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Thermodynamic Properties of Ketenes: Group Additivity Values from Quantum Chemical Calculations

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The geometries and thermodynamic properties (ΔH_f^{298}, S^{298}, and $C_p(T)$ (300−1500 K)) of 45 ketenes of four different types namely alkylketenes (set I), oxygenated alkylketenes (set II), 1,2- and 1,3-bisketenes (set III), and ketene-substituted alcohols (set IV) were determined by means of the CBS-Q procedure. The heats of formation of oxygenated ketenes were reevaluated using isodesmic reactions, and a systematic and consistent (∼1.5 kcal/mol) over prediction in the stability of *tert*-butyl substituted systems has been identified at the CBS-Q level. Nearly 20 new thermochemical groups for the ketene molecular family and 3 nonnext neighbor interaction terms were evaluated from the computed thermodynamic functions by simultaneous parameter estimation. The nonnext neighbor corrections account for an eclipsing interaction between the >CCO group and its β bonds. Statistical analysis of the ab initio data demonstrates the validity of the group additivity approximation. The derived group values describe the ab initio ΔH_f^{298}, S^{298}, and C_p(300 K) with an average deviation of less than 0.06 kcal/mol, 0.15 cal/(mol K), and 0.18 cal/(mol K), respectively. In most cases, these quantum-calibrated group additivity estimates are expected to be more accurate than the limited experimental data and empirical estimates; the only significant discrepancy (∼1.5 kcal/mol) is for substituted ketenes containing a *tert*-butyl group.

I. Introduction

Ketenes are basic building blocks in organic synthesis.[1] The regio- and stereoselective reactivity of ketenes is dictated by the localized HOMO and LUMO orbitals of the >CCO functional group which lie in two different planes perpendicular to each other. Ketenes are highly reactive compounds that can be synthesized by high-temperature pyrolysis[2] or photolysis.[3] Ketene and ketenyl radicals are produced in the combustion of acetylene,[4] acetone,[5] and other hydrocarbon fuels.[6] The concentrations of ketene and formaldehyde were both shown to increase dramatically in partially premixed flames.[7] Reactions of ketene and ketenyl radicals with other species are included in oxidation mechanisms of hydrocarbons.[8−10] The reduction of NO emission using propene as the secondary fuel has been shown[11] to involve the ketenyl radical intermediate. Knowledge of the thermodynamic properties of ketenes as well as the kinetic parameters of their reaction with other species is therefore needed for the description of pyrolysis and oxidation of fuels, as well as for photolytic reactions.[12,13] There is not much hope of getting this information soon through experimental means as few laboratories have the appropriate facilities and required expertise. There is a clear deficit of thermochemical information for the highly reactive ketenes that prevents a better understanding about their reactivity. There is a growing need for such information because of the changing trend in the modeling community to employ computers for kinetic model construction. The driving force for this changing approach is the expectation that the resultant computer generated model will be comprehensive comprising all kinetically significant species and reactions, which otherwise are likely to be missed in a man-made model. However, the cost of this comprehensiveness is that during the model construction process the thermodynamic properties of thousands of species must be estimated a priori. Group additivity approaches to the calculation of thermodynamic functions could meet the demands of rigorous model construction by computers. However, most group additivity studies have been focused on compounds where a wealth of experimental data are available; ketenes have largely been neglected because of the lack of experimental results. Recent years, however, have witnessed a remarkable improvement in the ability to predict molecular properties using sophisticated quantum chemical methods. We have recently[14−16] employed state-of-the-art quantum chemical calculations to derive group values (GVs) for transient species and transition structures for which direct experimental measurements are not feasible. In the present work, we derive GVs for the molecular family of ketenes using high-level quantum chemical calculations on a limited set of molecules. We have chosen 45 ketenes of four different types for the present study and we aim to develop nearly 20 GVs from the results of ab initio calculations.

II. Theoretical Methodology

A. Quantum Chemical Calculations. Standard ab initio molecular orbital theory calculations were carried out with the Gaussian 98 program.[17] Equilibrium geometries were completely optimized using the restricted Hartree−Fock method and second-order Møller−Plesset (MP2) perturbation theory with analytical gradients using the 6-31G(d′) basis set. The 6-31G(d′) basis is defined as having d-type polarization functions on the heavy atoms with exponents as in the 6-311G(d) basis. The harmonic vibrational frequencies and the moments of inertia for external rotation were computed at the HF/6-31G(d′) level. The energies were calculated using the complete basis set method, CBS-Q of Petersson et al.[18,19] which combines the

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extrapolated complete basis set second-order limit (CBS2) with higher order correlation (MP3, MP4, QCISD(T)) energies derived at a relatively smaller basis set for the accurate calculation of molecular energies. The method also includes an empirical correction and a correction for spin contamination in order to achieve improved agreement with experimental data. The calculated energies for this procedure show mean absolute deviations from the experiment for the standard test set of 4.2 kJ/mol. Procedures to convert the total energies obtained from the CBS-Q procedure to heats of formation at 0 K (ΔH_f^0) are well established.[20] The most commonly used procedure involves combining the calculated atomization energy for the molecule of interest with experimental values[21] of the heats of formation of the component atoms. The heat of formation at 298 K (ΔH_f^{298}) may be determined from the calculated ΔH_f^0 using the theoretical value of the difference in enthalpy between 0 and 298 K for the target molecule, obtained using scaled calculated HF/6-31G(d′) vibrational frequencies, together with experimental values of these enthalpy temperature corrections for the component elements in their standard states as obtained from the literature.[22] The atomization energy was further corrected for spin−orbit interaction in the energies of the atoms and isodesmic bond additivity corrections as suggested by Petersson et al.[23] The bond-additivity correction (BAC) for the >CCO group in the present work is taken as the sum of BAC for C═C (−0.08 kcal/mol) and C═O (0.55 kcal/mol) bonds, whereas for all other bonds, the values established by Petersson et al.[23] have been employed.

B. Calculation of Thermochemical Properties. The total partition function, Q_{tot}, of all species was calculated within the framework of the rigid-rotor-harmonic-oscillator approximation with corrections for internal rotation. Zero-point energies and vibrational frequencies were scaled by a factor of 0.91844 as recommended because of the systematic overestimation of the HF determined frequencies by about 10%. The scaled harmonic vibrational frequencies from the HF/6-31G(d′) level of calculation and the moments of inertia of molecular structures optimized at the MP2/6-31G(d′) level were used to calculate the rotational and vibrational partition functions, entropies, and heat capacities. All torsional motions about the single bonds between polyvalent atoms were treated as hindered internal rotations. The hindrance potential for the internal rotation was obtained at the HF/6-31G(d′) level by optimizing the 3N-7 internal coordinates, except for the dihedral angle, which characterizes the torsional motion. This dihedral angle was varied from 0° to 360° in increments of 20 or 30°. The potential energy surface thus obtained was then fitted to a Fourier series $\Sigma_m A_m \cos(m\phi) + B_m \sin(m\phi)$ with $m \leq 8$. Subsequently, the partition function for the hindered rotation was obtained by solving the Schrödinger equation

$$-\frac{h^2}{8\pi^2 I_{hir}}\frac{d^2\Psi(\Phi)}{d\Phi^2} + V(\Phi)\Psi(\Phi) = E(\Phi)\Psi(\Phi)$$

for the energy eigenvalues with the fitted hindrance potential using the free rotor basis. The reduced moment of inertia for rotation, I_{hir}, in the kinetic energy term was taken as the reduced moment of the two groups about an axis passing through the center of gravity of both the groups, $I^{(2,3)}$, in the notation of East et al.[24] Though I_{hir} is actually a function of ϕ and the vibrational coordinates, in the present work, I_{hir} was fixed at its value for the equilibrium geometry, and the rotating group was assumed to be rigid. The partition function for hindered rotation was evaluated by direct counting, whereas the thermodynamic properties H, S, and C_p were calculated from the ensemble energy averages and fluctuations in internal energy, respectively, $\langle E \rangle^2$ and $\langle E^2 \rangle$.

The thermodynamic functions are computed only for the lowest energy conformer of each ketene. Because the experimental value is an average value including contributions from minima of higher energy, we introduce some error. However, this error is expected to be systematic as the preferred conformation (as discussed in the next section) and the form of the rotational potential around each single bond between the polyvalent atoms is nearly the same in a particular type of ketene. A better way is to consider all minima and compute their thermodynamic functions separately and then perform a Boltzmann averaging of the functions based on their relative energy differences. Owing to the size of the systems investigated herein and the dimension of the conformational space, we restrict ourselves to the most stable conformer.

C. Group Values and Calculation of the Group Contributions. Definition and selection of the initial groups are critical to the development of a group additivity scheme for accurate property estimation. We have chosen four types of ketenes for the present study, viz., alkylketenes (set I; **1**−**11**), oxygenated (hydroxy and methoxy) alkylketenes (set II; **12**−**24**), bisketenes (1,2- (**39**−**44**) and 1,3- (**25**−**32**); set III), and ketenyl- substituted aliphatic alcohols (set IV; **33**−**38**). The ketene fragment >CCO as a whole has been considered as a single polyvalent unit, very similar to the way Benson has treated the carbonyl compounds. In aliphatic acyclic alkylketenes, the seven possible groups are {CCO/H2}, {CCO/H/C}, {CCO/C2}, {C/CCO/H3}, {C/CCO/C/H2}, {C/CCO/C2/H}, and {C/CCO/C3}. In the family of hydroxy- and methoxy-alkylketenes (set II), the five chemically distinguishable groups are {O/H/CCO}, {O/C/CCO}, {CCO/O/H}, {CCO/O/C}, and {CCO/O2}. The family of 1,2- and 1,3-bisketenes are characterized by {CCO/H/CCO}, {CCO/O/CCO}, {CCO/C/CCO}, {C/H2/CCO2}, {C/H/C/CCO2}, and {C/C2/CCO2}, whereas those of the ketenyl-substituted aliphatic alcohols considered in the present study are {C/CCO/O/H2}, {C/CCO/O/C/H}, and {C/CCO/O/C2}.

The simplest ketene, $CH_2═C═O$ is a unique molecule and forms the unique group {CCO/H2}. To estimate the remaining groups from the ab initio calculated thermochemical properties of a set of ketenes, we employ multivariate linear regression (MVLR) analysis. Unfortunately, the estimation of each of the six remaining group values in alkylketenes fails in consequence of their linear dependence. There is a similar problem in regressing the five group values for oxygenated ketenes. Consequently, we assign the group values of {C/CCO/H3} and {O/H/CCO} to be respectively equal to that of Benson's[25] {C/C/H3} and {O/C/H} groups. This is also a common practice adopted by Benson to overcome the problem of linear dependence while deriving groups with C_d, C_t, O, CO, etc.

We deduce the contributions coming from groups other than the new ketene groups, viz., {C/C/H3}, {C/O/H3}, and {O/C/H}, using Benson's group values.[25] By doing so, we assume that the chosen level of ab initio calculation and the associated protocol for estimation of thermochemical properties are capable of reproducing fairly well the true experimental values (because Benson's group values are derived from experiments). In a series of papers,[14−16] we have recently demonstrated the performance of the chosen method against empirical group addivity predictions for molecular families with varied functional groups such as alkanes, alkenes, alkynes, alcohols, ethers, acids, and esters.

