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Dimethyldioxirane, Carbonyl Oxide, and the Transition State Connecting Them: Electronic Structures, Relative Energies, and Vibrational Frequencies

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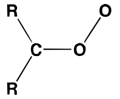
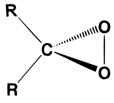
The electronic structures and vibrational frequencies of dimethyl-substituted carbonyl oxide and its cyclic isomer dimethyldioxirane have been investigated using high-level ab initio quantum mechanical techniques with large basis sets. The equilibrium geometries have been optimized at the self-consistent field (SCF), the single and double excitation configuration interaction (CISD), the coupled cluster with single and double excitation (CCSD), and the CCSD with connected triple excitations [CCSD(T)] levels of theory. The absolute and relative energies of carbonyl oxide, dimethyldioxirane, and the transition state between them have also been computed. At the highest level of theory employed in this study, TZP CCSD(T), dimethyldioxirane is predicted to be lower in energy than the carbonyl oxide by 23.2 kcal/mol with the inclusion of zero-point vibrational energy (ZPVE) corrections. The energy barrier for the cyclization of carbonyl oxide becomes 19.5 kcal/mol at the same level of theory. Harmonic vibrational frequencies and infrared (IR) intensities are determined at the DZP SCF and TZP SCF levels of theory for the dimethyl-substituted carbonyl oxide and the transition state, and at correlated levels (CISD and CCSD) with DZP and TZP basis sets for dimethyldioxirane. The experimental vibrational frequencies of dimethyldioxirane are assigned using the present theoretical predictions. It is hoped that the theoretical frequencies for the dimethyl carbonyl oxide isomer will stimulate new experiments.

Introduction

As reaction intermediates, carbonyl oxides (**1**) are known to play an important role in determining stereospecificities in organic syntheses.[1] However, because of its instability, the parent carbonyl oxide (**1a**) has not been observed directly in experiments, even though there is sufficient indirect evidence for the involvement of this intermediate in the ozonolysis of ethylene; the nature of **1a** in condensed phases (diradical or zwitterionic) is still an open question.[2] For example, Sander concluded that carbonyl oxides in the ground state are polar diradicals in 1990,[2] while Cremer et al. predicted **1a** possesses zwitterionic character in 1993.[3] Difficulties in identifying **1a** are caused by the rapid isomerization to its cyclic isomer, dioxirane. The parent dioxirane, **2a,** was first detected experimentally in the gas-phase ozonolysis of ethylene by Lovas and Suenram in 1977.[4]



1a, R=H
1b, R=CH_3



2a, R=H
2b, R=CH_3

Subsequently, extensive theoretical and experimental studies have been carried out to characterize this compound spectroscopically.[5−14] The energy separation between carbonyl oxide and dioxirane and the barrier for this cyclization have been predicted to be 25.6 and 19.2 kcal/mol, respectively, at the TZ2P CCSD(T) level of theory.[3] The only experimental observation of fundamental vibrational frequencies for the parent dioxirane was reported in 1991 by Sodeau and Whyte.[10] They obtained a FT-IR spectrum from the matrix photolysis of CH_3I in the presence of molecular oxygen and tentatively assigned 839 and 800.9 cm^{-1} to the C−O and O−O stretching modes of dioxirane. However, our 1996 paper concluded that these peaks should be reexamined.[15]

During the last decade, various substituted carbonyl oxides and dioxiranes have been isolated and utilized as powerful oxygen atom transfer reagents in organic syntheses.[16−22] Since dimethyldioxirane (**2b**) was first isolated in acetone solution and characterized spectroscopically by Murray in 1985,[16] spectral and chemical properties have been investigated such as NMR chemical shifts by Adam et al.[17] in 1987 and the UV spectrum by Baumstark et al.[18] in 1988. In addition, some oxygen transfer reactions including insertion and epoxidation have been reported.[23,24] The IR spectrum of dimethyldioxirane was reported without detailed assignments by Murray[16] in 1985, and theoretical investigations of the structure were carried out at the MP2/6-31G* level of theory by Cremer and co-workers in 1987.[17] More recently, the kinetic and theoretical investigations on the reaction paths of carbonyl oxide (**1b)** to dioxirane (**2b**) or to hydroperoxide have been reported.[25,26] However, the theoretical investigation of **1b** has been limited to energetics and kinetics,[27] and also there are no theoretical studies on the vibrational frequencies of dimethyldioxirane so far. In the present paper, we report geometrical parameters, vibrational frequencies, and relative energies for dimethyl carbonyl oxide, dimethyldioxirane, and the transition states for the internal

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rotation and the cyclization of carbonyl oxide predicted at a high level of theory using substantial basis sets. In addition, the intensities and detailed assignments of the infrared (IR) spectrum will be presented and compared with experimental observations.

