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Tautomeric Properties and Gas-Phase Structure of 3-Chloro-2,4-pentanedione

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The tautomeric properties of α-chlorinated acetylacetone, 3-chloro-2,4-pentanedione $CH_3C(O)$-CHCl−C(O)-CH_3, have been investigated by gas electron diffraction (GED) and quantum chemical calculations (B3LYP and MP2 approximations with different basis sets up to cc-pVTZ). Analysis of the GED intensities resulted in the presence of 100(2)% enol tautomer at 269(8) K. The following skeletal geometric parameters (r_{h1} values) of the molecule, which possesses C_s symmetry, were derived: $r(C{=}C) = 1.378(3)$ Å, $r(C{-}C) = 1.450(3)$ Å, $r(C{=}O) = 1.243(3)$ Å, $r(C{-}O) = 1.319(3)$ Å, $r(O{-}H) = 1.001(4)$ Å, $r(C{-}Cl) = 1.752(4)$ Å, $\angle C{-}C{=}C = 121.3(1.0)°$, $\angle C{=}C{-}O = 119.9(1.2)°$, $\angle C{-}C{=}O = 119.1(1.2)°$. Due to very small contributions of the keto tautomer in α-chlorinated acetylacetone and its parent species, the effect of α-chlorination on tautomeric properties cannot be derived from experimental data. Quantum chemical calculations (B3LYP/6-31G**, B3LYP/cc-pVTZ, and MP2/cc-pVTZ) predict that α-chlorination of acetylacetone has no pronounced effect on the tautomeric properties. On the other hand, similar calculations for 1-chloro-1,3-butanedion, ClC-(O)-CH_2−C(O)CH_3, demonstrate that chlorination in one β position destabilizes the enol tautomer. In both chlorinated species the enol form is strongly preferred.

Introduction

β-Diketones (β-dicarbonly compounds) have been widely studied both experimentally and theoretically, because they are important organic reagents and have interesting properties.[1] Keto−enol tautomerization of β-diketones has been investigated extensively. It is well known that the preference of the enol or keto tautomeric form of $R_1C(O){-}CHR_3{-}C(O)R_2$ depends strongly on the substituents R_1, R_2, and R_3. Furthermore, the keto/enol ratio also depends strongly on temperature, solvent and phase.[1]

Malonaldehyde (MA) or propandial ($R_1 = R_2 = R_3 = H$) is the most simple β-dicarbonyl compound. During the past decades, a considerable amount of experimental as well as theoretical work for MA has been reported. The predominance of the enol form of MA is confirmed in the gas phase at low pressure by FT-IR[2] and in chloroform solutions by NMR.[3] Microwave spectroscopy, as well, results in an enol structure with C_s symmetry.[4] CBS-4 calculations[5] predict the enthalpy of the enol form of MA to be lower by 3.53 kcal/mol than that for the keto tautomer. According to the calculated free energy difference $\Delta G^0_{298} = (G^0_{keto} - G^0_{enol}) = 1.48$ kcal/mol, the equilibrium composition of MA at 298 K is 7.6% of diketo and 92.4% of enol form. On the other hand, DFT/B3LYP calculations[6] predict $\Delta E = 7.6$ kcal/mol, corresponding to the exclusive enol form of MA at 298 K.

The dimethyl derivative of MA, acetylacetone (AcAc) ($R_1 = R_2 = CH_3$, $R_3 = H$) is known to exist in two forms, keto and enol, but rather different relative concentrations of the two tautomers were reported in the literature. NMR studies[7−10] show the predominance of the enol tautomer from 81% in pure liquid[10] to 91% in CCl_4 solution.[7] Temprado et al.[11] point out that the enol tautomer is more volatile and therefore its concentration in the gas phase should be even higher than that in the liquid (81%). Irving and Wadso[12] derived from the experimental enthalpy of vaporization (10.0 ± 0.1 kcal/mol) for the process

$$\text{AcAc (liquid, 81.4\% enol)} \rightarrow \text{AcAc (gas, 93.3\% enol)}$$

the tautomeric composition of AcAc in the gas phase. ^{1}H NMR studies[13] show that the enol form of AcAc predominates in the liquid, solution, and gas phase at all temperatures under investigation. In this study $\Delta H^0 = (H^0_{keto} - H^0_{enol}) = 4.66(18)$ kcal/mol, $\Delta S^0 = 8.26$ cal/(mol K) and $\Delta G^0_{298} = 2.20(45)$ kcal/mol was derived for the gas phase and the percentage of the diketo form at 298 K is 2.5(13) %. On the other hand, about 10% of the diketo tautomer was derived from matrix FT-IR spectra of AcAc.[2] From photoelectron spectra at different temperatures[14] the equilibrium constant for the keto ↔ enol reaction in the gas phase and its temperature dependence has been obtained. From the values of the equilibrium constant we derived enol concentrations of 73% at 25 °C, 60% at 100 °C, and about 50% at 175 °C.[14]

