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An Ab Initio and Density Functional Theory Study of Keto−Enol Equilibria of Hydroxycyclopropenone in Gas and Aqueous Solution Phase

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Keto−enol tautomerism in hydroxycyclopropenone (2-hydroxy-2-cyclopropen-1-one) has been studied using ab initio methods, the B3LYP functional of density functional theory, as well as complete basis set (CBS-QB3 and CBS-APNO) and G3 methods. Absolute and relative energies were calculated with each of the methods, whereas computations of geometries and harmonic frequencies for hydroxycyclopropenone and 1,2-cyclopropanedione were computed in the gas phase but were limited to HF, MP2 and CCSD levels of theory, and the B3LYP functional, in combination with the 6-31++G** basis set. Using the MP2/6-31++G** gas phase optimized structure, each species was then optimized fully in aqueous solution by employing the polarizable continuum model (PCM) self-consistent reaction field approach, in which HF, MP2 and B3LYP levels of theory were utilized, with the same 6-31++G** basis set. In both gas and aqueous solution phases, the keto form is higher in energy for all of the model chemistries considered. The presence of the solvent, however, is found to have very little effect on the bond lengths, angles and harmonic frequencies. From the B3LYP/6-31++G** Gibbs free energy, the keto−enol tautomeric equilibrium constant for 2-hydroxy-2-cyclopropen-1-one $\leftrightarrows$ 1,2-cyclopropanedione is computed to be $K_T(\text{gas}) = 2.35 \times 10^{-6}$, $K_T(\text{aq}) = 5.61 \times 10^{-14}$. It is concluded that the enol form is overwhelmingly predominant in both environments, with the effect of the solvent shifting the direction of equilibrium even more strongly in the favor of hydroxycyclopropenone. The almost exclusive nature of this species is attributed to stabilization resulting from aromaticity. Confirmation is provided by comparison of the simulated vibrational spectra of hydroxycyclopropenone with the measured infrared spectrum in an argon matrix.

1. Introduction

As a photochemical precursor to hydroxyacetylene, hydroxycyclopropenone (2-hydroxy-2-cyclopropen-1-one) is a molecule of considerable chemical interest. Although the former species had been previously observed in planetary atmospheres and interstellar clouds,[1] it was only generated terrestrially for the first time in 1986.[2] This achievement was considered noteworthy enough to warrant mention in the *Encyclopaedia Britannica* as one of the scientific highlights of the year.[3] Not long afterward, hydroxyacetylene was again prepared using two different processes involving the photodecarbonylation of hydroxycyclopropenone (see Figure 1.). One occurred at low temperature in an argon matrix,[4] whereas the other involved the laser flash photolysis of an aqueous solution at room temperature.[5] Despite its important role as a precursor, the laboratory synthesis of hydroxycyclopropenone has so far proved elusive, all such attempts to do so having so far failed,[6] and in general it has been little studied.

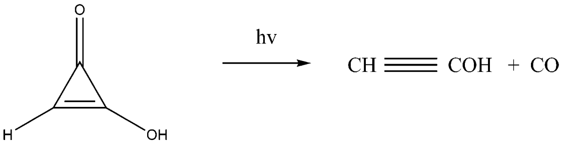

Figure 1. Photodecarbonylation of hydroxycyclopropenone to hydroxyacetylene.

This, however, is in marked contrast to other three- and even five- and seven-membered cyclic conjugated ketones, which have been the subject of a number of experimental[7−11] and theoretical studies[12−19] where their chemical and physical properties have been investigated. One well-known example is the seven-membered species tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), which has also been studied extensively.[20−28] Tropolone is of interest in relation to the present study on hydroxycyclopropenone in that it may undergo tautomeric equilibriation between the keto and enol forms as it provides an example of an aliphatic carbonyl compound possessing hydrogens α to the carbonyl group. When such structural features are present, the stabilization resulting from the carbonyl bond generally favors the keto form over the enol. Tropolone, however, is a system that does not follow this pattern, and of the possible tautomeric structures that this species may assume, the enol structure is observed almost exclusively. This is attributed to aromaticity present within the enol form, the delocalized ring structure containing six π electrons.[29] Hydroxycyclopropenone, which is a three-membered ring analogue of tropolone, would also be expected to possess a certain amount

