

Mass Spectral Study of Anthrone

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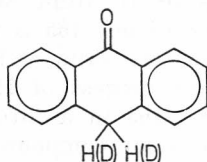
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Received July 6, 1987

The electron impact induced fragmentation of anthrone and its 10,10-dideuterated analogue has been studied in the mass spectrometer using low and high resolution, as well as ion kinetic energy measurements. The most important process observed in the mass spectra is loss of CO from the molecular ions with formation of ions of possible fluorenyl cation structure. Such ions, as shown earlier, undergo extensive hydrogen scrambling. In agreement with a fluorenyl cation structure, statistical loss of hydrogen in the fragmentation of anthrone is observed.

INTRODUCTION

Some years ago it was demonstrated that expulsion of neutral or radical fragments of various precursor ions leading to observation of a $[C_{13}H_9]^+$ ion (m/z 165) in the mass spectrometer is accompanied with extensive hydrogen scrambling within the precursor species.¹⁻⁷ On the other hand, the double loss of CO in anthraquinone leading finally to observation of an ion of presumably *o*-biphenylene structure (m/z 152) was shown to be a strictly two-step process with the second CO being expelled only after rearrangement of the $[M-CO]^+$ species into an *o*-carbonylbiphenyl radical ion.⁸ However, even the loss of the first CO fragment which requires cleavage of two carbon-carbon bonds in the starting molecule is also a process of considerable complexity as indicated by the observed kinetic energy release.⁹ The same holds also if only one CO unit is present in the molecule as has been demonstrated *e.g.* for tropone.¹⁰ Therefore, substantial hydrogen scrambling within molecular ions of such compounds prior to loss of CO can be expected. Not as clear is how a semiquinone, *i.e.* anthrone (1), would behave in this



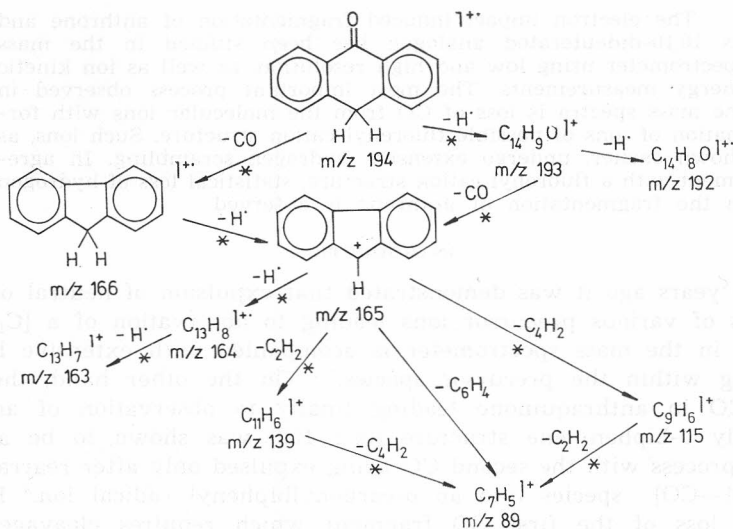
1 and 2

respect. With this in mind we have also prepared the corresponding d_2 analogue (2) and investigated the pair of compounds in the mass spectrometer

using the 1st and 2nd field free region (FFR) metastables and high resolution measurements to elucidate their fragmentation pathways.

RESULTS AND DISCUSSION

The uncorrected and normalized 70 eV mass spectra of 1 and 2 are shown in Figure 1. The fragmentation pathways for 1, as confirmed through observation of corresponding 1st FFR and 2nd FFR metastables and exact mass determination of the corresponding ions are given in Scheme 1. The pathways confirmed through the 1st FFR metastable are indicated by an arrow only and those by observation of the 2nd FFR by an asterisk. The mass spectra of the deuterated analogue 2, as well as determination of the relative intensities of its 1st FFR metastables, enable an insight into the extent of hydrogen scrambling in these compounds in the mass spectrometer.



