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A Density Functional Study of the Structures and Energetics of CXBrO where X = H, Cl, and Br

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The geometries, vibrational spectra, and relative energetics of CXBrO have been examined using density functional theory. The results show interesting structural trends for the bromination of formaldehyde. The thermodynamically most stable species is found to be CClBrO, with an estimated heat of formation of −38.2 kcal mol^{-1} at 298 K. The least stable CXBrO species is CBr_2O with a heat of formation of −25.8 kcal mol^{-1} at 298 K. The heat of formation of CBr_2O is in excellent agreement with experiments which determine the value from third-law kinetic studies.

I. Introduction

The release of bromine-containing organic compounds into the atmosphere has been suggested to be a source of atmospheric bromine which participates in ozone destruction cycles in the stratosphere.[1,2] Methyl bromide, CH_3Br, is one of the major bromine-containing organics prevalent in the stratosphere, accounting for nearly half of the total inorganic source (−20 pptv).[3] There are a number of other organic bromine compounds such as CH_2BrCl, $CHBrCl_2$, and $CHBr_3$, which have natural sources.[4−7] To understand the environmental impact of these compounds, knowledge of the atmospheric oxidation mechanism of these organic bromine species is required.

Laboratory studies show that the oxidation reactions of CH_2BrCl and $CHBrCl_2$,[8,9] following the extraction of hydrogen from these materials, led to the formation of an organobromine alkyl radical. Their subsequent reactions with O_2, followed by reactions with NO, led to the formation of organobromine alkoxy radicals, producing bromocarbonyl compounds in the process. Understanding the function and fate of bromocarbonyl compounds in the atmosphere presumes that the basic energetics of these compounds are well understood. The major bromocarbonyl compunds resulting from the atmospheric oxidation of CH_3Br, CH_2BrCl, $CHBrCl_2$, and $CHBr_3$ are CHBrO, CClBrO, and CBr_2O. In our survey of the literature, there is limited information available regarding the heat of formation of these species.

The aim of the present work is to carry out a theoretical characterization of the structures, vibrational spectra, and energetics of bromocarbonyl compounds, such as CHBrO, CClBrO, and CBr_2O. These data should assist in assessing chemical pathways for the formation and subsequent reaction of these atmospheric oxidation products.

II. Computational Methods

Ab initio molecular orbital calculations are performed using the GAUSSIAN 94 program.[10] All equilibrium geometries are fully optimized to better than 0.001 Å for bond distances and 0.1° for bond angles. The Becke's nonlocal three-parameter exchange with Lee−Yang−Parr correlation functional (B3LYP) method[11,12] is used with the 6-31G(d), 6-311G(d), 6-311G(2d), and 6-311++G(3df,3pd) basis sets. Harmonic vibrational frequencies and intensities of all species are calculated at the B3LYP level of theory with the same basis sets. The heats of formation for the set of bromocarbonyls are determined using isodesmic reactions. To improve the energetics, single-point energy calculations using the B3LYP/6-311++G(3df,3pd) optimized geometries are arrived at using the coupled cluster method, including singles, doubles, and triples [CCSD(T)] excitation with the 6-311++G(3df,3pd) basis set.

III. Results and Discussion

A. Geometries. The optimized structural parameters for the various CXBrO species at the different levels of theory are given in Table 1. There are some interesting trends in the structure in moving from the medium size, 6-31G(d), to the larger 6-311++G(3df,3pd) basis set. The CO bond length in CHBrO decreases with an increase in basis set size. This trend is observed for CClBrO and CBr_2O. For the CBr bond, the variation in the bond length with basis set size is less dramatic and systematic. The difference between the CBr bond lengths at the B3LYP/6-311G(d) levels of theory are 0.004, 0.002, and 0.002 Å for CHBrO, CClBrO, and CBr_2O, respectively. To assess these trends, calculations for formaldehyde are performed at the same levels of theory. The results are included in Table 1 along with experimental structural data. A similar trend in the CO bond length with increasing basis set size is seen for CH_2O, as observed for the CXBrO species, suggesting that the changes are an artifact of the basis set size. For the CH_2O model, the most reliable prediction of the geometry is at the B3LYP/6-311++G(3df,3pd) level of theory. The difference between experimental and theoretical predictions of the CO and CH bond length is ±0.005 Å.