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of aromatic character, and also to exist predominantly in the enol form. This, again, being justified by simple Hückel molecular orbital theory. Due to the scarcity of experimental data on hydroxycyclopropenone, it is the purpose of this study to evaluate the keto−enol equilibrium constant for this molecule in both the gas and aqueous solution phases, and to ascertain the most likely tautomeric structure adopted. To this end, ab initio and density functional theory calculations of the energy, Gibbs free energy and vibrational frequencies have been performed on the hydroxycyclopropenone−diketone system.

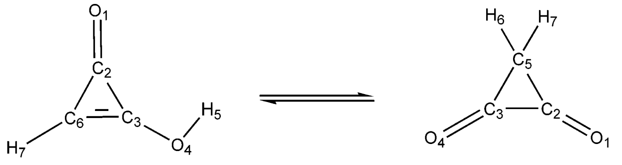
Although a number of measurements of the equilibrium constant for the tautomerization of a variety of keto−enol systems can be found in the literature,[30−33] only a relatively few theoretical investigations have been carried out.[34−36] In one study,[35] ab initio HF and MP2 calculations were used to compute the relative energy differences between phenol and 2,4- and 2,5-cyclohexadienone, from which an equilibrium constant for phenol $\rightleftharpoons$ 2,4-cyclohexadienone was evaluated to be 1.98×10^{-13}, in excellent agreement with the experimentally determined value of 1.86×10^{-13}, demonstrating that the direction of equilibrium is strongly in favor of the enol structure. In another, more recent investigation[36] using the CBS-QB3 method, a value of 7.15×10^{-14} was computed. From these works it may be concluded safely that electronic structure methods may be used to compute accurate and reliable relative energies of different tautomeric forms and to use these computational results to evaluate the equilibrium constant for tautomerization, especially in systems where aromatic stabilization plays a significant factor in determining which of the possible isomeric forms is energetically more favorable.

2. Computational Details

Ab initio[37] and density functional theory[38] calculations were carried out on 2-hydroxy-2-cyclopropen-1-one and 1,2-cyclopropanedione in both the gas phase and in aqueous solution. The former approach involved HF, MP2 and CCSD levels of theory (with all electrons treated in the last two methods) whereas in the latter description the B3LYP[39,40] functional was employed entirely. The standard 6-31++G** basis set[41] was used throughout. To assess whether the basis set selected was large enough, and to calculate accurate relative energies, gas phase computations were performed for comparison for the species of interest using two complete basis set approaches: CBS-QB3 and CBS-APNO, as well as the G3 method. All of the calculations in this study have been performed using the Gaussian 03[42] program running on a Linux Beowulf cluster at Wake Forest University.

For each of the species under investigation, using the appropriate symmetry as the only constraint imposed, geometries were optimized fully in the gas phase at each model chemistry, namely a minimum energy structure located together with a calculation of the vibrational frequencies. The latter calculation is necessary not only to ensure that the optimized geometry corresponds to a local minimum but also to generate thermochemical data to be used in the calculation of equilibrium constants, as well as for a comparison with recorded infrared spectra.

Solvent effects were studied by performing self-consistent reaction field (SCRF) calculations using the polarizable continuum model (PCM)[43] on the MP2(full)/6-31++G** gas phase optimized geometry of each species. In this method, the solute is placed into a cavity within the solvent, the latter being modeled as a continuum of uniform dielectric constant. In this solvent model, the number of tessarae on each sphere was set to 60. Only one strong polar solvent, namely water, was studied. Because analytical gradients are available for a number of theoretical levels using PCM, the geometries of each molecule were optimized fully in aqueous solution at the HF, MP2(full) and B3LYP levels.



