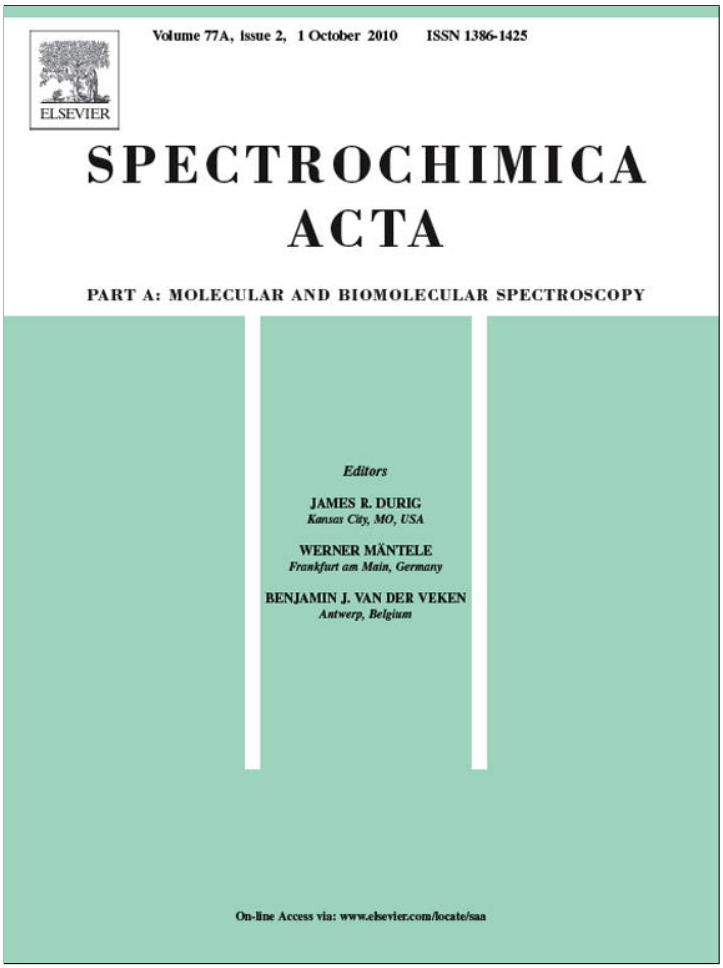


Spectrochimica Acta Part A 77 (2010) 367–373

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

3-Hydroxy-4-methyl-4-pentenonitrile and 4-methyl-3-oxo-4-pentenonitrile: Study of the tautomerics equilibria in gas phase and in solution

Juan M. Giussi[a,b], Agustín Ponzinibbio[a], M. Susana Cortizo[a,b], Patricia E. Allegretti[a,*]

[a] Laboratorio de Estudio de Compuestos Orgánicos (LADECOR), Facultad de Ciencias Exactas, calle 47 y 115 S/N, UNLP, C.P. 1900, Argentina
[b] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, calle 47 y 115 S/N, UNLP, C.P. 1900, Argentina

ARTICLE INFO

Article history:
Received 4 November 2009
Received in revised form 16 March 2010
Accepted 8 April 2010

Keywords:
Tautomerism
3-Hydroxy-4-methyl-4-pentenonitrile and 4-methyl-3-oxo-4-pentenonitrile
Mass spectrometry
Nuclear magnetic resonance

ABSTRACT

In the present work the tautomerics equilibria in 3-hydroxy-4-methyl-4-pentenonitrile and 4-methyl-3-oxo-4-pentenonitrile have been studied. The first compound presents two possible theoretical tautomers, nitrile and ketenimine. The second compound presents four possible theoretical tautomers ketonitrile, nitrile-enol (E and Z) and keto-ketenimine.

The study of the equilibrium in gas phase was performed by gas chromatography–mass spectrometry (GC–MS), and in solution by proton nuclear magnetic resonance spectrometry (^{1}H NMR).

In gas phase, the ketonitrile tautomer was favoured, a result which was supported by theoretical calculations by the use of AM1 semi-empiric calculation. The experimental tautomerization heat values were in good agreement with the theoretical ones.

The ^{1}H NMR spectra gave the additional evidence for the coexistence of the tautomers ketonitrile and enolnitrile for 4-methyl-3-oxo-4-pentenonitrile. The nitrile–ketenimine equilibrium for both compounds could not be observed by ^{1}H NMR spectra because of the low sensibility of this method. The ketonitrile–enolnitrile tautomerization heat of 4-methyl-3-oxo-4-pentenonitrile has been calculated and compared with the corresponding one in gas phase to evaluate the solvent effect.

1. Introduction

Nitrile compounds which present an α-hydrogen have the possibility of taumeric equilibrium towards ketenimine tautomer. Comparatively, keto-enol taumeric equilibria studies of carbonylic compounds [1,2] have been studied, but few reports related to the occurrence of nitrile–ketenimine tautomerism have been published [3–5].

The usefulness of the mass spectrometry for tautomeric studies has been widely demonstrated [6–18]. That is why this methodology has been chosen to study the nitrile–ketenimine equilibrium trying to find experimental evidence of the occurrence of the ketenimine tautomer through the interpretation of the mass spectral peaks of selected alkylidene malononitriles [19].

