

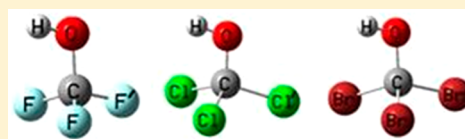
# Computational Study on Thermochemical Properties for Perhalogenated Methanols (CX<sub>3</sub>OH) (X = F, Cl, Br)

Ahmad I. Alrawashdeh\* and Raymond A. Poirier\*

Chemistry Department, Memorial University, Prince Phillip Drive, St. John's, Newfoundland A1B 3X7, Canada

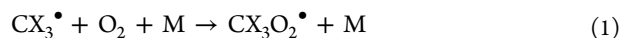
**S** Supporting Information

**ABSTRACT:** The perhalogenated methanols (CX<sub>3</sub>OH; X = F, Cl, and Br) are found in the atmosphere as products of the degradation of halocarbons. The thermochemical properties for these molecules have been calculated at the HF, MP2, and B3LYP levels of theories in conjunction with six different basis sets as well as at G3MP2 and CBS-QB3. Calculated properties include the gas-phase enthalpies of formation ( $\Delta_f H^0$ ), gas-phase acidities ( $\Delta_{\text{acid}} G^0$ ), gas-phase proton affinity, and bond dissociation energies of the C–O and O–H bonds of CX<sub>3</sub>OH. Excellent agreement is found between the results obtained using G3MP2 and CBS-QB3 methods and the available experimental data. The results obtained using MP2 are more consistent with the experimental, G3MP2, and CBS-QB3 values than those computed at B3LYP. In general, the 6-311+G(d,p) basis set when combined with the HF or MP2 level of theory produced better results than other basis sets considered in this study.

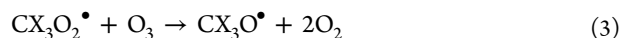
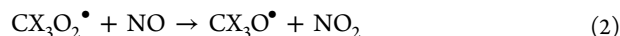


## 1. INTRODUCTION

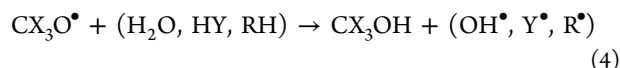
Chlorofluorocarbons (CFCs), halons, and related chemicals cause significant environmental impacts including deplete stratospheric ozone, produce noxious degradation products, and contribute to climate change as greenhouse gases.<sup>1,2</sup> Halons are important fire-extinguishing chemicals that are related to CFCs but contain the element bromine rather than chlorine.<sup>1</sup> With their large-scale use, an assessment of the atmospheric chemistry and hence environmental impact of CFCs and halons is needed.<sup>2,3</sup> The perhalogenated methyl radicals CF<sub>3</sub>•, CCl<sub>3</sub>•, and CBr<sub>3</sub>• occur in the atmosphere as intermediates in the degradation of CFCs and halons.<sup>4</sup> In an oxygen-rich atmosphere these radicals are converted into the corresponding methylperoxy structures CX<sub>3</sub>O<sub>2</sub>• (X = F, Cl, and Br).<sup>5,6</sup>



The CX<sub>3</sub>O<sub>2</sub>• then reacts with NO or O<sub>3</sub> generating trifluoro-, trichloro-, and tribromo-methoxy CX<sub>3</sub>O• radicals.<sup>5–7</sup>



While the processes that produce CX<sub>3</sub>O• are well-established, the subsequent fate of these radicals in the atmosphere is considerably less understood.<sup>2,5,7</sup> Laboratory kinetic studies suggest that the loss of CX<sub>3</sub>O• radicals in the lower atmosphere is related to hydrogen abstraction reactions from suitable donors, such as H<sub>2</sub>O, hydrogen halides (HY), or hydrocarbons (RH), leading to the formation of the perhalogenated methanols<sup>4</sup>



where X, Y = F, Cl, or Br.<sup>1,3</sup> The CX<sub>3</sub>OH alcohols are an interesting class of halocarbons due to their ability to act as a halogen reservoir. For this reason, these compounds have become the subject of several experimental and theoretical investigations.<sup>4–14</sup>

Understanding the thermochemical properties of these halocarbons is of fundamental importance in atmospheric chemistry. The determination of accurate enthalpies of formation and Gibbs energy of formation and other thermochemical properties of the species, implicated in ozone depletion, is essential in determining the concentration of these molecules in the stratosphere.<sup>15</sup> Estimates of the enthalpies of formation, proton affinities, gas-phase acidities, and other thermochemical properties of CF<sub>3</sub>OH, along with several other trifluoromethyl species, are available and have been used extensively in discussions of the decomposition of hydrofluorocarbons (HFCs) in the atmosphere.<sup>6–11,16,17</sup> Few studies of the thermochemical properties of CCl<sub>3</sub>OH and CBr<sub>3</sub>OH are available.<sup>18</sup> Several experiments have shown that the kinetics and mechanisms of the decomposition of CCl<sub>3</sub>OH and CBr<sub>3</sub>OH are very similar to those of CF<sub>3</sub>OH.<sup>4,7</sup>

Batt and Walsh<sup>19</sup> as well as Benson<sup>14</sup> used the group additivity approach to estimate the enthalpy of formation ( $\Delta_f H^0$ ) of CF<sub>3</sub>OH and other fluorocarbon compounds. They obtained values of  $\Delta_f H^0(\text{CF}_3\text{OH}) = -893.3 \pm 8.4$  and  $-899.6 \pm 4.2$  kJ mol<sup>–1</sup>, respectively, while Schneider and Wallington obtained a value of  $-910.9 \pm 8.4$  kJ mol<sup>–1</sup> using ab initio methods.<sup>17</sup> Montgomery et al.<sup>20</sup> and Sana et al.<sup>21</sup> also computed the  $\Delta_f H^0$  of CF<sub>3</sub>OH using ab initio methods. They found values of  $-910.9$  and  $-909.6$  kJ mol<sup>–1</sup>, respectively.

