Structures, Rotational Barriers, and Thermochemical Properties of Chlorinated Aldehydes and the Corresponding Acetyl ($CC^{\bullet}{=}O$) and Formyl Methyl Radicals ($C^{\bullet}C{=}O$) and Additivity Groups

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Received: August 9, 2001; In Final Form: October 18, 2001

Chlorinated formyl methyl radicals ($C^{\bullet}C{=}O$) are the stable keto forms of chlorovinoxy radicals formed by cleavage or abstraction of the weak O−H bonds of chlorovinyl alcohols. Thermochemical properties, $\Delta H_f°_{298}$, $S°_{298}$, and $C_p°(T)$ (5 K ≤ T ≤ 6000 K), are computed by density functional B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31G(d,p), and composite CBS-Q calculation methods for chlorinated aldehydes and the corresponding chlorinated acetyl and formyl methyl radicals: CH_3CHO (**1**), CH_3CClO (**2**), CH_2ClCHO (**3**), $CH_2ClCClO$ (**4**), $CHCl_2CHO$ (**5**), $CHCl_2CClO$ (**6**), CCl_3CHO (**7**), CCl_3CClO (**8**), $CH_3C^{\bullet}{=}O$ (**9**), $CH_2ClC^{\bullet}{=}O$ (**10**), $CHCl_2C^{\bullet}{=}O$ (**11**), $CCl_3C^{\bullet}{=}O$ (**12**), $C^{\bullet}H_2CH{=}O$ (**13**), $C^{\bullet}H_2CCl{=}O$ (**14**), *E*-$C^{\bullet}HClCH{=}O$ (**15**), *Z*-$C^{\bullet}HClCH{=}O$ (**16**), $C^{\bullet}Cl_2CH{=}O$ (**17**), *E*-$C^{\bullet}HClCCl{=}O$ (**18**), *Z*-$C^{\bullet}HClCCl{=}O$ (**19**), $C^{\bullet}Cl_2CCl{=}O$ (**20**). Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) level of theory. Vibration frequencies are scaled for zero-point energies and thermal corrections. Two to four isodesmic reactions are utilized at each calculation level to determine $\Delta H_f°_{298}$ of each species. Contributions to $S°_{298}$ and $C_p°(T)$ from translation, vibration, and external rotations are calculated using the rigid-rotor-harmonic-oscillator approximation based on the B3LYP/6-31G(d,p) structures. Hindered internal rotational contributions to entropies and heat capacities are calculated by summation over the energy levels obtained from direct diagonalizations of the Hamiltonian matrix of the internal rotation. The bond energies of C−H and C−Cl in chloroaldehydes are also calculated.

Introduction

Stable chlorovinyl alcohols are the important products from OH addition to vinyl chlorides because of the low energy for scission of weaker $C^{\bullet}C{-}Cl$ bonds relative to that for scission of $C^{\bullet}C{-}OH$ bonds.[1,2] The O−H bond is weak in a vinyl alcohol (about 86 kcal/mol), similar to the weak O−H bonds in phenols and hydroperoxides (about 87 kcal/mol). Facile abstraction of these weak vinoxy or phenolic H's results in vinoxy or phenoxy radicals, which undergo rapid electron rearrangement to the keto form (resonant structure), formyl methyl ($C^{\bullet}C{=}O$) radicals (reaction 1).

$$OH + CHCl{=}CHCl \rightarrow C^{\bullet}HCl{-}CHClOH \rightarrow CHCl{=}CHOH + Cl, \quad \Delta H_{rxn} = -19.1$$

$$CHCl{=}CHOH + C^{\bullet}H_3 \rightarrow CHCl{=}CHO^{\bullet} + CH_4, \quad \text{(exothermic)}, \quad \Delta H_{rxn} = -16.8$$

$$CHCl{=}CHO^{\bullet} \rightarrow C^{\bullet}HClCH{=}O, \quad \Delta H_{rxn} = -8.4 \qquad (1)$$

Talukdar et al.[3] point out that to determine the ozone depletion potential of a compound such as CH_3CCl_3 it is necessary to understand not only its atmosphere lifetime but also the degradation kinetics of its decomposition products. CCl_3CHO can be a stable product in atmospheric degradation of organic compounds containing more than two carbons and a CCl_3 group. CH_3CCl_3 is the primary source of CCl_3CHO in the atmosphere.[3]

The $\Delta H_f°_{298}$ values for some of the stable aldehydes, such as CH_3CHO, CH_3CClO, and CCl_3CClO, are relatively well-studied.[4−8] Melius calculated the structures, moments of inertia, and frequencies of most of the titled chlorinated radicals at the HF/6-31G(d) level of theory and calculated enthalpy and free energy using the BAC-MP4 method.[8] The $S°_{298}$ and $C_p°(T)$ values are almost unknown for all of these species, except CH_3CHO and CH_3CClO. In this work, we investigate the thermochemical properties ($\Delta H_f°_{298}$, $S°_{298}$, $C_p°(T)$) and bond energies for twenty chlorinated aldehydes and acetyl and formyl methyl radicals, using four different ab initio and DFT methods.

Calculations

All calculations are performed using the Gaussian 94 program suite.[9] The structures of all 20 species are fully optimized at the B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The B3LYP/6-31G(d,p) optimized geometrical parameters are used to obtain single total electronic energies in B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBS-Q single-point calculations.[10−12] B3LYP/6-31G(d,p) is chosen because it is reported to give accurate structural parameters and it includes electron correlation. B3LYP/6-311+G(3df,2p) is a larger basis set with diffuse functions allowing more overlap of the Cl electrons. QCISD(T)/6-31G(d,p) is considered a high-level ab initio method, and CBS-Q//B3LYP/6-31G(d,p) is a composite calculation method with corrections for electron type and spin contamination.

1. $\mathbf{\Delta H_f°_{298}}$**.** Standard enthalpies of formation for CH_3CHO (**1**), CH_3CClO (**2**), CH_2ClCHO (**3**), $CH_2ClCClO$ (**4**), $CHCl_2$-

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10.1021/jp0131424 CCC: $22.00

$CClO$ (**6**), CCl_3CHO (**7**), CCl_3CClO (**8**), $CH_3C^{\bullet}{=}O$ (**9**), and $C^{\bullet}H_2CH{=}O$(**13**) are available in the literature. Standard enthalpies of formation for $CHCl_2CHO$ (**5**), $CH_2ClC^{\bullet}{=}O$ (**10**), $CHCl_2C^{\bullet}{=}O$ (**11**), $CCl_3C^{\bullet}{=}O$ (**12**), $C^{\bullet}H_2CCl{=}O$ (**14**), *E*-$C^{\bullet}HClCH{=}O$ (**15**), *Z*-$C^{\bullet}HClCH{=}O$ (**16**), $C^{\bullet}Cl_2CH{=}O$ (**17**), *E*-$C^{\bullet}HClCCl{=}O$ (**18**), *Z*-$C^{\bullet}HClCCl{=}O$ (**19**), and $C^{\bullet}Cl_2CCl{=}O$ (**20**) are determined using total energies obtained by the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p), and CBS-Q calculation methods and generic isodesmic reactions for each species:

$$CHCl_2CH{=}O\ (\mathbf{5}) + CH_3CHO \rightarrow 2CH_2ClCHO \qquad (R5a)$$

$$2CHCl_2CH{=}O\ (\mathbf{5}) \rightarrow CH_3CH{=}O + CCl_3CCl{=}O \qquad (R5b)$$

$$CH_2ClC^{\bullet}{=}O\ (\mathbf{10}) + CH_3CHO \rightarrow CH_3C^{\bullet}{=}O + CH_2ClCH{=}O \qquad (R10a)$$

$$CH_2ClC^{\bullet}{=}O\ (\mathbf{10}) + CH_2O \rightarrow CHO + CH_2ClCH{=}O \qquad (R10b)$$

$$CH_2ClC^{\bullet}{=}O\ (\mathbf{10}) + C_2H_6 \rightarrow C_2H_5 + CH_2ClCH{=}O \qquad (R10c)$$

$$CH_2ClC^{\bullet}{=}O\ (\mathbf{10}) + C_2H_5Cl \rightarrow C_2H_5 + CH_2ClCCl{=}O \qquad (R10d)$$

$$CHCl_2C^{\bullet}{=}O\ (\mathbf{11}) + CH_3CClO \rightarrow CH_3C^{\bullet}{=}O + CHCl_2CCl{=}O \qquad (R11a)$$

$$CHCl_2C^{\bullet}{=}O\ (\mathbf{11}) + CH_2O \rightarrow CHO + CHCl_2CH{=}O \qquad (R11b)$$

$$CHCl_2C^{\bullet}{=}O\ (\mathbf{11}) + C_2H_6 \rightarrow C_2H_5 + CHCl_2CH{=}O \qquad (R11c)$$

$$CHCl_2C^{\bullet}{=}O\ (\mathbf{11}) + C_2H_5Cl \rightarrow C_2H_5 + CHCl_2CCl{=}O \qquad (R11d)$$

$$CCl_3C^{\bullet}{=}O\ (\mathbf{12}) + CH_3CClO \rightarrow CH_3C^{\bullet}{=}O + CCl_3CCl{=}O \qquad (R12a)$$

$$CCl_3C^{\bullet}{=}O\ (\mathbf{12}) + CH_2O \rightarrow CHO + CCl_3CH{=}O \qquad (R12b)$$

$$CCl_3C^{\bullet}{=}O\ (\mathbf{12}) + C_2H_6 \rightarrow C_2H_5 + CCl_3CH{=}O \qquad (R12c)$$

$$CCl_3C^{\bullet}{=}O\ (\mathbf{12}) + C_2H_5Cl \rightarrow C_2H_5 + CCl_3CCl{=}O \qquad (R12d)$$