Theoretical Approach

The basis sets used in this study are of double-ζ (DZ), DZ plus polarization (DZP), triple-ζ plus polarization (TZP), and TZ plus double polarization (TZ2P) quality. The DZ basis set consists of the standard Huzinaga[28] and Dunning[29] (9s5p/4s2p) contracted Gaussian functions for carbon and oxygen and the (4s/2s) set for hydrogen. The DZP basis is DZ plus a single set of polarization d functions on carbon and oxygen, and a set of p functions on hydrogen with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_p(H) = 0.75$. The TZP basis is of triple-ζ (TZ) quality with one set of polarization function (orbital exponents are the same with DZP), while the TZ basis consists of the Huzinaga[28] and Dunning[30] (10s6p/5s3p) set for C and O, and the (5s/3s) set for H. The TZ2P basis is of TZ quality with two sets of polarization function with exponents $\alpha_d(C) = 1.5, 0.375$, $\alpha_d(O) = 1.7, 0.425$, and $\alpha_d(H) = 1.5, 0.375$. The numbers of basis functions are 110, 136, and 184 with the DZP, TZP, and TZ2P basis sets.

The geometries of the dimethyl-substituted carbonyl oxide, dimethyldioxirane, and the transition states are fully optimized at the self-consistent field (SCF) level of theory using analytic techniques[31] with DZ, DZP, TZP, and TZ2P basis sets. The SCF equilibrium geometries are subsequently used as starting points to optimize structures at the single and double excited configuration (CISD) level with DZ, DZP, and TZP basis sets described above employing analytic CISD gradient methods.[32] The CISD geometries are finally used to obtain geometries optimized at the CCSD and CCSD(T) levels, which are the single and double excitation coupled cluster method and CCSD with the effects of connected triple excitations included perturbatively.[33] The CCSD and CCSD(T) optimized geometries were obtained employing the DZ, DZP, and TZP basis sets. In the CISD, CCSD, and CCSD(T) wave functions, the five corelike occupied SCF molecular orbitals are frozen (held doubly occupied) and the five highest virtual molecular orbitals are deleted from the correlation procedures. With the TZP basis set, the CISD wave functions (required for the frequency evaluations) include 350 602 configurations in C_{2v} symmetry, 715 458 configurations in Cs symmetry, and 1 388 611 in C_1 symmetry.

Harmonic vibrational frequencies and infrared (IR) intensities for dimethylcarbonyl oxide, dimethyldioxirane, and the transition states are evaluated using analytic second energy derivatives[34] at the SCF level. For dimethyldioxirane the computation has been extended to correlated methods CISD, CCSD, and CCSD(T) using finite displacements of analytic gradients. All four basis sets are used for SCF and CISD frequencies, while the DZ, DZP, and TZP basis sets are used for the CCSD and CCSD(T) frequencies. All computations described above are carried out with the PSI-2[35] suite of computer programs developed in our laboratory.

Results and Discussion

Geometrical Parameters and Energetics. Dimethyldioxirane has C_{2v} symmetry as shown in Figure 1 and its geometrical parameters at several levels of theory appear in Table 1. All geometries in figures were fully optimized at the TZP CCSD(T) level of theory. The effects of increasing the basis set from DZP to TZP are not very significant for the C−O and O−O bond distances at correlated levels of theory such as CISD, CCSD, and CCSD(T), while bond angles are largely stable with respect to both electron correlation and basis set size. The C−O bond distance is predicted to be slightly (about 0.01 Å) longer than that of the parent dioxirane, while the O−O bond length is little changed by methyl group substitution at the correlated levels of theory.[15] The predicted C−C−C bond angle of 117.6° at the highest level of theory employed is slightly larger than the H−C−H bond angle in the parent dioxirane due to the steric effect of the methyl group.[15]

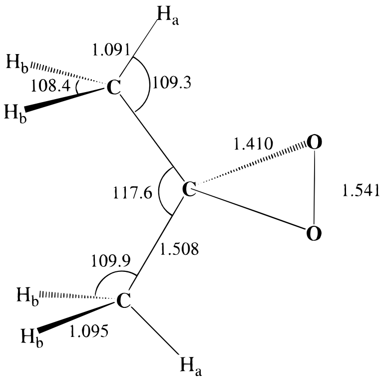

Figure 1. Predicted geometries for dimethyldioxirane at the TZP CCSD(T) level of theory. Bond lengths are in Å and bond angles are in deg.