Four different electron diffraction studies of AcAc have been reported with slightly conflicting results, as well.[15−18] Experimental intensities recorded at room temperature[16,17] have been interpreted in terms of the presence of the enol form only. A study performed at 105 °C resulted in an enol contribution of 66 ± 5%,[15] in good agreement with the value derived from the photoelectron spectra at 100 °C[14] (see above). An enol contribution of 78 ± 4% at 155 °C was reported in a recent GED investigation.[18] This value is in agreement with the concentration obtained from the gas-phase NMR values (79% enol at 155 °C).[13] It should be noted that the GED geometries of the enol tautomers reported in refs 15−18 as well as those of the diketo structures reported in refs 15 and 18 are rather different.

According to quantum chemical calculations, the keto ↔ enol equilibrium in the case of acetylacetone should be shifted

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TABLE 1: Optimized Relative Energies and Gibbs Free Energies of the Enol Tautomer and Diketo Conformers of 3-Chloro-2,4-pentanedione

	enol	diketo (ac,sp)	diketo (sc,sc)
		MP2/6-31G**	
τ(O1C2C1C3)	0.0	94.5	88.1
τ(O2C3C1C2)	0.0	16.9	90.7
E_{rel}, kcal/mol	0.0	2.21	1.56
G^0_{rel}, kcal/mol	0.0	−0.01	0.16
		MP2/cc-pVTZ	
τ(O1C2C1C3)	0.0	94.0	87.7
τ(O2C3C1C2)	0.0	17.6	91.4
E_{rel}, kcal/mol	0.0	5.47	4.98
G^0_{rel}, kcal/mol	0.0	3.29	3.46
		B3LYP/6-31G**	
τ(O1C2C1C3)	0.0	97.5	83.9
τ(O2C3C1C2)	0.0	23.7	92.3
E_{rel}, kcal/mol	0.0	7.64	7.17
G^0_{rel}, kcal/mol	0.0	5.56	5.65
		B3LYP/cc-pVTZ	
τ(O1C2C1C3)	0.0	95.6	84.9
τ(O2C3C1C2)	0.0	25.1	90.2
E_{rel}, kcal/mol	0.0	7.39	7.22
G^0_{rel}, kcal/mol	0.0	5.29	5.49

strongly to enol. CBS-4 calculations[5] performed for AcAc lead to a value of $\Delta G^0_{298} = (G^0_{\mathrm{keto}} - G^0_{\mathrm{enol}}) = 2.65$ kcal/mol and only 1.1% of diketo form at 298 K. DFT/B3LYP calculations[6] predict $\Delta G^0_{298} = 3.95$ kcal/mol and strong predominance of the enol tautomer (only 0.1% of diketo).

In the present study we are interested in the effect of chlorination at the α position on the tautomeric properties investigating 3-chloro-2,4-pentanedione ($R_1 = R_2 = CH_3$, $R_3 = Cl$). A previous GED study of malonyl dichloride ($R_1 = R_2 = Cl$, $R_3 = H$) reported that β−dichloro-substituted MA exists as a mixture of two nonplanar diketo conformers at 40 °C.[19] Thus, chlorination of MA at both β positions leads to strong preference of the diketo form and no enol tautomer was observed. In an NMR study of liquid 3-substituted pentane-2,4-diones[9] it was pointed out that electron-withdrawing substituents such as Cl in α position increases the enol content. Different NMR investigations of 3-chloro-2,4-pentanedione result in 84%[9] and 94%[8,10] of enol form in the pure liquid at room temperature and in 91% of enol in CCl_4 solution.[7] The IR spectra of 3-chloro-2,4-pentanedione[20] show some amount of the keto form in the liquid phase. To determine the tautomeric properties of 3-chloro-2,4-pentanedione in the gas phase, we performed a GED study, which is supplemented by quantum chemical calculations. Furthermore, the influence of one Cl-atom in β position was studied by performing quantum chemical calculations for 1 chloro-1,3-butanedione, ClC(O)-CH_2−C(O)-CH_3, ($R_1 = Cl$, $R_2 = CH_3$, $R_3 = H$).