If we examine the CO bond length across the series, i.e., CH_2O, CHBrO, CClBrO, and CBr_2O, we observe another interesting trend for the calculations of the B3LYP level of theory with the large 6-311++G(3df,3pd) basis set. There is a systematic decrease in the CO bond length upon increased halogenation of the carbon. In going from CH_2O to CBr_2O, there is a difference of 0.031 Å in the CO bond length.

No experimental structural parameters could be found in the literature for CHBrO and CClBrO, although some studies were

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TABLE 1: Optimized Structures

			levels of theory			
species	coordinates[a,b]	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(d)	B3LYP/ 6-311G(2d)	B3LYP/ 6-311++G(3df,3pd)	exptl
CH_2O	υ(CO)	1.206	1.200	1.198	1.199	1.2032[c]
	υ(CH)	1.111	1.110	1.108	1.106	1.1005
	θ(HCO)	122.4	122.1	122.3	121.9	121.85
CHBrO	υ(CO)	1.184	1.175	1.173	1.174	
	υ(CBr)	1.971	1.982	1.984	1.967	
	υ(CH)	1.098	1.097	1.095	1.097	
	θ(BrCO)	123.9	123.8	123.8	123.7	
	θ(HCO)	127.1	127.1	127.6	127.1	
	τ(HCOBr)	180.1	180.0	180.0	180.0	
CClBrO	υ(CO)	1.179	1.170	1.169	1.171	
	υ(CCl)	1.768	1.774	1.772	1.754	
	υ(CBr)	1.937	1.944	1.942	1.935	
	θ(ClCO)	124.2	123.8	124.1	124.1	
	θ(BrCO)	123.9	123.9	123.9	123.7	
	τ(ClCOBr)	180.0	180.0	180.0	180.0	
CBr_2O	υ(CO)	1.177	1.168	1.167	1.168	1.1755[d], 1.178 ± 0.009[e], 1.173 ± 0.009[e]
	υ(CBr)	1.941	1.951	1.950	1.939	1.9166, 1.923 ± 0.005, 1.918 ± 0.004
	θ(COBr)	124.0	123.6	123.8	123.6	112.36, 123.9 ± 0.04, 123.9 ± 0.4
	τ(BrCOBr)	180.0	180.0	180.0	180.0	

[a] Bond lengths in angstroms. [b] Bond angles in degrees. [c] Duncan, J. L. *Mol. Phys.* **1978**, *28*, 1177. [d] Carpenter, J. H.; Smith, J. G.; Thompson, I. H.; Whiffen, D. H. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 384. [e] Nakata, M.; Tsutomo, F.; Wilkins, D. J.; Kuchitsu, K. *J. Mol. Struct.* **1981**, *71*, 195.

found for CBr_2O. There was an early electron diffraction study performed by Dornte,[13] who reported the CO bond length to be 1.13 ± 0.02, and the CBr bond length to be 2.05 ± 0.04 Å. A later microwave study by Nakata et al.[14] reported a more accurate structure, with the CO bond length of 1.173 ± 0.009 Å, and a CBr bond length of 1.918 ± 0.004 Å. Electron diffraction studies[14] reported values for the CBr bond length of 1.923 ± 0.005 Å. If we use the uncertainties estimated for the CO bond length as determined from comparing CH_2O with the B3LYP/6-311++G(3df,3pd) geometries, we find that the CO bond length predicted for CBr_2O is within the error bars of both the microwave and electron diffraction results. A comparison of the experimental and theoretical C−Br bond length shows that at the B3LYP/6-311++G(3df,3pd) level of theory, the CBr bond is overestimated by 0.016 Å. We note that the best estimate of the CBr bond length is with a basis set that employs three d-polarization functions and one set of *f*-polarization functions. Using a smaller basis set would only increase the magnitude of the error in the predicted CBr bond length with B3LYP wave functions.

