Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Levulinic esters from the acid-catalysed reactions of sugar and alcohol as part of bio-refinery

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S1 Experimental details

Materials

All chemicals used in this study were analytical grade and were used without purification. Levoglucosan was obtained from Carbosynth Limited (U. K.). 2-(dimethoxymethyl)-5-(methoxymethyl)furan (DMMF) was bought from LC Scientific Inc. (Canada). Methanol is obtained from Merck Australia. Glucose, methyl α-D-glucopyranoside (MGP), ethyl α-D-glucopyranoside (EGP), methyl levulinate, ethyl levulinate, levulinic acid, and ethanol were purchased from Sigma Aldrich. Amberlyst 70 was used as the catalyst. Its physicochemical properties are available in the web: http://www.dow.com/products/product_detail.page?product=1120277. According to the datasheet, Amberlyst 70 can be used at the temperature as high as 190°C, however, the stability may be reduced under aqueous conditions. Hence, in order to determine if any leaching of the sulfonate groups occurred during the reaction, we performed the recycling experiments at the maximum reaction temperature of this study, 170°C, and determined the concentration of acid sites in the spent catalysts. The results showed that the leaching of sulfonate groups is insignificant under the conditions employed in this study.

Experimental procedure

The experiments were carried out in a stainless steel, high pressure batch reactor (Parr 4572, Parr Instrument Co.) equipped with an electrical heating jacket, a gas inlet, a sample outlet and a mechanical stirrer. For each experiment, weighed levoglucosan/ glucose, methanol, water, and Amberlyst 70 were mixed and then introduced into reactor. Volume of the reactants is typically ca. 390 ml (ca. 339 g). Initial concentration of levoglucosan/glucose is 5.58 wt% and the catalyst dosage is 5 wt% for all experiments. The methanol/water mass ratio depends on the given experiments. The autoclave was sealed after charging with reactants, and the air in it was replaced by purging with nitrogen for three times. The reactants were then brought to the desired temperature by external heating with a stirring rate of 600 rpm. The initial pressure in autoclave is ca. 1 bar before heating and the final pressure depends on the reaction temperature and the reaction medium. A sample was taken immediately after reaching the reaction temperature, and other samples were taken at 20 min intervals. The holding time at the reaction temperature is 180 min. For the experiments performed at 170^{o}C, it takes 28 min to reach the required reaction temperature of 170^{o}C. To gain insights in progress of the reaction during the heating-up process, samples were also taken during the heating-up periods. The catalytic results in the Figures are therefore divided into a nonisothermal zone before 28 min and an isothermal zone after 28 min.

Collected samples were filtered and stored in the refrigerator before analysis. Some special experiments were performed to measure formation of solid humins. In that case, no samples were taken and other conditions were the same. After 180 min at the reaction temperature, the reactants were extracted through the sampling valve to stop the reaction. After cooling down to the room temperature, the autoclave was opened. The catalyst with solid humins was collected. The solid humins adhered on the reactor wall was scrubbed as clean as possible, and the solid humins suspended in the solution were filtered. After that, the collected catalyst, scrubbed humins, and filtered humins were dried in a vacuum oven at 100^{o}C for 4 h to constant mass and total mass of solid humins was calculated. The definitions of levoglucosan conversion and product selectivities are as follows:

$$X(\text{mol }\%) = (1 - \text{moles of levoglucosan in product/moles of levoglucosan loaded in reactor}) \times 100\%$$

$$S(\text{mol }\%) = (\text{moles of product produced/moles of levoglucosan converted}) \times 100\%$$

Analytical methods

Analysis of the samples was carried out using a Hewlett-Packard GC-MS (HP6890 series GC with an HP5973 MS detector) with a capillary column (Agilent: HP-5MS, HP19091S-433) (length, 30 m; internal diameter, 250 mm; film thickness, 0.25 μm). Standard solutions covering the concentration range of the samples were used to obtain the calibration curve for calculating concentration of the compounds of interest. It was not possible to obtain standards for all the compounds identified in the GC/MS chromatograms. Consequently, signal intensity of the un-calibrated was normalized to compare trend of their concentration versus experimental parameters. The procedures for detection of the samples are generally as follows. A 1 μL sample was injected into the injection port set at 250°C with a split ratio of 50:1. The column was operated in a constant flow mode using 1.1 mL/min of helium as carrier gas. The column temperature was initially maintained at 40°C for 3 min before increasing to 300°C at a heating rate of 15°C/min. A solvent delay of 1.3 min was employed. The identification of each compound was achieved based on the matching mass spectrum in the spectral library. Moreover, the identification will further be confirmed by comparing the retention time and mass spectrum with the standards. As for the determination of D-glucose, the derivatization method was used and the procedure is generally following the literature.[1]

