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Molecular Structure, Vibrational Frequencies, and Energetics of the HCO, HOCO, and HCO_2 Anions

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The structures and vibrational spectra for HCO^-, $HOCO^-$, and HCO_2^- have been calculated at high levels of electronic structure theory. The changes in the structure of HCO^- relative to neutral HCO are consistent with the predictions based on photodetachment experiments. Of the two isomers, HCO_2^- and $HOCO^-$, the HCO_2^- anion is predicted to be the more stable. For $HOCO^-$, the cis conformer is of lower energy as compared to the trans. Conversely, for neutral HOCO, the trans conformer is lower in energy. The electron affinity of HCO is predicted to be 0.308 eV in excellent agreement with the experimental value of 0.313 eV. The electron affinity of HOCO is predicted to be 1.42 eV and there is no known experimental measurement. The electron affinity of $HCO_2(^2A_1)$ is predicted to be 3.51 eV as compared to the experimental value of 3.498 ± 0.015 eV. The $^2A_1$ state of HCO_2 is predicted to be the ground state on the basis of theoretical calculations, which are in agreement with the experimental assignment determined from the photoelectron spectra.

Introduction

The formyl radical, HCO, is an important intermediate that has attracted experimental and theoretical attention because of its role in both atmospheric and combustion oxidation processes. The radical was first detected in hydrocarbon flames.[1] Since these seminal studies, there have been many studies of its infrared and UV spectra.[2] There have also been a number studies of the cation of HCO, which corresponds to protonated CO.[3,4] In contrast, there have been relatively few studies of the anion, HCO^-. The anion was first observed in negative ion mass spectroscopy studies of alcohols by using the ion cyclotron resonance technique. A number of groups[5−8] have studied the gas-phase chemistry of HCO^-. The only gas-phase spectroscopic study of HCO^- was reported by Lineberger and co-workers.[9] These studies provided the first experimental structure of HCO^- based on the changes in geometry when an electron is detached from HCO^-. The only theoretical study of HCO^- that we found is the set of MNDO, HF, and MP2 calculations of carbonyl anions by Schleyer and co-workers.[10] To the best of our knowledge, there are no high level ab initio studies of this anion.

The formyloxyl radical, HCO_2, and its isomer, HOCO, are also important radicals that have both combustion and atmospheric chemistry roles. The HCO_2 radical has proven to be very difficult to observe experimentally, whereas the more stable isomer, HOCO, has been observed in the gas phase from laser difference frequency studies.[11] The first experimental structural determination came from gas-phase millimeter-wave studies.[12] The cation of HOCO has been observed and is the well-known protonated CO_2.[4] The first definitive identification came from submillimeter wave and infrared spectroscopic studies.[13] The only studies of the HCO_2 anion are those of Neumark and co-workers,[14] who reported the photoelectron spectra of HCO_2^- and DCO_2^- and observed vibrationally resolved progressions dominated by the CO_2 bend. There are no theoretical or experimental studies of the HOCO anion reported in the literature.

We have recently reported[15] detailed theoretical studies of the structures, frequencies, and thermochemistry of the HCO, HOCO, and HCO_2 radicals and here we extend these studies to their corresponding anions. An interesting aspect of the previous study is that HOCO is significantly more stable than HCO_2 and HOCO is barely bound with respect to the H + CO_2 asymptote. However, on the bases of simple chemical models, we would expect HCO_2^- to be resonance stabilized and to be much more stable than $HOCO^-$.

Computational Approach. We have been developing an approach[16] to the reliable calculation of molecular thermodynamic properties, notably heats of formation, on the basis of ab initio molecular orbital theory. This approach starts with coupled cluster theory, including a perturbative triples correction (CCSD(T)),[17−19] combined with the correlation-consistent basis sets[20,21] extrapolated to the complete basis set limit. This is followed by a number of smaller corrections including core-valence interactions and relativistic effects. For the present study, we used the augmented correlation consistent basis sets aug-cc-pV*n*Z for H, C, and O (*n* = D, T, and Q).[22] Only the spherical components (5-*d*, 7-*f*, 9-*g*, and 11-*h*) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs.[23] The open-shell CCSD(T) calculations were carried out at the R/UCCSD(T) level unless noted below, where a restricted open shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[24−26] The CCSD(T) total energies were extrapolated to the CBS limit

