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Determination of thermodynamic parameters of tautomerization in gas phase by mass spectrometry and DFT calculations: Keto-enol *versus* nitrile–ketenimine equilibria

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ABSTRACT

The study of tautomerics equilibria is really important because the reactivity of each compound with tautomeric capacity can be determined from the proportion of each tautomer. In the present work the tautomeric equilibria in some γ,δ-unsaturated β-hydroxynitriles and γ,δ-unsaturated β-ketonitriles were studied. The first family of compounds presents two possible theoretical tautomers, nitrile and ketenimine, while the second one presents four possible theoretical tautomers, keto-nitrile, enol (E and Z)-nitrile and keto-ketenimine.

The equilibrium in gas phase was studied by gas chromatography–mass spectrometry (GC–MS). Tautomerization enthalpies were calculated by this methodology, and results were compared with those obtained by density functional theory (DFT) calculations, observing a good agreement between them. Nitrile tautomers were favored within the first family of compounds, while keto-nitrile tautomers were favored in the second family.

1. Introduction

Nitriles compounds, which present a α-hydrogen, can undergo ketenimine tautomerism. While keto–enol tautomeric equilibria of carbonylic compounds have been studied extensively [1,2], there are few reports on the occurrence of nitrile–ketenimine tautomerism [3–5].

The usefulness of mass spectrometry for tautomeric studies has been widely demonstrated [6–10]. This methodology has been applied to the study of the nitrile–ketenimine equilibrium, trying to find experimental evidence for the occurrence of the ketenimine tautomer through the interpretation of the mass spectral peaks of selected alkylidene malononitriles [11].

The analysis of temperature variation in 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 reaching the equilibrium inside the injection system. Besides that, there are no reports on the contribution of radical ions tautomerization to the mass spectral data (used to evaluate these equilibria) [12,13]. In fact, there is no evidence of tautomerism of ionic species [14].

The examination of β-diketones mass spectra demonstrated that fragmentation patterns are influenced by the keto–enol content. This analysis might have the disadvantage that the ion abundances may not only depend on the tautomerization, but also on bond strength differences.

Some studies on selected β-diketones and open-closed chain tautomerization have shown that changes in injection temperature result in changes of peak intensities for fragments assigned to the enol form, while the ion source temperature does not exert any effect [15,16]. The simplest interpretation takes into account the pressure at different points of the instrument. Intermolecular collisions can occur inside the injection system (tautomerization is bimolecular), while in the ion source only unimolecular processes can take place. Of course an intramolecular mechanism on the low pressure side could also explain these results.

This methodology has been already used to calculate the heats of tautomerization of selected thioamides, and good results have been found. Acceptable correlations with semi-empirical AM1 calculations for such thermodynamic property have supported this approach [17].

The reactivity of β-ketonitriles is related to their structure and their tautomeric equilibria; that is why it should be useful to determine their spectral behavior in different conditions. Some studies have been carried out by infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectrometries using solvents of differ-

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ent polarity. Aprotic solvents, like dimethyl sulfoxide (DMSO) and pyridine, generally favor the enol forms [18].

Tautomeric equilibrium constants of unsaturated β-ketoesters in different solvents have been established by NMR spectrometry, in order to estimate the reactivity of the ketonic and enolic tautomers of this kind of compounds as monomers in radical polymerization [19,20], considering their interesting technological applications [21].

To estimate the stability of different tautomers in some compounds and to predict the abundances of peaks assignable to each tautomer in mass spectra, DFT calculations were used. [22,23].

Estimations of thermodynamic parameters by mass spectrometry and its comparisons with DFT calculations were not reported at the present. The aim of this work was applied these methodologies to a series of γ,δ-unsaturated β-hydroxynitriles, which presents nitrile–ketenimine tautomerism and γ,δ-unsaturated β-ketonitriles with nitrile–ketenimine and keto–enol tautomerism. In addition, we study the effect of different structural modification on heat of tautomerization.

2. Materials and methods

2.1. Synthesis of compounds

Two groups of compounds were studied. The HM compounds, 3-hydroxy-5-phenyl-4-pentenonitrile (HM1), 3-hydroxy-2-methyl-5-phenyl-4-pentenonitrile (HM2) and 3-hydroxy-4-methyl-4-pentenonitrile (HM3) and the CM compounds, 3-oxo-5-phenyl-4-pentenonitrile (CM1), 2-methyl-3-oxo-5-phenyl-4-pentenonitrile (CM2) and 4-methyl-3-oxo-4-pentenonitrile (CM3).