S2 Effects of reaction temperature on levoglucosan conversion and product distribution

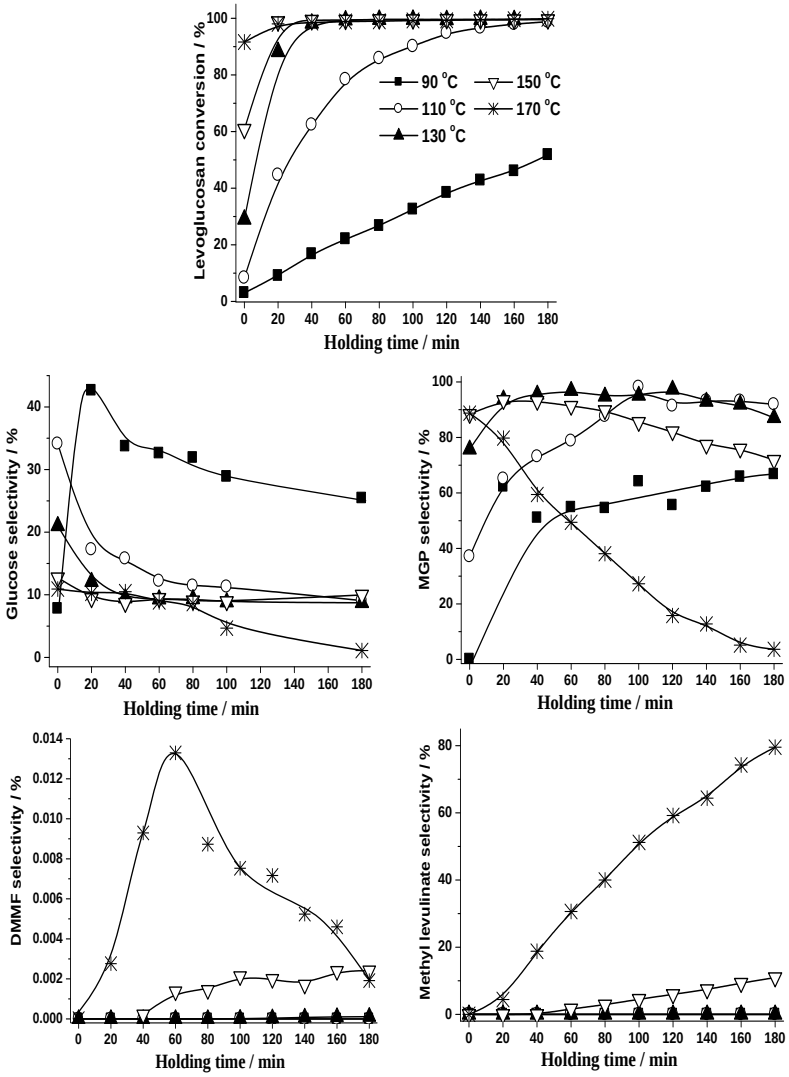
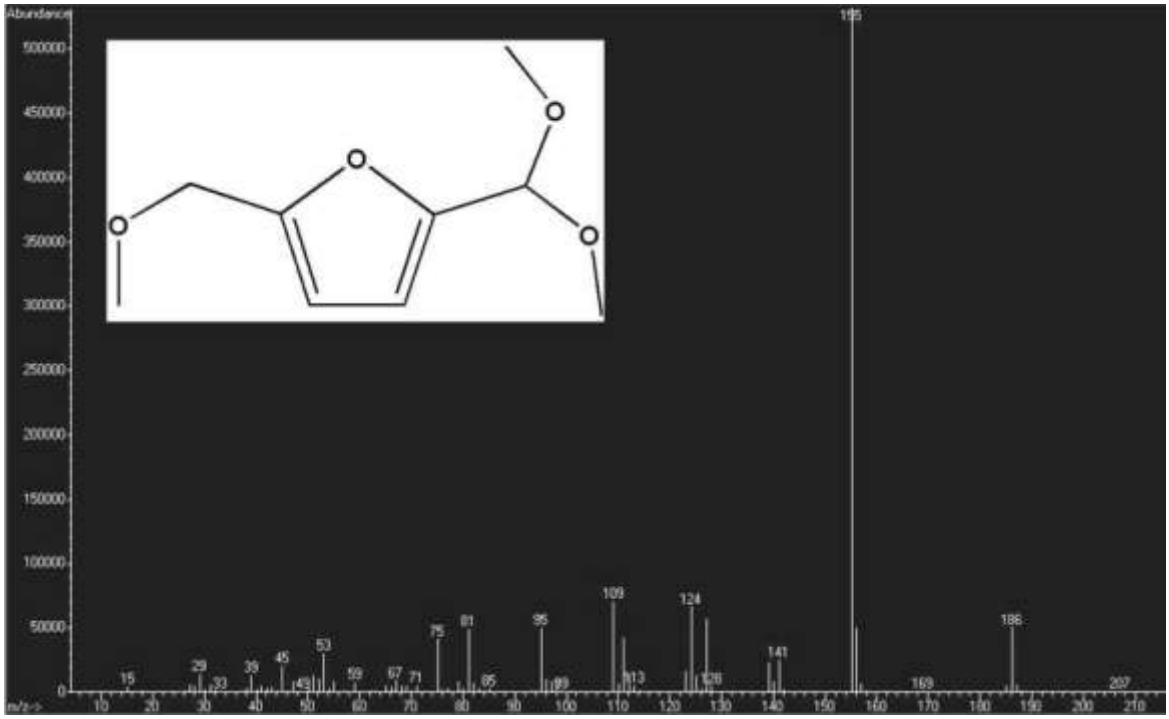