(1) (3)

Figure 2. Tautomerization of hydroxycyclopropenone. In enol structure **1** the $C_3-O_4-H_5$ bond angle is 108.8°. Not shown is the second enol structure (**2**) in which the orientation of the hydroxy group hydrogen atom 5 produces a $C_3-O_4-H_5$ reflex angle of 250.7°. Structure **3** is the diketone.

The changes in total energy, enthalpy, ΔH, and Gibbs free energy, ΔG, at a temperature T of 298.15 K are readily obtained from the results of electronic structure calculations. The last of these quantities is given by $\Delta G = \Delta H - T\Delta S$, where ΔS is the change in entropy. The equilibrium constant for tautomerization, K_T, is directly related to the Gibbs free energy, being defined by

$$K_T = \exp(-\Delta G/RT) \quad (1)$$

with $pK_T = -\log K_T$.

3. Results and Discussion

Ab initio and density functional theory calculations were performed on three structural isomers of $C_3H_2O_2$, whose molecular structures are illustrated in Figure 2, together with their atomic center numbers. They comprise two hydroxycyclopropenonone structures, corresponding to the enol form, and are labeled **1** and **2**. They differ in the orientation of the hydroxy group hydrogen atom. In structure **1** the MP2(full)/6-31++G** gas phase optimized $C_3-O_4-H_5$ bond angle is 108.8°, whereas for structure **2** (not shown in Figure 2) the reflex angle is 360° − 109.3° = 250.7°, the difference in orientations of the hydrogen in the two molecules being the obtuse angle 141.9°. Both of these species belong to the C_s point group. The third molecule, cyclopropanedione, labeled **3**, is the keto form and has C_{2v} symmetry.

Results are given in Tables 1 and 2 for the absolute and relative electronic energy in gas phase and in aqueous solution, respectively, computed at HF, MP2, CCSD and B3LYP-DFT, using the 6-31++G** basis set, and complete basis set and G3 methods. The polarizable continuum model was used to calculate the effect of the solvent. At each model chemistry considered, and irrespective of the phase, the keto form is higher in energy than the two enolates. For instance in the gas phase, at the MP2 level, cyclopropanedione is 10.0 kcal mol^{-1} higher in energy than species **1**, this difference increasing to 20.6 kcal mol^{-1} in the liquid medium. In general, the relative energy between keto and enol forms increases in solution in comparison to that found in the gas phase.

Presented in Table 3 are the gas and aqueous solution phase Gibbs free energy differences, evaluated at a temperature of 298.15 K and a pressure of 1 atm, at HF, MP2 and B3LYP levels of theory, and gas phase CBS-QB3, CBS-APNO and G3 results. Trends similar to that observed when electronic energies are compared are seen when the Gibbs free energy is examined. It is to be noted that the 6-31++G** basis set is large enough,

TABLE 1: Gas Phase Absolute Electronic Energy in Atomic Units (Hartrees) and Relative Energies (kcal mol^{-1}) for Hydroxycyclopropenone (Species 1 and 2) and Cyclopropanedione (Molecule 3), Evaluated at Different Levels of Theory, with the 6-31++G Basis Set**[a]

species	HF	MP2	CCSD	B3LYP	CBS-QB3	CBS-APNO	G3
1	−264.41348	−265.17853	−265.18937	−265.88964	−265.55045	−265.86794	−265.76506
2	+1.825	+1.737	+1.626	+1.662	+1.643	+1.603	+1.600
3	+13.999	+9.994	+8.358	+10.300	+10.926	+10.981	+10.628

[a] Also included are corresponding results obtained using the CBS-QB3, CBS-APNO and G3 methods.