Multivariate linear regression of the vector h of thermochemical properties computed from quantum chemistry (e.g., the array of heats of formation, **h** = (ΔH_1, ΔH_2, ..., ΔH_i) of a set of *i* species) with their dependence on the associated vector **g** of group values **g** = (g_1, g_2, ..., g_j) being expressed as **h** = **Xg** yields the best values for the parameters **g**. **X** is a matrix specifying the pattern of occurrence of *j* groups in the chosen *i* molecules. Marsi et al.[26] recently applied a similar procedure to arrive at group values of enthalpies of formation for alkanes and alkyl radicals. The main difference between the two protocols is that in the present work we do not allow for a change in the group values established by Benson, viz., {C/C/H3} and {O/C/H} groups. MVLR is expected to provide more reliable results than successive evaluation of group values from a subset of molecules, an alternative procedure often employed in the literature[27,28] because of the scarcity of input thermochemical data. Furthermore, MVLR allows a statistical proof of the results of the simultaneous estimation, revealing whether the assumption of group additivity is valid and if so, to what extent. Because the experimental heats of formation are not available for most of the ketenes investigated in this study, we employ an unweighted MVLR. Because quantum chemical calculations are known to have systematic errors in describing a specific bond type, MVLR is performed on several combinations of sets to check for the consistency of the derived group values.

III. Results and Discussion

In this section, we first analyze the optimized geometries and identify the favored orientation of groups with respect to each other. Next, we compare the calculated enthalpy of formation of ketene and methyl ketene with literature values. To check the reliability of the CBS-Q atomization energies, we recomputed ΔH_f^{298} of some of the oxygenated ketenes using isodesmic reactions. We then discuss the methyl substituent effect in comparison with olefins on going from (i) ketene to methylketene, (ii) methylketene to dimethylketene, and (iii) alkylketenes to methylalkylketenes and identify the need to account for nonnext neighbor contributions to enthalpies of formation. Thereafter, the group additivity scheme and GVs derived via MVLR are presented followed by a discussion on the parallelism in GVs of ketenes, olefins, and carbonyls. Finally, the groups values for entropy and heat capacity are derived, and the hindered internal rotor potentials for various substituted ketenes are presented and discussed.

A. Geometries. Alkylketenes can be categorized as aldoketenes (RCH=C=O) and ketoketenes (R_2C=C=O). The latter can further be subdivided as alkylmethylketenes (RC(CH_3)=C=O) and dialkylketenes R_2C=C=O. Previous publications[1] have addressed in detail the issue of the structure of H_2C=C=O and demonstrated[29−32] a good agreement between the structure optimized at the MP2/6-311+G(2df,p) level and the experimental value.[33−36] Both methylketene (**1**) and dimethylketene (**5**) have also been investigated extensively by theoretical methods,[29−32] and the geometries obtained were shown to be in good agreement with the scarcely available experimental data. The important observation regarding the conformational preference of alkylketenes is that the β C−H or the C−C bonds of the alkyl group prefer an eclipsed conformation with the >CCO group (Figure 1a), and they constitute the minimum of the rotational potential well around the C−C(CO) bond. Similar preference in conformation has earlier been observed in the case of carbonyl compounds. In this regard, the ketenyl group (>CCO) behaves very much like a carbonyl (>CO) group. In systems with both β C−H and C−C bonds, eclipsing interaction with the latter bond is usually energetically more favored than the former. In Table 1, we tabulate the absolute energies of the conformers of alkylketenes with eclipsing β C−H and β C−C bonds. As can be seen, even in dialkylketenes, conformers with two eclipsing β C−C bonds are more favored over those with a β C−H and a β C−C interaction. The energy difference between these conformers (Table 1) is not a constant in all of the alkylketenes as it is associated with a change in the number of gauche interactions.

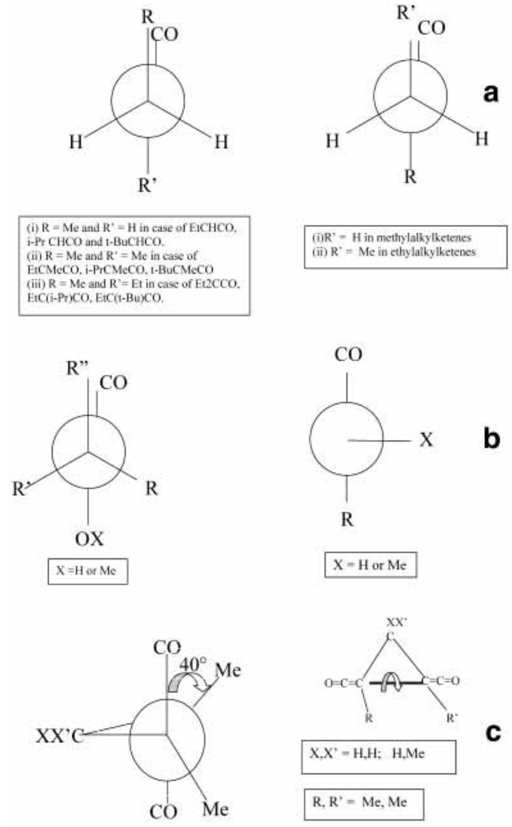

Figure 1. (a) Newman projection diagram for the preferred eclipsed conformation with the >CCO group in alkylketenes. (b) Newman projection diagram for the preferred eclipsed and perpendicular conformations respectively around the C- - -C(CO) and C(CO)- - -O bonds in oxygenated ketenes. (c) Newman projection diagram for the preferred anti conformations around the (CO)C- - -C(CO) bond in 1,3-bisketenes.

TABLE 1: CBS-Q Calculated Absolute Energies in au and the Relative Energy ΔE in kcal/mol between the C−H and C−C Eclipsed Conformers of Some Selected Ketenes[a]

species	C−H (eclipsed)	C−C (eclipsed)	Δ*E* (kcal/mol)
	Alkylketenes		
MeCH=C=O (**1**)	−191.598382	NA	
EtCH=C=O (**2**)	−230.824521	−230.824361	−0.100
i-PrCH=C=O (**3**)	−270.053686	−270.054446	0.477
t-BuCH=C=O (**4**)	NA	−309.285944	
Me_2C=C=O (**5**)	−230.826322	NA	
MeC(Et)=C=O (**6**)	−270.052327	−270.053501	0.737
MeC(i-Pr)=C=O (**7**)	−309.281128	−309.283114	1.246
MeC(t-Bu)=C=O (**8**)	NA	−348.514777	
Et_2C=C=O (**9**)	−309.279795	−309.281496	1.067
EtC(i-Pr)=C=O (**10**)	−348.509650	−348.511682	1.275
EtC(t-Bu)=C=O (**11**)	NA	−387.743398	
EtC(OH)=C=O (**19**)	−305.953615	−305.953505	−0.069
i-PrC(OH)=C=O (**20**)	−345.182892	−345.183590	0.438
EtC(OMe)=C=O (**22**)	−345.164753	−345.164845	0.058

[a] NA stands for not applicable cases. Ethyl substituents exert nearly the same preference for eclipsing the C−H or the C−C bond.

In conformers with a β-C−H eclipsing interaction, every *n*-alkyl, *iso*-alkyl, and *tert*-alkyl group in a dialkylketene introduces respectively one, two, and two gauche interactions, whereas the corresponding most favorable β C−C orientation results in respectively zero, one, and two gauche interactions around the C−C(CO) bond. It is, therefore, essential to arrive at a correction factor for the heat of formation with respect to the nature of the eclipsing β bond rather than solely in terms of simple destabilizing gauche interactions.

The simplest oxygenated ketene is hydroxyketene (HOCH═C═O) (**12**). It is a valence tautomer of dihydroxyacetylene (HOC≡COH) and glyoxal (O═CHCH═O). The interconversion of these isomers has been investigated theoretically.[37] The two bonds adjacent to the ketenyl group in hydroxy-/alkoxy-alkylketenes are C−C(CO) and O−C(CO). Although the C−C(CO) bond exhibits a very similar preferential pattern as observed in alkylketenes (e.g., eclipsing with β bonds of the alkyl groups), the preferred conformation around the XO−C(CO)R (X = H or Me) bond is with X being approximately perpendicular to the OC(CO) plane. Consequently, with secondary and tertiary alkyl groups, one encounters respectively one and two gauche interactions between R and the OX group (Figure 1b). However, the origin of the gauche interaction is stated by Benson to result from the repulsion of H atoms attached to too-close methyl groups. Following Benson, we do not expect any nonnext neighbor gauche effects between OX and R groups. In dihydroxy- (**14**), hydroxyalkoxy- (**16**) and dialkoxyketenes (**15**), $(XO)_2C{=}C{=}O$ (X=H,Me), the relative orientation of both X groups appears to be dictated by the lone pair electrons on the oxygen atoms. Although there is no bond between the two oxygens, the X groups form a dihedral angle (XO- - - - - -OX) of about 120° as observed in stable peroxides (ROOH).

Bisketenes consist of two ketene groups bonded either directly to each other (1,2-bisketenes) or separated by other atoms, e.g., by a CH_2 group as in 1,3-bisketenes. The most stable structure of the 1,2-bisketenes is the twisted form with the ketenyl groups being approximately perpendicular to each other. The preference for the twisted conformation suggests a destabilizing interaction or the lack of conjugative stabilization between the two ketenyl groups. 1,3-Bisketenes considered in the present study can be visualized as diketenyl-substituted alkanes and are characterized by two torsional modes between the aliphatic and the ketenyl carbon. In contrast to the R_3C−C(CO) bond in alkylketenes, where R is either a hydrogen or an alkyl group, in 1,3-bisketenes, one of the R's is a ketenyl group. The ketenyl substituent also prefers an eclipsed conformation; the preferential order is C−R > C−H ≥ C−C(CO). Besides these two torsions, the ketenyl groups are disposed anti to each other ((OC)C- - - - -C(CO) is around 180°; Figure 1c), if they are eclipsed with the former two bonds. As a result, with methylketenyl groups, a stabilizing 1,5- interaction is possible between the hydrogen of the methyl group and the >CCO of the other ketenyl moiety. The HOMO of the $>C_\beta C_\alpha O$ group is perpendicular to its plane with the highest coefficient on carbon, C_β. The distance between one of the hydrogens of the methyl group and C_β is 2.87 Å.

The preparation procedures for all of the ketenes considered in this study are available in Tidwell's book[1] on ketenes except for the ketenyl substituted alcohols (**33**−**38**). However, there are many plausible pathways leading to ketenyl-substituted alcohols in combustion and pyrolysis, so we have computed their thermochemistry as well. Ketenyl-substituted alcohols exhibit the same preferential eclipsing interaction around the C(CO)- - - -C(X_2)OH bond (X = H or Me) with {C−C} being more favored than the {C−H}. The OH group is always staggered with respect to the ketenyl group (OCH_2−CH═CO = −60°). The favored conformation around the C(X_2)-(CO)- - - - - -OH bond is with H making a dihedral angle of −60° with the ketenyl carbon (H− O− CX_2−C(CO) = −60°).

B. Enthalpies of Formation. The calculated ΔH_f^{298}s of 45 ketenes of four different types are listed in Table 2a−c. The calculated heat of formation for ketene is in very good agreement with the experimental value of −11.40 kcal/mol recommended in the Lias Compendium.[21] In contrast to the present work, the heats of formation reported earlier by Scott and Radom[32] at the CBS-Q level did not include the recommended CBS-Q bond-additivity and spin−orbit corrections. Furthermore, in that work, the thermal corrections to enthalpy were made by treating the torsional modes as harmonic vibrations rather than as hindered rotations. The heats of formation of methyl- (**1**) and dimethylketene (**5**) were originally a matter of dispute,[38−40] and only very recently, a consensus has been reached between the experimental and theoretical value. From appearance energy measurements using threshold photoionization mass spectrometry, Trager[41] obtained the ΔH_f^{298} for methylketene (**1**) (−16 ± 1.1 kcal/mol) and dimethylketene (**5**) (≤−20.55 kcal/mol) that are in very good agreement with the predictions of Radom et al.,[32] namely, −16.25 and −21.99 kcal/mol from the CBS-APNO level of calculation. The results obtained from the CBS-Q level in the present study are also in good agreement with the experimental value. Not much is known about the thermochemistry of other alkyl ketenes investigated in this study; 1,1-disubstituted ketenes are less reactive and do not show the tendency to dimerize, but it is not clear whether this is more than just a kinetic effect.