$$C^{\bullet}H_2CCl{=}O\ (\mathbf{14}) + CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_3CClO \qquad (R14a)$$

$$C^{\bullet}H_2CCl{=}O\ (\mathbf{14}) + CH_3C({=}O)CH_3 \rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_3CClO \qquad (R14b)$$

$$E\text{-}C^{\bullet}HClCH{=}O\ (\mathbf{15}) + CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_3CClO \qquad (R15a)$$

$$E\text{-}C^{\bullet}HClCH{=}O\ (\mathbf{15}) + CH_3C({=}O)CH_3 \rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_3CClO \qquad (R15b)$$

$$Z\text{-}C^{\bullet}HClCH{=}O\ (\mathbf{16}) + CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_3CClO \qquad (R16a)$$

$$Z\text{-}C^{\bullet}HClCH{=}O\ (\mathbf{16}) + CH_3C({=}O)CH_3 \rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_3CClO \qquad (R16b)$$

$$C^{\bullet}Cl_2CH{=}O\ (\mathbf{17}) + CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_2ClCClO \qquad (R17a)$$

$$C^{\bullet}Cl_2CH{=}O\ (\mathbf{17}) + CH_3C({=}O)CH_3 \rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_2ClCClO \qquad (R17b)$$

$$E\text{-}C^{\bullet}HClCCl{=}O\ (\mathbf{18}) + CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_2ClCClO \qquad (R18a)$$

$$E\text{-}C^{\bullet}HClCCl{=}O\ (\mathbf{18}) + CH_3C({=}O)CH_3 \rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_2ClCClO \qquad (R18b)$$

$$Z\text{-}C^{\bullet}HClCCl{=}O\ (\mathbf{19}) + CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_2ClCClO \qquad (R19a)$$

$$Z\text{-}C^{\bullet}HClCCl{=}O\ (\mathbf{19}) + CH_3C({=}O)CH_3 \rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_2ClCClO \qquad (R19b)$$

$$C^{\bullet}Cl_2CCl{=}O\ (\mathbf{20}) + CH_3CHO \rightarrow C^{\bullet}H_2CHO + CHCl_2CClO \qquad (R20a)$$

$$C^{\bullet}Cl_2CCl{=}O\ (\mathbf{20}) + CH_3C({=}O)CH_3 \rightarrow C^{\bullet}H_2C({=}O)CH_3 + CHCl_2CClO \qquad (R20b)$$

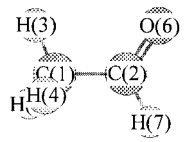
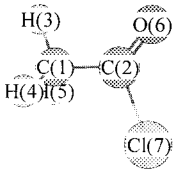
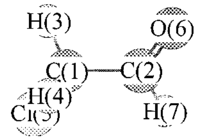
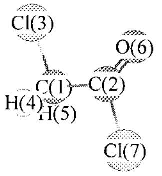
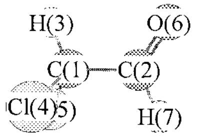
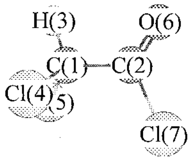
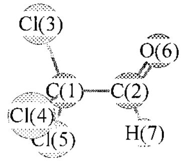
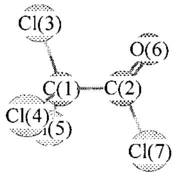
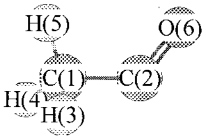
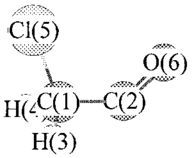
The use of isodesmic reactions to determine $\Delta H_f{}^{\circ}{}_{298}$ is based on the relationship shown in eq I:

$$\begin{aligned}\Delta H_{\mathrm{rxn},298} &= \sum(\text{total energies})_{298} \text{ of products} - \sum(\text{total energies})_{298} \text{ of reactants} \\ &= \sum(\text{experimental } \Delta H_f{}^{\circ}{}_{298} \text{ of products}) - \sum(\text{experimental } \Delta H_f{}^{\circ}{}_{298} \text{ of reactants}) \qquad (I)\end{aligned}$$

The method of isodesmic reactions relies on the similarity of the bonding environments in the reactants and products that leads to partial cancellation of systematic errors in the density functional and ab initio molecular orbital calculations.[13] Redfern et al. have compared the deviation of enthalpies of formation from experimental data for C_1 to C_{16} *n*-alkanes using the B3LYP method.[14] They clearly illustrate that use of a bond isodesmic working reaction or a homodesmotic working reaction with B3LYP calculations significantly improves the absolute accuracy in the calculations. For example, the error of computed enthalpies of formation, $\Delta H_f{}^{\circ}{}_{298}$, using B3LYP/6-31G(d,p) for *n*-alkanes is reduced to 0.1 kcal/mol per carbon in the chain length, as opposed to 2 kcal/mol per carbon in the chain length obtained using heats of atomization reaction schemes. This translates to ±1 versus ±20 kcal/mol for *n*-decane.

2. S°_{298}, $C_p{}^{\circ}(T)$ (5 K ≤ *T* ≤ 6000 K), and the Contributions of Hindered Internal Rotations to the Thermodynamic Properties. Contributions to S°_{298} and $C_p{}^{\circ}(T)$ from translation, vibrations, and external rotation (TVR) of species **1**−**20** are obtained using the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure. The ZPVE and frequencies are scaled by factors of 0.9806 and 0.9989, respectively, according to calibration by Scott and Radom.[15] Lazarou et al. have recently proposed a scaling factor of 1.0090 for vibrational frequencies at the B3LYP/6-311G(d) level.[16] The

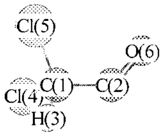
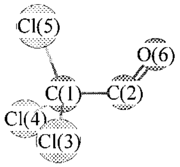
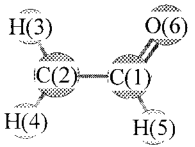
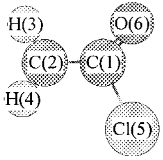
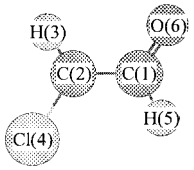
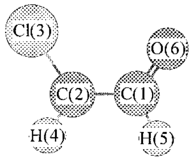
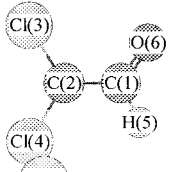
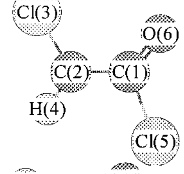
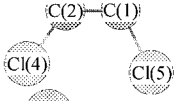
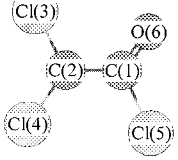
TABLE 1: Most Stable Geometries of Species 1−20 Optimized at the B3LYP/6-31G(d,p) Level of Theory

Species (ID#) σ = Symmetry #	Structure	Bond length	(angstrom)	Bond angle	(degree)	Dihedral angle	(degree)
CH_3CH=O (**1**) σ = 3		r21	1.507				
		r31	1.091	∠312	110.52		
		r41	1.097	∠412	109.75	∠4123	-121.55
		r51	1.097	∠512	109.75	∠5123	121.58
		r62	1.211	∠621	124.65	∠6213	0.08
		r72	1.114	∠721	114.77	∠7213	-179.93
CH_3CCl=O (**2**) σ = 3		r21	1.502				
		r31	1.091	∠312	109.04		
		r41	1.093	∠412	109.66	∠4123	-121.08
		r51	1.093	∠512	109.66	∠5123	121.07
		r62	1.187	∠621	128.11	∠6213	0.07
		r72	1.835	∠721	111.68	∠7213	-179.92
CH_2ClCH=O (**3**) σ = 1		r21	1.522				
		r31	1.090	∠312	110.07		
		r41	1.094	∠412	109.35	∠4123	-119.91
		r51	1.804	∠512	111.58	∠5123	121.32
		r62	1.207	∠621	121.74	∠6213	33.33
		r72	1.110	∠721	115.58	∠7213	-148.02
CH_2ClCCl=O (**4**) σ = 1		r21	1.516				
		r31	1.788	∠312	112.64		
		r41	1.092	∠412	108.82	∠4123	-121.01
		r51	1.092	∠512	108.80	∠5123	120.99
		r62	1.183	∠621	129.39	∠6213	-0.07
		r72	1.824	∠721	108.96	∠7213	179.95
$CHCl_2CH$=O (**5**) σ = 1		r21	1.529				
		r31	1.088	∠312	110.78		
		r41	1.797	∠412	108.52	∠4123	-118.93
		r51	1.797	∠512	108.54	∠5123	118.96
		r62	1.204	∠621	121.78	∠6213	0.05
		r72	1.107	∠721	114.41	∠7213	-179.96
$CHCl_2CCl$=O (**6**) σ = 1		r21	1.536				
		r31	1.088	∠312	106.77		
		r41	1.789	∠412	110.90	∠4123	-116.97
		r51	1.789	∠512	110.87	∠5123	116.94
		r62	1.190	∠621	122.14	∠6213	0.00
		r72	1.781	∠721	115.31	∠7213	180.00
CCl_3CH=O (**7**) σ = 3		r21	1.553				
		r31	1.770	∠312	112.05		
		r41	1.803	∠412	106.23	∠4123	-121.48
		r51	1.803	∠512	106.27	∠5123	121.51
		r62	1.198	∠621	123.92	∠6213	0.04
		r72	1.106	∠721	111.67	∠7213	-179.96
CCl_3CCl=O (**8**) σ = 3		r21	1.567				
		r31	1.782	∠312	108.95		
		r41	1.794	∠412	108.86	∠4123	-119.72
		r51	1.794	∠512	108.73	∠5123	119.66
		r62	1.185	∠621	123.99	∠6213	-0.30
		r72	1.779	∠721	113.74	∠7213	179.74
CH_3C•=O (**9**) σ = 3		r21	1.516				
		r31	1.094	∠312	108.70		
		r41	1.094	∠412	108.70	∠4123	-116.30
		r51	1.096	∠512	111.53	∠5123	121.86
		r62	1.189	∠621	127.90	∠6213	-121.86
CH_2ClC•=O (**10**) σ = 1		r21	1.495				
		r31	1.092	∠312	108.34		
		r41	1.092	∠412	108.36	∠4123	-117.56
		r51	1.830	∠512	115.87	∠5123	121.21
		r62	1.182	∠621	132.72	∠6213	-121.16

torsion frequency corresponding to the intramolecular rotor (C−C) is not included in the TVR calculations.

