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The Molecular Structures and Energetics of Cl_2CO, ClCO, Br_2CO, and BrCO

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The heats of formation of ClCO, Cl_2CO, BrCO, and Br_2CO have been calculated at high levels of ab initio molecular orbital theory. Geometries and frequencies for the two closed shell molecules were calculated at the MP2 level. The geometries of the two radicals were calculated at the level of coupled cluster theory with single and double excitations including a perturbative treatment of the connected triple excitations (CCSD(T)) with the augmented correlation consistent triple-ζ basis set (aug-cc-pVTZ). Extrapolation of the total energies (aug-double, aug-triple, aug-quadruple) to the complete 1-particle basis set limit was performed to further reduce the basis set truncation error. Additional improvements in the atomization energy were achieved by applying corrections for core/valence correlation, scalar relativistic effects, and spin−orbit coupling. Zero point energies were based on MP2 calculated values. Using restricted open shell treatments for the atoms, we find the following heats of formation (kcal/mol) at 0 K: $\Delta H_f[C(O)Cl_2] = -51.6 \pm 0.5$ (calc.) vs -52.2 ± 0.8 (expt.); $\Delta H_f(ClCO) = -4.6 \pm 0.5$ (calc.) vs -5.6 ± 0.7 (expt.); and $\Delta H_f[C(O)Br_2] = -22.7 \pm 1.0$ (calc.) vs -23.3 ± 0.1 (expt.), and $\Delta H_f[BrCO] = 0.7 \pm 1.5$ (calc). The radical BrCO is predicted to be only weakly bound with a long quasi-linear Br−C bond length of 3.09 Å, and a Br−CO binding energy (ΔE_{elec}) of only 1.6 kcal/mol calculated at the CCSD(T) estimated basis set limit. Inclusion of both molecular and atomic spin−orbit coupling effects reduces this to just 0.3 kcal/mol.

Introduction

The halogenated derivatives of formaldehyde have been considered to play a potential role in the chemistry of the upper troposphere and in the stratosphere. Given the potential importance of these compounds, there have been few studies that yield reliable structural and energetic information, especially for radicals such as XCO where X is a halogen. We have recently reported the results of highly accurate calculations for the structural parameters, vibrational frequencies, and energetics for X = H and X = F and the associated closed shell molecules, $C(O)H_2$ and $C(O)F_2$.[1] These results allowed us to confirm the reported heat of formation for HCO, reduce the error limits on this value, and provide a much higher quality ΔH_f^0 for FCO. These results clearly show that breaking the X-CO bond is much easier than breaking the X−C(O)X bond, with X−CO bond energies of 14.4 kcal/mol for X = H and 35.5 kcal/mol for X = F, as compared to X−C(O)X bond energies of 86.6 for X = H and 119.6 kcal/mol for X = F. It is thus of interest to predict the bond energies for X = Cl and X = Br in XCO and C(O)-X_2, as these compounds could serve as potential atmospheric reservoirs for Cl and Br and the C−Cl and C−Br bond energies are weaker than the C−H and C−F bond energies. For example, the C−Cl bond energies in CH_3Cl and CF_3Cl are 82.3 and 84.9 kcal/mol, respectively, and the C−Br bond energies in CH_3Br and CF_3Br are 68.5 and 68.7 kcal/mol, respectively. These can be compared to C−H bond energies of 103.4 and 104.8 kcal/mol in CH_4 and CF_3H, respectively, and C−F bond energies of 108.2 and 128.4 kcal/mol for CH_3F and CF_4, respectively. (All bond energies calculated at 0 K.[2−4])