**Received:** February 5, 2015

**Revised:** March 20, 2015

**Published:** March 23, 2015

Hence, ab initio and group additivity calculations disagree by as much as 18 kJ mol<sup>-1</sup>. The ab initio values are, however, closer to the experimental value of  $-908.8 \pm 3.8$  kJ mol<sup>-1</sup> determined by Asher and coworkers<sup>11</sup> using photoionization mass spectrometry. Chyall et al.<sup>5</sup> used translational energy threshold measurements for reactions involving of CF<sub>3</sub>OH<sub>2</sub><sup>+</sup> to compute  $\Delta_f H^0(\text{CF}_3\text{OH}) = -923.4 \pm 13.4$  kJ mol<sup>-1</sup>. This experimental value is slightly lower than the ab initio and group additivity values. They also used the same technique to obtain a value of  $-632.2 \pm 7.1$  kJ mol<sup>-1</sup> for the gas-phase proton affinity (PA) of CF<sub>3</sub>OH.

The gas-phase acidity ( $\Delta_{\text{acid}} G^0$ ) of CF<sub>3</sub>OH was measured by Huey and coworkers<sup>8</sup> to be  $-1351.4 \pm 6.7$  kJ mol<sup>-1</sup>. They used the flowing afterglow technique to evaluate the thermochemistry of CF<sub>3</sub>OH and related compounds. Segovia and Ventura<sup>22</sup> computed  $\Delta_{\text{acid}} H^0 = -1376$  kJ mol<sup>-1</sup> for CF<sub>3</sub>OH using density functional theory (B3LYP and B3PW91).

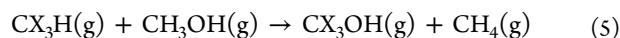
The (CF<sub>3</sub>O–H) and (CF<sub>3</sub>–OH) bond dissociation energies (BDEs) were first determined by Batt and Walsh<sup>19</sup> to be 456.1 and 486.2 kJ mol<sup>-1</sup>, respectively, using a combination of experimental data. Kim and Son<sup>23</sup> predicted these BDEs to be 500.0 and 477.4 kJ mol<sup>-1</sup>, respectively, at the CCSD/TZP level of theory. Using photoionization mass spectrometry, Asher and coworkers<sup>11</sup> obtained BDEs for CF<sub>3</sub>O–H and CF<sub>3</sub>–OH of  $491.6 \pm 7.9$  and  $482.0 \pm 1.3$  kJ mol<sup>-1</sup>, respectively. Schneider and coworkers<sup>24</sup> obtained BDEs of 495.0 and 402.9 kJ mol<sup>-1</sup>, respectively, at the MP2/6-31G(d,p) level of theory. Kim and Son<sup>23</sup> found that BDEs of the (CX<sub>n</sub>H<sub>3–n</sub>O–H) and (CX<sub>n</sub>H<sub>3–n</sub>–OH) {X = F, Cl or Br} increase with the degree of halogenation (*n*). This increase is not a linear function of *n*, with fluorine substituents having the greatest effect and bromine substituents having a lowest effect.

In this study, the thermochemical properties of CF<sub>3</sub>OH, CCl<sub>3</sub>OH, and CBr<sub>3</sub>OH are investigated with both wave function and density functional theories. Computed thermochemical properties include the enthalpies of formation, gas-phase acidity, the PA, and dissociation energies of the C–O and O–H bonds. The primary aims of the present computational investigation are to provide computed thermochemical properties of the perhalogenated methanols and to investigate how well modern electronic structure techniques are able to reproduce the available experimental data.

## 2. COMPUTATIONAL DETAILS

All calculations were performed with Gaussian 09.<sup>25</sup> Full geometry optimizations of all species considered were achieved at the HF, MP2, and B3LYP level of theory (unrestricted for open shells) using the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), and 6-311++G(df,p) basis sets as well as at the G3MP2 and CBS-QB3 levels of theory. Frequency calculations ensured that the minima had no imaginary frequencies.

Enthalpies of formation for the three perhalogenated methanols,  $\Delta_f H^0(\text{CX}_3\text{OH})$  at 298.15 K were calculated using the following gas-phase isodesmic reaction



where X = F, Cl, or Br. The gas-phase enthalpy of formation for the perhalogenated methanols,  $\Delta_f H^0(\text{CX}_3\text{OH})$ , is determined from the calculated enthalpy of reaction 5,  $\Delta_{\text{rxn}} H^0$ , and the known enthalpies of formation of the other species involved in the reaction using eq 6

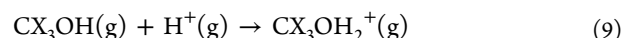
$$\begin{aligned} \Delta_f H^0(\text{CX}_3\text{OH}) &= \Delta_{\text{rxn}} H^0 - \Delta_f H^0(\text{CH}_4) \\ &\quad + \Delta_f H^0(\text{CH}_3\text{OH}) + \Delta_f H^0(\text{CX}_3\text{H}) \end{aligned} \quad (6)$$