In our earlier publications,[14−15] we have systematically investigated the performance of the CBS-Q method for predicting the thermochemical properties of alkanes, alkenes, aldehydes, acids, alcohols, and ethers. We observed a systematic overestimation of the stability of systems with tertiary butyl substituent at the CBS-Q level: $tBuCH_3$ (CBS-Q −41.57, expt −40.14 kcal/mol); t-BuCH═CH_2 (CBS-Q −15.7 kcal/mol, expt −14.5 kcal/mol); t-BuCHO (CBS-Q −60.2 kcal/mol, expt −58.5 kcal/mol); t-Bu-C(O)OH (CBS-Q −123.45 kcal/mol, expt −122.0 kcal/mol); t-BuOH (CBS-Q −75.9 kcal/mol, expt −74.5 kcal/mol); tBuOMe (CBS-Q −69.4 kcal/mol, expt −67.7 kcal/mol). The CBS-Q heats of formation are consistently below the experimental value by 1.5 kcal/mol. It is not clear whether the calculated or the experimental values are systematically in error. A similar unresolved discrepancy exists for the *tert*-butyl radical.[42] From our experience, we anticipate a similar systematic mismatch in the predicted stability of *tert*-butyl substituted ketenes using CBS-Q calculations.

All of the results given in Table 2a−c come from atomization energies. Although we do not have much experimental values for comparison, we checked the calculated heats of formation of some of the ketenes using isodesmic reactions. It is known that the cancellation of errors in theoretical estimates of the energies of isodesmic reaction generally leads to further improvement in the calculation of theoretical energies[32,43] as compared to the BAC factors in the atomization energy method. (The BAC are derived by fitting to a small set of molecules containing a particular bond.) Because the experimental data on thermochemical properties of oxygenated ketenes are too scarce, we cross-check the heat of formation of hydroxyalkylketenes with the aid of isodesmic reactions shown in Table 3. The CBS-Q absolute energies in au, the thermal correction in kcal/mol, and the experimental heats of formation in kcal/mol

TABLE 2: CBS-Q Calculated Data on Thermodynamic Properties of Alkylketenes, Oxygenated Alkylketenes, and Bisketenes[a]

species	ΔH_f^{298}	S^{298}	C_p (300 K)	C_p (400 K)	C_p (500 K)	C_p (600 K)	C_p (800 K)	C_p (1000 K)	C_p (1500 K)
Alkylketenes (set I)									
$CH_2=C=O$	−11.34	57.47	12.08	13.91	15.40	16.64	18.61	20.10	22.47
$CH_2=C=O$(expt)	*−11.40*	*57.8*	*12.4*	*14. 2*	*15.6*	*16.9*	*18.8*	*20.2*	*22.5*
MeCH=C=O (**1**)	−15.14	68.20	16.48	19.53	22.33	24.79	28.77	31.77	36.41
MeCH=C=O(expt)	*−16.0(1.1)*		*17.1*	*20.1*	*22.8*	*25.2*	*29.1*	*32.0*	*36.5*
EtCH=C=O (**2**)	−20.67	77.61	22.00	26.60	30.74	34.31	39.97	44.20	50.72
i-PrCH=C=O (**3**)	−28.57	84.05	27.70	33.94	39.48	44.16	51.48	56.88	65.18
t-BuCH=C=O (**4**)	−37.75	87.66	33.50	41.55	48.58	54.45	63.46	69.99	79.92
$Me_2C=C=O$ (**5**)	−21.73	74.92	22.44	26.61	30.47	33.91	39.57	43.88	50.56
$Me_2C=C=O$(expt)	<*−20.65*		*22.8*	*26.9*	*30.8*	*34.2*	*39.8*	*44.0*	*50.6*
MeC(Et)=C=O (**6**)	−27.97	85.84	27.53	33.36	38.68	43.31	50.74	56.31	64.89
MeC(i-Pr)=C=O (**7**)	−35.76	92.13	33.12	40.57	47.23	52.95	62.02	68.78	79.21
MeC(t-Bu)=C=O (**8**)	−44.87	95.68	39.12	48.29	56.42	63.30	74.04	81.92	93.95
$Et_2C=C=O$ (**9**)	−34.66	93.66	32.55	40.04	46.84	52.68	61.93	68.77	79.25
EtC(i-Pr)=C=O (**10**)	−42.52	101.41	39.15	47.84	55.79	62.63	73.45	81.47	93.75
EtC(t-Bu)=C=O (**11**)	−51.76	104.35	44.81	55.33	64.78	72.82	85.36	94.55	108.51
Oxygenated Ketenes (set II)									
HOCH=C=O (**12**)	−35.82	67.30	15.45	17.90	19.80	21.26	23.37	24.88	27.23
MeOCH=C=O (**13**)	−31.33	75.68	20.52	23.96	26.92	29.45	33.51	36.56	41.27
$(HO)_2C=C=O$ (**14**)	−73.22	70.23	20.12	24.16	27.05	28.89	30.75	31.64	32.97
$(MeO)_2C=C=O$ (**15**)	−64.74	86.97	29.49	35.90	41.42	45.64	51.38	55.24	61.13
(MeO)C(OH)=C=O (**16**)	−68.94	80.20	25.22	30.26	34.17	37.01	40.72	43.16	46.92
MeC(OH)=C=O (**17**)	−44.90	75.73	21.40	24.92	27.83	30.25	34.04	36.87	41.31
Me(OMe)C=C=O (**18**)	−40.15	84.34	26.09	30.42	34.49	38.13	44.09	48.57	55.43
EtC(OH)=C=O (**19**)	−50.42	84.85	26.81	31.96	36.26	39.80	45.28	49.32	55.63
i-PrC(OH)=C=O (**20**)	−58.29	91.63	32.47	39.32	45.05	49.73	56.86	62.06	70.11
t-BuC(OH)=C=O (**21**)	−68.88	95.04	38.46	47.07	54.25	60.05	68.79	75.08	84.76
EtC(OMe)=C=O (**22**)	−45.77	94.10	31.84	37.45	42.78	47.52	55.20	60.94	69.72
i-PrC(OMe)=C=O (**23**)	−54.08	100.17	37.59	44.91	51.66	57.52	66.83	73.72	84.25
t-BuC(OMe)=C=O (**24**)	−64.68	103.36	42.89	52.49	60.92	67.98	78.91	86.89	99.04
Oxygenated Ketenes (set IV)									
$HC(CO)CH_2OH$ (**33**)	−51.60	77.65	21.45	24.55	27.31	29.72	33.58	36.49	41.07
$MeC(CO)CH_2OH$ (**34**)	−58.53	85.64	27.77	31.90	35.64	38.97	44.46	48.64	55.23
$HC(CO)CH(CH_3)OH$ (**35**)	−61.18	85.32	28.23	32.64	36.57	39.95	45.29	49.29	55.57
$MeC(CO)CH(CH_3)OH$ (**36**)	−68.83	94.02	33.56	39.30	44.42	48.86	55.97	61.31	69.66
$HC(CO)C(CH_3)_2OH$ (**37**)	−72.47	88.83	35.74	41.85	46.81	50.96	57.51	62.42	70.22
$MeC(CO)C(CH_3)_2OH$ (**38**)	−79.94	97.06	40.88	48.25	54.47	59.73	68.11	74.40	84.30
Bisketenes (set III)									
$CH_2(HCCO)_2$ (**25**)	−15.18	85.48	27.06	31.49	35.24	38.39	43.32	46.93	52.38
CH_2(HCCO)(MeCCO) (**26**)	−22.85	95.48	32.95	38.52	43.41	47.59	54.24	59.14	66.59
$CH_2(MeCCO)_2$ (**27**)	−30.98	102.69	38.98	45.73	51.68	56.82	65.11	71.30	80.76
$CHMe(HCCO)_2$ (**28**)	−23.64	94.48	33.37	39.60	44.66	48.82	55.23	59.90	66.99
CHMe(HCCO)(MeCCO) (**29**)	−31.73	102.13	38.62	45.88	52.19	57.51	65.82	71.89	81.10
$CHMe(MeCCO)_2$ (**30**)	−39.88	110.27	44.65	53.07	60.44	66.75	76.73	84.09	95.29
$CMe_2(HCCO)_2$ (**31**)	−32.93	97.07	39.95	47.46	53.78	59.04	67.12	72.95	81.70
CMe_2(HCCO)(MeCCO) (**32**)	−41.51	108.11	45.37	54.18	61.76	68.13	77.96	85.10	95.87
$(HCCO)_2$ (**39**)	−10.03	76.91	21.07	24.75	27.57	29.77	32.99	35.23	38.51
(HCCO)(MeCCO) (**40**)	−17.06	86.75	26.94	31.61	35.46	38.64	43.59	47.18	52.56
$(MeCCO)_2$ (**41**)	−24.12	94.42	32.53	38.09	42.98	47.21	54.00	59.02	66.59
(HCCO)(HOCCO) (**42**)	−41.32	85.70	25.85	29.82	32.82	35.11	38.30	40.44	43.52
(HOCCO)(MeCCO) (**43**)	−48.89	94.76	31.66	36.46	40.50	43.82	48.85	52.39	57.61
$(HOCCO)_2$ (**44**)	−72.35	92.25	30.59	34.73	37.92	40.33	43.59	45.72	48.68

[a] ΔH_f^{298} values are given in kcal/mol, and S^{298} and $C_p(T)$ values are in cal/(mol K). Experimental values are given in italics.

at 298 K for the species used in isodesmic reactions are tabulated in Table 4. The calculated CBS-Q energies for these reactions are used in conjunction with the appropriate experimental ΔH_f^{298} values for the remaining three species in the reactions to get additional estimates of the heats of formations of the unknown ketene species. The isodesmic analyses in this case yield values of −36.17 and −36.34 kcal/mol for ΔH_f^{298} for hydroxyketene (**12**) at the CBS-Q level of theory. Our calculated value based on atomization energy is in good agreement. As can be seen from Tables 3 and 2, except for *tert*-butylhydroxyketene (**21**) and *tert*-butylketene (**4**), the difference in the calculated ΔH_f^{298} between the two procedures is rather small and the agreement is very reasonable. The isodesmic procedure shifts the computed energy of *tert*-butyl substituted ketenes by about 1.5 kcal/mol, the typical difference noted above between CBS-Q and experimental values for *tert*-butyl substituted species. This discrepancy systematically affects only the {C/C3/CCO} group value. The {C/C3/CCO} group enthalpy value given in Table 6 is consistent with all of the CBS-Q calculations but may be 1.5 kcal/mol too negative because of this unresolved discrepancy.