Quantum Chemical Calculations

All quantum chemical calculations were performed with the program set GAUSSIAN 03.[21] The geometries of the enol and diketo tautomers of 3-chloro-2,4-pentanedione and 1-chloro-1,3-butanedione were optimized with the MP2 and B3LYP methods and 6-31G** and cc-pVTZ basis sets. The relative energies ($\Delta E = E_{\mathrm{keto}} - E_{\mathrm{enol}}$) and relative free energies ($\Delta G^0 = G^0_{\mathrm{keto}} - G^0_{\mathrm{enol}}$) obtained with the different computational methods are summarized in Tables 1 and 2.

TABLE 2: Optimized Dihedral Angles, Relative Energies and Gibbs Free Energies of the Enol and Diketo Conformers of 1-Chloro-1,3-butanedione

	enol 1[a]	enol 2[a]	diketo (sp,ac)	diketo (ac,sp)
		MP2/6-31G**		
τ(OC(Cl)CC)	0.0	0.0	1.3	101.3
τ(OC(CH_3)CC)	0.0	0.0	109.4	−13.7
E_{rel}, kcal/mol	0.0	7.84	1.91	2.22
G^0_{rel}, kcal/mol	0.0	6.62	−0.82	−0.36
		MP2/cc-pVTZ		
τ(OC(Cl)CC)	0.0	*b*	2.1	101.5
τ(OC(CH_3)CC)	0.0	*b*	106.7	−15.7
E_{rel}, kcal/mol	0.0	*b*	5.21	5.30
G^0_{rel}, kcal/mol	0.0	*b*	2.21	2.49
		B3LYP/6-31G**		
τ(OC(Cl)CC)	0.0	*b*	4.1	101.6
τ(OC(CH_3)CC)	0.0	*b*	119.5	−14.8
E_{rel}, kcal/mol	0.0	*b*	6.27	7.01
G^0_{rel}, kcal/mol	0.0	*b*	3.35	4.04
		B3LYP/cc-pVTZ		
τ(OC(Cl)CC)	0.0	*b*	4.1	99.0
τ(OC(CH_3)CC)	0.0	*b*	116.1	−13.5
E_{rel}, kcal/mol	0.0	*b*	6.81	7.31
G^0_{rel}, kcal/mol	0.0	*b*	3.69	4.27

[a] Enol 1: O−H bond is adjacent to the methyl group, ClC(O)−CH═C(OH)CH_3. Enol 2: O−H bond is adjacent to Cl, ClC(OH)═CH−C(O)CH_3. [b] Not stable conformer according to this method.

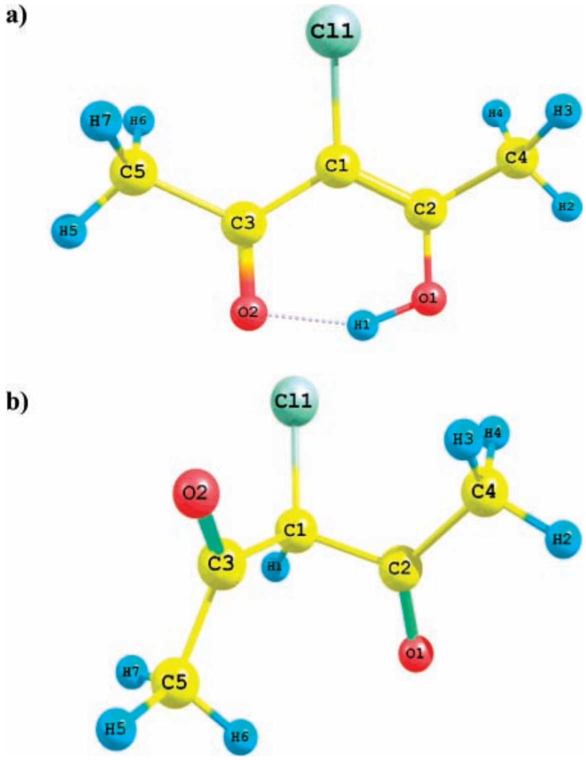

Figure 1. Molecular structures of enol tautomer (a) and diketo tautomer (b) of 3-chloro-2,4-Pentanedione.