B. Vibrational Analysis. The vibrational properties of each brominated carbonyl species are given in Table 2. The vibrational description is based on calculations using the 6-311++G-(3df,3pd) basis set. For the brominated carbonyl species, there are a total of six vibrational frequencies comprised of three stretching modes and three bending modes. Of the CHBrO, CClBrO, and CBr_2O species, perhaps CBr_2O is the most well-studied in terms of its vibration spectrum. It is a planar symmetrical molecule which belongs to the C_{2v} point group, which could be represented by

$$\Gamma = 3A_1 + 0A_2 + 2B_1 + 1B_2$$

All the modes are active in both infrared and Raman spectra. The most intense vibrational bands are predicted to be the υ_1 (CO stretch) and the υ_4 (asymmetric CBr stretch) at 1885.8 and 714 cm^{-1}, respectively, at the B3LYP/6-311++G(3df,3pd) level of theory. These computational results agree with the experimental observations of Overend and Evans,[15] who observed υ_1 and υ_4 at 1828 and 757 cm^{-1}, respectively. Schneider and Stokr[16] report these respective modes at 1826.6 and 743.3 cm^{-1}. The three bending modes consist of a weak BrCBr bend at 173 cm^{-1} at the B3LYP/6-311++G(3df,3pd) level of theory, in good agreement with the experimental values at 179.5 and 181 cm^{-1}; a CBrO bend at 341 cm^{-1} at the B3LYP/6-311++G(3df,3pd) level of theory compared with the experimental values at 353 and 350 cm^{-1}; and an out-of-plane wave motion at the 509 cm^{-1} at the B3LYP/6-311++G(3df,3pd) level of theory, compared with the experimental value at 511.1 and 512 cm^{-1}.

It is interesting to note that, for CBr_2O, the CBr stretching modes (both symmetric and asymmetric) are much lower in frequency than the CO stretching mode. An examination of potential energy distribution for the calculated frequencies reveals that the CO stretch mode is uncoupled from the stretching and bending modes, and could be considered a local mode for the set of vibrational modes of CBr_2O.

The only experimental report of the infrared spectra of CClBrO is by Overend and Evans.[15] The CClBrO molecule is planar, like CBr_2O, but belongs to the point group C_s, for which the vibrational modes span the representation

$$\Gamma = 5a' + 1a''$$

Like CBr_2O, the vibrational modes of CClBrO are all active in both infrared and Raman spectra. Overend and Evans[15] observed the two most intense bands at 1828 and 806 cm^{-1}, which they assign to υ_1 the CO stretching mode and υ_2 the asymmetric CCl stretch, respectively. Our examination of the potential energy distribution for the calculated frequencies for CClBrO show that the dominant motion for the υ_2 mode is the CCl stretch. The frequency at 369 cm^{-1} (υ_4), predicted at the B3LYP/6-311++G(3df,3pd) level of theory, is characterized by the CBr stretch. Overend and Evans[15] based the assignment of the υ_2 and υ_4 modes for CClBrO on the analogous symmetric and asymmetric stretching modes in CCl_2O and CBr_2O, with approximate mode description.

TABLE 2: Vibrational Frequencies[a,b] and Assignments for CXBrO (where X = H, Cl, and Br)

				B3LYP/6-31G(d)		B3LYP/6-311G(d)		B3LYP/6-311G(2d)		B3LYP/6-311++G(3df,3pd)		
species	mode number	symmetry	description	frequency	absolute intensity[d]	frequency	absolute intensity[d]	frequency[c]	absolute intensity[d]	frequency	absolute intensity[d]	exptl
CHBrO	1	a′	CH stretch	3079	25.7	3047	28.1	3033	19.3	3047	12.4	
	2		CO stretch	1882	412.9	1879	474.7	1877	446.6	1862	469.2	
	3		Out-of-plane wag	905	3.2	903	4.0	901	3.7	911	4.6	
	4		HCBr bend	642	158.1	635	167.1	631	162.2	637	169.5	
	5		CBr stretch	355	9.9	354	13.8	350	12.8	357	12.1	
	6	a″	HCO bend	1318	62.6	1312	71.4	1296	63.6	1293	54.7	
COClBr	1	a′	CO stretch	1907	332.5	1902	377.1	1894	335.4	1878	357.2	1828[a]
	2		CCl stretch	786	505.9	768	548.7	766	510.8	778	478.7	806
	3		in-plane bend	508	11.3	502	12.9	499	10.6	510	10.2	517
	4		CBr stretch	364	3.8	366	6.2	364	4.9	369	3.6	372
	5		ClCBr bend	241	0.3	237	0.4	234	0.5	238	0.6	240
	6	a″	out-of-plane wag	548	5.4	548	4.7	550	3.4	554	2.9	547
CBr_2O	1	a_1	CO stretch	1911	325.4	1906	373.0	1900	329.8	1886	182	1826.6[b], 1828[a]
	2		CBr sym. stretch	403	6.7	405	7.5	402	5.9	409	6.2	425.6, 425
	3		BrCBr bend	178	0.3	172	0.3	171	0.4	173	0.5	179.5, 181
	4	b_1	CBr asym. stretch	7.3	468.7	716	517.1	710	480.2	714	466.1	743.3, 757
	5		CBrO bend	332	7.1	338	9.7	336	8.5	341	6.8	353, 350
	6	b_2	out-of-plane wag	507	3.1	505	3.1	505	2.1	509	1.8	511.1, 512

