

Soviet-era science, translated into English

**Academician B. A.
ARBUZOV, Yu. Ya.
EFREMOV, V. L. TAL'
ROZE**

1964

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196401.11059>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Fig. 1. Structural formulas of the β -form of Δ^3 -carene oxide, α -form of Δ^3 -carene oxide, β -pinene oxide, and camphene oxide.

Figure 1: Fig. 1. Structural formulas of the β -form of Δ^3 -carene oxide, α -form of Δ^3 -carene oxide, β -pinene oxide, and camphene oxide.

Reaction scheme: α -form \rightarrow diol under H^+ \rightarrow tosylate \rightarrow β -form under KOH.

Figure 2: Reaction scheme: α -form \rightarrow diol under H^+ \rightarrow tosylate \rightarrow β -form under KOH.

Abstract

Full Text

Academician B. A. ARBUZOV, Yu. Ya. EFREMOV, V. L. TAL' ROZE

MASS SPECTROSCOPY OF THE OXIDES OF CERTAIN BICYCLIC TERPENES

The problem of identification in the analysis of natural substances is one of the most difficult. In recent years, mass spectrometry has achieved considerable success in this field. The present work is devoted to the mass spectrometry of Δ^3 -carene oxide (α - and β -forms), camphene oxide, and β -pinene oxide (Fig. 1).

Fig. 1

The mass spectra of the terpenes themselves have been studied in a number of works (¹⁻⁴). Oxides of bicyclic terpenes exhibit various kinds of isomerism, including stereoisomerism, which makes it possible to study the influence of different factors on the mass spectra.

The substances studied were synthesized from the corresponding hydrocarbons by oxidation with peracetic acid in diethyl ether solution, except for the β -form of Δ^3 -carene oxide. The β -form was obtained from the α -form according to the following scheme (⁵):

where T_s denotes the residue $CH_3C_6H_4SO_2$. The compounds obtained were purified by distillation on a column of 17 theoretical plates with glass packing, except for camphene oxide, which was purified by simple distillation. The properties of the indicated compounds fully correspond to the literature data (^{6,5}).

The mass spectra were recorded on an MI-1305 mass spectrometer equipped with a glass inlet system (⁷), which made it possible to operate at temperatures up to 300°C. The main part of the spectra was obtained at an electron energy of 50 eV. In some cases spectra were recorded at an electron energy of 9 ± 0.5 eV.

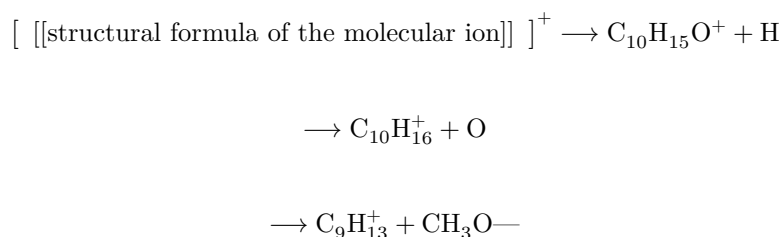
Since the readout device of the voltmeter did not allow the voltage between the cathode and the ionization chamber to be measured with the accuracy required for such work, the reproducibility of the results was ensured by keeping the anode voltage unchanged during the recording of all mass spectra. The mass spectra obtained and the formulas of the fragment ions (in those cases where this can be done) are given in Table 1. The spectra are normalized in such a way that the sum of the intensities of all lines is taken as 100. The most probable directions of dissociative ionization

of terpene oxides is the elimination of a methyl group (peak with $m/e = 137$), an isopropyl group (peaks with $m/e = 93$ and 94), and other cleavages of C—C bonds.

Since the presence of methyl groups at a quaternary carbon atom, of an isopropyl group, of a six-membered ring, and of an oxide ring is characteristic of all the isomers under consideration, their mass spectra are similar in their main features. However, even among the most pronounced decomposition pathways there are some which, while very probable for some isomers, are comparatively unlikely for others. We note these differences, since identification must be based precisely on them. Moreover, the differences in question are differences of order of magnitude: it is precisely such differences that make it possible, by mass spectrometry, to determine the presence of a percent or a fraction of a percent of one isomer in another.