Contributions to entropy and heat capacities from intramolecular rotation (C−C) are determined using direct integration over energy levels of the internal rotation potential energy in which barriers are determined at the B3LYP/6-31G(d,p) level. A program, "ROTATOR",[17] is used for this integration. This technique employs expansion of the hindrance potential in the

TABLE 1 (Continued)

Species (ID#) σ = Symmetry #	Structure	Bond length	(angstrom)	Bond angle	(degree)	Dihedral angle	(degree)
CHCl$_2$C•=O		r21	1.528				
(11)		r31	1.089	∠312	108.98		
		r41	1.798	∠412	106.74	∠4123	-115.54
		r51	1.807	∠512	114.05	∠5123	119.70
		r62	1.179	∠621	129.89	∠6213	-128.56
CCl$_3$C•=O		r21	1.551				
(12)		r31	1.792	∠312	106.13		
σ = 3		r41	1.793	∠412	106.08	∠4123	-118.18
		r51	1.800	∠512	112.80	∠5123	120.92
		r62	1.177	∠621	128.48	∠6213	-121.06
C.H$_2$CH=O		r21	1.425				
(13)		r32	1.085	∠321	119.29		
σ = 2		r42	1.085	∠421	121.33	∠4213	179.97
		r51	1.108	∠512	116.59	∠5123	179.98
		r61	1.239	∠612	122.98	∠6123	0.00
C•H$_2$CCl=O		r21	1.434				
(14)		r32	1.084	∠321	117.53		
σ = 2		r42	1.081	∠421	121.68	∠4213	-179.99
		r51	1.828	∠512	121.92	∠5123	-179.98
		r61	1.205	∠612	126.63	∠6123	0.00
E-C•HClCH=O		r21	1.431				
(15)		r32	1.084	∠321	121.80		
σ = 1		r42	1.715	∠421	121.57	∠4213	179.98
		r51	1.107	∠512	116.54	∠5123	-179.99
		r61	1.233	∠612	121.22	∠6123	0.00
Z-C•HClCH=O		r21	1.434				
(16)		r32	1.706	∠321	121.68		
σ = 1		r42	1.085	∠421	122.33	∠4213	-179.99
		r51	1.109	∠512	113.28	∠5123	179.98
		r61	1.230	∠612	125.09	∠6123	0.00
C•Cl$_2$CH=O		r21	1.447				
(17)		r32	1.707	∠321	121.24		
σ = 2		r42	1.720	∠421	120.16	∠4213	-179.93
		r51	1.106	∠512	113.79	∠5123	179.96
		r61	1.225	∠612	123.33	∠6123	-0.07
E-C•HClCCl=O		r21	1.440				
(18)		r32	1.700	∠321	119.86		
σ = 1		r42	1.081	∠421	122.80	∠4213	-179.94
		r51	1.824	∠512	110.29	∠5123	179.93
		r61	1.200	∠612	128.23	∠6123	-0.07
Z-C•HClCCl=O		r21	1.441				
(19)		r32	1.083	∠321	117.42		
σ = 1		r42	1.697	∠421	125.93	∠4213	-179.98
		r51	1.804	∠512	116.52	∠5123	179.99
		r61	1.207	∠612	122.37	∠6123	0.00
C•Cl$_2$CCl=O		r21	1.457				
(20)		r32	1.709	∠321	117.62		
σ = 2		r42	1.706	∠421	124.63	∠4213	-179.94
		r51	1.800	∠512	114.95	∠5123	179.98
		r61	1.203	∠612	123.98	∠6123	-0.03

Fourier series (eq II), calculation of the Hamiltonian matrix on the basis of wave functions of the free internal rotor, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix.[18−20] The torsional potential calculated at discrete torsion angles is represented by a truncated Fourier series:

$$V(\Phi) = a_0 + \sum a_i \cos(i\Phi) + \sum b_i \sin(i\Phi) \qquad i = 1, 2, 3, ... \quad \text{(II)}$$

Values of the coefficients (a_0, a_i, and b_i) are calculated to provide the minimum and maximum of the torsional potentials

TABLE 2: B3LYP/6-31G(d,p) Harmonic Vibrational Frequencies and Moments of Inertia (amu bohr^2)

	frequency (cm^{-1}, not scaled)	I_a	I_b	I_c
1	157, 505, 776, 889, 1129, 1139, 1388, 1438, 1473, 1485, 1840, 2884, 3038, 3099, 3163	31.73	178.89	199.48
2	138, 342, 428, 514, 598, 963, 1049, 1117, 1399, 1475, 1479, 1917, 3068, 3144, 3173	179.06	375.55	543.41
3	52, 275, 454, 696, 794, 1032, 1041, 1191, 1274, 1415, 1456, 1838, 2948, 3085, 3165	56.16	679.80	714.68
4	83, 198, 295, 431, 477, 716, 781, 917, 970, 1201, 1315, 1448, 1934, 3101, 3160	203.07	1231.98	1423.75
5	80, 253, 273, 322, 432, 700, 773, 1016, 1056, 1219, 1250, 1410, 1842, 2979, 3176	585.65	639.54	1164.22
6	47, 166, 172, 260, 406, 501, 577, 620, 780, 783, 1072, 1258, 1260, 1875, 3171	875.29	1260.61	1494.17
7	80, 199, 245, 269, 317, 322, 434, 619, 700, 833, 1012, 1021, 1395, 1861, 2993	996.98	1116.40	1207.40
8	43, 167, 171, 240, 279, 286, 356, 423, 508, 613, 738, 789, 832, 1007, 1894	1222.45	1807.53	1942.23
9	111, 463, 853, 952, 1049, 1365, 1470, 1471, 1937, 3037, 3132, 3134	21.76	182.00	192.61
10	179, 211, 580, 662, 796, 836, 1184, 1268, 1431, 1975, 3100, 3158	107.42	504.06	600.16
11	73, 194, 271, 370, 581, 670, 735, 813, 1207, 1249, 1968, 3158	514.47	652.04	1092.32
12	57, 178, 255, 262, 311, 383, 432, 573, 738, 778, 825, 1961	1007.24	1107.72	1191.16
13	458, 503, 753, 977, 980, 1162, 1408, 1486, 1568, 2956, 3162, 3279	26.96	158.22	185.18
14	320, 360, 433, 552, 602, 758, 1027, 1161, 1463, 1723, 3184, 3313	160.14	364.46	524.60
15	188, 278, 472, 652, 886, 969, 1162, 1265, 1426, 1611, 2974, 3237	34.94	675.87	710.81
16	215, 320, 574, 682, 826, 955, 1086, 1344, 1416, 1621, 2947, 3222	97.96	477.14	575.10
17	186, 213, 292, 337, 470, 672, 952, 975, 1200, 1408, 1652, 2982	451.14	696.05	1147.19
18	123, 201, 310, 431, 524, 633, 761, 858, 1110, 1338, 1771, 3263	198.04	1192.16	1390.19
19	139, 179, 407, 489, 516, 569, 658, 898, 1199, 1311, 1712, 3240	356.12	831.57	1187.69
20	65, 189, 261, 268, 347, 423, 521, 602, 777, 995, 1210, 1749	706.22	1227.88	1934.10

TABLE 3: Enthalpies of Formation for Reference Species (and Literature Citations)[a]

