1 Structure, Bonding, and Thermochemistry of Ketenes

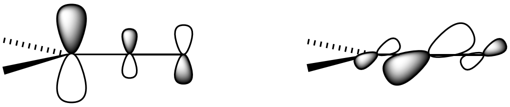
1.1 THEORETICAL AND COMPUTATIONAL STUDIES OF KETENES

Computational methods are increasingly used not only for the elucidation of the structures, energies, and properties of ketenes, but also as an adjunct to a wide variety of ketene studies. Consequently, the use of computational studies appears throughout this book and only a few of the more fundamental studies devoted to computation of ketene properties are noted here, while others are included in appropriate sections throughout the book.

A comprehensive review of theoretical studies on ketene appeared in 1980,[1] and this and other earlier studies[2,3] will not be repeated here. These provide the fundamental basis for understanding the properties of ketenes. The emphasis is now on the application of computational studies for understanding the properties of different types of ketenes and the myriad reactions that they undergo.

1.1.1 Molecular and Electronic Structure and Energy

The unique properties of ketenes derive from their cumulene structure, with the highest occupied molecular orbital (HOMO) perpendicular to the ketene plane and the lowest unoccupied molecular orbital (LUMO) in the ketene plane (Figure 1.1).[4] These reveal that ketene has substantial negative charge on oxygen and C_2, while there is positive charge on C_1 (the carbonyl carbon) in the ketene plane. As a consequence, electrophiles are expected to attack ketenes at oxygen or perpendicular to the ketene plane at C_2, while nucleophiles approach in the ketene plane at C_1.



The important resonance structures for ketene are **1a–c**, and these predict the negative charge on C_2 and the positive charge on C_1. These resonance structures were used by Hannay and Smyth[5] to explain the dipole moment of ketene (1.45

Ketenes II, by Thomas T. Tidwell

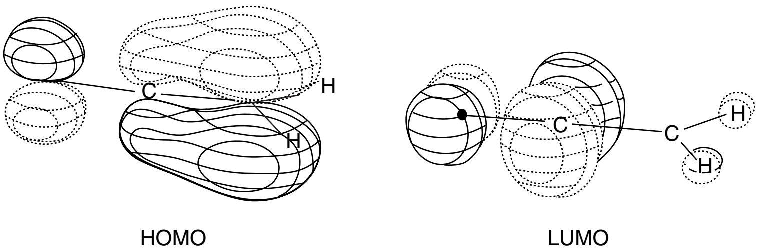
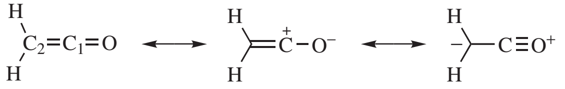


Figure 1.1 Frontier molecular orbitals of ketene (reproduced from reference 4 by permission of the American Chemical Society).

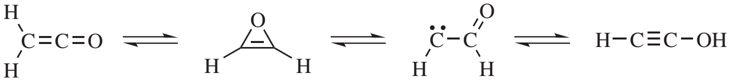
Debye [D]), which is less than those of formaldehyde (2.27 D) or acrolein (3.04 D), suggesting negative charge buildup on C_2 and the possibility of less negative charge on oxygen than in most aldehydes and ketones (Section 2.4). An alternative interpretation by Walsh[6] was that the sp hybridization of C_1 reduces the negative charge on oxygen, but this did not explain the propensity for electrophilic attack at C_2.



1a **1b** **1c**

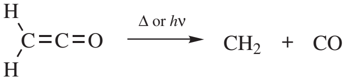
High-level *ab initio* calculations of the electronic states of ketene[7–10] have been reported. Calculated vertical excitation energies of ketene agree well with experimental values.[7] The calculation of the molecular structure and vibrational infrared (IR) spectrum of ketene, as calculated by post-Hartree-Fock and density functional theory methods, show that good agreement with experimental values can be obtained by either method.[9] *Ab initio* calculations of the electronic structures of $CH_2{=}C{=}O$ and C_3O_2 give the dipole polarizabilities of these molecules and the results provide a basis for predicting experimental properties.[10]

The structures and stabilities of the C_2H_2O isomers ketene (**1**), oxirene (**2**), formylmethylene (**3**), and hydroxyacetylene (**4**) and their interconversion by the Wolff rearrangement have been the subject of many computational studies (equation 1).[11–17] Investigations using (AM1) were particularly concerned with the possibility of competing hydrogen rearrangement[18] and the effects of substituents in aryl derivatives.[19] Calculations of the isomerization of vibrationally excited ketene via oxirene (equation 1) agree with experimental results.[20] This reaction has also been studied by density functional theory (DFT) methods, including the role of formylcarbene.[21] The nature of the stationary point of oxirene has been examined using a variety of density functional methods, and the results with the largest basis sets agree with previous high-level correlated methods that this species is an energy minimum.[22,23] This problem is discussed further in Section 3.3.



