ($CCO-C^{\bullet}$, $C2CO-C^{\bullet}$, and $C3CO-C^{\bullet}$ bonds). Points are calculated values at the B3LYP/6-31G(d) level of theory for $CCO-C^{\bullet}$, $C2CO-C^{\bullet}$, and $C3CO-C^{\bullet}$, in circles, squares, and triangles, respectively. Lines are results of the Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S2).

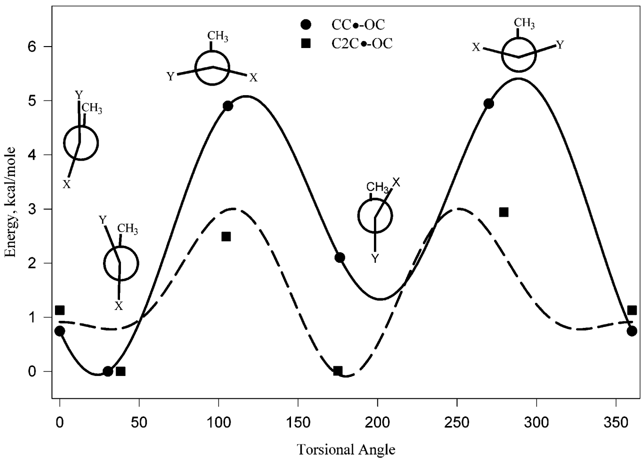


Figure 6. Calculated potential curve for the rotation of the $-C^{\bullet}C$ and $-C^{\bullet}C2$ groups on $CC^{\bullet}OC$ and $C2C^{\bullet}OC$ radicals, respectively. Points are calculated values at the B3LYP/6-31G(d) level of theory for $CC^{\bullet}-O-C$ and $C2C^{\bullet}=OC$, in circles and squares, respectively. Lines are results of the Fourier expansion equation, F1, with the coefficients listed in the Supporting Information (Table S2).

for rotation of the $-C^{\bullet}H_2$ group in $C3^{\bullet}COC$ is higher than corresponding barriers in $C^{\bullet}COC$ and $C2^{\bullet}COC$ radicals by 0.36 and 0.17 kcal/mol, respectively.

The barriers for rotation of $-C^{\bullet}H_2$ radicals bonded to an ether carbon are lower than the corresponding barriers in the parent molecules by 1.77, 1.56, and 1.31 kcal/mol for $C^{\bullet}-COC$, $C2^{\bullet}-COC$, and $C3^{\bullet}-COC$, respectively. This is consistent with the rotational barrier of the ethyl radical (0.1 kcal/mol[41]), which has a much lower barrier than CH_3-CH_3 in ethane (2.9 kcal/mol[42]).

Rotation about $-C^{\bullet}H_2$ in Alkoxymethyl Radicals ($CCOC^{\bullet}$, $C2COC^{\bullet}$, and $C3COC^{\bullet}$). Figure 5 shows the calculated potential curve for rotation of the $-C^{\bullet}H_2$ group in alkoxymethyl radicals ($CCO-C^{\bullet}$, $C2CO-C^{\bullet}$, and $C3CO-C^{\bullet}$). The $-C^{\bullet}H_2$ torsions are approximated by a 2-fold rotation potential. The maxima occur at the unpaired electron orbital of the $-C^{\bullet}H_2$ group eclipsed and anti with the alkyl group ($CC^{\bullet}$, $C2C^{\bullet}$, and $C3C^{\bullet}$). In contrast with the rotational barriers on the $-C^{\bullet}H_2$ radicals bonded to ether carbons, the rotational barriers for $-C^{\bullet}H_2$ bonded to an ether link are significantly higher than barriers in parent molecules: barriers are 3.0, 4.75, and 3.92 kcal/mol for $CCO-C^{\bullet}$, $C2CO-C^{\bullet}$, and $C3CO-C^{\bullet}$, respectively. The radical electron is delocalized between the carbon and the oxygen atom in a π^* orbital for the lowest energy conformer.

Rotation about $-C^{\bullet}C$ and $-C^{\bullet}C2$ Groups in $CC^{\bullet}OC$ and $C2^{\bullet}COC$. Figure 6 shows the calculated potential curve for rotation of the $-C^{\bullet}C$ and $-C^{\bullet}C2$ groups on $CC^{\bullet}OC$ and $C2C^{\bullet}OC$ radicals, respectively. Two minima are located when the unpaired electron orbital of the $-C^{\bullet}C$ and $-C^{\bullet}C2$ groups hyperconjugate with the antibonding orbital of the oxygen atom. The rotational barrier of the $-C^{\bullet}C$ group is higher than the barrier of rotation about the $-C^{\bullet}C2$ group by 2 kcal mol^{-1}, due to the stabilization resulting from the hyperconjugation and the repulsion between two methyl groups bonded to the ether carbon and the ether link.

3. Thermodynamic Properties: ΔH°_{f298}, $S^{\circ}(T)$'s, and $C_p(T)$'s ($50 \leq T/K \leq 5000$). *ΔH°_{f298}.* Total energies, zero-point vibration energies, and thermal contributions to enthalpy calculated at levels of theory in this study are listed in Table 4. The zero point vibration energy (ZPVE) are scaled by 0.9806 and 0.9608 for B3LYP/6-31G(d) and MP2/6-31G(d,p) theoretical frequencies, respectively. The frequencies are not scaled in calculation of the vibration component of the thermal contribution to enthalpy. Enthalpies of formation (ΔH°_{f298}) and uncertainties for species used in the working reactions were adopted from literature data listed in Table 5. The accuracy of our theoretical ΔH°_{f298} values is controlled by several factors: the choice of the working chemical reactions used to cancel errors, the level of sophistication (method + basis set) applied to calculate the electronic energy, the uncertainty of the ZPVE's and thermal corrections, and the reliability of the ΔH°_{f298} of reference compounds. The enthalpies of isodesmic reaction 1 listed in Table 6 are all within +0.2 to −4.13 kcal/mol of being thermoneutral; this signifies that both products and reactants have similar energies and that the chosen isodesmic reaction will likely have good cancellation of the errors. The maximum uncertainty in enthalpy values for the reference compounds and the statistical standard deviations from the all calculation levels in the isodesmic reactions are also listed in Table 6. We assumed that our calculations on species in the isodesmic reactions have similar error ranges for the ZPVE's and thermal corrections, and we assigned the cumulative uncertainty corrections to be 0.44 kcal/mol from Scott and Radom reported errors. The energy difference values at the B3LYP/6-31G(d) level were used to calculate the statistical distribution of rotation conformers. The energy difference of the conformers and relative fraction are listed in Table 3.

Table 7 lists the calculated ΔH°_{f298} for three ethers and the corresponding radicals at various levels. Our recommended ΔH°_{f298} data listed in the last column of Table 7 and in column 3 in Table 8 are the average values of the six levels (MP2/6-311+G(2df,2p)//MP2/6-31G(d,p), B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p), CBSQ//B3LYP/6-31G(d,p), CBSQ//MP2/6-31G(d,p), G3MP2//MP2/6-31G(d,p), and G3MP2//B3LYP/6-31G(d,p)), in which the statistical distribution of rotation conformers is included. Analysis of the data from these six calculation levels using the work reaction analysis shows that enthalpies for each species are all within ±1.26 kcal/mol. The errors of ΔH°_{f298} were calculated by summing the deviations between various levels, the errors from the ZPVEs and thermal corrections, and the maximum uncertainties in enthalpy of the reference compounds.

