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The evidence for the occurrence of tautomeric structures for selected aldehydes and thioaldehydes

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ABSTRACT

Mass spectra of selected aldehydes and thioaldehydes have been analyzed and specific fragmentation assignments have been done to keto and enol tautomers, although many peaks can be assigned to both forms (i.e. mass spectra are superimposed on one another).

The enolization rate for aldehydes is generally favored by the increase in the steric effect caused by α substitution to the carbonyl group.

The analysis of the corresponding mass spectra has allowed to establishing an acceptable correlation between selected ion abundances ratios and approximate enolization equilibrium constants (carried out by means of DFT calculations).

The influence of temperature on the enol/keto selected fragments abundance ratios (for different aldehydes and thioaldehydes and for different pair of ions of the same compound whenever possible) is studied in order to estimate the enthalpy difference for the tautomeric equilibria.

The results indicate that the thioketo–thioenol equilibrium can be studied by mass spectrometry and the ionization in the ion source have negligible effect on the position of that equilibrium.

1. Introduction

The understanding of the nature of tautomeric equilibria is relevant to study several issues from both organic chemistry and biochemistry [1,2].

There has been a considerable interest in the enolization of carbonyl compounds for many years [3] and excellent methods have been developed for the generation of simple enols of aldehydes and ketones in solution [4,5]. Monofunctional enols have been found to be reactive intermediates in numerous organic reactions, e.g., electrophilic substitution to carbonyl compounds, oxy-Cope, Conia, and Carrol rearrangements, retro-Diels alder reactions, etc. In many of these reactions, the enolization of the carbonyl compound is the rate-determining step. Therefore, a change in the reaction conditions (e.g., substituent effect) can decrease the activation energy for the enolization and lead to an increase in reaction rate and yield [6].

Data about stability and the short lifetime of aldehyde and ketone enol can be found in the literature [7]. Guthrie [8] published that the enol content of simple carbonyl compounds can be estimated as the ratio of rate constants for acid catalyzed enolization of the carbonyl compound and acid-catalyzed hydrolysis of the corresponding methyl enol ether.

The enol isomers of simple monofunctional aldehydes and ketones are generally quite unstable and revert to their carbonyl tautomers rapidly. A notable exception to this behavior is provided by a group of crowded enols studied by Fuson et al. [9,10] in a classic series of investigations. Fuson's enols have bulky aryl substituents, such as mesityl or duryl, attached to their carbon–carbon double bonds. They are stable substances that can be isolated, and, if the crowding is sufficiently severe, they resist conversion to their keto isomers strongly. Keto-enol equilibrium constants for some of these crowded systems have been determined only recently, and these new studies have shown that these enols are stable, not only because the barriers for their keto-enol interconversion are high but also because the enols themselves have unusual thermodynamic stability.

However, enols can be dramatically stabilized by the introduction of bulky group onto the α carbon to the carbonyl group [11,12]; in some cases the enol may then be the thermodynamically stable tautomer [13], not kinetically though [14]. The chemistry of enols, particularly those derived from carbonyl containing compounds other than ketones, including carboxylic acids and esters, has been of some interest [15,16].

Mass spectrometry represents a very sensitive method for the study of tautomeric equilibria since it is capable of detecting tau-

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tomeric forms which make only minor contributions and which might go undetected using other techniques. Previous studies examine the effect of the nature of substituents on the tautomerism of 5-triazinones in gas phase using mass spectrometry [17]. The other compounds like 2,4-hidroxyquinolines were also studied by this technique [18].

All studies of keto-enol tautomers of carbonyl compounds were conducted on ions produced in the gas phase [19–21].

The mass spectrometry seems to be very informative for studying and identifying tautomers, because in this case external factors like solvents, intermolecular interactions, etc., can be excluded by transferring the tautomeric system into the gas phase, where the process becomes truly unimolecular [22]. It has been proved in the case of keto-enol tautomerism of a series of 1- and 3-substituted acetylacetones [23] and a variety of carbonylic and thiocarbonilic compounds [24–33].

On the other hand, the tautomerism of organic compounds has been subject of extensive theoretical studies using various quantum-mechanical statistical–physical approaches [34].

In previous studies [27,29] theoretical calculation has proved to be useful in the assignation of tautomeric structures based on mass spectrometric data. Besides, the route to the several fragmentations can only be rationalized by invoking a specific tautomer for the parent ions [35].

This work deals with the study of keto-enol equilibria for some aldehydes and thio analogues by resorting to mass spectrometry and DFT-B3LYP with the 6-31G(d,p) basis sets calculations.