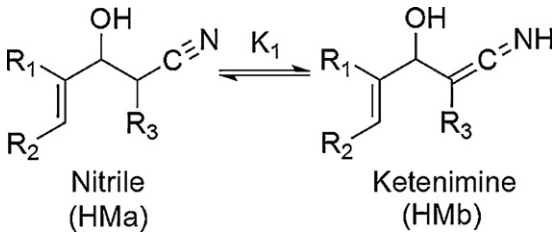
All the compounds were synthesized and purified according to published procedures [24,25].

2.2. Structural determinations

2.2.1. Gas chromatography–mass spectrometry

These determinations were performed by injection of methanol solutions (1 μl) in an HP 5890 Chromatograph coupled to an HP 5972 A mass selective detector under the following conditions:

Column: HP5-MS, 30 m × 0.25 mm × 5 μm.
Carrier gas: helium, 0.6 ml/min.
Temperatures set points:
Injector: 200 °C, 250 °C, 275 °C and 300 °C.
Oven: 40 °C (5 min), 20 °C/min, 290 °C.
Interface: 300 °C.



Scheme 1. Nitrile–ketenimine equilibrium for HM compounds.

Ion source: 185 °C.
Quadrupole: 150 °C.
Electron energy: 70 eV.

The pressure in the mass spectrometer, 10^{-3} Pa, precludes ion-molecule reactions.

2.2.2. Gas chromatography–mass spectrometry-ion trap

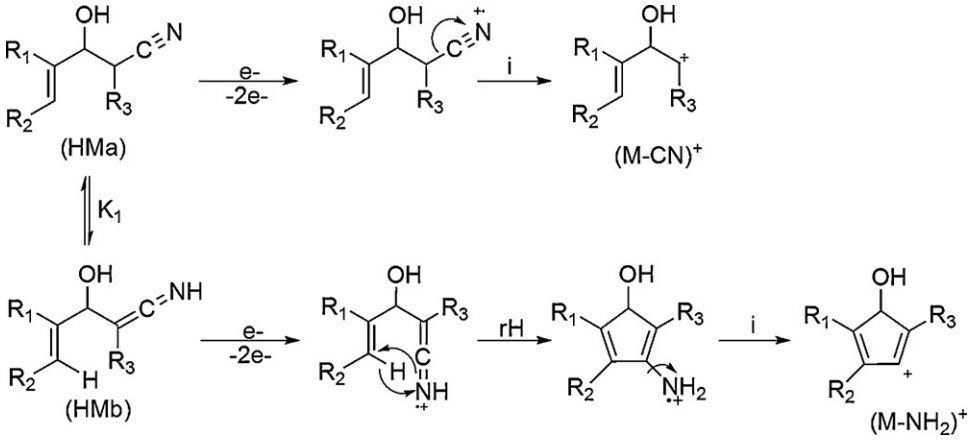
These determinations were performed by injection of methanol solutions (1 μl) in a Thermo Quest Trace 2000 coupled to Finnigan Polaris ion trap detector (unit mass resolution) under the same experimental conditions already mentioned for the single quadrupole GC/MS system. This instrumentation was utilized to confirm proposed fragmentation pathways by CID (collision induced dissociation) using helium as the damping gas, a CID voltage of 5–7 eV and an excitation energy of 0.35–0.45 (values were optimized for each ion transition). These experiments were done by selecting a precursor ion from the full-scan spectrum and carrying out the corresponding MS/MS product ion scan (Schemes 2, 4 and 5).

3. Theory/calculation

The molecules under study were subjected to geometry optimizations using the density functional theory (DFT) [26,27]. For this purpose, the B3LYP hybrid exchange-correlation functional [28,29] together with the 6-31G(d,p) basis set as implemented in the Gaussian 03 package [30] was used. All geometrical parameters were optimized without constraints.

We obtained the harmonic vibration frequencies of all molecules under study. The frequencies were calculated at the same level as the geometry optimization.