Fig. S1 Effects of reaction temperature on levoglucosan conversion and product distribution. Methanol/water mass ratio: 4.5; catalyst dosage: 5 wt%; stirring rate: 600 rpm.

Fig. S1 shows levoglucosan conversion and product selectivities at different temperatures in methanol/water medium. All experiments were carried out in an autoclave in which the reaction mixture was firstly heated (at ca. 6 K min^{-1}) to the required temperature and then held for 180 min. "0 min" of the holding time in Fig. S1 refers to the time when the required reaction temperature was just reached. Liquid samples were then withdrawn from the autoclave regularly for analysis. At a low temperature of 90°C, levoglucosan conversion reached only ca. 50% at the end. Glucose and MGP were produced as the main products. While the hydrolysis of levoglucosan gives glucose, the reactions of glucose or levoglucosan or both with methanol give MGP. At 110°C, levoglucosan became very reactive and MGP was produced as the main product.

Prolonged reaction time at 130°C led to slight decreases in MGP selectivity. Meanwhile, trace DMMF was formed from MGP. In addition to DMMF, 5-(methoxymethyl)-2-furancarboxadhyde (ether of HMF), 5-(hydroxymethyl)-2-(dimethoxymethyl)furan (acetal of HMF) were detected as well in the mass spectrum with small peaks. However, due to difficulty to get the standards, we did not quantify them and mainly focused on the catalytic behaviors of DMMF in this paper. DMMF can be regarded as the ether and acetal of HMF. Its identification was based on its mass spectrum presented in Scheme S1 and subsequently was confirmed by the standards. At 150°C, the conversion of MGP became remarkable and significant amounts of methyl levulinate were produced via DMMF. Methyl formate was also formed, but its peak in GC-MS chromatogram was largely overlapped with the methanol peak and hence hard to be quantified. In the acid treatment of glucose, levulinic acid and formic acid are generally formed with a 1:1 molar ratio in line with the reaction stoichiometry,[2] so the molar ratio between methyl formate and methyl levulinate is also expected to be 1:1. At 170°C, the methyl levulinate selectivity increased to ca. 80% after 180 min. DMMF selectivity versus reaction time showed an inverted-U shape and its concentration remained at a trace level. The conversion from DMMF to methyl levulinate was a relatively easy step. Once DMMF was formed from MGP, it was soon converted to methyl levulinate.



