MASS-SPECTROMETRIC CHARACTERISTICS OF GLYCIDYL AND THIOGLYCIDYL ETHERS

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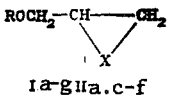
The principles of the fragmentation of the simplest glycidyl and thioglycidyl ethers under the influence of electron impact, which were discovered by comparison of the spectra of homologs using data from photoelectronic spectroscopy and optical mass spectrometry, are examined as a manifestation of the general characteristics of the fragmentation of bifunctional compounds.

The simplest oxygen-containing heterocyclic compounds — oxiranes — are included among substances with principles of fragmentation under the influence of electron impact that have been characterized in rather great detail but still remain anomalously complex [1]. This feature of them is responsible for the urgency of mass-spectrometric investigations of homologous series of compounds that contain three-membered heterorings, particularly when there are other heteroatoms in the molecules. The data available on thiiranes are limited primarily to methyl-substituted homologs [1].

As a rule, a second heteroatom or functional group changes the mass-spectrometric characteristics of such compounds significantly as a consequence of the possibility of alternative localization of the positive charge in the molecular ions on two centers. The fragmentation of a number of the simplest bifunctional oxiranes — α,β-epoxy ketones — have been analyzed from these points of view [1]. Simple glycidyl (I) and thioglycidyl (II) ethers, which are examined in the present paper, constitute another class of similar substances.



Ia-gIIa.c-f

I X=O; II X=S; a R=CH_3; b R=C_2H_5; c R=C_3H_7, d R=C_4H_9; e R=C_3H_5, f R=C_6H_5, g R=*p*-$CH_3C_6H_4$

The mass spectra of glycidyl ethers have been described only in [2]; some peculiarities of the fragmentation of the simplest representatives of this series and two diglycidyl ethers were characterized in the same paper. A previously published atlas [3] includes the mass spectrum of indole (R = H) that is markedly distorted by impurities. The spectra of glycidol and ethers Ia, b, f have been presented in an atlas [4] in an uninformative graphical form. However, the common mass-spectrometric characteristics of a homologous series of alkylglycidyl ethers are not available, and thioglycidyl ethers have not been investigated at all.

A comparison of the mass spectra of compounds of the I series recorded under different conditions and presented in [2] revealed significant differences in the intensities of the individual peaks, including the major peaks. For this reason, in the present research we have attempted for the first time to discuss the statistically treated mass spectra calculated by averaging of the data obtained with different instruments and different techniques for introducing the samples. The abbreviated mass spectra of the investigated compounds (the ion peaks with relative intensities higher than 10%, but no less than 10 major peaks) are presented in Table 1. Statistical treatment makes it possible to detect the individual signals with

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TABLE 1. Mass Spectra of Glycidyl (Ia-g) and Thioglycidyl (IIa, c-f) Ethers (70 eV)

Compound	m/z (relative intensity, %)*	ΣIΔI
Ia	88 (5) M, 72 (5), 58 (75), 57 (60), 45 (100), 43 (30), 42 (9), 31 (35), 30 (9), 29 (47)	408
Ib	59 (43), 58 (62), 57 (48), 45 (43), 44 (39), 43 (36), 41 (8), 31 (100), 30 (8), 29 (77)	137
Ic	59 (47), 58 (48), 57 (54), 45 (16), 44 (18), 43 (100), 41 (44), 39 (13), 31 (86), 29 (66)	165
Id	*87* (25), 73 (58), 71 (18), 59 (29), 58 (55), 57 (100), 56 (60), 55 (75), 45 (49), 44 (52), 43 (61), 42 (20), 41 (85), 39 (39), 31 (80), 30 (35), 29 (96)	369
Ie	114 (2) M, *84* (18), *83* (22), *71* (34), 59 (13), 58 (100), 57 (97), 56 (29), 55 (68), 45 (37), 44 (17), 43 (98), *42* (46), 41 (80), 39 (56), 31 (67), *30* (29), 29 (81)	381
If	150 (70) M, 120 (13), 107 (24), 94 (100), 91 (18), 79 (15), 66 (22), 65 (25), 57 (28), 51 (23), *41* (19), *39* (40), 31 (31), 29 (40)	343
Ig	164 (91) M, 134 (10), 121 (25), 108 (100), 107 (56), 93 (11), 91 (52), 79 (15), 77 (26), 65 (13), 57 (22), 51 (11), 39 (11), 31 (28), 29 (37)	153
IIa	104 (98) M, *77* (27), 76 (30), 74 (16), 73 (51), 72 (18), 71 (100), 59 (15), 58 (41), *57* (22), 47 (12), 45 (94), *43* (29), 41 (54), 39 (27), 29 (31)	422
IIc	132 (34) M, 90 (29), 75 (16), 74 (47), 73 (46), 59 (14), 58 (13), 57 (62), 45 (49), 43 (100), 41 (47), 39 (19)	120
IId	146 (100) M, 91 (14), 90 (31), 89 (17), *87* (25), 74 (63), 73 (55), 58 (27), 57 (76), 56 (26), 55 (19), 45 (34), 41 (70), 39 (20), 29 (51)	440
IIe	130 (1) M, 75 (13), 74 (85), 73 (100), 59 (14), 58 (11), 57 (27), 55 (14), 45 (63), 41 (95), 39 (46), 29 (14)	255
IIf	166 (100) M, 134 (15), 120 (20), 94 (23), 91 (14), 77 (48), 75 (30), 74 (29), 73 (78), 69 (20), 65 (35), 51 (30), 47 (24), 45 (68), 41 (42), 39 (56)**	