The gas-phase acidities for perhalogenated methanols,  $\Delta_{\text{acid}} G^0(\text{CX}_3\text{OH})$ , at 298.15 K were evaluated as the Gibbs energy of reaction 7 according to eq 8



$$\begin{aligned} \Delta_{\text{acid}} G^0(\text{CX}_3\text{OH}) &= \Delta G^0(\text{H}^+) + \Delta G^0(\text{CX}_3\text{O}^-) \\ &\quad - \Delta G^0(\text{CX}_3\text{OH}) \end{aligned} \quad (8)$$

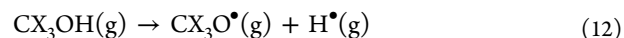
The gas-phase PAs for perhalogenated methanols, PA(CX<sub>3</sub>OH), at 298.15 K were evaluated as the negative enthalpy of reaction 9 using eq 10



$$\begin{aligned} \text{PA}(\text{CX}_3\text{OH}) &= \Delta H^0(\text{CX}_3\text{OH}) + \Delta H^0(\text{H}^+) \\ &\quad - \Delta H^0(\text{CX}_3\text{OH}_2^+) \end{aligned} \quad (10)$$

where the gas-phase  $\Delta G^0(\text{H}^+)$  and  $\Delta H^0(\text{H}^+)$  are  $-26.28$  and  $6.19$  kJ mol<sup>-1</sup> at 298.15 K, respectively.<sup>26,27</sup>

The C–O and O–H BDEs of the perhalogenated methanols at 298.15 K were computed as the enthalpy change of reactions 11 and 12 using eqs 13 and 14, respectively



$$\begin{aligned} \text{BDE}(\text{C–O}) &= \Delta H^0(\text{CX}_3^\bullet) + \Delta H^0(\text{OH}^\bullet) \\ &\quad - \Delta H^0(\text{CX}_3\text{OH}) \end{aligned} \quad (13)$$

$$\begin{aligned} \text{BDE}(\text{O–H}) &= \Delta H^0(\text{CX}_3\text{O}^\bullet) + \Delta H^0(\text{H}^\bullet) \\ &\quad - \Delta H^0(\text{CX}_3\text{OH}) \end{aligned} \quad (14)$$

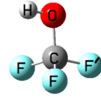
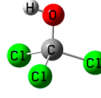

## 3. RESULTS AND DISCUSSION

The HF, MP2, and B3LYP optimized structures for CF<sub>3</sub>OH, CCl<sub>3</sub>OH, and CBr<sub>3</sub>OH are shown in Table 1. The results for the enthalpies of formation ( $\Delta_f H^0$ ), gas-phase acidities ( $\Delta_{\text{acid}} G^0$ ), gas-phase PAs, and the C–O and O–H BDEs of the three perhalogenated methanols at different levels of theory are given in Tables 2–6.

**3.1. Geometries.** The key structural parameters corresponding to the optimized structures of the CX<sub>3</sub>OH molecules at various levels of theory with the 6-31G(d) and 6-311++G(df,p) basis sets are presented in Table 1. The three molecules are found to have a staggered conformation of C<sub>s</sub> symmetry, confirming previous experimental<sup>28,29</sup> and theoretical<sup>30,31</sup> investigations. In general, for the three molecules, bond lengths decrease with increasing basis set size at the HF, MP2, and B3LYP levels of theory, while bond angles do not vary significantly. Electron correlation lengthens bond lengths in going from HF to MP2 and B3LYP but does not have any significant effect on bond angles except for the COH bond angle. In CX<sub>3</sub>OH there is one short and two equal longer C–X bonds at all levels of theory and basis sets. This is due to the Jahn–Teller effect (or distortion).<sup>32</sup>

**3.2. Gas-Phase Enthalpies of Formation.** The enthalpies of formation for perhalogenated methanols at different levels of

**Table 1.** Optimized Structural Parameters for CF<sub>3</sub>OH, CCl<sub>3</sub>OH, and CBr<sub>3</sub>OH<sup>a</sup>

Molecule	Parameter	6-31G(d)			6-311++G(df,p)		
		HF	MP2	B3LYP	HF	MP2	B3LYP
	$r(\text{CF})$	1.320	1.352	1.351	1.313	1.334	1.348
	$r(\text{CF}')$	1.305	1.332	1.331	1.297	1.315	1.326
	$r(\text{CO})$	1.331	1.356	1.352	1.328	1.344	1.345
	$r(\text{OH})$	0.949	0.974	0.971	0.943	0.962	0.965
	$\angle(\text{FCF})$	108.7	108.8	108.8	108.6	108.7	108.5
	$\angle(\text{FCF}')$	106.7	106.4	106.5	106.7	106.6	106.4
	$\angle(\text{OCF})$	111.9	112.2	112.2	111.9	112.2	112.3
	$\angle(\text{COH})$	110.3	108.2	108.6	110.8	108.3	109.8
	$r(\text{CCl})$	1.784	1.791	1.825	1.786	1.781	1.822
	$r(\text{CCl}')$	1.759	1.760	1.782	1.759	1.752	1.780
	$r(\text{CO})$	1.346	1.368	1.353	1.339	1.358	1.349
	$r(\text{OH})$	0.952	0.978	0.975	0.944	0.964	0.967
	$\angle(\text{ClCCl})$	109.9	110.1	109.8	109.8	110.1	109.7
	$\angle(\text{ClCCl}')$	108.4	108.1	107.5	108.1	108.1	107.5
	$\angle(\text{OCCl})$	110.7	111.1	111.3	111.0	111.1	111.3
	$\angle(\text{COH})$	110.3	108.2	108.8	110.9	108.3	109.9
	$r(\text{CBr})$	1.955	1.977	1.996	1.956	1.957	1.998
	$r(\text{CBr}')$	1.925	1.937	1.948	1.926	1.923	1.949
	$r(\text{CO})$	1.343	1.371	1.350	1.340	1.357	1.346
	$r(\text{OH})$	0.952	0.980	0.976	0.945	0.966	0.968
	$\angle(\text{BrCBr})$	109.7	109.7	109.5	109.9	110.0	109.9
	$\angle(\text{BrCBr}')$	108.2	107.5	107.2	108.4	107.9	107.5
	$\angle(\text{OCBr})$	110.9	111.5	111.5	111.1	111.2	111.3
	$\angle(\text{COH})$	110.2	108.0	108.7	110.8	108.3	110.3

