MASS-SPECTROMETRIC AND QUANTUM-CHEMICAL STUDY OF
FRAGMENTATION OF DiallyL ESTERS OF DICARBOXYLIC ACIDS

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In a mechanistic study of thermal breakdown of diallyl polymers, six diallyl esters of dicarboxylic
acids have been investigated by means of mass spectrometry. A characteristic feature of the
fragmentation of these compounds is the low stability of the molecular ions and detachment of the allyl
cation, the peak of which is usually the highest in the mass spectrum. In interpreting such an unusual
path of fragmentation of esters, quantum-chemical calculations have been carried out in the MINDO/3
approximation; the preferred conformation of the diallyl maleate molecule and the distribution of
electron density in this conformation have been determined, and the most stable cyclic structure of the
intermediate cation \[CH=CH(CO)_{2}OH\]^+ has been established. The nature of the "bridge" between the
carboxyl groups in diallyl esters of dicarboxylic acids has practically no influence on the direction of
fragmentation. The decisive factor in the fragmentation is the electrostatic interaction of charges on the
atoms of carboxyl carbon and ester oxygen of the second carboxyl group. A fragmentation scheme with
the formation of intermediate cyclic cations is proposed.

Diallyl esters of dicarboxylic acids serve as monomers in the production of polymers used as materials in the
electronics and optical industries, and also polymers used in the form of reinforced plastics [1, 2]. The properties of
these polymers are predetermined to a certain degree by the structure of the monomer molecule; however, this
relationship has not been investigated adequately. Here we are reporting on a mass-spectrometric investigation of the
fragmentation of a series of diallyl esters of dicarboxylic acids. In the interest of completeness in interpreting the
results, we also carried out a quantum-chemical study of the electronic and spatial structure of certain diallyl esters
and intermediate products of their fragmentation.

The objects of investigation were the esters I-VIII: R'--O--C--R--C--O--R', I) R = --CH=CH--, R' =
--CH2--CH=CH2; II) R = --CH2--CH2--, R' = --CH2--CH=CH2; III) R = (--CH2--)4, R' = --CH2--CH=CH2; IV) R =
(--CH2)--2, R' = --CH2--CH=CH2; V) R = o-C6H4, R' = --CH2--CH=CH2; VI) R = m-C6H4, R' = --CH2--CH=CH2; VII) R =
o-C6H4, R' = --CH2--CH2--CH3; VIII) allyl benzoate. The mass-spectrometric measurements were performed in an
MKh-1320 instrument with ionization by electron impact (70 ev). In order to avoid the thermal decomposition that
occurs upon heating low-volatility substances, the samples were introduced directly into the ion source chamber.

In Table 1 we show the principal peaks in the mass spectra of the esters I-VIII. The peaks of the molecular
ions (MIs) are low in intensity; in some cases, they are even difficult to register. The relative intensities of the MI
peaks in esters — and this means the stability of the MIs — depends on the number of carboxyl groups and the
character of the substituent in the ester fragment. Thus, for the methyl ester of benzoic acid, the relative intensity of
the MI is 50%; when the change is made to dicarboxylates, this drops to 20%, and for tricarboxylates to 2-5% [3]. In
the esters that we have investigated, the presence of two allyl-carboxyl groups gives a still greater reduction in
stability of the MI, so that it decomposes rapidly. The stability of the MIs is determined to a considerable degree by
intramolecular electronic effects, as can be seen by the increase in stability from the ortho isomer (compound V) to the
meta isomer (compound VI, m/z 246, 12.9%).

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A characteristic feature of the fragmentation of the diallyl esters is that almost all of them have a maximal peak with m/z 41, corresponding to the allyl cation \([\text{CH}_2=\text{CH}--\text{CH}_2]^+\); the exception is compound VI, in view of the stability of its MI. For the esters I–V, the peaks with the largest mass number correspond to the cations \([\text{MI} -- \text{OR}']^+\) (these are underlined in Table 1); the relative intensities of the peaks of these cations vary from 15% to 50%; for compounds VI and VIII, this intensity is 100%. The absence of MI peaks from the spectra indicates that they readily split out an \(\text{OR''}\) group and are converted into the relatively stable cation \([\text{MI} -- \text{OR}']^+\). The structure of the bridge R influences the stability of these cations and governs the subsequent course of the fragmentation. The high intensity of the peaks pertaining to the cations \([\text{R'}]^+\), along with the presence of the cations \([\text{MI} -- \text{OR}']^+\), suggests that the detachment of the \(\text{OR''}\) fragment from the MI is followed by splitting out the \([\text{R'}]^+\) fragment in the second ester group.