Chemical Ionization Mass Spectrometry Studies. Nitric Oxide as a Reagent Gas

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Summary Preliminary results indicate that it may be possible to identify the functional group present in many organic compounds from chemical ionization mass spectra recorded with nitric oxide as the reagent gas.

IN chemical ionization mass spectrometry (CIMS) sample molecules are ionized in the gas phase by ion-molecule reactions rather than by the conventional electron bombardment technique.[1] Reagent ions are generated in the ion source by bombarding suitable gases at relatively high pressures (*ca.* 1 Torr). Sample molecules are introduced in the usual manner and undergo chemical reactions on collision with reagent ions. To date most CI spectra have been obtained using methane as reagent gas.[1] Under electron bombardment at 1 Torr, methane affords $C_2H_5^+$ and CH_5^+ ions in high abundance and these two ions function either as Brønsted acids or hydride abstractors toward neutral sample molecules.

We have explored the utility of a number of different gases as reagents in CI and have found previously that methane–acetaldehyde and methane–acetone mixtures can be used to distinguish ketones from aldehydes and to differentiate primary, secondary, and tertiary alcohols;[2] ND_3 can be used to differentiate primary, secondary, and tertiary amines;[3] active hydrogen in organic compounds can be determined with deuterium oxide;[4] argon–water mixtures afford spectra containing abundant $M + 1$ ions as well as all the fragment ions expected from EI spectra.[5]

We present here results of preliminary experiments using nitric oxide as a reagent gas. CI(NO) spectra of several pesticides and benzophenones have been discussed previously.[5]

Electron bombardment of nitric oxide at *ca.* 0·5 Torr produces NO^+ (*m/e* 30) in high abundance and this ion, in turn, functions as an electron acceptor, hydride abstracting agent, and electrophile towards organic sample molecules in the ion source of the mass spectrometer.

The major peak in the CI(NO) mass spectra of ketones, esters, and carboxylic acids corresponds to $M + 30$, and results from attachment of the reagent ion, NO^+, to the sample molecule.† Relatively low abundances of M^+ and $M + 1$ ions are also observed in some cases and the carboxylic acids suffer loss of OH to give an abundant $M - 17$ ion. Generation of M^+ ions presumably occurs by electron transfer between the sample molecule and the NO^+ reagent ion. Proton transfer from water as a contaminant probably accounts for the $M + 1$ ions.

In contrast to the above results the most abundant ion in the CI(NO) spectra of aldehydes and ethers corresponds to $M - 1$. Attachment of NO^+ to the sample is also observed for aldehydes but not for ethers.

Treatment of the primary and secondary alcohols with NO^+ produces abundant ions corresponding to $M - 1$, $M - 17$, and $M - 2 + 30$. An $M - 3$ ion is also generated from primary but not secondary alcohols. Tertiary alcohols afford a single ion corresponding to $M - 17$. Although the detailed steps involved in the reactions leading to the $M - 1$, $M - 3$, and $M - 2 + 30$ ions are not known at present, the CI(NO) spectrum of [1-$^2H_1$]cyclohexanol indicates that it is the hydrogen at C(1) that is lost exclusively in the formation of the $M - 1$ ion from cyclohexanol. Since [2,2,6,6-$^2H_4$]cyclohexanol forms an abundant $M - 2 + 30$ ion by selective loss of two hydrogen atoms, it also seems probable that this type of ion is pro-

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† A comparison of the $M + 1$ ion abundance in CI(CH_4) and $M + 30$ ion abundance in CI(NO) spectra of ketones indicates that the sensitivities of the two techniques are comparable.

duced by oxidation of the alcohol and subsequent attachment of NO^+ to the resulting ketone. Formation of the $M - 3$ ion from the primary alcohols may involve hydride abstraction from an intermediate aldehyde.

The above results suggest that once the molecular weight of the sample has been determined by $CI(CH_4)$ mass spectrometry, it should be possible to identify the functional groups in many organic compounds by recording a second CI mass spectrum using nitric oxide as the reagent gas.

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