PHOTOIONIZATION MASS SPECTROMETRY OF ALIPHATIC MONOTERPENE ALCOHOLS

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Recently, considerable advances have been achieved in the application of ultraviolet radiation to the formation of ions in the source of a mass spectrometer. Thanks to a number of basic and methodical advantages, photoionization mass spectrometry can be used successfully to investigate the mechanism of ionization processes [1, 2].

The aim of the present work was to determine the basic processes of dissociative photoionization of monoterpene alcohols and to compare them with the processes taking place on electron impact. Figures 1-3 give the photoionization mass spectra of geraniol, nerol, and linalool, and also the corresponding spectra obtained by the electron-impact method.

Geraniol. On photoionization, the splitting out of water in the decomposition of the molecular ion leads to the appearance of an ion with m/e 136 as the strongest in the mass spectrum. It is difficult to determine accurately the structural formula of the radical cation formed in this process: apparently we are dealing with a set of distinct isomeric structures.

The splitting out of water may be accompanied by cleavage of the C−C bonds of the side chains. The elimination of a methyl radical gives an ion with m/e 121, and the splitting out of an isopropyl radical an ion with m/e 93.

Of the cleavages not induced by an oxygen atom, the most probable is the cleavage of the allyl bond. This bond is in the β position to two probable points of localization of the charge − the quaternary centers of the structure with double bonds − and is readily broken on electron impact [3] with the formation of an ion with m/e 69 ($M^+ \rightarrow 69^+ + 85$), which decomposes with the ejection of ethylene and gives a strong peak of an allyl cation (m/e 41).

On photoionization, the ion with m/e 69 has an insignificant intensity, but together with it an ion with m/e 84 appears which has a low intensity on electron impact.

In the field of low mass numbers, the photoionization mass spectrum of geraniol shows a strong peak of an ion with m/e 59. Since in the electron-impact mass spectra of monoterpene hydrocarbons no ion with such a value of the mass number is observed [4], it may be regarded as a homolog of the hydroxonium ion.

No fragmentary ions in the regions of mass numbers below 59 are formed in the photoionization of geraniol. This is apparently due to the low excitation energy of the heavy fragmentary ions.

A characteristic feature of the photoionization mass spectrum of geraniol is the increase in the relative intensities of the characteristic ions with high mass numbers. The relative magnitude of the peak of the molecular ion in photoionization is 25 times greater than on electron impact. The intensity of the characteristic ion with m/e 136 increases 20-fold. The characteristics of the photoionization mass spectra permit the question to be put of the possibility of the effective analysis of isomeric compounds.

Nerol. Nerol is a stereoisomer of geraniol. As is known [5], trans isomers are more stable to photon and electron impacts. This is confirmed by differences in the photoionization mass spectra of geraniol, which is a trans isomer, and nerol, which is the corresponding cis isomer.

The ratio of the intensities of the peaks of the molecular ions of the cis and trans isomers that we studied is $I_{cis}/I_{trans} = 1:4$. The intensity of the molecular ion as a fraction of the total ion current is 6%

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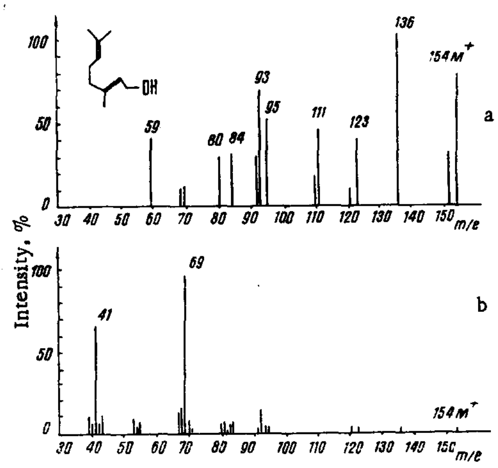

Fig. 1. Mass spectra of geraniol: a) on photoionization; b) on electron impact.