[a] Overend, J.; Evans, J. C. *Trans. Faraday Soc.* **1959**, *55*, 1817. [b] Schneider, B.; Stokr, J. *Collect. Czech. Chem. Commun.* **1961**, *26*, 1221. [c] In units of cm^{-1}. [d] In units of km mol^{-1}.

The rms error between the B3LYP/6-311++G(3df,3pd) calculated and experimental vibrational frequencies is 2.2% for CClBrO. The root-mean-square error for CBr_2O is found to be 3.6%. Because there are no reported vibrational frequencies for CHBrO, the probable error in the predicted vibrational frequencies for CHBrO should be 4%, conservatively.

For CHBrO, the vibrations span the irreducible representation as

$$\Gamma = 5A' + 1A''$$

The CH stretch is calculated to be a relatively weak band at 3047 cm^{-1}. The CO stretch is the most intense peak, resonating at 1862 cm^{-1}. The CBr stretch is also fairly weak, occurring at 357 cm^{-1}. There are three bending modes; two moderately intense hydrogen wagging modes at 1293 and 911 cm^{-1}, and a strong HCBr bend at 637 cm^{-1}.

Overend and Scherer[17,18] examined a series of molecules of the CXYO type molecules in order to examine the effects of mass and force constant effects on the carbonyl stretching frequency. A series of acetyl, carbony, and benzoyl halides were examined. The important finding by Overend and Scherer[17,18] is that there is considerable variation in the CO stretching mode, which is greater than the mass and force constant corrections. The authors attributed this to the electronic effects of the substituent groups (X and Y) on the carbonyl bond. We find support for the observation of Overend and Scherer[18] in the correlation of the CO stretching frequency with the CO bond distance. The r(CO) bond length and υ(CO) frequency are, respectively, 1.174 Å and 1862 cm^{-1} for CHBrO, 1.171 Å and 1878 cm^{-1} for CClBrO, and 1.168 Å and 1886 cm^{-1} for CBr_2O at the B3LYP/6-311++G(3df,3pd) level of theory, and these values support the correlations observed by Overend and Scherer.[18] Bellamy and Williams[19] describe this effect in terms of electrostatic interaction between the halogen atom and the carbonyl bond.

C. Thermodynamic Properties. CCSD(T) energies of each species are listed in Table 3. The total energies are corrected to 0 K by adding the zero-point energy to the predicted total energy. To obtain the energy at 298 K, the thermal energy of each species is added to its total energy instead of the zero-point energy. The reaction enthalpy at 0 or 298 K can then be obtained by use of the corrected energy along with the following equation:

$$\Delta H = \Delta E - \Delta nRT$$

For a reaction with the same number of products as reactants, the change in molecularity Δn is zero, and $\Delta H = \Delta E$.

To improve the accuracy of the method, isodesmic reactions were used. Isodesmic and isogeric reactions are those in which reactants and products contain the same type of bonds, same number of bonds, and the same spin multiplicity. Because of the electronic similarity between the reactants and products, errors in the calculated energy between them may cancel. Table 4 lists thermodynamic properties for all species used in the isodesmic reactions, while Table 5 lists the heat of formation of each carbonyl species at 298 K. The isodesmic species listed in Table 5 involve methane, formaldehyde, chloromethane, and bromomethane. Thus, the accuracy of the present results relies on the reliability of the heats of formation for these species. CH_2O has a known heat of formation, at 298 K, of −26.0 kcal mol^{-1}. The substitution of a hydrogen atom for a bromine atom to form CHBrO has a slight impact on its heat of formation, which is found to be −29.9 kcal mol^{-1} at the CCSD(T)/-311G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory. Further substitution of the remaining hydrogen atom by a chlorine atom results in increased stabilization, whereas substitution by a bromine atom results in decreased stabilization. The 298 K heat of formation of CClBrO and CBr_2O are −38.2 and −25.8 kcal mol^{-1}, respectively, at the CCSD(T)/-311G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory.