Our most reliable predicted geometries of the dimethyl-substituted carbonyl oxide and the transition state for the internal rotation of methyl group are presented in Figure 2. The geometrical parameters at other levels of theory are listed in Table 2. In general, bond distances decrease with increasing basis set size, while electron correlation increases the bond distances. The geometries of dimethyl carbonyl oxide (see Figure 2a) are comparable to those of the lowest singlet state of the related dimethyl carbene molecule in their analogous parameters.[36] The C−C−C bond angle, 124.8°, of carbonyl oxide falls between that of the lowest triplet (130.7°) state and the singlet state (111.5°) of dimethyl carbene.[36] The relative stability of the staggered conformation in comparison with the eclipsed form of dimethylcarbonyl oxide may be explained by the pseudo-π conjugation between the p orbital of the terminal oxygen atom and the π-type combination of the C−H bonds of the methyl group. This kind of π-stabilization is also shown in the monomethyl-substituted carbonyl oxide, and the relative stability for the methyl group rotation was reported to be 2.5 kcal/mol,[37] which is comparable to our predicted value of 1.9 kcal/mol in dimethyl-substituted carbonyl oxide at the TZP CCSD(T) level of theory. The geometric structure of the transition state for the internal rotation of the methyl group in Figure 2b is found to be of C_s symmetry and closely resembles carbonyl oxide except for the rotation of the methyl group about the C−C bond. The C−O bond distance of 1.28 Å at the TZP CCSD(T) level of theory in both structures shows the double bond character, which implies that their electronic structures are preferred to the zwitterionic forms.

The predicted geometry of the transition state for the cyclization of dimethyl carbonyl oxide to dimethyldioxirane has C_1 symmetry and is shown in Figure 3 . The C−O bond length for the transition state is predicted to be 1.299 Å at the DZP CCSD(T) level of theory, which is slightly elongated (about 0.011 Å) from the carbonyl oxide. However, the O−O bond distance is significantly lengthened from 1.389 Å for the carbonyl oxide to 1.505 Å for the transition state, and the

TABLE 1: Absolute Energies and Geometrical Parameters of Dimethyldioxirane at Various Levels of Theory[a]

method	energy (hartrees)	R(C−O)	R(O−O)	R(C−C)	R(C−H$_a$)	R(C−H$_b$)	θ(CCC)	θ(CCH$_a$)	θ(CCH$_b$)	θ(HCH)
DZP SCF	−266.764 914	1.370	1.441	1.506	1.083	1.087	117.6	109.6	110.0	108.3
TZP SCF	−266.791 986	1.370	1.445	1.503	1.081	1.085	117.6	109.7	110.0	108.3
TZ2P SCF	−266.797 662	1.367	1.444	1.502	1.078	1.082	117.6	109.6	110.0	108.3
DZP CISD	−267.446 212	1.386	1.474	1.504	1.086	1.089	117.7	109.5	110.0	108.3
TZP CISD	−267.514 817	1.385	1.473	1.498	1.082	1.086	117.6	109.5	110.0	108.3
DZP CCSD	−267.587 018	1.403	1.517	1.511	1.094	1.097	117.6	109.5	110.0	108.3
TZP CCSD	−267.664 339	1.402	1.516	1.505	1.090	1.093	117.6	109.4	110.0	108.3
DZP CCSD(T)	−267.614 451	1.409	1.540	1.513	1.096	1.099	117.6	109.4	110.0	108.3
TZP CCSD(T)	−267.698 990	1.410	1.541	1.508	1.091	1.095	117.6	109.3	109.9	108.4

[a] All bond lengths are in angstroms and bond angles are in degrees.

