



Quantitative correlations between collision induced dissociation mass spectrometry coupled with electrospray ionization or atmospheric pressure chemical ionization mass spectrometry – Experiment and theory

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ARTICLE INFO

Article history:

Received 1 December 2017

Received in revised form

27 December 2017

Accepted 28 December 2017

Available online 2 January 2018

Keywords:

Collision induced dissociation mass spectrometry

Electrospray ionization

Kinetics

Atmospheric pressure chemical ionization

Quantum chemistry

ABSTRACT

The problematic that we consider in this paper treats the quantitative correlation model equations between experimental kinetic and thermodynamic parameters of coupled electrospray ionization (ESI) mass spectrometry (MS) or atmospheric pressure chemical ionization (APCI) mass spectrometry with collision induced dissociation mass spectrometry, accounting for the fact that the physical phenomena and mechanisms of ESI[−] and APCI[−] ion formation are completely different. There are described forty two fragment reactions of three analytes under independent ESI[−] and APCI[−] measurements. The developed new quantitative models allow us to study correlatively the reaction kinetics and thermodynamics using the methods of mass spectrometry, which complementary application with the methods of the quantum chemistry provide 3D structural information of the analytes. Both static and dynamic quantum chemical computations are carried out. The object of analyses are [2,3-dimethyl-4-(4-methyl-benzoyl)-2,3-di-p-tolyl-cyclobutyl]-p-tolyl-methanone (**1**) and the polycyclic aromatic hydrocarbons derivatives of dibenzoperylen (**2**) and tetrabenzo [*a,c,f,g,op*]naphthacene (**3**), respectively. As far as (**1**) is known to be a product of [2π+2π] cycloaddition reactions of chalcone (1,3-di-p-tolyl-propenone), however producing cyclic derivatives with different stereo selectivity, so that the study provide crucial data about the capability of mass spectrometry to provide determine the stereo selectivity of the analytes. This work also first provides quantitative treatment of the relations '3D molecular/electronic structures'–'quantum chemical diffusion coefficient'–'mass spectrometric diffusion coefficient', thus extending the capability of the mass spectrometry for determination of the exact 3D structure of the analytes using independent measurements and computations of the diffusion coefficients. The determination of the experimental diffusion parameters is carried out within the 'current monitoring method' evaluating the translation diffusion of charged analytes, while the theoretical modelling of MS ions and computations of theoretical diffusion coefficients are based on the Arrhenius type behavior of the charged species under ESI[−] and APCI[−] conditions. Although the study provide certain sound considerations for the quantitative relations between the reaction kinetic–thermodynamics and 3D structure of the analytes together with correlations between 3D molecular/electronic structures–quantum chemical diffusion coefficient–mass spectrometric diffusion coefficient, which contribute significantly to the structural analytical chemistry, the results have importance to other areas such as organic synthesis and catalysis as well.

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1. Introduction

The methods of mass spectrometry (MS) have evolved into versatile approaches for highly precise, selective and accurate chemical analyses with irreplaceable application in many *trans*- and *multi*-disciplinary areas, for instance, environmental

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analysis; agricultural and/or food sciences and technologies; Public's Security; drugs—discovery and pharmacy; medicine; etc. What is important to highlight in this context is that the great applicability of MS is chiefly determined by its superior instrumental features such as: (i) flexible scheme of instrumental design; (ii) superior method performances; (iii) fast operation techniques; (iv) capability for analysis of molecular weights from low molecular weight analytes to (bio)polymers and other (bio)macromolecules with weights \in 10–100 kDa; (v) analysis of homogeneous and heterogeneous samples, for instance, aerosols, liquid and semi liquid compounds as well as substances in the solid—state; (vi) direct assay of living systems such as for example, living cells, whole organs and bodies as well as a capability to employ imaging techniques; etc. [1]. One important instrumental characteristic associated with point (i) mentioned above is its employment in different coupling instrumental schemes with high performance liquid chromatography (HPLC) and/or gas—chromatography (GC), direct liquid injection analyses, high super critical fluid chromatography, etc. [2], which has resulted to utilization of LC—MS and/or GC—MS as routine analytical approaches to many research fields [3]. Among different ionization techniques, electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) have been broadly employed in hybrid instrumental schemes owing to their high ionization efficiency applicable to volatile, non—volatile and polar analytes. The former approach (*i.e.* ESI) belongs to the so—called soft ionization methods producing singly and multiply charged ions of analyses from solution within the unimolecular reaction of protonation/deprotonation depending on the modes of operation (negative or positive polarity) and avoiding fragmentation of analytes, thus yielding to important qualitative, quantitative and structural information about the substances in solution, including, most importantly, 3D molecular structural information, because of there is obtained data about non—covalent interactions as well [1b,4–6]. Regarding the latter application of the soft ionization MS methods in analytical chemistry, which essentially go beyond the routine quantification of analytes in the quantitative analytical chemistry, despite the fact that we determine 3D structure of these analytes via complex quantitative procedure involving experimental reaction kinetics and thermodynamics as well as theoretical modelling of the molecular and electronic structures of the analytes using computational quantum chemistry, where the quantitative treatment is based on evaluation of the free Gibbs energy, we should underline that in this study we additionally correlate theoretical quantum chemical and experimental mass spectrometric diffusion coefficients of the molecular species. We will show in this work that the latter correlative approach provides independent and accurate information and relatively salient illustration about great prospective and applicability of the MS methods in 3D structural determination in solution and in the gas—phase. In this context an important point should be noted at the juncture of the striking experimental results from the mass spectrometry mentioned above. It is that, methodological developments of MS methods themselves have great impact and contributions to many interdisciplinary research fields. On this other hand, as far as the results presented in this work are not only consistent with methodological development of the mass spectrometry for exact 3D structural analysis, but are highly relevant to applied aspects of the organic synthesis and catalysis we have chosen to consider in this section of the paper some important application aspects of the studied analytes as well. Thus, chalcones (1,3—diaryl—2—propen—1—ones, CL) are naturally occurring products or synthetic derivatives from flavonoid type [7]. It is, in general, acknowledged that study *into* direction biological activity of chalcones has been shown a broad range of functions, for instance, anti—*invasive* [7a] and anti—*inflammatory* activities [7b] as well as antioxidant,