TABLE 2: Absolute and Relative Electronic Energy in Atomic Units and kcal mol^{-1}, Respectively, at Different Levels of Theory for the Three Molecules in Aqueous Solution Using the Polarizable Continuum Solvent Reaction Field Model, with the 6-31++G Basis Set**

species	HF	MP2	B3LYP
1	−264.43654	−265.175563	−265.90890
2	+0.267	+0.440	+0.430
3	+24.670	+20.637	+20.339

TABLE 3: Gas (g) and Aqueous Solution Phase (PCM) Gibbs Free Energy Differences (in Atomic Units and kcal mol^{-1}) Evaluated at 298.15 K and 1 atm for the Three Molecules at Different Levels of Theory with the 6-31++G Basis Set**[a]

	1	**2**	**3**
HF (g)	−264.39309	+1.776	+12.637
MP2 (g)	−265.16212	+1.669	+8.173
B3LYP (g)	−265.87355	+1.552	+7.679
CBS-QB3 (g)	−265.53468	+1.569	+7.904
CBS-APNO (g)	−265.85116	+1.578	+9.567
G3 (g)	−265.74977	+1.561	+9.522
HF (PCM)	−264.42441	+0.180	+23.325
MP2 (PCM)	−265.16780	+0.259	+18.953
B3LYP (PCM)	−265.90118	+0.258	+18.078

[a] Also included are the corresponding results obtained with the use of CBS-QB3, CBS-APNO and G3 methods in the gas phase.

TABLE 4: PCM MP2(full)/6-31++G Calculated Optimized Geometry (Bond Lengths/Å and Angles/Degrees) in Aqueous Solution for the Three Isomers of $C_3H_2O_2$**[a]

1	**2**	**3**
C2−O1 = 1.2368	C2−O1 = 1.2375	C2−O1 = C3−O4 = 1.2163
C3−C2 = 1.4284	C3−C2 = 1.4213	C2−C3 = 1.483
C3−O4 = 1.3215	C3−O4 = 1.3197	C2−C5 = C3−C5 = 1.5151
O4−H5 = 0.9986	O4−H5 = 0.9992	C5−H6 = C5−H7 = 1.0929
C2−C6 = 1.4252	C2−C6 = 1.4274	A(1,2,3) = A(2,3,4) = 153.4
C3−C6 = 1.3619	C3−C6 = 1.3645	A(1,2,5) = A(4,3,5) = 145.9
C6−H7 = 1.0853	C6−H7 = 1.0854	A(3,2,5) = A(2,3,5) = 60.7
A(1,2,3) = 152.1	A(1,2,3) = 152.3	A(2,5,3) = 58.6
A(2,3,4) = 156.0	A(2,3,4) = 150.1	A(6,5,7) = 114.6
A(3,4,5) = 109.5	A(3,4,5) = 109.5	A(2,5,6) = A(3,5,6) = 118.1
A(1,2,6) = 150.9	A(1,2,6) = 150.5	A(2,5,7) = A(3,5,7) = 118.1
A(3,2,6) = 57.0	A(3,2,6) = 57.2	
A(2,3,6) = 61.4	A(2,3,6) = 61.6	
A(4,3,6) = 142.6	A(4,3,6) = 148.3	
A(2,6,3) = 62.2	A(2,6,3) = 61.2	
A(2,6,7) = 150.7	A(2,6,7) = 151.2	
A(3,6,7) = 147.7	A(3,6,7) = 147.6	

[a] See Figure 2 for atomic center numbers.

TABLE 5: Gas and Aqueous Solution Phase Equilibrium Constant, Reciprocal Equilibrium Constant and p*K* Value between the Various Isomeric Forms of $C_3H_2O_2$, Evaluated at the B3LYP/6-31++G Level**[a]

	K	K^{-1}	p*K*
	Gas Phase		
2 versus **1**	7.286×10^{-2}	13.72	1.138
3 versus **1**	2.351×10^{-6}	4.253×10^{5}	5.629
3 versus **2**	3.227×10^{-5}	3.099×10^{4}	4.491
	CBS-APNO		
2 versus **1**	6.969×10^{-2}	14.35	1.157
3 versus **1**	9.712×10^{-8}	1.030×10^{7}	7.013
3 versus **2**	1.394×10^{-6}	7.176×10^{5}	5.856
	PCM		
2 versus **1**	0.6471	1.545	0.1890
3 versus **1**	5.607×10^{-14}	1.784×10^{13}	13.25
3 versus **2**	8.665×10^{-14}	1.154×10^{13}	13.06