The analysis of temperature changes on the injection system of a mass spectrometer has demonstrated that hydrogen/deuterium exchange (via enol form) occurs inside the injection system prior to ionization, which can be considered as an evidence of the reach of the equilibrium into the injection system and the lack of any contribution to the mass spectral data (used to evaluate these equilibria) by tautomerization of radical ions [36,37]. In fact, it has been claimed that tautomerization also occurs in the molecular ions proposed that enolization should be considered to occur before ionization, since no evidence of tautomerism of ionic species could be observed [38].

This methodology has been already used for the calculation of heats of tautomerization of selected thioamides and measurably good results have been found. Very good correlations with theoretical data for such thermodynamic property have given for supporting to this approach [39].

2. Experimental

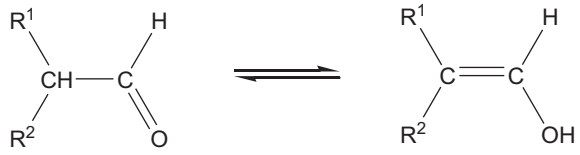
2.1. Materials

Ethanal, Carlo Erba RPE.
Propanal, Carlo Erba RE.
Methylpropanal ≥99%, Aldrich.
3-Phenylpropanal was synthesized and purified according to literature procedure [40].
Phenylethanal ≥90%, Aldrich.
2-Phenylpropanal 98%, Aldrich.
Cyclopentanecarbaldehyde 97%, Aldrich.
Cyclohexanecarbaldehyde 97%, Aldrich.
Methanol, Carlo Erba RPE.
Thioaldehydes non-commercially available were synthesized and purified according to the literature procedures [41].

2.2. Gas chromatography–mass spectrometry

These determinations were done by injection of methanol solutions (1 μL) in an HP 5890 Series II Plus chromatograph coupled to an HP 5972 A mass spectrometric detector under the following conditions:

Column: HP5-MS, 30 m × 0.25 mm × 5 μm.
Carrier gas: helium.
Injector temperature: 200 °C.
Oven temperature: 80 °C, 10 °C/min, 200 °C.
Interface temperature: 300 °C.
Ion source temperature: 185 °C.
The pressure in the mass spectrometer, 10^{-5} Torr, precludes ion-molecule reactions.
Electron energy: 70 eV.



Scheme 1. Possible tautomeric structures for aldehydes.

2.3. Computational procedure

The calculations were performed using the GAUSSIAN 03 [42] program package. Optimum equilibrium geometries were computed for the singlet ground states of all pertinent molecular systems using DFT-B3LYP with the 6-31G(d,p) basis sets. Numerous conformations were computed in order to ensure that the lowest energy conformation was obtained for each molecular system.

3. Results and discussion

Scheme 1 shows the possible tautomeric structures for aldehydes.

The relevance of spectrometric data as a predictive tool in regard to tautomeric equilibria depends mainly on the fact that the contribution due to tautomerization of molecular ions in the gas phase does not take place or can be ignored. The importance of this point comes from the physicochemical properties of ionic and radical species, quite different from the neutral ones. Since temperature effects are relevant to the determination of enthalpy differences, both sample introduction system (GC) and ion source (MS) temperatures were modified to find evidence regarding the involvement of neutral or ionic species in the spectrometric results produced by tautomerism occurrence. For the studied compounds, no significant changes are observed when modified the ion source temperature (data not shown).

Table 1 depicts mass spectral data which is relevant to the study of tautomerism of these compounds. Since coexisting tautomers are not separated by chromatography in these conditions, the mass spectra are the result of mass spectra superposition, so that accurate fragments should be selected for proper comparison. Contrarily, in our previous work, we reported chromatographic separation of the tautomeric forms for β-ketoesters [24].

From the analysis of the mass spectrometric data of selected aldehydes, the loss of OH and/or H_2O $(M-OH)^+$ and $(M-H_2O)^{+\bullet}$ from the molecular ion could be assigned to the enol form and the $(M-CHR^1R^2)^+$ to the keto form. A relative estimation of the tautomers occurrence could be the ratio $[(M-R)^+]/[(M-OH)^+]$ or $[(M-R)^+]/[(M-H_2O)^+]$.

The ion abundances in Table 1 were calculated as follows: (1000 × ion abundance/total ion abundance).

Table 1
Relevant mass spectral data of selected aldehydes and thioaldheydes for the study of tautomerism. Enol-keto heats of formation difference (kcal/mol) by calculation and approximate equilibrium constant values for the enolization reaction (DFT calculation) for the selected aldehydes.

