

GAS PHASE “HYDROLYSIS” OF ALKYL ESTERS: A SELECTED-ION FLOW TUBE STUDY

Gregory J. Francis, Daniel B. Milligan, and Murray J. McEwan.

SYFT Ltd., 3 Craft Place, Middleton, Christchurch 8024, New Zealand.

Department of Chemistry, University of Canterbury, Christchurch 8041, New Zealand.

Selected-ion flow tube mass spectrometry (SIFT-MS) is a relatively new technique for quantifying trace analytes in whole air samples. Esters, which have been studied here, are often responsible for the smell and flavour of many fruits such as banana (butyl acetate) and pineapple (methyl butyrate).

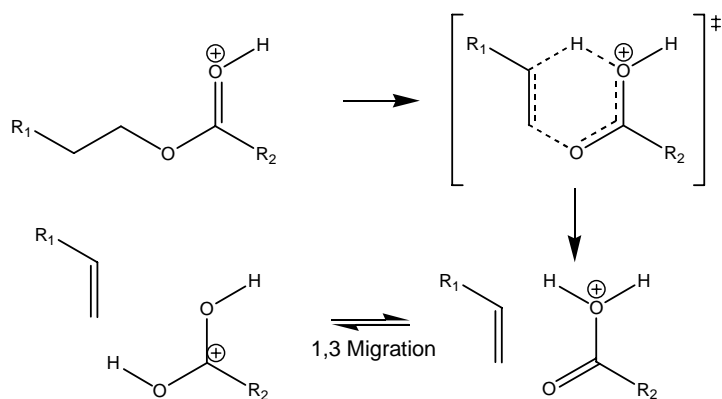
A Syft Technologies VOICE¹⁰⁰ SIFT-MS instrument has been used to measure the rate coefficients and branching ratios of 17 alkyl esters with H_3O^+ , NO^+ and O_2^+ . The observed branching ratios were found to be highly complex with unexpected products corresponding to protonated carboxylic acid being formed from a substantial percentage of collisions. A mechanism has been previously proposed for alkylcyclohexyl benzoates by Denekamp and Stanger,¹ where a 1,5 migration of an H atom from a beta carbon to the carbonyl oxygen occurs induced by H_3O^+ protonation via a cyclic six-membered intermediate. A similar mechanism is proposed here for alkyl esters and is given as figure 1.

Density functional theory and accurate energy G2MP2 calculations have been used to study these mechanisms in further detail.

The esters studied are then used as an example of how to create a SIFT-MS analytical method for the detection of trace analytes related to aspects of border security, and process control.

The presentation will link a fundamental gas-phase ion chemical study to real-world analytical measurement.

Figure 1. Proposed mechanism for H migration. $\text{R}_1 = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$; $\text{R}_2 = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$.



¹ Denekamp C. & Stanger A. *Journal of Mass Spectrometry*, 2002, **37**, 336-42.