Thus, it proves possible to determine in mixtures of isomers comparatively small impurities of camphene oxide (from the $m/e = 111$ line) and to identify clearly β -pinene oxide, sufficiently free of impurity, from the $m/e = 94$ line with use of the $m/e = 83$ line.

However, it is very difficult to distinguish the stereoisomers of Δ^3 -carene oxide, especially when camphene and β -pinene oxides are present along with them. It was therefore natural, for the purpose of distinguishing stereoisomers, to turn to the low-intensity lines of the spectrum, i.e., to the unlikely pathways of dissociative ionization of the molecules. The greatest differences between the intensities of comparatively weak, but still satisfactorily measurable, lines correspond to the decompositions:



It is noteworthy that these greatest differences relate to the elimination of the H atom and, apparently, of the O atom and the radical $\text{CH}_3\text{O}\text{—}$. It is precisely the

relative arrangement of the oxygen and the methyl groups (and, correspondingly, of their hydrogen atoms) that changes most substantially in passing from one stereoisomer to the other.

It may be concluded that the cis position of the methyl groups and oxygen facilitates all the cleavages listed.

Three usual hypotheses may be advanced concerning the causes of the influence of stereoisomerism on mass spectra: 1) the mutual influence of groups in the cis position somewhat weakens the strength of certain bonds (for example, the

C–H bond and the O bond in our example), 2) new decomposition pathways

become possible in the case of one of the forms which do not exist in the other form (formation of the CH_3O — radical from the ion of the cis form), 3) owing to the existence of a definite probability of excitation of two electrons in the molecule, the relative arrangement of the group could substantially influence the character of the reaction. The importance of the last hypothesis in each particular case can apparently be readily tested by studying low-voltage spectra, since if the decomposition pathways considered are connected with excitation of two electrons, then at electron energies close to the ionization potential these processes will in general be practically excluded. Comparison of mass spectra obtained at different electron energies shows that, with decreasing energy, the relative intensity of the lines under consideration increases. Thus, the first two remain as possible causes of the stereoisomeric effect for the indicated lines. However, lowering the electron energy leads to the observation of yet another fact, striking from the authors' point of view,

Table 1

m/e of the resulting ion	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for Δ_α^3 -carene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for Δ_β^3 -carene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for camphene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for β -pinene	$V_u = 9 \text{ V}; \frac{I}{\Sigma I} \cdot 100$ for Δ_α^3 -carene	$V_u = 9 \text{ V}; \frac{I}{\Sigma I} \cdot 100$ for Δ_β^3 -carene	Proposed reaction of ion formation
152	0,43	0,33	0,16	0,26	1,50	3,40	$\text{C}_{10}\text{H}_{16}\text{O} + e \rightarrow \text{C}_{10}\text{H}_{16}\text{O}^+$
151	0,09	0,02	0,62	0,02			$\text{C}_{10}\text{H}_{16}\text{O}^+ \rightarrow \text{C}_{10}\text{H}_{15}\text{O}^+ + \text{H}$
138	0,29	0,15	0,90	0,12	1,30	0,70	
137	3,92	1,45	10,00	1,00	17,40	8,30	$\rightarrow \text{C}_9\text{H}_{13}\text{O}^+ + \text{CH}_3$
136	0,24	0,02	0,24	0,02	2,90	0,14	$\rightarrow \text{C}_{10}\text{H}_{16}^+ + \text{O}$
134	0,48	0,21		0,14	4,30	0,90	
124	0,14	0,16	0,24	0,28	0,52	0,32	
123	1,53	0,80	0,44	4,00	5,20	2,45	$\rightarrow \text{C}_8\text{H}_{11}\text{O}^+ + \text{C}_2\text{H}_5$
122	0,12	0,04	0,23	0,04	0,07		
121	0,7	0,09	1,00	0,35	1,30	0,11	$\rightarrow \text{C}_9\text{H}_{13}^+ + \text{CH}_3\text{O}$