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TABLE 1: Frozen Core QCISD(T) and CCSD(T) Geometries and Energies for HCO_x^{-a}

		coordinates				
species	basis	r(CH)	r(CO)	R(CO′)	θ(HCO) or HOC	θ(OCO)
$HCO^-(\tilde{X}^1A')$	aug-cc-pVDZ	1.242	1.257		109.4	
		1.241	1.257		109.4	
	aug-cc-pVTZ	1.218	1.246		109.6	
		1.217	1.246		109.5	
	aug-cc-pVQZ	1.215	1.242		109.6	
$HCO_2^-(\tilde{X}^1A_1)$	aug-cc-pVDZ	1.141	1.270		114.9	130.2
		1.141	1.269		114.8	130.3
	aug-cc-pVTZ	1.130	1.258		114.9	130.2
		1.129	1.257		114.9	130.2
	MP2/6-31++G**[b]	1.125	1.267			130.2
	exptl crystal (Na^+)[c]	1.106	1.246			126.4
$HOCO^-$ $(\tilde{X}^1A')$ cis	aug-cc-pVDZ	0.984	1.493	1.244	102.2	111.4
		0.984	1.489	1.244	102.3	111.5
	aug-cc-pVTZ	0.981	1.459	1.235	102.3	111.8
		0.980	1.458	1.235	102.3	111.8
	aug-cc-pVQZ	0.978	1.454	1.232	102.3	111.8
$HOCO^-$ $(\tilde{X}^1A')$ trans	aug-cc-pVDZ	0.970	1.576	1.224	99.9	109.9
		0.969	1.568	1.224	100.1	109.9
	aug-cc-pVTZ	0.964	1.523	1.217	100.3	110.6
		0.964	1.520	1.216	100.4	110.6
	aug-cc-pVQZ	0.961	1.515	1.214	100.5	110.7

[a] Bond distances in angstroms and bond angles in degrees. First line is the QCISD(T) optimized geometry, and the second line is the CCSD(T) optimized geometry. [b] Reference 14. [c] Reference 35.

by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\mathrm{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \qquad (1)$$

where $n = 2$ (DZ), 3 (TZ), and 4(QZ), as first proposed by Peterson et al.[27] This extrapolation method has been shown to yield atomization energies in closest agreement with experiment by a small measure as compared to other extrapolation approaches up through $n = 4$. The geometries were optimized at the frozen core CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels of theory. The CCSD(T)/aug-cc-pVTZ geometries were used for the CCSD(T)/aug-cc-pVQZ calculations. In addition, geometries were optimized at the QCISD(T) level[28a] with the aug-cc-pVDZ and aug-cc-pVTZ basis sets for all of the anions and for HCO^- and $HOCO^-$, also with the aug-cc-pVQZ basis set. Vibrational frequencies were calculated at the CCSD(T) and QCISD(T) levels with the aug-cc-pVDZ basis set. The QCISD(T) calculations were done using the Gaussian 98 program.[28b] All of the calculations were performed on SGI computers.

Core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[29] Scalar relativistic corrections ΔE_{SR}, which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI−SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and one-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[30] The atomic spin−orbit corrections to the total atomization energies are taken from Moore's tables.[31]

By combining our computed $\sum D_0$ values with the known heats of formation[32] at 0 K for the elements ($\Delta H_f^0(\mathrm{O}) = 58.98$ kcal mol^{-1}, $\Delta H_f^0(\mathrm{C}) = 169.98 \pm 0.1$ kcal mol^{-1}, and $\Delta H_f^0(\mathrm{H}) = 51.63$ kcal mol^{-1}), we can derive ΔH_f^0 values for the molecules under study in the gas phase. We can obtain heats of formation at 298K by following the procedures outlined by Curtiss et al.,[33] and by using the stationary electron convention, i.e., we do not ascribe a change in the heat of formation of the electron as a function of temperature.

Results and Discussion

The geometry information for the anions is reported in Table 1 and the vibrational frequencies of the anions are reported in Table 2. The geometry and frequency information for the neutrals has previously been reported.[15] The energy contributions for the neutral radicals and the anions are reported in Table 3. We report the neutral energetics again to make comparison of the various contributions easier for the reader. The geometries obtained at the CCSD(T) and QCISD(T) levels are essentially identical. The calculated frequencies obtained with the two approaches are very similar, being in agreement within 10 cm^{-1}.