<sup>a</sup>Bond lengths ( $r$ ) in angstroms and angles ( $\angle$ ) in degrees.

theory and basis sets as well as the experimental value for CF<sub>3</sub>OH are listed in Table 2. The  $\Delta_f H^0$  for the three molecules were obtained using isodesmic (which should lead to cancelation of errors) reactions (eq 5) in combination with the experimental  $\Delta_f H^0$  of CH<sub>3</sub>OH, CH<sub>4</sub>, CF<sub>3</sub>H, CCl<sub>3</sub>H, and CBr<sub>3</sub>H.<sup>33</sup> Asher and coworkers<sup>11</sup> obtained a value of  $-908.8 \pm 3.8$  kJ mol<sup>-1</sup> for  $\Delta_f H^0$  of CF<sub>3</sub>OH using photoionization mass spectrometry. The  $\Delta_f H^0(\text{CF}_3\text{OH})$  computed at G3MP2, CBS-QB3, HF/6-311+G(d,p), HF/6-311++G(d,p), MP2/6-311+G(d,p), and MP2/6-311++G(d,p) are in excellent agreement with the experimental value of Asher and coworkers,<sup>11</sup> differing by no more than 1 kJ mol<sup>-1</sup> (Table 2). The calculated  $\Delta_f H^0$  for CF<sub>3</sub>OH at B3LYP with diffuse basis functions is in good agreement with the experimental value differing by no more than 8 kJ mol<sup>-1</sup> (Table 2).

There is no experimental data for the  $\Delta_f H^0$  (and the other properties investigated in this study) for CCl<sub>3</sub>OH and CBr<sub>3</sub>OH. Therefore, it was difficult to test the accuracy of the  $\Delta_f H^0$  results for these compounds. It is well known that the use of composite methods usually leads to accurate energetics, especially for reactions involving small molecular systems, with

an error that does not usually exceed 6 kJ mol<sup>-1</sup>.<sup>34</sup> Hence, the accuracy of the HF, MP2, and B3LYP results is tested by comparing the calculated  $\Delta_f H^0$  values for CCl<sub>3</sub>OH and CBr<sub>3</sub>OH at these levels of theory with the G3MP2 and CBS-QB3 values.

The addition of diffuse functions on the heavy atoms is found to play an important role in the accuracy of the  $\Delta_f H^0$  computed at HF, MP2, and B3LYP levels of theory (Table 2). There is no effect of adding diffuse functions or p-type polarization functions on hydrogen on the  $\Delta_f H^0$  for these three molecules. As shown in Table 2, the  $\Delta_f H^0$  values obtained with 6-311+G(d,p) and 6-311++G(d,p) are identical, and those obtained using 6-31G(d) and 6-31G(d,p) are almost the same. The largest deviations from experiment in the G3MP2 and CBS-QB3  $\Delta_f H^0$  for the three molecules were at B3LYP and for basis sets without diffuse functions (Table 2). According to these results, it is hard to determine which of the methods was the most accurate; however, HF and MP2 with the 6-311+G(d,p) and 6-311++G(d,p) basis sets led to the best results.

**3.3. Gas-Phase Acidity.** The gas-phase acidities ( $\Delta_{\text{acid}} G^0$ ) of perhalogenated methanols at different levels of theory and basis sets as well as the experimental value for CF<sub>3</sub>OH are listed in Table 3. The calculated  $\Delta_{\text{acid}} G^0$  for CF<sub>3</sub>OH at G3MP2 and CBS-QB3 levels of theory are in excellent agreement with the experimental value of  $1351.4 \pm 6.7$  kJ mol<sup>-1</sup> determined by Huey and coworkers,<sup>8</sup> and both values are within the experimental error. As can be seen from the results in Table 3, there is a significant improvement in the calculated acidities at HF and MP2 levels in going from the 6-31G(d,p) to the 6-311+G(d,p) basis set. This reflects the importance of diffuse functions in properly treating anions. Adding diffuse functions on hydrogen has a negligible effect.

The acidities of the three molecules computed at MP2 using basis sets with diffuse functions are in reasonable agreement with the G3MP2 and CBS-QB3 values and differ by no more than 16 kJ mol<sup>-1</sup> (Table 3). B3LYP when combined with basis sets with diffuse functions leads to results that are less accurate compared with those obtained using basis sets without diffuse functions. The  $\Delta_{\text{acid}} G^0$  of CF<sub>3</sub>OH obtained at B3LYP using basis sets with diffuse functions is as much 39 kJ mol<sup>-1</sup> too low compared with experiment, while the  $\Delta_{\text{acid}} G^0$  for CCl<sub>3</sub>OH and CBr<sub>3</sub>OH differ from the G3MP2 and CBS-QB3 values by as much as 47 kJ mol<sup>-1</sup>. The best  $\Delta_{\text{acid}} G^0$  evaluated by B3LYP are 1367 kJ mol<sup>-1</sup> with 6-311G(d,p) for CF<sub>3</sub>OH and 1260 and 1238 kJ mol<sup>-1</sup> for CCl<sub>3</sub>OH and CBr<sub>3</sub>OH, respectively, using 6-31G(d,p), as shown in Table 3.