Finally, from the analysis of vibrations, it was possible to obtain thermodynamic information about the system under study.For validated the use of the density functional theory, in the optimized geometries single point calculations was performed. For this pur-



Scheme 2. Specific fragments assigned to each tautomer for HM compounds.

pose, the MP2 level together with the 6-31G(d,p) basis set as implemented in the Gaussian 03 package.

4. Results and discussion

4.1. Gas chromatography–mass spectrometry

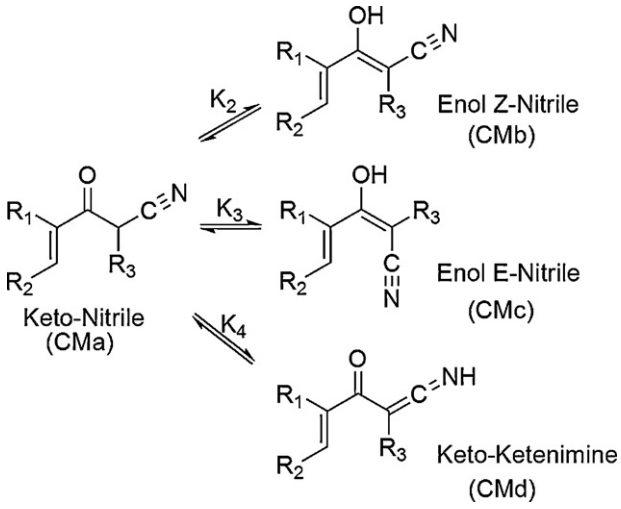
Scheme 1 shows all the possible tautomeric structures for HM compounds (in supplementary material it is show their mass spectra).

In order to evaluate the occurrence of the tautomers, specific fragmentations must be assigned. From the analysis of the mass spectrometric data, the peaks at $m/z=(M–NH_2)^+$ were assigned to the ketenimine forms (Scheme 2), and the ion at $m/z=(M–CN)^+$ were assigned to nitrile forms (Scheme 2).

The fragmentation pathways were confirmed by GC/MS ion trap experiments (Table 1).

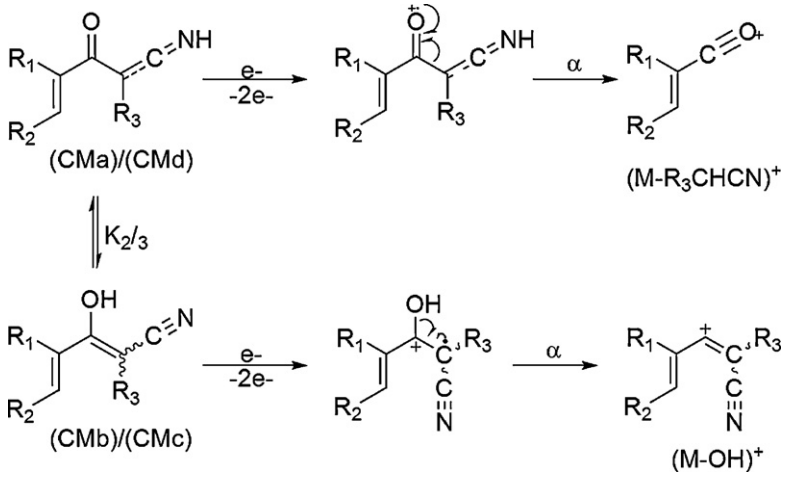
Scheme 3 shows all the possible tautomeric structures for CM compounds (in supplementary material it is show their mass spectra).

The $m/z=(M–R_3CHCN)^+$ peak could be assigned only to the keto tautomers, keto-nitrile and keto-ketenimine (Scheme 4), while the $m/z=(M–OH)^+$ peak could be assigned only to enol-nitrile forms (Scheme 4). The $m/z=(M–CN)^+$ peak could be assigned exclusively to nitrile forms, ketonitrile and enol-nitrile (Scheme 5) and the $m/z=(M–NH_2)^+$ peak could be assigned exclusively to keto-ketenimine forms (Scheme 5). The fragmentation pathways were confirmed by GC/MS ion trap experiments (Table 2).