(a) 3-Chloro-2,4-pentanedione. To detect all possible diketo conformers, the two-dimensional potential energy surface has been scanned with the B3LYP/6-31G** method. The torsional angles τ(O1C2C1C3) and τ(O2C3C1C2) were varied in steps of 20° with full optimization of all other parameters (see Figure 1 for atom numbering). The potential surface (Figure 2) possesses two minima for (ac,sp)[22] conformer with τ(O1C2C1C3) about 100° and τ(O2C3C1C2) about 20° and for (sc,sc)[22] conformer in which both dihedral angles are close to 90°.

The values in Table 1 indicate that the predicted relative energies of diketo and enol tautomers depend strongly on the computational method. For comparison of calculated and experimental tautomeric composition, Gibbs free energies must

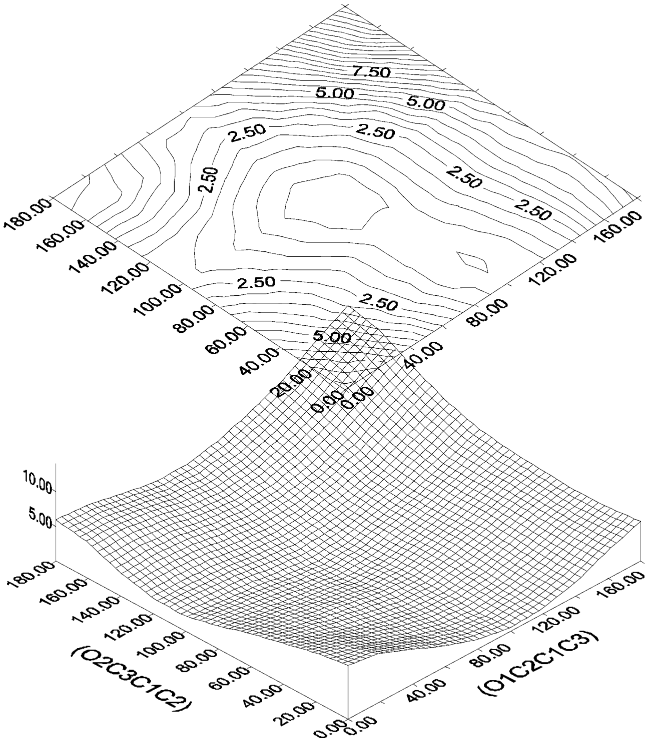

Figure 2. Potential energy surface for 3-chloro-2,4-pentanedione obtained by rotation around C−C bonds.

be applied, instead of the relative energies. G^0 values include zero-point energies, temperature corrections, and entropies. These contributions depend primarily on low-frequency vibrations, which differ appreciably between keto and enol tautomers. For example, the lowest frequency for the diketo form is predicted to be 42 and 47 cm^{-1} (for (ac,sp) and (sc,sc) conformers, respectively) and that of the enol form to be 70 cm^{-1} (B3LYP/cc-pVTZ). Predictions concerning the tautomeric equilibrium depend strongly on the computational method, as well. Whereas both B3LYP and MP2/cc-pVTZ calculations predict a strong preference of the enol tautomer, the MP2 method with small basis sets predicts small ΔG^0 values (−0.01 and 0.16 kcal/mol for (ac,sp) and (sc,sc) conformers, respectively), corresponding to about equal contributions of both, enol and keto tautomers.

The geometric parameters for the enol tautomer that were derived with the MP2 and B3LYP methods with the same basis sets (cc-pVTZ) are listed in Table 3, together with the experimental results. Vibrational amplitudes and corrections, $\Delta r = r_{h1} - r_a$, were derived from theoretical force fields (B3LYP/cc-pVTZ) with the method of Sipachev, using the program SHRINK.[23] The values for the enol form are listed in Table 4.

(b) 1-Chloro-1,3-butanedione. A scan of the potential energy surface with the B3LYP/6-31G** method in steps of 20° of the dihedral angles τ(OC(Cl)CC) and τ(OC(CH$_3$)CC) demonstrates the existence of two stable diketo forms of 1-chloro-1,3-butanedione (Figure 3). Calculations for two possible enol conformers were performed. According to both B3LYP and MP2/cc-pVTZ calculations only one stable enol form with the O−H bond adjacent to the methyl group, ClC(O)−CH═C(OH)-CH$_3$ (enol 1), exists. If a starting geometry with the O−H bond adjacent to Cl, ClC(OH)═CH−C(O)CH$_3$, is used, the O−H bond flips from Cl to the acetyl group and the geometry optimization converges toward the “enol 1” form. For this compound as well, the predicted tauomeric properties depend strongly on the computational method. The data in Table 2 show that both B3LYP calculations and the MP2 approximation with large basis sets predict a strong preference for the enol form, whereas the MP2 method with small basis sets predicts a preference for the keto tautomer.