TABLE 2: Absolute and Relative Energies, and Geometrical Parameters for Dimethyl-Substituted Carbonyl Oxide and the Transition State for the Internal Rotation of a Methyl Group at Various Levels of Theory[a]

method	energy (hartrees)	ΔE[b] (kcal/mol)	R(C−O)	R(O−O)	R(C$_1$−C$_2$)	R(C$_1$−C$_3$)	R(C$_2$−H$_6$)	R(C$_2$−H$_8$)	θ(CCC)	θ(COO)	θ(C$_1$C$_3$H$_7$)
Dimethyl-Substituted Carbonyl Oxide											
DZP SCF	−266.728 975	22.6(21.6)	1.219	1.456	1.498	1.494	1.082	1.087	120.8	116.8	110.7
TZP SCF	−266.757 258	21.8(20.9)	1.217	1.458	1.494	1.489	1.080	1.085	120.8	116.7	110.8
DZP CISD	−267.401 663	28.0(27.0)	1.242	1.404	1.493	1.485	1.086	1.090	122.7	116.7	110.6
TZP CISD	−267.471 768	27.0(26.1)	1.238	1.409	1.486	1.477	1.082	1.082	122.5	116.4	110.8
DZP CCSD	−267.545 025	26.4(25.4)	1.269	1.398	1.499	1.490	1.094	1.098	124.0	116.7	110.4
TZP CCSD	−267.623 738	25.5(24.6)	1.264	1.406	1.492	1.481	1.090	1.090	123.7	116.4	110.6
DZP CCSD(T)	−267.574 897	24.8(23.8)	1.288	1.389	1.501	1.491	1.096	1.096	125.0	116.8	110.3
TZP CCSD(T)	−267.660 608	24.1(23.2)	1.285	1.397	1.494	1.481	1.092	1.091	124.8	116.5	110.5
Transition State for the Internal Rotation of a Methyl Group (C_s Symmetry)											
DZP SCF	−266.727 032	23.8(22.5)	1.218	1.463	1.502	1.497	1.082	1.087	119.6	119.1	110.4
TZP SCF	−266.755 124	23.1(21.9)	1.215	1.467	1.497	1.492	1.080	1.085	119.5	118.9	110.5
DZP CISD	−267.463 877	29.6(28.3)	1.241	1.408	1.496	1.489	1.086	1.090	121.4	119.0	110.5
TZP CISD	−267.468 883	28.8(27.6)	1.237	1.413	1.489	1.482	1.082	1.086	121.0	118.8	110.6
DZP CCSD	−267.542 008	28.2(26.9)	1.268	1.399	1.502	1.495	1.094	1.098	122.5	119.1	110.4
TZP CCSD	−267.620 460	27.5(26.3)	1.263	1.407	1.494	1.487	1.090	1.094	122.1	118.9	110.6
DZP CCSD(T)	−267.571 725	26.8(25.5)	1.288	1.388	1.503	1.496	1.096	1.100	123.5	119.4	110.3
TZP CCSD(T)	−267.657 119	26.3(25.1)	1.284	1.396	1.495	1.488	1.092	1.089	123.1	119.1	110.5

[a] All bond lengths are in angstroms and bond angles are in degrees. [b] Relative to dimethyldioxirane; energies in parentheses include zero-point vibrational energy (ZPVE) corrections.

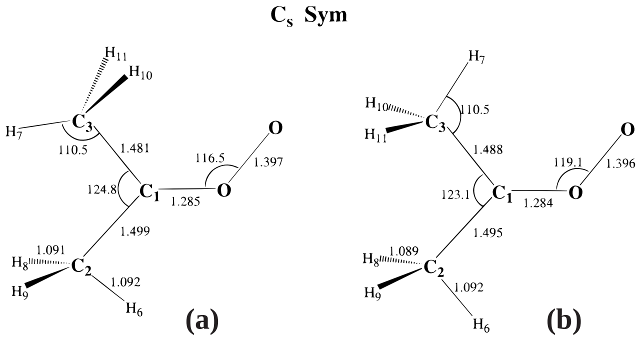

Figure 2. Predicted geometries for (a) the dimethyl-substituted carbonyl oxide and (b) the transition state for the internal rotation of a methyl group at the TZP CCSD(T) level of theory. Bond lengths are in Å and bond angles are in deg.

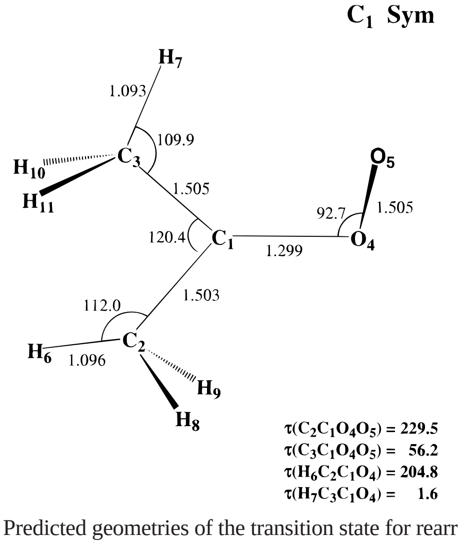

Figure 3. Predicted geometries of the transition state for rearrangement of the carbonyl oxide to the dioxirane at the DZP CCSD(T) level of theory. Bond lengths are in Å and bond angles are in deg.