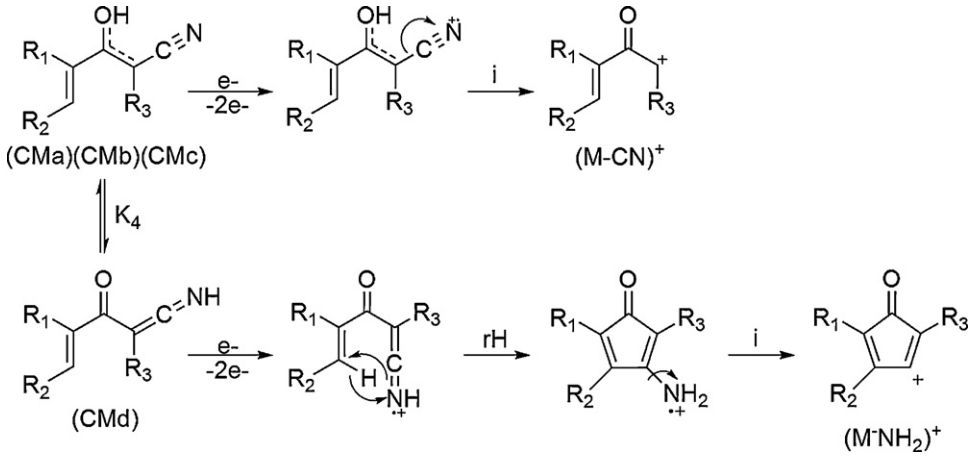


Scheme 3. Nitrile–ketenimine and keto–enol equilibria for CM compounds.

Nedeltcheva et al. [31] suggest the following equations, which could give rough estimate for the molar fractions of the



Scheme 4. Specific fragments assigned to each tautomer for CM compounds (keto–enol equilibrium).



Scheme 5. Specific fragments assigned to each tautomer for CM compounds (nitrile–ketenimine equilibrium).

Table 1
MS^2 data for HM compounds.

Compound	Precursor ion (m/z)	Relevant product ions (m/z)
HM1	173	157, 156, 155, 147, 146, 133, 104, 103, 91
	157	140
	156	115, 52
	146	145
HM2	187	172, 171, 170, 169, 161, 145, 133, 91
	169	140
	156	154, 115, 103
	103	77
	91	65, 39
	77	51
	187	172, 171, 170, 169, 161, 145, 133, 91
HM3	111	95, 94, 93, 85, 84, 71, 43, 42
	93	53
	84	83, 69, 44

Table 2
MS^2 data for CM compounds.

Compound	Precursor ion (m/z)	Relevant product ions (m/z)
CM1	171	155, 154, 153, 145, 144, 131
	131	103
	103	77
	77	51
CM2	185	169, 168, 167, 159, 158, 145, 131, 91
	167	152, 141
	131	106, 103
	103	77
	91	65
	77	51
	65	39
CM3	109	93, 92, 91, 83, 82, 69, 68, 43
	69	41
	68	40

tautomers:

$$X_E\ (\%) = \frac{Ie}{Ie + Ik}, \quad X_K\ (\%) = \frac{Ik}{Ie + Ik}, \quad X_{KE}\ (\%) = \frac{Ike}{Ike + In}$$

$$X_N\ (\%) = \frac{In}{Ike + In}$$

where

$$Ie = \frac{I \text{ from enol form}}{I \text{ from enol form} + I \text{ from keto form}}$$

$$Ik = \frac{I \text{ from keto form}}{I \text{ from enol form} + I \text{ from keto form}}$$

$$In = \frac{I \text{ from nitrile form}}{I \text{ from nitrile form} + I \text{ from ketenimine form}}$$

$$Ike = \frac{I \text{ from ketenimine form}}{I \text{ from nitrile form} + I \text{ from ketenimine form}}$$

where I is the relative intensity of the corresponding peaks.

We compared keto (nitrile or ketenimine) *versus* enol (nitrile) equilibria, and the nitrile (keto or enol) *versus* ketenimine (keto) equilibria. In the case of nitrile–ketenimine equilibrium, the I values for HM1, HM2 and HM3 compounds, are presented in Table 3.

We can see that HM2 has a highest relative content of ketenimine tautomer, which can be attributed to the bulky substituent on double bond (methyl group instead hydrogen atom).

Table 3
Relative intensity of tautomeric structures of HM compounds.