[a] The corresponding gas phase CBS-APNO results are also given. In the first row of each section, *K* refers to K_{eq} (equilibrium) and in the last two rows *K* refers to K_T (tautomerism).

the differences in relative energy and Gibbs free energy changing little with the use of complete basis set methods. The small differences in ΔG, however, will have a large effect on the value of the equilibrium constant (see below).

Displayed in Table 4 are the optimized bond lengths and angles for the three molecules in aqueous solution calculated with PCM at the MP2(full)/6-31++G** model chemistry. On comparing these results with those obtained in the gas phase at the same theoretical level, we see very little difference. Comparable bond lengths are found to agree to within 0.02 Å whereas respective bond angles differ by no more than a degree. The structural differences between the keto and enol forms are readily apparent from Table 4. Two different carbon−oxygen bond lengths occur in the enolates, C_2-O_1 and C_3-O_4, both of which are equal in the symmetric diketone. Again due to symmetry, two of the three carbon−carbon bond lengths are identical in cyclopropanedione, in contrast to the respective separations in the other two compounds, which are all unique, and in fact are all shorter. The order of the relative energies for the three species may be related to characteristic structural features present. In particular, relative stability in these isomers is influenced largely by the relative positions assumed by the two hydrogen atoms, whether both are bonded to carbon, as in the case of 1,2-cyclopropanedione, or to one carbon and one oxygen atom, as occurs in the two other conformers.

Table 5 contains gas and aqueous solution phase results for the equilibrium constant when the two enol structures are compared, and tautomeric equilibrium constants for the keto form relative to these two isomers, using the Gibbs free energy evaluated at the B3LYP/6-31++G** level, and eq 1. Also listed are the corresponding reciprocal constants, and values of $pK_i = -\log K_i$, i = eq (equilibrium), T (tautomerism). The corresponding gas phase CBS-APNO results are also presented. It is clear that hydroxycyclopropenone exists predominantly in the enol form with the ratio of enol **1** to the keto form (**3**) being approximately 425 000:1 in the gas phase at the B3LYP/6-31++G** model chemistry. With the CBS-APNO method this ratio increases to approximately 1.03×10^7:1, illustrating the importance of computing highly accurate free energy differences. The analogous ratios for the other enol, **3** versus **2**, are ∼31 000:1 using density functional theory, and ∼718 000:1 with the CBS-APNO method, each more than an order of magnitude less than that relative to species **1**, as indicated by their relative pK_T values. In solution phase the equilibrium is driven more strongly in the favor of the enol structures. The

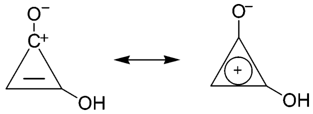


Figure 3. Aromatic resonance forms of hydroxycyclopropenone.

PCM approach yields $K_T = 5.61 \times 10^{-14}$ for **3** versus **1**, and 8.67×10^{-14} for **3** versus **2**, a 7.6 and 8.6 difference in pK_T values, respectively, over the B3LYP/6-31++G** results obtained in gas phase. The extra stability of the enol in aqueous solution is partly attributed to its greater polarity. This is confirmed by comparing the MP2(full)/6-31++G** computed dipole moments using PCM. For species **1** and **2** the dipole moments are 5.48 and 9.08 D whereas for cyclopropanedione it is calculated to be 4.26 D. A similar conclusion was drawn for cyclopropenone,[7] whose molecular electric dipole moment was measured by Stark shift to be 4.39 D, the large value due to the highly polar C═O bond. It is interesting to compare the gas phase results obtained in this study with those previously calculated for phenol.[35] In the present case, from Table 5 the pK_T for structure **1** relative to cyclopropanedione (**3**) is 5.6 compared to a value of 12.7 for the phenol−cyclohexadienone system. The direction of equilibrium is driven far more strongly in favor of the enol form in the latter system (by 7 orders of magnitude) than when compared to hydroxycyclopropenone. This may be attributed to the greater aromatic character exhibited in phenol, hydroxycyclopropenone being commonly termed as “pseudoaromatic”, rather than aromatic, which applies genuinely to phenol. Nevertheless, the direction of equilibrium is pushed greatly to the advantage of the enol structures due to the additional stabilization afforded by aromaticity in hydroxycyclopropenone, even overriding the effects of ring strain.