C−O−O bond angle is reduced from 116.8° to 92.7° due to the cyclization of carbonyl oxide to dioxirane. Also, the torsional angle, C$_3$−C$_1$−O−O, is predicted to be 56.2° and the methyl group in the C$_2$ position is rotating about 24.8°.

The absolute and relative energies for dimethyldioxirane, dimethyl carbonyl oxide, and the transition states are listed in Tables 1−3. The energy differences between dimethyldioxirane and carbonyl oxide (or the transition state) decrease with expansion of the basis sets. The correlation effects increase the energy separation (ΔE) in going from SCF to CISD but decrease ΔE in going from CISD to CCSD or CCSD(T). The TZP CCSD(T) energy of the transition state was obtained at the TZP CCSD optimized geometry. At the highest level of theory employed in this study, dimethylcarbonyl oxide is predicted to lie 24.1 kcal/mol higher in energy than dimethyldioxirane and the energy barriers for the internal rotation and the cyclization of carbonyl oxide are predicted to be 2.2 and 21.0 kcal/mol, respectively. Inclusion of the zero-point vibrational energy (ZPVE) corrections lowers the energy separation (ΔE) to 23.2 kcal/mol and the energy barriers to 1.9 and 19.5 kcal/mol. These results are in good agreement with previous theoretical predic-

TABLE 3: Absolute and Relative Energies, and Geometrical Parameters of the Transition State (C_1 Symmetry) for Isomerization to Dimethyldioxirane at Various Levels of Theory

	SCF		CISD		CCSD		CCSD(T)	
	DZP	TZP	DZP	TZP	DZP	TZP	DZP	TZP[b]
energies (hartrees)	−266.700419	−266.729097	−267.366188	−267.437450	−267.509995	−267.589898	−267.540252	−267.627103
ΔE[a] (kcal/mol)	40.5 (38.1)	39.5 (37.2)	50.2 (47.8)	48.5 (46.2)	48.3 (45.9)	46.7 (44.4)	46.6 (44.2)	45.1 (42.7)
R(C−O)	1.232	1.231	1.261	1.259	1.286	1.282	1.299	
R(O−O)	1.662	1.645	1.520	1.519	1.510	1.512	1.505	
R(C$_1$−C$_2$)	1.500	1.495	1.494	1.486	1.501	1.492	1.503	
R(C$_1$−C$_3$)	1.498	1.493	1.494	1.486	1.503	1.494	1.505	
R(C$_2$−H$_6$)	1.084	1.082	1.086	1.082	1.094	1.090	1.096	
R(C$_2$−H$_8$)	1.089	1.087	1.092	1.089	1.100	1.096	1.101	
R(C$_2$−H$_9$)	1.083	1.082	1.088	1.084	1.096	1.092	1.098	
R(C$_3$−H$_7$)	1.079	1.077	1.082	1.078	1.091	1.086	1.093	
R(C$_3$−H$_{10}$)	1.089	1.088	1.093	1.089	1.101	1.097	1.103	
R(C$_3$−H$_{11}$)	1.086	1.084	1.089	1.085	1.097	1.093	1.098	
θ(CCC)	118.9	119.0	119.4	119.4	119.9	119.9	120.4	
θ(COO)	92.9	93.2	92.3	92.4	92.3	92.3	92.7	
θ(C$_2$C$_1$O)	118.9	118.8	116.7	116.7	115.8	115.8	115.4	
θ(C$_1$C$_2$H$_6$)	112.6	112.7	112.8	112.9	112.3	112.5	112.0	
θ(C$_1$C$_3$H$_7$)	110.5	110.7	110.6	110.9	110.2	110.5	109.9	
θ(H$_8$C$_2$H$_9$)	108.0	107.9	107.5	107.4	107.5	107.5	107.6	
θ(H$_{10}$C$_3$H$_{11}$)	107.7	107.6	107.7	107.6	107.8	107.6	107.8	
τ_{2145}	247.2	246.3	234.0	234.8	230.6	231.4	229.5	
τ_{3145}	69.4	68.7	59.6	59.9	57.2	57.5	56.2	
τ_{6214}	202.0	201.0	199.9	199.7	203.1	202.9	204.8	
τ_{7314}	−6.1	−6.1	−1.0	−1.2	0.9	0.4	1.6	

[a] Relative to dimethyldioxirane; energies in parentheses include zero-point vibrational energy (ZPVE) corrections. All bond lengths are in angstroms and bond angles are in degrees. [b] The TZP CCSD(T) energy is a single-point energy which is obtained at the TZP CCSD optimized geometry.

