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Mass Spectrometry: Insightful Window for Organic Chemistry

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Editorial

Just recently, Vijaya Krishna Varanasi represented the advantages of open access journals [1], thus we want to share some ideas based on our mass spectrometric researches for organic chemistry in "Organic Chemistry: Current Research". Mass spectrometer, as a tool of weighing the ions, is applied widely in natural science. With massive progress in ionization techniques and mass analysers recently, modern mass spectrum characterized by sensitivity, speed, specificity and stoichiometry [2], opens an insightful window for deepening the understanding of the organic chemistry. As the key point in understanding the mechanisms of organic reactions, the identification of reactive intermediates is nearly always a challenging task because they are short-lived and hardly separated from other related complexes. Electrospray ionization (ESI) is a method of transferring real-world ions from solution to the gas phase [3]. Because reactive species are almost infinitely stable due to high-vacuum conditions in the gas phase [4] and active species with a charge can be probed selectively, ESI-MS has become increasingly popular in characterization of active intermediates especially combined with tandem mass spectrometric (MS^n) methods [4-9].

Since Aliprantis et al. studied the catalytic intermediates in the Suzuki reaction by ESI-MS in 1994 [10], ESI-MS has been widely used in studies of the intermediates and mechanisms of metal-catalyzed reactions. We systematically studied the Ru-olefin metathesis catalysts [11,12], the Ru-catalyzed olefin metathesis reactions [13,14] and the CH_3CN-assisted decomposition reaction of the 1st Grubbs catalyst [15]. These work made those proposed mechanisms be proved to some extent and will help to optimize and develop the reaction conditions and application scope of catalysts. Other than mechanisms of metal-catalyzed reactions, ESI-MS is also applied in studies on the mechanism of organocatalysis reactions [16,17] and free radical reactions [18-20]. We have studied the interaction of radical traps (Tempo and Dmpo) and radicals produced in the electrophilic fluorination of olefins and Selectfluor by ESI-MS, which provides evidence for presence of a single-electron transfer mechanism in electrophilic fluorination [21,22]. The limitation of ESI-MS method is that the species have to be charged. However, possible omission of important neutral reaction intermediates can be circumvented by the introduction of an easily ionizable group to a remote position of the catalyst or the substrate [23]. Furthermore, combined with microreactor, on-line ESI-MS have proven to be particularly effective in the investigation of systems involving relatively unstable products, which would not survive the normal handling, quenching, and storage practices typical of off-line strategies [5,24]. Thus, ESI-MS will applied in understanding the mechanisms of more organic reactions in the future.

The reaction mechanisms sometimes can be better revealed in the subtle details in the gas phase for which are always complicated by hydrogen bond and solvation effect in the condensed phase [25]. However, gas phase reactions are difficult to study in the normal experiment conditions. The modern mass spectrometer, as a complete chemical laboratory, provides an ideal tool [26]. Name reactions are foundation for organic chemistry and similar reactions could also occur in gas phase. Till now, two name reactions "McLafferty rearrangement" [27] and "Eberlin reaction" [28] occurred in mass spectrometry. Several interesting gas phase reactions have also been investigated by our group: like the *Smiles* and related rearrangements of aromatic systems [29-31], sulfonyl-sulfinate rearrangement [32,33], retro-Michael type fragmentation reactions [34], *Clasien* rearrangement reaction [35] and *Favorskii* rearrangement [36]. We also used tandem mass spectrometry to predict chemical transformations of 2-pyrimidinyloxy-*N*-arylbenzyl amine derivatives in solution based on study of intrinsic properties of reactions in gas phase before [37]. "Gas phase firstly and then condensed phase", this idea puts insight into quick discovery of complexes' potential reactive centers.

Learning the world via mass, mass spectrum has great advantages in understanding the mechanisms of organic reactions and the gas-phase reactions [38]. Combined with contemporary new technologies, we are confident that mass spectrum will give more surprises to the organic chemists. Significant challenges still remain to be overcome in study of mechanisms in both gas phase and solution organic reactions by mass spectrometry and related technologies. The journal "Organic chemistry: Current Research" from OMICS Publishing Group would provide more opportunities to present key issues in advances in the use of mass spectrometric methods to solve the organic chemistry problems.

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