species	$\Delta H_f{}^{\circ}{}_{\times b0298}$ (kcal/mol)
CH_4	*−17.89 ± 0.07* (Cox[5]), −17.78 ± 0.1 (Pedley[4]), −17.82 (TRC[7]), −17.90 (JANAF[32]), −17.9 (Benson[6]), −17.89 ± 1.00 (Melius[8]), −17.83 ± 0.07 (Gurvich[33])
CH_3	*34.97 ± 0.12* (Gurvich[33]), 34.82 (JANAF[32]), 35.09 (TRC[7]), 34.3 (Benson[6]), 34.88 ± 1.18 (Melius[8]), 35.68 (Seetula[34])
C_2H_6	*−20.2 ± 0.1* (Benson[6]), 20.03 ± 0.10 (Pedley[4]), −20.24 ± 0.12 (Cox[5]), −20.24 (SWS[35]), −20.03 (TRC[7])
C_2H_5	*28.80 ± 0.50* (Marshall[36]), 25.89 (TRC[7]), 28.80 (JANAF[32]), 26.5 (Benson[6]), 28.26 ± 1.29 (Melius[8]), 25.57 ± 1.43 (Gurvich[33]), 28.78 (Seetula[34])
C_2H_5Cl	*−26.79 ± 0.26* (Pedley[4]), −26.1 ± 0.4 (Cox[5]), −26.84 (TRC[7]), −26.80 (JANAF[32]), −26.7 (Benson[6]), −27.17 ± 1.02 (Melius[8])
CH_3CCl_3	*−34.56 ± 0.41* (Pedley[4]), −34.00 (TRC[7]), −33.55 ± 1.97 (Melius[8])
CH_2O	*−25.96 ± 0.12* (Pedley[4]), −26.0 (Benson[6]), −25.94 (TRC[7]), −26.27 (JANAF[32]), −25.98 ± 0.12 (Gurvich[33])
CHO	*10 ± 1* (Tsang[37]), 10 ± 1.2 (Gurvich[33]), 10.4[38]
acetone	*−51.94 ± 0.17* (Pedley[4]), −51.90 ± 0.12 (Cox[5]), −51.90 (TRC[7]), −51.7 (Benson[6]), −49.88 ± 1.10 (Melius[8]), −52.23 (Wiberg[39])
$C^{\bullet}H_2C({=}O)CH^3$	*−8.53 ± 1.15*[c], −6.0 (Benson[6]), −5.7[40]
CH_3CHO (**1**)	*−39.70 ± 0.12* (Pedley[4]), −39.73 ± 0.12 (Cox[5]), −39.72 (TRC[7]), −39.7 (Benson[6]), −38.55 ± 1.05 (Melius[8]), −40.80 (Wiberg[39])
CH_3CClO (**2**)	*−58.03 ± 0.19* (Pedley[4]), −58.40 ± 0.20 (Cox[5]), −58.02 (TRC[7]), −58.9 (Benson[6]), −56.93 ± 1.06 (Melius[8]), −60.07 ± 0.12,[41] −58.40 ± 0.20,[42] −58.94[43]
CH_2ClCHO (**3**)	*−41.67 ± 1.05* (Melius[8]), −41.97 ± 1[c]
$CH_2ClCClO$ (**4**)	*−58.70 ± 1.00*[b] (Cox[5]), −58.33 ± 1.22 (Melius[8]), −59.59 ± 3[c]
$CHCl_2CClO$ (**6**)	*−57.70 ± 1.00*[b] (Cox[5]), −57.98 ± 1.68 (Melius[8]), −57.46 ± 3[c]
CCl_3CHO (**7**)	*−45.52 ± 2.96* (Melius[8]), −47.01 ± 3[c]
CCl_3CClO (**8**)	*−57.31 ± 2.06* (Pedley[4]), −56.60 ± 2.10 (Cox[5]), −56.49 ± 3.99 (Melius[8]), −60.50,[42] −56.74 ± 0.7[c]
$CH_3C^{\bullet}{=}O$ (**9**)	*−2.90 ± 0.70* (Tsang[37]), −3.43 ± 2[c], −2.67[d]
$C^{\bullet}H_2CHO$ (**13**)	*3.55 ± 1.00*[b] (Melius[8]), 2.76 ± 2[c], 3.93[d]

[a] Italicized values are used in this work. [b] Uncertainty is estimated. [c] Calculated in this work. [d] Other work in this group.[44]

with allowance of a shift of the theoretical extreme angular positions. The program input is further discussed below in the results section, and a complete example of input and output data is provided in the Supporting Information, Appendix.

Results and Discussion

1. Geometries and Vibrational Frequencies. The most stable geometries, optimized at the DFT B3LYP/6-31G(d,p) level, for all twenty species are listed in Table 1 with vibrational frequencies and moments of inertia in Table 2. The optimized geometry shows a planar structure for each formyl methyl radical. Harmonic vibrational frequencies and moments of inertia are calculated on the basis of these optimized geometries at this level of theory. The frequency corresponding to the C−C bond torsion of each of species **1−12** is omitted in calculation of entropies and heat capacities; we substitute the contributions with values from internal hindered rotator analysis (discussed above). The internal rotation barriers are high (above 9 kcal/mol) for each of the formyl and chloro formyl methyl radicals (species **13−20).** We therefore treat these as vibrations and use the torsion frequencies in calculation of entropy and heat capacity.

Total energies for species **1−20** and all reference species in the isodesmic reactions (R5a, R5b, R10a−R20b) are calculated at the B3LYP/6-31G(d,p) level and at the B3LYP/6-311+G (3df,2p), QCISD(*T*)/6-31G(d,p), CBS-Q levels based on the B3LYP/6-31G(d,p) structure. Total energies are corrected by ZPVEs (scaled by 0.9806[15]) and thermal corrections from 0 to 298 K[13] and listed in Supporting Information, Table S1.

The literature values of the reference species in the isodesmic reactions are reviewed in Table 3. Most hydrocarbons in this table are relatively well-established. Chloroethane and 1,1,1-trichloroethane are among the few chlorocarbons for which the literature enthalpies of formation are consistent. There are, however, larger discrepancies for chlorinated aldehydes **2**, **3**,

TABLE 4: Calculation of $\Delta H_f{}^\circ{}_{298}$ (kcal/mol) for $C^{\bullet}H_2C(=O)CH_3$ Radical

isodesmic reactions	B3LYP/6-31G(d,p) //B3LYP/6-31G(d,p)	B3LYP/6−311 +G(3df,2p) //B3LYP/6-31G(d,p)	QCISD(T)/6-31G(d,p) //B3LYP/6-31G(d,p)	CBS-Q //B3LYP/ 6-31G(d,p)	uncertainty	
					SD[a]	expt[b]
$C^{\bullet}H_2C(=O)CH_3 + CH_4 \rightarrow$ acetone + CH_3	−10.24	−9.06	−7.43	−8.27	1.19	0.36
$C^{\bullet}H_2C(=O)CH_3 + C_2H_6 \rightarrow$ acetone + C_2H_5	−9.35	−8.22	−5.33	−8.55	1.75	0.77
final result					−8.53[c] ± 1.15[d]	

[a] Standard deviations for all four levels of theory. [b] Cumulative uncertainties from reference species in reactions (see also Table 3). [c] Average value of B3LYP/6-311+G(3df,2p) and CBS-Q levels of theory. [d] Standard deviation for B3LYP/6-311+G(3df,2p) and CBS-Q levels of theory plus 0.77 kcal/mol (maximum cumulative uncertainties from $\Delta H_f{}^\circ{}_{298}$ of reference species).

TABLE 5: Calculations of $\Delta H_f{}^\circ{}_{298}$ (kcal/mol) for Aldehydes 3−8

isodesmic reactions	B3LYP/ 6-31G(d,p) //B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G (3df,2p) //B3LYP/ 6-31G(d,p)	QCISD(T)/ 6−31G(d,p) //B3LYP/ 6-31G(d,p)	CBS-Q //B3LYP/ 6-31G(d,p)	avg[a]	literature range (see Table 3)
CCl_3CClO (**8**)+ $C_2H_6 \rightarrow CH_3CHO + CCl_3CH_3$	−54.98	−55.64	−57.96	−58.36	−56.74	−60.50 to −56.49
CH_2ClCHO (**3**)+ $C_2H_6 \rightarrow CH_3CHO + C_2H_5Cl$	−42.07	−41.91	−42.76	−42.16	−42.22	−41.97
$CH_2ClCClO$ (**4**)+ $CH_3CHO \rightarrow CH_3CClO + C_2H_5Cl$	−57.96	−57.97	−59.11	−58.98	−58.50	−59.59 to −58.33
$CHCl_2CHO$ (**5**) + $CH_3CHO \rightarrow 2CH_2ClCHO$	−42.91	−43.98	−43.64	−45.56		
$2CHCl_2CHO$ (**5**) $\rightarrow CH_3CHO + CCl_3CCl{=}O$	−46.48	−46.12	−45.65	−44.18		
final result for **5**					−44.96[b] ± 3.26[c]	
$CHCl_2CClO$ (**6**) + $CH_3CHO \rightarrow CHCl_2CHO + CH_3CClO$	−56.29	57.07	−57.93	−58.65	−57.49	−57.98 to −57.46
CCl_3CHO (**7**) + $CH_3CClO \rightarrow CH_3CHO + CCl_3CClO$	−48.01	−46.94	−45.93	−44.32	−46.30	−45.52

[a] Average value of all four levels. [b] Average value of B3LYP/6-311+G(3df,2p) and CBS-Q levels of theory. [c] Statistic standard deviation for B3LYP/6-311+G(3df,2p) and CBS-Q levels of theory plus maximum cumulative uncertainties from $\Delta H_f{}^\circ{}_{298}$ of reference species.

4, **6**, **7**, and **8**. We calculate them in this work, and the results are listed in Table 3. Our results are all in the error ranges of the selected literature data. $C^{\bullet}H_2C(=O)CH_3$ and $CHCl_2CH{=}O$ (**5**) are calculated in this work because to best of our knowledge no literature values are available.

2. $\Delta H_f{}^\circ{}_{298}$ of $C^{\bullet}H_2C(=O)CH_3$. This radical is used as a reference compound in the isodesmic reaction for formyl methyl radicals. The calculation for $\Delta H_f{}^\circ{}_{298}$ of the $C^{\bullet}H_2C(=O)CH_3$ is shown in Table 4. The result, −8.53 ± 1.15 kcal/mol, is lower than Benson's −6 kcal/mol.[6]

3. $\Delta H_f{}^\circ{}_{298}$ of 2, 3, 4, 5, 6, 7, and 8. It is seen from Table 3 that there are a few literature $\Delta H_f{}^\circ{}_{298}$ values for CH_3CClO (**2**), CH_2ClCHO (**3**), $CH_2ClCClO$ (**4**), $CHCl_2CClO$ (**6**), CCl_3CHO (**7**), and CCl_3CClO (**8**). In addition, we find no values for $\Delta H_f{}^\circ{}_{298}$ of $CHCl_2CHO$ (**5**). We calculate the $\Delta H_f{}^\circ{}_{298}$ of species **2**, **3**, **4**, **5**, **6**, **7**, and **8** using CH_3CHO (**1**), C_2H_6, and C_2H_5Cl as reference species with results shown in Table 5. Our results for **2**, **3**, **4**, **6**, **7**, and **8** are all within the error range of the available literature data. The literature $\Delta H_f{}^\circ{}_{298}$ values in Table 3 are, therefore, used for **2**, **3**, **4**, **6**, **7**, and **8**. Our calculated $\Delta H_f{}^\circ{}_{298}$ value is used for $CHCl_2CHO$ (**5**).