TABLE 4: Vibrational Frequencies (in cm^{-1}), Infrared (IR) Intensities (in km/mol), and Zero-Point Vibrational Energies (ZPVE, in kcal/mol) for Dimethyl-Substituted Carbonyl Oxide and the Transition State for Isomerization to Dimethyldioxirane at the DZP, SCF, and TZP SCF Levels of Theory

mode	approx assignment	carbonyl oxide (C_s)		transition state (C_1)	
		DZP SCF	TZP SCF	DZP SCF	TZP SCF
ω_1	CH str (a’)	3329(10)	3296(7)	3356(5)	3325(3)
ω_2	CH str (a’)	3318(12)	3284(10)	3320(12)	3287(10)
ω_3	CH asym str (a″)	3303(1)	3268(<1)	3283(11)	3249(8)
ω_4	CH asym str (a″)	3271(10)	3236(7)	3267(8)	3233(6)
ω_5	CH str (a’)	3219(14)	3195(12)	3202(3)	3176(2)
ω_6	CH str (a’)	3202(3)	3177(1)	3194(6)	3166(5)
ω_7	CO str (a’)	1898(233)	1877(227)	1818(374)	1792(350)
ω_8	Me wag (a’)	1600(11)	1597(7)	1603(13)	1603(11)
ω_9	Me twist (a″)	1594(16)	1595(15)	1590(8)	1589(8)
ω_{10}	HCH bend (a’)	1579(25)	1579(27)	1577(10)	1578(8)
ω_{11}	Me twist (a″)	1575(3)	1577(3)	1565(42)	1565(48)
ω_{12}	Me wag (a’)	1538(23)	1534(17)	1536(56)	1531(49)
ω_{13}	HCH bend (a’)	1520(31)	1519(33)	1513(16)	1512(20)
ω_{14}	CCO bend (a’)	1391(35)	1382(42)	1367(57)	1358(64)
ω_{15}	Me rock (a″)	1223(8)	1224(7)	1212(11)	1211(11)
ω_{16}	CCH bend (a’)	1173(3)	1174(4)	1168(5)	1167(6)
ω_{17}	CCH bend (a’)	1059(2)	1055(1)	1027(4)	1023(5)
ω_{18}	Me rock (a″)	985(<1)	986(<1)	957(1)	956(1)
ω_{19}	CC str (a’)	878(11)	873(13)	841(<1)	831(<1)
ω_{20}	CC str (a’)	764(38)	768(34)	608(83)	619(96)
ω_{21}	torsion (a″)	537(2)	537(2)	497(18)	498(18)
ω_{22}	OO str (a’)	534(2)	536(2)	406(4)	410(11)
ω_{23}	CCC bend (a’)	383(1)	387(1)	373(63)	391(52)
ω_{24}	COO bend (a’)	322(11)	325(11)	246*i*(2)	254*i*(4)
ω_{25}	torsion (a″)	264(1)	264(1)	227(11)	245(8)
ω_{26}	torsion (a″)	175(<1)	172(<1)	184(1)	187(1)
ω_{27}	torsion (a″)	142(1)	148(1)	85(2)	94(2)
ZPVE		59.3	58.0	56.9	56.6

tions of 22.9 kcal/mol for the energy separation and 20 kcal/mol for the isomerization barrier by Cremer et al.[38] The ZPVE corrections are based on the SCF frequencies with the corresponding basis set.