antimalarial, anticancer, antileishmanial, anticonvulsant, anti—Parkinson activities and mono—amino oxidase inhibitory function [7f,8]. Research development in context design of new non—linear optical materials (NLO) has been illustrated application of CLs as organic NLO—phores as well [9]. The broad biological activity of CLs is perhaps for reason that α,β —unsaturated propenone fragment participates in a large set of substitution and cyclization reactions yielding to a large number of different molecular scaffolds. They can act as starting materials obtaining isoxazolo [3—c,4] quinolines [10]; homo—1,2,4—triaryl benzenes [11]; many derivatives based on the classical [2+4] cycloaddition reactions [12]; 1,3,5—tiphenyl—pentane—1,5—diones [13a,b]; 2,4,6—Triarylpyridines [14]; substituted oxetanes *via* Rousseau's bromocyclization [15]; chiral pyryliums [16]; cyclohexenes [17]; 1,3,5—triarylbenzenes [18]; 2,4—diphenylfurans [19]; α —pyrones [20]; 1,3—diphenyl—2,3—epoxy—4—bromobutanones [21]; pyranocoumarins [22]; epoxy derivatives [23] and more. Looking at the collection of synthetic experimental conditions chalcones are obtained *via* Claisen—Schmidt condensation of substituted aldehydes and methylketones in alkali medium [7g] in polar protic solvents/solvent mixtures [7d,e,j,k] with reaction times $t \in$ 0.6–24 h [7b]. The known epoxidation reactions have been obtained in low polar solvents like toluene and MgO [7h], BaO—ZrO₂ and/or Ba(OH)₂, but again in alkali medium [23]. There is known only one report including CLs synthesis in acidic medium *via* heterogeneous catalysed process with participation of silica—H₂SO₄ efficient both in polar (CH₃OH) and low polar solvent (CH₂Cl₂) [7i]. Many studies devoted to mechanistic aspects of alkali catalysed Claisen—Schmidt condensation leading to CLs lend support to different views, based on examining of the kinetics of reactions and/or computational quantum chemical molecular modelling of the interactions [23–26], including concepts on mechanistic aspects of interactions in presence of BaO—ZrO₂ and Ba(OH)₂ in alkali medium [23]. There is important to note that despite the broad application of CLs for over two decades until more recently [24a] intelligibility of mechanisms of alkali catalysed Claisen—Schmidt condensation is disputable because of many of the proposed mechanisms only partially agree with available experimental data. In addition to the fact that to the only acidic catalysed Claisen—Schmidt condensation reported in [7i] there is a lack of proposed mechanism. In this context our goals in this study have been manifold. First, as mentioned above we have developed a quantitative models allowing to study the correlation between the reaction kinetics and thermodynamic parameters using the methods of mass spectrometry, thus allowing to obtain a 3D structural information of the analytes using complementary the methods of mass spectrometry and the quantum chemistry. Next, we have focused on a systematic analysis of observed parallel reactions yielding to chalcones in different amounts depending on the experimental conditions. This allows in the same time to consider for first time theoretically possible mechanisms of acidic catalysed Claisen—Schmidt condensation yielding to chalcones. A third line of our research efforts deals, among others, with both experimentally and theoretically with kinetics and thermodynamics of observed [2 π +2 π] cycloaddition reaction of CLs in acidic medium together with a consideration of firstly reported, here, possible mechanism explaining the unexpected regio— and stereoselectivities of the reaction. Given that, our research, not only underline the great advantages of the methods of mass spectrometry obtaining structural information of the analytes, but there is extended it capability to predict 3D structure of the analytes in addition to their enantioselectivity. In the connection with the issue of formation of [2 π +2 π] cycloaddition products, we should argue, here, that, in general, in the literature there are known only few studies reporting such as products of interaction of chalcones. As analytical data we well know that [2 π +2 π] cycloaddition

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