Scheme S1 Mass spectrum of DMMF

S3 Reaction pathway of levoglucosan in ethanol/water

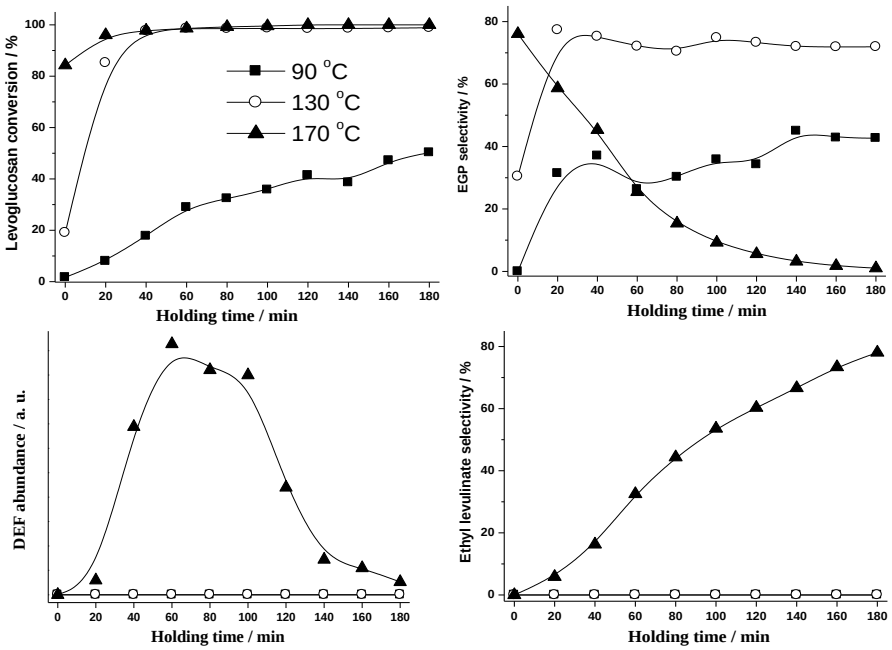
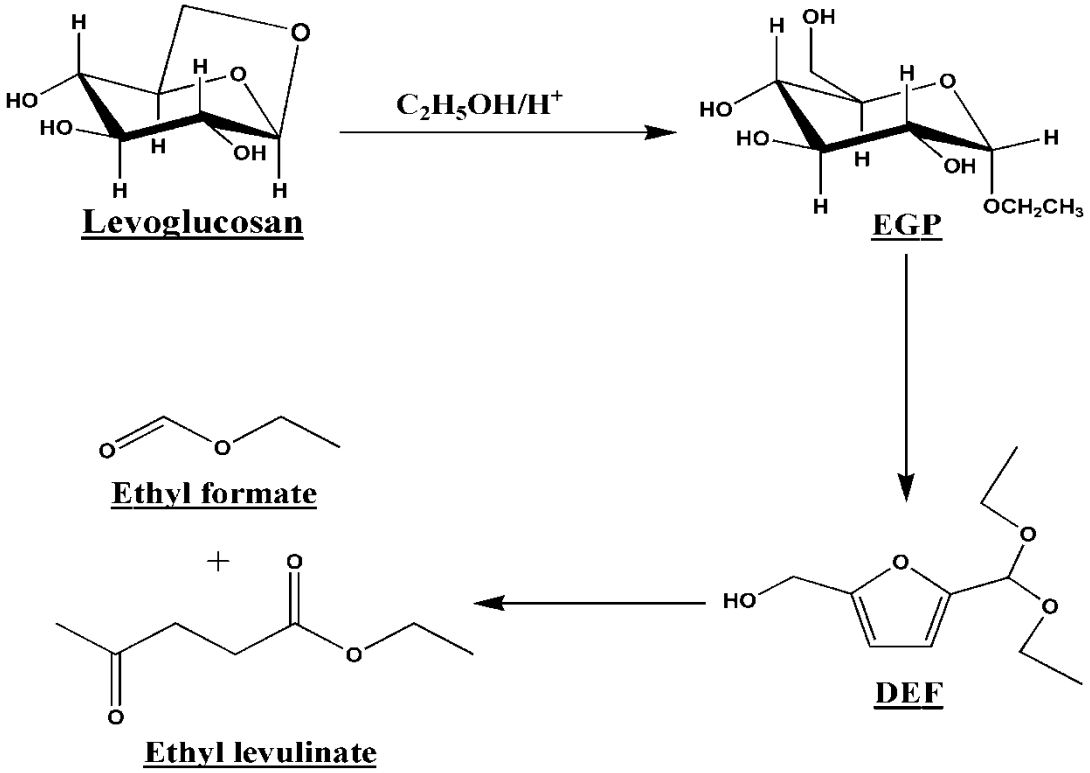


Fig. S2 Effect of temperature on levoglucosan conversion and product distribution in ethanol/water: ethanol/water mass ratio: 4.5; catalyst dosage: 5 wt%; isothermal reaction time: 180 min; stirring rate: 600 rpm.



