Mass Spectrometric Behaviour of Some Disalicyloxyalkanes under Electron Impact

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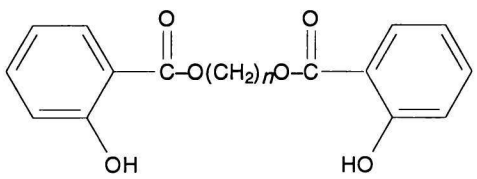
The mass spectral behaviour under electron impact (EI) of disalicylates of some α,ω-alkanediols is discussed. The mass fragmentation of these compounds is influenced by a strong intramolecular hydrogen bond between hydrogen of the OH group and oxygen of the neighbouring carboxyl group. Metastable transitions were used to substantiate the proposed fragmentation scheme.

While the electron impact mass spectra (EIMS) of alkyl esters of salicylic acid have been the subject of the extensive study [1—6], nothing has been published about the mass spectrometric behaviour of disalicylates of some α,ω-alkanediols which are used as the light stabilizers for various polymers [7]. Therefore, the aim of our work has been to study the mass fragmentation of this type of compounds with the general formula



where $n = 2$—6.

EXPERIMENTAL

The compounds investigated were synthesized according to the literature [7].

The EIMS of compounds investigated were recorded using a GCMS LKB 2091 instrument under the following conditions: electron beam energy 70 eV, accelerating voltage 3.5 kV, ionizing current 50 μA, and the temperature of the ion source 250 °C. Metastable peaks in the first field-free region were obtained on a Jeol-JMS-D 100 mass spectrometer equipped with MS-MT 01 Metastable Ion Detector by scanning accelerating voltage. During the MS analyses, the samples of the compounds investigated were introduced into the instrument with a direct insertion probe.

RESULTS AND DISCUSSION

The 70 eV EIMS of disalicylates of five α,ω-alkanediols, *i.e.* 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol presented in Fig. 1 are quite similar. On the basis of these spectra as well as appropriate metastable transitions and using general rules of the mass fragmentation of the alkyl esters of aromatic acids [8, 9], it was possible to determine the mass spectrometric behaviour of the compounds investigated. EI-induced mass fragmentation of this type of esters shows many common features. The intense molecular ions $M^{+\bullet}$ (with $I_r = 5$—25 %) are stabilized by the presence of two aromatic rings and intramolecular hydrogen bondings between the hydrogens of the OH groups (at the *ortho* positions to the ester substituent) and the oxygens of the carboxyl groups. The main fragmentation ions are formed, similarly as in the case of alkyl benzoates [10—12] and salicylates [1—6], by cleavages of the single C—OR and C—C ester bonds of the molecular ions $M^{+\bullet}$ In this way, the series of the ions *a*, *b*, and *c* are formed (Scheme 1). Moreover, α-cleavage of the ester C—O bond in the ion *c* is associated with a hydrogen transfer and elimination of the alkenyl radical occurs (McLafferty rearrangement) giving rise to the ion *f* at m/z = 138 having the $[o\text{-}HOC_6H_4COOH]^{+\bullet}$ structure. This ion may also be formed directly from the molecular ions $M^{+\bullet}$ in the same way. However, there are no metastable transitions which would confirm this route of the mass fragmentation. In contrast to the double hydrogen atom transfers occurring in the mass fragmentation processes of alkyl benzoates [10—12], only single atom transfers were detected in the mass spectra of the esters investigated. This fact is in a good agreement with analogous results obtained by *Tajima et al.* [5, 6] for isoalkyl salicylates and may be explained by the attraction of the hydrogen of the OH group by one of the oxygen atoms of the neighbouring carboxyl group. As a result of this, occurrence of the intramolecular hydrogen bond prevents the hydrogen transfer to the second oxygen atom of the carboxyl group which is a part of the hydrogen bond. If this were not so, the more intense peaks of the ions at m/z = 139 should be detected in the mass spectra studied (Fig. 1).