It is worthwhile to investigate the computed methyl substitution effect in ketenes as compared to that observed in olefins. The ΔH_f^{298} values calculated for ketene and methylketene lead to an $\Delta\Delta H_f^{298}$ value of −3.79 kcal/mol for methyl substitution in ketene. This in comparison with $\Delta\Delta H_f^{298}$ values for methyl substitution in alkenes (−7.661 kcal/mol) reveals that, compared to hydrogen, alkyl substituents are less stabilizing for ketenes than they are for alkenes. However, the methyl substituent effect in going from methylketene (**1**) to dimethylketene (**5**) amounts to −6.59 kcal/mol. Furthermore, the calculated $\Delta\Delta H_f^{298}$ value for the monoalkylketenes [EtCH=C=O (**2**), i-PrCH=C=O (**3**), and t-BuCH=C=O (**4**)] and the corresponding methyl substituted dialkylketenes [EtC(Me)=C=O) (**6**), i-PrC(Me)=C=O (**7**), and t-BuC(Me)=C=O) (**8**)] is comparable to that of alkenes

TABLE 3: Use of Isodesmic Reactions to Cross-Check the Heats of Formation of Ketenes[a]

isodesmic reactions	ΔH_{rxn}	calcd. ΔH_f^{298}
$\mathrm{CH_2{=}CH_2{+}CH(OH){=}C{=}O}$ (**12**) → $\mathrm{CH_2CO{+}CH(OH){=}CH_2}$	−17.51	−36.17
$\mathrm{CH_2{=}O{+}CH(OH){=}C{=}O}$ (**12**) → $\mathrm{CH_2CO{+}HC(O)OH}$	−39.51	−36.34
$\mathrm{CH_2CH_2{+}HC(OMe){=}C{=}O}$ (**13**) → $\mathrm{MeOCH{=}CH_2{+}CH_2CO}$	−18.18	−29.70
$\mathrm{CH_2O + HC(OMe){=}C{=}O}$ (**13**) → $\mathrm{HC(O)OMe + CH_2CO}$	−39.61	−30.72
$\mathrm{CH_2CH_2{+}CH_3C(OH){=}C{=}O}$ (**17**) → $\mathrm{MeCH{=}CH_2 + HC(OH){=}C{=}O}$(**12**)	1.38	−44.86
$\mathrm{CH_2O + CH_3C(OH){=}C{=}O}$ (**17**) → $\mathrm{CH_3C(O)OH + CH_2CO}$	−43.32	−45.34
$\mathrm{CH_2CH_2{+}CH_3C(OH){=}C{=}O}$ (**17**) → $\mathrm{HOCHCH_2{+}HC(CH_3){=}C{=}O}$(**1**)	−12.22	−45.26
$\mathrm{CH_2O{+}CH_3C(OH){=}C{=}O}$ (**17**) → $\mathrm{HC(O)OH + HC(CH_3){=}C{=}O}$(**1**)	−34.22	−45.43
$\mathrm{CH_2O + CH_3C(OMe){=}C{=}O}$ (**18**) → $\mathrm{HC(O)OMe + CH_3CH{=}C{=}O}$(**1**)	−34.60	−39.53
$\mathrm{CH_2O + CH_3C(OMe){=}C{=}O}$ (**18**) → $\mathrm{CH_3C(O)OMe + CH_2CO}$	−43.64	−39.72
$\mathrm{CH_2{=}CH_2 + EtC(OH){=}C{=}O}$ (**19**) → $\mathrm{EtCH{=}CH_2 + HC(OH){=}C{=}O}$(**12**)	1.91	−50.42
$\mathrm{CH_2{=}O + EtC(OH){=}C{=}O}$ (**19**) → $\mathrm{EtC(O)H + HC(OH){=}C{=}O}$(**12**)	−3.63	−50.57
$\mathrm{CH_2{=}O + EtC(OH){=}C{=}O}$ (**19**) → $\mathrm{EtC(O)OH + CH_2CO}$	−43.02	−50.73
$\mathrm{CH_2{=}CH_2 + i\text{-}PrC(OH){=}C{=}O}$ (**20**)→ $\mathrm{i\text{-}PrCH{=}CH_2 + HC(OH){=}C{=}O}$(**12**)	2.46	−57.32
$\mathrm{CH_2{=}O + i\text{-}PrC(OH){=}C{=}O}$ (**20**) → $\mathrm{i\text{-}PrC(O)H + HC(OH){=}C{=}O}$(**12**)	−2.75	−58.66
$\mathrm{CH_2{=}CH_2 + t\text{-}BuCH{=}C{=}O}$ (**4**) → $\mathrm{t\text{-}BuCH{=}CH_2 + H_2CCO}$	−2.48	−35.90
$\mathrm{CH_2{=}O + t\text{-}BuCH{=}C{=}O}$ (**4**) → $\mathrm{t\text{-}BuC(O)H + H_2CCO}$	−7.56	−36.30
$\mathrm{CH_2{=}CH_2 + t\text{-}BuC(OH){=}C{=}O}$ (**21**) → $\mathrm{t\text{-}BuCH{=}CH_2 + HC(OH){=}C{=}O}$(**12**)	4.18	−67.04
$\mathrm{CH_2{=}O + t\text{-}BuC(OH){=}C{=}O}$ (**21**) → $\mathrm{t\text{-}BuC(O)H + HC(OH){=}C{=}O}$(**12**)	−0.90	−67.44
$\mathrm{CH_2{=}O + t\text{-}BuC(OH){=}C{=}O}$ (**21**) → $\mathrm{t\text{-}BuC(O)OH + H_2C{=}C{=}O}$	−39.64	−67.72

[a] The CBS-Q heats of reactions ΔH_{rxn} and the inferred heats of formation ΔH_f^{298} of the substituted ketenes are given in kcal/mol. The other ΔH_f^{298}'s used in isodesmic reactions come from experiment (Table 4).

TABLE 4: CBS-Q (0 K) Absolute Energies (in au), Thermal Corrections (in kcal/mol), and Experimental Heats of Formation at 298 K (in kcal/mol) for the Species Used in Isodesmic Reactions Given in Table 3

species	energy	thermal corr.	expt ΔH_f^{298}
$\mathrm{CH_2{=}CH_2}$	−78.415693	2.50	12.54
$\mathrm{CH_2{=}O}$	−114.342730	2.39	−25.98
$\mathrm{CH_2{=}CHOH}$	−153.563892	3.00	−29.80
$\mathrm{CH_2{=}CHOCH_3}$	−192.775467	3.59	−24.00
$\mathrm{HC(O)OH}$	−189.525529	2.60	−90.49
$\mathrm{CH_3C(O)OH}$	−228.763160	3.33	−103.30
$\mathrm{CH_3CH_2C(O)OH}$	−267.989221	4.49	−108.39
$\mathrm{(CH_3)_3CC(O)OH}$	−346.447349	5.91	−122.00
$\mathrm{HC(O)OCH_3}$	−228.736748	3.54	−84.97
$\mathrm{CH_3C(O)OMe}$	−267.974412	4.36	−98.00
$\mathrm{CH_3CH{=}CH_2}$	−117.645036	3.22	4.88
$\mathrm{CH_3CH_2CH{=}CH_2}$	−156.870214	4.05	−0.15
$\mathrm{i\text{-}PrCH{=}CH_2}$	−196.099425	5.08	−6.50
$\mathrm{t\text{-}BuCH{=}CH_2}$	−235.330251	5.56	−14.50
$\mathrm{CH_3C(O)H}$	−153.580816	3.12	−40.80
$\mathrm{CH_3CH_2C(O)H}$	−192.806489	4.20	−44.36
$\mathrm{i\text{-}PrCH{=}O}$	−232.034486	4.79	−51.57
$\mathrm{t\text{-}BuCH{=}O}$	−271.265297	5.40	−58.50

and is consistently around −7.2 kcal/mol suggesting an increased stabilization upon disubstitution. This increased stabilization can be attributed to the increasing number of eclipsing interactions while going from unsubstituted ketene to mono (1 β C−C), to alkylmethyl (1 β C−C and 1 β C−H), and to dialkyl (2 β C−C) ketenes. It must be stated that in alkenes the methyl substituent effect is nearly a constant while going from ethylene → propene (7.66 kcal/mol), propene → methylpropene (8.66 kcal/mol), or but-1-ene→ 2-methylbut-1-ene (7.66 kcal/mol). As can be seen from the following section, MVLR of the $\Delta_f H^{298}$ of the alkylketenes without any nonnext neighbor (NN) corrections results in significant deviation (−0.56 kcal/mol) for the theoretically and experimentally established $\Delta_f H^{298}$ of methylketene and mediocre fit between the group additivity estimates and the quantum chemical enthalpies of formation. Consequently, while deriving the groups, we considered nonnext neighbor corrections to enthalpy based on the number and nature of the eclipsing β bond.

C. Group Additivity Scheme and Group Enthalpy Values from MVLR Analysis. The group additivity scheme for alkylketenes is shown in Table 5. In the present scheme, we introduce NN corrections only when two bonds are simultaneously eclipsed with the >CCO group namely with 2 C−H (NN0) or a C−H and a C−C (NN1) or 2 C−C (NN2) bonds. NN0 is taken as zero. The difference in the enthalpy of formation between methylketene (**1**) and dimethylketene (**5**) corresponds to {CCO/H/C}-{CCO/C2}-{C/H3/CCO}. Also, the difference between mono- and the corresponding methyl-alkylketenes should amount to the same group contribution minus NN1; this allowed us to set NN1 = −0.5 kcal/mol. Similarly, the difference in the heats of formation between ethyl-alkylketene and the sum of ethylketene (**2**) and the corresponding methyl-alkylketene should correspond to {CCO/C/H} + {C/H3/CCO} and should be equal to ΔH_f^{298} of methylketene. For example

TABLE 5: Group Additivity Scheme for Alkyl Ketenes after Deducting for Benson's {C/C/H3} Groups[a]

species	{CCO/H/C}	{CCO/C2}	{C/C/H2/CCO}	{C/C2/H/CCO}	{C/C3/CCO}	NN I	NN II	gauche
$\mathrm{CH_2{=}C{=}O}$	0	0	0	0	0	0	0	0
$\mathrm{MeCH{=}C{=}O}$(**1**)	1	0	0	0	0	0	0	0
$\mathrm{EtCH{=}C{=}O}$(**2**)	1	0	1	0	0	0	0	0
$\mathrm{i\text{-}PrCH{=}C{=}O}$(**3**)	1	0	0	1	0	0	0	0
$\mathrm{t\text{-}BuCH{=}C{=}O}$(**4**)	1	0	0	0	1	0	0	0
$\mathrm{Me_2C{=}C{=}O}$(**5**)	0	1	0	0	0	0	0	0
$\mathrm{MeC(Et){=}C{=}O}$(**6**)	0	1	1	0	0	1	0	0
$\mathrm{MeC(i\text{-}Pr){=}C{=}O}$(**7**)	0	1	0	1	0	1	0	1
$\mathrm{MeC(t\text{-}Bu){=}C{=}O}$(**8**)	0	1	0	0	1	1	0	2
$\mathrm{Et_2C{=}C{=}O}$(**9**)	0	1	2	0	0	0	1	0
$\mathrm{EtC(i\text{-}Pr){=}C{=}O}$(**10**)	0	1	1	1	0	0	1	1
$\mathrm{Et(t\text{-}Bu)C{=}C{=}O}$(**11**)	0	1	1	0	1	0	1	2

[a] NNI and NN II correspond to nonnext neighbor interation terms. NN1 (−0.5 kcal/mol) is the stabilization from simultaneous {C−C} and {C−H} bonds eclipsing the >CCO group, whereas NNII (−1.6 kcal/mol) results from two {C−C} bonds simultaneously eclipsing the >CCO. Gauche correction inferred in this work amounts to 0.1 kcal/mol.