Vibrational Frequencies and Infrared (IR) Intensities. Table 4 gives the harmonic vibrational frequencies, IR intensities, and zero-point vibrational energies for the optimized geometries of the dimethyl carbonyl oxide and the transition state for isomerization at the SCF level of theory with the DZP and TZP basis sets. The real vibrational frequencies for carbonyl oxide and a single imaginary vibrational frequency for the transition state confirm the existence of a potential minimum and a true transition state, respectively. To our knowledge, no experimental observations have been reported for any vibrational feature of dimethyl carbonyl oxide. The predicted C−O stretching vibrational frequency (ω_7) of 1877 cm^{-1} at the TZP SCF level of theory for dimethyl carbonyl oxide shows the double bond character, which is consistent with the geometrical prediction for the C−O bond distance. The methyl wagging mode (ω_8) in the eclipsed form of carbonyl oxide is predicted to have a relatively high vibrational frequency, which can be explained by the stabilizing interaction of the methyl group with the π orbital on the terminal oxygen atom. The C−O and O−O stretching frequencies of the transition state are relatively lower than those of carbonyl oxide, which is consistent with increasing C−O and O−O bond distances in the transition state by the ring closure to dioxirane.

The harmonic vibrational frequencies and IR intensities of dimethyldioxirane at various levels of theory are presented in Table 5. There are five IR inactive a$_2$ modes among the total 27 vibrational frequencies including nine a$_1$, six b$_1$, and seven b$_2$ modes. The IR spectrum of dimethyldioxirane may be specified by 12 strong peaks which have relatively large IR intensities (>10 km/mol). When comparing the harmonic vibrational frequencies with the five experimental fundamentals, it is important to remember that SCF and CISD frequencies are typically 10% and 5% high, respectively. The CCSD and CCSD(T) frequencies can reduce this error to 3% with sufficiently large basis sets.[39] The first and only measurement of the IR spectrum for dimethyldioxirane was reported without

TABLE 5: Vibrational Frequencies (in cm^{-1}) with IR Intensities (in km/mol) in Parentheses and Zero-Point Vibrational Energies (kcal/mol) for Dimethyldioxirane at Various Levels of Theory

		SCF			CISD		CCSD		CCSD(T)	
sym	assignment	DZP	TZP	TZ2P	DZP	TZP	DZP	TZP	DZP	expt[a]
a_1	CH sym str	3313(20)	3281(16)	3289(15)	3298(15)	3267(10)	3212(14)	3177(10)	3196(15)	3012
a_1	CH sym str	3208(18)	3184(16)	3193(17)	3181(13)	3159(11)	3094(14)	3069(12)	3077(14)	2999
a_1	Me sym bend	1658(70)	1644(43)	1642(27)	1599(38)	1590(21)	1537(12)	1531(5)	1520(4)	
a_1	Me sym bend	1576(73)	1572(81)	1569(78)	1524(72)	1518(78)	1467(59)	1457(55)	1448(46)	
a_1	CO str	1528(18)	1526(24)	1525(39)	1477(17)	1474(19)	1423(33)	1416(38)	1399(48)	
a_1	Me sym rock	1174(3)	1173(3)	1172(4)	1130(2)	1130(2)	1085(2)	1082(3)	1069(2)	
a_1	CC str + OO str	1005(<1)	1001(1)	990(1)	955(<1)	954(<1)	874(<1)	872(<1)	838(<1)	
a_1	OO str + CC str	781(4)	775(4)	771(4)	758(4)	755(3)	706(3)	705(3)	671(3)	
a_1	CCC bend	377(2)	379(1)	379(2)	366(1)	368(1)	356(1)	357(1)	352(1)	
a_2	CH asym str	3272(0)	3237(0)	3243(0)	3262(0)	3227(0)	3176(0)	3137(0)	3160(0)	
a_2	Me asym bend	1591(0)	1592(0)	1600(0)	1545(0)	1543(0)	1500(0)	1494(0)	1490(0)	
a_2	Me asym rock	1077(0)	1078(0)	1083(0)	1043(0)	1040(0)	1012(0)	1006(0)	1002(0)	
a_2	CO2 twist	423(0)	422(0)	424(0)	406(0)	403(0)	387(0)	384(0)	380(0)	
a_2	torsion	172(0)	174(0)	182(0)	167(0)	167(0)	159(0)	158(0)	157(0)	
b_1	CH asym str	3280(47)	3246(40)	3252(39)	3269(41)	3234(33)	3182(40)	3143(33)	3166(39)	3005
b_1	Me asym bend	1612(17)	1613(16)	1621(15)	1566(14)	1565(13)	1520(13)	1516(12)	1510(13)	
b_1	Me asym rock	1254(7)	1253(5)	1254(5)	1224(4)	1220(2)	1188(3)	1182(1)	1174(2)	
b_1	CO asym str	914(20)	900(19)	885(18)	908(21)	897(20)	872(16)	861(16)	850(14)	899
b_1	CO2 rock	467(<1)	466(<1)	468(<1)	448(1)	447(1)	431(1)	429(1)	425(1)	
b_1	torsion	229(<1)	230(<1)	233(<1)	227(11)	228(11)	222(10)	222(10)	221(9)	
b_2	CH asym str	3311(14)	3279(13)	3287(13)	3297(17)	3266(16)	3210(17)	3175(1)	3195(17)	
b_2	CH asym str	3201(8)	3177(5)	3186(4)	3176(4)	3153(2)	3090(4)	3064(<1)	3073(5)	
b_2	Me asym bend	1594(<1)	1594(<1)	1600(<1)	1549(3)	1549(<1)	1504(2)	1502(<1)	1494(1)	
b_2	Me asym bend	1554(37)	1547(33)	1550(32)	1506(42)	1496(39)	1457(40)	1445(47)	1442(40)	
b_2	CC asym str	1370(38)	1358(41)	1358(39)	1341(23)	1329(25)	1304(24)	1289(36)	1292(25)	1209
b_2	Me asym rock	1019(<1)	1014(<1)	1017(<1)	992(2)	987(3)	963(3)	956(6)	953(3)	
b_2	CO_2 wag	501(20)	501(19)	501(19)	486(31)	484(29)	471(28)	470(26)	466(27)	
	ZPVE (kcal/mol)	59.3	58.9	59.0	58.4	57.8	56.3	55.9	55.8	56.3