**Table 2.** Gas-Phase Enthalpies of Formation ( $\Delta_f H^0$ ) for CF<sub>3</sub>OH, CCl<sub>3</sub>OH, and CBr<sub>3</sub>OH in kJ mol<sup>-1</sup> at 298.15 K

	CF <sub>3</sub> OH			CCl <sub>3</sub> OH			CBr <sub>3</sub> OH <sup>a</sup>		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
6-31G(d)	-927	-929	-922	-264	-289	-279	-102	-128	-124
6-31G(d,p)	-927	-929	-923	-266	-288	-280	-102	-127	-124
6-311G(d,p)	-920	-924	-918	-262	-284	-278	-90	-117	-114
6-311+G(d,p)	-908	-909	-900	-259	-282	-271	-86	-113	-105
6-311++G(d,p)	-908	-908	-900	-259	-282	-271	-86	-113	-105
6-311++G(df,p)	-913	-915	-903	-262	-271	-272	-64	-116	-106
G3MP2		-910			-279			-111	
CBS-QB3		-909			-278			-111	
experimental	$-908.8 \pm 3.8$								

<sup>a</sup>In this case, there may be a small error due to relativistic effects.<sup>36</sup>

Table 3. Gas-Phase Acidities ( $\Delta_{\text{acid}}G^0$ ) for  $\text{CF}_3\text{OH}$ ,  $\text{CCl}_3\text{OH}$ , and  $\text{CBr}_3\text{OH}$  in  $\text{kJ mol}^{-1}$  at 298.15 K

	$\text{CF}_3\text{OH}$			$\text{CCl}_3\text{OH}$			$\text{CBr}_3\text{OH}^a$		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
6-31G(d)	1398	1367	1392	1297	1263	1245	1266	1218	1223
6-31G(d,p)	1416	1396	1407	1314	1292	1260	1284	1248	1238
6-311G(d,p)	1398	1384	1367	1294	1274	1227	1263	1240	1200
6-311+G(d,p)	1366	1335	1312	1291	1266	1222	1254	1224	1188
6-311++G(d,p)	1367	1335	1313	1291	1267	1222	1254	1225	1188
6-311++G(df,p)	1375	1341	1321	1294	1275	1225	1260	1236	1194
G3MP2		1347			1269			1234	
CBS-QB3		1345			1269			1230	
experimental		1351.4 $\pm$ 6.7							

<sup>a</sup>In this case there may be a small error due to relativistic effects.<sup>36</sup>Table 4. Gas-Phase Proton Affinities (PA) for  $\text{CF}_3\text{OH}$ ,  $\text{CCl}_3\text{OH}$ , and  $\text{CBr}_3\text{OH}$  in  $\text{kJ mol}^{-1}$  at 298.15 K

	$\text{CF}_3\text{OH}$			$\text{CCl}_3\text{OH}$			$\text{CBr}_3\text{OH}^a$		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
6-31G(d)	609	617	636	646	669	675	667	669	687
6-31G(d,p)	627	641	649	662	683	688	683	693	699
6-311G(d,p)	618	634	630	660	682	690	681	696	719
6-311+G(d,p)	610	615	611	659	679	701	676	688	728
6-311++G(d,p)	610	615	611	659	679	701	676	688	728
6-311++G(df,p)	617	619	616	661	691	703	703	685	732
G3MP2		616			680			687	
CBS-QB3		614			683			691	
experimental		632.2 $\pm$ 7.1							

<sup>a</sup>In this case there may be a small error due to relativistic effects.<sup>36</sup>Table 5. (C–O) Bond Dissociation Energies (BDEs) for  $\text{CF}_3\text{OH}$ ,  $\text{CCl}_3\text{OH}$ , and  $\text{CBr}_3\text{OH}$  in  $\text{kJ mol}^{-1}$  at 298.15 K

	$\text{CF}_3\text{OH}$			$\text{CCl}_3\text{OH}$			$\text{CBr}_3\text{OH}^a$		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
6-31G(d)	335	492	464	219	400	366	218	407	339
6-31G(d,p)	337	493	466	220	401	367	220	408	372
6-311G(d,p)	333	490	459	221	401	363	201	390	352
6-311+G(d,p)	321	480	442	218	401	353	198	390	342
6-311++G(d,p)	321	480	442	218	401	353	198	390	342
6-311++G(df,p)	326	500	444	221	403	354	176	407	342
G3MP2		483			388			375	
CBS-QB3		485			390			380	
experimental		482.0 $\pm$ 1.3							

<sup>a</sup>In this case there may be a small error due to relativistic effects.<sup>36</sup>