TABLE 6: Group Values (GVs) for Enthalpy of Formation (kcal/mol)[a]

	I = alkylketenes		I = corrected		II = oxy ketenes				III = bisketenes		recommended	
groups	set 1	SE	set 1	SE	set II	SE	set I&II	SE	set I−III	SE	set I−IV	SE
{C/H3/CCO}	−10.08	N/A	−10.08	N/A	−10.08	N/A	−10.08	N/A	−10.08	N/A	−10.08	N/A
{O/H/CCO}	−37.90	N/A	−37.90	N/A	−37.90	N/A	−37.90	N/A	−37.90	N/A	−37.90	N/A
{CCO/H/C}	−4.497	0.22	−4.945	0.05			−4.951	0.07	−4.947	0.06	−4.947	0.06
{CCO/C2}	−1.600	0.25	−1.629	0.06			−1.644	0.08	−1.650	0.06	−1.644	0.06
{C/C/H2/CCO}	−6.514	0.18	−5.743	0.04	−5.650	0.16	−5.722	0.05	−5.720	0.05	−5.723	0.05
{C/C2/CCO/H}	−4.186	0.26	−3.641	0.06	−3.595	0.16	−3.631	0.07	−3.630	0.06	−3.634	0.06
{C/C3/CCO}	−3.363	0.26	−2.884	0.06	−4.195	0.16	−2.893	0.07	−2.892	0.06	−2.896**	0.06
{O/CCO/C}					−23.390	0.08	−23.390	0.05	−23.392	0.05	−23.390	0.05
{CCO/O/H}					2.110	0.12	2.110	0.09	2.111	0.08	2.110	0.08
{CCO/O/C}					3.250	0.12	3.270	0.06	3.269	0.06	3.273	0.06
{CCO/O2}					2.405	0.12	2.406	0.09	2.406	0.08	2.403	0.08
{C/H2/CCO2}									−5.304	0.13	−5.301	0.13
{C/H/C/CCO2}									−3.723	0.13	−3.714	0.13
{C/C2/CCO2}									−2.983	0.13	−2.987	0.13
{CCO/H/CCO}									−4.998	0.13	−4.998	0.13
{CCO/C/CCO}									−2.070	0.13	−2.070	0.13
{CCO/O/CCO}									1.607	0.13	1.607	0.13
{C/CCO/O/H2}											−8.680	0.09
{C/CCO/O/C/H}											−8.370	0.09
{C/CCO/O/C2}											−9.725	0.09
NN1	0.0		−0.5		−0.5		−0.5		−0.5		−0.5	
NN2	0.0		−1.6		−1.6		−1.6		−1.6		−1.6	
NN3	0.0		−0.9		−0.9		−0.9		−0.9		−0.9	

[a] For set I, the results of regression are given for both uncorrected and corrected scenario with respect to nonnext neighbor interaction for disubstituted ketenes. The results of other sets correspond to the corrected case. {C/H3/CCO} and {O/H/CCO} GVs are assumed to be equal to Benson's groups {C/H3/C} and {O/H/C}, respectively. SE stands for the standard error in the statistical analysis (99% confidence).

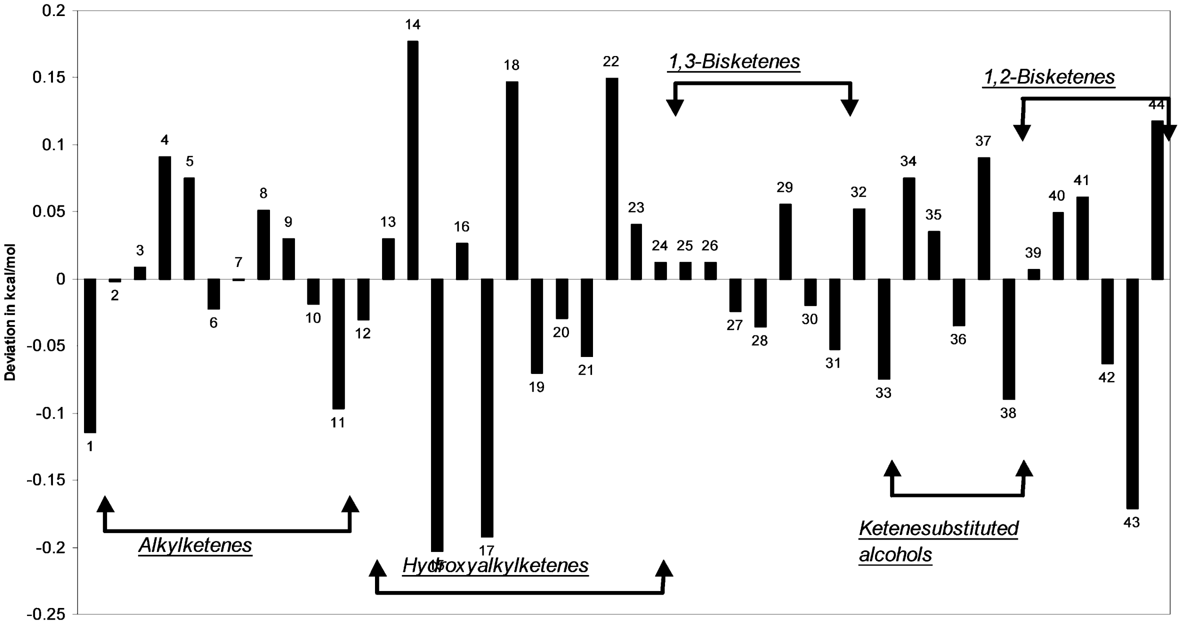

Figure 2. Enthalpy deviations between values calculated by using the newly derived groups via MVLR versus the calculated value using the method of atomization energy at the CBS-Q level.

$$\Delta_f H^{298}(\mathrm{Et_2C{=}C{=}O}) = 2\{\mathrm{C/H3/C}\} + \{\mathrm{CCO/C2}\} + 2\{\mathrm{C/C/H2/CCO}\} + \mathrm{NN2}$$

$$\Delta_f H^{298}(\mathrm{EtCMe{=}C{=}O}) = \{\mathrm{C/H3/C}\} + \{\mathrm{C/H3/CCO}\} + \{\mathrm{C/C/H2/CCO}\} + \{\mathrm{CCO/C2}\} + \mathrm{NN1}$$

$$\Delta_f H^{298}(\mathrm{EtCH{=}C{=}O}) = \{\mathrm{C/H3/C}\} + \{\mathrm{C/C/H2/CCO}\} + \{\mathrm{CCO/H/C}\}$$

$$\Delta_f H^{298}(\mathrm{EtC(Me)CO}) + \Delta_f H^{298}(\mathrm{EtCHCO}) - \Delta_f H^{298}(\mathrm{Et_2CCO}) = \{\mathrm{CCO/C/H}\} + \{\mathrm{C/H3/CCO}\} + \mathrm{NN2} + \mathrm{NN1}$$

This provides a correction factor NN2= −1.6 for the simultaneous interaction of two eclipsing C−C bonds with a >CCO group.

1,3-Bisketenes share {CCO/H/C} and {CCO/C2} groups with other sets of ketenes (sets I and IV). Consequently, the difference in the $\Delta_f H^{298}$ for the pairs (i) CH$_2$(HCCO)$_2$ (**25**) and CH$_2$(HCCO)(MeCCO) (**26**), (ii) CH$_2$(HCCO)(MeCCO) (**26**) and CH$_2$(MeCCO)$_2$ (**27**), (iii) CHMe(HCCO)$_2$ (**28**) and CHMe(HCCO)(MeCCO) (**29**), (iv) CHMe(HCCO)(MeCCO) (**29**) and CHMe(MeCCO)$_2$ (**30**), and (iv) CMe$_2$(HCCO)$_2$ (**31**) and CMe$_2$(HCCO)(MeCCO) (**32**) corresponds to {CCO/H/C}-{CCO/C2}-{C/H3/CCO} which is well characterized from the experimental heat of formation of methylketene (**1**) and dimethylketene (**5**). This constraint provided the way to arrive at a correction factor of NN3 = −0.9 kcal/mol for the 1,5 interaction between the methyl group of MeCCO and the CO group of the other ketenyl bonded to the same carbon atom.

The thermochemistry of bisketenes is hardly known though their formation in pyrolysis and photolysis of cyclic enediones

TABLE 7: HF/6-31G(d′) Calculated Torsional Frequencies (in cm^{-1}) and Rotational Barrier Heights (in kcal/mol) for All of the Rotors in the Investigated Ketenes[a]