The calculated electron affinity of HCO is 0.308 eV, in excellent agreement with the experimentally measured value of 0.313 ± 0.005 eV.[9] Murray et al. performed a Franck−Condon analysis of the HCO^- photoelectron spectra and, based on the spectral analysis, they calculated that r(CO) should increase by 0.04 ± 0.02 Å, r(CH) should increase by 0.14 ± 0.02 Å, and ∠(HCO) should decrease by 16 ± 2° in the anion as compared to the neutral. The experimental deltas for r(CO) and ∠(HCO) are in excellent agreement with our calculated deltas of 0.062 Å and 14.9°. The experimental delta for r(CH) is somewhat larger than our calculated delta of 0.096 Å, but the authors do note that their largest error in the Franck Condon analysis is for this geometric parameter because of the flat potential energy surface along this mode due to the low C−H bond energy. The dramatic changes for the geometry on adding an electron are consistent with the changes in the frequencies. The calculated C−H stretch drops by almost 900 cm^{-1} in the anion as compared to the neutral and the C−O stretch drops by ∼500 cm^{-1} in the anion. In contrast, the HCO bending frequency increases in the anion. These values are consistent with the significant lengthening of the C−H and C−O bonds and the significant decrease in <HCO in the anion as compared to the neutral.

TABLE 2: Frozen Core QCISD(T) and CCSD(T) Harmonic Vibrational Frequencies (cm^{-1})

species	mode number	mode symmetry	mode description	QCISD(T) aug-cc-pVDZ	CCSD(T) aug-cc-pVDZ	exptl[a]
$HCO^-(\tilde{X}^1A')$	1	a′	CH stretch	1740	1751	
	2		CO stretch	1326	1332	
	3		HCO bend	1257	1260	
$HCO_2^-(\tilde{X}^2A_1)$	1	a_1	CH stretch	2658	2659	2830
	2		CO symmetric stretch	1302	1307	1361
	3		CO_2 bend	721	724	775
	4	b_1	H out of-plane wag	1026	1027	1068
	5	b_2	CO asymmetric stretch	1612	1619	1607
	6		H in-plane wag	1357	1365	1367
$HOCO^-(\tilde{X}^1A')$	1	a′	OH stretch	3508	3514	
cis	2		C═O stretch	1545	1551	
	3		HO′C bend	1158	1170	
	4		C−O stretch	651	661	
	5		OCO bend	498	510	
	6	a″	torsion	619	624	
$HOCO^-(\tilde{X}^1A')$	1	a′	OH stretch	3754	3762	
trans	2		C═O stretch	1635	1639	
	3		HO′C bend	1066	1083	
	4		C−O stretch	604	612	
	5		OCO bend	361	380	
	6	a″	torsion	486	485	

[a] Reference 36.

TABLE 3: Contributions to the Total Energy for HCO_x and HCO_x^- and Relative Energies

contribution[a]	HCO ($^2A'$)	HCO^- ($^1A'$)	HOCO trans ($^2A'$)	$HOCO^-$ cis ($^1A'$)	$HOCO^-$ trans ($^1A'$)	$HCO_2(^2B_2)$	$HCO_2(^2A_1)$	HCO_2^- ($^1A_1$)
aug-cc-pVDZ[b]	−113.600071	−113.605937	−188.695569	−188.744680	−188.742759	−188.672545	−188.669629	−188.798105
aug-cc-pVTZ[b]	−113.692517	−113.700207	−188.851970	−188.902204	−188.899877	−188.827271	−188.825304	−188.957409
aug-cc-pVQZ[b]	−113.721047	−113.729397	−188.900834	−188.951494	−188.949107	−188.875152	−188.873581	−189.007244
Est. CBS Eq 1[c]	−113.737131	−113.745865	−188.928450	−188.979359	−188.976945	−188.902161	−188.900812	−189.035415
ΔE_{elec} CBS eq 1[d]	278.12	283.60	395.47	427.41	425.90	379.3	378.4	462.59
ΔE_{CV}[e]	1.05	0.75	1.35	1.00	1.01	1.29	1.39	1.32
ΔE_{SR}[f]	−0.27	−0.36	−0.52	−0.64	−0.64	−0.43	−0.48	−0.76
ΔE_{SO}[g]	−0.30	−0.30	−0.52	−0.52	−0.52	−0.52	−0.52	−0.52
ΔE_{ZPE}[h]	−8.16	−6.20	−12.81	−11.47	−11.37	−12.2	−9.6	−12.43
ΣD_0[i]	270.4	277.5	383.0	415.8	414.4	367.4	369.2	450.2
$\Delta H_f(0K)$[j]	10.2	3.1	−43.4	−76.2	−74.8	−27.8	−29.6	−110.6
$\Delta H_f(298K)$[k]	10.3	3.2	−44.4	−77.2	−75.8	−28.8	−30.4	−111.6
EA(calc)[l]	7.1 (0.308)		32.8 (1.42) cis 31.4 (1.36) trans				82.8 (3.59)$^2B_2$[m] 81.0 (3.51)$^2A_1$[m]	
EA(expt)[l]	7.22 (0.313)[n]						80.66 (3.498 ± 0.015)[o]	