The calculated ΔH°_{f298} (in kcal/mol) for CCOC and C2COC in this work are -52.22 ± 0.84 and -60.13 ± 0.94, which are in good agreement with the results of Pilcher,[1] -51.73 ± 0.16

TABLE 4: Total Energies, Zero-Point Vibration Energies (ZPVE, Unscaled) and Thermal Corrections to Enthalpies ($H^\circ_{298} - H^\circ_0$)

	//B3LYP/6-31G(d,p)					//MP2/6-31G(d,p)				
	total energy (0 K, hartree)					total energy (0 K, hartree)				
	CBSQ	G3MP2	B3LYP/6-311+G(3df,2p)	ZPVE[a] (hartree)	$[H^\circ_{298} - H^\circ_0]$[b] (kcal/mol)	CBSQ	G3MP2	MP2/6-311+G(2df,2p)	ZPVE	$[H^\circ_{298} - H^\circ_0]$ (kcal/mol)
$CH_3CH_2OCH_3$	−193.9804122	−194.0185491	−194.3140999	68.05	4.06	−193.9795772	−194.0076506	−193.8242518	70.15	4.02
$C^\bullet H_2CH_2OCH_3$	−193.3190384	−193.3562787	−193.6555715	58.27	4.31	−193.3178869	−193.3453429	−193.1672286	60.30	4.23
$CH_3C^\bullet HOCH_3$	−193.3313591	−193.3678148	−193.6690351	59.23	4.23	−193.3300967	−193.3567877	−193.1782715	61.29	4.15
$CH_3CH_2OC^\bullet H_2$	−193.3288905	−193.3657838	−193.6656962	59.33	4.11	−193.3277187	−193.3548207	−193.1766571	61.31	4.01
$(CH_3)_2CHOCH_3$	−233.2106547	−233.2591013	−233.6158115	85.61	4.87	−233.2096532	−233.2457446	−233.0183852	88.22	4.81
$C^\bullet H_2CH(CH_3)OCH_3$	−232.5500476	−232.5974631	−232.9579039	76.28	5.01	−232.5488215	−232.5840959	−232.3620025	78.76	4.90
$(CH_3)_2C^\bullet OCH_3$	−232.5617017	−232.6082701	−232.9719157	76.98	5.03	−232.5603759	−232.5948317	−232.3720286	79.69	4.88
$(CH_3)_2CHOC^\bullet H_2$	−232.5604424	−232.6077034	−232.9688658	76.94	4.84	−232.5591336	−232.5942738	−232.3722070	79.45	4.71
$(CH_3)_3COCH_3$	−272.4417741	−272.4997255	−272.9151776	103.00	5.69	−272.4406734	−272.4839076	−272.2129960	106.13	5.62
$C^\bullet H_2(CH_3)_2COCH_3$	−271.7811931	−271.8381653	−272.2576048	93.62	5.88	−271.7796785	−271.8221693	−271.5564203	96.74	5.66
$(CH_3)_3COC^\bullet H_2$	−271.7919267	−271.8483829	−272.2684608	94.26	5.69	−271.7904517	−271.8324315	−271.5667294	97.33	5.50
H	−0.4998179	−0.5021409		0.00	1.48	−0.4998179	−0.5018389		0.00	1.48
C	−37.7851517	−37.7907852		0.00	1.48	−37.7851518	−37.7893382		0.00	1.48
O	−74.9870573	−74.9920641		0.00	1.48	−74.9870595	−74.9897741		0.00	1.48

[a] Unscaled zero-point vibrational energies. In the calculation of reaction enthalpies, ZPVE is scaled 0.9806 and 0.9608 for B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels, respectively. [b] Thermal correction: Thermal corrections are calculated as follows for $T = 298.15$ K: $H^\circ_T - H^\circ_0 = H_{trans}(T) + H_{rot}(T) + \Delta H_{vib}(T) + RT$; $H_{trans}(T) = (3/2)RT$, $H_{rot}(T) = (3/2)RT$, $\Delta H_{vib}(T) = N_A h \sum \nu_i/(\exp(h\nu_i/kT) - 1)$, where N_A is the Avogadro constant, h is the Planck constant, k is the Boltzmann constant, and ν_i is the vibrational frequency.

TABLE 5: ΔH°_{f298} for Species in Isodesmic Reactions and Bond Energy Calculations

species	ΔH°_{f298} (kcal/mol)	ref
CH_3OH	−48.07 ± 0.05	44
C_2H_5OH	−56.23 ± 0.12	44
$(CH_3)_2CHOH$	−65.19	45
$(CH_3)_3COH$	−74.72 ± 0.21	46
CH_3OCH_3	−43.99 ± 0.12	1
C_2H_6	−20.24±0.12	47
$CH_3^\bullet$	34.82	48
s-C_3H_7	22 ± 0.5	49
t-C_4H_9	11 ± 0.7	49
$CH_3OC^\bullet H_2$	0.31 ± 0.69	*a*, *b*
$CH_3O^\bullet$	4.1 ± 1.	49
$CH_3CH_2O^\bullet$	−2.65 ± 1.97	*a*, *c*
$(CH_3)_2CHO^\bullet$	−11.75 ± 1.83	*a*, *c*
$(CH_3)_3CO^\bullet$	−20.86 ± 2.08	*a*, *c*
species	ΔH°_{f0} (kcal/mol)[d]	ref
H	51.63	50
C	169.58	50
O	58.99	50

[a] Based on average values of B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p), MP2/6-311+G(2df,2p)//MP2/6-31G(d,p), CBSQ, and G3(MP2) with B3LYP/6-31G(d,p) and MP2/6-31G(d,p) calculations. [b] Using the isodesmic reaction $CH_3OC^\bullet H_2 + C_2H_6 = CH_3OCH_3 + C_2H_5$ and bond dissociation enthalpies of $\Delta H^\circ_{298}(CH_3CH_2{-}H)$ (101.1 kcal/mol). [c] Using the isodesmic reaction $(CH_3)_xCH_{3-x}O^\bullet + CH_3OH = (CH_3)_xCH_{3-x}OH + CH_3O^\bullet$ ($x = 1-3$). [d] Experimental values of ΔH°_{f0}(elements) for calculation. ΔH°_{f298} values based on atomization procedures.

and 60.24 ± 0.23; Pedley,[5] −51.72 ± 0.17 and −60.23 ± 0.24; Cohen,[6] −51.89 and −60.21; and Verevkin,[7] −51.94 and −60.13. The ΔH°_{f298} of C3COC = −67.78 ± 1.44 kcal/mol in this work is also in agreement with data of Fenwick,[2] −67.68 ± 0.31 kcal/mol; Pedley,[5] −67.76 ± 0.26 kcal/mol; Cohen,[6] −68.81 kcal/mol; and Verevkin,[7] −67.81 kcal/mol, but 2.3 kcal/mol higher than the Smutny[3] value of −70.00 kcal/mol. We note that Cox et al.[4] reanalyzed Smutny's value for pressure correction and reported the value of −67.45 ± 0.45 kcal/mol.

The recommended ΔH°_{f298} values (in kcal/mol) are −1.67 ± 0.98, −10.06 ± 0.8,5 and −17.74 ± 1.13 for C•COC, C2•COC, and C3•COC, respectively, −7.93 ± 1.81, −16.75 ± 1.71, and −24.54 ± 1.97 for CCOC•, C2COC•, and C3COC•, respectively, and −9.31 ± 2.18 and −17.33 ± 2.38 for CC•OC and C2C•OC.

The calculated ΔH°_{f298} values based on atomization procedures ($\Delta H^\circ_{f298,AT}$) are compared with the above recommended ΔH°_{f298} group balance isodesmic reaction analysis in Table 9. The mean deviations (MDs), mean absolute deviations (MADs), and largest deviations (LDs) are also shown in Table 9. The $\Delta H^\circ_{f298,AT}$ values from CBSQ with both DFT and MP2 geometries have best overall agreement with recommended ΔH°_{f298} values. The $\Delta H^\circ_{f298,AT}$ values from G3MP2//MP2/6-31G(d,p) show a systematic deviations which increases with increasing size of molecule.