The analysis of changes in temperature 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 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 [20,21]. In fact, it has been claimed that tautomerization also occurs in the molecular ions proposing that enolization should be considered to occur before ionization, since no evidence of tautomerism of ionic species could be observed [22].

The examination of β-diketones mass spectra demonstrated that fragmentation patterns are influenced by the keto-enol content of these compounds. This simplified analysis might have the disadvantage that the ion abundances may not only depend on tautomerization but also, among other parameters, on bond strength differences although it has been demonstrated not to be the case.

Some studies on selected β-diketones and open-closed chain tautomerization have shown that changes in injection temperature results in changes of peak intensities for fragments assigned to the enol form, while changes in the ion source temperature did not exert any effect [23,24].

The simplest interpretation takes into account the pressure at different instrument points: the injection system where intermolecular collisions can occur (tautomerization is bimolecular) and the ion source where only unimolecular processes can take place, of course an intramolecular mechanism on the low pressure side could also explain the results.

This methodology has been already used for the calculation of heats of tautomerization of selected thioamides and measurably

* Corresponding author. Tel.: +54 221 4243104.
E-mail address: pallegre@quimica.unlp.edu.ar (P.E. Allegretti).

1386-1425/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2010.04.003

good results have been found. Very good correlations with theoretical data for such thermodynamic property have supported this approach [18].

The reactivity of β-ketonitriles is related to their structure and their tautomeric equilibria; that is why it should be useful to determine the spectral behaviour in different conditions in order to study the tautomeric distribution. Some studies have been carried out by IR, UV and NMR spectrometries using solvents of different polarities. Aprotic solvents, like DMSO and pyridine, generally favours the enol forms [25].

Tautomeric constants equilibria of insaturated β-ketoesters in different solvents have been established by nuclear magnetic resonance spectrometry, in order to analyze the reactivity of the ketonic and the enolic tautomer of this kind of compounds as monomers in radical polymerization [26,27], considering their interesting technological applications [28].

To carry out calculations by the Hartree-Fock model [29] (starting point to converge towards Schrodinger equation solutions by invoking additional approximations or adding additional determinants) implies high computational time and costs which scale as the third of fourth power of the number of basic functions due to the number of two-electron integrals that are necessary to build the Fock matrix are reached. Semi-empirical methods reduce these integrals [30] by considering only the valence electrons (actually involved in chemical bonding), the core electrons being subsumed into the nuclear core [31]. Orthogonal Slater-type s, p and d orbitals are always used which enables further simplifications. The Austin Model 1 (AM1) method was designed to eliminate the tendency to overestimate repulsions between atoms which are separated by the sum of their respective van der Walls radii. Gaussian functions (repulsive and attractive) are used leading to a significant improvement over similar semi-empirical methods. Parameterization against experimental data includes effects of electron correlation, so that some allowance for these effects is implicit in the calculation of heat of formation [32].

The aim of the present work is to study the nitrile–ketenimine equilibrium and keto-enol equilibrium by mass spectrometry in order to find experimental evidence of the occurrence of the ketenimine and enol tautomers of 3-hydroxy-4-methyl-4-pentenonitrile and 4-methyl-3-oxo-4-pentenonitrile.

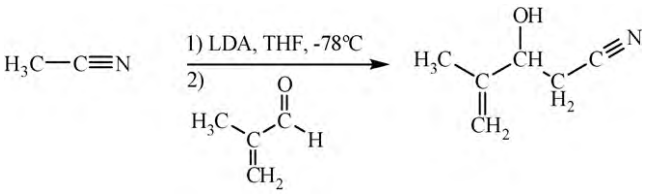
2. Materials and methods

2.1. Synthesis of 3-hydroxy-4-methyl-4-pentenonitrile and 4-methyl-3-oxo-4-pentenonitrile

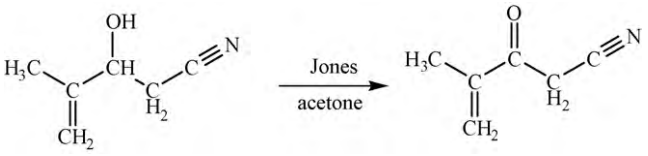
3-Hydroxy-4-methyl-4-pentenonitrile and 4-methyl-3-oxo-4-pentenonitrile were synthesized and purified according to literature procedures [33].

2.1.1. 3-Hydroxy-4-methyl-4-pentenonitrile (Scheme 1)