Aldehyde	$[M^+]$	$[(M-XH)^+]$	$[(M-H_2X)^{+\bullet}]$	$[(M-CHR^1R^2)^+]$	$[(M-XH)^+]/[(M-CHR^1R^2)^+]$	$[(M-H_2X)^{+\bullet}]/[(M-CHR^1R^2)^+]$	Neutral molecule		Radical cation	
							ΔHenol Z-keto	ΔHenol E-keto	ΔHenol Z-keto	ΔHenol E-keto
Ethanal	95.4	35.3	30.8	146.1	0.24	0.21	10.46	–	−11.13	–
Thioethanal	181.0	202.3	26.9	98.9	2.05	0.27				
Propanal	166.9	2.9	6.5	244.5	0.012	0.03	11.85	10.47	−27.70	−22.65
Thiopropanal	246.4	297.2	162.0	212.2	1.40	0.76				
Methylpropanal	117.0	5.0	7.1	118.3	0.042	0.06	9.87	–	−18.41	–
Methylthiopropanal	245.8	156.6	95.3	68.1	2.3	1.40				
3-Phenylpropanal	113.2	2.6	2.8	95.4	0.027	0.03	10.93	11.36	−5.67	−3.74
Phenylethanal	96.7	3.7	3.8	39.2	0.094	0.10	7.89	6.75	−15.88	−17.80
2-Phenylpropanal	2.9	5.9	7.5	47.4	0.12	0.16	6.74	5.17	−11.94	−20.73
Cyclopentane carbaldehyde	2.8	7.2	39.7	36.0	0.20	1.10	0.23	–	−21.85	–
Cyclohexane carbaldehyde	8.8	2.30	12.7	13.2	0.17	0.96	9.68	–	−27.68	–

X = O,S.

As it can be observed, the equilibrium position depends on the substituent nature regarding electronic and steric effects [22,43].

From Table 1, the tendency observed from selected aldehydes is easily explained in terms of the steric hindrance produced by the substituent R^1 and R^2 next to the carbonyl group (Scheme 1).

For ethanal it should be regarded that, for such small molecules, unspecific rearrangements can occur, in which case the enol/keto ratio (from the selected fragments) does not correspond.

Bulky substituents in the α carbon to the carbonyl group shift the equilibrium towards the enol form; this can be observed when comparing the data shown in Table 1 for propanal and methylpropanal (0.012 vs 0.042 for the ratio $[(M-OH)^+]/[(M-CHR^1R^2)^+]$ or 0.027 vs 0.060 for the ratio $[(M-H_2O)^+]/[(M-CHR^1R^2)^+]$) and 2-phenylpropanal and phenylethanal (0.12 vs 0.094 for the ratio $[(M-OH)^+]/[(M-CHR^1R^2)^+]$ or 0.16 vs 0.098 for the ratio $[(M-H_2O)^+]/[(M-CHR^1R^2)^+]$) or 2-phenylpropanal vs 3-phenylpropanal (0.12 vs 0.027 for the ratio $[(M-OH)^+]/[(M-CHR^1R^2)^+]$ and 0.16 vs 0.030 for the ratio $[(M-H_2O)^+]/[(M-CHR^1R^2)^+]$).

For phenylethanal or 3-phenylpropanal vs 2-phenylpropanal, both the size of the substituents and the additional stabilization by the extended conjugation of the corresponding enol are relevant.

In the case of cyclopentanecarbaldehyde vs cyclohexanecarbaldehyde, (0.20 vs 0.17 for the ratio $[(M-H_2O)^+]/[(M-CHR^1R^2)^+]$ and 1.1 vs 0.96 for the ratio $[(M-H_2O)^+]/[(M-CHR^1R^2)^+]$) the tautomeric equilibria involves a change in the carbon bond angle from about 109.5° to about 120°. This change is highly favored in cyclopentanecarbaldehyde because it relieves eclipsing strain. In cyclohexanecarbaldehyde, this factor is absent because lacks eclipsing strain.

Notwithstanding, to support that the observed tautomeric equilibria distributions come from the molecular species with negligible contribution from tautomerism of molecular ions, theoretical calculations of heats of formation were carried out for both species.

Table 1 also shows the enol-keto heats of formation differences for the selected molecules and corresponding molecular ions. A reasonable good correlation with the mass spectra observations is achieved only in the case of the neutral molecule. When considered the radical ion, not only is there no correlation with the experimental data but also no logical tendencies are observed (e.g. compare methylpropanal with propanal; 2-phenylpropanal vs phenylethanal and cyclohexanecarbaldehyde with cyclopentanecarbaldehyde).