TABLE 3: Experimental and Calculated Geometric Parameters of the Enol Tautomer of 3-Chloro-2,4-pentanedione[a]

parameters	GED (r_{h1}, α_{h1})[b]	B3LYP/cc-pVTZ	MP2/cc-pVTZ
r(C1−C2)	1.378(3)	1.374	1.371
r(C1−C3)	1.450(3)[c]	1.445	1.447
r(C2−C4)	1.497(3)[c]	1.492	1.489
r(C3−C5)	1.508(3)[c]	1.503	1.499
r(C2−O1)	1.319(3)	1.321	1.324
r(C3−O2)	1.243(3)[c]	1.245	1.247
r(C4−H2)	1.079(4)	1.087	1.085
r(C4−H3)	1.083(4)[c]	1.091	1.089
r(C5−H5)	1.078(4)[c]	1.086	1.085
r(C5−H6)	1.083(4)[c]	1.091	1.089
r(C5−H7)	1.083(4)[c]	1.091	1.089
r(O1−H1)	1.001(4)[c]	1.009	1.007
r(C1-Cl)	1.752(4)	1.758	1.735
∠C2C1C3	121.3(1.0)	121.6	121.2
∠C1C2O1	119.9(1.2)	120.6	120.9
∠C1C3O2	119.1(1.2)	119.7	120.1
∠C1C2C4	124.5(2.2)	124.6	123.9
∠C1C3C5	121.0(2.2)	120.6	119.6
∠H2C4C2	108.2(2.5)	109.3	109.1
∠H3C4C2	109.6(2.5)[c]	110.6	110.3
∠H5C5C3	108.0(2.6)	108.9	108.9
∠H6C5C3	109.9(2.6)[c]	110.8	110.4
∠H3C4H2	110.3(3.9)	109.8	110.0
∠H6C5H5	110.3(3.9)[c]	109.8	110.0
∠H1O1C2	106.1[d]	106.1	104.8

[a] Distances in Å and angles in degrees. For atom numbering see Figure 1. [b] Uncertainties in r_{h1} $\sigma = (\sigma_{sc}^2 + (2.5\sigma_{LS})^2)^{1/2}$ ($\sigma_{sc} = 0.002r$, σ_{LS}, standard deviation in least-squares refinement), for angles $\sigma = 3\sigma_{LS}$. [c] Difference to previous parameter fixed to calculated (B3LYP/cc-pVTZ) value. [d] Not refined.

Structure Analysis

The heaviest ion in the mass spectrum was the parent ion $[C_5H_7O_2Cl]^+$ (Table 6).This proves that monomers are present in the vapor at the conditions of the GED experiment. The experimental radial distribution function (Figure 4) was derived by Fourier transformation of the experimental intensities. Model calculations for 3-chloro-2,4-pentanedione, CH$_3$C(O)−CHCl−C(O)CH$_3$, demonstrate that radial distribution functions for enol and keto tautomers differ very strongly (see Figure 4). Differences occur in the region of bonded distances as well as for nonbonded distances. The experimental curve can be reproduced reasonably well only with the enol tautomer.

Therefore, in the least-squares analysis only the enol form was considered. The differences between all C−H and O−H bond lengths, between the C3−O2 and C2−O1 bond lengths and between all C−C bond lengths were restrained to calculated values (B3LYP/cc-pVTZ) as well as the orientation of CH$_3$ groups. A planar skeleton with overall C_s symmetry was assumed. Starting parameters from B3LYP/cc-pVTZ calculation were refined by a least-squares procedure of the molecular intensities. Independent r_{h1} parameters were used to describe the molecular structure. Vibrational amplitudes were refined in groups with fixed differences. With the above assumptions four bond distances and eight bond angles (see Table 3) were refined simultaneously with eight groups of vibrational amplitudes. There were three correlation coefficients, that had values larger than |0.7|: (∠C1C2O1)/(∠C1C3O2) = −0.95, (∠C1C2C4)/(∠C1C3C5) = −0.99, (∠H2C4C2)/(∠H5C5C3) = −0.94.