[a] Total energies in Hartrees and energy differences in kcal/mol. [b] Valence electron only CCSD(T) total energy with the given basis set. [c] Estimated frozen core, complete basis set energy obtained from eq 1 using the CCSD(T)/aug-cc-pVxZ (x = D, T, and Q) energies. [d] Valence electron atomization energy from extrapolated total energies obtained with eq 1. [e] Core/valence correction obtained from R/UCCSD(T)/cc-CVTZ calculations. [f] Scalar relativistic correction obtained from CISD/cc-pVTZ calculations. [g] Net spin−orbit correction to the atomization energy. [h] Zero point vibrational energy contribution. [i] $\Sigma D_0 = \Delta E_{elec} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} + \Delta E_{ZPE}$. [j] Heat of formation at 0 K. [k] Heat of formation at 298 K. [l] Electron affinity in kcal/mol. Values in parentheses are in eV. [m] Electron affinities for the two lowest states of HCO_2. The HCO_2 state labels are given. [n] Reference 9. [o] Reference 14.

For HOCO, the electron affinity is calculated to be 1.42 eV, significantly larger than the electron affinity of HCO. The cis structure of the anion is more stable than the trans structure by 1.4 kcal/mol. In contrast, the trans structure of the neutral is ∼2 kcal/mol more stable than the cis structure.[15] The HOCO radical can be considered to be a carbonyl with an OH bonded to the carbon. Thus, similar changes in the geometry should be found on addition of an electron to HOCO as were found for adding an electron to HCO. The C═O bond distance increases by 0.048 Å in the cis anion as compared to the trans radical and the C−O bond distance increases by 0.109 Å in the cis anion, again as compared to the trans radical. The OH distance increases slightly by 0.015 Å in the anion as compared to the radical. Consistent with the increases in the bond distances, the ∠(OCO) decreases by 15.2° and the ∠(HOC) by 5.4° in the cis anion as compared to the trans radical. There are different changes when an electron is added to form the trans anion. The C═O bond lengthens by only 0.034 Å in the trans anion but the C−O bond distance increases by 0.17 Å and the OH bond distance showing essentially no change. The ∠OCO and ∠HOC become smaller by 16.3° and 7.2°, respectively. The frequencies track the bond distance changes. The C−H stretch decreases by more than 250 cm^{-1} in the cis isomer of the anion as compared to the trans radical and essentially no change is found for the C−H stretch in the trans anion. The C═O stretch decreases by ∼ 300 cm^{-1} in the cis anion and by about 200 cm^{-1} in the trans anion. The C−O stretch decreases by 350−400 cm^{-1} in the anions. The in plane bends are also sensitive to the addition of the electron and significantly decrease. The torsion is not as sensitive to the addition of the electron, increasing in the cis anion and decreasing in the trans isomer.

The potential energy surface for photodetachment of an electron from HCO_2^- is complicated by the significant number of low-lying states for the HCO_2 radical and by the instability of the radical with respect to the H + CO_2 dissociation channel. This instability means that it is very difficult to calculate the frequencies for the radical. The vibrationless, electronic energy ordering for HCO_2 (in kcal/mol) is 0.0 ($^2B_2/\sigma$), 0.9 ($^2A_1/\sigma$), 1.9 ($^2A'/\sigma$), and 11.1 ($^2A_2/\pi$). The zero point energies of the various states are highly dependent on the method used to compute them. At the UCCSD(T)/aVDZ level, the zero point energies in kcal/mol are 12.2 ($^2B_2/\sigma$), 9.6 ($^2A_1/\sigma$), and 11.8 ($^2A'/\sigma$). At the CASPT2/ANO level, the zero point energies in kcal/mol are 12.2 ($^2B_2/\sigma$), and 10.5 ($^2A_1/\sigma$) and the $^2A'/\sigma$ state has an imaginary frequency. The calculated frequencies for the $^2B_2/\sigma$ state are close to what would be expected for the structure based on a qualitative chemical analysis. Due to the long C−H bond distance in the $^2A_1/\sigma$ state, the C−H stretch is much lower than in the $^2B_2/\sigma$ state helping to explain the large difference in zero point energies for the two states. For the $^2A_1/\sigma$ state, the UCCSD(T)/aVDZ and the CASPT2/ANO frequencies are essentially the same except for the lowest b_2 frequency where the UCCSD(T)/aVDZ value of 157 cm^{-1} is much lower than the CASPT2/ANO frequency of 642 cm^{-1}. When the zero point energies are included, the $^2A_1/\sigma$ state is 1.8 kcal/mol below the $^2B_2/\sigma$ state with the UCCSD(T)/aVDZ frequencies and 0.9 kcal/mol below with the CASPT2/ANO frequencies.

