

NOTIZEN

Hydrogen Scrambling in 1-Naphthol under Electron Impact

L. KLASINC * and H. GÜSTEN

Institut für Radiochemie, Kernforschungszentrum Karlsruhe
Karlsruhe, Germany

(Z. Naturforsch. 27 a, 1681—1682 [1972]; received 18 October 1972)

The fragmentation of 1-naphthol and the scrambling of the hydroxyl group hydrogen under electron impact has been studied by means of deuterium labelling. The mass spectra of 1-naphthol (I), 1-naphthol-OD (II), 2,3,4,5,6,7,8-heptadeutero-1-naphthol (III) and perdeutero-1-naphthol (IV) indicate that only the hydrogen of the hydroxyl group is involved in the dehydration of the molecular ion. The loss of 29 mass units from the molecular ion yielding m/e 115 ($[M-HCO]^+$) is preceded by hydrogen scrambling to an extent of 25%, while in the further decomposition of the $[M-HCO]^+$ -ion complete hydrogen randomization is involved.

Introduction

Recent mass spectral studies on aromatic and heterocyclic compounds by means of deuterium labelling showed that practically complete hydrogen randomization in these molecules occurs under electron impact¹⁻⁹. The mass spectra of these compounds are characterized by having the molecular ion as the base peak and it can be argued that its stability is responsible for the phenomenon of hydrogen scrambling.

In the present study we were interested to what extent the hydrogen of a hydroxyl group attached to an aromatic compound scrambles with other hydrogens in the molecule under electron impact. The compound investigated was 1-naphthol (I) and the labelled 1-naphthol-OD (II), 2,3,4,5,6,7,8-heptadeutero-1-naphthol (III) and perdeutero-1-naphthol (IV).

Results and Discussion

In the mass spectrum of 1-naphthol at 70 eV (Fig. 1) the molecular ion $[M]^+$ is the base peak although fragmentation to $[M-HCO]^+$ - and $[M-CO]^+$ -ions is highly operative. The hydrogen loss from the molecular ion is small (about 3% of the base peak). Also small but interesting is the dehydration of the molecular ion which precedes hydrogen scrambling since the initial hydrogen of the hydroxyl group is always included in the eliminated water. Thus, (I) shows a loss of 18 mass units (Fig. 1), (II) and (III) of 19 mass units and (IV) of 20 mass units with equal yields.

The most important fragmentation of the molecular ion is the loss of neutral CO and HCO fragments¹⁰. The elimination of carbon monoxide is characteristic for phenols and quinones¹⁰. Recently it was shown by ¹³C-labelling that the original C—O bond of phenol is not broken before elimination of carbon monoxide⁴. Present results show by observation of metastable peaks in the first and second field-free region that loss of 29 mass units is a two step process taking place either as $(H^+ + CO)$ or as $(CO + H^+)$ expulsion from the molecular ion. The elimination of CO from the molecular and the $[M-1]^+$ -ions of 1-naphthol is associated with abundant not resolved metastable peaks, m_1^* and m_2^* , in the second field-free region. The loss of CO in (I) amounts to approximately 1/3 of the base peak whereas the ratio of $[M-CO]/[M-HCO]^+$ -ions (corrected for ¹³C) is 0.39. Taking their ¹³C corrections into account, the actual deuterium content of (II), (III) and (IV), as well as the percentage of CO loss, a nearly constant value of about 0.4 is obtained for the ratios of $[M-CO]/([M-HCO]^+ + [M-DCO]^+)$ ions in the mass spectra of the deuterated 1-naphthols. Since the observed ratio of $[M-HCO]^+/[M-DCO]^+$ in (II) is = 3,

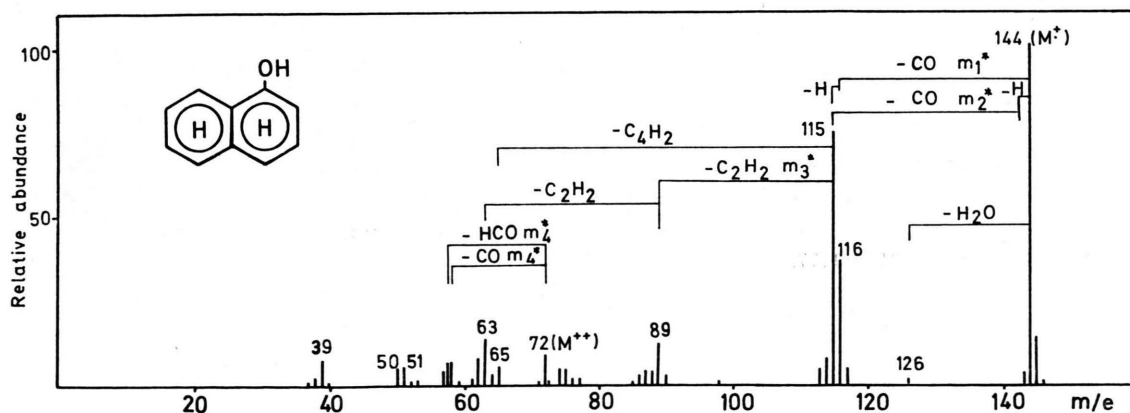


Fig. 1. Mass spectrum of 1-naphthol (I) at 70 eV.