Compound	I nitrile	I ketenimine	K_1
HM1	9.99×10^{-1}	2.70×10^{-6}	2.70×10^{-6}
HM2	9.99×10^{-1}	3.93×10^{-6}	3.93×10^{-6}
HM3	9.99×10^{-1}	1.02×10^{-6}	1.02×10^{-6}

Table 4 shows the results of relative intensity of tautomeric structures corresponding to keto enol and nitrile ketenimine equilibria for CM1, CM2 and CM3 compounds.

The relative content of the enol tautomer increase in the order: CM1, CM2, CM3. The highest content of enol tautomer in CM3 compound can be attributed to the lower stability of the keto form, because it has not extension of conjugation (presence of phenyl group in CM1 and CM2). CM2 has a higher relative content of enol tautomer than CM1, probably because the highest stability of double bond by the presence of methyl group.

The relevance of spectrometric data as a predictive tool in regard to tautomeric equilibria depends mainly on the assumption that tautomerization of molecular ions in the gas phase does not occur 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 changes, both sample introduction system (GC) and ion source (MS) temperatures were modified to determine whether neutral or ionic species were involved in the spectrometric results produced by tautomerism occurrence. For the studied compounds, no significant changes were observed when the ion source temperature was modified (data not shown).

The sample introduction system temperature was modified, and relevant data for the mass spectra of the selected compounds are shown in Table 5. No chromatographic separation was observed, indicating that their mass spectra were the result of the individual tautomer mass spectra superposition (probable due to the fast interconversion rate). Experimental determinations were done independently by quintuplicate.

The ionic abundances observed in the mass spectra of different compounds are directly related to the atomic binding forces. In order to compare relative abundances of structurally related compounds, a normalization using the following expression was applied (Eq. (1)):

$$[\text{ion}] = \frac{\text{ion abundance} \times 1000}{\sum \text{total ion abundances}} \tag{1}$$

Eq. (2) provides a simple method to determine the heat of nitrile–ketenimine tautomerization (ΔH).

$$\ln K = \ln \frac{[\text{ketenimine}]}{[\text{nitrile}]} = \ln \frac{[\text{f ketenimine}]}{[\text{f nitrile}]} = -\frac{\Delta H}{RT} + C \tag{2}$$

where [f ketenimine] and [f nitrile] are the abundances of the fragments corresponding to the ketenimine and nitrile forms.

Eq. (3) provides a simple method to determine the heat of keto–enol tautomerization for the compounds studied.

$$\ln K = \ln \frac{[\text{enol}]}{[\text{keto}]} = \ln \frac{[\text{f enol}]}{[\text{f keto}]} = -\frac{\Delta H}{RT} + C \tag{3}$$

where [f enol] and [f keto] are the abundances of the fragments corresponding to the enol and keto forms.

Table 4
Relative intensity of tautomeric structures of CM compounds.

Compound	Ik	Ie	In	Ike	$K_{2/3}$	K_4
CM1	9.99×10^{-1}	1.30×10^{-5}	9.99×10^{-1}	9.11×10^{-6}	1.30×10^{-5}	9.11×10^{-6}
CM2	9.99×10^{-1}	4.70×10^{-4}	9.99×10^{-1}	1.17×10^{-5}	4.70×10^{-4}	1.17×10^{-5}
CM3	9.98×10^{-1}	1.08×10^{-3}	9.98×10^{-1}	1.93×10^{-5}	1.08×10^{-3}	1.93×10^{-5}

Table 5
Mass spectral data of selected compounds at different temperatures.