1 **2** **3** **4** (1)

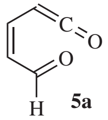
The dissociation of ketene into CH_2 and CO by photochemical or thermal methods (equation 2) is a classical problem in chemistry, particularly regarding the energy distribution and electronic states of the products (Sections 5.2, 5.3).[24,25]



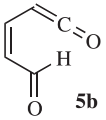
$$H_2C{=}C{=}O \xrightarrow{\Delta \text{ or } h\nu} CH_2 + CO \qquad (2)$$

1

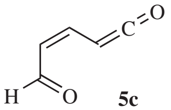
Examples of recent studies of ketenes include calculations of the structures, conformations and IR spectra of 5-oxo-2,4-pentadienal (**5**), and it was concluded that of the previously claimed structures, conformer **5a** does not exist as an energy minimum and that only **5b–d** occur.[26] Structures of the cyclized forms **6** and α-pyrone (**7**) were also calculated, as well as that for the transition state for the degenerate rearrangement of **5b** by hydrogen migration. Structures of hydroxycumulenones **8** were also calculated.[26] Structures, conformations, and vibrational spectra have been calculated for the haloacyl and acetyl ketenes **9**.[27,28] The dipole polarizabilities of ketene and carbon suboxide (C_3O_2) have also been calculated by *ab initio* methods.[10]



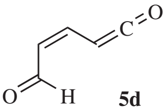
5a



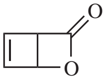
5b



5c



5d



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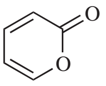

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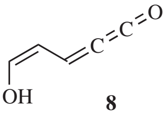

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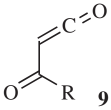
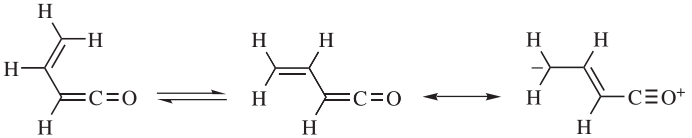


9 (R = F, Cl, Br, CH_3)

The moleculecular structure of vinylketene (**10**) has been of interest, and the C–C rotational barrier has also been determined by computations (equation 3).[29] The dipole moment and ^{13}C NMR (nuclear magnetic resonance) spectrum (Section 4.1.2) of **10** have been interpreted as showing the importance of electron delocalization to C_4, as shown in resonance structure **10a**.



s-cis-**10** *s-trans*-**10** **10a**

(3)

Molecular mechanics force fields for studies of ketenes have also been presented,[30] and the use of natural valence coordinates for ketene computations have been tested.[31]

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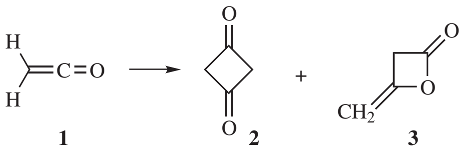
1.1.2 Theoretical and Computational Studies of Ketene Reactions

The mechanisms and energetics of many different reactions of ketenes have been analyzed by computational and theoretical methods and provide useful insights into the understanding of ketene reactivity. Many of these studies are included in later sections dealing with the preparation and properties of ketenes, but a brief survey of the approaches to some of the most common ketene reactions is presented here.

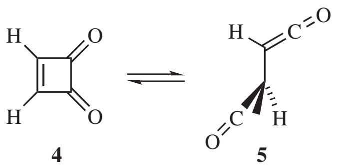
The dimerization of ketene (**1**) has been studied using *ab initio* molecular dynamics calculations, 1–5 which lead to the conclusion in the most recent calculation[1] that the β-lactone dimer **3** is the most stable, (equation 1),[1] with a free energy change of –5.5 kcal/mol, while formation of 1,3-cyclobutanone **2** has a free energy change of –4.5 kcal/mol. Previous calculations predicted a lower barrier for forming **3**,[2–5] in agreement with experiment. Dynamics calculations, however, predicted a lower barrier for formation of **2**, and appear to be less reliable in this regard.[1]



1 **2** **3**

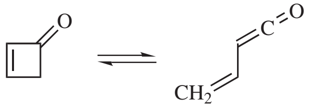
(1)

The equilibrium between cyclobuten-3,4-dione **4** and 1,2-bisketene **5**, which is shown by theory and experiment to have a twisted, almost perpendicular conformation, is considered in Section 4.9 (equation 2). Ring opening of cyclobutenone **6** to vinylketene **7** (equation 3) is discussed in Section 5.4.4, as well as the opening of the corresponding aza- and oxa-cyclobutenones to form imidoylketene (**8**) and formylketene (**9**), respectively.



4 **5**

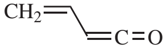
(2)



6 **7**

(3)

Computations using DFT have been used to examine the [4+2] and [2+2] cycloadditions of vinylketene (**7**), imidoylketene (**8**), and formylketene (**9**) with formaldimine (**10**).[6] For the [2+2] cycloaddition, both stepwise mechanisms involving zwitterionic intermediates and transition states for concerted reactions were located, and it was suggested that multiple transition states may be involved. For the [4+2] cycloadditions, both stepwise and concerted pseudopericyclic pathways were also calculated.[6]



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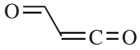
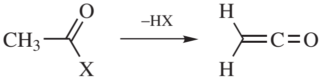


9

$CH_2{=}NH$

10

A theoretical study of the conversion of acetyl cyanide, acetyl isocyanide and acetyl fluoride (**11a–c**) to ketene and other products has also been reported (equation 4).[7,8]

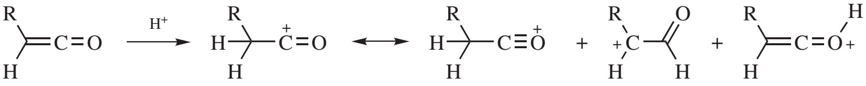


11 (X = CN, NC, F) **1**

(4)

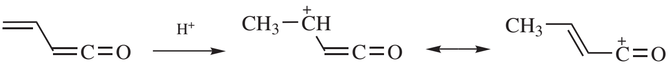
A DFT computational study of the [2+2] cycloaddition of ketene with $CH_2{=}CH_2$, $CH_2{=}O$, and $(C_5H_5)Re(O)_2{=}O$ discusses the role of orbital interactions, electrostatics, and repulsions due to the Pauli principle on the activation energies.[9]

