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CHEMICAL IONIZATION MASS SPECTROMETRY STUDIES. I. IDENTIFICATION OF ALCOHOLS

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In mass spectra of alcohols generated by electron impact (EI), the molecular ion (M) is generally absent or present in very low abundance.[1] Most of the ion current is carried by smaller oxygen-containing fragment ions. Consequently, identification of alcohols by mass spectrometry is often difficult or impossible. Methane and isobutane chemical-ionization (CI) mass spectra of alcohols also exhibit ions of low abundance in the molecular-weight region.[2] In contrast to EI spectra, however, fragment ions formed from the alkyl portion of the molecule dominate the CI spectra.

In this report we describe the results of preliminary experiments in which protonated acetone (1) and protonated acetaldehyde (2) were employed as reagents to obtain CI mass spectra of alcohols. This procedure affords abundant ions at the high mass end of the spectra of primary, secondary, and tertiary alcohols and provides a means of distinguishing between the above isomers.

Strong Brönsted acids, CH_5^+ and $C_2H_5^+$, are produced when methane at a pressure of 1 torr is bombarded with 500 eV electrons.[3]

$$CH_4 + e^- \longrightarrow CH_4^{+\cdot} + CH_3^+$$

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + CH_3^\cdot$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$

Although these species are inert to further reaction with methane, they do protonate carbonyl compounds such acetaldehyde and acetone readily. As a result if a mixture of CH_4 and CH_3CHO (20:1) or CH_4 and $(CH_3)_2CO$ (20:1) is subjected to electron impact, the only abundant ions formed are those derived from the carbonyl compound at m/e values corresponding to M+1 and 2M+1,*

$$CH_5^+ \ (C_2H_5^+) + (CH_3)_2CO \longrightarrow CH_4 \ (C_2H_4) + [(CH_3)CO]H^+ \qquad M+1$$

$$[(CH_3)_2CO]H^+ + (CH_3)_2CO \longrightarrow [(CH_3)_2CO]_2H^+ \qquad 2M+1$$

Addition of cyclohexanol (3) to the CI source containing protonated acetone $CH_3\overset{+}{C}OHCH_3$, affords the spectrum shown in Figure 1.** Peaks derived from the alcohol appear at m/e 97, 99, 155, 157, 193, 195, 197. In the spectrum of 1-d_1-cyclohexanol the relative abundance of ions formed by loss of deuterium and hydrogen atoms from the molecular ion is 8:1. Thus, in the formation of the M-1 ion (m/e 99) from 3, it is the hydrogen at C-1 that is lost preferentially. We suggest that this occurs by a pathway involving hydride transfer

Figure 1

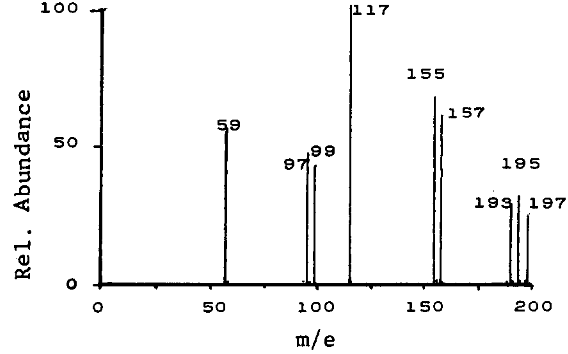
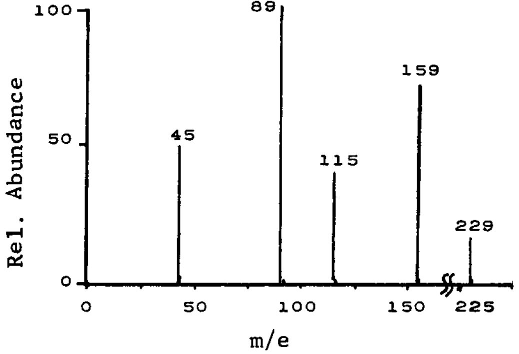


Figure 2



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* M+1 and 2M+1 ions could also be produced by a reaction between either acetaldehyde and acetone and the radical cation, $CH_4^{+\cdot}$. The latter ion is the initial product formed when methane is subjected to electron impact.