S°(T)'s, and $C_p(T)$'s (50 ≤ T/K ≤ 5000). S°_{298} and $C_p(T)$ (300 ≤ T/K ≤ 1500) calculation results using B3LYP/6-31G(d,p) and MP2/6-31G(d,p) determined geometries and harmonic frequencies are summarized in Table 8. TVR represents the sum of the contributions from translations, external rotations, and vibrations for S°_{298} and $C_p(T)$'s. The frequencies were scaled by 1.0015 and 1.0232 for B3LYP/6-31G(d) and MP2/6-31G(d,p) theoretical frequencies, respectively, in calculation of the vibration component of the thermal contribution to entropy. The frequencies were not scaled in calculation of the vibration component of the thermal contribution to heat capacity. S°_{298} and $C_p(T)$ contributions from hindered rotors are represented as IR, which were calculated by direct integration over

TABLE 6: Isodesmic Reaction Enthalpies (298 K) for Ethers and the Corresponding Radicals

	//B3LYP/6-31G(d,p)			//MP2/6-31G(d,p)					
	G3MP2	CBSQ	B3LYP/6-311+G(3df,2p)	G3MP2	CBSQ	MP2/6-311+G(2df,2p)	$\Delta H_{\mathrm{rxn,lit.}}$[a]	SD[b]	limited errors[c]
$(CH_3)_xCH_{3-x}OCH_3 + CH_3OH \leftrightarrow (CH_3)_xCH_{3-x}OH + CH_3OCH_3$									
$x = 1$	0.13	0.17	−0.11	0.16	0.20	0.17	−0.35 ± 0.62	±0.11	±0.29
$x = 2$	−1.07	−0.88	−1.57	−0.74	−0.85	−0.67	−0.90 ± 0.62	±0.33	±0.17
$x = 3$	−2.71	−2.60	−4.13	−2.62	−2.54	−2.58	−2.39 ± 1.4	±0.62	±0.38
$C^{\bullet}H_2C(CH_3)_{x-1}CH_{3-x}OCH_3 + CH_3CH_3 \leftrightarrow (CH_3)_xCH_{3-x}OCH_3 + CH_3C^{\bullet}H_2$									
$x = 1$	−1.52	−1.55	−1.34	−1.60	−1.64	−1.68		±0.12	±0.42
$x = 2$	−1.01	−0.96	−0.84	−1.07	−0.98	−1.16		±0.11	±0.30
$x = 3$	−1.02	−0.99	−0.68	−1.08	−1.03	−1.23		±0.18	±0.51
$(CH_3)_xCH_{3-x}OC^{\bullet}H_2 + CH_3OCH_3 \leftrightarrow (CH_3)_xCH_{3-x}OCH_3 + CH_3OC^{\bullet}H_2$									
$x = 1$	0.04	0.04	0.14	0.00	0.01	−0.01		±0.06	±1.31
$x = 2$	0.97	0.94	1.14	0.95	0.94	0.97		±0.08	±1.19
$x = 3$	0.97	1.13	1.25	0.96	1.15	0.93		±0.13	±1.40
$C^{\bullet}(CH_3)_xH_{2-x}OCH_3 + CH_3OCH_3 \leftrightarrow (CH_3)_xCH_{3-x}OCH_3 + CH_3OC^{\bullet}H_2$									
$x = 1$	1.19	1.46	2.11	1.11	1.37	0.87		±0.43	±1.31
$x = 2$	1.13	1.53	2.86	1.13	1.55	0.69		±0.74	±1.19

[b] Literature values of ΔH°_{f298}(three title ethers) are listed in column 3 in Table 8. ΔH°_{f298}(alcohols and CH_3OCH_3) are listed in Table 5. [b] Statistical standard deviations. [c] Uncertainly in enthalpy values for the reference compounds.

TABLE 7: Calculated Enthalpies of Formation (ΔH°_{f298} (kcal/mol), 298 K) for Ethers and the Corresponding Radicals

	//B3LYP/6-31G(d,p)			//MP2/6-31G(d,p)			
	G3MP2	CBSQ	B3LYP/6-311+G(3df,2p)	G3MP2	CBSQ	MP2/6-311+G(2df,2p)	recommend[a]
$CH_3CH_2OCH_3$	−52.28	−52.32	−52.04	−52.31	−52.35	−52.32	−52.22 ± 0.84
$(CH_3)_2CHOCH_3$	−60.04	−60.23	−59.54	−60.37	−60.26	−60.44	−60.13 ± 0.94
$(CH_3)_3COCH_3$	−67.93	−68.04	−66.51	−68.02	−68.10	−68.06	−67.78 ± 1.44
$C^{\bullet}H_2CH_2OCH_3$	−1.76	−1.77	−1.70	−1.71	−1.71	−1.64	−1.67 ± 0.98
$C^{\bullet}H_2CH(CH_3)OCH_3$	−10.03	−10.27	−9.70	−10.30	−10.27	−10.28	−10.06 ± 0.85
$C^{\bullet}H_2(CH_3)_2COCH_3$	−17.91	−18.05	−16.83	−17.94	−18.07	−17.83	−17.74 ± 1.13
$CH_3CH_2OC^{\bullet}H_2$	−8.02	−8.06	−7.89	−8.02	−8.06	−8.01	−7.93 ± 1.81
$(CH_3)_2CHOC^{\bullet}H_2$	−16.71	−16.86	−16.37	−17.02	−16.89	−17.11	−16.75 ± 1.71
$(CH_3)_3COC^{\bullet}H_2$	−24.60	−24.87	−23.46	−24.68	−24.95	−24.70	−24.54 ± 1.97
$CH_3C^{\bullet}HOCH_3$	−9.17	−9.49	−9.86	−9.12	−9.42	−8.89	−9.31 ± 2.18
$(CH_3)_2C^{\bullet}OCH_3$	−16.87	−17.46	−18.09	−17.20	−17.51	−16.83	−17.33 ± 2.38

[a] The average values at six levels (MP2/6-311+G(2df,2p)//6-31G(d,p), B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p), CBSQ//B3LYP/6-31G(d,p), CBSQ//MP2/6-31G(d,p), G3MP2//MP2/6-31G(d,p), and G3MP2//B3LYP/6-31G(d,p)), in which the statistical distribution of rotation conformers is included.

energy levels of the exact potential curve obtained at the B3LYP/6-31G(d) level. We do not include a separate calculation for the entropy of mixing because the calculation of a partition function for the corresponding internal rotor includes the contribution for each conformer. Entropies and heat capacities at temperatures from 50 to 5000 K are listed in Table 10. Differences are within 0.88 cal/(mol K) (S°_{900} of $C3COC^{\bullet}$) and 1.09 cal/(mol K) ($C_p(500)$ of $C3COC^{\bullet}$) for MP2 and DFT-determined $S^{\circ}(T)$'s and $C_p(T)$'s, respectively.

Our calculated values of $S^{\circ}_{298}(CCOC) = 74.71$, $S^{\circ}_{298}(C2COC) = 82.31$, and $S^{\circ}_{298}(C3COC) = 86.55$ are higher than the data of Stull,[11] 74.24 (CCOC), 80.86 (C2COC), and 84.36 (C3COC), by ca. 0.5, 1.5, and 2.0 cal/(mol K), respectively, and ca. 1 cal/(mol K) higher than the results from Andon,[10] $S^{\circ}_{298}(C2COC) = 81.64$ and $S^{\circ}_{298}(C3COC) = 85.52$, and Guthrie,[12] $S^{\circ}_{298}(C2COC) = 81.33$. The calculated S°_{298} values (in cal/(mol K)) for corresponding radicals of three title ethers are $S^{\circ}_{298}(C^{\bullet}COC) = 80.18$, $S^{\circ}_{298}(C2^{\bullet}COC) = 83.54$, $S^{\circ}_{298}(C3^{\bullet}COC) = 92.37$, $S^{\circ}_{298}(CCOC^{\bullet}) = 77.97$, $S^{\circ}_{298}(C2COC^{\bullet}) = 83.74$, $S^{\circ}_{298}(C3COC^{\bullet}) = 88.89$, $S^{\circ}_{298}(CC^{\bullet}OC) = 76.34$, and $S^{\circ}_{298}(C2C^{\bullet}OC) = 84.62$.

The calculated heat capacities are in good agreement with the values of Stull[11] for three title ethers and with Chao's[9] value for CCOC at 300 K; but they are ca. 1−2 cal/(mol K) higher than values of Stull and Chao at 1000 K. $C_p(300)$ of methyl ethyl, methyl isopropyl, and methyl *tert*-butyl ethers and the corresponding radicals are determined to be $C_p(300)$ (CCOC) = 22.18 cal/(mol K), $C_p(300)$ (C2COC) = 26.69 cal/(mol K), $C_p(300)$ (C3COC) = 32.70 cal/(mol K), $C_p(300)$ ($C^{\bullet}COC$) = 21.14 cal/(mol K), $C_p(300)$ ($C2^{\bullet}COC$) = 28.07 cal/(mol K), $C_p(300)$ ($C3^{\bullet}COC$) = 33.80 cal/(mol K), $C_p(300)$ ($CCOC^{\bullet}$) = 20.81 cal/(mol K), $C_p(300)$ ($C2COC^{\bullet}$) = 27.02 cal/(mol K), $C_p(300)$ ($C3COC^{\bullet}$) = 33.11 cal/(mol K), $C_p(300)$ ($CC^{\bullet}OC$) = 21.35 cal/(mol K), and $C_p(300)$ ($C2C^{\bullet}OC$) = 27.15 cal/(mol K).