species	σ	torsional frequencies in cm^{-1}(ν)	rotational barrier heights in kcal/mol
CH$_2$═C═O	2	NA	NA
MeCH═C═O(**1**)	3	163(C−Ck)	1.395(C−Ck)
EtCH═C═O(**2**)	3	77(C−Ck),289(C−C)	1.730(C−Ck), 3.633(C−C)
i-PrCH═C═O(**3**)	9	63(C−Ck),260(C−C), 293(C−C)	1.909(C−Ck), 3.938(C−C)
t-BuCH═C═O(**4**)	81	58(C−Ck), 255(C−C), 313(C−C), 314(C−C)	1.610(C−Ck), 4.569(C−C)
Me$_2$C═C═O(**5**)	18	191(C−Ck), 192(C−Ck)	2.176(C−Ck)
MeC(Et)═C═O(**6**)	9	78(C−Ck), 190(Me-Ck), 244(C−C)	3.608(C−Ck), 3.706(C−C), 2.133(Me-Ck)
MeC(i-Pr)═C═O(**7**)	27	45(C−Ck), 173(Me-Ck), 221(C−C), 259(C−C)	3.032(C−Ck),3.523(C−C), 1.800(Me-Ck)
MeC(t-Bu)═C═O(**8**)	243	39(C−Ck), 166(Me-Ck), 270(C−C), 303(C−C), 327(C−C)	2.629(C−Ck), 4.262(C−C), 1.843(Me-Ck)
Et$_2$C═C═O(**9**)	18	60(C−Ck), 82(C−Ck), 223(C−C), 282(C−C)	3.831(C−Ck), 3.736(C−C)
EtC(i-Pr)═C═O(**10**)	27	40(C−Ck), 60(C−Ck), 254(C−C), 282(C−C), 302(C−C)	3.151(C−Ck), 6.919(Et-Ck), 3.587(C−C), 3.863(C−C)
EtC(t-Bu)═C═O(**11**)	243	38(C−CK), 58(C−Ck), 290(C−C), 259(C−C), 300(C−C), 330(C−C)	2.403(C−Ck), 8.343(Et-Ck), 4.192(C−C), 3.962(C−C)
HOCH═C═O(**12**)	1	350(HO−Ck)	3.503(HO−Ck)
MeOCH═C═O(**13**)	3	94(O−Ck), 185(C−O)	2.108(O−Ck), 3.069(C−O)
(HO)$_2$C═C═O(**14**)	2	390(HO−Ck),400(HO−Ck)	5.481(HO−Ck)
(MeO)$_2$C═C═O(**15**)	18	93(O−Ck), 103(O−Ck), 152(C−O), 155(C−O)	1.506(O−Ck), 7.115(C−O)
(MeO)C(OH)═C═O(**16**)	3	104(O−Ck), 157(C−O), 389(HO−Ck)	5.947(MeO−Ck), 1.532(C−O), 5.088(HO−Ck)
MeC(OH)═C═O(**17**)	3	210(C−Ck), 341(HO−Ck)	2.535(Me-Ck), 3.454(HO−Ck)
Me(OMe)C═C═O(**18**)	9	74(O−Ck), 163(C−O), 196(C−Ck)	2.250(Me-Ck), 5.456(MeO−Ck), 1.587(C−O)
EtC(OH)═C═O(**19**)	3	91(C−Ck), 251(C−C), 335(HO−Ck)	3.609(C−Ck), 3.482(C−C), 3.430(HO−Ck)
i-PrC(OH)═C═O(**20**)	9	74(C−Ck), 238(C−C), 260(C−C), 340(HO−Ck)	3.514(C−C), 3.873(C−C), 4.027(HO−CK), 3.247(C−Ck)
t-BuC(OH)═C═O(**21**)	81	62(C−Ck),247(C−C), 302(C−C), 307(C−C), 351(HO−Ck)	4.479(HO−Ck), 4.079(C−C), 3.870(C−Ck)
EtC(OMe)═C═O(**22**)	9	68(C−Ck),80(O−Ck), 171(C−O), 285(C−C)	4.038(C−Ck), 5.856(O−Ck), 1.522(C−O), 3.520(C−C)
i-PrC(OMe)═C═O(**23**)	27	51(C−Ck), 79(O−Ck), 166(C−O), 251(C−C), 277(C−C)	3.852(C−Ck), 3.922(C−C), 8.128(O−Ck), 1.345(C−O)
t-BuC(OMe)═C═O(**24**)	243	56(C−Ck), 88 (O−Ck), 169(C−O), 250(C−C), 306(C−C), 320(C−C)	11.693(O−Ck), 1.213(C−O), 3.10(C−Ck), 4.571(C−C)
HC(CO)CH$_2$OH(**33**)	1	101(C−Ck), 370(HO−C)	2.836(HO−C), 2.736(C−Ck)
MeC(CO)CH$_2$OH(**34**)	3	103(C−Ck), 165(Me-Ck),396(HO−C)	1.862(Me-Ck), 4.178(C−Ck), 2.554(HO−Ck)
HC(CO)C*H(Me)OH(**35**)	3	81(C−Ck), 271(C−C), 379(HO−Ck)	2.771(C−Ck), 4.149(C−C), 3.049(HO−C)
MeC(CO)C*H(Me)OH(**36**)	9	67(C−Ck), 164(Me-Ck), 284(C−C), 368(HO−C))	1.894(Me-Ck), 4.172(C−C), 2.779(HO−C), 3.426(C−Ck)
HC(CO)C(Me)$_2$OH(**37**)	9	68(C−Ck), 262(C−C), 303(C−C), 385(HO−C)	2.911(C−Ck), 3.274(HO−C), 4.457(C−C)
MeC(CO)C(Me)$_2$OH(**38**)	27	59(C−Ck),172(Me-Ck), 255(C−C), 308(C−C), 380(HO−C)	4.198(C−C), 1.693(Me-Ck), 2.891(HO−C), 3.506(C−Ck)
CH$_2$(HCCO)$_2$(**25**)	2	60(C−Ck), 70(C−Ck)	2.602(C−Ck)
CH$_2$(HCCO)(MeCCO) (**26**)	3	60(C−Ck), 60(C−Ck), 177(Me-Ck)	1.466(Me-Ck), 4.056(C−Ck), 3.322(C−Ck)
CH$_2$(MeCCO)$_2$(**27**)	18	45(C−Ck),60(C−Ck),178(Me-Ck), 182(Me-Ck)	1.466(Me-Ck), 4.056(C−Ck)
CHMe(HCCO)$_2$(**28**)	3	54(C−Ck),60(C−Ck),283(C−C)	2.845(C−Ck), 1.960(C−Ck), 4.656(C−C)
C*HMe(HCCO)(MeCCO) (**29**)	9	49(C−Ck), 56(C−Ck), 172(Me-Ck), 285(C−C)	1.463(Me-Ck), 4.342(C−C), 4.696(C−Ck), 2.843(C−Ck)
CHMe(MeCCO)$_2$(**30**)	27	42(C−Ck), 51(C−Ck), 173(Me-Ck), 183(Me-Ck), 275(C−C)	4.056(C−Ck), 1.729(Me-Ck), 1.976(Me-Ck), 4.185(C−C)
CMe$_2$(HCCO)$_2$(**31**)	18	52(C−Ck), 56(C−Ck), 289(C−C), 329(C−C)	5.192(C−C), 2.889(C−Ck)
CMe$_2$(HCCO)(MeCCO) (**32**)	27	48(C−Ck), 54(C−Ck), 173(Me-Ck), 295(C−C), 335(C−C)	3.272(C−Ck), 4.10(C−Ck), 1.743(Me-Ck), 4.792(C−C)
(HCCO)$_2$(**39**)	2	68(Ck-Ck)	4.737(Ck-Ck)
(HCCO)(MeCCO) (**40**)	3	64(Ck-Ck), 186(Me-Ck)	4.739(Ck-Ck),2.039(Me-Ck)
(MeCCO)$_2$(**41**)	18	53(Ck-Ck), 171(Me-Ck), 178(Me-Ck)	1.779(Me-Ck), 1.820(Me-Ck), 6.235(Ck-Ck)
(HCCO)(HOCCO) (**42**)	1	76(Ck-Ck), 338(HO−Ck)	6.476(Ck-Ck), 3.965(HO−Ck)
(HOCCO)(MeCCO) (**43**)	3	66(Ck-Ck), 165(Me-Ck), 360(HO−Ck)	4.732(HO−Ck), 1.699(Me-Ck), 7.363(Ck-Ck)
(HOCCO)$_2$(**44**)	2	67(Ck-Ck), 355(HO−Ck), 370(HO−Ck)	4.732(HO−Ck), 10.852(Ck-Ck)

[a] Symmetry numbers σ are also listed. C_k corresponds to the pivot carbon of the >CCO group.

and triones has been evidenced. The set of molecules considered in the family of 1,2-bisketenes is rather small because of computational limitations, as these have a minimum of six heavy atoms. Furthermore, many of the groups for 1,2-bisketenes are unique to this family. Consequently, the groups {CCO/H/CCO}, {CCO/C/CCO}, and {CCO/O/CCO} were derived from the best fit of the thermochemical properties of the six 1,2-bisketenes.

MVLR of the ΔH_f^{298} corrected for nonnext neighbor interaction shows a maximum deviation of only 0.20 kcal/mol. The GVs for enthalpy derived via MVLR are presented in Table 6. The GVs in five columns were obtained through a different combination of the set of molecules. Molecules in sets I andset II have the following three groups in common, {C/C/CCO/H2}, {C/C2/CCO/H}, and {C/C3/CCO}, whereas those in sets I, III, and IV have {CCO/H/C} and {CCO/C2} groups in common. The {C/C3/CCO} group values derived from sets I (corrected, −2.89 ± 0.06; uncorrected, −3.36 ± 0.26 kcal/mol for nonnext neighbor interaction) and II (−4.19 ± 0.16 kcal/mol) differ from

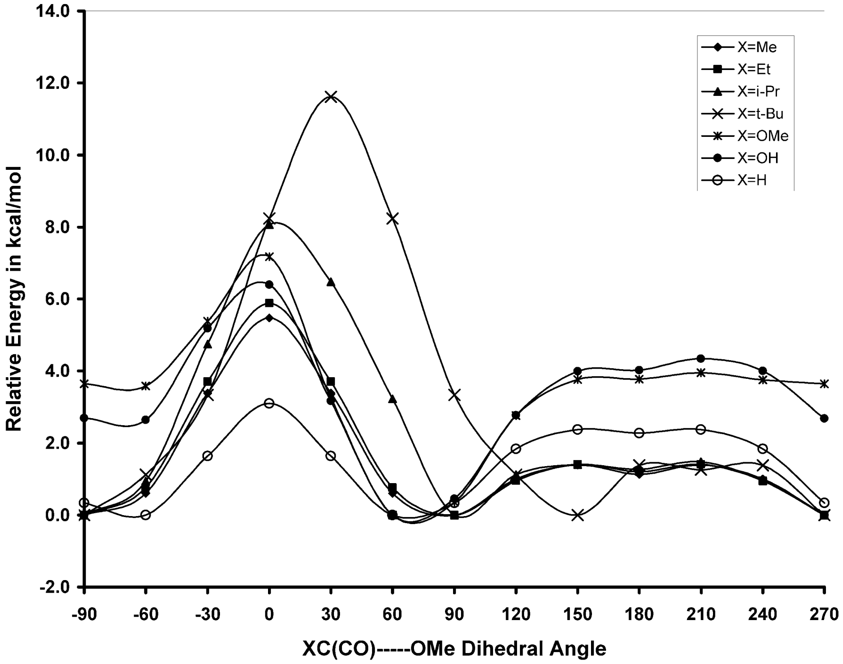

Figure 3. HF/6-31G(d′) PES for internal rotation about the CX(CO)- - -OCH$_3$ bond in methoxyalkylketenes from set II, for various substituents X.

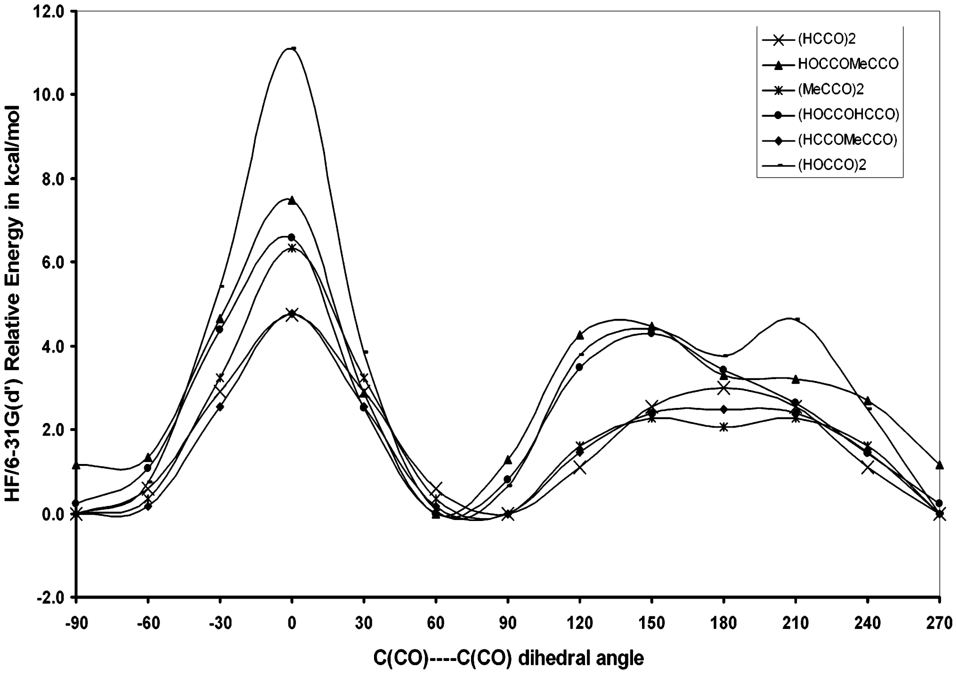

Figure 4. HF/6-31G(d′) PES for internal rotation about the C(CO)- - -C(CO) bond in 1,2-bisketenes from set III.

each other by 1.3 kcal/mol. In set II, the enthalpy value of {C/C3/CCO} is lower than that of {C/C2/H/CCO}. This is in contrast to the general understanding about the enthalpy of groups, viz., 1° < 2° < 3° carbon. Consequently, in set II, we tend to believe that both *tert*-butylhydroxy- (**21**) and *tert*-butylmethoxyketenes (**24**) are stabilized additionally by 1.3 kcal/mol. However, we could not identify any special stabilizing interaction specific to these systems. When we reanalyzed the ΔH_f^{298} using isodesmic reactions, we had hoped to see a mismatch with these two oxygenated species. However, isodesmic reactions reveal a systematic offset even for *tert*-butylketene (**4**). Consequently, of the 20 groups derived here, the {C/C3/CCO} group has large uncertainty (1.3 kcal/mol). Besides this group, the common feature of all sets is that the estimation was successful. The GVs obtained were capable of describing all of the 45 ab initio data within an average error of ≤0.06 kcal/mol and with the highest deviation of <0.21 kcal/mol. The worst agreement was found for dimethoxyketene. A comparison of the ΔH_f^{298} obtained via ab initio calculations and from GVs is depicted in Figure 2. The agreement of these data indicates that the GA method is applicable for the calculation of standard enthapies of formation and suggests that it could provide reliable data for the ketenes not considered in this study. The multiple correlation coefficient of 0.9999 confirms the appropriateness of simple linear GA rules for ketenes. The condition number of **X** matrix is 10 suggesting that any errors in the ab initio data could be amplified by up to a factor of 10 in the derived