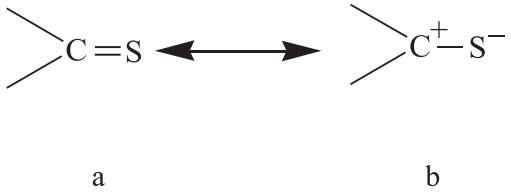
Then these findings are consistent with the tautomerism occurrence for the neutral species before ionization.

Approximate calculation of the equilibrium constant values for tautomerization can be done using these data regarding that the corresponding entropy changes are near neglectable or at least very similar.

The correlation between the equilibrium constants and the mass spectral data is very good what gives additional support to the predicting value of the proposed ion abundances ratio.

Table 1 depicts mass spectral data which is relevant to the study of tautomerism of selected aldehydes and thioanalogues, too. By analyzing this table, the enol occurrence is not very significant for the selected oxygenated aldehydes but with the exchange in heteroatom (O–S) a strong equilibrium shift towards the enol tautomer is observed (even for propanal or methylpropanal).

The thione group is relatively unstable in the monomeric form and tends to turn into a stable C–S single bond [44]. As already



Scheme 2.

established in previous work, the heteroatom O–S exchange causes a noticeable effect on the equilibrium position [45]. Thus, aliphatic thioketones exist in equilibrium with their enethiols [46].

This results arised from the greater polarization of the thiocarbonyl group (Scheme 2) (i.e. greater contribution of the canonical form b, see below) when compared with carbonyl group, because of the greater difficulty of the larger sulfur atom to form π-bonds with carbon [47,48].

This effect seems to outweigh the greater electronegativity of oxygen [49].

Comparing the mass spectral data for propanethial and 2-methylpropanethial, it is clear that the substituent size impacts the equilibrium position: the larger the substituent, the more noticeable the shift towards to the enol form.

The sample introduction system temperature has been modified and Table 2 depicts relevant data for the mass spectra of selected compounds.

Experimental determinations are done independently by triplicate.

Eq. (1) provides a simple method to determine the heat of keto-enol tautomerization for the studied compounds.

$$\ln K = \ln\frac{[\text{enol}]}{[\text{keto}]} = \ln\frac{[\text{f enol}]}{[\text{f keto}]} = \frac{-\Delta H}{RT} + C \qquad (1)$$

Table 2
Modification of K_1 and K_2 with the temperature for some compounds selected.

Aldehyde	T (°C)	$K_1 = [(M-OH/SH)^+]/[(M-R)^+]$	$K_2 = [(M-H_2O/H_2S)^+]/[(M-R)^+]$
Acetaldehyde	200	0.2400	0.2100
	250	2.2909	1.2274
	275	4.7863	9.5940
	300	9.5499	96.8278
Ethanethial	200	2.0500	0.2700
	250	7.7620	0.9900
	275	10.2330	1.2600
	300	10.7150	2.6500
Propionaldehyde	200	0.0120	0.0270
	250	0.0760	0.5980
	275	0.2630	0.9480
	300	0.8910	0.4810
Propanethial	200	1.4000	0.7600
	250	1.5500	0.8280
	275	1.7800	0.9350
	300	1.8600	0.9420
Isobutyraldehyde	200	0.0420	0.0600
	250	0.1660	0.3404
	275	3.3884	1.1117
	300	5.6234	1.3614
2-Methylpropanethial	200	2.3000	1.4000
	250	1.6596	0.9057
	275	1.0839	0.9705
	300	1.0328	0.6194

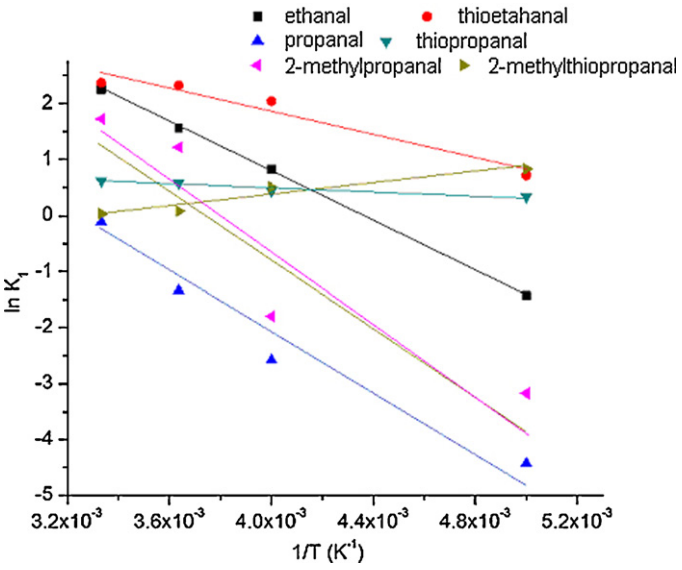


Fig. 1. Ln K_1 vs $1/T$ plot for selected aldehydes.

where [f enol] and [f keto] are the abundance of the fragments corresponding to the enol and keto forms, assuming that the concentration ratios are proportional to the ion fragment abundance ratios. The calculated slope from figures can be used directly to determine the enthalpy differences (Eq. (1)).