That hydroxycyclopropenone possesses aromatic character is most simply understood on the basis of elementary Hückel molecular orbital theory.[29] The conventional depiction of the enols **1** and **2** is that given in Figure 2. These structures are not aromatic, however. The three membered ring contains three π electrons. The aromatic forms are illustrated in Figure 3. It is in this sense that hydroxycyclopropenone is pseudoaromatic, being a combination of nonaromatic and aromatic resonance structures. The enols therefore have a cyclopropenone structure that satisfies the $4n + 2$ rule, with $n = 0$ in this case corresponding to a delocalized ring system with two π electrons. It is well-known that such cyclic species have extra aromatic stability. The keto isomer (**3**) on the other hand, with its methylene group, does not. As in cyclopropenone,[7] the effect of the carbonyl group in the enol is to withdraw electrons from the ring into the polar C═O bond resulting in the two π electron configuration. This is confirmed by considering Mulliken atomic charges in hydroxycyclopropenone. For O_1 and C_2 atoms at the MP2(full)/6-31++G** model chemistry in the gas phase, these are computed to be −0.66 and +0.51, respectively, giving rise to a polar carbonyl bond. It should also be mentioned that the aromatic nature of cyclopropenone (and other five-, seven-, and nine-membered cyclic polyenes), and the resulting stabilization produced by resonance, is well established.[7,29] In one recent study,[19] newly developed computational criteria for aromaticity were applied to fulvenes, ketocyclopolyenes, fulvenones, and diazocyclopolyenes, and their cations. These criteria included magnetic susceptibility exaltations, isomerization energies, aromatic stabilization energies, and nucleus independent chemical shifts. It was found that the trends observed from these new measures agreed with that predicted by Hückel theory. Although these new methods could be applied to the systems of interest in this study, they are beyond the scope of the present work but could, nonetheless, form the basis of a future investigation.

TABLE 6: Gas Phase Harmonic Frequencies (cm^{-1}), Zero-point Energies (kcal mol^{-1}), and Infrared Intensities (km mol^{-1}) for the Three Species Evaluated at the MP2(full)/6-31++G Level of Theory as Well as the Measured Infrared Frequencies of Hydroxycyclopropenone in an Ar Matrix Taken from Ref 4**

Measured IR Spectrum of Hydroxycyclopropenone in Ar Matrix[4]						
ν(O−H):	3589.5 m	3583.6 m	3491.0 m			
ν(C═O):	1859.6 m	1859.0 s	1857.2 s	1856.6 s	1853.2 s	
ν(C═C):	1659.3 s	1658.4 s	1657.6 s	1657.0 vs		
δ(O−H):	1336.9 m	1333.6 m	1319.3 m	1316.2 m	1308.0 m	1303.6 m

