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Gas phase protonation of α, β and γ-dicarbonyls: Thermochemistry and structures

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A paper dedicated to the memory of Sharon Lias

Abstract

An experimental and theoretical study of the protonation of representative dicarbonyl compounds M = 2,3-butanedione (biacetyl), **1**, 2,4-pentanedione (acetylacetone), **2**, 2,5-hexanedione (acetonylacetone), **3**, and methyl-acetoacetate, **4** has been carried out. The experimental proton affinities and protonation entropies have been obtained by the extended kinetic method using the orthogonal distance regression (ODR) treatment. Theoretical proton affinities are calculated at the G2MP2 level of theory while protonation entropies were estimated after a detailed treatment of the internal rotations. The data show that protonation of **1** and **2** is associated with negligible protonation entropies while significant negative values are obtained for molecules **3** and **4**. Protonation of 2,3-butanedione, **1a**, is associated with a tautomerisation inside the proton transfer complex thus leading to protonated 2-hydroxy-butenone, **1bH⁺**. Protonation thermochemistry of 2,4-pentanedione **2** may be simply rationalized by the protonation of its most stable tautomer, the 4-hydroxy-3-pentene-2-one, **2b**, to give its most stable protonated form **2bH⁺** stabilized by a strong intramolecular hydrogen bond. Protonation of 2,5-hexanedione **3a** most probably produces a cyclic structure stabilized by a covalent bonding, **3aHc⁺**. The structure of neutral methyl acetoacetate **4** sampled during protonation in mass spectrometry experiments appears to be its diketonic form **4a**; its protonation leading to an internally hydrogen bonded stabilized structure **4aH⁺**.

Keywords: Proton affinity; Protonation entropy; Gas phase basicity; Dicarbonyl; Diketones

1. Introduction

In the last decades, it has long been recognized that, by its ability to handle isolated ions, mass spectrometry is an essential tool for the study of gas phase ion kinetics and thermochemistry. In this context, determination of intrinsic basicities of individual molecules has been, and is still, a field of stimulating research in the mass spectrometry community. The current NIST tabulation established by Hunter and Lias [1] is probably the most evident and useful illustration of this fundamental activity.

Proton is the simplest monocharged cation, it is unique in having no electron around its nucleus and thus has the smallest radius as compared to all other ions (10^{-15} m against $\sim 10^{-10}$ m). One consequence of this characteristic is a considerable electrostatic and polarizing power on neighbour atoms or molecular entities. This phenomenon is, in particular, at the origin of the strength of the hydrogen bond in protonated molecules. Accordingly, since a hydrogen bond energy between two molecules is typically equal to ca. 10–20 kJ/mol, this quantity attains values in the range 100 to 150 kJ/mol if one partner is a protonated specie [2]. This large stabilization energy has consequences on the structure of hydrogen bonded ion-molecule adducts and allows chemistry to occur inside the ion-molecule complex. From this latter point of view, the most frequently encountered chemical process is proton transfer reactions. However, more extensive changes in covalent structure, leading for example to isomerization or dissociation, may also take place. Similarly, in polyfunctional molecules, the formation of intramolecular

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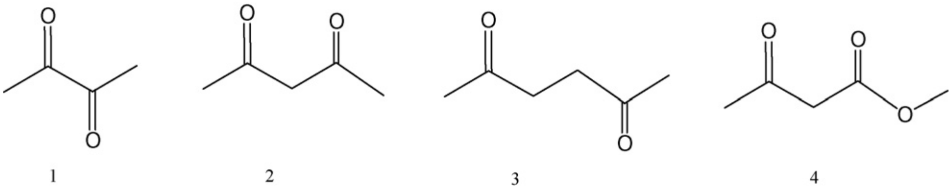

Scheme 1.

hydrogen bond may be also at the origin of structural changes which have consequences on the intrinsic basicity or acidity of the considered species [1–3] but may also favour isomerisation or dissociation processes.

Polycarbonyls constitute an important class of molecules prone to tautomerism, to internal hydrogen bonding and to interfunctional interactions eventually leading to structural changes upon protonation. In the present study we (re)examine the protonation thermochemistry of a series of representative dicarbonyl molecules: 2,3-butanedione (biacetyl), **1**, 2,4-pentanedione (acetylacetone), **2**, 2,5-hexanedione (acetonylacetone), **3**, and methyl-acetoacetate, **4** (Scheme 1).