Protonation of ketenes and bisketenes has been the subject of a number of studies.[10–15] Protonation of ketene (**1**) at C_2 forming the acylium ion **12** is strongly favored relative to protonation at C_1 forming α-formyl carbocation **13**, but for substituted ketenes **14**, strongly electron-donating substituents R enhance the possibility of formation of **13** (equation 5).[13,15] Protonation at oxygen forming **15** is not as favorable as protonation at C_2 in the cases studied. For vinylketene protonation at C_4 forming the allylic cation **16** is the lowest energy pathway (equation 6).[11]



14 (**1**, R = H) **12** **13** **15**

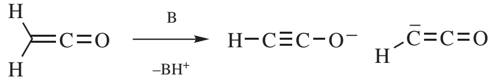
(5)



10 **16**

(6)

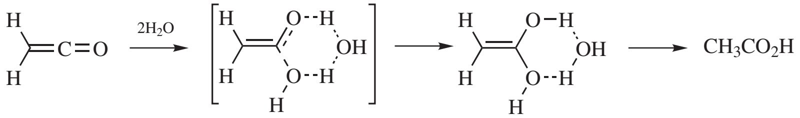
Proton abstraction from ketene (**1**) forming the ynolate anion **17** has been the subject of computational study, and the linear structure for **17** with negative charge delocalized between oxygen and C_2 is favored over a bent structure **18** that could have negative charge concentrated on C_2 (equation 7).[16,17]



1 **17** **18**

(7)

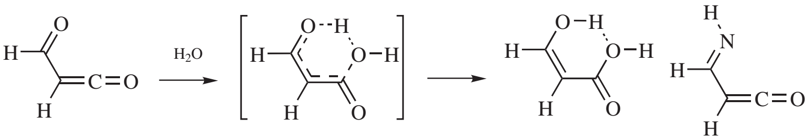
The hydration of ketene has been the subject of numerous computational studies, and reaction with two water molecules through a cyclic transition state **19** forming the acid enol **20** is favored over addition of a single H_2O molecule or addition of two H_2O molecules to the C–C double bond, forming acetic acid directly (equation 8).[18–21] This is the accepted mechanism for hydration of aldehydes and ketones forming hydrates in both experimental and theoretical studies.[22–25]



1 **19** **20**

(8)

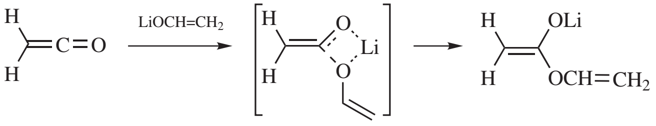
Reaction of formylketene (**21**)[26] with H_2O was predicted to occur with coordination of the H_2O to the formyl oxygen through pseudopericyclic transition state **22** forming **23** (equation 9).[26,27] Imidoylketene **24** was found to behave similarly[27]



21 **22** **23** **24**

(9)

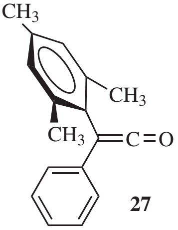
The reactions of LiH, and $LiCH_3$ with ketene are predicted to occur through initial lithium coordination to the ketenyl oxygen and then bond formation to the carbonyl carbon.[28] The addition of the lithium enolate of acetaldehyde was predicted to occur similarly, with C–O bond formation giving **25**, even though C–C bond formation gives a more stable product (equation 10).[29] This result was confirmed experimentally (Section 5.5.2.2)



1 **25** **26**

(10)

The structure of mesitylphenylketene **27** has been calculated at the HF/3–21G level and has been found to have a twisted structure of the mesityl perpendicular to the ketene plane, with the bond distances (**27a**) and bond angles (**27b**) shown.[30] The transition state for addition of MeLi was also calculated, and the preferential attack from the side of the mesityl group was explained by the perpendicular conformation adopted by this substituent to minimize steric interactions.[30]



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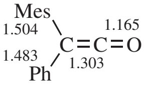
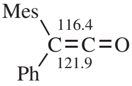


27a



27b

Other theoretical studies include the possible formation of metal-complexed ketenes from vinyl carbene complexes (Section 3.5),[31] radical cyclization of ketenes (Section 5.7),[32] and the reaction of ketenes with diazomethanes (Section 5.10).[33]

The structure of the complex of ketene with $Cr(CO)_4OH_2$ was calculated using the B3LYP(6-31)G$^+$) basis set for C, H, and O, and a double (ζ) basis set for Cr (Figure 3.1, Section 3.5).[15]

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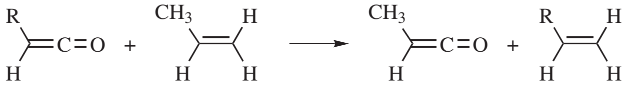
1.1.3 Substituent Effects on Ketenes

The effects of substituents on the stability of ketenes were studied by *ab initio* calculations of the structures and energies of the ketenes and isodesmic comparison with alkenes (equation 1).[1–3] The energy change (kcal/mol) in the conversion of a substituted ketene **1** and propene (**2**) to methylketene **3** and the substituted alkene **4** was taken as the stabilization energy (*SE*) of that substituent on ketenes (Table 1.1). The choice of CH_3 as the standard of comparison is arbitrary, but emphasizes that by this method many alkyl, alkenyl, and aryl groups (Me, cyclopropyl, CF_3, vinyl, phenyl) are calculated to have similar effects, and the *SE* values are small. The results are consistent using HF/3–21G, HF/6–31G*, and MP2/6–31G* level calculations, which produces confidence that the conclusions will not be affected by higher-level calculations.