Scheme S2 Main reaction pathway of levoglucosan in ethanol/water

Similar like that of methanol, ethanol also can be used to esterify the organic acid in bio-oil. The catalytic behaviours of levoglucosan in ethanol/water were also investigated. The experiments were performed at 90, 130, and 170 °C, which represent the low, medium, and high temperatures in esterification. The catalytic results are shown in Fig. S2. The

reaction mixture was firstly heated (at ca. 6°C min^{-1}) to the required temperature and then held for 180 min. "0 min" of the holding time in Fig. S2 refers to the time when the required reaction temperature was just reached, at which time sampling also commenced. Reaction temperature significantly affects levoglucosan conversion and product distributions. At 90°C, levoglucosan conversion reaches ca. 50%, which is similar with that in methanol/water. However, the selectivity to EGP (ca. 40%) is much lower than that of MGP in methanol/water (ca. 60%), which may result from the steric effect, due to the bigger size of ethanol molecule. Glucose was also quantified in some samples, selectivity of which is ca. 60% at the beginning and ca. 40% at the end at 90°C. Increasing temperature to 130°C efficiently promotes the conversion of levoglucosan. EGP is produced as the main product and no remarkable degradation of it is observed. At 170°C, significant degradation of EGP to 5-(diethoxymethyl)-2-furanmethanol (DEF) is observed. Owing to the difficulty to get the standard, DEF is recognized through its mass spectrum, which will be discussed below. The abundance of DEF in the products versus reaction time shows an inverted-U shape. Ethyl levulinate is the degradation product of DEF, and its selectivity reaches ca. 78% at the end. Like methyl levulinate, ethyl levulinate also can be used as a gasoline fuels additive and fragrance additive. In addition, ethyl formate also is formed at 170°C, but its peak in mass spectrum is largely overlapped with ethanol peak and hence hard to be quantified. Like that of formic acid and levulinic acid in the acid treatment of glucose, the molar ratio between ethyl formate and ethyl levulinate may also be 1:1. A simple scheme about the reaction pathway of levoglucosan in ethanol is given in Scheme S2.

Identification of DEF by the mass spectrum

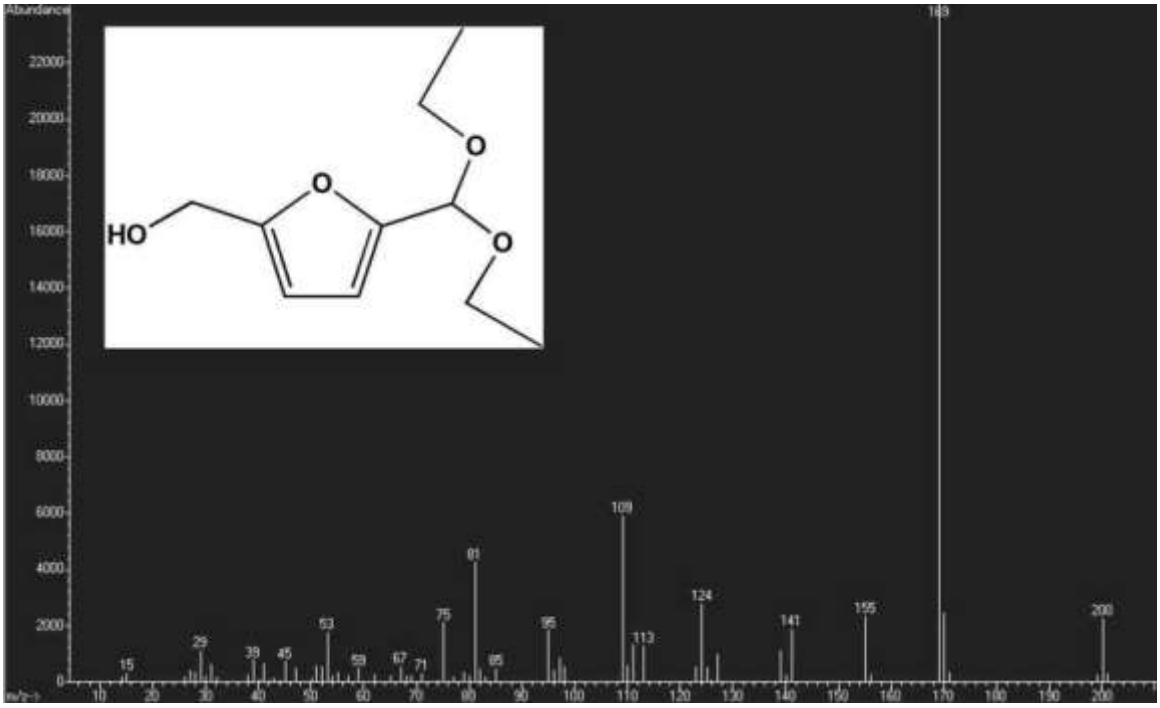
In the methanol/water mixture, the further degradation of MGP gives DMMF as the product. Similarly, the further degradation of EGP should give the 2-(diethoxymethyl)-5-(ethoxymethyl)-Furan as the product. However, detailed analysis of the mass spectrum shows that the formation of DEF is more reasonable. Due to difficulty to get the standard, the mass spectrum (Scheme S3) is used as an evidence for its identification. Detailed analysis of degradation pathways of DEF in GC/MS is presented in Scheme S4and S5, respectively. The ionized molecule in electric and magnetic fields will undergo further degradation to neutral fragment and/or fragment ion. Some of the fragment ion is characteristic, which is very useful for identifying the integral structure of the unknown molecule.