m/e of the resulting ion	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: Δ_α^3 -carene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: Δ_β^3 -carene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: camphene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: β -pinene	$V_u = 9 \text{ V}; \frac{I}{\Sigma I} \cdot 100$ for oxide: Δ_α^3 -carene	$V_u = 9 \text{ V}; \frac{I}{\Sigma I} \cdot 100$ for oxide: Δ_β^3 -carene	Proposed reaction of ion formation
120	0,17	0,06	0,02	0,03	0,65	0,18	
119	2,64	1,06	0,20	0,30	5,20	1,60	
112	0,003	0,01	0,21				
111	0,004	0,14	3,53	0,09	0,09	0,09	$\rightarrow \text{C}_7\text{H}_{11}\text{O}^+ + \text{C}_3\text{H}_5$
110	0,34	0,40	0,36	0,43	3,00	2,80	
109	6,10	3,53	5,34	1,85	24,30	14,70	$\rightarrow \text{C}_7\text{H}_9\text{O}^+ + \text{C}_3\text{H}_7$
108	0,25	0,17	0,72	0,71	1,50	1,63	
107	0,71	0,30	1,20	0,22			
106	0,08	0,04	0,07	0,05			
105	0,58	0,37	0,73	0,22			
98	0,02	0,02	0,07	0,51			
97	0,31	0,32	0,28	0,20			
96	0,41	0,18	0,35	0,39	0,54	0,42	
95	2,96	2,66	1,41	1,26	2,14	3,77	
94	1,83	3,71	6,18	0,16	6,94	30,85	$\rightarrow \text{C}_7\text{H}_{10}^+ + \text{C}_3\text{H}_6\text{O}$
93	4,30	3,20	4,74	0,90	4,70	3,60	$\rightarrow \text{C}_7\text{H}_9^+ + \text{C}_3\text{H}_7\text{O}$
92	0,87	0,25	0,81	0,31	3,00	1,40	
91	3,20	2,10	2,53	1,77			
85	0,20	0,04	1,00	0,37			
84	0,23	0,34	0,33	0,27	0,23	0,10	
83	0,89	0,76	0,46	3,86	0,14	0,64	
82	1,60	2,55	0,32	6,40	1,20	7,80	
81	4,82	4,30	2,40	6,15	2,16	1,00	
80	0,82	0,91	0,73	0,45	2,00	1,20	
79	3,37	8,71	6,28	4,14	2,10	8,80	
78	0,44	0,11	0,52	0,28	0,34		
77	2,48	2,07	2,24	1,77			
75	0,03	0,09		0,03			
72	0,02	0,07	0,15	0,04	0,14	0,18	
71	0,42	0,75	0,22	0,34			
70	0,29	0,07	0,36	2,24	0,23		
69	1,52	1,40	3,82	8,60	1,60	0,14	
68	1,84	0,81	0,89	1,22	0,11	0,14	
67	7,69	7,47	6,84	9,18			
66	0,47	0,53	1,35	0,51			
65	1,22	1,15	1,05	0,75			
63	0,16	0,21	0,07	0,17	0,63	1,10	$\text{C}_{10}\text{H}_{16}\text{O}^+ \rightarrow \text{C}_3\text{H}_7\text{O}^+ + \text{C}_7\text{H}_9$
59	0,38	0,53	0,03	0,07			