For this purpose, the gas phase basicity, GB(M), and the proton affinity, PA(M), of molecules M = **1**–**4**, defined by the Gibbs free energy change $\Delta_1 G^\circ$ and the enthalpy $\Delta_1 H^\circ$ of reaction (1) at 298 K [1]:

$$\mathrm{MH^+} \rightarrow \mathrm{M} + \mathrm{H^+} \qquad (1)$$

together with the protonation (or "half-reaction") entropy $\Delta_p S^\circ(\mathrm{M}) = S^\circ(\mathrm{MH^+}) - S^\circ(\mathrm{M})$ were determined both experimentally and theoretically [1].The experimental proton affinity and protonation entropy of molecules M = **1**–**4** were determined by the extended kinetic method [4,5] and compared with previous determinations obtained by the equilibrium method [22,23]. Molecular orbital calculations conducted up to the G2MP2 level have been used to perform conformational analysis of M and $\mathrm{MH^+}$ and to obtain reliable theoretical proton affinities. Theoretical protonation entropies were estimated using statistical thermodynamic calculations using an improved treatment of the internal hindered rotations.

2. Experimental and computational section

2.1. MIKE and CID-MIKE experiments

The experimental data presented below were obtained on a B-E tandem mass spectrometer of the type VG ZAB 2F operating in the mass analyzed ion kinetic energy (MIKE) mode or in the collision induced dissociation (CID) mode. The ion source was operating under chemical ionization conditions (electron energy: 250 V; emission current: 500 μA; source temperature: 480 K; accelerating voltage 7800 V). For each molecule M = **1**–**4**, a series of reference bases $\mathrm{B_i}$ has been used to produce the relevant proton bound dimer $M\mathrm{HB_i}^+$. Equal amounts (ca 10 μl) of both samples were introduced in the heated inlet system. In these conditions, the ion source pressure is sufficient to allow thermalization and self-chemical ionization of the samples. In MIKE experiments, $\mathrm{MHB_i}^+$ ions were selected by the magnetic sector B and allowed to spontaneously dissociate before analysis of the fragments ions by the electric sector E. In CID experiments, $\mathrm{MHB_i}^+$ ions are also selected by the magnet B but further activated by collisions with argon in the collision cell located between the sectors B and E before analysis of the fragment ions by the electric sector. Product ions $\mathrm{MH^+}$ and $\mathrm{B_iH^+}$ abundances were measured from peak intensities (peak height) of the corresponding ions, and, when necessary, with addition of their subsequent dissociation products. For each adduct $\mathrm{MHB_i}^+$ a mean of four experiments has been done by different experimentalists at several months interval. The mean values have been used for the kinetic method treatment described in Section 3.1.

2.2. Computational methods

Molecules **1**–**4** and their protonated forms were examined at the MP2/6-31G(d) level in order to locate the most favourable conformations and to determine the rotational barriers used in the entropy calculations (see below). Zero point vibrational energies, ZPVE, and thermal contributions to the enthalpy at 298 K, $\mathrm{H_{298}(M) - H_0(M)}$, were estimated from the scaled (by a factor 0.893) harmonic frequencies calculated at the HF/6-31G(d) level of theory.

Proton affinities are computed, according to reaction (1), from the standard enthalpy change given by:

$$\mathrm{PA_{calc}(M)} = E_{\mathrm{tot}}(\mathrm{M}) - E_{\mathrm{tot}}(\mathrm{MH^+}) + \Delta_1\mathrm{ZPVE} + \Delta_1 H_{0\rightarrow 298}$$

with E_{tot} being the calculated total energy of the considered species, Δ_1ZPVE the zero point vibrational energy difference ZPVE(M)–ZPVE($\mathrm{MH^+}$) and $\Delta_1 H_{0\rightarrow 298}$ the thermal correction to enthalpy including the 298 K enthalpy contribution of the proton (i.e., $\Delta_1 H_{0\rightarrow 298} = [H_{298}(\mathrm{M}) - H_0(\mathrm{M})] - [H_{298}(\mathrm{MH^+}) - H_0(\mathrm{MH^+})] + 6.2\ \mathrm{kJ\,mol^{-1}}$). It has been demonstrated that in order to obtain accurate (±5 $\mathrm{kJ\,mol^{-1}}$) proton affinities by this procedure, very high levels of correlation and very large basis sets must be used [6]. Various protocols are available, ranging from W1, W2 [7], G2, G3 [8] to CBS-Q [9] procedures. In the present study, we have adopted the method of highest accuracy practicable owing to the size of the investigated systems i.e., the G2MP2 method. All calculations have been undertaken using the Gaussian98 and Gaussian03 suites of programmes [10].

To compare experimental and computed gas-phase basicities, GB(M), it is necessary to know the entropy change associated with reaction (1) since, at a temperature T, GB(M) = PA(M) − $T\,\Delta_1 S^\circ$. As noted in the beginning of this section, the entropy difference $\Delta_1 S^\circ$ may be expressed by $[S^\circ(\mathrm{H^+}) - \Delta_p S^\circ(\mathrm{M})]$ where