The best agreement factor resulted for 100% enol form with R_f = 4.6%. Several least-squares refinements were performed

TABLE 4: Interatomic Distances, Vibrational Amplitudes and Vibrational Corrections for the Enol Conformer (Excluding Nonbonded Distances Involving Hydrogen)[a]

	r_{h1}	l(GED)	l (B3LYP/ cc-pVTZ)	$r_{h1} - r_a$
O1−H	1.001(4)	0.082(3) *l*1	0.080	−0.0008
C5−H5	1.078(4)	0.078(3) *l*1	0.076	0.0017
C4−H2	1.079(4)	0.078(3) *l*1	0.077	0.0017
C4−H4	1.083(4)	0.079(3) *l*1	0.077	0.0018
C4−H3	1.083(4)	0.079(3) *l*1	0.077	0.0018
C5−H7	1.083(4)	0.078(3) *l*1	0.077	0.0018
C5−H6	1.083(4)	0.078(3) *l*1	0.077	0.0018
C3−O2	1.243(3)	0.042(3) *l*1	0.040	−0.0004
C2−O1	1.319(3)	0.045(3) *l*1	0.044	0.0010
C1−C2	1.378(3)	0.046(3) *l*1	0.044	0.0002
C1−C3	1.450(3)	0.050(3) *l*1	0.049	0.0020
C2−C4	1.497(3)	0.051(3) *l*1	0.049	0.0003
C3−C5	1.508(3)	0.052(3) *l*1	0.050	0.0006
C1−Cl	1.752(4)	0.050(3) *l*2	0.049	0.0008
C1···O2	2.324(12)	0.048(3) *l*3	0.054	0.0026
C1···O1	2.335(11)	0.047(3) *l*3	0.054	0.0022
C5···O2	2.385(24)	0.052(3) *l*3	0.058	0.0044
C4···O1	2.385(22)	0.054(3) *l*3	0.060	0.0040
C2···C3	2.464(6)	0.049(3) *l*3	0.055	0.0042
O1···O2	2.471(10)	0.080(3) *l*3	0.086	−0.0036
C1···C4	2.545(23)	0.055(3) *l*3	0.061	0.0026
C1···C5	2.574(24)	0.057(3) *l*3	0.063	0.0024
C2···Cl	2.708(6)	0.056(2) *l*4	0.060	0.0037
C3···Cl	2.768(6)	0.058(2) *l*4	0.062	0.0075
C2···O2	2.771(17)	0.065(2) *l*4	0.069	0.0017
C3···O1	2.789(20)	0.068(2) *l*4	0.072	0.0025
C5···Cl	3.094(44)	0.095(3) *l*5	0.096	0.0043
C4···Cl	3.099(43)	0.094(3) *l*5	0.095	0.0040
C2···C5	3.841(18)	0.061(2) *l*6	0.064	0.0098
C3···C4	3.871(16)	0.062(2) *l*6	0.064	0.0095
O2···Cl	3.914(10)	0.056(2) *l*6	0.059	0.0106
O1···Cl	3.938(10)	0.056(2) *l*6	0.059	0.0080
C4···O2	4.268(18)	0.080(8) *l*7	0.075	0.0071
C5···O1	4.296(21)	0.083(8) *l*7	0.078	0.0104
C4···C5	5.119(11)	0.095(10) *l*8	0.078	0.0170

[a] Values in Å. Error limits for the amplitudes are 3σ values. For atom numbering see Figure 1.

for mixtures of enol and keto tautomers. R_f factors of 5.3 and 5.7% were obtained for 2 or 5% contributions of the (sc,sc) keto conformer and of 5.4 and 6.2% for 2 and 5% contributions of the (ac,sp) keto conformer. Using Hamilton's criteria[24] we obtain a tautomeric composition of 100(2)% enol. Final results of the least-squares analysis are given in Table 3 (geometric parameters) and Table 4 (vibrational amplitudes). The refined geometrical parameters are rather similar to those predicted by the quantum chemical calculations.

Discussion

The primary interest of this study was the effect of chlorination in α position of AcAc on the tautomeric properties. According to an NMR study of pure liquids at 33 °C the enol contribution increases from 81% in AcAc to 94% in 3-chloro-2,4-pentanedione.[10] Rather different values for the enol contribution of AcAc in the gas phase at room temperature have been reported, ranging from 97.5(13)% to 73% (see Introduction). According to our results the enol contribution of 3-chloro-2,4-pentanedione in the gas phase is 100(2)%. Thus, the observed trend that α-chlorination of AcAc stabilizes the enol form in the liquid state[9,10] cannot be confirmed by the experiments in the gas phase, since the keto contribution is very small in both compounds and equal within the experimental uncertainties.