4. Bond Energies. The C−H, C−C, and C−O bond energies for methyl ethyl, methyl isopropyl, and methyl *tert*-butyl ethers at various calculation levels are presented in Table 11 with ΔH°_{f298} of alkyl and alkoxy radicals in Table 5. The recommended values are listed in column 8 in Table 11. Average values of C−H bond energies on primary carbons removed from the ether oxygen atom by one carbon are 102.1−102.7 kcal/mol, which is about 1 kcal/mol greater than a primary C−H bond on ethane, propane, etc. Carbon−hydrogen bond strengths on methyl groups adjacent to the ether oxygen are range from 95.3 to 96.4 kcal/mol. Carbon−hydrogen bonds on both secondary and tertiary sites adjacent to the oxygen atoms are similar and average values are 95.0 and 94.9 kcal/mol. Methoxy−carbon bonds range from 82.9 to 86.2 kcal/mol and alkoxy−methyl bonds are 81.7−84.4 kcal/mol. Methyl−carbon bonds on the ether carbons range from 85.3 to 87.3 kcal/mol for tertiary to primary, respectively. Alkoxy−methyl bonds in CCOC and C3COC are ca. 1 kcal/mol weaker than energies of methoxy−carbon bonds, which are also ca. 2 kcal/mol weaker than energies of methyl−carbon bonds.

TABLE 8: Ideal Gas-Phase Thermodynamic Properties, ΔH°_{f298}, S°_{298}, and C_p(300−1500)

species (symmetry no.)		ΔH°_{f298}[a]	S°_{298}[b,e]	$C_p(300)$[b]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$
$CH_3CH_2OCH_3$ (9)	TVR[c,f]		60.91	14.40	19.23	24.12	28.55	35.78	41.24	49.76
			60.63	*14.03*	*18.76*	*23.58*	*27.95*	*35.1*	*40.54*	*49.17*
	IR[d]									
	$CH_3-CH_2OCH_3$		4.29	2.14	2.18	2.08	1.94	1.68	1.49	1.25
	$CH_3CH_2-OCH_3$		5.11	3.67	3.12	2.62	2.24	1.75	1.42	0.90
	$CH_3CH_2O-CH_3$		4.54	2.16	2.08	1.91	1.75	1.50	1.35	1.17
	total[g]	**−52.22 ± 0.84**	**74.72**	**22.18**	**26.37**	**30.46**	**34.18**	**40.37**	**45.15**	**52.78**
	Stull[11]	−51.73 ± 0.16[1]	74.24	21.53	26.08	30.53	34.58	41.19	46.18	
	Pedley[5]	−51.72 ± 0.17								
	Cohen[6]	−51.89								
	Pilcher[1]	−51.73 ± 0.16								
	Verevkin[7]	−51.94								
	Chao[9]			22.30	27.22	31.71	35.63	41.96	46.75	54.24
$C^{\bullet}H_2CH_2OCH_3$ (3)	TVR		64.95	15.31	19.71	23.96	27.73	33.80	38.37	45.55
			64.81	*14.95*	*19.19*	*23.37*	*27.09*	*33.13*	*37.71*	*45.02*
	IR									
	$C^{\bullet}H_2-CH_2OCH_3$		4.80	1.58	1.38	1.26	1.19	1.11	1.07	1.03
	$C^{\bullet}H_2CH_2-OCH_3$		5.99	2.26	2.10	1.93	1.77	1.50	1.27	0.83
	$C^{\bullet}H_2CH_2O-CH_3$		4.51	2.16	2.09	1.93	1.77	1.52	1.37	1.18
	total	**−1.67 ± 0.98**	**80.19**	**21.14**	**25.02**	**28.79**	**32.14**	**37.60**	**41.75**	**48.33**
$CH_3C^{\bullet}HOCH_3$ (9)	TVR		62.27	14.63	18.99	23.29	27.12	33.32	38.00	45.34
			62.05	*14.15*	*18.39*	*22.63*	*26.43*	*32.63*	*37.34*	*44.82*
	IR									
	$CH_3-C^{\bullet}HOCH_3$		5.23	1.73	1.51	1.36	1.26	1.16	1.10	1.04
	$CH_3C^{\bullet}H-OCH_3$		3.84	3.36	3.94	3.89	3.52	2.67	2.02	1.12
	$CH_3C^{\bullet}HO-CH_3$		5.11	1.86	1.63	1.46	1.34	1.21	1.14	1.06
	total	**−9.31 ± 2.18**	**76.35**	**21.34**	**25.76**	**29.66**	**32.90**	**38.00**	**41.92**	**48.30**
$CH_3CH_2OC^{\bullet}H_2$ (3)	TVR		64.48	14.9	19.37	23.67	27.45	33.52	38.11	45.34
			64.21	*14.34*	*18.71*	*22.98*	*26.76*	*32.86*	*37.47*	*44.85*
	IR									
	$CH_3-CH_2OC^{\bullet}H_2$		4.30	2.14	2.18	2.07	1.93	1.67	1.48	1.24
	$CH_3CH_2-OC^{\bullet}H_2$		6.24	2.13	1.83	1.67	1.56	1.37	1.19	0.82
	$CH_3CH_2O-C^{\bullet}H_2$		3.09	1.92	2.14	2.27	2.31	2.22	2.04	1.64
	total	**−7.93 ± 1.81**	**77.97**	**20.81**	**25.19**	**29.33**	**32.90**	**38.45**	**42.51**	**48.80**
$(CH_3)_2CHOCH_3$ (27)	TVR		63.06	18.18	24.55	30.8	36.35	45.33	52.1	62.68
			62.88	*17.71*	*23.86*	*29.99*	*35.49*	*44.44*	*51.23*	*61.99*
	IR									
	$(CH_3)_2-CHOCH_3$		4.32	2.14	2.18	2.07	1.93	1.67	1.48	1.24
	$(CH_3)_2-$CHOCH3		4.41	2.16	2.15	2.02	1.86	1.60	1.43	1.21
	$(CH_3)_2CH-OCH_3$		5.43	2.40	2.37	2.33	2.26	2.07	1.88	1.52
	$(CH_3)_2CHO-CH_3$		4.93	2.04	1.82	1.63	1.49	1.30	1.20	1.09
	total	**−60.13 ± 0.94**	**82.20**	**26.69**	**32.71**	**38.39**	**43.35**	**51.30**	**57.30**	**66.81**
	Stull[11]	−60.24 ± 0.23[1]	80.86	26.67	32.97	38.90	44.17	52.67	59.08	
	Pedley[5]	−60.23 ± 0.24								
	Cohen[6]	−60.21								
	Pilcher[1]	−60.24 ± 0.23								
	Verevkin[7]	−60.13								
	Andon[10]		81.64							
	Guthrie[12]		81.33							
$C^{\bullet}H_2CH(CH_3)OCH_3$ (9)	TVR		67.17	18.96	24.91	30.52	35.41	43.24	49.12	58.39
			66.94	*18.44*	*24.21*	*29.74*	*34.6*	*42.41*	*48.32*	*57.76*
	IR									
	$C^{\bullet}H_2-CH(CH_3)OCH_3$		4.64	1.90	1.58	1.40	1.29	1.16	1.11	1.04
	$CH_3-CH(C^{\bullet}H_2)OCH_3$		4.37	2.15	2.16	2.05	1.90	1.64	1.46	1.23
	$C^{\bullet}H_2CH(CH_3)$-OCH_3		2.66	3.22	3.05	2.77	2.52	2.14	1.86	1.48
	$C^{\bullet}H_2CH(CH_3)O-CH_3$		4.82	2.10	1.92	1.72	1.57	1.36	1.25	1.11
	total	**−10.06 ± 0.85**	**83.54**	**28.07**	**33.27**	**38.07**	**42.28**	**49.13**	**54.40**	**62.94**
$(CH_3)_2C^{\bullet}OCH_3$ (27)	TVR		64.67	18.06	23.85	29.49	34.50	42.61	48.72	58.25
			64.36	*17.57*	*23.17*	*28.7*	*33.67*	*41.74*	*47.86*	*57.57*
	IR									
	$(CH_3)_2-C^{\bullet}OCH_3$		4.94	2.02	1.80	1.61	1.47	1.29	1.19	1.09
	$(CH_3)_2-C^{\bullet}OCH_3$		4.94	2.02	1.80	1.61	1.47	1.29	1.19	1.09
	$(CH_3)_2C^{\bullet}$-OCH_3		5.44	3.19	2.93	2.60	2.28	1.73	1.33	0.75
	$(CH_3)_2C^{\bullet}O-CH_3$		4.79	2.11	1.93	1.74	1.58	1.37	1.25	1.12
	total	**−17.33 ± 2.38**	**84.63**	**27.15**	**31.97**	**36.66**	**40.88**	**47.86**	**53.26**	**61.95**
$(CH_3)_2CHOC^{\bullet}H_2$ (9)	TVR		66.66	18.58	24.6	30.26	35.19	43.06	48.97	58.28
			66.33	*17.89*	*23.77*	*29.38*	*34.3*	*42.2*	*48.16*	*57.66*
	IR									
	$(CH_3)_2-CHOC^{\bullet}H_2$		4.33	2.15	2.17	2.07	1.92	1.66	1.47	1.24
	$(CH_3)_2-CHOC^{\bullet}H_2$		4.28	2.13	2.19	2.10	1.97	1.70	1.51	1.26
	$(CH_3)_2CH-OC^{\bullet}H_2$		5.71	2.29	2.29	2.22	2.08	1.74	1.42	0.86
	$(CH_3)_2CHO-C^{\bullet}H_2$		2.91	2.22	2.30	2.36	2.38	2.28	2.10	1.69
	Total	**−16.75 ± 1.71**	**83.75**	**27.02**	**33.14**	**38.57**	**43.10**	**50.01**	**55.07**	**63.02**