Our laboratory has recently been developing a composite theoretical approach that is intended to reliably predict a variety of thermodynamic quantities, including heats of formation, without recourse to empirical parameters.[1,5−13] As described below, our approach starts with existing, reliable thermodynamic values (obtained from either experiment or theory). Missing pieces of information are then computed by using high-level ab initio electronic structure methods, such as coupled cluster methods including single, double, and connected triple excitations, with the latter being handled perturbatively.[14−16] This method, known conventionally as CCSD(T), is capable of recovering a large fraction of the correlation energy for molecules that can qualitatively be described by a single electronic configuration.[9,12] To further reduce the magnitude of the finite basis set (1-particle) error, the CCSD(T) energies are extrapolated to the complete basis set (CBS) limit. To improve the agreement with experiment, corrections for core/valence

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correlation, atomic spin−orbit effects, molecular scalar relativistic effects, and the remaining correlation energy are required. In addition, vibrational zero point energies (ZPEs) must also be carefully considered, as significant errors can inadvertently be introduced through the noncritical adoption of low-level estimates of vibrational contributions to heats of formation. The composite approach that we have developed has been shown to yield reliable atomization energies for a growing number of molecules. Application of this method to a group of 73 molecules, many of which were taken from the G2 and G2/97 test set, yielded a mean absolute deviation with respect to experiment of 0.7 to 0.8 kcal/mol.[9,12]

Computational Approach

For the 1-particle expansion, we use the correlation-consistent (cc) basis sets from Dunning and co-workers[17−21] because of the regularity with which they approach the CBS limit. We have previously found that convergence of the energy is improved if the cc basis sets are augmented by an additional shell of diffuse functions, especially for polar molecules. These basis sets are conventionally denoted aug-cc-pV*n*Z, $n = \mathrm{D}$ (double), T (triple), etc.; throughout the text we will abbreviate these basis set labels to aVDZ, aVTZ, etc. Currently available complete basis set extrapolation methods (described below) require that calculations be carried out through at least the quadruple-ζ level. Only the spherical components (5-*d*, 7-*f*, and 9-*g*) of the Cartesian polarization functions were used.

As noted above, the primary contribution to ΣD_e is the electronic energy difference between the molecule and the constituent atoms obtained from frozen core (FC) CCSD(T) calculations. Most of the coupled cluster calculations were performed with the MOLPRO program suite.[22] The MP2 calculations were performed with the *Gaussian 98* program.[23] Both the MOLPRO and *Gaussian 98* calculations were performed on SGI computers. Some of the larger CCSD(T) calculations were run with NWChem[24,25] on the 512-node IBM-SP massively parallel computer in the Molecular Science Computing Facility in the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory.

The geometries and frequencies for $C(O)Cl_2$ and $C(O)Br_2$ were calculated at the MP2 level of theory[26] with the cc-pVTZ basis set. The geometries of ClCO and BrCO were calculated at the CCSD(T) level of theory with the cc-pVDZ, aVDZ, and aVTZ basis sets. The frequencies for these radicals were calculated at the MP2/aVDZ level. All calculations were started from geometries optimized at the local density functional theory level with a polarized double-ζ basis set (either DZVP2 or DZVP).[27−29] The open shell coupled cluster calculations used restricted open shell Hartree−Fock (ROHF) orbitals followed by a relaxation of the spin constraint in the coupled cluster calculation, denoted R/UCCSD(T).[16,30,31]

The raw atomization energies can be improved by extrapolating to the CBS limit, especially when the largest basis set is aVQZ. Experience with similar systems showed only a small spread in the effectiveness of various CBS extrapolations, and we choose to use a mixed exponential/Gaussian function of the form

$$E(x) = \mathrm{A}_{\mathrm{CBS}} + \mathrm{B}\exp[-(n-1)] + \mathrm{C}\exp[-(n-1)^2] \quad (1)$$

where $n = 2$ (DZ), 3 (TZ) etc., which was first proposed by Peterson et al.[32]

The next largest contribution to the atomization energy is due to the molecular zero point energy. The zero point energies were calculated from the average of the harmonic frequencies (ω_i) calculated at the MP2 level and the experimental anharmonic fundamental frequencies (when available) via the expression

$$\mathrm{ZPE} = [0.5^*\Sigma\nu_i(\mathrm{expt.}) + 0.5^*\Sigma\omega_i(\mathrm{MP2})]/2 \quad (2)$$