1 **2** **3** **4** (1)

From a qualitative viewpoint, the *SE* values (Table 1.1) are consistent with experience, for example in the known stability of silyl-substituted ketenes and the high reactivity of haloketenes, especially fluoroketenes. This suggested a correlation with substituent electronegativity, and indeed, a reasonable correlation

TABLE 1.1 Comparative Calculated Stabilization Energies (kcal/mol) (MP2/6–31G*//MP2/6–31G* and HF/6–31G*//HF/6–31G*) for Ketenes RCH=C=O for the Isodesmic Reaction of Equation 1[1,3]

R	ΔE (MP2)	ΔE (HF)	χ_{BE}[a]
H	3.9	3.3	2.20
Li	30.1	27.9	1.00
BeH	19.6	18.1	1.47
BH_2	18.7	16.8	1.93
CH_3	0.0	0.0	2.56
NH_2	−9.3	−7.2	3.10
OH	−14.5	−14.2	3.64
F	−16.9	−17.2	4.00
Na	34.3	29.2	1.00
MgH	23.2	21.9	1.33
AlH_2	20.1	18.7	1.62
SiH_3	11.5	10.9	1.91
PH_2	6.3	6.3	2.17
SH	0.2	1.3	2.63
Cl	−7.7	−7.5	3.05
CF_3	—	−0.1	2.68
c-Pr	—	−1.8	2.56
$CH{=}CH_2$[b]	—	−0.2	2.61
$CH{=}O$[c]	5.4	3.6	2.60
Ph	—	0.9	2.58
CO_2H	—	4.7	2.66
$C{\equiv}CH$	0.5	0.2	2.66
CN	0.6	−0.4	2.69
$CH{=}C{=}CH_2$	—	−1.6	
$CH{=}C{=}O$	—	−5.3[d]	2.58
$N{=}O$	—	−0.1	3.06
NO_2	1.9	−3.2	3.22
$N{\equiv}C$[e]	—	−8.5	3.30

[a] Group electronegativity from refs. 4, and 5, except Pauling electronegativity for H.

[b] Transcoid.

[c] Ciscoid.

[d] For the process $(CH{=}C{=}O)_2 + (CH_2{=}CH)_2 \rightarrow 2\ CH_2{=}CHCH{=}C{=}O$.

[e] Isocyano.

(Figure 1.2) was found with the group electronegativities χ_{BE} provided by Boyd, Boyd, and Edgecombe (equation 2).[4,5] Thus, ketenes are expected to be stabilized by electropositive substituents, which are capable of σ-π electron donation from the R–C_2 bond to the carbonyl group, and destabilized by electronegative groups. Electronegative atoms such as O, N, and the halogens also have lone pairs of electrons, which have a repulsive interaction with C_2 of ketenes, which bears a high negative charge, as found by the computations, and as seen in the remarkably high field ^{13}C

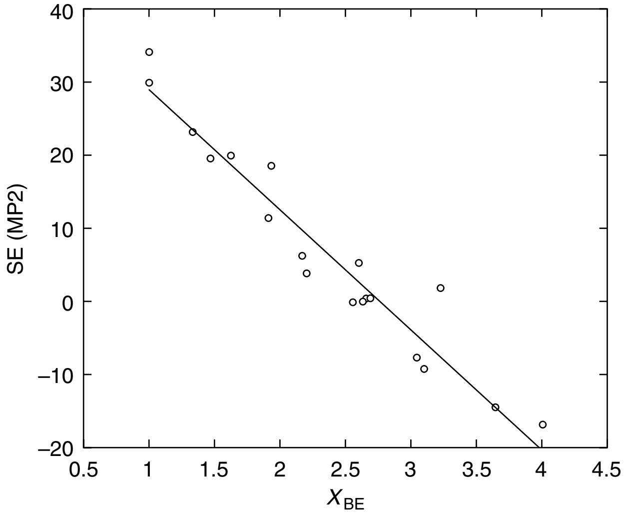
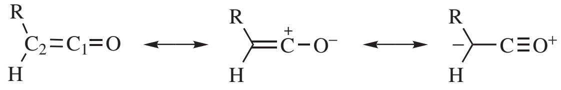


Figure 1.2 Plot of MP2/6–31G* calculated stabilization energies for substutued ketene versus substituent group electronegativities (X_{BE}).

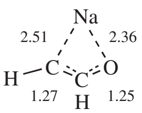
NMR shifts of this carbon (Section 2.1), and as expected by the resonance structure **1c**.

$$SE_{(\mathrm{MP2})} = -17.0_{\chi\mathrm{BE}} + 46.4 \quad (r = 0.97) \tag{2}$$



1a **1b** **1c**

As shown in Figure 1.2, there are some deviations from the correlation, and those for the substituents Na, BH_2 and CH=O are all significantly above the correlation line (obs: 34.3, 18.7, and 5.4, respectively, calculated from equation 2: 29.4, 13, and 2.2, respectively), indicating greater stabilization than expected from these substituents on the basis of their electronegativities. The extra stabilization of sodioketene (**5**) can be understood as arising from the bridged structure **5** calculated for this ketene (bond distances in Å shown), while boranylketene (**6**) and formylketene (**7**) are stabilized by conjugation.



