Solution injection laser pyrolysis: a novel technique for gas phase pyrolysis of involatile compounds

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The gas phase pyrolysis of involatile species has been studied by injection of solutions in inert solvents into SF_6 gas heated by CO_2 laser radiation; the gas phase chemistry reflects the distribution of species present in solution, and may potentially be controlled through parameters such as solution pH.

IR laser powered homogeneous pyrolysis (LPHP) has been successfully exploited for over 20 years in the investigation of the mechanisms of thermal decomposition of volatile organic and organometallic compounds.[1,2] The advantages of the technique are well known; very small quantities of materials are needed, initiation of reaction is unambiguously homogeneous, and intermediates are readily trapped.[3,4] Among its shortcomings are difficulties in defining and measuring effective temperatures, although this may be overcome through the use of compounds of well known kinetic parameters. In addition, previous work has been restricted to compounds of at least moderate volatility (> 1 Pa). Here, we show that the latter limitation may be removed by a simple adaptation of the technique, and report some preliminary results.

The modification of IR LPHP described in this study is referred to as solution injection laser pyrolysis, SILP. Saturated solutions of target species in suitable solvents were introduced directly into the SF_6 gas heated by the CO_2 IR laser by means of a Hamilton syringe inserted through a rubber septum. In order to ensure rapid vaporisation of the solvent, the needle orifice was mechanically modified to produce a fine spray, and the needle tip heated to somewhat below red heat by positioning at the perimeter of the heated zone. Effective temperatures were not otherwise monitored in the present work although these are clearly needed in quantitative studies. Gaseous pyrolysis products were identified after injection by FTIR, and quantified with the aid of commercial software. For very soluble species, solution volumes of 10–50 µl yielded strong product IR spectra. In some experiments, additional gaseous reagents were introduced into the pyrolysis cell before solution injection in order to trap reactive intermediates, or the solution pH varied to modify the dominant solute species.

The volumes of solution injected are such that the vapour pressure of the solvent is usually exceeded in the pyrolysis cell; as a result, interpretation of observations might conceivably involve the partial dissolution of gaseous pyrolysis products in residual liquid solvent. In cases where evaluation of this complicating feature was possible, it proved to play no significant role, and has therefore been discounted. It is also possible that partial pyrolysis of solute might take place in solution within the heated needle tip before ejection. Again, investigations correlating product yield with needle tip location indicated that this was not the case; this conclusion is consistent with those from the early development of thermospray mass spectrometry, where orifice temperatures as high as 1000 °C were employed.[5]

The physical processes that occur as solution emerges from the needle tip into the heated gas zone are a matter of vigorous debate in the literature. In the most widely accepted model proposed by Iribarne and Thomson,[6] the majority of the solvent is vaporised into a fine spray as the solution leaves the capillary;

the droplets that result may be charged, positively or negatively, in a statistical manner reflecting the distribution of ionic species in solution. As further solvent evaporates from the droplets, the charge density increases and eventually results in a series of 'Coulomb explosions' in which ions, either naked or solvated, are ejected into the gas phase. However, in contrast with electrospray or thermospray mass spectrometry, the principal focus of the present work is the subsequent thermal chemistry of solute species. This process also differs substantially from the suite of 'spray pyrolysis' methods developed for the generation of ceramic materials, where the major pyrolysis processes involve micro-aggregates of solute at heated surfaces.[7] The preliminary results described below confirm the viability of the technique, and illustrate its potential in mechanistic investigations.

Zinc oxoacetate and zinc acetate in toluene. The covalent zinc oxoacetate {hexakis[µ-(acetato-$O:O'$)]-μ_4-oxotetrazinc}, $Zn_4O(MeCO_2)_6$, provides a convenient reference point for the investigation of the gas phase pyrolysis chemistry of metal acetates; although little is known of the vapour of this compound, pyrolysis of the solid is known to produce largely CO_2 and acetone.[8] Its very slight volatility, and its stable tetrahedral Zn_4O unit, have also attracted interest in the parent compound as a potential precursor in the chemical vapour deposition of zinc oxide films.[9] In the present work, toluene was selected as the solvent, as it proved thermally inert at the temperatures employed. FTIR spectra (Fig. 1) of the gaseous products of SILP of saturated toluene solutions of Zn_4O-$(MeCO_2)_6$ were dominated by solvent vapour and ketene, with smaller amounts of CO_2 and CH_4, and traces of CO, C_2H_4 and C_2H_2; no trace of acetone was detected. Clearly, pyrolysis pathways for isolated molecules in the vapour are very different from those in the bulk solid. Very similar results were found for the less soluble zinc acetate, although the yield of ketene was lower, and that of methane higher. In fully deuterated toluene, CH_3D was produced as well as CH_4, indicating the involvement of methyl radicals. These results concur with the known routes for decomposition of isolated acetate groups on oxide surfaces, and indicate that analogues of zinc oxoacetate may serve as molecular mimics for surface chemistry.[10]