An additional set of corrections to the CCSD(T)(FC) binding energies also needs to be included if the goal is to predict molecular heats of formation to an accuracy of ±1 kcal/mol or better. Core/valence corrections to the dissociation energy were obtained from fully correlated (1s2s2p electrons of C and O, 2s2p3s3p electrons of Cl, and 3s3p3d4s4p electrons of Br) CCSD(T) calculations with cc-pCVTZ and cc-pwCVTZ basis sets.[33] (The Br calculations employed a preliminary cc-pwCVTZ basis set.[33c]) These basis sets include additional functions that allow for effective correlation of the core electrons. Experience has shown that the cc-pCVTZ basis set recovers ∼75% or more of the effect seen with the larger cc-pCVQZ basis. In the following, these corrections will be labeled ΔE_{CV}.

The next set of corrections deals with the effect of relativity. Most popular electronic structure packages do not correctly describe the lowest energy spin multiplet of an atomic state, such as the ^{3}P state of carbon. Instead, the energy is a weighted average of the available multiplets. To correct for this effect, we apply an atomic spin−orbit correction of 0.08 kcal/mol for C, 0.24 for O, 0.84 for Cl, and 3.51 for Br based on the experimental excitation energies of Moore.[34] The sign of the correction is negative, indicating that when added to the theoretical value of ΣD_e the binding energy *decreases*, since the energy of the atoms was underestimated without the correction. For the radicals ClCO and BrCO there is also a molecular spin−orbit splitting that should be taken into account. In the present work, frozen-core single and double excitation configuration interaction, CISD(FC), calculations with the 1- and 2-electron Breit−Pauli operator within the framework of first-order perturbation theory were carried out as described in the work of Nicklass et al.[35] These calculations employed the cc-pCVTZ basis set with diffuse *s* and *p* functions taken from the aVTZ sets for Cl and Br, and the cc-pVTZ set for C and O. The *f* polarization functions were not included in these calculations and the *sp* sets for C and O were left uncontracted.

Besides atomic spin−orbit effects, there are also scalar relativistic corrections which are intended to account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms. As in our previous studies, we evaluated the scalar relativistic correction, ΔE_{SR}, with CISD(FC) wave functions using the cc-pVTZ basis set (CISD/VTZ). ΔE_{SR} was represented as the sum of the expectation values of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[36] Comparisons between this approach and published 4-component results, or Douglas-Kroll (DK) scalar relativistic corrections,[9,11,37] suggested that CISD/VTZ should be accurate to ∼ ±0.2 kcal/mol. The number of comparisons was limited due to the scarcity of published 4-component and DK results. Recently, however, Bauschlicher[38] have criticized the use of CISD wave functions and the cc-pVTZ basis set, arguing that such a level does not yield ΔE_{SR} values that are as accurate as we had initially found. The source of the errors varies from molecule to molecule, with some having larger errors than others. We have used our formalism as it should not introduce errors larger than 0.5 kcal/mol.

By combining our computed ΣD_0 values with the known[2] heats of formation at 0 K for the elements $\Delta H_f^0(\mathrm{C}) = 169.98 \pm 0.1$ kcal/mol, $\Delta H_f^0(\mathrm{O}) = 58.9$ kcal/mol, $\Delta H_f^0(\mathrm{Cl}) = 28.59$

TABLE 1: Geometry Parameters[a] Calculated in the Present Work

	X^1A_1 C(O)Cl_2		X^2A' ClCO			
parameter	MP2/VTZ	exp[b]	MP2/aVDZ	CCSD(T)/VDZ	CCSD(T)/aVDZ	CCSD(T)/aVTZ
C−O	1.195	1.166	1.175	1.168	1.171	1.163
C−Cl	1.741	1.746	1.810	1.866	1.857	1.818
<OCCl	124.2	124.4	129.3	128.9	129.0	129.1
<ClCCl	111.6	111.3				
	X^1A_1 C(O)Br_2		$X^2\Sigma^+$ BrCO			
	MP2/VTZ	exp[b]	MP2/aVDZ	CCSD(T)/VDZ	CCSD(T)/aVDZ	CCSD(T)/aVTZ
C−O	1.182	1.172	1.149	1.144	1.146	1.135
C−Br	1.909	1.917	3.128	3.299	3.142	3.094
<OCBr	123.9	123.8	180	180	180	180
<BrCBr	112.2	112.3				