4. $\Delta H_f{}^\circ{}_{298}$ of Acetyl Radicals and Formyl Methyl Radicals. The $\Delta H_f{}^\circ{}_{298}$ values for $CH_3C^{\bullet}{=}O$ (**9**) and $C^{\bullet}H_2CHO$ (**13**) are taken from review of the literature in Table 3. The $\Delta H_f{}^\circ{}_{298}$ values for radicals **10**−**12** and **14**−**20** are obtained using the isodesmic reaction method at different levels of theory.

The enthalpy changes of the isodesmic reactions are calculated from the total energies (Table 6). The calculated $\Delta H_f{}^\circ{}_{298}$ values for **10**−**12** and **14**−**20** are shown in Table 7. We take the average of two levels, B3LYP/6-311+G(3df,2p) and CBS-Q, for our recommended $\Delta H_f{}^\circ{}_{298}$.

The accuracy of $\Delta H_f{}^\circ{}_{298}$ in this computation methodology is governed by several factors: (i) the choice of the working chemical reactions used to cancel calculation errors; (ii) the level of sophistication (method + basis set) applied to calculate the electronic energy; (iii) the uncertainty of the ZPVE's and thermal corrections; (iv) the reliability of the $\Delta H_f{}^\circ{}_{298}$ of reference compounds. We use acetaldehyde, formaldehyde, ethane, and chloroethane in four isodesmic reactions for each of the three acetyl radicals **10**−**12** (eqs R10, R11, and R12 series). Differences in $\Delta H_f{}^\circ{}_{298}$ between the three working reactions are small. The reactions using CH2 versus CCl2 result in a similar value in this system. We select aldehyde and acetone in our isodesmic reactions R14−R20 because they have similar chemical structures with the target species **14**−**20**. Most enthalpies of reaction in Table 6 are less than 10 kcal/mol indicating similar energy structures on both sides of the equations and suggesting a reasonable cancellation of errors. ZPVEs and thermal corrections have small contributions to the errors on a relative base. Scott and Radom report rms errors after scaling (0.9806 for B3LYP/6-31G(d)) of ±0.1 kcal/mol for ZPVE in their study on 39 molecules incorporating 1066 known vibrations. They also report a rms error of about ±0.01 kcal/mol for thermal correction from 0 to 298 K in DFT.[15] We assume that our calculations on species in the isodesmic reactions have the same error ranges and assign the accumulative uncertainties in $\Delta H_f{}^\circ{}_{298}$ from ZPVEs and thermal corrections to be ±0.44 kcal/mol. Other sources of error listed in Table 7 comprise the standard deviation of four calculated $\Delta H_f{}^\circ{}_{298}$ values (two selected levels and two to four isodesmic reactions), plus the cumulative uncertainties in $\Delta H_f{}^\circ{}_{298}$ for the reference species. Our results are in agreement (within ±1 kcal/mol) with the web data of Melius,[8] in those cases for which comparisons can be made. The recommended $\Delta H_f{}^\circ{}_{298}$ values are summarized in Table 8.

5. Internal Rotational Barriers. The potential barrier for internal rotation around the C−C bond is calculated at the B3LYP/6-31G(d,p) level. Potential energy as a function of dihedral angle is determined by scanning the torsion angle of C−C from 0° to 360° at 15° intervals and allowing the remaining molecular structural parameters to be optimized. Geometries at all maximum and minimum values are fully optimized in separate calculations. Diagrams for potential energy (ZPVE and thermal corrections included) changes with torsion angle are shown in Figures 1−3. The values of the coefficients of the Fourier expansion, a_i and b_i in eq II, are obtained from the fitting program in SigmaPlot version 2.0 and then used in

TABLE 6: Calculated $\Delta H_{rxn,298}$ (kcal/mol) for Radicals

isodesmic reactions	B3LYP/ 6-31G(d,p) //B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G(3df,2p) //B3LYP/ 6-31G(d,p)	QCISD(T)/ 6-31G(d,p) //B3LYP/ 6-31G(d,p)	CBS-Q //B3LYP/ 6-31G(d,p)
(R10a) **10** + $CH_3CHO \rightarrow CH_2ClCHO + CH_3C^{\bullet}{=}O$	1.07	0.63	−0.29	−0.35
(R10b) **10** + $CH_2O \rightarrow CH_2ClCHO + CHO$	0.04	−0.10	−1.55	−1.17
(R10c) **10** + $C_2H_6 \rightarrow CH_2ClCHO + C_2H_5$	13.14	12.17	9.12	11.89
(R10d) **10** + $C_2H_5Cl \rightarrow CH_2ClCClO + C_2H_5$	3.02	2.13	−0.64	2.04
(R11a) **11** + $CH_3CClO \rightarrow CHCl_2CClO + CH_3C^{\bullet}{=}O$	4.35	2.82	2.22	0.54
(R11b) **11** + $CH_2O \rightarrow CHCl_2CHO + CHO$	−3.68	−4.13	−4.41	−4.92
(R11c) **11** + $C_2H_6 \rightarrow CHCl_2CHO + C_2H_5$	9.43	8.14	6.26	8.14
(R11d) **11** + $C_2H_5Cl \rightarrow CHCl_2CClO + C_2H_5$	3.86	2.05	−0.12	1.43
(R12a) **12** + $CH_3CClO \rightarrow CCl_3CClO + CH_3C^{\bullet}{=}O$	6.57	5.22	4.13	1.92
(R12b) **12** + $CH_2O \rightarrow CCl_3CHO + CHO$	−4.20	−4.18	−4.79	−4.95
(R12c) **12** + $C_2H_6 \rightarrow CCl_3CHO + C_2H_5$	8.90	8.09	5.88	8.11
(R12d) **12** + $C_2H_5Cl \rightarrow CCl_3CClO + C_2H_5$	6.07	4.45	1.80	2.80
(R14a) **14** + $CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_3CClO$	−2.83	−3.04	−2.64	−2.73
(R14b) **14** + acetone $\rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_3CClO$	−1.62	−1.82	−1.50	−1.70
(R15a) **15** + $CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_3CClO$	−9.44	−8.87	−8.98	−8.63
(R15b) **15** + acetone $\rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_3CClO$	−8.24	−7.65	−7.84	−7.60
(R16a) **16** + $CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_3CClO$	−10.18	−9.69	−9.59	−9.57
(R16b) **16** + acetone $\rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_3CClO$	−8.98	−8.47	−8.44	−8.54
(R17a) **17** + $CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_2ClCClO$	−4.19	−3.00	−3.82	−2.25
(R17b) **17** + acetone $\rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_2ClCClO$	−2.99	−1.78	−2.67	−1.23
(R18a) **18** + $CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_2ClCClO$	5.12	5.73	4.30	4.80
(R18b) **18** + acetone $\rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_2ClCClO$	6.32	6.95	5.45	5.82
(R19a) **19** + $CH_3CHO \rightarrow C^{\bullet}H_2CHO + CH_2ClCClO$	3.86	4.45	3.37	4.29
(R19b) **19** + acetone $\rightarrow C^{\bullet}H_2C({=}O)CH_3 + CH_2ClCClO$	5.06	5.68	4.52	5.32
(R20a) **20** + $CH_{3CHO} \rightarrow C^{\bullet}H_2CHO + CHCl_2CClO$	9.75	9.90	8.12	8.75
(R20b) **20** + acetone $\rightarrow C^{\bullet}H_2C({=}O)CH_3 + CHCl_2CClO$	10.95	11.12	9.27	9.77

TABLE 7: $\Delta H_f{}^{\circ}{}_{298}$ (kcal/mol) for Radicals by Isodesmic Reactions and Theoretical Calculation Methods

		B3LYP/6-31G(d,p) //B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p) //B3LYP/6-31G(d,p)	QCISD(T)/6-31G(d,p) //B3LYP/6-31G(d,p)	CBS-Q //B3LYP/6-31G(d,p)	avg[a]	uncertainty		Melius[8]
							SD[a]	ref[b]	
10	(R10a)	−5.94	−5.50	−4.58	−4.52			1.87	
	(R10b)	−5.75	−5.61	−4.16	−4.54			2.17	
	(R10c)	−5.81	−4.84	−1.79	−4.56			1.65	
	(R10d)	−6.13	−5.24	−2.47	−5.15	−4.99	0.44	1.76	
11	(R11a)	−6.92	−5.39	−4.79	−3.11			1.89	
	(R11b)	−5.32	−4.87	−4.59	−4.08			4.38	
	(R11c)	−5.39	−4.10	−2.22	−4.10			3.86	
	(R11d)	−5.97	−4.16	−1.99	−3.54	−4.17	0.71	1.76	
12	(R12a)	−8.75	−7.40	−6.31	−4.10			2.95	
	(R12b)	−4.10	−4.12	−3.51	−3.35			4.08	
	(R12c)	−5.42	−4.61	−2.40	−4.63			1.21	
	(R12d)	−7.79	−6.17	−3.52	−4.52	−5.18	1.10	1.96	−5.28
14	(R14a)	−11.95	−11.74	−12.14	−12.05			1.31	
	(R14b)	−13.00	−12.80	−13.12	−12.92	−12.60	0.49	1.55	−11.53
15	(R15a)	−5.34	−5.91	−5.80	−6.15			1.31	
	(R15b)	−6.38	−6.97	−6.78	−7.02	−6.51	0.57	1.55	−6.02
16	(R16a)	−4.60	−5.09	−5.19	−5.21			1.31	
	(R16b)	−5.64	−6.15	−6.18	−6.08	−5.63	0.56	1.55	−5.43
17	(R17a)	−11.26	−12.45	−11.63	−13.20			2.12	
	(R17b)	−12.30	−13.51	−12.62	−14.06	−13.30	0.67	2.32	−12.45
18	(R18a)	−20.57	−21.18	−19.75	−20.25			2.12	
	(R18b)	−21.61	−22.24	−20.74	−21.11	−21.20	0.82	2.32	−20.32
19	(R19a)	−19.31	−19.90	−18.82	−19.74			2.12	
	(R19b)	−20.35	−20.97	−19.81	−20.61	−20.30	0.58	2.32	−19.42
20	(R20a)	−24.20	−24.35	−22.57	−23.20			2.12	
	(R20b)	−25.24	−25.41	−23.56	−24.06	−24.26	0.91	2.36	−24.27

[a] Average and standard deviations for B3LYP/6-311+G(3df,2p) and CBS-Q levels of theory. [b] Cumulative uncertainties from reference species in isodesmic reactions (see Table 3).

the program "ROTATOR"[17,18,21] to calculate the contributions of internal rotors to S°_{298} and $C_p{}^{\circ}(T)$ (5 K ≤ T ≤ 6000 K). These coefficients are listed in Supporting Information Table S2.