TABLE 8 (Continued)

species (symmetry no.)		ΔH°_{f298}[a]	S°_{298}[b,e]	$C_p(300)$[b]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$
$(CH_3)_3COCH_3$ (243)	TVR		62.66	22.47	30.32	37.81	44.40	55.03	63.04	75.63
			62.32	*21.81*	*29.42*	*36.79*	*43.34*	*53.95*	*62*	*74.81*
	IR									
	$(CH_3)_3-COCH_3$		4.25	2.12	2.20	2.12	1.99	1.72	1.53	1.27
	$(CH_3)_3-COCH_3$		4.25	2.12	2.20	2.12	1.99	1.72	1.53	1.27
	$(CH_3)_3-COCH_3$		4.27	2.13	2.19	2.11	1.97	1.71	1.52	1.26
	$(CH_3)_3C-OCH_3$		6.32	2.31	2.21	2.00	1.76	1.34	1.03	0.58
	$(CH_3)_3CO-CH_3$		5.13	1.87	1.64	1.46	1.35	1.21	1.14	1.06
	total	**−67.78 ± 1.44**	**86.74**	**32.70**	**40.30**	**47.11**	**52.92**	**62.20**	**69.27**	**80.66**
	Stull[11]	−70 ± 1.2[3]	84.36	32.22	40.18	47.70	54.28	64.36	71.66	
	Pedley[5]	−67.76 ± 0.26								
	Cohen[6]	−68.81								
	Verevkin[7]	−67.81								
	Fenwick[2]	−67.68 ± 0.31								
	Smutny[3]	−70 ± 1.2								
	Cox[4]	−67.45 ± 0.45								
	Andon[10]		85.52							
$C^{\bullet}H_2(CH_3)_2COCH_3$ (27)	TVR		68.9	23.21	30.65	37.51	43.45	52.92	60.05	71.32
			68.48	*22.49*	*29.73*	*36.5*	*42.42*	*51.9*	*59.08*	*70.57*
	IR									
	$C^{\bullet}H_2$-$(CH_3)_2COCH_3$		4.46	2.04	1.75	1.55	1.41	1.24	1.16	1.07
	$C^{\bullet}H_2(CH_3)_2-COCH_3$		4.26	2.13	2.19	2.11	1.98	1.72	1.52	1.27
	$C^{\bullet}H_2(CH_3)_2-COCH_3$		4.26	2.13	2.19	2.11	1.98	1.72	1.52	1.27
	$C^{\bullet}H_2(CH_3)_2C-OCH_3$		5.58	2.76	2.75	2.55	2.27	1.73	1.32	0.73
	$C^{\bullet}H_2(CH_3)_2CO-CH_3$		5.11	1.90	1.66	1.49	1.37	1.22	1.15	1.06
	total	**−17.74 ± 1.13**	**92.36**	**33.80**	**40.75**	**46.82**	**51.94**	**60.06**	**66.25**	**76.35**
$(CH_3)_3COC^{\bullet}H_2$ (81)	TVR		66.37	22.91	30.39	37.29	43.25	52.75	59.91	71.22
			65.92	*22.05*	*29.35*	*36.2*	*42.17*	*51.72*	*58.94*	*70.49*
	IR									
	$(CH_3)_3-COC^{\bullet}H_2$		4.30	2.14	2.19	2.09	1.95	1.69	1.50	1.25
	$(CH_3)_3-COC^{\bullet}H_2$		4.30	2.14	2.19	2.09	1.95	1.69	1.50	1.25
	$(CH_3)_3-COC^{\bullet}H_2$		4.30	2.14	2.19	2.09	1.95	1.69	1.50	1.25
	$(CH_3)_3C-OC^{\bullet}H_2$		6.57	2.20	1.96	1.72	1.51	1.19	0.95	0.58
	$(CH_3)_3CO-C^{\bullet}H_2$		3.28	2.01	2.20	2.27	2.25	2.09	1.88	1.51
	total	**−24.54 ± 1.97**	**88.90**	**33.11**	**40.59**	**47.01**	**52.33**	**60.58**	**66.76**	**76.70**

[a] Units in kcal/mol; average values are calculated at various levels in this study and include statistical distribution of rotation conformers. [b] Units in cal/(mol/K). [c] The sum of contributions from translations, external rotations, and vibrations. [d] Contribution from internal rotations. [e] Symmetry number is taken into account. [f]Based on B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels of theory. MP2/6-31G(d,p) is shown in italics. [g] S°_{298} and $C_p(T)$'s contributions from TVR are average values from MP2/6-31G(d,p) and B3LYP/6-31G(d,p) calculations.

TABLE 9: Comparison between Calculated ΔH°_{f298} Values Based on Atomization Procedures ($\Delta H^\circ_{f298,AT}$)[a] and Values Calculated by Our Group Isodesmic Reaction Method (Recommended ΔH°_{f298})

species	recommended ΔH°_{f298} (kcal/mol)	$\Delta H^\circ_{f298,AT}$			
		CBSQ		G3MP2	
		//B3LYP/6-31G(d,p)	//MP2/6-31G(d,p)	//B3LYP/6-31G(d,p)	//MP2/6-31G(d,p)
$CH_3CH_2OCH_3$	−52.22 ± 0.84	−52.01	−51.43	−50.53	−49.33
$C^{\bullet}H_2CH_2OCH_3$	−1.67 ± 0.98	−2.51	−1.69	−1.93	−0.45
$CH_3C^{\bullet}HOCH_3$	−9.31 ± 2.18	−10.16	−9.27	−9.09	−7.56
$CH_3CH_2OC^{\bullet}H_2$	−7.93 ± 1.81	−8.49	−7.65	−7.69	−6.19
$(CH_3)_2CHOCH_3$	−60.13 ± 0.94	−59.51	−58.8	−58.05	−56.55
$C^{\bullet}H_2CH(CH_3)OCH_3$	−10.06 ± 0.85	−10.38	−9.48	−9.73	−7.99
$(CH_3)_2C^{\bullet}OCH_3$	−17.33 ± 2.38	−17.72	−16.71	−16.54	−14.71
$(CH_3)_2CHOC^{\bullet}H_2$	−16.75 ± 1.71	−16.73	−15.76	−15.99	−14.19
$(CH_3)_3COCH_3$	−67.78 ± 1.44	−67.56	−66.77	−65.62	−63.85
$C^{\bullet}H_2(CH_3)_2COCH_3$	−17.74 ± 1.13	−18.51	−17.31	−17.41	−15.18
$(CH_3)_3COC^{\bullet}H_2$	−24.54 ± 1.97	−25.06	−23.91	−23.64	−21.46
MDs[b]		−0.29	0.61	0.84	2.55
MADs[c]		0.40	0.31	0.63	0.62
LDs[d]		−0.84	1.33	2.16	3.93

[a] $\Delta H^\circ_{f298,AT}(X)$ = [total energy at 0 K of (X) − ∑(total energy at 0 K of (elements)] × 627.51 + ∑[experimental values of ΔH°_{f0}(elements)] − thermal correction to enthalpies ([$H^\circ_{298} - H^\circ_0$]). Experimental values of ΔH°_{f0}(elements) are listed in Table 5. [b] Mean deviations. [c] Mean absolute deviations. [d] Largest deviations.