[a] Bond distances in Å and bond angles in degrees. Open shell CCSD(T) calculations were done with the R/UCCSD(T) method. [b] Reference 39.

TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) Calculated at the MP2 Level of Theory with the cc-pVTZ [C(O)Cl_2, C(O)Br_2] and aug-cc-pVDZ (ClCO, BrCO) Basis Sets

	C(O)Cl_2		C(O)Br_2			ClCO			BrCO
sym	calc	expt[a]	calc	expt[a]	sym	calc	expt[b]	sym	calc
a_1	1831	1827	1823	1828	a′	1917	1877	Σ	2082
	583	567	444	425		637	570		65
	308	285	187	181		373	335	Π	47
b_1	595	580	532	512					
b_2	858	849	762	757					
	448	440	357	350					

[a] Reference 42. [b] References 40 and 43.

TABLE 3: Total Energies (a.u.) at the CCSD(T) Level of Theory[a]

basis set	C(O)Cl_2	ClCO	C(O)Br_2	BrCO
aVDZ	−1032.413080	−572.689715	−5258.127005	−2685.562655
aVTZ	−1032.643645	−572.847391	−5258.466273	−2685.771005
aVQZ	−1032.714486	−572.896286	−5258.532014	−2685.816109
CBS(mix)[b]	−1032.754389	−572.923878	−5258.564675	−2685.839369
CBS(exp)[c]	−1032.74591	−572.918263	−5258.54781	−2685.82857
CBS($1/l_{max}$)[d]	−1032.75537	−572.924506	−5258.56996	−2685.84214

[a] The MP2/VTZ geometries were used throughout for C(O)Cl_2 and C(O)Br_2, while the CCSD(T)/aVTZ geometries were used for the aVQZ calculations on ClCO and BrCO (optimal geometries used for aVDZ and aVTZ). [b] Equation 1. [c] Equation 3. [d] Equation 4.

TABLE 4: Energy Components (kcal/mol) for Calculating ΣD_e and ΔH_f^0 (0K)

energy term	C(O)Cl_2	C(O)Br_2	ClCO	BrCO
ΔE_{elec}(mix)[a]	345.61	320.14	266.85	260.61
ΔE_{elec}(exp)[b]	345.42	316.87	266.73	258.33
$\Delta E_{elec}(1/l_{max})$[c]	345.54	320.11	266.80	260.58
ΔE_{CV}[d]	1.54	1.90	1.09	0.72
ΔE_{SO}[e]	−2.00	−7.34	−1.16	−1.65
ΔE_{SR}[f]	−0.83	−0.83	−0.56	−0.12
ZPE(calc)[g]	6.61	5.87	4.18	3.20
ZPE(expt)[h]	6.50	5.79	3.97	
ZPE(avg)	6.56	5.83	4.08	3.20
ΣD_e[i]	337.76	308.04	262.14	256.36
ΔH_f^0 (0K)calc	−51.6 ± 0.5	−22.7 ± 1.0	−4.6 ± 0.5	0.7 ± 1.5
ΔH_f^0 (0K)exp[j]	−52.2 ± 0.8	−23.3 ± 0.1	−5.6 ± 0.7	