* Guest from the institute "Ruder Bošković", Zagreb, Croatia, Yugoslavia.



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roughly 1/4 of the eliminated hydrogen in this process must have been bound initially to the oxygen. In other words, hydrogen scrambling or equivalence of the hydroxyl group hydrogen and other naphthalene ring hydrogens seems to occur in a high percentage (~70%). A large isotope effect can be excluded by the inspection of the mass spectrum of (III). Assuming the same ratios for (III) as found in (II), i.e. $[M]/[M-CO]=3$, $[M-CO]/([M-HCO'] + [M-DCO']) = 0.4$ and $[M-DCO']/[M-HCO'] = 3$, a good agreement with the observed intensities of m/e 120, 121, 122 and 123 in the mass spectrum of (III) (corrected for ^{13}C) is obtained. Together with the mass spectrum of (IV) which shows that the relative heights of $[M]^+$, $[M-CO]$ and $[M-DCO']$ -ions are not changed on deuteration, the results prove that 3/4 of the initial hydroxyl group hydrogen in 1-naphthol remains in the $[M-HCO']$ -ion.

Evidence for the incorporation of the hydroxyl group hydrogen into the naphthalene ring and its further fate can be obtained from the fragmentation of the $[M-HCO']$ -ion. This ion decomposes by loss of twice a C_2H_2 and a C_4H_2 (?) neutral fragment. Only the first loss of C_2H_2 from (I) is associated with a very weak metastable peak m_3^* in the second field-free region at 68.9 mass units. Calculations show that in the C_2H_2 elimination from (II) and (III) statistical distribution of hydrogen and deuterium must be assumed to explain the obtained ion ratios. This leads to the conclusion of complete hydrogen randomization in the $[M-H(D)CO']$ -ion.

Experimental

All mass spectra were recorded under identical operating conditions on an Atlas MAT CH 5 mass spectrometer at 70 eV using a direct inlet system at 90 °C. The metastables formed in the first field-free region were obtained with a double-focusing mass spectrometer (CEC 21-110 C) by decoupling the accelerating

voltage power supply by means of a device constructed at the "Jožef Stefan" institute. Deuterium analysis was carried out by nmr technique on a Varian HA 100 instrument.

1-Naphthol (I), (Merck p.a.), was recrystallized from distilled water, white needles, m.p. 95 °C.

1-Naphthol-OD (II) was prepared by repeated equilibration of (I) in D_2O (99.7%) and recrystallization from D_2O , m.p. 95 °C.

Deuterium: 97% D_1 .

Perdeutero-1-naphthol (IV) was prepared according to the method of KHARASCH¹¹ by oxidation of perdeutero-1-naphthyl-magnesium bromide. Octadeuteronaphthalene, 99% D, (Merck), was brominated with bromine in CCl_4 and purified by column chromatography on silica gel in ligroin in 40% yield. The resulting Grignard solution, perdeutero-1-naphthyl magnesium bromide in ether, was oxidized with carbon dioxide free oxygen at 0°.

After the first two days an equivalent of isopropyl magnesium iodide was added and the oxidation continued for another two days. The reaction mixture was decomposed with D_2SO_4 and D_2O , extracted with dry ether, purified by column chromatography on silica gel in ligroin and finally recrystallized from D_2O , m.p. 94–95 °C.

Deuterium: 86% D_8 , 14% D_7 .

2,3,4,5,6,7,8-heptadeutero-1-naphthol (III) was prepared by repeated equilibration of IV in distilled water and recrystallization from H_2O , m.p. 95 °C.

Deuterium: 86% D_7 , 14% D_6 .

Acknowledgement

The authors thank Dr. J. MARSEL from the "J. Stefan" Institute, Ljubljana, for first field-free region metastable measurements. — Diese Arbeit wurde im Rahmen der deutsch-jugoslawischen Zusammenarbeit auf wissenschaftlich-technischem Gebiet durchgeführt. Wir danken dem Internationalen Büro in Jülich (Kernforschungsanlage) für finanzielle Unterstützung.

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