**3.4. Gas-Phase Proton Affinities.** Table 4 reports gas-phase PAs for the perhalogenated methanols at various levels of theory and basis sets used in this study as well as the experimental value for  $\text{CF}_3\text{OH}$ . In general, the calculated PAs of  $\text{CF}_3\text{OH}$  at all levels of theory and basis sets used in this study are in reasonable agreement with the experimental value ( $632 \pm 7.1 \text{ kJ mol}^{-1}$ )<sup>5</sup> differing by no more than  $24 \text{ kJ mol}^{-1}$  (Table 4). Except for HF/6-31G(d), the PAs of  $\text{CCl}_3\text{OH}$  calculated at the HF, MP2, and B3LYP levels are all in good agreement with G3MP2 and CBS-QB3 and differ by no more than  $23 \text{ kJ mol}^{-1}$  (Table 4). The calculated PA of  $\text{CBr}_3\text{OH}$  at B3LYP using basis sets with diffuse functions differs from the PA calculated at G3MP2 and CBS-QB3 by as much as  $45 \text{ kJ mol}^{-1}$ . As shown in Table 4, B3LYP with 6-31G(d) or 6-31G(d,p) gave results in excellent agreement with the G3MP2 and CBS-QB3 values. The PA of  $\text{CBr}_3\text{OH}$  at the HF level with all basis sets (except 6-31G(d)) differs from G3MP2 and CBS-QB3 values by a

maximum of  $16 \text{ kJ mol}^{-1}$ . MP2 performed very well with all basis sets (except 6-31G(d)) for calculating the PA of  $\text{CBr}_3\text{OH}$  as well as for  $\text{CF}_3\text{OH}$ , while the PA of  $\text{CCl}_3\text{OH}$  calculated at MP2, with all basis sets used in this study, is in good agreement with the G3MP2 and CBS-QB3 values, differing by no more than  $11 \text{ kJ mol}^{-1}$  (Table 4). The addition of diffuse functions contributes very little improvement to the predicted PA values, while the addition of p-type polarization functions is important.

**3.5. Gas-Phase C–O and O–H Bond Dissociation Energies.** The C–O and O–H BDEs of the perhalogenated methanols at different levels of theory and basis sets used in this study as well as the experimental values for the  $\text{CF}_3\text{–OH}$  and  $\text{CF}_3\text{O–H}$  bonds are listed in Tables 5 and 6, respectively. The C–O and O–H BDEs of  $\text{CF}_3\text{OH}$  calculated at G3MP2 and CBS-QB3 are in excellent agreement with the experimental values. It can be seen from Tables 5 and 6 that the effect of basis set is small for the calculated values of BDE, while



Table 6. (O–H) Bond Dissociation Energies (BDEs) for CF<sub>3</sub>OH, CCl<sub>3</sub>OH, and CBr<sub>3</sub>OH in kJ mol<sup>−1</sup> at 298.15 K

	CF <sub>3</sub> OH			CCl <sub>3</sub> OH			CBr <sub>3</sub> OH <sup>a</sup>		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
6-31G(d)	328	452	456	302	425	413	295	412	386
6-31G(d,p)	346	482	471	319	454	427	313	442	407
6-311G(d,p)	346	488	474	319	461	427	309	444	406
6-311+G(d,p)	347	493	478	320	463	427	310	447	407
6-311++G(d,p)	348	493	478	320	464	427	310	448	407
6-311++G(df,p)	347	499	478	322	454	427	286	453	406
G3MP2		497			457			436	
CBS-QB3		498			461			440	
experimental		491.6 ± 7.9							

<sup>a</sup>In this case there may be a small error due to relativistic effects.<sup>36</sup>

electron correlation plays an essential role. For this reason, HF performs very poorly in describing BDEs. At HF the BDEs of CF<sub>3</sub>OH differ from experiment by as much as 164 kJ mol<sup>−1</sup>. MP2 BDEs are in good agreement with the G3MP2 and CBS-QB3 values for all three molecules. For CF<sub>3</sub>OH, MP2 when combined with 6-311G(d,p), 6-311+G(d,p), and 6-311++G(d,p) basis sets gives results that are close to the experimental value, differing by <8 kJ mol<sup>−1</sup>. For CBr<sub>3</sub>OH, MP2 when paired with the same three basis sets produces results that differ by no more than 15 and 10 kJ mol<sup>−1</sup> from the G3MP2 and CBS-QB3 results, respectively, while for CCl<sub>3</sub>OH, MP2 BDEs differ by less than 15 and 13 kJ mol<sup>−1</sup> from the G3MP2 and CBS-QB3 results, respectively, with all basis sets used in this study (except 6-31G(d)). In general, B3LYP performs poorly for calculating BDEs of perhalogenated methanols; see Tables 5 and 6. The CX<sub>3</sub>–OH and CX<sub>3</sub>O–H bond strengths decrease from X = F to X = Br. This has been attributed to a decrease in ionic character of these bonds.<sup>35</sup>

#### 4. CONCLUSIONS

Thermochemical properties ( $\Delta_f H^0$ ,  $\Delta_{\text{acid}} G^0$ , PA, and BDE) of perhalogenated methanols (CF<sub>3</sub>OH, CCl<sub>3</sub>OH, and CBr<sub>3</sub>OH) have been calculated at HF, MP2, and B3LYP levels of theory using six different basis sets as well as at G3MP2 and CBS-QB3. The three molecules are predicted to have staggered conformations with C<sub>s</sub> symmetry. The thermochemical properties (except PA) for CF<sub>3</sub>OH evaluated using G3MP2 and CBS-QB3 theories are in excellent agreement with experimental values differing by no more than 4 and 6 kJ mol<sup>−1</sup>, respectively. The choice of the basis set plays a significant role in calculating thermochemical properties of perhalogenated methanols. The MP2 level combined with the 6-311+G(d,p) basis set provided results that in good agreement with experimental, G3MP2, and CBS-QB3 values. The addition of diffuse functions on hydrogen to the 6-311+G(d,p) basis set has no effect on the computed properties. B3LYP performed poorly (especially when combined with basis sets containing diffuse functions) in calculating the thermochemical properties of these molecules. This study indicates that the order of acidity for the perhalogenated methanols is CBr<sub>3</sub>OH > CCl<sub>3</sub>OH > CF<sub>3</sub>OH, which corresponds to the reverse order of the CX<sub>3</sub>O–H bond strength: CBr<sub>3</sub>O–H < CCl<sub>3</sub>O–H < CF<sub>3</sub>O–H.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Full geometries and energies of all structures at all levels of theory discussed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

##### Corresponding Authors

\*R.A.P.: E-mail: [rpoirier@mun.ca](mailto:rpoirier@mun.ca).