[a] Equation 1. [b] Equation 3. [c] Equation 4. [d] Core/valence corrections obtained with the cc-pCVTZ and cc-pwCVTZ basis sets as described in the text. A positive sign indicates that CV effects increase the stability of the molecule relative to the atomic asymptotes. [e] Correction due to the improper treatment of the atomic asymptotes as an average of spin multiplets. For BrCO, this includes a molecular SO effect of +1.77 kcal/mol. The SO splitting in ClCO was calculated to be just 2 cm^{-1} and has been neglected. For BrCO, ΔE_{SO} was calculated as described in the text. Use of the experimental splitting for Br as compared to the calculated one leads to $\Delta E_{SO} = -2.06$ kcal/mol and to BrCO being slightly unbound with respect to the Br + CO asymptote. [f] The scalar relativistic correction is based on CISD(FC)/cc-pVTZ calculations of the 1-electron Darwin and mass-velocity terms. [g] MP2 harmonic zero point energies. [h] References 42 and 43. [i] $\Sigma D_e = \Delta E_{elec}(\text{mix}) + \Delta E_{CV} + \Delta E_{SO} + \Delta E_{SR} - \text{ZPE(avg)}$. [j] References 2−4, 49, 50.

kcal/mol, and $\Delta H_f^0(\text{Br}) = 28.18$ kcal/mol we can derive ΔH_f^0 values for the molecules under study. The uncertainties in our theoretical approach (see below) are probably large enough that the uncertainties in the experimental heats of formation of the atoms are negligible.

Results and Discussion

The calculated geometry parameters are given in Table 1 and the calculated frequencies are given in Table 2. The required total energies are given in Table 3 and the components for calculating the ΣD_e are given in Table 4. The calculated geometry parameters for C(O)Cl_2 and C(O)Br_2 are in reasonable agreement with the experimental results.[39] However, we note that the difference of 0.03 Å in the CO bond length for C(O)Cl_2 is larger than what we would expect for such molecules at this level, especially since we do get within 0.01 Å for the CO bond length in C(O)Br_2. The calculated geometry for ClCO at the MP2/aVDZ level of theory is in good agreement with the previous MP2 calcuations of Schnöckel et al.,[40] as well as those of Chien et al.[41] In the latter study, however, their MP2 bond angle is nearly 15° smaller, which is presumably due to the lack of diffuse functions in their basis set. Our CCSD(T)/aVTZ values should be the most reliable to date. The calculated harmonic vibrational frequencies for C(O)Cl_2 and C(O)Br_2 are in excellent agreement with the experimental values, which were measured in the gas phase.[42] The excellent agreement between the calculated and experimental values for the C═O stretch in C(O)Cl_2 is accidental, as the calculated value is a harmonic frequency and the experimental value is an anharmonic frequency. The calculated C═O bond is too long, leading to a lowering of the harmonic value so that it is very close to the experimental anharmonic one. The agreement is somewhat worse for ClCO where the experimental values were obtained from a matrix isolation experiment.[40,43] The calculated zero point energies are in excellent agreement with experiment (taken as one-half of the fundamentals) being within 0.1 kcal/mol for C(O)Cl_2 and C(O)Br_2 and within 0.2 kcal/mol for ClCO.

The most interesting result in Table 1 is for the structure of BrCO. At the CCSD(T)/aVTZ level, the molecule is predicted to be a loose complex with a very long Br−C bond length of 3.094 Å and a linear bond angle, albeit with a very low bending frequency of just 47 cm^{-1}. In addition, the calculated CO stretching frequency, 2082 cm^{-1}, is very similar to that of free CO, 2144 cm^{-1}, at the same level of theory.[44] Hence BrCO can be qualitatively described as a van der Waals complex between CO and Br atoms, with the singly occupied p_z orbital of Br directed toward the CO bond axis. Not unexpectedly, it was found that an excited $^2\Pi$ state (formed from the ^2P_x and ^2P_y components of the Br atom) was only 6 kcal/mol above the ground $^2\Sigma^+$ state. The initial DFT geometry was bent with a bond angle of 130° and a short Br−C bond length of 2.11 Å, much like that of ClCO. At the CCSD(T)/aug-cc-pVTZ level of theory, however, the energy of the DFT optimized geometry is 2.35 kcal/mol above the final linear geometry with the long Br−C bond.