Tautomeric properties predicted by quantum chemical calculations for AcAc and for α- and β-chlorinated derivatives depend strongly on the computational method. Results for AcAc which have been reported in the literature predict enol contributions of 98.9%[5] and 99.9%.[6] Our calculations for AcAc predict enol percentages of 100% (B3LYP/6-31G** and B3LYP/cc-pVTZ), of 99.9% (MP2/cc-pVTZ), and of 70% (MP2/6-31G**). Thus, all except one calculation predict the enol contribution of AcAc to be higher than 98%. These calculations reproduce closely the gas-phase NMR value (97.5(13)%).[13] Only the MP2/6-31G** method predicts a much smaller enol contribution of 70% at room temperature. Previous tautomeric studies of $CH_3C(O)-CH_2-C(O)OCH_3$[25] and of $CH_3C(O)-CH_2-C(O)NH_2$,[26] have demonstrated, that the MP2/6-31G** method strongly underestimates the enol contribution compared to results derived from GED experiments. Thus, we expect that this method also fails to predict the tautomeric properties of AcAc.

For 3-chloro-2,4-pentanedione the experimental result (enol contribution 100(2)%) is reproduced correctly by most computational methods which predict 100% enol. For this compound

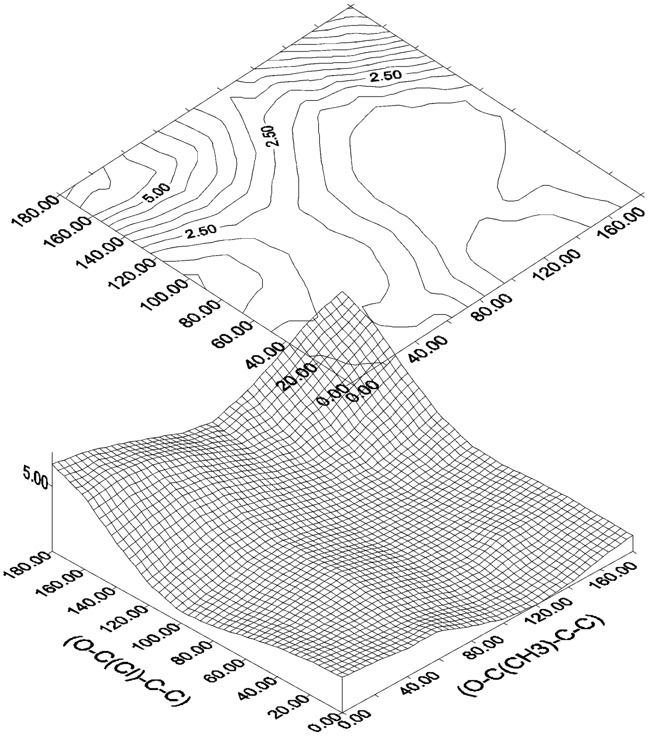

Figure 3. Potential energy surface for 1-chloro-1,3-butanedione obtained by rotation around C−C bonds.

TABLE 5: Conditions of GED Experiment

nozzle-to-plate distance, mm	338	598
fast electrons beam, μA	0.46	0.45
accelerating voltage, kV	70.5	70.4
electron wavelength, Å	0.04470(4)	0.04472(3)
temperature of effusion cell, K	267(5)	271(5)
ionization voltage, V	50	50
exposure time, s	70−80	50−60
residual gas pressure, Torr	2.8×10^{-6}	5.1×10^{-6}

TABLE 6: Mass Spectral Data of the Vapor of $C_5H_7O_2Cl$[a]

ion[b]	m/e	relative abundance, %
$[M]^+$	136	8.7
	134	27.3
$[M-CH_3]^+$	121	15.0
	119	46.5
$[M-C(O)CH_3]^+$	91	5.7
$[CC(O)CH_3]^+$	55	15.1
$[C(O)CH_3]^+$	43	100

[a] Only peaks with abundance ≥5%. [b] M = $C_5H_7O_2Cl$.

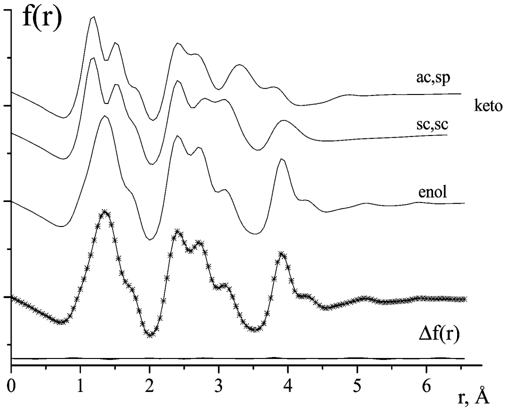

Figure 4. Experimental and calculated radial distribution functions and difference curve for the enol.