\*A.I.A.: E-mail: [aia638@mun.ca](mailto:aia638@mun.ca).

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

We acknowledge Compute Canada and the Atlantic Computational Excellence Network (ACEnet) for computer time. We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. A.I.A. acknowledges the AlHussein Bin Talal University for his Ph.D. fellowship.

#### ■ REFERENCES

- (1) Hill, M. K. *Understanding Environmental Pollution*; Cambridge University Press, New York, 2004.
- (2) Wallington, T. J.; Schneider, W. F.; Worsnop, D. R.; Nielsen, O. J.; Sehested, J.; Debruyne, W. J.; Shorter, J. A. The Environmental Impact of CFC Replacements HFCs and HCFCs. *Environ. Sci. Technol.* **1994**, *28*, 320A–326A.
- (3) Wallington, T. J.; Hurley, M. D.; Nielsen, O. J.; Sulbaek Andersen, M. P. Atmospheric Chemistry of CF<sub>3</sub>CFHCF<sub>2</sub>OCF<sub>3</sub> and CF<sub>3</sub>CFHCF<sub>2</sub>OCF<sub>2</sub>H: Reaction with Cl Atoms and OH Radicals, Degradation Mechanism, and Global Warming Potentials. *J. Phys. Chem. A* **2004**, *108*, 11333–11338.
- (4) Brudnik, K.; Jodkowski, J. T.; Sarzyński, D.; Nowek, A. Mechanism of the Gas-Phase Decomposition of Trifluoro-, Trichloro-, and Tribromomethanols in the Presence of Hydrogen Halides. *J. Mol. Model.* **2011**, *17*, 2395–2409.
- (5) Chyall, L. J.; Squires, R. R. The Proton Affinity and Absolute Heat of Formation of Trifluoromethanol. *J. Phys. Chem.* **1996**, *100*, 16435–16440.
- (6) Barone, S. B.; Turnipseed, A. A.; Ravishankara, A. R. Kinetics of the Reactions of the CF<sub>3</sub>O Radical with Alkanes. *J. Phys. Chem.* **1994**, *98*, 4602–4608.
- (7) Brudnik, K.; Wójcik-Pastuszka, D.; Jodkowski, J. T.; Leszczynski, J. Theoretical Study of the Kinetics and Mechanism of the Decomposition of Trifluoromethanol, Trichloromethanol, and Tribromomethanol in the Gas Phase. *J. Mol. Model.* **2008**, *14*, 1159–1172.
- (8) Huey, L. G.; Dunlea, E. J.; Howard, C. J. Gas-Phase Acidity of CF<sub>3</sub>OH. *J. Phys. Chem.* **1996**, *100*, 6504–6508.