To predict error bounds for the calculated heats of formation, we used additional CBS extrapolation formulas. Besides the expression given above, we also used two alternative functional forms, a simple exponential[45,46]

$$E(n) = \mathrm{A}_{\mathrm{CBS}} + \mathrm{B}\exp(-\mathrm{C}n) \tag{3}$$

and an expansion in $1/l_{\max}$

$$E(l_{\max}) = \mathrm{A}_{\mathrm{CBS}} + \mathrm{B}/(l_{\max} + 0.5)^4 \tag{4}$$

where $l_{\max}$ is the maximum l value for the basis set ($l = 0$, 1, 2, ... for *s*, *p*, *d*, etc.).[47,48] The values obtained from using eqs 1, 3, and 4 were within 0.2 kcal/mol of each other for $C(O)Cl_2$ and ClCO. For $C(O)Br_2$, the extrapolations from eqs 1 and 4 are in excellent agreement with each other, but the extrapolation based on the simple exponential differed by 3.3 kcal/mol from the other two values. For BrCO, we find a similar result with the extrapolated values from eqs 1 and 4 in almost exact agreement and the value from the simple exponential (eq 3) 2.3 kcal/mol lower. Since this difference is quite large and we find such good agreement between the extrapolations from eqs 1 and 4, we estimate the error in the extrapolation to be smaller than the difference between the extrapolated value from eq 1 and eq 3 for $C(O)Br_2$ and BrCO, on the order of 1.0 kcal/mol. The final quoted uncertainties include the estimated errors in the extrapolation and our assessment of the likely errors arising from each of the smaller corrections. These include errors arising from the use of harmonic frequencies (if necessary) and the core/valence and scalar relativistic corrections. Our error analysis assumes no cancellation of error, although given the variations in sign of the different effects, some cancellation is likely to occur.

The various energy components for calculating ΣD_e show some interesting behavior. The core valence contribution is not negligible as expected from our previous work, ranging from a low of 1.1 kcal/mol for ClCO to a high of 1.9 kcal/mol for $C(O)Br_2$. The core valence correction for BrCO is smaller, consistent with the molecular structure showing only a weak complex between Br and CO. The scalar relativistic effects are predicted to lower ΣD_e and are all similar, with those for $C(O)Cl_2$ and $C(O)Br_2$ being the same. The scalar relativistic correction for BrCO is very small as compared to the other ΔE_{SR} values. The spin−orbit correction is much larger than found for most first-row compounds due to the large spin−orbit corrections of 0.84 kcal/mol for Cl and 3.51 kcal/mol for Br. For ClCO and BrCO, molecular spin−orbit corrections were calculated to be ~0 (2 cm^{-1}) and 1.8 kcal/mol, respectively (their total energies are lowered by these amounts). Because the effect in the atom for Br is so large and the binding energy for Br−CO is so small (see below) we have calculated the spin−orbit splitting for Br at the same level as for BrCO. The total experimental spin−orbit splitting for Br is 3685 cm^{-1} as compared to our calculated value of 3259 cm^{-1}. Better agreement with experiment would require the inclusion of significant core/valence correlation in these calculations.[35] The calculated value leads to an atomic spin−orbit correction of 3.10 kcal/mol as compared to the experimental value of 3.51 kcal/mol. Thus, for the calculation of the atomization of BrCO, we have used our calculated value for Br for calculating ΔE_{SO}. For BrCO, the molecular spin−orbit correction has the effect of decreasing the large contribution of the atomic spin−orbit splitting of Br atom to ΣD_e by almost one-half.