m/e of the resulting ion	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: Δ_α^3 -carene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: Δ_β^3 -carene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: camphene	$V_u^* = 50 \text{ V}; \frac{I^{**}}{\Sigma I} \cdot 100$ for oxide: β -pinene	$V_u = 9 \text{ V}; \frac{I}{\Sigma I} \cdot 100$ for oxide: Δ_α^3 -carene	$V_u = 9 \text{ V}; \frac{I}{\Sigma I} \cdot 100$ for oxide: Δ_β^3 -carene	Proposed reaction of ion formation
57	0,32	0,32	0,33	0,71			
56	0,45	0,60	0,28	0,55			
55	3,43	3,66	2,74	4,21			
54	0,60	0,75	0,36	1,28			
53	2,38	3,22	2,21	2,78			
52	0,30	0,26	0,26	0,20			
51	0,72	0,75	0,63	0,59			
50	0,15	0,17	0,04	0,15			
45	0,31	0,56	0,07	0,02			
44	0,33	0,42	0,07	0,15			
43	9,36	11,71	2,28	2,29	0,81	0,36	$\rightarrow \text{C}_3\text{H}_7^+ + \text{C}_7\text{H}_9\text{O}$
42	0,56	0,40	0,60	0,65			
41	7,74	7,45	9,19	11,11			$\rightarrow \text{C}_3\text{H}_5^+ + \text{C}_7\text{H}_{11}\text{O}$
40	0,64	0,40	0,58	0,35			
39	4,30	5,77	4,16	3,72			
29	1,51	2,10	1,53	2,43			
27	3,00	4,64	2,65	3,66			
15	0,56	0,77	0,30	0,25			$\rightarrow \text{CH}_3^+ + \text{C}_9\text{H}_{13}\text{O}$

* V_u –ionizing voltage.

** I –line intensity.

of a stereoisomeric effect—a sharp fall in the relative intensity of the $m/e = 79$ line in the case of the α -isomer, with the relative intensity of this line in the spectrum of the β -isomer practically preserved.

Formally, the ion with $m/e = 79$ may be the C_6H_7^+ ion. This corresponds, at least, to the cleavage of two bonds in the six-membered ring. It is surprising,

that stereoisomerism has such a strong influence on such an “energy-intensive” cleavage. This effect shows how cautiously one must treat conclusions about the pathways of dissociative ionization that are based on an analogy between the structure of the excited ion formed upon electron impact and the known structure of the neutral molecule. In any case, it is clear that in such a consideration it is necessary to take into account to which part of the excited ion the positive charge tends to be localized.

Some differences in the mass spectra of stereoisomers in a number of compounds have also been observed earlier (⁸, ⁹). However, the differences in the case of

stereoisomers of Δ^3 -carene oxide are apparently among the especially large ones. It is not excluded that this is due to a substantial difference in the electronegativity of the groups, whose mutual arrangement is determined by stereoisomerism. In precisely this case, the location of the positive charge in the excited ion may be substantially different for the cis and trans isomers.

The mass-spectral study carried out shows, in any event, that by using both intense and weak lines in the mass spectra of terpene oxides, it is possible not only to identify pure substances, including stereoisomers, but also to detect comparatively small impurities (on the order of percent) of some isomers in others.

Institute of Organic Chemistry
Academy of Sciences of the USSR
Kazan

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
10 VI 1964

CITED LITERATURE

¹ L. Friedman, A. P. Wolf, *J. Am. Chem. Soc.*, **80**, 2424 (1958). ² T. Gilchrist, R. J. Reed, *Experientia*, **16**, 134 (1960). ³ R. J. Reed, In: F. W. McLafferty, *Mass Spectrometry of Organic Ions*, N.Y.—London, 1963, p. 637. ⁴ Ragnar Ryhage, Erik von Sydow, *Chemica Scandinavica*, **17**, 2025 (1963). ⁵ Henryk Kuczynski; Zenon Chabudzinski, *Roczn. Chem.*, **34**, 177 (1960). ⁶ B. A. Ar-buzov, Z. G. Isaeva, *ZhOKh*, **24**, 1250 (1954). ⁷ Yu. Ya. Efremov, T. A. Bikbulatov, B. Ya. Teitelbaum, *Pribory i tekhn. eksperim.*, No. 6, 180 (1963). ⁸ J. H. Beynon, R. A. Saunders, A. E. Williams, *Appl. Spectroscopy*, **14**, 95 (1960). ⁹ P. Natalis, *Bull. Soc. Chem. Belg.*, **69**, 519 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.