Input and output data for $CH_2ClC^{\bullet}{=}O$ (**10**) is shown and described in Supporting Information, Appendix, as an example application of this program. The "ROTATOR" calculation takes the 3D structure for the lowest energy conformer of the molecule, information about each atom's coordinate (x, y, z), and the respective connection to atoms of the bond about which rotation is occurring. The code calculates the reduced moment of inertia not about the bond but about the rotation axis—a method described by Pitzer and Gwinn[22−25] for this type of internal rotation. One can observe the results in the appendix of Supporting Information, in which the occurrence of near degenerate eigenenergies is observed with increase in energy

TABLE 8: Calculated Ideal Gas-Phase Thermochemical Properties[a,b]

				$C_p°(T)$							
		$\Delta H_f°_{298}$	$S°_{298}$	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	note
$CH_3CH{=}O$ (**1**)	TVR		57.92	11.34	13.95	16.50	18.77	22.49	25.31	29.69	
	I.R.		5.23	1.54	1.36	1.25	1.18	1.10	1.07	1.03	
	total		63.15	12.88	15.31	17.75	19.95	23.59	26.38	30.72	
		−39.70 ± 0.12	63.10	13.30	15.79	18.27	20.56	24.19	26.81	31.10	use[c]
$CH_3CCl{=}O$ (**2**)	TVR		65.34	14.56	17.30	19.69	21.71	24.88	27.22	30.81	
	I.R.		5.42	1.53	1.35	1.24	1.17	1.10	1.06	1.03	
	total		70.76	16.09	18.65	20.93	22.88	25.98	28.28	31.84	
		−58.03 ± 0.19	70.59	16.28	18.89	21.20	23.19	26.32	28.62	32.00	use[c]
$CH_2ClCH{=}O$ (**3**)	TVR		66.94	13.84	16.74	19.32	21.49	24.84	27.25	30.88	
	I.R.		6.08	2.07	2.02	1.91	1.77	1.49	1.24	0.81	
	total	−41.67 ± 1.05	73.02	15.91	18.76	21.23	23.26	26.33	28.49	31.69	*d*
$CH_2ClCCl{=}O$ (**4**)	TVR		73.43	17.07	20.07	22.49	24.42	27.24	29.19	32.04	
	I.R.		6.24	3.85	3.19	2.37	1.74	1.01	0.64	0.27	
	total	−58.70 ± 1.00	79.67	20.92	23.26	24.86	26.16	28.25	29.83	32.31	*e*
$CHCl_2CH{=}O$ (**5**)	TVR		73.86	17.23	20.14	22.55	24.49	27.34	29.30	32.12	
	I.R.		5.31	3.75	3.19	2.62	2.18	1.61	1.26	0.76	
	total	−44.96 ± 3.26	79.17	20.98	23.33	25.17	26.67	28.95	30.56	32.88	*f*
$CHCl_2CCl{=}O$ (**6**)	TVR		79.39	20.34	23.40	25.68	27.40	29.76	31.27	33.31	
	I.R.		7.68	1.51	1.30	1.10	0.92	0.65	0.47	0.25	
	total	−57.70 ± 1.00	87.07	21.85	24.70	26.78	28.32	30.41	31.74	33.56	*e*
$CCl_3CH{=}O$ (**7**)	TVR		77.43	21.30	24.18	26.30	27.90	30.12	31.55	33.49	
	I.R.		6.39	2.13	1.94	1.74	1.56	1.28	1.06	0.68	
	total	−44.26 ± 3.14	83.82	23.43	26.12	28.04	29.46	31.40	32.61	34.17	*d*
$CCl_3CCl{=}O$ (**8**)	TVR		82.71	24.62	27.60	29.56	30.92	32.61	33.58	34.70	
	I.R.		7.87	1.65	1.29	1.00	0.77	0.49	0.34	0.16	
	total	−57.31 ± 2.06	90.58	26.27	28.89	30.56	31.69	33.10	33.92	34.86	*g*
$CH_3C^{\bullet}{=}O$ (**9**)	TVR		58.82	10.95	13.02	14.98	16.72	19.55	21.69	25.07	
	I.R.		5.49	1.16	1.09	1.06	1.04	1.02	1.01	1.00	
	total	−2.90 ± 0.70	64.31	12.11	14.11	16.04	17.76	20.57	22.70	26.07	*h*
$CH_2ClC^{\bullet}{=}O$ (**10**)	TVR		68.67	13.55	15.91	17.88	19.49	21.92	23.66	26.28	
	I.R.		3.84	2.73	3.33	3.50	3.35	2.73	2.17	1.35	
	total	−4.99 ± 3.05	72.51	16.28	19.24	21.38	22.84	24.65	25.83	27.63	*f*
$CHCl_2C^{\bullet}{=}O$ (**11**)	TVR		75.04	16.86	19.28	21.10	22.48	24.43	25.73	27.54	
	I.R.		6.30	2.09	1.83	1.62	1.48	1.26	1.10	0.81	
	total	−4.17 ± 5.53	81.34	18.95	21.11	22.72	23.96	25.69	26.83	28.35	*f*
$CCl_3C^{\bullet}{=}O$ (**12**)	TVR		78.80	21.10	23.41	24.90	25.93	27.23	27.99	28.90	
	I.R.		6.83	1.58	1.36	1.24	1.17	1.05	0.95	0.71	
	total	−5.18 ± 5.62	85.63	22.68	24.77	26.14	27.10	28.28	28.94	29.61	*f*
$C^{\bullet}H_2CH{=}O$ (**13**)		3.55 ± 1.00	60.45	12.60	15.12	17.32	19.15	21.97	24.04	27.25	*d*
$C^{\bullet}H_2CCl{=}O$ (**14**)		−12.60 ± 3.13	68.53	16.19	18.73	20.68	22.20	24.44	26.02	28.41	*f*
E-$C^{\bullet}HClCH{=}O$ (**15**)		−6.51 ± 2.52	69.90	15.29	17.76	19.86	21.56	24.08	25.83	28.40	*f*
Z-$C^{\bullet}HClCH{=}O$ (**16**)		−5.63 ± 2.51	69.66	15.02	17.62	19.77	21.50	24.06	25.82	28.40	*f*
$C^{\bullet}Cl_2CH{=}O$ (**17**)		−13.30 ± 3.43	75.75	18.37	20.78	22.70	24.20	26.34	27.72	29.59	*f*
E-$C^{\bullet}HClCCl{=}O$ (**18**)		−21.20 ± 3.58	77.57	18.71	21.23	23.11	24.53	26.50	27.78	29.55	*f*
Z-$C^{\bullet}HClCCl{=}O$ (**19**)		−20.30 ± 3.34	77.25	18.64	21.19	23.09	24.53	26.51	27.80	29.57	*f*
$C^{\bullet}Cl_2CCl{=}O$ (**20**)		−24.26 ± 3.67	83.02	21.85	24.26	25.96	27.20	28.79	29.71	30.78	*f*

[a] $\Delta H_f°_{298}$ in kcal/mol; $S°_{298}$ and $C_p°(T)$ in cal/mol K. [b] TVR = translational + vibrational + external rotational; I.R. = internal rotational. [c] $\Delta H_f°_{298}$ from Pedley;[4] $S°_{298}$ and $C_p°(T)$ from TRC.[7] [d] $\Delta H_f°_{298}$ from Melius;[8] $S°_{298}$ and $C_p°(T)$ from B3LYP/6-31G(d,p) calculation. [e] $\Delta H_f°_{298}$ from Cox;[5] $S°_{298}$ and $C_p°(T)$ from B3LYP/6-31G(d,p) calculation. [f] $\Delta H_f°_{298}$ from theoretical calculation in this group; $S°_{298}$ and $C_p°(T)$ from B3LYP/6-31G(d,p) calculation. [g] $\Delta H_f°_{298}$ from Pedley;[4] $S°_{298}$ and $C_p°(T)$ from B3LYP/6-31G(d,p) calculation. [h] $\Delta H_f°_{298}$ from Tsang;[37] $S°_{298}$ and $C_p°(T)$ from B3LYP/6-31G(d,p) calculation.

from the bottom of the well. This is a very satisfying demonstration and reinforces this occurrence of degenerate energy levels, which are illustrated via ammonia inversion in many textbooks.

Figure 1 shows the internal rotational barriers for the eight chlorinated aldehyde species **1**−**8**. All of them have three minima for ∠OCCH (∠OCCCl in **8,** see Table 1) of 0°, 120°, and 240°, except CH_2ClCHO (**3**). The lowest barriers are observed in CH_3CHO and CH_3CClO, about 1.1 kcal/mol; the highest barrier is in $CHCl_2CHO$, 4.25 kcal/mol.