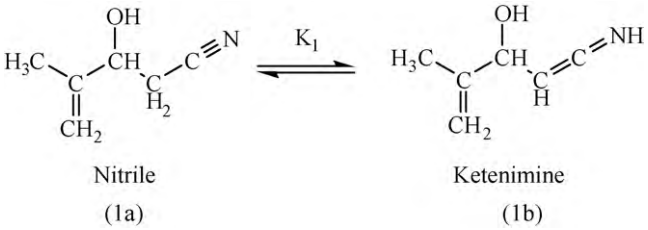
A dry, two-necked, round-bottomed flask (200 ml), capped with septa and equipped with argon inlet, magnetic stirring bar, was charged with dry tetrahydrofuran (40 ml) and diisopropylamine (22 mmol, 3.1 ml, 2.23 g). The solution was cooled to −30 °C and butyllithium (13.75 ml, 22 mmol, 1.6 M solution in hexanes), was added. The reaction was stirred for 15 min and cooled to −76 °C to −78 °C. Dry acetonitrile (20 mmol, 0.84 g, 1.08 ml) was added dropwise so that the internal reaction temperature remains below −66 °C (addition time 5–10 min). When addition of the acetonitrile was complete, the reaction was stirred for 50 min at −70 °C to −78 °C. A solution of freshly distilled metacrolein (20 mmol, 1.4 g, 1.65 ml) and 10 ml of dry tetrahydrofuran is then added rapidly via a cannula. The reaction was stirred for 5 min and quenched by the rapid addition of saturated aqueous ammonium chloride at acid pH. The reaction mixture was immediately poured into a separatory funnel containing diethyl ether (50 ml). The reaction flask was rinsed with 10 ml of distilled water and 10 ml of diethyl ether. After thorough mixing, the layers were separated and the aqueous layer was extracted with diethyl ether (three, 10 ml portions). The combined organic layers were washed with brine (20 ml), dried over magnesium sulfate, filtered, and evaporated under reduced pressure. 3-Hydroxy-4-methyl-4-pentenonitrile was purified by Kugelrohr distillation at 0.20 mm (oven temperature 65 °C) using a dry ice/isopropyl alcohol cold bath to cool the receiver (87% yield).



Scheme 1. Reaction to obtain 3-hydroxy-4-methyl-4-pentenonitrile.



Scheme 2. Oxidation of 3-hydroxy-4-methyl-4-pentenonitrile.

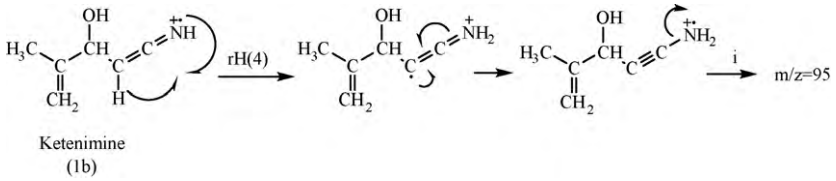


Scheme 3. Possible tautomeric structures for 3-hydroxy-4-methyl-4-pentenonitrile.

2.1.2. 4-Methyl-3-oxo-4-pentenonitrile (Scheme 2)

A 100 ml, round-bottomed flask equipped with a magnetic stirring bar and pressure-equalizing dropping funnel was charged with 3-hydroxy-4-methyl-4-pentenonitrile and 40 ml of acetone. The mixture was cooled in an ice bath and Jones reagent[1] (17.5 ml) was added dropwise via the dropping funnel (addition time is approximately 30 min). When addition of the Jones reagent was completed, the reaction mixture was allowed to slowly warm to room temperature and was stirred overnight. Methanol (2 ml) was added to quench excess Jones reagent and the reaction mixture was poured into a separatory funnel containing diethyl ether (80 ml). After thorough mixing, the layers were separated and the aqueous layer was extracted with diethyl ether (three 20 ml portions). The combined organic layers were washed with brine (two 20 ml portions), dried over $MgSO_4$, filtered, and the solvent was removed by simple distillation. Final purification was accomplished by Kugelrohr distillation at 0.20 mm (oven temp 48 °C) with a 25 ml receiving bulb

[1] Jones reagent was prepared by dissolving chromium oxide (CrO_3) (2.035 g) in concentrated sulfuric acid (2.1 ml) with cooling and then diluting with distilled water to give a total volume of 17.5 ml.



Scheme 4. Fragmentation pathway of ketenimine tautomer.

cooled to −78 °C using a dry ice/isopropyl alcohol cold bath (yield 49%).

2.2. Structural determinations

2.2.1. Gas chromatography–mass spectrometry

These determinations were performed by the 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; ion source: 185 °C; quadrupole: 150 °C.
Electron energy: 70 eV.
The pressure in the mass spectrometer, 10^{-5} Torr, precludes ion molecule reactions.

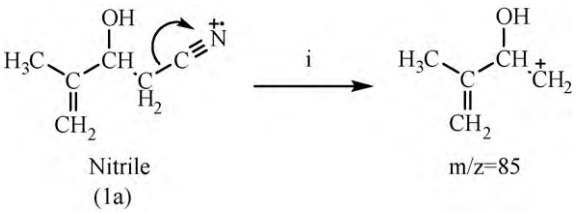
2.2.2. Gas chromatography–mass spectrometry—ion trap

These determinations were performed by the 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 2–10).

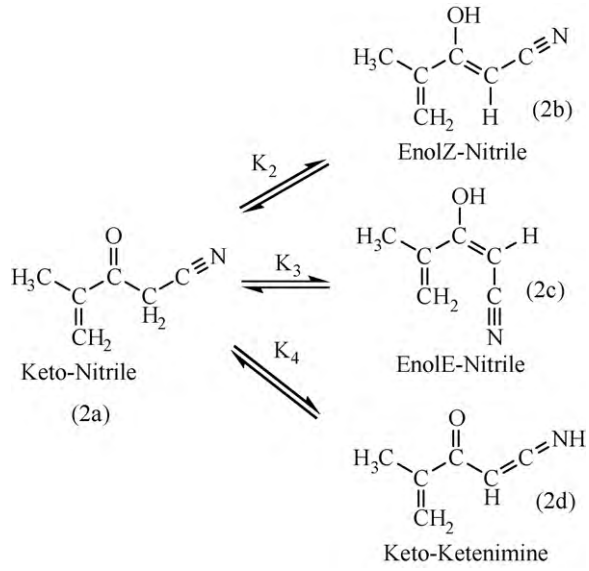
2.2.3. Nuclear magnetic resonance

The nuclear magnetic resonance (NMR) spectra, ^{1}H NMR, were registered with a Varian Mercury Plus Spectrometer, 200 MHz.