The heats of formation of $C(O)Cl_2$ and $C(O)Br_2$ are reasonably well-established, with the best value being for $\Delta H_\mathrm{f}^0[C(O)Cl_2]$. The calculated and experimental values for $\Delta H_\mathrm{f}^0[C(O)Cl_2]$ at 0 K are in excellent agreement, with the calculated value slightly more positive as expected from our other studies. The heat of formation of $C(O)Br_2$ has been reported in a number of summaries[2−4,49] as ΔH_f^0(298K) = −20.1 ± 0.1, −27.1 ± 0.1, and −23.0 kcal/mol, with the latter value yielding ΔH_f^0(0 K) = −19.2 kcal/mol. Correcting the other two values from 298 to 0 K gives −16.3 ± 0.1 and −23.3 ± 0.1 kcal/mol. The latter (most recent) value is in excellent agreement with our calculated value of −22.7 kcal/mol. The calculated 0 K value for $\Delta H_\mathrm{f}0$(ClCO), −4.6 ± 0.5 kcal/mol, falls within the ±0.7 kcal/mol experimental error bounds of Wine and co-workers[50] and clearly demonstrates that the older experimental value[2] of −15.4 ±10 kcal/mol is much too large. Our result for ClCO is also in good agreement with the G3 value (−5.2 kcal/mol) calculated by Chien et al.[41] For ΔH_f^0(BrCO), our value is the only one available.

The following reaction energies at 0 K based on the calculated ΔH_f^0's for the halogenated compounds and the known heats of formation of the atoms and CO (ΔH_f^0(CO) = −27.2 ± 0.04 kcal/mol vs −27.1 kcal/mol calc.[1]) provide insight into the stability of the various compounds:

$$C(O)Cl_2 \rightarrow ClCO + Cl \qquad \Delta H(0\ \mathrm{K}) = 75.7\ \mathrm{kcal/mol} \tag{5}$$

$$C(O)Cl_2 \rightarrow CO + 2Cl \qquad \Delta H(0\ \mathrm{K}) = 81.6\ \mathrm{kcal/mol} \tag{6}$$

$$COCl \rightarrow CO + Cl \qquad \Delta H(0\ \mathrm{K}) = 5.9\ \mathrm{kcal/mol} \tag{7}$$

$$C(O)Br_2 \rightarrow BrCO + Br \qquad \Delta H(0\ \mathrm{K}) = 51.6\ \mathrm{kcal/mol} \tag{8}$$

$$C(O)Br_2 \rightarrow CO + 2Br \qquad \Delta H(0\ \mathrm{K}) = 51.9\ \mathrm{kcal/mol} \tag{9}$$

$$COBr \rightarrow CO + Br \qquad \Delta H(0\ \mathrm{K}) = 0.3\ \mathrm{kcal/mol} \tag{10}$$

The Cl−C bond energy in $C(O)Cl_2$ of 75.7 kcal/mol is 6 to 10 kcal/mol smaller than the bond energies of 82 to 85 kcal/mol given in the Introduction for simple chlorinated methanes. The loss of the second Cl from ClCO occurs very easily with a bond energy of only 5.9 kcal/mol. It is possible to calculate the simultaneous loss of 2 Br atoms from $C(O)Br_2$, a value of 51.9 kcal/mol. This is 16.8 kcal/mol below the value of a Br−C bond in methanes as noted above. The bond energy for Br−CO is very low, only 0.3 kcal/mol at 0 K. Thus if $C(O)Br_2$ absorbs enough energy to lead to loss of a Br atom, the second can be very easily removed. The terms that go into the bond energy of Br−CO provide some interesting insights. At the CCSD(T)/CBS limit, the electronic contribution to the bond energy is 1.61 kcal/mol. The spin−orbit in the atom is quenched by 1.3 kcal/mol based on our calculated spin−orbit splittings, so the spin−orbit terms essentially cancel ΔE_{elec} leading to the very low bond energy as the other terms are approximately zero. (Use of the experimental value for the spin−orbit splitting in Br actually leads to BrCO being unbound by 0.1 kcal/mol.) For comparison, the ΔE_{elec} contribution to the Cl−CO bond energy at the CCSD(T)/CBS limit is 7.85 kcal/mol. In ClCO, where the molecular spin−orbit effect is calculated to be completely quenched, the CCSD(T)/CBS bond energy (D_e) is reduced only to 7.01 kcal/mol, a significant binding energy as compared to BrCO.