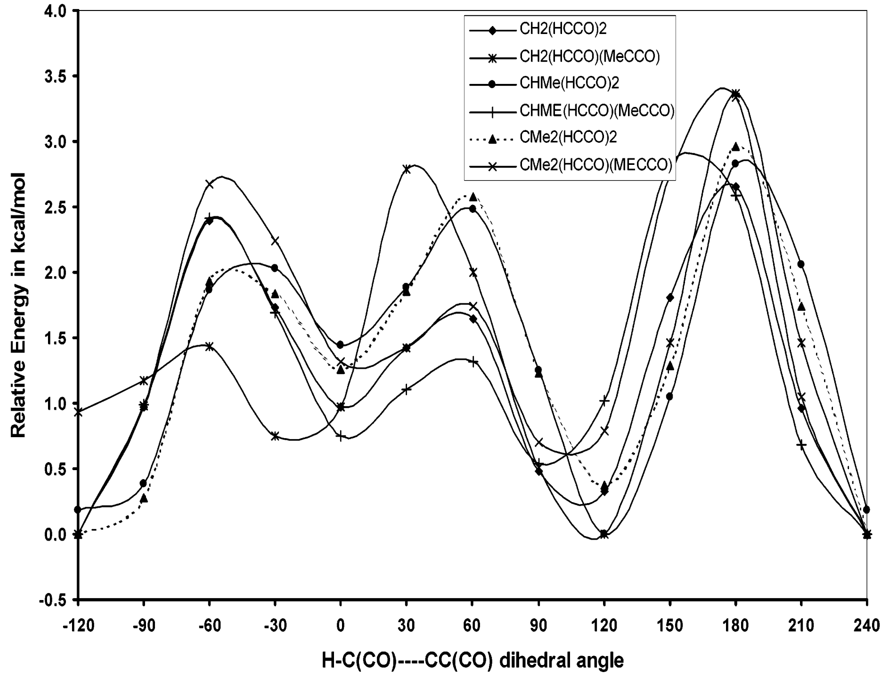

Figure 5. HF/6-31G(d′) PES for rotation of the HCCO group, i.e., rotation around the HC(CO)- - -CX$_2$C(CO)Y bond (X = H or Me; Y = H or Me) in 1,3-bisketenes from set III.

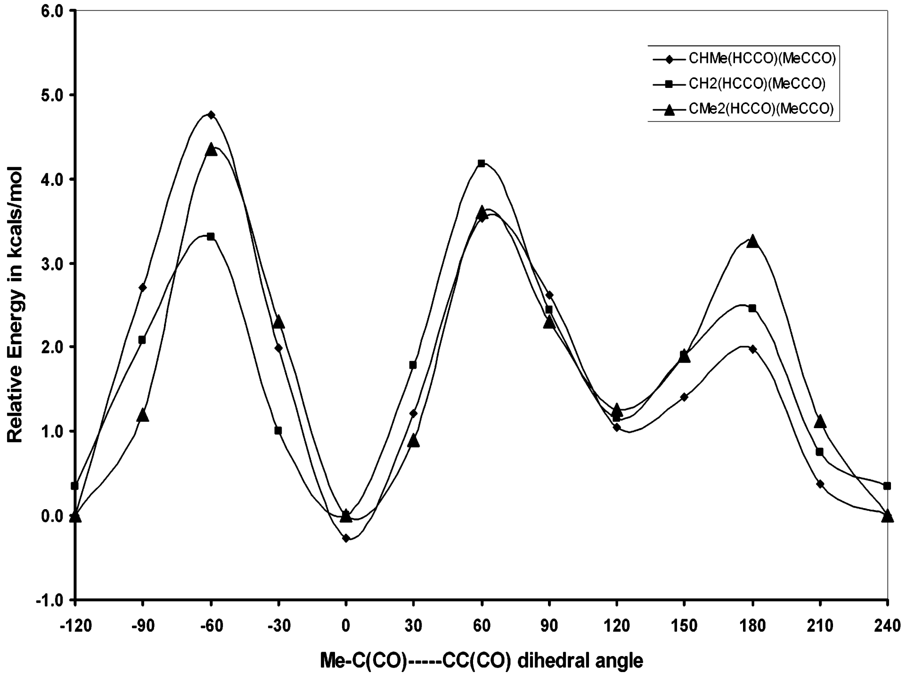

Figure 6. HF/6-31G(d′) PES for rotation of the MeCCO group, i.e., rotation around the MeC(CO)- - -CX2C(CO)Y bond (X = H or Me; Y = H or Me) in 1,3-bisketenes from set III.

group values. The Durbin−Watson test[44] for autocorrelation (2.818) suggests that the error deviations are uncorrelated.

The group values for enthalpy are presented in Table 6. Under alkylketenes, in the first column, GVs derived without using any nonnext neighbor corrections (i.e., NN1 = NN2 = NN3 = 0) are shown. Although the fitting is good, several group values seem to differ from set to set and they are not consistent with the experimentally established enthalpy of formation of methylketene and dimethylketene. After accounting nonnext neighbor interactions, using NN1 = −0.5 (for simultaneously eclipsed C−H and C−C bonds β to CCO), NN2 = −1.6 (for two simultaneously eclipsed C−C bonds β to CCO), and NN3 = −0.9 (for 1,5 stabilizing interaction between methyl group and >CCO in 1,3-bisketenes), the results in the second column were obtained. In the next column, the results of the regression of set II (oxyketenes) are given, whereas in the later columns, the results of the regression of combined sets are tabulated. In these combined sets, both *tert*-butylhydroxy- (**21**) and *tert*-butylmethoxyketenes (**24**) have been omitted.

D. Parallelism in GVs of Ketenes, Olefins, and Carbonyls. The ketenyl group consists of an olefinic and a carbonyl carbon. The most distinguishing features of the electronic structure of ketene are the polarity of the $>C_\beta{}^{\delta-}C_\alpha{}^{\delta+}O^{\delta-}$ group and the fact the localized HOMO and LUMO orbitals are perpendicular to each other. Consequently, it is interesting to compare the trends in the enthalpy of the newly derived ketene groups with

TABLE 8: Group Values for Intrinsic Entropy of Formation (cal/(mol K))[a]

	I = alkyl ketenes		II = oxy ketenes				III = bisketenes		recommended	
groups	set I	SE	set II	SE	sets I&II	SE	sets I−III	SE	sets I−IV	SE
{CCO/H/C}	40.14	0.15			40.12	0.13	40.09	0.13	40.04	0.14
{CCO/C2}	19.95	0.17			19.91	0.15	19.95	0.14	20.02	0.15
{C/C/H2/CCO}	9.38	0.12	9.55	0.25	9.41	0.10	9.40	0.11	9.37	0.12
{C/C2/CCO/H}	−12.29	0.18	−12.23	0.25	−12.28	0.13	−12.29	0.14	−12.31	0.15
{C/C3/CCO}	−34.85	0.18	−34.65	0.25	−34.84	0.13	−34.85	0.14	−34.87	0.15
{O/CCO/C}			9.40	0.12	9.34	0.10	9.34	0.11	9.34	0.12
{CCO/O/H}			38.16	0.19	38.17	0.16	38.17	0.18	38.17	0.19
{CCO/O/C}			18.48	0.19	18.55	0.12	18.56	0.13	18.58	0.14
{CCO/O2}			13.39	0.19	13.42	0.16	13.42	0.18	13.42	0.19
{C/H2/CCO2}							6.94	0.30	7.18	0.31
{C/H/C/CCO2}							−14.04	0.30	−14.12	0.31
{C/C2/CCO2}							−36.50	0.30	−36.46	0.33
{CCO/H/CCO}							39.06	0.08	39.06	0.08
{CCO/C/CCO}							19.65	0.08	19.65	0.08
{CCO/O/CCO}							17.73	0.08	17.73	0.08
{C/CCO/O/H2}									8.43	0.23
{C/CCO/O/C/H}									−13.04	0.23
{C/CCO/O/C2}									−36.50	0.23

[a] The symmetry number used for each molecule is tabulated separately in Table 7. {C/H3/CCO} and {O/H/CCO} GVs are assumed to be equal to Benson's groups {C/H3/C} and {O/H/C}, respectively. SE stands for standard error in statistical analysis (99% confidence).

those of the corresponding olefin and carbonyl groups. The enthalpies of the {CCO/H2}, {CCO/H/C}, and {CCO/C2} groups follow an increasing trend similar to the alkene groups {C_d/H2}< {C_d/H/C} < {C_d/C2}, whereas the carbonyl group follows a reverse order {CO/H2} > {CO/H/C} > {CO/C2}. The same is true with respect to the {CCO/O/H} and {CCO/O/C} groups. In the case of olefins and carbonyls, {C_d/O/C_d} and {CO/O/CO} are taken by Benson as equal to respectively {C_d/C/C_d} and {CO/C/CO} groups. In ketenes, however, the enthalpy of {CCO/O/CCO} is higher than {CCO/C/CCO}, which in turn is higher than that of the {CCO/H/CCO} group. Thus, ketenyl groups behave more like olefins than carbonyls as expected from their polarity. A comparison of the primary, secondary, tertiary, and quaternary alkyl groups with a ketene substituent, namely, {C/CCO/H3}, {C/CCO/C/H2}, {C/CCO/C2/H}, and {C/CCO/C3} groups, follows the same order (Me < 1° < 2° <3°) as in groups of the C_d and CO family. The enthalpies of diketenyl substituted alkane groups, viz., {C/H2/CCO2} (−5.13 kcal/mol) and {C/H/C/CCO2} (−3.67), are comparable respectively to that of the monoketenyl groups {C/H2/C/CCO} (−5.71 kcal/mol) and {C/H/C2/CCO} (−3.65 kcal/mol) groups.

E. Hindered Rotor Barrier Heights and Harmonic Frequency of Torsional Vibrations. The barriers for internal rotations are calculated as the difference between the classical energy of each conformation and that of the global equilibrium. In Table 7, we have compiled the hindered rotor barrier heights of all of the torsional motions and their corresponding harmonic vibrational frequencies along with their rotational symmetry numbers. Besides the barrier height, the form of the potential is very important for an accurate calculation of the partition function associated with an asymmetric rotor. The hindrance potential around the C−C(CO) bond in an alkylketene is characterized by 3 minima each corresponding to an eclipsed conformation of the >CCO group with one of the three β bonds. The rotational potential of HO−C(CO) has minima at approximately a perpendicular orientation of H with respect to >CCO. The XC(CO)- - -OCH_3 rotational potential energy surface for all of the alkoxyketenes (X = H, Me, Et, i-Pr, t-Bu, OH, and OCH_3) investigated in this study is shown in Figure 3. Interestingly, the rotational potential of MeO- - -CR(CO) has one pronounced maximum with Me eclipsing with R and a minimum near about a perpendicular orientation of Me with respect to the >CCO group. However, the conformer with an eclipsing Me and >CCO group turns out to be another shallow minimum on the surface. With the bulky *tert*-butyl substituent, the hindered rotor potential differs somewhat from other members of the same class.