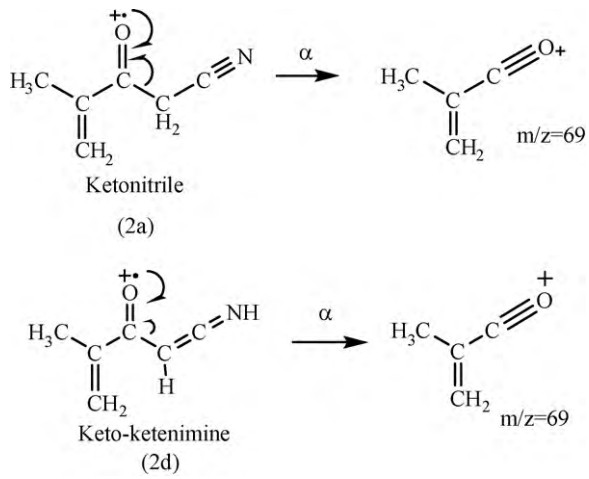
^{1}H NMR spectra in chloroform-d_1, acetona-d_6, carbon tetrachloride, acetonitrile-d_3 and dimethyl-d_6 sulfoxide (DMSO-d_6) were recorded. The typical spectral conditions were as follows: spectral width 3201 Hz, acquisition time 4.09 s and 8–16 scans per spectrum. Digital resolution was 0.39 Hz per point. Deuterium from the solvent was used as the lock and TMS as the internal standard. Sample concentration was 0.41%P/V and the selected temperature was 10 °C, 20 °C, 30 °C and 40 °C.



Scheme 5. Fragmentation pathway of nitrile tautomer.



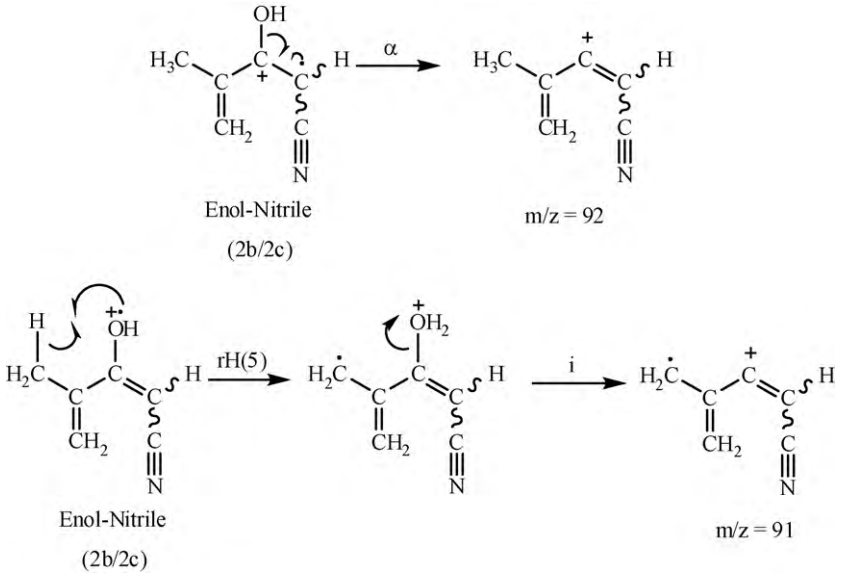
Scheme 6. Possible tautomeric structures for 4-methyl-3-oxo-4-pentenonitrile.



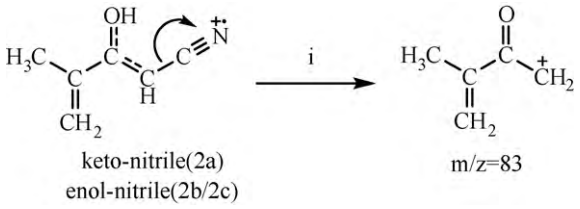
Scheme 7. Fragmentation pathway of keto tautomers.

3. Theory/calculation

AM1 (Austin Model 1) calculations were run using the standard Hyper Chem package [34], by choosing the Polak-Ribiere first-order minimization algorithm frequently employed in molecular modelling. The method gradually changes the co-ordinates to the minimum point by successive steps of interaction. Since it has been resorted to heat of formation values and the AM1 technique has been specially parameterized to reproduce this sort of experimental data, it is thought this choice is a sensible one for the molecular set under study.



Scheme 8. Fragmentation pathway of enol tautomer.



Scheme 9. Fragmentation pathway of nitrile tautomers.

Table 1
Mass spectral data of 3-hydroxy-4-methyl-4-pentenonitrile at different temperatures.