The carbonyl halides, CX_2O (where X = Cl or Br) have been found to be major products of the photolysis of chlorinated and brominated methane in the presence of oxygen.[51−55] They result from the reaction of trihalomethyl radicals with molecular oxygen and from the dissociation of CX_3O radicals. In particular, CCl_2O results from the oxidation of CCl_4, and CBr_2O results from oxidation of CBr_3H. There are few studies that have characterized the atmospheric consequences of $C(O)Cl_2$ and $C(O)Br_2$. In the case of $C(O)F_2$, its photochemical oxidation is well known to produce $FC(O)O_x$ species,[56] because the FCO radical, which results from breaking the CF bond in $C(O)F_2$, is quite stable as noted above. With the information calculated above for ClCO and BrCO, we can address the issue of the atmospheric fate of the ClCO and BrCO radicals, especially with respect to reactions in the stratosphere. Specifically, are these radicals sufficiently stable to allow reaction with molecular oxygen to dominate, thereby leading to the formation $XC(O)O_x$ species analogous to the fluorine analogues? Photodissociation of CCl_2O into ClCO and Cl is known to take place with unit quantum yield with wavelengths ≤184.9 nm.[57] It is assumed that the C−Cl bond cleavage is the primary photolytic route.[57] The energy of the 184.9 nm photon is about 154 kcal/mol, and the present calculations suggest that the dissociation limit for breaking the C−Cl bond is 75.7 ± 1 kcal/mol; together this leads to 78.3 kcal/mol excess energy remaining in the ClCO fragment. The ClCO binding energy is only 5.9 kcal/mol. Since the excess energy in the ClCO fragment exceeds the C−Cl bond dissociation energy by more than 70 kcal/mol, it is unlikely that the ClCO fragment would live long enough to participate in bimolecular reactions with O_2 or NO. Similarly, $C(O)Br_2$ has a broad-feature UV absorption band starting at 320 nm.[58] The energy of the 320 nm photon is 89.3 kcal/mol, and the endothermicity of the dissociation reaction of $C(O)Br_2 \rightarrow BrCO + Br$ is 51.6 kcal/mol; together this leads to 37.7 kcal/mol of excess energy remaining in the BrCO fragment, which is only bound by <1 kcal/mol. The BrCO fragment is even less likely than ClCO to survive long enough to be involved in other atmospheric reactions. The present work thus leads to an interesting conclusion regarding the atmospheric oxidation of $C(O)Cl_2$ and $C(O)Br_2$. Photolysis of these compounds in the stratosphere leads to the formation of CO and the release of either two chlorine atoms or two bromine atoms, which could participate in catalytic ozone destruction cycles.

Conclusion

Very high level ab initio molecular orbital theory has been used to predict the geometries, vibrational spectra, and heats of formation at 0 K for ClCO, Cl_2CO, BrCO, and Br_2CO. The calculations are able to accurately predict the heats of formation of Cl_2CO and Br_2CO using the method described above based on extrapolating CCSD(T) energies to the CBS limit and then carefully including zero point, core-valence, scalar relativistic, and spin−orbit energy corrections. The calculated value for ΔH_f(ClCO) confirms the recent value of Wine and co-workers.[50] The radical BrCO is predicted to be only weakly bound with a long quasi-linear Br−C bond length of 3.09 Å, and a Br−CO binding energy of only 0.3 kcal/mol when both molecular and atomic spin−orbit coupling effects are included; thus, this species is very weakly bound. The calculated results suggest that photolysis of $C(O)Cl_2$ and $C(O)Br_2$ in the stratosphere will lead quickly to the formation of CO and the release of either two chlorine atoms or two bromine atoms. The released halogen atoms are then able to participate in catalytic ozone destruction cycles.

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