Degradation of the ionized molecule is generally rather complicated. Homolytic or heterolytic cleavage of the chemical bonds or the rearrangement of the atoms may be included. To simplify, we assume that the positive charge mainly locates on the oxygen atom of the furan ring and the divalent ions are not considered. DEF has the furan ring which has some aromaticity due to the conjugated π bonds. Hence it easily loses one of the unpaired electron in furan ring oxygen, forming the molecular ion (m/z = 200). The homolytic cleavage of the C–C bond between the hydroxymethyl group and furan ring will give the fragment ion with m/z of 169. After the cleavage, the carbon atom in the furan ring contains an unpaired electron, which is difficult to combine with the unpaired electron in the oxygen of furan ring to form a new C=O bond, otherwise the furan ring has to be opened, leading to an unstable form of fragment ion. Instead, the rearrangement of the atoms may occur through a ring transition state, and one of the hydrogen in the ethoxy group will migrate and combine with the carbon in furan ring to form a relatively stable fragment ion (base peak, m/z = 169). Since the base peak has the highest abundance, so its isotopic peak may be visible. The fragment ion with m/z of 170 may be its isotopic ion. The abundance ratio between base peak and the fragment ion of m/z = 170 is ca. 10.67%, while theoretical abundance ratio between the isotopic peak and base peak is ca. 10.51%. The closed ratio of the abundance is another evidence for the composition of the base peak. The consecutive loss of the two methylene groups of the base peak will give the two fragment ions with m/z = 155 and m/z = 141, respectively. Continuous and