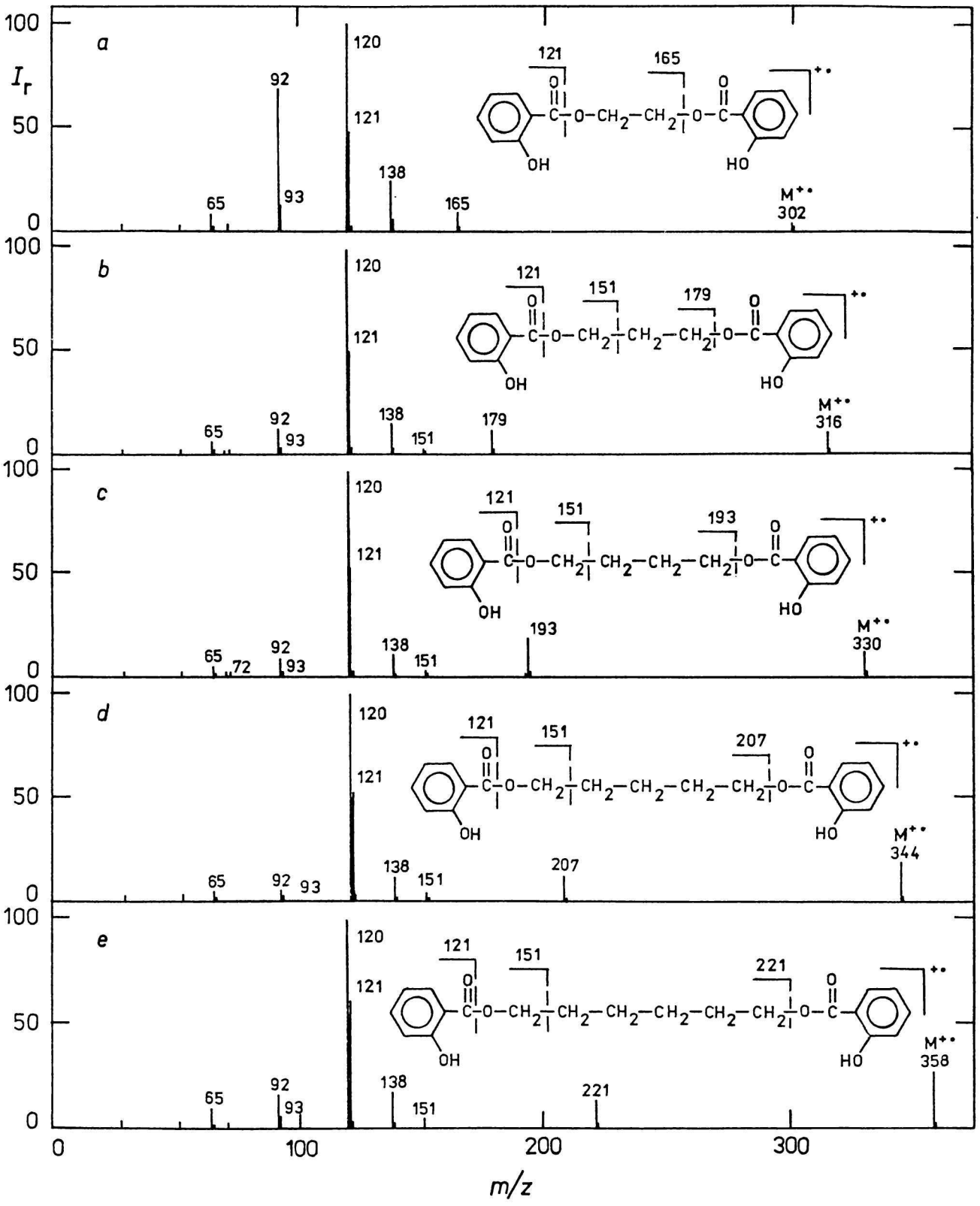
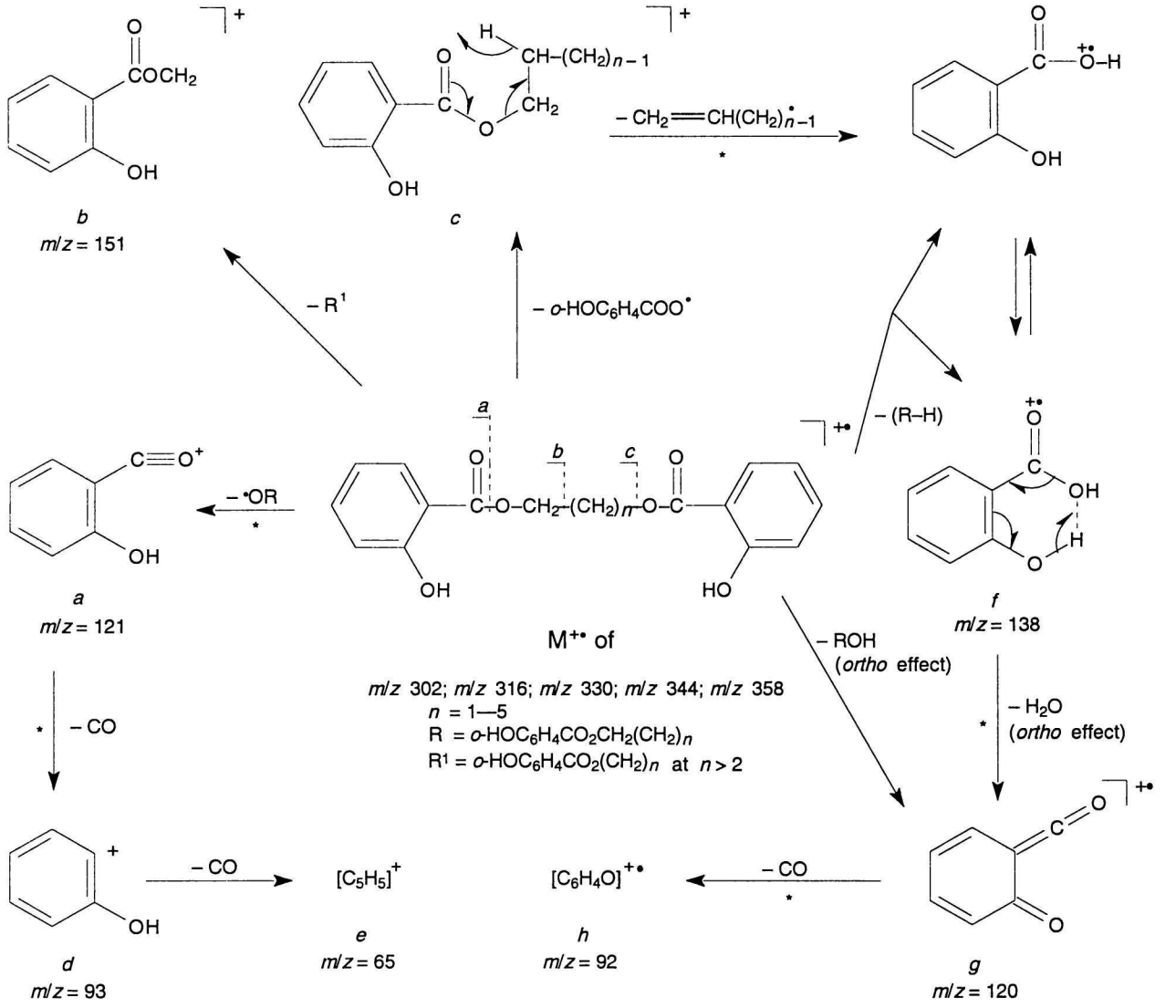