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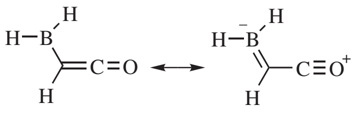

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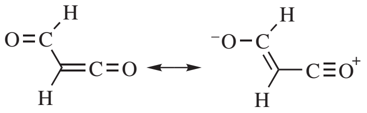

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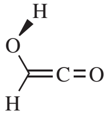
The nonplanar geometries of hydroxyketene (**8**) and aminoketene (**9**) are another structural feature revealed by the computations.[1,3] These ketenes with n-π donor groups adopt these conformations to minimize repulsive interactions between the π-electrons concentrated at C_2 and the lone pairs. The suggestion of a bonding interaction between the nitrogen lone pair and the carbonyl carbon in **9** was discounted, as the calculated bond order between these atoms is negative.[1]



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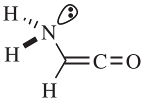

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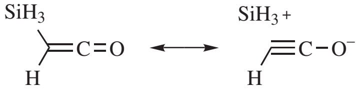
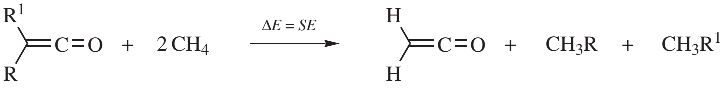
The stabilization of silylketenes **10** and others with electropositive substituents may be ascribed to hyperconjugative electron donation, as shown in **10a** (Section 4.5). This is an example of the β-silicon effect, as observed in β-silyl carbocations.[6]



10 **10a**

A limited study using computations at the G3(MP2)//B3LYP level for an isodesmic comparison of ketenes with substituted methanes was carried out, which included disubstituted ketenes (equation 3).[7] The results are given in Table 1.2. This treatment compares the substituent effects for ketenes to those for substituted methanes and also includes substituent effects on disubstituted ketenes.



$$R^1RC{=}C{=}O + 2\,CH_4 \xrightarrow{\Delta E = SE} H_2C{=}C{=}O + CH_3R + CH_3R^1 \qquad (3)$$

11 **1** **12** **13**

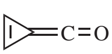
Because of the different references used, the results in Tables 1.1 and 1.2 are not directly comparable. The magnitudes of the ΔE values are larger for the comparisons in Table 1.1, and this is evidently due to the difference of the substituent effects in $RCH{=}CH_2$ as compared to RCH_3. In Table 1.1 the magnitude of the F/OH and F/Cl differences are 2.4 and 11.6 kcal/mol, respectively, compared to 6.4 and 6.2 kcal/mol, respectively, in Table 1.2. Thus, while the magnitude of the substituent effects is F > OH > Cl for both sets, there are quantitative differences. More striking are the effects in the disubstituted ketenes (Table 1.2), which, rather

TABLE 1.2 Calculated Stabilization Energies (kcal/mol) (G3MP2//B3LYP) for Ketenes $RR^1CH{=}C{=}O$ for the Isodesmic Reaction of Equation 3[7]

Ketene	ΔE (kcal/mol)
$HOCH{=}C{=}O$	−5.6
$MeOCH{=}C{=}O$	−6.1
$ClCH{=}C{=}O$	−5.8
$ClC(OH){=}C{=}O$	−4.3
$ClC(OMe){=}C{=}O$	−3.7
$FCH{=}C{=}O$	−12.0
$FC(OH){=}C{=}O$	−5.4
$FC(OMe){=}C{=}O$	−5.4

than being additive, are actually less for the disubstitued cases. This suggests that stabilizing effects are present when there are two electronegative substituents on C_2 of ketene. Further study to test the generality of this effect is warranted.

Substituent effects in ketenylketenes are considered in Section 4.9 and those in allenylketenes in Section 4.18.[8] Computational studies of antiaromatic destabilization in trifulvenone **14** and heptafulvenone **16**, and of aromatic stabilization of pentafulvenone **15**, are discussed in Section 4.1.10.[9,10]



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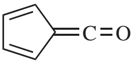

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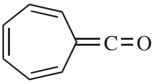

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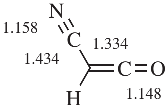
1.2 MOLECULAR STRUCTURE DETERMINATIONS

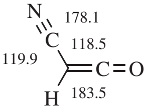
Molecular structures of many ketenes[1] have been examined experimentally by microwave,[2–15] electron diffraction,[16–18] and X-ray techniques,[19–27] and many more by computations at various theoretical levels. Experimental data for some simple ketenes are given in Table 1.3, with calculated values for comparison.

Structures have been determined using microwave spectroscopy for $CH_2{=}C{=}O$ (**1**),[2–6] $NCCH{=}C{=}O$ (**2**),[7] $FCH{=}C{=}O$ (**3**),[8,9] $ClCH{=}C{=}O$ (**4**),[10] $CH_3CH{=}C{=}O$ (**5**),[11] and $BrCH{=}C{=}O$ (**6**).[12] The microwave spectrum of vinylketene (**7**) was measured, but only the dipole moment was obtained from the data.[13] The microwave spectrum of $(CH_3)_2C{=}C{=}O$ (**8**) was measured and the structure obtained with the assumption of the same $C{=}O$ bond length as in $CH_3CH{=}C{=}O$.[14] The ketene $Cl_2C{=}C{=}O$ (**9**) had a negligible dipole moment and the microwave spectrum could not be measured,[15] but the structure was determined using electron diffraction.[16] A molecular structure for thioketene ($CH_2{=}C{=}S$, **10**) was also determined.[17] The experimental bond distances, bond angles, and dipole moments obtained are summarized in Table 1.3, along with comparative computational results.

Gas phase pyrolysis of the acyl chloride with appropriate isotopic labeling at 750°C gave cyanoketene (**2**) with ^{2}H, ^{15}N, ^{13}N, carbonyl ^{13}C, or ^{18}O labeling for determination of the molecular structure by microwave spectroscopy.[7] The molecule had a dipole moment of 3.542(15) D, and the molecular structure was in reasonable agreement with the calculated structure (Table 1.3). See also Section 4.1.3.