On average the DFT geometry results in about 0.1 kcal/mol lower energy than the MP2 geometry. The DFT and MP2 calculations both yield good results compared to the composite methods. The largest deviations are in the B3LYP/6-311+G(3df,2p) results, showing deviations of more than 1 kcal/mol (low) for bonds relating to the tertiary carbon.

5. Group Additivity Values and Hydrogen Bond Increment (HBI) Groups for Radicals. The method for derivation of central groups and HBI groups has been illustrated in previous studies.[36,37,43] The oxygen−carbon−carbon group (O/C2) was derived from thermodynamic property data of three title ethers (CCOC, C2COC, and C3COC) and dimethyl ether (listed in

TABLE 10: Ideal Gas-Phase Thermodynamic Properties, $C_p(T)$'s, $S^\circ(T)$'s, and Thermal Correction to Enthalpy ($50 \leq T/K \leq 5000$)

	$CH_3CH_2OCH_3$			$C^{\bullet}H_2CH_2OCH_3$			$CH_3C^{\bullet}HOCH_3$			$CH_3CH_2OC^{\bullet}H_2$		
T (K)	$[C_p^\circ]^a$	$[S^\circ]^a$	$[H_T^\circ - H_0^\circ]^b$	$[C_p^\circ]^a$	$[S^\circ]^a$	$[H_T^\circ - H_0^\circ]$	$[C_p^\circ]^a$	$[S^\circ]^a$	$[H_T^\circ - H_0^\circ]$	$[C_p^\circ]^a$	$[S^\circ]^a$	$[H_T^\circ - H_0^\circ]$
50	9.54	48.87	0.42	11.67	52.62	0.42	10.08	49.94	0.42	10.43	51.82	0.42
100	12.46	56.37	0.94	14.13	61.51	0.96	13.48	58.07	0.97	13.35	59.97	0.94
150	15.35	61.98	1.58	16.07	67.63	1.65	15.61	63.97	1.65	15.44	65.81	1.57
200	17.89	66.76	2.32	17.70	72.49	2.44	17.34	68.71	2.42	17.07	70.49	2.31
298.15	22.10	74.72	4.04	21.07	80.19	4.27	21.26	76.35	4.19	20.74	77.97	4.06
300	22.18	74.86	4.08	21.14	80.32	4.31	21.34	76.48	4.23	20.81	78.10	4.10
400	26.37	81.84	6.29	25.02	86.96	6.60	25.76	83.26	6.45	25.19	84.72	6.33
500	30.46	88.21	9.01	28.79	92.99	9.34	29.66	89.48	9.12	29.33	90.83	9.02
600	34.18	94.14	12.20	32.14	98.58	12.49	32.90	95.22	12.19	32.90	96.54	12.13
700	37.47	99.70	15.81	35.06	103.80	15.98	35.64	100.54	15.63	35.90	101.88	15.59
800	40.37	104.94	19.78	37.60	108.69	19.78	38.00	105.49	19.38	38.45	106.88	19.36
900	42.92	109.89	24.06	39.81	113.29	23.84	40.08	110.13	23.40	40.63	111.58	23.39
1000	45.15	114.57	28.62	41.75	117.62	28.14	41.92	114.49	27.65	42.51	116.00	27.65
1100	47.11	119.00	33.41	43.44	121.72	32.63	43.54	118.59	32.11	44.14	120.16	32.12
1200	48.83	123.22	38.41	44.92	125.60	37.29	44.97	122.48	36.75	45.55	124.10	36.76
1300	50.32	127.22	43.60	46.21	129.28	42.12	46.22	126.16	41.54	46.78	127.83	41.56
1400	51.64	131.04	48.94	47.34	132.78	47.07	47.33	129.66	46.47	47.86	131.37	46.49
1500	52.78	134.67	54.42	48.33	136.11	52.14	48.30	132.99	51.52	48.80	134.73	51.54
1600	53.79	138.15	60.01	49.19	139.29	57.31	49.15	136.17	56.67	49.63	137.94	56.69
1700	54.67	141.47	65.72	49.95	142.32	62.57	49.91	139.20	61.91	50.35	141.00	61.94
1800	55.45	144.65	71.52	50.63	145.22	67.91	50.57	142.10	67.24	50.99	143.92	67.26
1900	56.14	147.69	77.40	51.22	148.00	73.32	51.16	144.88	72.63	51.55	146.72	72.66
2000	56.75	150.62	83.35	51.74	150.67	78.80	51.69	147.54	78.09	52.05	149.40	78.12
2500	58.94	163.67	113.95	53.63	162.56	106.88	53.57	159.41	106.12	53.84	161.35	106.14
3000	60.22	174.65	145.51	54.74	172.54	135.78	54.68	169.38	134.99	54.89	171.36	134.99
3500	61.00	184.09	177.66	55.44	181.12	165.18	55.35	177.95	164.36	55.55	179.96	164.36
4000	61.49	192.35	210.20	55.88	188.63	194.91	55.77	185.45	194.08	55.96	187.48	194.07
4500	61.79	199.69	243.00	56.17	195.29	224.87	56.03	192.10	224.02	56.23	194.16	224.01
5000	61.98	206.28	275.99	56.36	201.28	255.00	56.18	198.07	254.13	56.40	200.15	254.12

	$(CH_3)_2CHOCH_3$			$C^{\bullet}H_2CH(CH_3)OCH_3$			$(CH_3)_2C^{\bullet}OCH_3$			$(CH_3)_2CHOC^{\bullet}H_2$		
T (K)	$[C_p^\circ]$	$[S^\circ]$	$[H_T^\circ - H_0^\circ]$	$[C_p^\circ]$	$[S^\circ]$	$[H_T^\circ - H_0^\circ]$	$[C_p^\circ]$	$[S^\circ]$	$[H_T^\circ - H_0^\circ]$	$[C_p^\circ]^a$	$[S^\circ]$	$[H_T^\circ - H_0^\circ]$
50	10.80	51.65	0.43	9.85	52.20	0.41	10.42	52.66	0.42	10.61	52.82	0.41
100	14.84	60.42	1.00	14.87	60.58	0.98	15.61	61.48	1.02	15.30	61.70	0.96
150	18.20	67.10	1.75	19.15	67.47	1.75	19.72	68.65	1.81	18.43	68.54	1.69
200	21.05	72.75	2.66	22.53	73.47	2.69	22.54	74.75	2.74	21.13	74.22	2.58
298.15	26.58	82.20	4.84	27.97	83.54	4.95	27.07	84.63	4.96	26.91	83.75	4.78
300	26.69	82.37	4.89	28.07	83.72	5.00	27.15	84.80	5.00	27.02	83.91	4.82
400	32.71	90.91	7.74	33.27	92.56	7.92	31.97	93.31	7.83	33.14	92.58	7.69
500	38.39	98.88	11.24	38.07	100.56	11.42	36.66	101.00	11.24	38.57	100.62	11.15
600	43.35	106.39	15.34	42.28	107.94	15.46	40.88	108.12	15.18	43.10	108.12	15.16
700	47.62	113.46	19.96	45.93	114.79	19.96	44.60	114.76	19.60	46.85	115.11	19.63
800	51.30	120.12	25.03	49.13	121.19	24.85	47.86	120.99	24.42	50.01	121.63	24.50
900	54.50	126.41	30.49	51.93	127.20	30.08	50.73	126.84	29.59	52.73	127.74	29.71
1000	57.30	132.35	36.29	54.40	132.85	35.61	53.26	132.37	35.07	55.07	133.47	35.22
1100	59.74	137.98	42.39	56.57	138.19	41.40	55.48	137.60	40.82	57.12	138.86	40.98
1200	61.87	143.32	48.74	58.48	143.24	47.41	57.43	142.56	46.80	58.90	143.96	46.98
1300	63.74	148.40	55.32	60.16	148.03	53.61	59.14	147.27	52.98	60.46	148.78	53.17
1400	65.38	153.23	62.10	61.64	152.59	59.99	60.64	151.76	59.34	61.82	153.36	59.54
1500	66.81	157.84	69.04	62.94	156.93	66.52	61.95	156.03	65.85	63.02	157.70	66.06
1600	68.07	162.23	76.14	64.08	161.07	73.19	63.11	160.10	72.50	64.08	161.85	72.71
1700	69.18	166.44	83.37	65.09	165.02	79.97	64.12	164.00	79.27	65.00	165.80	79.48
1800	70.15	170.46	90.72	65.98	168.81	86.85	65.02	167.73	86.14	65.82	169.57	86.36
1900	71.02	174.32	98.17	66.77	172.43	93.82	65.82	171.30	93.10	66.55	173.19	93.32
2000	71.78	178.02	105.71	67.48	175.91	100.87	66.52	174.73	100.15	67.19	176.65	100.37
2500	74.54	194.53	144.45	70.01	191.42	137.07	69.05	190.03	136.32	69.51	192.07	136.53
3000	76.14	208.41	184.40	71.51	204.46	174.33	70.53	202.89	173.57	70.87	205.01	173.77
3500	77.12	220.36	225.08	72.43	215.67	212.25	71.42	213.95	211.47	71.71	216.12	211.68
4000	77.72	230.81	266.24	73.01	225.48	250.60	71.96	223.62	249.82	72.23	225.83	250.01
4500	78.08	240.08	307.74	73.37	234.19	289.25	72.29	232.21	288.46	72.55	234.44	288.65
5000	78.30	248.41	349.47	73.59	242.02	328.10	72.48	239.91	327.31	72.75	242.18	327.50