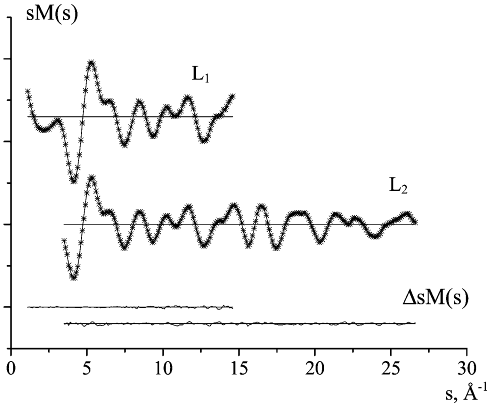

Figure 5. Experimental (dots) and calculated (solid lines) modified molecular intensity curves and residuals (experimental-theoretical) at two nozzle-to-plate distances ($L_1 = 598$ mm, $L_2 = 338$ mm).

again the MP2/6-31G** method which results in only 36% of enol contribution at room temperature, fails to reproduce tautomeric properties. The experimental trend for liquid AcAc that α-chlorination stabilizes the enol form, is not confirmed by our calculations, which predict slightly lower ΔG^0 values for the chlorinated species (see Table 1) than for AcAc ($\Delta G^0 = 5.56$ vs 5.99 kcal/mol from B3LYP/6-31G**, 5.29 vs 7.04 kcal/mol from B3LYP/cc-pVTZ, and 3.29 vs 3.89 kcal/mol from MP2/cc-pVTZ).

After having established, that of α-chlorination in AcAc has no pronounced effect on the tautomeric properties in the gas phase, we are interested in the effect of β-chlorination. In previous studies we established a rule that diketones of the kind $R_1C(O)-CH_2-C(O)R_2$ exist predominantly in the enol form, if R_1 and R_2 belong to group 1 (H, CH_3, $C(CH_3)_3$, and CF_3) and as keto tautomers, if R_1 and R_2 belong to group 2 (F, Cl, OCH_3, and NH_2).[26] Thus, a previous GED study for $ClC(O)-CH_2-C(O)Cl$, in which both methyl groups in AcAc are substituted by chlorine, demonstrated that this compound exists only in the diketo form. Two GED studies for diketones with R_1 from group 1 and R_2 from group 2 ($CH_3C(O)-CH_2-C(O)-OCH_3$ and $CH_3C(O)-CH_2-C(O)NH_2$) resulted in mixtures of enol and keto forms.[25,26] Therefore, one might expect such a mixture of both tautomers to exist also for $CH_3C(O)-CH_2-C(O)Cl$, which contains substituents from both groups.

Since no experimental data are available for this compound, calculations were performed with the same methods as applied for the α-chlorinated AcAc. The results are summarized in Table 2. Excluding the result of the MP2/6-31G** method, which has failed to predict tautomeric properties in many other cases, the calculations predict again a strong preference of the enol form (96−100%). The ΔG^0_{rel} values for the keto forms of $CH_3C(O)-CH_2-C(O)Cl$ are slightly lower than those of AcAc and the α-chlorinated species. Thus, our calculations predict that β-chlorination in AcAc slightly destabilizes the enol tautomer.

Experimental Section

The electron diffraction patterns and mass spectra were recorded simultaneously using the techniques described previously.[27,28] The conditions of the GED/MS experiment and the relative abundance of the characteristic ions of $C_4H_7O_2Cl$ are shown in the Tables 5 and 6, respectively.

The temperature of the molybdenum effusion cell was measured by a W/Re-5/20 thermocouple that was calibrated by the melting points of Sn and Al. The wavelength of electrons was determined from diffraction patterns of polycrystalline ZnO. The optical densities were measured by a computer controlled MD-100 (Carl Zeiss, Jena) microdensitometer.[29] The molecular intensities sM(s) were obtained in the s-ranges 3.5−26.6 and 1.1−14.6 $Å^{-1}$ for the short and long nozzle-to-plate distance, respectively ($s = (4\pi/\lambda) \sin \theta/2$, λ is electron wavelength and θ is scattering angle). The experimental and theoretical intensities sM(s) are compared in the Figure 5.

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