The mass spectrum of 1 exhibits, besides the molecular ion, m/z 194, which is the base peak, the prominent m/z 165 of presumably fluorenyl cation structure. There are two pathways to this ion, *i. e.* either by loss of a hydrogen atom from the M^+ and subsequent expulsion of CO or first the loss of CO and then that of H^\cdot takes place. Comparison of the 1st FFR metastables indicates that loss of H^\cdot from M^+ is about three times more intensive, and that the formation of m/z 165 is ten times more intensive from m/z 166 than from m/z 193; thus the ratio of $\text{M}-\text{CO}-\text{H}$ vs. $\text{M}-\text{H}-\text{CO}$ seems to be roughly 3. A direct process of HCO loss was not found. The subsequent fragmentation of m/z 165 in anthrone is the same as previously found for this ion in other precursor compounds, such as fluorene, stilbene, diphenylmethane, 3,10-dihydrophenanthrene and others, *i. e.* formation of m/z 139, m/z 115 and m/z 89 by loss of C_2H_2 , C_4H_2 and C_6H_4 units is observed.¹⁻⁷ The ratio of the 1st FFR metastables for the first two processes is roughly 1.

On the basis of low energy mass spectra the dideuterated analogue 2 contained 88% d_2 -, 10% d_1 - and 2% d_0 -molecules, *i. e.* without the label in

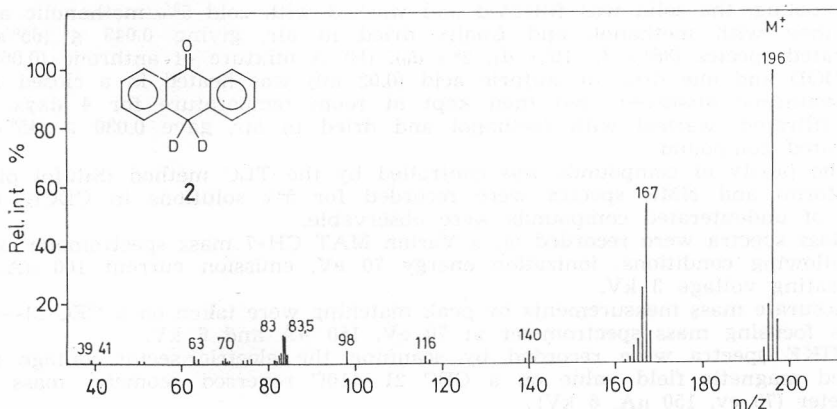
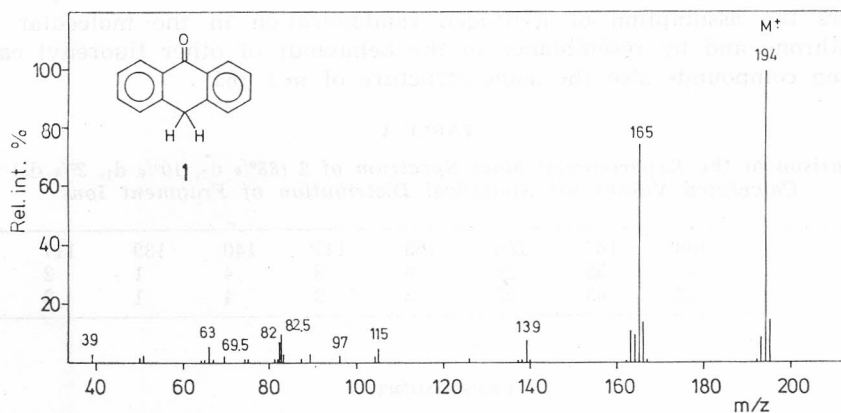


Figure 1. The 70 eV mass spectra of anthrone (1) and its 10,10- D_2 analogue (2).