Fig. 1. Electron impact mass spectra (70 eV) of disalicylates of 1,2-ethanediol (*a*), 1,3-propanediol (*b*), 1,4-butanediol (*c*), 1,5-pentanediol (*d*), and 1,6-hexanediol (*e*).



Scheme 1
The main mass fragmentation pathways of the disalicyloxyalkanes studied.

The most intense peaks which are present in all the mass spectra of disalicyloxyalkanes correspond to the ion *g* at *m/z* = 120. This ion is formed by the expulsion of H_2O molecule from the ion *f via* a six-membered transition state (*ortho* effect) followed by the loss of CO molecule to yield the ion *h* at *m/z* = 92. In general, this fragmentation pathway is typical for the formation of the most abundant ions at *m/z* = 120 in the case of alkyl salicylates. Also, the ion *g* (*m/z* = 120) may be directly formed as a result of elimination of the neutral ROH molecules (*ortho* effect) from molecular ions $M^{+\bullet}$ of disalicyloxyalkanes studied. However, the appropriate metastable transition for this fragmentation reaction was not observed.

In conclusion, although the results presented in this paper relate only to mass spectrometric studies of a few disalicyloxyalkanes, while emphasizing the important role of the intramolecular hydrogen bondings, they permit us to determine many general features of the mass spectral fragmentation of this type of esters.

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REFERENCES

1. Emery, E. M., *Anal. Chem. 32*, 1495 (1960).
2. Nakata, H., Tatematsu, A., Yoshizumi, H., and Naga, S., *Chem. Lett. 1973*, 75.
3. McLafferty, F. W., *Interpretation of Mass Spectra,* Chapter 4. The Benjamin Cummings Publishing Company, New York, 1973.
4. Gross, M. L., DeRoss, F. L., and Hoffman, A. C., *Org. Mass Spectrom. 12*, 258 (1977).

5. Tajima, S., Azami, T., Shizuka, H., and Tsuchiya, T., *Org. Mass Spectrom. 14*, 499 (1979).
6. Tajima, S., Azami, T., and Tsuchiya, T., *Mass Spectrosc. 27*, 247 (1979).
7. *U.S.* 3022268 (1962).
8. Budzikiewicz, H., Djerassi, C., and Williams, D. H., *Mass Spectrometry of Organic Compounds.* Holden-Day, San Francisco, 1967.
9. Beynon, J. H., Saunders, R. A., and Williams, A. E., *The Mass Spectra of Organic Molecules.* Elsevier Publishing Company, Amsterdam, 1968.
10. Djerassi, C. and Fenselau, C., *J. Am. Chem. Soc. 87*, 5756 (1965).
11. Levsen, K. and Beckey, H. D., *Int. J. Mass Spectrom. Ion Phys. 15*, 333 (1974).
12. Benoit, F. M. and Harrison, A. G., *Org. Mass Spectrom. 11*, 1056 (1976).