The hindrance potential corresponding to syn, anti isomerization in 1,2-bisketenes is shown in Figure 4. The syn isomer (with >CCO groups on the same side) corresponds to a maximum on the PES. Although the anti isomer (C(CO)−C(CO) = 180°) correlates to a minimum in the potential well, the most preferred relative orientation of two ketenyl groups is a skewed one (C(CO) −C(CO) = ~90°). The planar syn and anti isomers are not favored. The 1,3-bisketenes have two polar groups attached to the same carbon. Consequently, the rotation of one ketene group at some conformation results in a change in the relative orientation of the other ketenyl groups. In other words, the rotational potentials are coupled to each other and the coupling is stronger with two MeCCO groups attached to each other through a CX_2 (X = H or Me) group. However, it can be realized from Table 7 that the magnitude of the harmonic frequency corresponding to the torsional vibration of ketenyl or methylketenyl rotation in all of the eight bisketenes is nearly the same. Consequently, treating this mode as a vibration results in a constant group contribution (see the Supporting Information, Table C).

Because problems were encountered in obtaining the energies of some of the partially optimized conformers along the MeC(CO)- - -CH_2C(Me)CO (**27**) and MeC(CO)- - -CH(Me)C(Me)CO (**30**) rotational PESs, the corresponding rotational potentials are taken as equivalent to the torsional potential in the corresponding (HCCO)CX_2- - -C(Me)CO (X = H or Me) systems. The PESs of HCCO rotation in $CX_2(HCCO)_2$ systems and MeCCO rotation in CX_2(HCCO)(MeCCO) [X = H or Me] systems are shown respectively in Figures 5 and 6.

The rotational symmetry numbers ($\sigma_{ext}*\sigma_{int}$) in Table 7 are the product of external and internal rotational symmetry corrected for optical isomers. The ketenes with asymmetric carbon are indicated with an asterisk, and their entropies have been corrected by a factor of R ln 2 for every chiral center. The total molecular entropies of all ketenes at 298 K are tabulated in Table 2. Similar to Benson, while deriving the groups, we employ the intrinsic entropies for MVLR. Intrinsic entropies are obtained by adding $R\ \ln(\sigma_{ext}*\sigma_{int}/n_i)$ where n_i is the total

TABLE 9: Group Values for Substituted Ketenes Heat Capacity at 300 K in cal/(mol K)[a]

	I = alkyl ketenes		II = oxy ketenes				III = bisketenes		recommended	
groups	set 1	SE	set II	SE	set I&II	SE	set I−III	SE	set I−IV	SE
{CCO/H/C}	10.32	0.19			10.32	0.15	10.30	0.14	10.31	0.15
{CCO/C2}	9.81	0.22			9.80	0.16	9.84	0.14	9.82	0.15
{C/C/H2/CCO}	5.31	0.16	5.54	0.24	5.36	0.12	5.35	0.11	5.35	0.12
{C/C2/CCO/H}	4.97	0.23	5.01	0.24	4.97	0.15	4.96	0.15	4.96	0.16
{C/C3/CCO}	4.56	0.23	4.43	0.24	4.48	0.15	4.47	0.15	4.48	0.16
{O/CCO/C}			2.90	0.11	2.90	0.12	2.90	0.12	2.90	0.13
{CCO/O/H}			11.29	0.18	11.29	0.19	11.29	0.18	11.29	0.20
{CCO/O/C}			10.86	0.18	10.91	0.13	10.92	0.13	10.91	0.14
{CCO/O2}			11.56	0.18	11.56	0.19	11.56	0.18	11.56	0.20
{C/H2/CCO2}							6.67	0.30	6.68	0.32
{C/H/C/CCO2}							6.32	0.30	6.33	0.32
{C/C2/CCO2}							6.74	0.32	6.73	0.34
{CCO/H/CCO}							10.55	0.03	10.55	0.03
{CCO/C/CCO}							10.10	0.03	10.10	0.03
{CCO/O/CCO}							11.01	0.03	11.01	0.03
{C/CCO/O/H2}									7.15	0.24
{C/CCO/O/C/H}									7.20	0.24
{C/CCO/O/C2}									8.39	0.24

[a] {C/H3/CCO} and {O/H/CCO} GVs are assumed to be equal to Benson's groups {C/H3/C} and {O/H/C}, respectively. SE stands for standard error in statistical analysis (99% confidence).

TABLE 10: Group Values for Substituted Ketenes Heat Capacity at Temperatures Ranging from 400 to 1500 K in cal/(mol K) with Fitting Variances for 99% Confidence[a]

	C_p(400 K)		500 K		600 K		800 K		1000 K		1500 K	
groups	sets I−IV	SE	sets I−IV	SE	sets I−IV	SE	sets I−IV	SE	sets I−IV	SE	sets I−IV	SE
{CCO/H/C}	11.72	0.11	12.94	0.11	13.98	0.09	15.71	0.07	16.95	0.05	18.78	0.04
{CCO/C2}	10.74	0.12	11.53	0.11	13.22	0.10	13.46	0.07	14.28	0.05	15.35	0.04
{C/C/H2/CCO}	6.83	0.09	8.25	0.09	9.45	0.08	11.19	0.06	12.46	0.04	14.34	0.03
{C/C2/CCO/H}	6.35	0.13	7.61	0.11	8.54	0.10	9.65	0.07	10.35	0.05	11.19	0.04
{C/C3/CCO}	6.06	0.13	7.31	0.11	8.07	0.10	8.59	0.07	8.66	0.05	8.29	0.04
{O/CCO/C}	2.29	0.10	2.33	0.09	2.53	0.08	3.15	0.06	3.58	0.04	3.98	0.03
{CCO/O/H}	13.67	0.16	15.10	0.14	16.10	0.13	17.36	0.09	18.25	0.06	19.75	0.05
{CCO/O/C}	12.65	0.11	13.59	0.10	14.22	0.09	15.00	0.07	15.48	0.05	16.28	0.04
{CCO/O2}	15.58	0.16	17.69	0.14	18.67	0.13	18.78	0.09	18.40	0.07	18.01	0.05
{C/H2/CCO2}	8.28	0.25	9.58	0.23	10.61	0.21	12.04	0.15	13.13	0.11	14.87	0.08
{C/H/C/CCO2}	7.96	0.25	9.13	0.23	9.91	0.21	10.70	0.15	11.19	0.11	11.81	0.08
{C/C2/CCO2}	8.10	0.27	9.02	0.24	9.53	0.22	9.66	0.16	9.52	0.11	8.93	0.08
{CCO/H/CCO}	12.41	0.04	13.82	0.04	14.91	0.03	16.51	0.02	17.62	0.01	19.24	0.01
{CCO/C/CCO}	11.24	0.04	12.12	0.04	12.84	0.03	14.00	0.02	14.75	0.01	15.72	0.01
{CCO/O/CCO}	12.97	0.04	14.17	0.04	14.97	0.03	15.80	0.02	16.26	0.01	16.88	0.01
{C/CCO/O/H2}	8.67	0.18	9.75	0.17	10.65	0.15	11.93	0.11	12.97	0.08	14.86	0.06
{C/CCO/O/C/H}	8.49	0.18	9.33	0.17	9.92	0.15	10.50	0.11	10.92	0.08	11.71	0.06
{C/CCO/O/C2}	9.66	0.18	10.03	0.17	10.07	0.15	9.64	0.11	9.26	0.08	8.74	0.06
Abs. Deviation	0.14		0.12		0.11		0.07		0.05		0.04	
Max. Deviation	0.30		0.28		0.35		0.26		0.19		0.12	

[a] {C/H3/CCO} and {O/H/CCO} GVs are assumed to be equal to Benson's groups {C/H3/C} and {O/H/C}, respectively.

number of energetically equivalent optical isomers. In Table 2, we compare the calculated thermochemical properties with the available experimental data. The calculated $C_p(T)$'s for ketene, methylketene (**1**), and dimethylketene (**5**) are consistently lower compared to the experimental value by a few tenths of a cal/(mol K). This is very likely due to the low-frequency C═C═O bending mode which according to our calculations absorbs at around 160 cm^{-1} for all substituted ketenes. Scott and Radom[45] have suggested different scaling factors (i) for different methods (like G2, CBS-Q, etc.), (ii) for reproducing low- and high-frequency fundamental vibrations, and (iii) for reproducing zero-point vibrational energy corrections. However, the scarcity of experimental data prevents us from introducing a new scaling factor for this fundamental absorption, so throughout, we have employed a single scaling factor equal to that of the CBS-Q method.

The group values for entropy and heat capacity derived via MVLR are presented in Tables 8−10. As discussed earlier, GVs were obtained through combinations of different sets of molecules. In all of the cases, MVLR was successful and the GVs obtained are capable of predicting all of the ab initio entropy data with an average deviation of 0.14 cal/(mol K) and with a highest deviation of <0.47 cal/(mol K). The worst agreement was found for ethylmethoxyketene (**22**) and *tert*-butylethylketenes (**11**). Despite significant variations in the hindrance potential, the results of regression for entropy and C_p at low temperatures are very satisfactory. As observed for the enthalpy, the entropy also follows a similar trend reported earlier with alkene C_d groups. Going from {CCO/H/C} to {CCO/C2}, the entropy value decreases by roughly the same 20 cal/(mol K) suggested for olefinic groups. A similar observation holds good in going from Me to 1°, to 2°, and to 3° in both the mono, viz., {C/H3/CCO} > {C/C/H2/CCO} > {C/C2/H/CCO} > {C/C3/CCO} as well as in the diketene substituted groups, e.g., {C/H2/CCO2} >{C/H/C/CCO2} > {C/C2/CCO2}.

The effects of low frequency vibrations and hindrance potentials are prominent in entropy and low temperature heat capacity data. Consequently, we have tabulated the results of regression using different sets of ketenes in Tables 8 and 9. The results of the regression essentially reveal that ab initio computed thermochemical properties of a homologous series follow the group additivity rule of Benson despite the variations in the magnitude of the frequencies, barrier heights, and the reduced moment of hindered rotors. It is probably so due to the fact that the most stable conformer is nearly the same in every homologous series, and in many cases, the barriers to internal rotation are relatively high. In Table 10, we have tabulated the results of regression for $C_p(T)$ values of all of the groups in the temperature range 400−1500 K along with the statistical analysis of the regression. As expected, the average as well as the maximum deviation decreases with increase in temperature. This is due to the relative insensitivity of the partition function with respect to frequencies of large magnitude. Also the partition function of a hindered rotor slowly evolves into a free rotor whose heat capacity is a constant at high temperatures. With state-of-the-art quantum chemical methods, it is now possible to compute thermochemical functions within the experimental uncertainty for small molecules with less than 15 heavy atoms. The GVs derived from these high quality results using the MVLR procedure are the best practical method for reliably estimating ΔH_f^{298}, S^{298}, and $C_p(T)$ (300−1500 K) on larger ketenes and for other systems where no thermodynamic data or accurate estimation techniques are available.

Conclusions

Benson groups were developed for the estimation of thermodynamic properties of four different types of ketenes. The group values were derived using the thermodynamic properties of a few dozen ketenes calculated by statistical mechanical methods in conjunction with ab initio molecular parameters. A nonnearest neighbor correction is necessary to account for interactions between the CCO group and eclipsing bonds which affect the enthalpy of formation. The protocol presented here provides a viable method for calculating the thermodynamic properties of systems where experimental data are scarce and for accurately estimating the properties of larger molecules, where high quality quantum chemical calculations would be impractical.

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Supporting Information Available: The MP2/6-31G(d′) optimized geometries, unscaled HF/6-31G(d′) harmonic frequencies in (cm^{-1}), and rotational constants (in GHz) of all of the ketenes are given in Tables A and B. The thermodynamic functions of 1,3-bisketenes wherein the ketenyl and methylketenyl rotations are treated as torsional vibrations are given in Table C. The deviation plot between the predicted and calculated entropy and C_p (300 K) for all 45 ketenes are given in Figures A and B, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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