2a



2b

The gas phase molecular structure of $(CF_3S)_2C{=}C{=}O$ (**11**) has been determined by electron diffraction and displays C_2 symmetry, with the CF_3–S bonds perpendicular above and below the molecular plane.[18] This geometry is that predicted by molecular orbital calculations, and minimizes repulsion between the lone pairs on sulfur and the electron-rich HOMO at C_2 of the ketene.

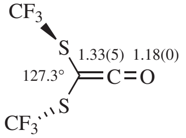


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TABLE 1.3 Experimental and Calculated (HF/6-31G*//HF/6-31G*)(Parentheses) Bond Distances, Bond Angles (Deg), and Dipole Moments of Ketenes $RR^1C_2C_1C{=}O$

R	R^1	C=O	$C_1{=}C_2$	C_2-R_1	C_2-R	OC_1C_2	RC_1C_2	RC_2R_1	$R_1C_2C_1$	μ (Debye)	Ref
H	H	1.164	1.3165	1.0800	1.0800	180.0	119.01	121.98	119.01	1.41	3
		1.1626	1.3147	1.0905	1.0905	180.0	118.27	123.46	118.27		2
		(1.145)	(1.306)	(1.075)		(180.0)	(119.3)	(121.4)	(119.3)	(1.63)	22
		(1.1681)	(1.3166)	(1.0745)	(1.0745)	(180.0)	(119.4)	(121.2)	(119.38)		2[a]
F	H	1.167	1.317	1.080	1.356	178.0	119.5	118.2	122.3	1.29	8,9
		(1.147)	(1.308)	(1.067)	(1.339)	(177.9)	(120.1)	(117.4)	(122.5)	(1.59)	22
		(1.181)	(1.323)	(1.074)	(1.363)	(178.1)	(120.0)	(117.7)	(122.3)		9[b]
Cl	H	1.161	1.316	1.082	1.726	180.0	120.9	119.3	119.8	1.2	10
		(1.142)	(1.308)	(1.068)	(1.731)	(179.2)	(120.5)	(118.7)	(120.8)	(1.39)	22
Br	H	1.162	1.316	1.082	1.880	180.0	118.5	120.6	120.9		12
CH_3	H	1.171	1.306	1.083[c]	1.518	180.5	122.6[d]	123.7	113.7	1.79	11
		(1.149)	(1.305)	(1.074)	(1.512)	(180.0)	(123.2)	(120.8)	(116.0)	(1.99)	22
NC	H	1.148	1.334		1.434	176.5	118.5	119.9		3.542(15)	7
		1.133	1.321	(1.072)	(1.424)	(178.7)		(121.3)	(120.6)	(3.72)	22
$CH{=}CH_2$	H									0.97	12
										(1.20)	22
Cl	Cl	1.160	1.299	1.726	1.726	180.0	120.4	119.2	120.4		16
		(1.161)	(1.306)	(1.726)	(1.726)	(180.0)	(120.7)	(118.6)	(120.7)	(0.07)	16a
CH_3	CH_3	1.171	1.300	1.514		180.0	120.6	118.8	120.6		14
CF_3S	CF_3S	1.18	1.33					127.3			18

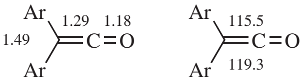
[a] MP3/6–31G**.

[b] MP2/4–31G**.

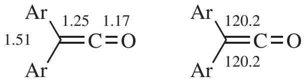
[c] For CH_3 C-H 1.083 ((1.084), 1.11.

[d] H–C–H 109.9, 108.8; H–C–C_2 111.1 (111.4).

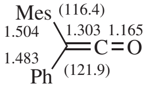
Structures have been obtained by X-ray studies of dimesitylketene (**12**) and bis(3,5-dibromomesityl)ketene (**13**).[19] Both structures have propeller conformations of the aryl groups, and in **12** these are nonequivalent, with dihedral angles of 48.8° and 56.8°, while in **13** these are equivalent, with dihedral angles of 56.8°. The structure of mesitylphenylketene **14** has been calculated at the HF/3–21G level, with the indicated bond distances and bond angles (parentheses).[20]



12 (Ar = 2,4,6-$Me_3C_6H_2$)



13 (Ar = 2,4,6-$Me_3C_6Br_2$)



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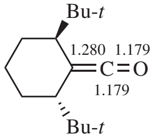
Structures determined by X-ray for the aliphatic ketene **15**,[21] the alkenylketene **16** with a chromiun tricarbonyl complexed to the side chain,[22] and the tetraketene **17**[23] have also been reported. There are systematic differences in the ketenyl C=C bond lengths determined by X-ray, which are all between 1.25 and 1.29 Å, and those obtained by microwave spectroscopy or electron diffraction reported in Table 1.3, which are all greater than 1.30 Å, and those calculated at the MP2/6–31G* level, which are all also greater than 1.30 Å, with the exception of those to the highly electropositive Li, Na, and MgH substituents, none of which are known experimentally.[24,25]



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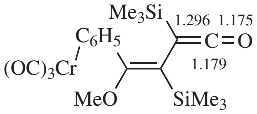

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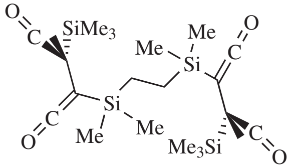
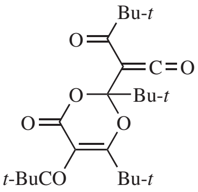


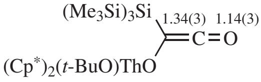
17

The X-ray structure of ketene **18**, derived from the dimerization of dipivaloylketene,[26] revealed that the ketenyl C=O and C=C bond lengths of 1.13 and 1.35 Å are distinctly shorter and longer, respectively, than the average of those of four previous ketene X-ray structure determinations of 1.18 and 1.28 Å, respectively, but are very similar to recently determined values of 1.14 and 1.34 Å for a (metaloxy)silylketene **19**.[27] The shorter C=O and longer C=C bonds for **18** are consistent with acyl conjugation of the ketene as proposed for other acylketenes (**20**; see also Section 4.1.4), but the C–C bond length of the silylketene was not shortened, as could be expected by resonance structure **21**.