The electron affinity to the $^2B_2$ state for HCO_2 is 3.59 eV, which is almost 0.1 eV higher than the experimental value of 3.50 ± 0.015 eV, clearly outside the error limits that we would expect for our calculation of the electron affinity. Using the UCCSD(T)/aVDZ frequencies, the electron affinity to the $^2A_1$ state is 3.51 eV (81.0 kcal/mol), in excellent agreement with the experimental value. Using the CASPT2/ANO frequencies for the $^2A_1$ state, the electron affinity is 3.55 eV. On the basis of the quality of the calculated electron affinity for HCO and for those of other molecules, we expect to be able to predict the electron affinity of HCO_2 to within a few hundredths of an eV. These results then show that the lowest state for HCO_2 is the $^2A_1$ and that the UCCSD(T) frequencies provide the best set of results. This implies that the lowest b_2 frequency in the $^2A_1$ state of HCO_2 has a low value (~157 cm^{-1} based on the UCCSD(T)/aug-cc-pVDZ frequencies) and is probably very anharmonic. In addition, it shows for surfaces dominated by very flat potential energy regions that the determination of reliable vibrational energy corrections is key if we wish to calculate energetic/thermodynamic quantities to better than 1 kcal/mol. The calculated values for the electron affinities show that the experimental assignment of Neumark and co-workers[14] for the ground state of HCO_2 based on interpreting the photoelectron spectra of the anion is correct. The heat of formation of the anion has been measured by determining the acidity of HC(O)OH in the gas phase by using mass spectrometric techniques.[34] The experimental heat of formation at 298 K of -110.9 ± 2.3 kcal/mol is in excellent agreement with our calculated value of -111.6 kcal/mol.

The $^2A_1$ state of the radical shows a very large <OCO (144.6°) and a long C−H bond (1.158 Å). The anion has C_{2v} symmetry and the <OCO moves toward the value of 120° expected for sp^2 hybridization at a trivalent carbon reaching a value of 130.2°. The C−O bond distance only increases by 0.027 Å in the anion and the C−H bond distance actually decreases by 0.028 Å in the anion. The calculated structures of HCO_2^- with the aug-cc-pVDZ basis set are in good agreement with the previously calculated MP2/6-31++G** structure.[14] The calculated structures for HCO_2^- with the aug-cc-pVTZ basis set are in good agreement with the experimental crystal structure.[35] The calculated structure is within 0.01 Å for the C−O bond length from the structure with the Na^+ counterion but the calculated C−H bond distance is longer by 0.023 Å as compared to the crystal structure value. This is not surprising as it is extremely difficult to accurately measure C−H bond distances by using X-ray diffraction techniques. The calculated OCO bond angle is surprisingly 4° larger than the crystal structure value, suggesting the possibility of crystal deformation forces as noted previously.[14] Finally, we note that there is very good agreement between the experimental frequencies measured in the solid state[36] for HCO_2^- and the calculated values with the aug-cc-pVDZ basis set.

Conclusions

The electron affinities of HCO, HCO_2 and HOCO have been calculated by using high levels ab initio electronic structure theory. The agreement between theory and experiment for the electron affinities of HCO and HCO_2 is excellent within 0.02 eV and suggests that the calculated electron affinity of HOCO is within 0.02 eV of the unknown experimental value. The calculated value for the electron affinity of HCO_2 strongly suggests that the ground state of HCO_2 is the $^2A_1$ state. This state is higher in energy at the electronic energy level than the $^2B_2$ state but the $^2A_1$ state becomes lower in energy when the zero point energy is included because of its smaller zero point energy. The calculated electron affinity results also imply that the lowest b_2 vibrational mode for the $^2A_1$ state of HCO_2 has a low frequency on the order of 150 cm^{-1}.

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