

Microreactor-Electrospray Ionization Mass Spectrometry, a Novel Tool for the Investigation of Reactive Intermediates in Solution

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Introduction

Simple methods for the direct detection of reactive intermediates, if possible under the conditions of the preparative reaction, are essential for elucidating and understanding the mechanisms of synthetically important reactions in solution. Electrospray ionization mass spectrometry (ESI MS), and atmospheric pressure chemical ionization mass spectrometry (APCI MS) can be used to study liquid-phase solutions.

Methods

By using a simple microreaction system coupled online to the mass spectrometer we developed a method for the mass spectrometric investigation of chemical reactions in solution, the direct detection of the occurring reactive intermediates as well as their characterization by MS/MS. Thus, substrates, intermediates and final products can be monitored using our novel method. Our work has been focused on the detection of radicals^[1] and radical cations^[2] as reactive intermediates in preparatively important organic reactions in solution.

Preliminary Results

Herewith, we are reporting on our investigations of electron transfer initiated radical cation chain reactions in solution and the direct detection of the transient radical cations. We studied the Diels-Alder reaction of cyclopentadiene and phenyl vinyl sulfide to give 5-(phenylthio)norbornene initiated by tris(*p*-bromophenyl)aminium hexachloroantimonate.^[3] This radical cation chain reaction proceeds via the transients phenyl vinyl sulfide^{•+} and 5-(phenylthio)norbornene^{•+} which were detected and characterized unambiguously and directly in the reacting solution under quasistationary conditions by ESI MS/MS. In addition we are able to monitor easily substrate and product in the reacting solution by APCI MS.^[2]

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