1	**2**	**3**
3836 (a′,143)	3794 (a′,69)	3245 (b_1,1)
3320 (a′,3)	3310 (a′,2)	3145 (a_1,7)
1948 (a′,498)	1964 (a′,514)	1876 (a_1,52)
1721 (a′,306)	1692 (a′,425)	1781 (b_2,229)
1339 (a′,303)	1389 (a′,13)	1400 (a_1,26)
1179 (a′,5)	1139 (a′,177)	1090 (a_1,133)
1107 (a′,3)	1099 (a′,4)	1077 (b_2,23)
878 (a′,12)	871 (a′,5)	1063 (a_2,0)
793 (a″,63)	790 (a′,30)	807 (a_1,18)
792 (a′,55)	780 (a″,38)	750 (b_2,14)
638 (a″,11)	645 (a″,2)	543 (b_2,1.3)
598 (a′,3)	597 (a′,8)	501 (b_1,0.3)
491 (a″,130)	501 (a″,118)	304 (a_1,4)
282 (a″,3)	280 (a″,34)	218 (a_2,0)
265 (a′,5)	278 (a′,6)	143 (b_1,14)
ZPE = 27.4 kcal mol^{-1}	ZPE = 27.3 kcal mol^{-1}	ZPE = 25.6 kcal mol^{-1}

In addition to evaluating equilibrium constants from thermochemical properties obtained from the results of a frequency calculation, the computed vibrational frequencies may themselves be compared with values obtained from experimentally measured infrared spectra. For hydroxycyclopropenone in an argon matrix the infrared spectrum has been recorded,[4] and the vibrational frequencies are given in Table 6, along with computed values at the MP2/6-31++G** level of theory in the gas phase, for this species and 1,2-cyclopropanedione. Also listed in Table 6 are the symmetry assignments and infrared intensities, as well as the zero point energy. On comparing the measured and simulated spectra, it is clear that hydroxycyclopropenone predominates over cyclopropanedione. In the experimental spectrum a band of medium intensity spanning approximately 50 cm^{-1}, centered around 3540 cm^{-1}, is attributed to O−H stretch, which occurs at ~3836 and 3794 cm^{-1} in the gas phase computed spectra of **1** and **2**, respectively. Additional O−H vibrations measured in the 1300−1335 cm^{-1} range occur at 1339 cm^{-1} in the gas phase spectrum of **1**. This stretching mode is obviously absent in cyclopropanedione, confirming the presence of the enol structure. A strong measured band spanning a range of 3 cm^{-1} around 1856 cm^{-1} is assigned to the C═O stretch and agrees well with the high-intensity peak computed at 1948 cm^{-1} in the gas phase spectrum of structure **1**, with the corresponding frequency in the keto form occurring at both lower wavenumber (1876 cm^{-1}) and intensity (52 km mol^{-1}). The high-intensity band at ~1720 cm^{-1} in the computed spectra of the enol, due to C═C stretch, compares nicely with those measured at ~1655 cm^{-1}, whereas the analogous band in the keto structure is found at a much higher wavenumber, 1781 cm^{-1}. Overall agreement between computed and observed values increases if the former are multiplied by a scale factor of 0.9427, the figure recommended[44] for frequency calculations performed at the MP2 level of theory. Needless to say, caution should of course be exercised when one compares frequencies measured in a matrix with those computed for systems in the gas phase.

The additional stabilization energy gained by the enol structures due to aromaticity is the major reason for driving the equilibrium in the direction of the enol form rather than in the direction of the keto structure, overcoming even the effects of ring strain present in these three-membered species. This is well-known in the case of phenol, where aromaticity is attributed to the preponderance of the former over cyclohexadienone, for which the equilibrium constant for this system has recently been calculated using ab initio methods[35] and found to agree remarkably well with the experimentally determined value. In addition to resonance stabilization, the greater polarity of hydroxycyclopropenone, due to the polar C═O bond, as reflected in its electric dipole moment, accounts for the predominance of the enol form over the keto structure in aqueous solution, as well as for the difference between the gas and solution phase equilibrium constant. The effects arising from aromaticity on the direction of equilibrium of the species investigated in this study (as well as their monothio- and dithio-substituted analogues[45]), and of phenol, is in contrast to other systems in which keto−enol tautomerism occurs and where aromaticity is not a factor, in which stabilization by the carbonyl bond generally favors the keto form in aliphatic carbonyl compounds possessing α-hydrogens.

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