T (°C)	$[(M-NH_2)^+]$	$[(M-CN)^+]$	$K_1 = [(M-NH_2)^+]/[(M-CN)^+]$
200	0.11	160.76	0.68×10^{-3}
250	1.05	158.23	6.63×10^{-3}
275	1.77	150.60	11.75×10^{-3}
300	5.89	141.59	41.60×10^{-3}

4. Results and discussion

4.1. Gas chromatography–mass spectrometry

Scheme 3 shows all the possible tautomeric structures for 3-hydroxy-4-methyl-4-pentenonitrile and Fig. S1 shows its mass spectrum.

In order to evaluate the occurrence of the tautomers, specific fragmentations should be assigned. From the analysis of the mass spectrometric data, the peaks at m/z 95 $(M-NH_2)^+$ can be only assigned to the ketenimine (Scheme 4) and the ion at m/z 85 $(M-CN)^+$ could be only assigned to nitrile form (Scheme 5).

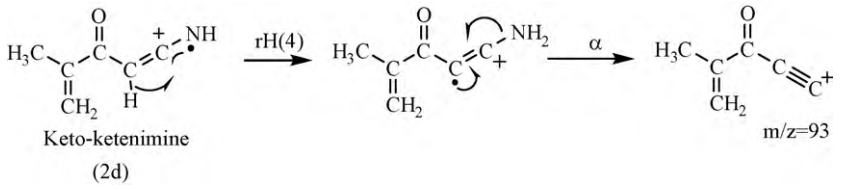
Scheme 6 shows all the possible tautomeric structures for 4-methyl-3-oxo-4-pentenonitrile and Fig. S2 shows its mass spectrum.

The $m/z = 69$ peak $(M-{}^{\bullet}CH_2CN)^+$ can be only assigned to the keto tautomer, ketonitrile and ketenimine-keto (Scheme 7), while the $m/z = 92$ $(M-OH)^+$ and $m/z = 91$ $(M-H_2O)$ peaks could be only assigned to enolnitrile forms (Scheme 8). The $m/z = 83$ peak can be exclusively assigned to nitrile form, ketonitrile and enolnitrile (Scheme 9) and the $m/z = 93$ peak can be exclusively assigned to keto-ketenimine form (Scheme 10). The $m/z = 83$ peak may come of ketonitrile and enolnitrile form.

We compare keto (nitrile or ketenimine) versus enol (nitrile) equilibria and the nitrile (keto or enol) versus ketenimine (keto) equilibria.

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 changes, 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 were observed when modifying the ion source temperature (data not shown).

The sample introduction system temperature has been modified and Tables 1 and 2 show relevant data for the mass spectra of 3-hydroxy-4-methyl-4-pentenonitrile and of 4-methyl-3-hydroxy-4-pentenonitrile, respectively. No chromatographic



Scheme 10. Fragmentation pathway of keto-ketenimine tautomer.

separation was observed so 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.

For better correlation the abundances were calculated as follows:

$$[\text{ion}] = \frac{\text{ion abundance} \times 1000}{\text{total ion abundances}}.$$

Eq. (1) provides a simple method to determine the heat of nitrile–ketenimine tautomerization for the compounds studied:

$$\ln K = \ln\frac{[\text{ketenimine}]}{[\text{nitrile}]} = \ln\frac{[\text{f ketenimine}]}{[\text{f nitrile}]} = -\frac{\Delta H}{RT} + C \quad (1)$$

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

Eq. (2) provides a simple method to determine the heat of tautomerization keto-enol:

$$\ln K = \ln\frac{[\text{enol}]}{[\text{keto}]} = \ln\frac{[\text{f enol}]}{[\text{f keto}]} = -\frac{\Delta H}{RT} + C \quad (2)$$

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

Tables 1 and 2 depict mass spectral data which are relevant to the study of tautomerism of these compounds.

Since coexisting tautomers are not separated by chromatography in the working conditions, the mass spectra are the result of mass spectra superposition, so that adequate fragments should be selected for proper comparison. In the case of compound (**1**), only nitrile–ketenimine equilibrium can occur. Since only the form nitrile (**1a**) may lose the CN radical such fragmentation $(M-CN)^+$ can only come from this tautomer. On the other hand, the loss of NH_2 (Scheme 2) can only submit the ketenimine isomer (**1b**), whereby the fragment $(M-NH_2)^+$ can be assigned as coming exclusively from (**1b**).

For the compound (**2**) two balances are possible: keto-enol and nitrile–ketenimine. The keto form can be presented as ketonitrile (**2a**) or keto-ketenimine (**2d**). The alpha breakdown presented in Scheme 5 is considered to come only from these tautomeric forms. The loss of OH (Scheme 6) comes only from enolnitrile structures (**2b** and **2c**) because the ketenimine form (**2d**) cannot produce the enol tautomer. It is worth noting that this methodology is not possible to distinguish between the isomers (**2b**) and (**2c**), so that K_2 and K_3 will not be evaluated individually. For the evaluation of nitrile–ketenimine balance must take into account that the only structure that can lead to the isomer (**2d**) is (**2a**). The fragment $(M-CN)^+$ can come only from (**2a**) and the loss of NH_2 from (**2d**), as explained in the case of compound (**1**).

The approach consists in using the abundances ratio $[(M-NH_2)^+]/[(M-CN)^+]$ in both compounds and additionally $(M-OH)^+/\alpha$ in the case of 4-methyl-3-oxo-4-pentenonitrile for the estimation of the tautomerization position assuming that the response factor for each tautomer is similar.