- (9) Wallington, T. J.; Hurley, M. D.; Schneider, W. F.; Sehested, J.; Nielsen, O. J. Atmospheric Chemistry of Trifluoromethoxy Radicals: Reaction with Water. *J. Phys. Chem.* **1993**, *97*, 7606–7611.
- (10) Wallington, T. J.; Schneider, W. F. The Stratospheric Fate of  $\text{CF}_3\text{OH}$ . *Environ. Sci. Technol.* **1994**, *28*, 1198–1200.
- (11) Asher, R. L.; Appelman, E. H.; Tilson, J. L.; Litorja, M.; Berkowitz, J.; Ruscic, B. A Photoionization Study of Trifluoromethanol,  $\text{CF}_3\text{OH}$ , Trifluoromethyl Hypofluorite,  $\text{CF}_3\text{OF}$ , and Trifluoromethyl Hypochlorite,  $\text{CF}_3\text{OCl}$ . *J. Chem. Phys.* **1997**, *106*, 9111–9121.
- (12) Turnipseed, A. A.; Barone, S. B.; Jensen, N. R.; Hanson, D. R.; Howard, C. J.; Ravishankara, A. R. Kinetics of the Reactions of  $\text{CF}_3\text{O}$  Radicals with CO and  $\text{H}_2\text{O}$ . *J. Phys. Chem.* **1995**, *99*, 6000–6009.
- (13) Schneider, W. F.; Wallington, T. J.; Huie, R. E. Energetics and Mechanism of Decomposition of  $\text{CF}_3\text{OH}$ . *J. Phys. Chem.* **1996**, *100*, 6097–6103.
- (14) Benson, S. W. Thermochemistry of  $\text{CF}_3\text{O}$  Radical and  $\text{CF}_3\text{OH}$ . *J. Phys. Chem.* **1994**, *98*, 2216–2216.
- (15) Abramowitz, S.; Chase, M. W. Thermodynamic Properties of Gas Phase Species of Importance to Ozone Depletion. *Pure Appl. Chem.* **1991**, *63*, 1449–1454.
- (16) Schneider, W.; Wallington, T. Thermochemistry of  $\text{COF}_2$  and Related Compounds. *J. Phys. Chem.* **1994**, *98*, 7448–7451.
- (17) Schneider, W. F.; Wallington, T. J. Ab Initio Investigation of the Heats of Formation of Several Trifluoromethyl Compounds. *J. Phys. Chem.* **1993**, *97*, 12783–12788.
- (18) Wallington, T.; Schneider, W.; Barnes, I.; Becker, K.; Sehested, J.; Nielsen, O. Stability and Infrared Spectra of Mono-, Di-, and Trichloromethanol. *Chem. Phys. Lett.* **2000**, *322*, 97–102.
- (19) (a) Batt, L.; Walsh, R. A Reexamination of the Pyrolysis of Bis Trifluoromethyl Peroxide. *Int. J. Chem. Kinet.* **1982**, *14*, 933–944. (b) Batt, L.; Walsh, R. A Reexamination of the Pyrolysis of Bis Trifluoromethyl Peroxide. Addendum: Concerning  $\text{D}(\text{CF}_3\text{O}_2\text{--CF}_3)$  and  $\text{D}(\text{CF}_3\text{--O}_2)$ . *Int. J. Chem. Kinet.* **1983**, *15*, 605–607.
- (20) Montgomery, J. A.; Michels, H. H.; Francisco, J. S. Ab Initio Calculation of the Heats of Formation of  $\text{CF}_3\text{OH}$  and  $\text{CF}_2\text{O}$ . *Chem. Phys. Lett.* **1994**, *220*, 391–396.
- (21) Sana, M.; Leroy, G.; Peeters, D.; Wilante, C. The Theoretical Study of the Heats of Formation of Organic Compounds Containing the Substituents  $\text{CH}_3$ ,  $\text{CF}_3$ ,  $\text{NH}_2$ ,  $\text{NF}_2$ ,  $\text{NO}_2$ , OH and F. *J. Mol. Struct.: THEOCHEM* **1988**, *164*, 249–274.
- (22) Segovia, M.; Ventura, O. N. Density Functional and G2 Study of the Strength of the OH Bond in  $\text{CF}_3\text{OH}$ . *Chem. Phys. Lett.* **1997**, *277*, 490–496.
- (23) Kim, S. J.; Son, H. S. Ab Initio Quantum Mechanical Study for the Photolysis and Unimolecular Decomposition Reactions in the Atmosphere of  $\text{CF}_3\text{OH}$ . *Bull. Korean Chem. Soc.* **1999**, *20*, 1493–1500.
- (24) Schneider, W. F.; Nance, B. I.; Wallington, T. J. Bond Strength Trends in Halogenated Methanols: Evidence for Negative Hyperconjugation? *J. Am. Chem. Soc.* **1995**, *117*, 478–485.
- (25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- (26) Uddin, K. M.; Warburton, P. L.; Poirier, R. A. Comparisons of Computational and Experimental Thermochemical Properties of  $\alpha$ -Amino Acids. *J. Phys. Chem. B* **2012**, *116*, 3220–3234.
- (27) Vessecchi, R.; Galembeck, S. E. Evaluation of the Enthalpy of Formation, Proton Affinity, and Gas-Phase Basicity of Gamma-Butyrolactone and 2-Pyrrolidinone by Isodesmic Reactions. *J. Phys. Chem. A* **2008**, *112*, 4060–4066.
- (28) Diodati, F. P.; Bartell, L. S. Electron Diffraction Study of the Molecular Structure of Trifluoromethyl Hypofluorite. *J. Mol. Struct.* **1971**, *8*, 395–400.
- (29) Buckley, P.; Weber, J. P. The Microwave Spectrum of Trifluoromethyl Hypofluorite. *Can. J. Chem.* **1974**, *52*, 942–945.
- (30) Kwon, O.; Kwon, Y. Theoretical Molecular Structures for Trifluoromethyl Hypohalites,  $\text{CF}_3\text{OX}$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}$ ): Ab Initio and DFT Calculations. *J. Mol. Struct.: THEOCHEM* **1999**, *489*, 119–130.
- (31) Fernández, L. E.; Varetti, E. L. A Theoretical Study of the Vibrational Properties of Trifluoromethanol and the Trifluoromethyl Hypohalites,  $\text{CF}_3\text{OX}$  ( $\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}$ ). *J. Mol. Struct.: THEOCHEM* **2003**, *629*, 175–183.
- (32) Wang, J.; Boyd, R. J. The First-Order Jahn–Teller Distortion and the Symmetry of the Electron Density in the  $\text{BH}_3^+$  Radical. *J. Chem. Phys.* **1992**, *96*, 1232–1239.
- (33) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. Assessment of Gaussian-2 and Density Functional Theories for the Computation of Enthalpies of Formation. *J. Chem. Phys.* **1997**, *106*, 1063–1079.
- (34) Mandal, D.; Mondal, B.; Das, A. K. The Association Reaction between  $\text{C}_2\text{H}$  and 1-Butyne: A Computational Chemical Kinetics Study. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4583–4595.
- (35) Wiberg, K. B.; Rablen, P. R. Substituent Effects. 5. Vinyl and Ethynyl Derivatives. An Examination of the Interaction of Amino and Hydroxy Groups with Carbon-Carbon Double and Triple Bonds. *J. Am. Chem. Soc.* **1993**, *115*, 9234–9242.
- (36) Martin, J. M. L.; Taylor, P. R. A Definitive Heat of Vaporization of Silicon through Benchmark ab Initio Calculations on  $\text{SiF}_4$ . *J. Phys. Chem. A* **1999**, *103*, 4427–4431.