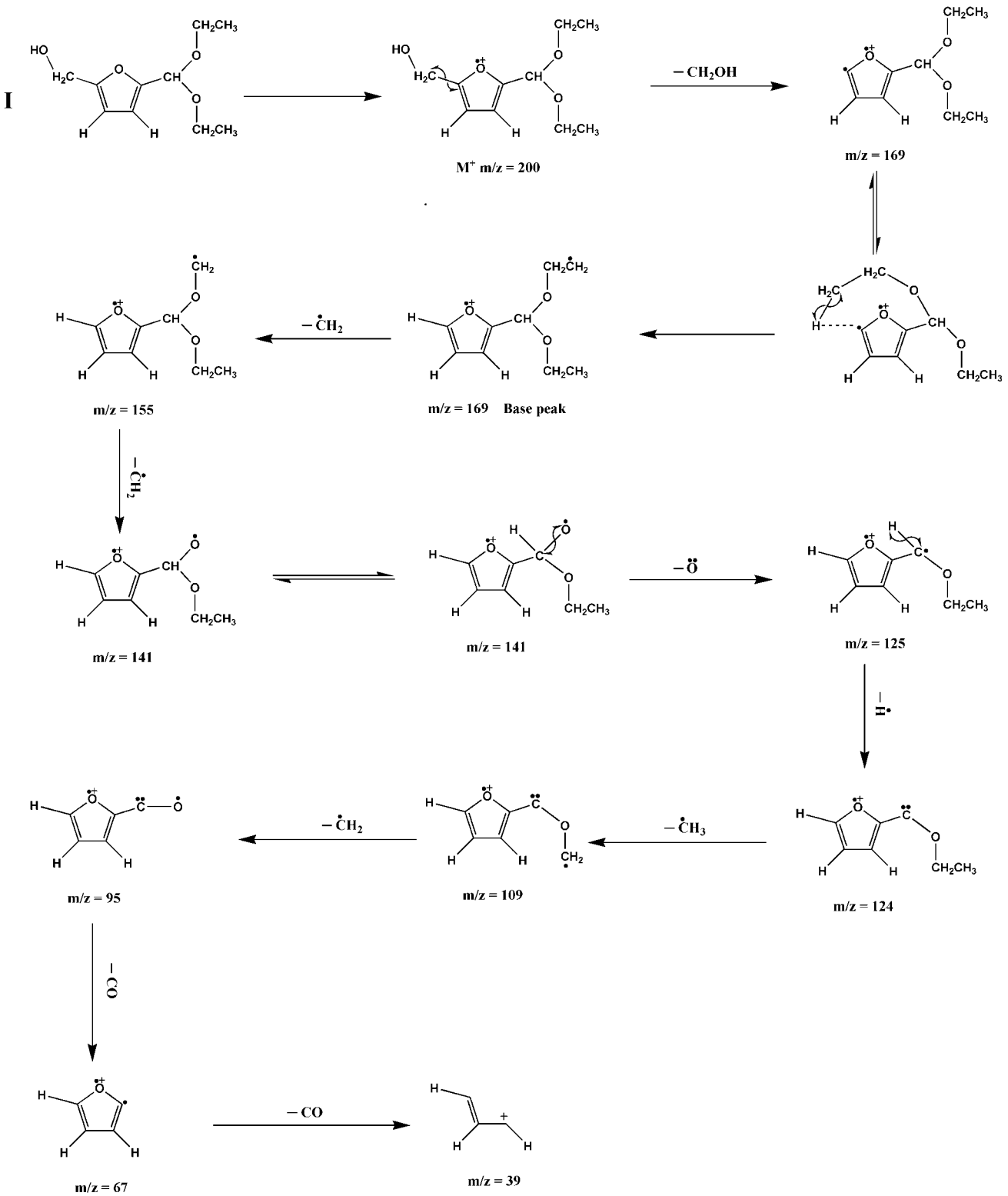
consecutive loss of an oxygen atom and a hydrogen atom will give the fragment ions with m/z = 125 and 124, respectively. Similarly, loss of the methyl group and further loss of the methylene group in the ethoxy group will give the fragment ions with m/z = 109 and m/z = 95. The further loss of a neutral CO molecule will give the fragment ion with m/z = 67, and the loss of another CO molecule will give the fragment ion with m/z = 39.

In addition to the above routes, other pathways also may exist and should account for the formation of other fragment ions (Scheme S5). The hydrogen in the ethoxy group of the fragment ion with m/z = 141 may undergo rearrangement to oxygen through a six-membered cyclic transition state. The formed fragment ion can undergo the consecutive cleavages and lose the two methylene groups, giving the fragment ions with m/z = 127 and m/z = 113, respectively. The further loss of one oxygen in the fragment ion with m/z = 113 will give the fragment ion with m/z = 97. Similarly, the rearrangement of the fragment ion with m/z = 109 and simultaneously loss of one neutral CO molecule will give a fragment ion with m/z = 81. Further loss of another neutral CO molecule will give the fragment ion with m/z of 53, degradation of which will give a fragment ion with m/z = 39.