The ion abundances in Tables 1 and 2 were calculated as follows: (1000 × ion abundance/total ion abundance).

Fig. 1 shows the effect of the temperature on all equilibrium constant determined. Applying the Van't Hoff expression (Eqs. (1) and (2)) the heats of tautomerization were calculated.

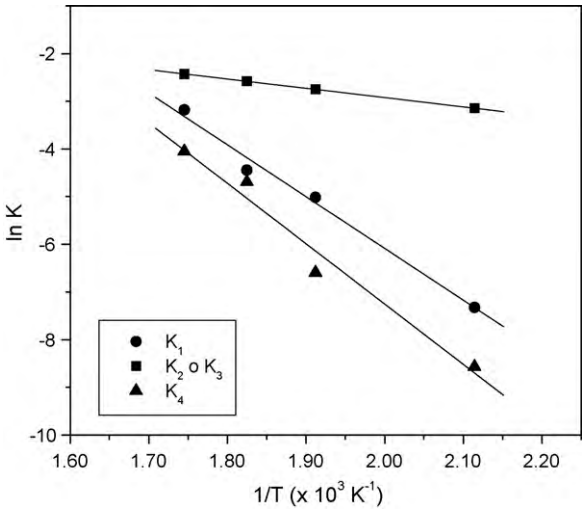


Fig. 1. Representation of $\ln K$ vs $1/T$. Study of equilibria nitrile–ketenimine and keto-enol for both compounds.

Table 3
Heats of formation of different tautomers evaluated by AM1 calculation.

Tautomer	ΔH_f (kcal/mol)
1a	−17.10
1b	3.56
2a	4.62
2b	8.09
2c	9.02
2d	30.27

4.2. Theoretical calculations

As in previous works [6–8,10–14], semi-empirical AM1 results were used to determine the heats of formation differences which follow the same tendency observed by mass spectrometric results. The heats of tautomerization were evaluated from the difference between the calculated heats of formation of each involved tautomers. A very important aspect of the enolnitrile structure is the possibility of isomerism E–Z and its incidence on the experimental behaviour. AM1 semi-empirical calculations were carried out on both tautomers. Table 3 presents these results and put in evidence that z-isomer is most stable.

After applying the Van't Hoff equation ((3) and (4)) to the experimental data (Fig. 1), the values for the experimental heats of tautomerization were obtained. Table S1 shows experimental and theoretical heats of tautomerization for the selected molecules. It is possible to see that, within the experimental error, a good agreement was found.

4.3. Nuclear magnetic resonance

Figs. 2 and 3 show the ^1H NMR spectra in chloroform of 3-hydroxy-4-methyl-4-pentenonitrile and 4-methyl-3-oxo-4-pentenonitrile.

Table 2
Mass spectral data of 4-methyl-3-oxo-4-pentenonitrile at different temperatures.

T (°C)	α	$[(M-OH)^+]$	$[(M-NH_2)^+]$	$[(M-CN)^+]$	$K_{2/3} = [(M-OH)^+]/\alpha$	$K_4 = [(M-NH_2)^+]/[(M-CN)^+]$
200	203.6	8.75	0.014	73.96	0.043	0.19×10^{-3}
250	192.9	12.34	0.098	71.36	0.064	1.37×10^{-3}
275	185.3	14.08	0.645	70.23	0.076	9.18×10^{-3}
300	178.2	15.69	1.207	69.39	0.088	17.40×10^{-3}

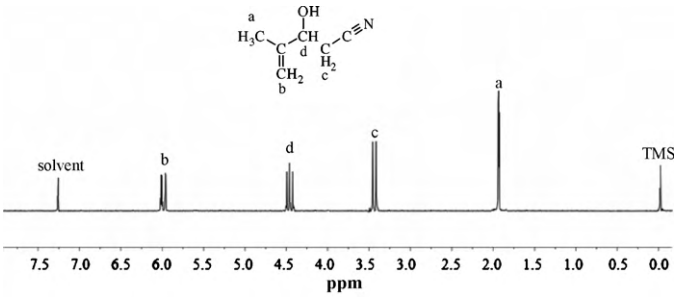


Fig. 2. ^{1}H NMR spectrum in chloroform of 3-hydroxy-4-methyl-4-pentenonitrile.

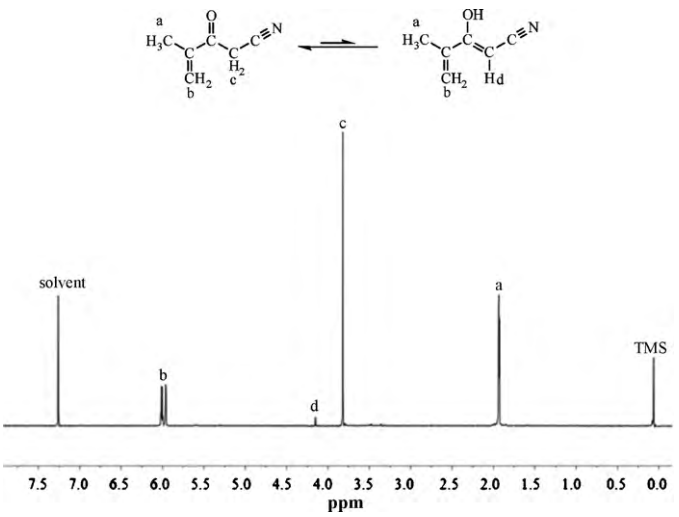


Fig. 3. ^{1}H NMR spectrum in chloroform of 4-methyl-3-oxo-4-pentenonitrile.