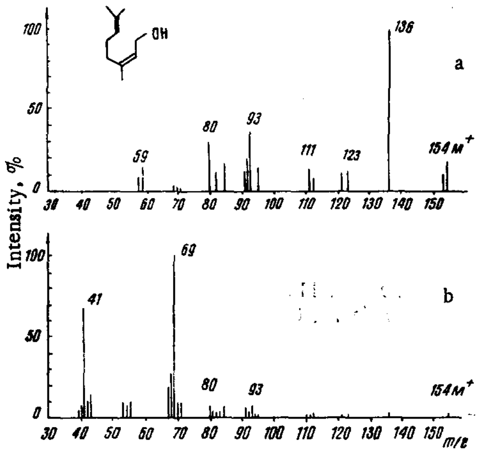

Fig. 2. Mass spectra of nerol: a) on photoionization; b) on electron impact.

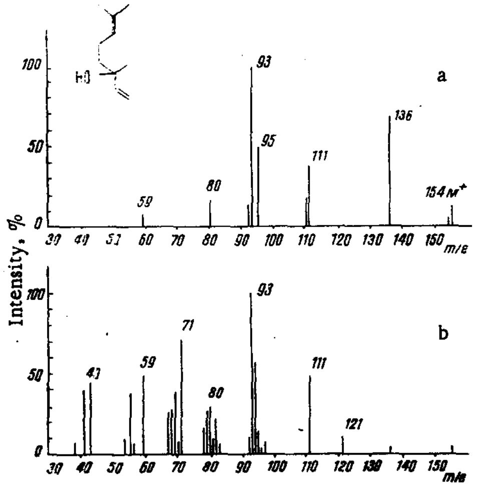

Fig. 3. Mass spectra of linalool: a) on photoionization; b) on electron impact.

for nerol and 14% for geraniol, i.e., the stability of the cis isomer is 2.3 times smaller than for the trans isomer.

On ionization with electrons having an energy of 40 eV, the ratio of stabilities of the molecular ions of geraniol and nerol is 1.4. It can be seen from this that in the case of photoionization we have a more characteristic value of the stability for each of the isomers than on electron impact.

Linalool. In contrast to the monoterpene alcohols that we have considered above, linalool is a tertiary alcohol. In addition to this structural difference it lacks a readily-cleaved doubly allyl bond.

The molecular ions of tertiary alcohols are characterized by low stability [6], and therefore the peak of the molecular ion on photoionization is considerably inferior in intensity to the peak of the molecular ion in the mass spectra of a primary alcohol. The relative intensities of the molecular ions for geraniol and linalool are, respectively, 14 and 1%. The relative intensities of the ions $M^{+\cdot}$ and $(M-18)^{+\cdot}$ formed in the photoionization of linalool are, respectively, 25 and 20 times greater than on electron impact.

On photoionization, the process leading to the formation of the ion with m/e 71 which arises in the decomposition of the molecular ion at the C_5-C_6 bond is unlikely.

It must be mentioned that, in the photoionization mass spectrum, ions are observed the formation of which is connected with the migration of hydrogen (ions with m/e 136, 111, 95, 80, 59). At the same time, ions with m/e 71 and 69, the appearance of which takes place with simple bond cleavage and the energetic favorability of which is obvious, are absent from the mass spectra.

EXPERIMENTAL

The photoionization mass spectra were recorded on an apparatus constructed on the basis of a MI-1301 mass spectrometer. For the photoionization of the vapors of the compounds under investigation, unresolved light was introduced into the ionization chamber through a window formed from a lithium fluoride crystal. The source of vacuum ultraviolet radiation was a high-voltage hydrogen lamp [7]. The maximum energy of the photons passing into the ionization chamber was limited by the transmission of the window and did not exeeed 11.8 eV.

On photoionization, the ion currents did not exceed 10^{-14} A, and they were recorded by means of an ion-optical converter.

The electron-impact mass spectra were taken on the same apparatus with an ionization voltage of 40 V. The temperature of the inlet system and of the ionization chamber was 100°C in both cases.

SUMMARY

1. The dissociative processes observed in the photoionization of monoterpene alcohols have been investigated. It has been established that the relative intensities of the peaks of the heavy ions, including the molecular ions, are higher on photoionization than on electron impact.

2. It has been found that the mass spectra of the isomeric alcohols obtained on photoionization differ from one another to a greater degree than the electronic mass spectra.

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