TABLE 10 (Continued)

T (K)	$(CH_3)_3COCH_3$			$C^{\bullet}H_2(CH_3)_2COCH_3$			$(CH_3)_3COC^{\bullet}H_2$		
	$[C_p^\circ]$	$[S^\circ]$	$[H_T^\circ - H_0^\circ]$	$[C_p^\circ]$	$[S^\circ]$	$[H_T^\circ - H_0^\circ]$	$[C_p^\circ]$	$[S^\circ]$	$[H_T^\circ - H_0^\circ]$
50	10.21	52.75	0.46	11.25	56.30	0.42	9.92	55.38	0.41
100	15.59	61.42	1.06	16.65	65.70	1.03	15.06	63.73	0.99
150	20.68	68.75	1.91	21.89	73.49	1.91	20.34	70.87	1.83
200	24.90	75.31	2.99	26.24	80.42	3.01	24.90	77.38	2.90
298.15	32.56	86.74	5.65	33.66	92.36	5.77	32.96	88.90	5.60
300	32.70	86.94	5.71	33.80	92.57	5.83	33.11	89.11	5.66
400	40.30	97.46	9.24	40.75	103.32	9.41	40.59	99.74	9.20
500	47.11	107.27	13.55	46.82	113.16	13.74	47.01	109.58	13.49
600	52.92	116.46	18.59	51.94	122.23	18.71	52.33	118.70	18.43
700	57.90	125.08	24.24	56.29	130.64	24.24	56.78	127.19	23.94
800	62.20	133.17	30.42	60.06	138.48	30.25	60.58	135.09	29.92
900	65.96	140.79	37.07	63.35	145.82	36.67	63.88	142.49	36.32
1000	69.27	147.98	44.13	66.25	152.71	43.45	66.76	149.43	43.09
1100	72.17	154.79	51.53	68.81	159.21	50.54	69.29	155.98	50.16
1200	74.72	161.24	59.24	71.07	165.35	57.91	71.52	162.17	57.52
1300	76.96	167.37	67.22	73.06	171.18	65.51	73.47	168.03	65.11
1400	78.93	173.21	75.44	74.81	176.71	73.33	75.19	173.59	72.92
1500	80.66	178.77	83.85	76.35	181.98	81.33	76.70	178.88	80.91
1600	82.19	184.08	92.45	77.71	187.01	89.49	78.04	183.93	89.06
1700	83.53	189.16	101.21	78.92	191.80	97.80	79.21	188.74	97.36
1800	84.71	194.01	110.10	79.98	196.39	106.23	80.25	193.35	105.78
1900	85.77	198.67	119.12	80.92	200.79	114.77	81.18	197.76	114.31
2000	86.70	203.14	128.24	81.76	205.00	123.41	82.00	201.98	122.94
2500	90.06	223.09	175.13	84.79	223.80	167.74	84.96	220.82	167.25
3000	92.02	239.88	223.45	86.58	239.59	213.38	86.70	236.65	212.87
3500	93.21	254.31	272.66	87.66	253.17	259.83	87.76	250.24	259.30
4000	93.93	266.94	322.45	88.34	265.05	306.80	88.41	262.13	306.27
4500	94.37	278.15	372.64	88.76	275.59	354.14	88.81	272.68	353.59
5000	94.62	288.22	423.11	89.01	285.06	401.74	89.05	282.15	401.19

[a] Units in cal/(mol K); S_T° and $C_p(T)$'s contribution from TRV (translational, external rotational, and vibrational) are average values from MP2/6-31G(d,p) and B3LYP/6-31G(d,p) calculations. Internal rotation contributions are calculated on the basis of barrier potential at B3LYP/6-31G(d) level. [b] Thermal corrections in kcal/mol: Thermal corrections are calculated as follows for $T = 298.15$ K: $H_T^\circ - H_0^\circ = H_{trans}(T) + H_{rot}(T) + \Delta H_{vib}(T) + RT$; $H_{trans}(T) = (3/2)RT$, $H_{rot}(T) = (3/2)RT$, $\Delta H_{vib}(T) = N_A h \sum \upsilon_i / (\exp(h\upsilon_i/kT) - 1)$, where N_A is the Avogadro constant, h is the Planck constant, k is the Boltzmann constant, and υ_i is the vibrational frequency.

TABLE 11: Bond Energies[a] at 298 K

reaction series	//B3LYP/6-31G(d,p)			//MP2/6-31G(d,p)			recommended[b]
	G3MP2	CBSQ	B3LYP/ 6-311+G(3df,2p)	G3MP2	CBSQ	MP2/ 6-311+G(2df,2p)	
			H−ROC				
$CH_3CH_2OCH_3 \rightarrow C^{\bullet}H_2CH_2OCH_3 + H$	102.62	102.65	102.44	102.70	102.74	102.78	102.65 ± 1.82
$(CH_3)_2CHOCH_3 \rightarrow C^{\bullet}H_2CH(CH_3)OCH_3 + H$	102.11	102.06	101.94	102.17	102.08	102.26	102.17 ± 1.79
$(CH_3)_3COCH_3 \rightarrow C^{\bullet}H_2C(CH_3)_2OCH_3 + H$	102.12	102.09	101.78	102.18	102.13	102.33	102.14 ± 2.57
			ROC−H				
$CH_3CH_2OCH_3 \rightarrow CH_3CH_2OC^{\bullet}H_2 + H$	96.36	96.36	96.26	96.40	96.39	96.41	96.39 ± 2.65
$(CH_3)_2CHOCH_3\ (CH_3)_2CHOC^{\bullet}H_2 + H$	95.43	95.46	95.26	95.45	95.46	95.43	95.48 ± 2.65
$(CH_3)_3COCH_3 \rightarrow (CH_3)_3COC^{\bullet}H_2 + H$	95.43	95.27	95.15	95.44	95.25	95.47	95.34 ± 3.41
			RC(−H)OC				
$CH_3CH_3OCH_3 \rightarrow CH_3C^{\bullet}HOCH_3 + H$	95.21	94.94	94.29	95.29	95.03	95.53	95.01 ± 3.02
$(CH_3)_2CHOCH_3 \rightarrow (CH_3)_2C^{\bullet}OCH_3 + H$	95.27	94.87	93.54	95.27	94.85	95.71	94.90 ± 3.32
			R−OC				
$CH_3CH_2OCH_3 \rightarrow CH_3CH_2^{\bullet} + CH_3O^{\bullet}$	85.14	85.18	84.90	85.17	85.21	85.18	85.08 ± 1.84
$(CH_3)_2CHOCH_3 \rightarrow (CH_3)_2CH^{\bullet} + CH_3O^{\bullet}$	86.14	86.33	85.64	86.47	86.36	86.54	86.23 ± 2.44
$(CH_3)_3COCH_3 \rightarrow (CH_3)_3C^{\bullet} + CH_3O^{\bullet}$	83.03	83.14	81.61	83.12	83.20	83.16	82.88 ± 3.14
			RO−C				
$CH_3CH_2OCH_3 \rightarrow CH_3CH_2O^{\bullet} + CH_3$	84.46	84.49	84.21	84.48	84.52	84.49	84.39 ± 2.81
$(CH_3)_2CHOCH_3 \rightarrow (CH_3)_2CHO^{\bullet} + CH_3$	83.11	83.30	82.61	83.44	83.33	83.51	83.20 ± 2.77
$(CH_3)_3COCH_3 \rightarrow (CH_3)_3CO^{\bullet} + CH_3$	81.89	82.00	80.48	81.98	82.07	82.02	81.74 ± 3.52
			C−ROC				
$CH_3CH_2OCH_3 \rightarrow CH_2^{\bullet}OCH_3 + CH_3$	87.42	87.45	87.17	87.44	87.48	87.45	87.35 ± 1.53
$(CH_3)_2CHOCH_3 \rightarrow CH_3C^{\bullet}HOCH_3 + CH_3$	85.69	85.56	84.50	86.07	85.66	86.37	85.64 ± 3.12
$(CH_3)_3COCH_3 \rightarrow (CH_3)_2C^{\bullet}OCH_3 + CH_3$	85.87	85.40	83.24	85.64	85.42	86.05	85.27 ± 3.82