The ^{1}H NMR spectra give the additional evidence for the coexistence of the tautomers ketonitrile and enolnitrile for 4-methyl-3-oxo-4-pentenonitrile. The nitrile–ketenimine equilibrium for both compounds could not be observed due to the low sensibility of this method.

The signals at $\delta = 3.81$ and $\delta = 4.37$ in the ^{1}H NMR spectrum of 4-methyl-3-oxo-4-pentenonitrile are assigned to the methylene and methine protons, respectively, and the other protons exhibit the same chemical shifts for both tautomers. Experimental determinations were done independently by triplicate.

The rate of keto-enol interconversion is sufficiently slow on the NMR time scale to calculate the equilibrium constant from the areas obtained by integration of the peaks at $\delta = 3.81$ and $\delta = 4.37$. As it can be seen from Table 4, the ketonic fraction in 4-methyl-3-oxo-4-pentenonitrile decreases with increasing polarity of the solvents (Fig. 4).

Table 4
Modification of the fraction keto and the K_T with solvent and temperature.

Solvent (dielectric constant)	Temperature (°C)	Fraction keto	K_T[a]
Carbon tetrachloride (2.2)	20	0.990	0.010
Chloroform (4.8)	10	0.965	0.036
	20	0.974	0.027
	30	0.981	0.019
Acetone (20.7)	10	0.690	0.450
	20	0.694	0.440
	30	0.699	0.431
Acetonitrile (37.5)	20	0.352	1.841
DMSO (46.7)	20	0.128	6.812
	30	0.127	6.874
	40	0.125	7.000

[a] K_T = [tautomer enolnitrile]/[tautomer ketonitrile].

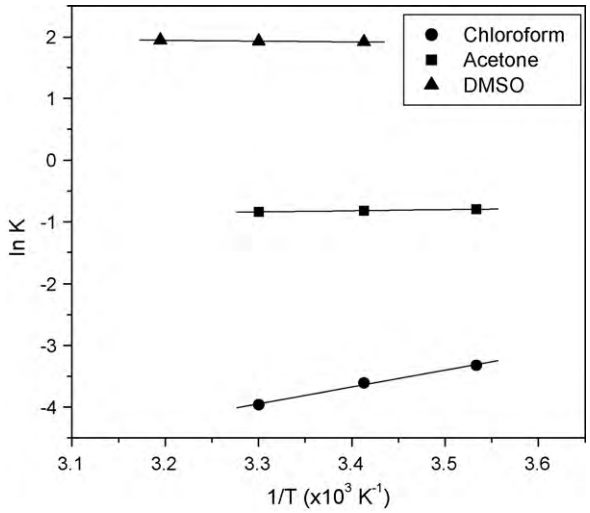


Fig. 4. Representation of ln K vs $1/T$ for 4-methyl-3-oxo-4-pentenonitrile in chloroform, acetone and dimethylsulfoxide.

Table 5
Heats of tautomerization ketonitrile–enolnitrile in 4-methyl-3-oxo-4-pentenonitrile. Solvent effect.

Solvent	Experimental ΔH (kcal/mol)
Chloroform	−5.44 ± 0.1
Acetone	−0.37 ± 0.02
DMSO	0.25 ± 0.01

Eq. (3) provides a simple method to determine the heat of tautomerization keto-enol for 4-methyl-3-oxo-4-pentenonitrile in solution:

$$\ln K = \ln\frac{[\text{enol}]}{[\text{keto}]} = \ln\frac{[\text{Int. } \delta = 4.37]}{[\text{Int. } \delta = 3.81]} = -\frac{\Delta H}{RT} + C \quad (3)$$

where [Int. $\delta = 4.37$] and [Int. $\delta = 3.81$] are the integrations of the signals at $\delta = 4.37$ corresponding methine protons to the enol form and $\delta = 3.81$ corresponding methylene protons to the keto forms.

Table 5 shows the heats of tautomerization ketonitrile–enolnitrile in 4-methyl-3-oxo-4-pentenonitrile in the selected solvents.

5. Conclusions

The results show that the keto-enol and nitrile–ketenimine equilibrium can be studied by mass spectrometry. The values for the experimental heats of tautomerization are in good agreement with the theoretical ones.

In solution by nuclear magnetic resonance, the nitrile–ketenimine equilibrium for both compounds could not be observed due to the low sensitivity of this method.

In solution, the results obtained by NMR spectrometry show that the rise in the solvent polarity increases the content of the enolnitrile tautomer and as temperature rises in selected solvents there is an increase in the content of the ketonitrile tautomer.

In solution, the experimental heats of tautomerization calculated by NMR spectrometry depend on solvent polarity. The results show that the rise in the solvent polarity increases the heat of tautomerization ketonitrile–enolnitrile in 4-methyl-3-oxo-4-pentenonitrile.

Acknowledgments

We are indebted to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata for financial support and to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), República Argentina.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.04.003.