Figure 2 shows the internal rotational barriers for four chlorinated formyl methyl radicals **9**−**12**. It is seen that $CH_2ClC^{\bullet}{=}O$ has two minima and $CHCl_2C^{\bullet}{=}O$ has three minima. This results from the interaction between lone pair electrons on oxygen and the C−Cl antibonding orbital, which can be ascribed as the anomeric effect.[26] In $CH_2ClC^{\bullet}{=}O$ (**10**), the two minima are the Cl and O eclipsed conformer (∠ClCCO = 0°) and the anti conformer (∠ClCCO = 180°). In $CHCl_2C^{\bullet}{=}O$ (**11**), the minima include the two Cl and O eclipsed conformers (∠ClCCO = 0°) with the third minimum of the anti conformer (∠ClCCO = 180°). The lowest barriers are observed in $CH_3C^{\bullet}{=}O$, 0.6 kcal/mol, and $CH_2ClC^{\bullet}{=}O$ has the highest barriers, about 4.5 kcal/mol.

The rotational barrier increases significantly in acetyl radicals **13**−**20**, relative to their stable parent species, as shown in Figure 3. The two lowest energy conformers for each species in Figure 3 are planar, which have ∠OCCH or ∠OCCCl equal to 0° and 180° (see Table 1). The species *E*-$C^{\bullet}HClCH{=}O$ (**15**) and *Z*-$C^{\bullet}HClCH{=}O$ (**16**) and *E*-$C^{\bullet}HClCCl{=}O$ (**18**) and *Z*-$C^{\bullet}HClCCl{=}O$ (**19**) are two pairs of isomers that share the same curves in Figure 3. The *E* isomers (∠6123 = 0°) are about 0.5 kcal/mol lower in energy than the *Z* isomers (∠6123 = 180°). The high

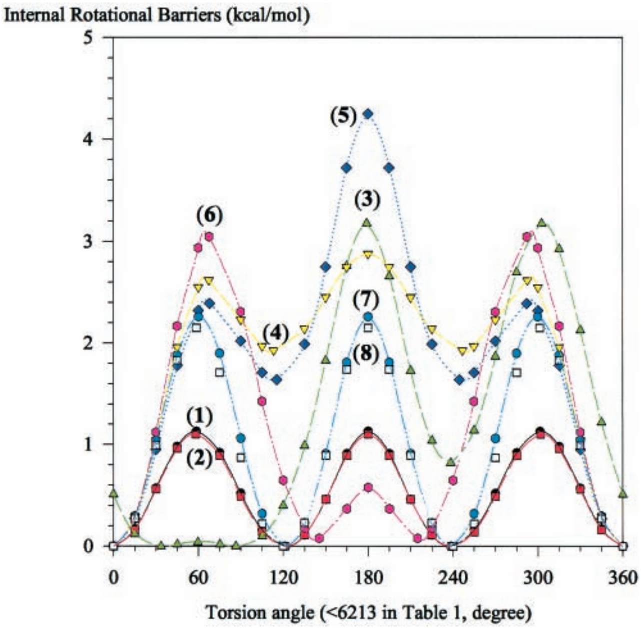


Figure 1. Internal rotational barriers of species **1**−**8**.

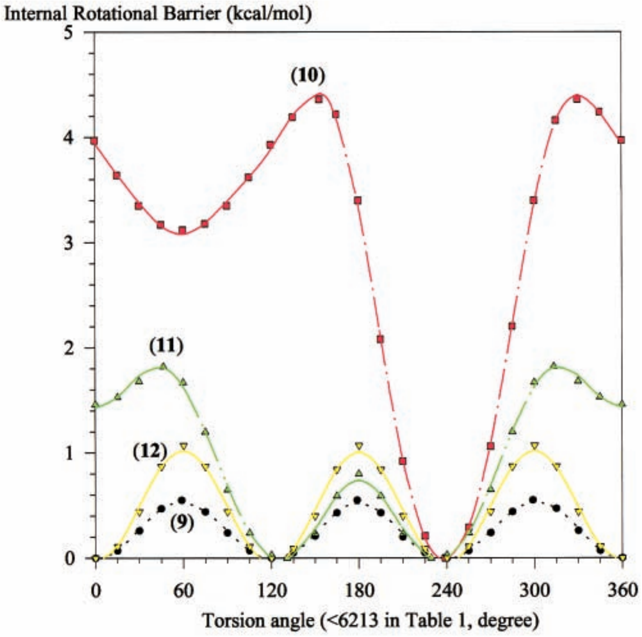


Figure 2. Internal rotational barriers of species **9**−**12**.

rotational barriers (9−16 kcal/mol) for species **13**−**20** result from breaking $C^{\bullet}-C=O$ π overlap resonance when the species are varied from the planar structures.

6. Standard Entropies and Heat Capacities. The $S°_{298}$ and $C_p°(T)$ (5 K $\leq T \leq$ 6000 K) contributions from translation, external rotation, and vibrations (TRV) are calculated from B3LYP/6-31G(d,p) determined geometries and frequencies with a "SMCPS" computer program.[21] TRV plus the contributions from internal rotations (IR) are listed in Table 8 for each species. Our calculated standard entropies and heat capacities for CH_3CHO and CH_3CClO are close to the TRC literature data.[7] Table 8 summarizes the thermochemical properties, $\Delta H_f°_{298}$, $S°_{298}$, and $C_p°(T)$ (300 K $\leq T \leq$ 1500 K), for all 20 species discussed in this work. Thermochemical parameters of species **1**−**20** at temperature ranges of 5−6000 K are available in the Supporting Information, Table S3.

7. Group Additivity Values and C−H and C−Cl Bond Energies. Benson groups for species **1**−**20** including the groups for parents and the corresponding hydrogen bond increment (HBI) groups[27] for radicals are tabulated in Table 9. All groups relevant to compounds of this study, both previously assigned and newly derived, are listed in Table 10. The method for derivation of both central groups and hydrogen bond increment (HBI) groups is described by Sun and Bozzelli.[28] As a brief summary, the enthalpy value in a HBI group is the carbon− or oxygen−hydrogen bond enthalpy ($\Delta H_{rxn,298}$ for bond cleavage) at the indicated site. The entropy and heat capacity terms are values that when added to the parent (nonradical molecule) result in the corresponding value for the radical. Entropy values are intrinsic (include no symmetry component for either the radical or parent). The entropy value does include correction for spin degeneracy of the electron and loss of the optical isomer, when appropriate.

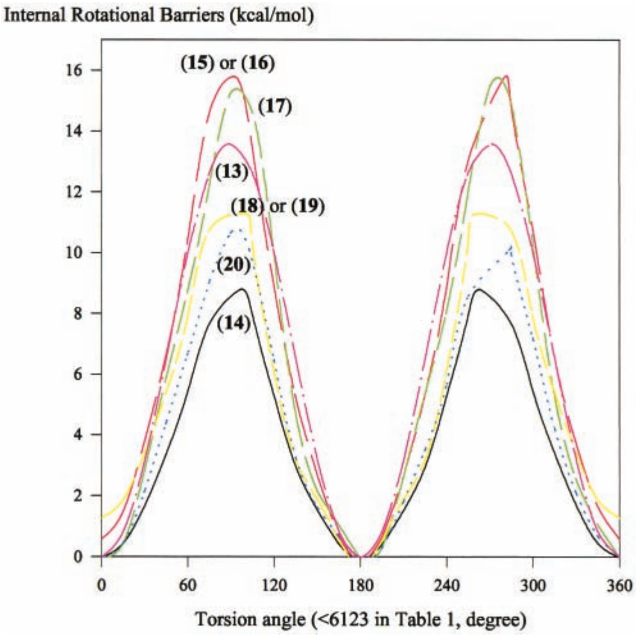


Figure 3. Internal rotational barriers of species **13**−**20**.

The C−H and C−Cl bond energies in acetone, (chloro)-aldehydes (**1**, **3**, **5**, **7**), and acetyl chlorides (**2**, **4**, **6**, **8**) are determined using the corresponding enthalpy change of the bond dissociation reactions and the thermochemical data of each species as listed in Table 8. From $CHCl_2CH{=}O \rightarrow CHCl_2\text{-}C^{\bullet}{=}O + H$, we get $BE(O{=}C{-}H) = \Delta H_{rxn,298} = 92.9$; from $CHCl_2CH{=}O \rightarrow CHCl^{\bullet}CH{=}O + Cl$, we get $BE(H_2C{-}Cl) = \Delta H_{rxn,298} = 67.4$.

The bond energies in acetone and the chlorinated aldehydes are illustrated in Figure 4. We first discuss this figure going across (from left to right), in the direction of increasing Cl substitution on the methyl carbon. The carbonyl carbon−hydrogen bond energies in di- or trichloroaldehydes are about 4 kcal/mol higher than CH_3CHO and CH_2ClCHO (first row) because of the strong electronegativity of the added Cl atoms on the methyl carbon. The carbonyl carbon−chlorine bond energy also decreases about 3 kcal/mol from CH_3CClO to CCl_3CClO (second row). Both methyl carbon−hydrogen and methyl carbon−chlorine bond energies decrease about 15 kcal/mol in first and second rows because of the steric and stabilization effects.