[a] Units in kcal/mol. [b] Recommend bond energies are calculated from the ΔH_{f298}° listed in Table 5 and column 3 in Table 8. Errors are sum of uncertainties in enthalpy values for the reactants and products.

TABLE 12: Central Group and Hydrogen Bond Increment (BHI) Group for Radicals

group	compound	ΔH°_{f298}[a]	S°_{298}[b]	$C_p(300)$[b]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$
Benson/Cohen Groups[51,6]										
$C/C/H_3$		−10.2	30.41	6.19	7.84	9.4	10.79	13.02	14.77	17.58
$C/C/H_2/O$		−8.1	9.8	4.99	6.85	8.3	9.43	11.11	12.33	14.66
$C/C_2/H/O$		−7.2	−11	4.8	6.64	8.1	8.73	9.81	10.4	11.51
$C/C_3/O$		−6.6	−33.56	4.33	6.19	7.25	7.7	8.2	8.24	8.09
$C/H_3/O$		−10.1	30.41	6.19	7.84	9.4	10.79	13.03	14.77	17.58
Group Additivity Values, This Work										
O/C_2	CH_3OCH_3	−24.01	8.75	3.35	3.12	3.04	3.00	3.12	3.13	3.03
	$CH_3CH_2OCH_3$	−24.14	8.47	4.81	3.84	3.36	3.17	3.21	3.28	2.96
	$(CH_3)_2CHOCH_3$	−24.23	8.32	3.81	3.20	2.88	2.92	3.11	3.21	2.96
	$(CH_3)_3COCH_3$	−23.76	9.18	4.61	4.05	3.84	3.41	3.29	3.20	3.06
		−24.04	**8.68**	**4.14**	**3.55**	**3.28**	**3.13**	**3.18**	**3.21**	**3.00**
	Benson[51]	−23.2	8.68	3.4	3.7	3.7	3.8	4.4	4.6	
ether gauche	$(CH_3)_2CHOCH_3$	1.12	−0.09	−0.76	−0.93	−1.11	−0.84	−0.75	−0.62	−0.44
	$(CH_3)_3COCH_3$	1.43	0.48	−0.23	−0.37	−0.47	−0.51	−0.63	−0.63	−0.37
		1.27	**0.19**	**−0.50**	**−0.65**	**−0.79**	**−0.67**	**−0.69**	**−0.63**	**−0.40**
	Benson[51]	0.5								
HBI Group Values, This Work										
ROCJ	$CH_3CH_2OC^{\bullet}H_2$	96.39	1.07	−1.36	−1.19	−1.13	−1.28	−1.92	−2.65	−3.98
	$(CH_3)_2CHOC^{\bullet}H_2$	95.48	−0.64	0.34	0.43	0.18	−0.25	−1.28	−2.22	−3.79
	$(CH_3)_3COC^{\bullet}H_2$	95.34	−0.02	0.41	0.29	−0.10	−0.60	−1.62	−2.51	−3.96
		95.74	**0.14**	**−0.21**	**−0.16**	**−0.35**	**−0.71**	**−1.61**	**−2.46**	**−3.91**
RJCOC	$CH_2^{\bullet}CH_2OCH_3$	102.65	3.28	−1.04	−1.35	−1.67	−2.04	−2.78	−3.41	−4.46
	$C^{\bullet}H_2CH(CH_3)OCH_3$	102.17	−0.84	1.38	0.56	−0.32	−1.07	−2.17	−2.90	−3.87
	$C^{\bullet}H_2C(CH_3)_2OCH_3$	102.14	1.26	1.10	0.45	−0.28	−0.98	−2.14	−3.01	−4.31
		102.32	**1.23**	**0.48**	**−0.11**	**−0.76**	**−1.36**	**−2.36**	**−3.11**	**−4.21**
RCJOC	$CH_3C^{\bullet}HOCH_3$	95.01	1.63	−0.83	−0.61	−0.80	−1.28	−2.37	−3.23	−4.49
	$(CH_3)_2C^{\bullet}OCH_3$	94.90	2.43	0.47	−0.74	−1.73	−2.47	−3.44	−4.03	−4.86
		94.96	**2.03**	**-0.18**	**-0.68**	**-1.27**	**-1.88**	**-2.90**	**-3.63**	**-4.67**

[a] Units in kcal/mol. [b] Units in cal/(mol/K).

Table 12). The correction term for the nonnearest neighbor interaction, “ether gauche”, is also derived to account for the gauche interaction of two methyl groups within the alkyl chain across an ether link.

Three sets of HBI group values (ROCJ, RJCOC, and RCJOC; J = radical site) are derived from 8 radicals and also listed in Table 12. The enthalpy values of the HBI group are all similar when the chemical environments are similar. The entropy and heat capacity are slightly different within the same series; with the differences less than 4 and 2 cal/(mol K) for values of entropy and heat capacity, respectively.

Summary

Thermodynamic properties of three title ethers and the corresponding radicals were determined by ab initio and density functional calculations. ΔH°_{f298} values were calculated using group balance isodesmic reactions based on MP2/6-311+G(2df,2p)//MP2/6-31G(d,p), B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p), CBSQ//MP2/6-31G(d,p), CBSQ//B3LYP/6-31G(d,p), G3MP2//MP2/6-31G(d,p), and G3MP2//B3LYP/6-31G(d,p) levels and include the statistical distribution of rotational conformers. $S^\circ(T)$'s and $C_p(T)$'s ($50 \le T/\mathrm{K} \le 5000$) were determined with B3LYP/6-31G(d,p) and MP2/6-31G(d,p) optimized geometries and frequencies, hindered internal rotational contributions to $S^\circ(T)$'s and $C_p(T)$'s were calculated by intramolecular torsion potential curves, and the entropy corrections for the mixing of rotational conformers are included. The C−H, C−C, and C−O bond energies were estimated using the ΔH°_{f298} of the three ethers and the corresponding radicals with alkyl and alkoxy radicals at each calculation levels. Thermodynamic properties of the O/C2 group and the ether gauche interaction term were determined for group additivity application. The hydrogen bond increment group values for ROCJ, RJCOC, and RCJOC were also derived.

Acknowledgment. We thank Chad Sheng (NJIT) for use of his SMCPS (Statistical Mechanics for Heat Capacity and Entropy) computer code to calculate $S^\circ(T)$'s and $C_p(T)$'s terms plus ZPVE and thermal energy from Gaussian data files. We acknowledge funding from the USEPA Northeast Regional Research Center and the USEPA Airborne Organics Research Center.

Supporting Information Available: Full parameters of optimized structures (Table S1) and coefficients of the Fourier expansion components, a_i and b_i in eq F1 (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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