References

[1] P.E. Allegretti, M.M. Schiavoni, E.A. Castro, J.J.P. Furlong, World J. Chem. 2 (2) (2007) 25–62.
[2] G. Angelini, P. De Maria, A. Fontana, M. Pierini, G. Siani, J. Org. Chem. 72 (2007) 4039–4047.
[3] S. Trofimenko, E.L. Little Jr., H.F. Mower, J. Org. Chem. 27 (1962) 433–438.
[4] T.R. Kasturi, B.N. Mylari, A. Balasubramanyam, C.N.R. Rao, Can. J. Chem. 40 (1962) 2272–2286.
[5] T.R. Kasturi, V.K. Sharma, A. Srinivasan, G. Subrahmanyam, Tetrahedron 29 (1973) 4103–4109.
[6] P.E. Allegretti, G.R. Labadie, M. González Sierra, J.J.P. Furlong, Afinidad LVII No. 485 (2000) 41–49.
[7] P.E. Allegretti, E.A. Castro, J.J.P. Furlong, J. Mol. Struct. (Theochem) 499 (2000) 121–126.
[8] P.E. Allegretti, L. Gavernet, E.A. Castro, J.J.P. Furlong, J. Mol. Struct. (Theochem) 532 (2000) 139–142.
[9] P.E. Allegretti, M.M. Schiavoni, H. Di Loreto, J.J.P. Furlong, C.O. Della Védova, J. Mol. Struct. (Theochem) 560 (2001) 327–335.
[10] P.E. Allegretti, A.S. Cánepa, R.D. Bravo, E.A. Castro, J.J.P. Furlong, Asian J. Spectrosc. 4 (2000) 133–137.
[11] P.E. Allegretti, L. Gavernet, E.A. Castro, J.J.P. Furlong, Asian J. Spectrosc. 5 (2) (2001) 63–68.
[12] P.E. Allegretti, C.B. Milazzo, E.A. Castro, J.J.P. Furlong, J. Mol. Struct. (Theochem) 589–590 (2002) 161–170.
[13] P.E. Allegretti, M.S. Cortizo, C. Guzmán, E.A. Castro, J.J.P. Furlong, Arkivoc X (2003) 24–31.
[14] P.E. Allegretti, V. Peroncini, E.A. Castro, J.J.P. Furlong, Int. J. Chem. Sci. 1 (1) (2003) 1–12.
[15] P.E. Allegretti, D. Asens, M.M. Schiavoni, M.S. Cortizo, R.D. Bravo, E.A. Castro, J.J.P. Furlong, Arkivoc XV (2003) 134–142.
[16] P.E. Allegretti, M.M. Schiavoni, M.S. Cortizo, E.A. Castro, J.J.P. Furlong, Int. J. Mol. Sci. 5 (2004) 294–300.
[17] P.E. Allegretti, C.B. Milazzo, J.J.P. Furlong, Eur. J. Mass Spectrom. 11 (2005) 53–64.
[18] P.E. Allegretti, E.A. Castro, J.J.P. Furlong, Eur. J. Mass Spectrom. 12 (2006) 317–330.
[19] H. Saraví Cisneros, S. Laurella, D.L. Ruiz, P.E. Allegretti, J.J.P. Furlong, Int. J. Spectrosc. (2009) 18, Article ID 408345.
[20] P. Petrientt, A. Kalandarishivilli, Mass Spectrom. Rev. 15 (1966) 339–345.
[21] M. Masur, H.F.M. Nooshabadi, K. Aghapoor, H. Reza Darabi, M.M. Mojahedi, Tetrahedron Lett. 40 (1999) 7549–7556.
[22] (a) J.K. MacLeod, P.R. Jones, Chem. Rev. 63 (1963) 461–489;
(b) J.K. MacLeod, J.B. Thomson, C. Djerassi, Tetrahedron 23 (1967) 2095–2103.
[23] L. Zamir, B.S. Jensen, E. Larsen, Org. Mass Spectrom. 2 (1969) 49–61.
[24] M.E. Rennekamp, J.V. Paukstelis, R.G. Cooks, Tetrahedron 27 (1971) 4407–4415.
[25] L. Aspart-Pascot et, J. Lematre, Bull. Soc. Chim. France 2 (1971) 483–488.
[26] J. Spencer, E. Holmboe, M. Kirshenbaum, D. Firth, P. Pinto, Can. J. Chem. 60 (1982) 1178–1182.
[27] S. Masuda, M. Tanaka, T. Ota, Makromol. Chem. 187 (1986) 1087–1092.
[28] A. Arostegui, M. Sarrionandia, J. Aurrekoetxea, I. Urrutibeascoa, Polym. Deg. Stabil. 91 (11) (2006) 2768–2774.
[29] A. Szabó, N.S. Ostlund, Modern Quantum Chemistry, McGraw-Hill, New York, USA, 1958.
[30] J. Sadlej, Semi-Empirical Methods in Quantum Chemistry, John Wiley & Sons, New York, USA, 1985.
[31] F. Jensen, Introduction to Computational Chemistry, John Wiley & Sons, New York, USA, 1999.
[32] J.M. Goodman, Chemical Applications of Molecular Modelling, Royal Society of Chemistry, London, UK, 1998.
[33] Organic Syntheses, 71 (1993) 236.
[34] Hyper Chem® 6.03 for windows Molecular Modeling System, Hypercube, Inc., Gainesville, FL, USA, 2000.