Compound	T (°C)	$[(M–R_3CHCN)^+]$	$[(M–OH)^+]$	$[(M–NH_2)^+]$	$[(M–CN)^+]$	$K_{2/3} = [(M–OH)^{\pm}]/[(M–R_3CHCN)^+]$	K_1 or $K_4 = [(M–NH_2)^{\pm}]/[(M–CN)^+]$
HM1	200	–	–	1.05	3.87×10^5	–	2.72×10^{-6}
	250	–	–	7.05	2.57×10^3	–	2.74×10^{-3}
	275	–	–	41.17	1.10×10^4	–	3.74×10^{-3}
	300	–	–	375.10	4.07×10^3	–	9.22×10^{-2}
HM2	200	–	–	0.99	2.52×10^5	–	3.91×10^{-6}
	250	–	–	7.53	1.81×10^4	–	4.17×10^{-4}
	275	–	–	56.33	6.74×10^4	–	8.36×10^{-4}
	300	–	–	274.20	7.77×10^4	–	3.53×10^{-3}
HM3	200	–	–	0.91	8.97×10^5	–	1.01×10^{-6}
	250	–	–	5.61	1.65×10^5	–	3.40×10^{-5}
	275	–	–	6.67	1.08×10^5	–	6.16×10^{-5}
	300	–	–	89.69	1.15×10^5	–	7.80×10^{-4}
CM1	200	245.5	0.0032	0.11	1.23×10^5	1.30×10^{-5}	9.11×10^{-6}
	250	222.9	0.0056	7.79	9.09×10^4	2.50×10^{-5}	7.12×10^{-4}
	275	207.9	0.0104	22.39	4.87×10^4	5.00×10^{-5}	2.50×10^{-3}
	300	198.7	0.0145	95.84	8.05×10^3	7.30×10^{-5}	1.19×10^{-2}
CM2	200	216.9	0.1020	0.13	1.09×10^4	4.70×10^{-4}	1.17×10^{-5}
	250	200.4	0.2120	1.77	9.63×10^3	1.06×10^{-3}	1.84×10^{-4}
	275	242.7	0.2930	14.42	8.69×10^3	1.21×10^{-3}	1.66×10^{-3}
	300	179.8	0.3850	53.39	7.98×10^3	2.14×10^{-3}	6.69×10^{-3}
CM3	200	322.5	0.3480	0.18	9.28×10^3	1.08×10^{-3}	1.93×10^{-5}
	250	192.9	0.6650	3.27	8.77×10^3	3.45×10^{-3}	3.73×10^{-4}
	275	185.3	0.8650	22.19	8.07×10^3	4.67×10^{-3}	2.75×10^{-3}
	300	178.2	1.0960	31.70	7.00×10^3	6.15×10^{-3}	4.53×10^{-3}

Table 5 depicts mass spectral data which are relevant to the study of tautomerism of these compounds. Since coexisting tautomers were not separated by chromatography in these working conditions, the mass spectra were the result of mass spectra superposition, so that adequate fragments should be selected for proper comparison. In the case of HM compounds, only the nitrile–ketenimine equilibrium can occur. Since only the nitrile form (HMa) may lose the CN radical, such fragmentation $(M–CN)^+$ can only come from this tautomer (Scheme 2). On the other hand, the loss of NH_2 (Scheme 2) can only submit the ketenimine isomer (HMb), so that the fragment $(M–NH_2)^+$ can be assigned as coming exclusively from HMb.

For the CM compounds two balances are possible: keto–enol and nitrile–ketenimine. The keto form can be present as keto-nitrile (CMa) or keto-ketenimine (CMd). The alpha breakdown presented in Scheme 4 is considered as coming only from these tautomeric forms. The loss of OH (Scheme 4) comes only from enol-nitrile structures (CMb and CMc), since the ketenimine form (CMd) cannot produce the enol tautomer. Since this methodology did not allow to distinguish between the CMb and CMc isomers, K_2 and K_3 could not be evaluated individually. For the evaluation of nitrile–ketenimine balance it was necessary to take into account that the only structure that can lead to the CMd isomer is CMa. The $(M–CN)^+$ fragment can come only from CMa and the loss of NH_2 from CMd (Scheme 5), as explained in the case of HM compounds.

The approach consists in using the abundances ratio $[(M–NH_2)^+]/[(M–CN)^+]$ in both family compounds, and additionally $[(M–OH)^+]/[(M–R_3CHCN)^+]$ in the case of CM compounds, for the estimation of the tautomerization position assuming that the response factors of each tautomer are similar.

The ion abundances shown in Table 5 were calculated as mentioned (ion abundance × 1000/∑total ion abundances).

Fig. 1 shows the correlation between the temperature and the equilibrium constant. The heats of tautomerization were calculated applying the Van't Hoff expression (Eqs. (2) and (3)).