Aqueous alkali metal acetates. There have been several reports on the dominant ionic species observed in the electro-
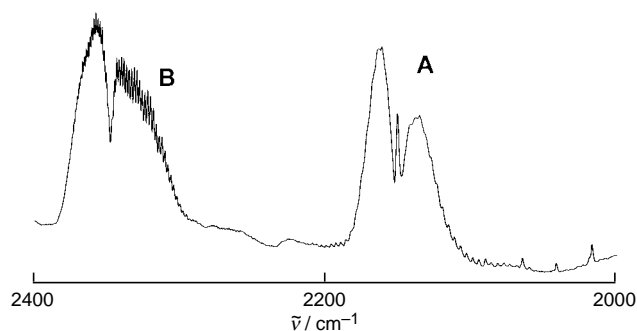

Fig. 1 Partial FTIR spectrum of the products of SILP of zinc oxoacetate in toluene, indicating the production of ketene (A) and CO_2 (B)

spray mass spectra of alkali metal acetates;[11] these include clusters of the form $[M_n(OAc)_{n \mp 1}]^\pm$. In the SILP system, at high laser powers, the SF_6 photosensitiser was attacked, presumably by metal atoms or ions, resulting in the production of large quantities of SO_2 and extensive etching of the cell walls and windows. This reaction route was not explored in any detail; however, the observation of a blue chemiluminescence within the heated gas zone (presumably electronically excited SO_2) did provide clear visual confirmation of the homogeneous nature of reaction. At lower powers, all the alkali metal acetates behaved identically, and most experiments were conducted with saturated solutions of the potassium salt. In H_2O, the major products were CO_2 and CH_4, together with small amounts of CO and C_2H_2; no ketene was observed, in line with the known ready hydrolysis of ketenes.[12] In D_2O solution, extensive deuteration of C_2H_2 (as both C_2HD and C_2D_2) was observed, suggestive perhaps of ion–molecule reactions, but none of CH_4. Copyrolysis with H_2 resulted in almost complete suppression of CO_2 and CO, and a marked increase in CH_4 production; copyrolysis with D_2 resulted in some CH_3D, but no deuterated acetylenes. Conversely, copyrolysis with O_2 suppressed both hydrocarbons and increased the yield of oxides. Pyrolysis of a saturated solution of potassium acetate in 2 mol l^{-1} NaOH yielded no CO_2, and a marked increase in both CH_4 and C_2H_2.

Aqueous glycine. Many electrospray studies have focussed on systems of biological interest such as amino acids; in particular, the gas-phase chemistry of glycine-related anions and cations has been the subject of a number of experimental and theoretical investigations.[13] The IR-detectable gas phase products of SILP of aqueous solutions of glycine were CO_2, CO, NH_3, HCN, CH_4 and traces of C_2H_2. From 2 mol l^{-1} NaOH solution, no HCN was observed; from acidified solutions, no traces of CH_4, C_2H_2 or NH_3 were detected. With the ^{13}C-labelled $H_2N^{13}CH_2CO_2H$, only $H^{13}CN$ was observed, and both $^{13}CO_2$ and ^{13}CO were also detected at levels dependent on solution pH. From acidic solution, the ratio of $^{13}CO_2:^{12}CO_2$ was $1:5$, and that of $^{13}CO:^{12}CO$ $1:1$; from basic solutions, no labelled carbon oxides were generated. Unlike the alkali metal acetates, none of the solute species present in glycine solution are appreciably volatile, and we may conclude that these variations in pyrolysis products reflect changes in the major species appearing in the gas phase.

The above preliminary results indicate that the SILP technique provides the potential for the investigation of pyrolysis of isolated involatile species in the gas phase, most significantly of cations and anions, which are not readily produced by other methods.

Notes and References

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