Figs. 1 and 2 show the representation of $\ln K$ vs $1/T$ for selected aldehydes and thio analogues.

Regarding the experimental results obtained by mass spectrometry, it is interesting to observe the consistency of the calculations with the indicated fragmentation pathways. After applying the van't Hoff equation (Eq. (1)) to the slopes of the figures, it can be seen that the values for the experimental heats of tautomerization are in excellent agreement with the theoretical ones (Table 3).

The correlation between the heats of tautomerization calculated from the slopes of Fig. 1 and those determined by quantum chemical calculations are excellent.

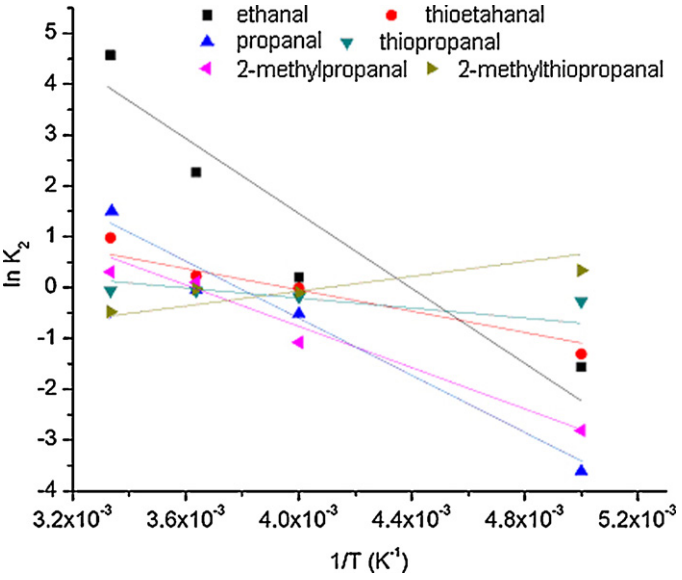


Fig. 2. Ln K_2 vs $1/T$ plot for selected aldehydes.

Table 3
Heat of tautomerization obtained from the slopes of the plots and heat of tautomerization obtained from GAUSSIAN 03 calculations.

Compound	Average slopes from Fig. 1	Average slopes from Fig. 2	Experimental ΔH, kJ mol^{-1}	Calculated ΔH, kJ mol^{-1}
Ethanal	$y = -4346.9x + 8.5874$ $R^2 = 0.9939$	$y = -6916.5x + 13.701$ $R^2 = 0.9178$	9 ± 2 (ΔH_1) 14 ± 3 (ΔH_2)	10.45
Thioethanal	$y = -2042x + 4.6797$ $R^2 = 0.9203$	$y = -2569.8x + 4.8571$ $R^2 = 0.9811$	4 ± 2 (ΔH_1) 5 ± 1 (ΔH_2)	4.29
Propanal	$y = -4971.7x + 8.504$ $R^2 = 0.9836$	$y = -5121.7x + 9.3451$ $R^2 = 0.9666$	9.9 ± 0.9 (ΔH_1) 10 ± 2 (ΔH_2)	11.852 (E) 10.466 (Z)
Thiopropanal	$y = -363.34x + 0.901$ $R^2 = 0.9591$	$y = -270.83x + 0.4492$ $R^2 = 0.9275$	0.7 ± 0.2 (ΔH_1) 0.5 ± 0.3 (ΔH_2)	0.760 (E)
Methylpropanal	$y = -6102.5x + 11.344$ $R^2 = 0.8961$	$y = -3862.7x + 6.9427$ $R^2 = 0.977$	12 ± 3 (ΔH_1) 7.2 ± 0.9 (ΔH_2)	11.934
Methylthiopropanal	$y = 1003.1x - 1.7431$ $R^2 = 0.9415$	$y = 840.47x - 1.6222$ $R^2 = 0.8517$	-2.0 ± 0.8 (ΔH_1) -2 ± 1 (ΔH_2)	−1.923

4. Conclusion

The application of mass spectrometry techniques together with theoretical calculations gives us a suitable way to analyze the enolization occurrence for the chosen set of aldehydes and thio analogues. It has been shown that the sensible employment of these two different methods enables one to achieve a predictive capability to study the enolization effect of the compounds under consideration in this work.

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