[a] Reference 16.

detailed assignments for each peak by Murray et al. in 1985.[16] The probable assignments (based on our theoretical results) for the experimental frequencies appear in Table 4.

The three observed IR peaks around 3000 cm^{-1} may be assigned to C−H stretching vibrational frequencies and are in good agreement with our predictions. The two C−H asymmetric stretching modes (b_2) might be superposed with the symmetric stretching mode (a_1). The C−O symmetric stretching vibrational frequency is predicted to be 1416 cm^{-1} at the TZP CCSD level of theory, and 24 cm^{-1} lower with CCSD(T). This is comparable with experimental results for some substituted dioxiranes.[15] The C−C and O−O symmetric stretching vibrational frequencies are strongly coupled to each other and predicted to be 872 and 705 cm^{-1}, respectively, with very weak IR intensities. These peaks might be too weak to be observed in the IR spectrum of dimethyldioxirane. The predicted C−O and C−C asymmetric stretching frequencies of 861 cm^{-1} (22 cm^{-1} lower with CCSD(T)) and 1289 cm^{-1} (12 cm^{-1} lower with CCSD(T)) may be compared with the experimental fundamentals of 899 and 1209 cm^{-1}. Even though there are no pertinent experimental observations, there should be four or more IR peaks in the range 1300−1500 cm^{-1} due to methyl bending modes and few peaks below 500 cm^{-1}.

Concluding Remarks

The molecular structure of dimethyl-substituted carbonyl oxide has C_s symmetry with a staggered conformation. The predicted C−O bond distance of 1.28 Å at the TZP CCSD(T) level of theory shows double bond character, which implies that the electronic structure of dimethylcarbonyl oxide prefers the zwitterionic form. The transition state for the cyclization of dimethyl carbonyl oxide to dimethyldioxirane has C_1 symmetry. The energy separation between dimethylcarbonyl oxide and dimethyldioxirane is predicted to be 23.2 kcal/mol and the energy barriers for the internal rotation and the cyclization of carbonyl oxide are computed to be 1.9 and 19.5 kcal/mol, respectively, including ZPVE corrections. The real vibrational frequencies for dimethylcarbonyl oxide and a unique imaginary vibrational frequency for the transition state confirm the potential minimum and a true transition state. The harmonic vibrational frequencies and IR intensities of dimethyldioxirane have been evaluated from its fully optimized equilibrium geometries at the corresponding levels of theory using sophisticated ab initio quantum mechanical methods. The C−O symmetric harmonic stretching frequency is estimated to be around 1392 cm^{-1}. The C−C and O−O symmetric harmonic stretching modes are strongly coupled to each other, and their frequencies are predicted to be 836 and 670 cm^{-1}, respectively, with very weak IR intensities. The C−O and C−C asymmetric harmonic stretching frequencies are predicted to be 839 and 1277 cm^{-1}, respectively, with relatively strong intensities. Probable assignments of available experimental frequencies for dimethyldioxirane are made using our theoretical predictions.

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