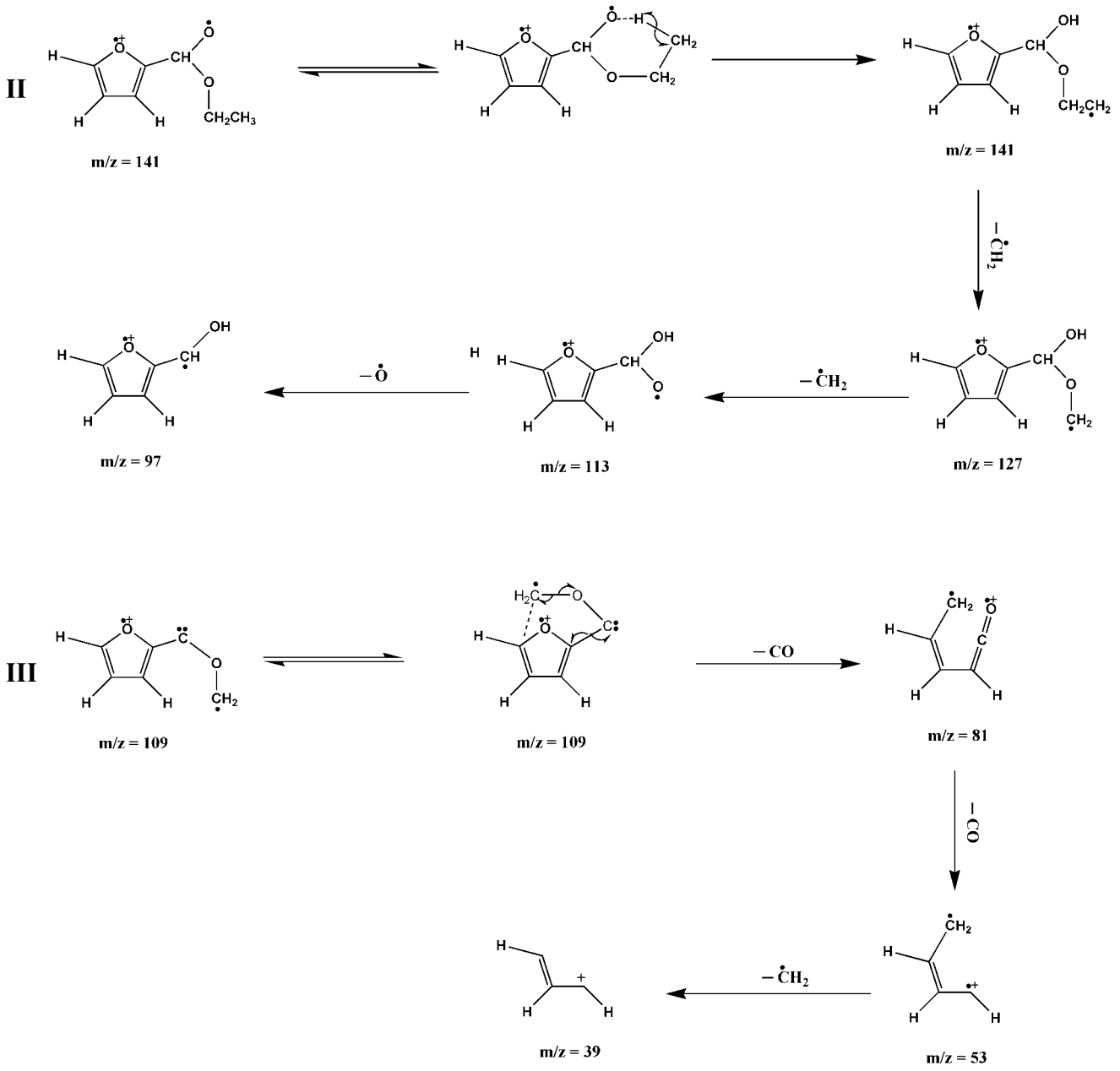
Mass spectrum is very useful to indentify structure of unknown compounds. The structure of DMMF was predicted through analysis of its mass spectrum in the similar way, and later was confirmed by the standard. However, although most mass-to-charge ratios in the mass spectrum are attributed to the specific fragment ion, it is still hard to say that the molecular structure predicted from the mass spectrum and the pathway for its degradation are correct. Other techniques are needed to confirm the structure of DEF.



Scheme S3 Mass spectrum of DEF



Scheme S4 Degradation pathway I for DEF in GC/MS



Scheme S5 Degradation pathway II and III for DEF in GC/MS

Reference

1 C. C. Chen and G. D. Mcginnis, *Carbohydr. Res.*, 1981, **90**, 127.

2 L. Peng, L. Lin, J. Zhang, J. Zhuang, B. Zhang and Y. Gong, *Molecules*, 2010, **15**, 5258.