** All mass spectra were obtained at a resolution of 2000 on an AEI MS-902 mass spectrometer equipped with a dual EI/CI ion source designed and build by Scientific Research Instrument Corporation, Baltimore, Md.

from cyclohexanol to protonated acetone as shown below.

3 4 m/e 99

The M-3 ion at m/e 97 in the spectrum of 3 probably corresponds to protonated cyclohexenone formed by the loss of hydrogen from 4 since the same ion appears in the CI spectrum (methane-acetone) at M-4 for 1-d_1- and 2,2,6,6-d_4-cyclohexanol, at M-1 for cyclohexanone and at M-2 for 2,2,6,6-d_4-cyclohexanone. Whether the loss of hydrogen is a concerted one step or multistep process is not known. The remaining ions in the spectrum of 3 occur at m/e values corresponding to dimeric structures containing a proton and various combinations of acetone (1), cyclohexanone (5) and cyclohexenone (6): 1-H^+-6(m/e 155); 1-H^+-5 (m/e 157); 6-H^+-6(m/e 193); 5-H^+-6 (m/e 195); and 5-H^+-5 (m/e 197).

A CI mass spectrum of cyclohexanol can also be obtained using protonated acetaldehyde as the ionizing reagent. Again M-1 and M-3 ions are produced in high abundance. Ions corresponding to dimeric structures are also formed and appear at m/e 141 (2-H^+-6); 143 (2-H^+-5), 193 (6-H^+-6), 195 (5-H^+-6) and 197 (5-H^+-5).

In contrast to the situation with a secondary alcohol such as 3, ionization of primary alcohols is affected by protonated acetaldehyde but not by protonated acetone. Thus 1-heptanol (7) affords the mass spectrum shown in Figure 2 when $CH_3\overset{+}{C}HOH$ is employed as the ionizing reagent. Abundant ions occur at m/e values corresponding to M-1 and the same types of dimeric structures produced from 3. No reaction occurs between 1-heptanol and protonated acetone because the required hydride transfer step is endothermic. The expected product ion, protonated 1-heptanal (8), is less stable than the reagent ion, $CH_3\overset{+}{C}OHCH_3$.

$$\underset{\textstyle 7}{CH_3(CH_2)_5CH_2OH} + CH_3\overset{+}{C}OHCH_3 \not\longrightarrow \underset{\textstyle 8}{CH_3(CH_2)_5\overset{+}{C}HOH} + CH_3CHOHCH_3$$

In general, the proton affinity of ketones is greater than that of aldehydes.[4] Thus even if the hydride transfer did take place from the primary alcohol to $CH_3\overset{+}{C}OHCH_3$, the product ion 8 would not be observed because it would immediately donate a proton to the excess acetone present in the CI source. This can be demonstrated by either adding 1-heptanal to a methane-acetone reagent-gas mixture or by adding acetone to a reagent-gas mixture composed of 1-heptanal and methane. In both cases the CI mass spectrum of 1-heptanal is completely suppressed and only ions derived from acetone are observed.

Hydride abstraction from tertiary alcohols to produce M-1 ions does not occur when either $CH_3\overset{+}{C}HOH$ or $CH_3\overset{+}{C}OHCH_3$ are employed as reagent ions. Thus, by obtaining two CI spectra, one with methane-acetaldehyde, and the other with methane-acetone as the reagent gases, it is possible to distinguish between primary, secondary and tertiary alcohols.*

Experiments are currently in progress to determine the limitations of the above technique and to explore the possibility of using CI mass spectrometry to make conformational assignments to hydroxyl groups in fused ring systems.

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REFERENCES

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*Alcohols that have been studied to date include; all isomeric butyl and amyl alcohols; benzyl, cyclopentyl and ferrocenyl alcohols; and several monosubstituted cyclohexanol derivatives.