There are no experimental estimates of the heat of formation for CHBrO and CClBrO for which the accuracy of the theoretical heat of formation could be assessed. However, there

TABLE 3: Energetics of Species Calculated Using B3LYP Methodology[a]

molecules	levels of theory	energies	thermal	ZPE
CH_2O	B3LYP/6-31G(d)	−114.500 471	0.02968	0.02682
	B3LYP/6-311G(d)	−114.533 368	0.02945	0.02658
	B3LYP/6-311G(2d)	−114.535 831	0.02934	0.02647
	B3LYP/6-311++G(3df,3pd)	−114.549 945	0.02940	0.02653
	CCSD(T)/6-311++G(3df,3pd)	−114.336 131		
CHBrO	B3LYP/6-31G(d)	−2685.62 390	0.02203	0.01864
	B3LYP/6-311G(d)	−2688.09 990	0.02192	0.01852
	B3LYP/6-311G(2d)	−2688.09 837	0.02183	0.01843
	B3LYP/6-311++G(3df,3pd)	−2688.11 768	0.02186	0.01847
	CCSD(T)/6-311++G(3df,3pd)	−2686.31 403		
CClBrO	B3LYP/6-31G(d)	−3145.22 303	0.01409	0.00991
	B3LYP/6-311G(d)	−3147.72 546	0.01403	0.00985
	B3LYP/6-311G(2d)	−3147.72 732	0.01401	0.00981
	B3LYP/6-311+G(3df)	−3147.74 868	0.01403	0.00986
	CCSD(T)/6-311++G(3df,3pd)	−3145.44 513		
CBr_2O	B3LYP/6-31G(d)	−5256.73 297	0.01360	0.00919
	B3LYP/6-311G(d)	−5261.64 811	0.01365	0.00921
	B3LYP/6-311G(2d)	−5261.64 276	0.01362	0.00917
	B3LYP/6-311+G(3df,3pd)	−5261.66 810	0.01362	0.00918
	CCSD(T)/6-311++G(3df,3pd)	−5258.27 855		
CH_4	B3LYP/6-31G(d)	−40.518 382	0.04806	0.04520
	B3LYP/6-311G(d)	−40.527 934	0.04768	0.04481
	B3LYP/6-311G(2d)	−40.528 255	0.04764	0.04477
	B3LYP/6-311++G(3df,3pd)	−40.537 396	0.04743	0.04456
	CCSD(T)/6-311++G(3df,3pd)	−40.438 209		
CH_3Cl	B3LYP/6-31G(d)	−500.108 464	0.04113	0.03811
	B3LYP/6-311G(d)	−500.146 420	0.04090	0.03788
	B3LYP/6-311G(2d)	−500.148 725	0.04071	0.03775
	B3LYP/6-311++G(3df,3pd)	−500.159 742	0.04070	0.03768
	CCSD(T)/6-311++G(3df,3pd)	−499.559 871		
CH_3Br	B3LYP/6-31G(d)	−2611.61 647	0.04056	0.03747
	B3LYP/6-311G(d)	−2614.06 893	0.04033	0.03724
	B3LYP/6-311G(2d)	−2614.06 440	0.04027	0.03718
	B3LYP/6-311++G(3df,3pd)	−2614.08 055	0.04017	0.03708
	CCSD(T)/6-311++G(3df,3pd)	−2612.39 525		

[a] All values in hartrees.