Moving from top to bottom in Figure 4 (direction of increasing Cl substitution on carbonyl carbon), one observes the methyl carbon−hydrogen bond energies increase by 1.7−2.3 kcal/mol because of the electron negativity of the Cl atom on the carbonyl carbon. The methyl carbon−chlorine bond

TABLE 9: Groups in Species 1−20

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Central Groups																				
$C/CO/H_3$	X	X							X				X	X						
$C/CO/H_2/Cl$			X	X						X					X	X		X	X	
$C/CO/H/Cl_2$					X	X					X						X			X
$C/CO/Cl_3$							X	X				X								
CO/C/H	X		X		X		X		X	X	X	X	X		X	X	X			
CO/C/Cl		X		X		X		X						X				X	X	X
Interaction Groups																				
INT/Cl_2				X														X	X	
INT/Cl_3						X														X
INT/Cl_4								X												
HBI Groups																				
$CC^\bullet{=}O$									X	X	X	X								
$C^\bullet C{=}O$													X							
$C^\bullet CCl{=}O$														X						
$C^\bullet ClC{=}O$															X	X				
$C^\bullet Cl_2C{=}O$																	X			
$C^\bullet ClCCl{=}O$																		X	X	
$C^\bullet Cl_2CCl{=}O$																				X

TABLE 10: Group Values ($\Delta H_f°_{298}$ in kcal/mol, $S°_{298}$ and $C_p°$ in cal/mol K)

groups	$\Delta H_f°_{298}$	$S°_{298}$	$C_p°(T)$							note
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	
Known Groups										
$C/CO/H_3$	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58	ref 6
CO/C/H	−29.10	34.90	7.00	7.80	8.80	9.70	11.20	12.20	13.60	ref 6
Int/Cl_2	2.54	−1.29	0.75	0.46	0.23	0.08	−0.05	−0.05	0.02	ref 45
Int/Cl_3	3.85	−1.86	0.58	0.33	0.04	−0.12	−0.24	−0.24	0.20	ref 45
Int/Cl_4	5.10	−2.15	0.05	−0.11	−0.26	−0.24	−0.10	0.43	0.73	ref 45
This Work, See Text										
CO/C/Cl	−47.95	42.36	10.09	11.05	11.80	12.40	13.30	13.85	14.42	from **2**
$C/CO/Cl/H_2$	−12.93	38.36	9.50	11.36	12.63	13.62	15.07	16.16	17.98	from **3**, **4**
$C/CO/Cl_2/H$	−14.73	45.42	12.58	14.43	15.66	16.51	17.55	18.25	19.11	from **5**, **6**
$C/CO/Cl_3$	−15.44	52.55	16.13	17.95	19.02	19.53	19.90	19.64	19.71	from **8**
HBI Group, This Work, See Text										
$CC^\bullet{=}O$	94.52	−0.64	−0.59	−0.88	−1.41	−1.90	−2.79	−3.33	−4.28	from **9** to **12**
$C^\bullet CH{=}O$	94.83	−4.86	−0.59	−0.52	−0.88	−1.34	−2.25	−2.93	−3.93	from **13**
$C^\bullet CCl{=}O$	97.53	−2.87	−0.09	−0.16	−0.52	−0.99	−1.88	−2.60	−3.59	from **14**
$C^\bullet ClCH{=}O$	88.20	−3.48	−1.34	−1.47	−1.62	−1.79	−2.20	−2.54	−3.18	from **15**, **16**
$C^\bullet ClCClO$	89.69	−2.02	−1.66	−1.66	−1.56	−1.57	−1.81	−2.17	−2.86	from **18**, **19**
$C^\bullet Cl_2CHO$	82.63	−3.19	−1.21	−1.45	−1.76	−2.01	−2.41	−2.73	−3.12	from **17**
$C^\bullet Cl_2CClO$	86.67	−1.52	−1.40	−1.55	−1.54	−1.59	−1.82	−2.15	−2.95	from **20**

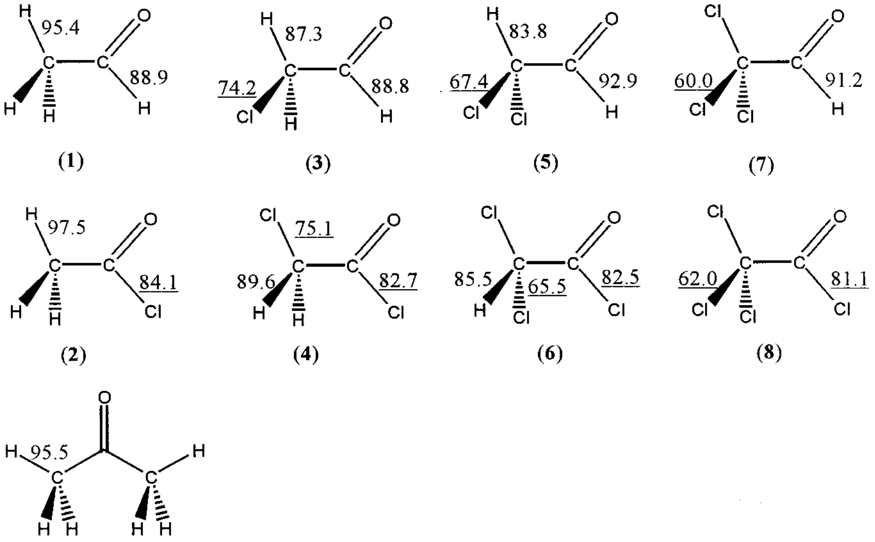


Figure 4. C−H and C−Cl bond energies in kcal/mol (bond lengths, angles, and atom sizes do not reflect actually optimized structures).

energies increase by 1−2 kcal/mol; one exception is the decrease in methyl carbon−chlorine bond energy from $CHCl_2CHO$ to $CHCl_2CClO$, −1.9 kcal/mol.

The data in Table 4 show (i) a Cl atom on the methyl carbon decreases bond energies on the carbonyl carbon−chlorine, the methyl carbon−hydrogen, and the methyl carbon−chlorine bonds but increases the carbonyl carbon−hydrogen bond energy and (ii) chlorination of the carbonyl carbon strengthens the bond energy of H (or Cl) on the vicinal carbon by 1−2 kcal/mol (the one exception is the methyl carbon−chlorine bond energy, which decreases from $CHCl_2CHO$ to $CHCl_2CClO$). These results are similar to the trends of chlorination effects on ethanes and ethyl radicals found by Seetula[29] and Sun and Bozzelli.[28] Seetula finds that the α-substituted Cl atom in chlorinated ethanes has a tendency to increase C_β−H bond strengths and decrease C_α−H bond strengths. The Cl atom has a tendency to make other C−Cl bonds weaker, both in chlorinated ethanes and in ethyl radicals. All β-chlorinated ethyl radicals have a weak C−Cl bond and facile elimination (β-scission) of the Cl atom to form ethylene, whereas α-chlorinated ethyl radicals are relatively stable at elevated temperature.

The C−H bond energy in acetone is 95.5 kcal/mol from our calculated $\Delta H_f{}^\circ{}_{298}$ of $C^\bullet H_2C(=O)CH_3$ in Table 4. This value is 1.5 kcal/mol higher than the estimated value by Bordwell and Harrelson (94 kcal/mol)[30] and 2.8 kcal/mol lower than the review value by McMillen and Golden (98.3 ± 1.8 kcal/mol).[31]

Summary

Structures, internal rotational barriers, and thermochemical properties of CH_3CHO (**1**), CH_3CClO (**2**), CH_2ClCHO (**3**), $CH_2ClCClO$ (**4**), $CHCl_2CHO$ (**5**), $CHCl_2CClO$ (**6**), CCl_3CHO (**7**), CCl_3CClO (**8**), $CH_3C^\bullet{=}O$ (**9**), $CH_2ClC^\bullet{=}O$ (**10**), $CHCl_2C^\bullet{=}O$ (**11**), $CCl_3C^\bullet{=}O$ (**12**), $C^\bullet H_2CH{=}O$ (**13**), $C^\bullet H_2CCl{=}O$ (**14**), *E*-$C^\bullet HClCH{=}O$ (**15**), *Z*-$C^\bullet HClCH{=}O$ (**16**), $C^\bullet Cl_2CH{=}O$ (**17**), *E*-$C^\bullet HClCCl{=}O$ (**18**), *Z*-$C^\bullet HClCCl{=}O$ (**19**), and $C^\bullet Cl_2CCl{=}O$ (**20**) are studied by B3LYP/6-31G(d,p) DFT calculation. The recommended $\Delta H_f{}^\circ{}_{298}$ of each species in $C^\bullet H_2C(=O)CH_3$, **5**, **10**, **11**, **12**, and **14**−**20** is the average value of data using isodesmic reactions calculated at B3LYP/6-311+G(3df,2p) and CBS-Q levels of calculation based on B3LYP/6-31G(d,p) optimized geometry. The $S^\circ{}_{298}$ and $C_p{}^\circ(T)$ (5 K ≤ T ≤ 6000 K) are determined by B3LYP/6-31G(d,p) optimized geometries and frequencies. The $\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, and $C_p{}^\circ(T)$ (300 K ≤ T ≤ 1500 K) of all species from **1** to **20** are summarized in Table 8. Group values for four central groups, CO/C/Cl, C/CO/Cl/H_2, C/CO/Cl_2/H, and C/CO/Cl_3, and seven HBI groups, $CC^\bullet{=}O$, $C^\bullet CH{=}O$, $C^\bullet CCl{=}O$, $C^\bullet ClCH{=}O$, $C^\bullet ClCCl{=}O$, $C^\bullet Cl_2CH{=}O$, and $C^\bullet Cl_2CCl{=}O$, are derived for use of group additivity estimation for higher chlorinated acetyl-containing molecules.

Acknowledgment. We acknowledge the USEPA Northeast Regional Research Centers and the USEPA Research Center on Airborne Organics for the funding. We acknowledge Chad Sheng for the "SMCPS" and the FORTRAN version of the "ROTATOR" computer code.

Supporting Information Available: Tables S1−S3 providing the total energies, coefficients for the truncated Fourier series, and thermochemical properties at T = 5−6000 K for **1**−**20** and an appendix containing an example of use of the "ROTATOR" program. This material is available free of charge via the Internet at http://pubs.acs.org.

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