the 10-position. The ratio of 1st FFR metastables for loss of hydrogen *vs.* deuterium from m/z 196 was found to be 4; thus, no preference for expulsion of the label was observed indicating that the hydrogen randomization already takes place in the molecular ion. Knowing the actual composition of 2 (88% d_2 , 10% d_1 , 2% d_0) and the fragmentation pattern of 1 one can calculate the distribution of the label in the daughter ions m/z 165–168, 139–141 and 116, 117 under the assumption that this distribution is statistical. The processes which should be considered, *e.g.* in the formation of m/z 163–168 from m/z 193–196, are loss of hydrogen and loss of CO from the parent C_{14} -ions and loss of hydrogen from the daughter C_{13} -ions. The observed ratio of metastable transitions for hydrogen *vs.* deuterium loss in the labelled parent molecules amounts to 4 and 9 for the dideuterated and monodeuterated compounds, respectively. Similarly, the fragmentation to m/z 139, 140, 141, 116 and 117 has been treated. The final result can be compared with the experimentally observed spectrum of 2 (Table I). This comparison clearly

favours the assumption of hydrogen randomization in the molecular ions of anthrone and by resemblance to the behaviour of other fluorenyl cation forming compounds also the same structure of m/z 165.

TABLE I

Comparison of the Experimental Mass Spectrum of 2 (88% d_2 , 10% d_1 , 2% d_0) with Calculated Values for Statistical Distribution of Fragment Ions

m/z	168	167	166	165	141	140	139	117	116
exp.	11	55	26	8	3	4	1	2	2
cal.	12	63	27	8	3	4	1	2	3

EXPERIMENTAL

10,10-Dihydroanthracene-9-one (anthrone) was of commercial origin (E. Merck). Its 10,10- d_2 -analogue was prepared by two methods. (A) A drop of piperidine (0.02 ml) was added to the mixture of anthrone (0.065 g) and CH_3OD (2 ml) the flask was immediately closed and then heated to 90 °C for 20 minutes with stirring. After cooling, the solid was filtrated and washed with cold 5% methanolic acetic acid, then with methanol, and finally dried in air, giving 0.043 g (65%) of deuterated species (88% d_2 , 10% d_1 , 2% d_0). (B) A mixture of anthrone (0.065 g), CH_3COOD and one drop of sulfuric acid (0.02 ml) was heated in a closed flask until anthrone dissolved, and then kept at room temperature for 4 days. The solid, filtrated, washed with methanol and dried in air, gave 0.030 g (45%) of deuterated compound.

The purity of compounds was controlled by the TLC method (Silufol plates, chloroform) and NMR spectra were recorded for 5% solutions in CDCl_3 . Only traces of undeuterated compounds were observable.

Mass spectra were recorded on a Varian MAT CH-7 mass spectrometer under the following conditions: ionization energy 70 eV, emission current 100 μA , ion accelerating voltage 3 kV.

Accurate mass measurements by peak matching were taken on a CEC 21-110C double focusing mass spectrometer at 70 eV, 150 μA and 6 kV.

MIKE spectra were recorded by scanning the electric sector voltage at a selected magnetic field value on a CEC 21-110C reversed geometry mass spectrometer (70 eV, 150 μA , 6 kV).

All samples were introduced into the ion source (source temperature 120 °C) via an unheated direct insertion probe.

Acknowledgement. — The authors are grateful to Dr. B. Kralj, »Jožef Stefan« Institute, Ljubljana for measurements of accurate masses and 1st FFR metastables on double focusing instruments.

S. M. S. acknowledges the stay as visiting scientist at the »Ruđer Bošković« Institute within the framework of the Yugoslav-Soviet exchange program.

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SAŽETAK

Studij spektra masa antrona

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Fragmentacija antrona i njegova 10,10-dideutero-analoga, izazvana elektronskim bombardiranjem, istraživana je u spektrometru masa koristeći nisko i visoko razlučivanje te mjereći kinetičke energije iona. Najvažniji proces opažen u spektrima masa jest gubitak CO iz molekularnog iona uz stvaranje iona vjerojatno fluorenil-kationske strukture. Takvi ioni, kao što je već ranije pokazano, podliježu izrazitom miješanju vodikovih atoma. U skladu s fluorenil-kationskom strukturom opažen je statistički gubitak vodika u fragmentaciji antrona.