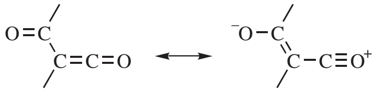


18

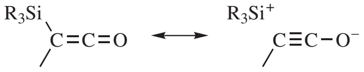
	obs bond lengths (Å)	ketene bond lengths from literature
C=O	1.13 (1)	1.18, 1.17, 1.18, 1.18 (1.18)
C=C	1.35 (2)	1.29, 1.25, 1.28, 1.30 (1.28)



19

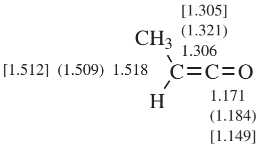


20



21

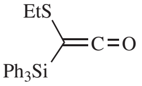
A molecular structure of $CH_3CH{=}C{=}O$ (**5**) calculated using the MP2/6–31G level (parentheses) shows no better agreement with experimental values than do previous HF/6–31G* calculations [brackets].[29]



5

Carbon suboxide C_3O_2 (O=C=C=C=O, **22**) has a quasilinear structure with a very small energy barrier for bending around the central carbon.[29–31] The structure of crystalline C_3O_2 has been determined by X-ray.[32]

Other molecular structures of ketenes have been determined by X-ray for the silyl stabilized ketene **23**,[33] and for a cobalt-complexed ketene.[34]



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1.3 THERMOCHEMISTRY OF KETENES

The determination of the thermodynamic properties of ketenes has been of continuing interest,[1–14] and these properties have been obtained by both experimental and computational methods. There have been significant differences in values from different sources, but resolution of these differences has apparently been achieved. Preferred values from the most recent reports for ketene, methylketene, and dimethylketene are given in Table 1.4, and a compilation of some of the other existing data is presented in Table 1.5.[1–21] The computational value for

TABLE 1.4 Thermodynamic Values for Simple Ketenes (kJ/mol; kcal/mol in brackets)

Ketene	ΔH^{o}_{f}	PA (kJ/mol) [kcal/mol]	GB (kJ/mol) [kcal/mol]	Ref
$CH_2{=}C{=}O$	-54 ± 5 [-12.9]	822.9 ± 3.4 [195]	790.1 ± 1.5 [188]	2, 5, 22
$CH_3CH{=}C{=}O$	-66.9 [-16.0]^{21}	839.8 ± 3.6 [200.7]	809.6 ± 3.3 [193.5]	1, 2, 5, 21
		845.4 ± 4.8		7
$(CH_3)_2C{=}C{=}O$	-92	855 [204]		4, 6

TABLE 1.5 Experimental and Theoretical Heats of Formation and Proton Affinities (kJ/mol; kcal/mol in brackets)

	ΔH^{o}_{f298}	PA	Ref
$CH_2{=}C{=}O$	-52		6
	-54 ± 5 [-12.9]	822.9 ± 3.4 [195]	2, 5
	$-47.7(-11.4)$		15
	(-14.7)		16
	-100 ± 10		18
$CH_2{=}C{=}O^{+\bullet}$	875 [209]		4, 6
$CH_3C(+){=}O$	658		6
$CH_3CH{=}C{=}O$	-68 [-16.3]		4, 6
	-97 ± 5		1, 2
		845 ± 4.8	7
		834.1	20
	-95.5 [-22.8]		5
	-86.6 [-20.6]	853	12
	-65.1 ± 10		3
	-105 [-25]		17, 19
$CH_3CH{=}C{=}O^{\pm\bullet}$	795 [190]		6
	797.0		3, 4
$CH_3CH_2C(+){=}O$	618 [148]		6
$(CH_3)_2C{=}C{=}O$	-92 [22]	855 (204)	4, 6
	-137 ± 5 [-32.7]		5
	-155 [-37]		19
$(CH_3)_2C{=}C{=}O^{+\bullet}$	726 (174)		4
	723 [173]		6
$(CH_3)_2CHC(\pm){=}O$	583 [139]		6
$NCCH{=}C{=}O$	-100.4 [-24 ± 5]		10
$NCCH_2C(+){=}O$	828 [198 ± 3]		10
$NCCH_2C(\bullet){=}O$	133.8 [32 ± 1]		10
$NCCH{=}C{=}O^{+\bullet}$	1061 [253 ± 3]		10
$PhCH{=}C{=}O$	25.1 [6] (est)		19
$Ph_2C{=}C{=}O$	121 [29] (est)		19
$CH_2{=}CHCH{=}C{=}O$	16.7 [4]		14
$CH_2{=}CHCH{=}C{=}O^{+\bullet}$	816 [195]		14

