Preferred Field Ionisation of Olefins at a Silver Nitrate Surface

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Summary The efficiency of ionisation of some olefins over that of corresponding paraffins is increased at an emitter partially coated with $AgNO_3$ under conditions where adsorption can occur.

Certain reactions of samples studied by field ionisation (FI) mass spectrometry are most easily explained by adsorption at the surface near which ionisation occurs in the classical FI mechanism: proton transfer to give ROH_2^+ and cluster formation to give $(ROH)_2H^+$ from alcohols,[1] γ hydrogen transfer with β cleavage,[2] chelation,[3,4] dissociative chemisorption of alkanes[5] and cycloalkanes,[6] and disproportionation of cyclic compounds.[7] Chemical reactivity related to adsorption on FI surfaces thus being widespread, we have studied the possibility of designing surface characteristics for the selective adsorption and FI of functional groups.

The formation of complexes with Ag^I by olefins[8] and aromatic compounds[9] has been known for a long time and used as the basis for chromatographic methods, including the removal of olefins, acetylenes, and aromatic compounds from samples prior to gas chromatographic analysis.[10] This well known selective retention suggested a sufficiently favourable equilibrium for application in FI. Emitters for field desorption–field ionisation mass spectrometry were partially coated with $AgNO_3$ by three immersions into a 25% aqueous solution with drying at room temperature each time. Visual inspection showed that this provides approximately one-third coverage of the emitter surface by $AgNO_3$ crystals. Equimolar mixtures of cyclohexane–cyclohexene, decane–dec-1-ene, and decalin–tetralin were analysed using a modified[3] AEI MS702 instrument with photographic plate recording. The following observations were made. (i) Only ions corresponding to the molecular weights of the compounds were detected. (ii) At 0 mA heating current the intensity of the ion from the unsaturated compound was 15—50% greater than that from the saturated (50%: tetralin–decalin; 15%: dec-1-ene–decane). (iii) At 15 mA heating current the intensities of both ions from the mixture were the same within 1%. (iv) When an emitter not coated with $AgNO_3$ was used with 0 mA heating current, the intensities of both ions were the same within 1%.

We conclude that the presence of $AgNO_3$ on a field anode causes partial selectivity not noted in its absence, but that when adsorption is prevented by heating FI shows no selectivity for either olefin or paraffin. More detailed experiments will indicate the applicability of such ideas to the study of the mechanism of field ionisation and specificity of adsorption. Selected compounds have been removed prior to gas chromatographic analysis by using pre-columns packed with materials which show a selectivity for certain functional groups; many of these pre-column packings should be applicable to selective FI methods. We propose that optimisation of salts for adsorption of specified functional groups, use of thin films of involatile solvents, and extension to involatile samples may possibly provide a new selective mass spectrometric method even more controllable than chemical ionisation with special reagent gases.

We thank the National Science Foundation for support.

(*Received*, 13*th April* 1977; *Com.* 347.)

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