TABLE 4: Heats of Formation[d] **for Species Used in Isodesmic Reactions**

species	ΔH_f^{0K}	ΔH_f^{298K}	ref
CH_4	−16.0 ± 0.1	−17.9 ± 0.1	*a*
CH_2O	−25.1 ± 1.5	−26.0 ± 1.5	*a*
CH_3Cl	18.1 ± 0.5	−19.6 ± 0.1	*b*,*c*
CH_3Br		−8.5 ± 0.03	*b*

[a] Curtiss, L. A.; Raghavachari, K.; Redfern, P. D.; Pople, J. A. *J. Chem. Phys.* **1997**, *106(3)*, 1063. [b] Yu-Ran, L.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 280. [c] Lias, S. G.; Bartness, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Ref. Data, Suppl.* **1988**, *17*. [d] In units of kcal mol^{-1}.

TABLE 5: Relative Energetics[a] **for CXBrO (where X = H, Cl, and Br) Isodesmic Reaction Schemes**

level of theory	reactions	ΔH_{rxn}^{298}	ΔH_f^{298}
CHBrO	$CHBrO + CH_4 \rightarrow CH_2O + CH_3Br$		
B3LYP/6-31G(d)		16.0	−32.6
B3LYP/6-311G(d)		16.1	−32.7
B3LYP/6-311G(2d)		16.7	−33.3
B3LYP/6-311++G(3df,3pd)		15.6	−32.2
CCSD(T)/6-311++G(3df,3pd)		13.3	−29.9
CClBrO	$CClBrO + 2CH_4 \rightarrow CH_2O + CH_3Cl + CH_3Br$		
B3LYP/6-31G(d)		22.3	−40.6
B3LYP/6-311G(d)		21.3	−39.6
B3LYP/6-311G(2d)		22.5	−40.8
B3LYP/6-311++G(3df,3pd)		21.7	−40.0
CCSD(T)/6-311++G(3df,3pd)		19.9	−38.2
CBr_2O	$CBr_2O + 2CH_4 \rightarrow CH_2O + 2CH_3Br$		
B3LYP/6-31G(d)		23.1	−30.3
B3LYP/6-311G(d)		21.2	−28.4
B3LYP/6-311G(2d)		22.4	−29.6
B3LYP/6-311++G(3df,3pd)		20.8	−28.0
CCSD(T)/6-311++G(3df,3pd)		18.6	−25.8

[a] All values in kcal mol^{-1}.

are three reports of experimental estimates of the heat of formation of CBr_2O in the literature. Cox and Pilcher[20] reported a value of −20.1 kcal mol^{-1}, estimated from equilibrium studies of the reaction of CO + Br_2. A calorimetric study[21] of the aqueous hydrolysis of bromophosgene yielded a heat of formation for CBr_2O as −27.3 ± 0.51 kcal mol^{-1}. This experimental estimate is in marked disagreement with the Cox and Pilcher[20] value. Dunning and Pritchard,[22] using a third-law treatment for the equilibrium between CO, Br_2 and CBr_2O, obtained a value of −27.13 ± 0.12 kcal mol^{-1}, in good agreement with the calorimetric results of −27.3 ± 0.51 kcal mol^{-1}. There is considerable experimental scatter for the 298 K heat of formation values for CBr_2O, although there is better agreement between the equilibrium and calorimetric values.

The computational estimate of the heat of formation for CBr_2O, at 298 K, is −25.8 kcal mol^{-1} at the CCSD(T)/-311G-(3df,3pd)//B3LYP/6-311++G(3df,3pd) level of theory. This value is within 1.5 kcal mol^{-1} of the experimental equilibrium determination of Dunning and Pritchard[22] and 1.3 kcal mol^{-1} of the calorimetric results.[21] The good agreement between our computational result and the equilibrium and calorimetric values suggests that experimental estimates are reliable. Moreover, it also suggests that computational estimates for the heats of formation for CHBrO and CClBrO, for which there are no experimental determinations available, should be reasonably well determined.

IV. Summary

The equilibrium structures, vibrational spectra, and heats of formation for CXBrO (where X = H, Cl, and Br) have been investigated. We find that the thermodynamically most stable structure of the series is CClBrO, with a heat of formation of -38.2 kcal mol^{-1} at 298 K. The least stable species is CBr_2O, with a heat of formation of -25.8 kcal mol^{-1}. We find that our best estimate of the heat of formation of CBr_2O is within ± 2 kcal mol^{-1} of the best experimental determinations. Results for CHBrO and CClBrO should be reasonably well determined.

References and Notes

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