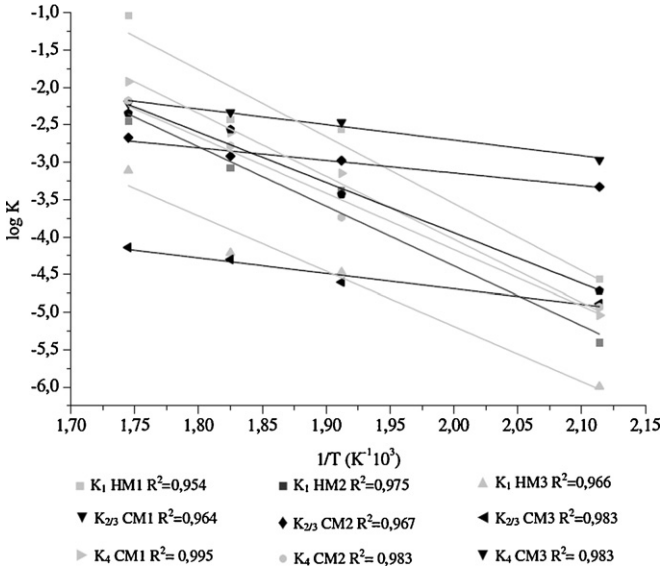


Fig. 1. Correlation between the temperature and the equilibrium constant.

4.2. Theoretical calculations

The geometries of the ketonitriles were optimized at the B3LYP/6-31G(d,p) level of DFT in order to investigate the stability of ketenimine, keto and enol forms in the gas phase. The values of heats of tautomerization (kcal/mol) for all the tautomeric equilibria are reported in Table 6. A very important aspect of the enol-nitrile structure is the possibility of E–Z isomerism and its incidence on the experimental behavior. DFT calculations were carried out on both tautomers.For validated the use of the density functional theory, in the optimized geometries single point calculations was performed. For this purpose, the MP2 level together with the 6-31G(d,p) basis set. The result obtained applied this methodology were coincident which obtained by DFT calculations. The principal difference is in the values of ketenimine forms with approximately 10 kcal/mol. However, both methods exhibited the same trends.

Table 6
Experimental and calculated heath of tautomerization (ΔH) for selected tautomeric equilibria.

Compound	Equilibrium	Experimental ΔH (kcal/mol)	Calculated ΔH (kcal/mol) B3LYP	Calculated ΔH (kcal/mol) MP2
HM1	a ⇌ b	18 ± 4	23.19	34.04
CM1	a⇌b/c	4 ± 1	5.63(Z) 4.97(E)	5.45 (Z) 4.87 (E)
CM1	a⇌b	17 ± 4	15.16	26.16
HM2	a⇌b	16 ± 3	20.09	31.23
CM2	a⇌b/c	3 ± 1	6.63(Z) 3.34(E)	6.83 (Z) 5.78 (E)
CM2	a⇌b	15 ± 4	16.78	27.97
HM3	a⇌b	21 ± 1	20.73	29.56
CM3	a⇌b/c	4 ± 1	2.88(Z) 6.65(E)	4.41 (Z) 7.82 (E)
CM3	a⇌b	25 ± 1	23.69	23.91

After applying the Vanĭt Hoff equation ((2) and (3)) to the experimental data (Fig. 1), the experimental values of heats of tautomerization were obtained. Table 6 shows experimental and theoretical heats of tautomerization for the selected molecules. It can be observed that, within the experimental error, a good agreement was found.

5. Conclusions

The results of the present study show that the keto–enol and nitrile–ketenimine equilibrium can be studied by mass spectrometry.

We found a good correlation between enthalpy change values obtained experimentally and those obtained by DFT calculations.

The equilibria here studied are endothermic. The ketonitrile tautomers were favored in the CM compounds, while the nitrile tautomers were favored in the HM ones.

Nitrile–ketenimine equilibria were those with the highest ΔH value, indicating that this equilibrium was the less favored.

Theoretical calculations showed that the E isomers displayed the highest enthalpic stability among CM1 and CM2 compounds, while the Z isomer was the most stable among CM3 compounds.

HM2 and CM2 compounds showed the lowest ΔH values for both equilibria, probably due to the inductive effect of the methyl groups.

The experimental ΔH value of HM compounds was lower than that calculated using DFT calculations, which may be due to the fact that some isotopic contributions were not considered in the analysis of the experimental values.

MP2 calculations validate the use of DFT calculations for the study of tautomeric equilibria for HM and CM compounds.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.12.050.

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