TABLE 1.6 CBS–Q Calculated ΔH_f^{298} and ΔS^{298} for Ketenes and Bisketenes

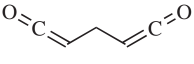
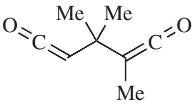
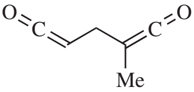
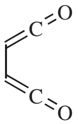
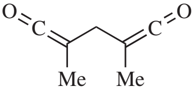
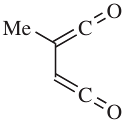
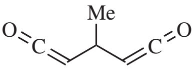
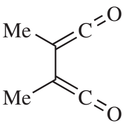
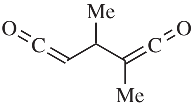
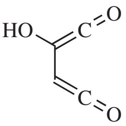
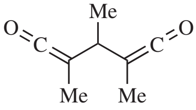
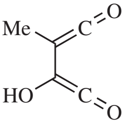
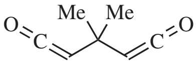
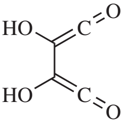
Ketene	ΔH_f^{298} (kcal/mol)	ΔS^{298} (cal/mol K)	Ketene	ΔH_f^{298} (kcal/mol)	ΔS^{298} (cal/mol K)
CH_2=C=O (**1**)	−11.34	57.47	MeOC(OH)=C=O (**17**)	−68.94	80.20
MeCH=C=O (**2**)	−15.14	68.20	MeC(OH)=C=O (**18**)	−44.90	75.73
EtCH=C=O (**3**)	−20.67	77.61	MeC(OMe)=C=O (**19**)	−40.15	84.34
i–PrCH=C=O (**4**)	−28.57	84.05	EtC(OH)=C=O (**20**)	−50.42	84.85
t–BuCH=C=O (**5**)	−37.75	87.66	*i*–PrC(OH)=C=O (**21**)	−58.29	91.63
Me_2C=C=O (**6**)	−21.73	74.92	*t*-BuC(OH)=C=O (**22**)	−68.88	95.04
MeCEt=C=O (**7**)	−27.97	85.84	EtC(OMe)=C=O (**23**)	−45.77	94.10
i–PrCMe=C=O (**8**)	−35.76	92.13	*i*-PrC(OMe)=C=O (**24**)	−54.08	100.17
t–BuCMe=C=O (**9**)	−44.87	95.68	*t*-BuC(OMe)=C=O (**25**)	−64.68	103.36
Et_2C=C=O (**10**)	−34.66	93.66	($HOCH_2$)CH=C=O (**26**)	−51.60	77.65
i–PrCEt=C=O (**11**)	−42.52	101.41	($HOCH_2$)CMe=C=O (**27**)	−58.53	85.64
t–BuCEt=C=O (**12**)	−51.76	104.35	(HOCHMe)CH=C=O (**28**)	−61.18	85.32
HOCH=C=O (**13**)	−35.82	67.30	(HOCHMe)CMe=C=O (**29**)	−68.83	94.02
MeOCH=C=O (**14**)	−31.33	75.68	($HOCMe_2$)CH=C=O (**30**)	−72.47	88.83
$(HO)_2$C=C=O (**15**)	−73.22	70.23	($HOCMe_2$)CMe=C=O (**31**)	−79.94	97.06
$(MeO)_2$C=C=O (**16**)	−67.74	86.97			
 **32**	−15.18	85.48	 **39**	−41.51	108.11
 **33**	−22.85	95.48	 **40**	−10.03	76.91
 **34**	−30.98	102.69	 **41**	−17.06	86.75
 **35**	−23.64	94.48	 **42**	−24.12	94.42
 **36**	−31.73	102.13	 **43**	−41.32	85.70

TABLE 1.6 (*Continued*)

Ketene	ΔH_f^{298} (kcal/mol)	ΔS^{298} (cal/mol K)	Ketene	ΔH_f^{298} (kcal/mol)	ΔS^{298} (cal/mol K)
 **37**	−39.88	110.27	 **44**	−48.89	94.76
 **38**	−32.93	97.07	 **45**	−72.35	92.25

ΔH_f^0 of -92 kJ/mol[4,6] for dimethylketene appears preferable to the experimental value of –137 kJ/mol,[5] as the latter value depends on reference values for other cations and a recently revised experimental value of $\Delta H^o{}_f$ for the propionyl cation necessitated a revision of the proton affinity for methylketene.[7] The trend in the values for the three ketenes also appears reasonable.

Based on an analysis of literature data, a revised value for the enthalpy of formation of ketene $\Delta H_f^0 = -100 \pm 10$ kJ mol^{-1} was proposed.[18] This differs significantly from the previously accepted value of $\Delta H_f^0 = -48$ kJ mol^{-1}, and further confirmation of this value appears warranted.

Heats of formation (kcal/mol values in parentheses) have been reported for the following species: NCCH=C=O (24±5), $NCCH_2C(+)=O$ (198±3), $NCCH_2C(\bullet)=O$ (32±1), and $NCCH=C=O^{+\bullet}$ (253±3).[7,10]

Sumathi and Green[11] have used MP2/6–31G*//MP2/6–31G* calculations to determine the heats of formation of 45 fairly simple monoketenes and bisketenes, as shown in Table 1.6. The calculated values were considered to be as accurate as the available experimental values and were used to derive group equivalents for the estimation of ΔH_f for other species.

Proton affinities (kJ/mol) of ketenes RCH=C=O for the groups R have been found by CBS-QB3 calculations as follows: H (820), CH_3 (844), NH_2 (917), OH (823), and F (793).[22] These results reflect the combined effect of the substituent on the stability of the ketene and on the cation $RCH_2C(+)=O$ such that the least favorable protonation for R = F was attributed to the great instability of the cation, FCHC(+)=O, while the most favorable process was for R = NH_2, where the initial product was the dissociating complex $H_2NCH^+ \bullet\bullet\bullet C=O$.[22]

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