*The signals with poorly reproducible intensities are given in italics.

**The data were obtained by averaging of two spectra; statistical treatment and evaluation of the ΣIΔI parameter were impossible.

relative errors I_{rel} both on the scale of the relative intensities and in percent of the overall ion current. In the opinion of the authors, the problem of the inclusion of such peaks in the fragmentation schemes requires special discussion.

The $\Sigma\bar{I}\Delta\bar{I}$ parameter, where $\bar{I}$ are the average values of the intensities in percent of the overall ion current, and $\Delta\bar{I}$ are their errors, which correspond to a confidence probability of 0.95, can serve as an "integral" characteristic of the interlaboratory error in the spectra as a whole; summation is carried out over all of the peaks of the spectra [5].

Molecular-ion peaks are virtually absent in the spectra of alkylglycidyl ethers at any ionization energy (W_M < 0.1%), with the exception of glycidol and its methyl ether (W_M ≈ 1%). Aryl ethers If,g are characterized by W_M ≈ 16-17%. The W_M values are close for both alkyl- and arylthioglycidyl ethers (~6-15%) but much smaller (0.1-0.2%) for allyl ethers. The W_M parameter correlates satisfactorily with the so-called critical energies [the differences between the ionization energies (IE) and the minimum appearance energies (AE) of the fragment ions] E_{cr} = AE − IE, determined from the photoionization spectra (Table 2).

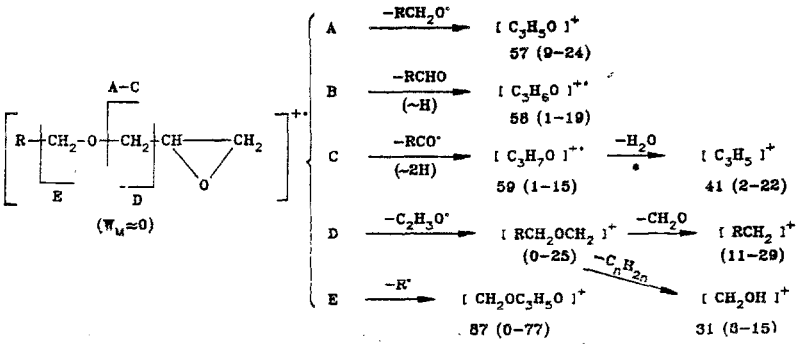
In the photoelectronic spectra of ethers I the first band corresponds to ionization of the orbital localized on the exocyclic oxygen atom [6]. In the case of thioglycidyl ethers II the highest occupied molecular orbital (HOMO) is localized on the sulfur atom. This assignment is confirmed by the fact that the ionization energies of ethers I virtually coincide with the range of IE of simple ethers (9.3 ± 0.2 eV), while the IE of the series of ethers II are considerably smaller and approach the values for dialkyl sulfides (8.4 ± 0.1 eV) (evaluated from the data in [7]). The advent of an isolated C=C bond in allyl ethers Ie and IIe is equivalent to the development of a third center of charge localization and leads to anomalous fragmentation of these compounds.

Information regarding the primary charge localization in the molecular ions can be used in discussing the schemes of the fragmentation of the compounds of the I and II series. Comparison of the spectra of homologs is the principal method used to establish the general principles of the fragmentation of the series [5]. However, the complexity of the fragmentation

TABLE 2

Compound	W_M (70 eV)	IE± 0.1 eV	E_{CI}±0.1 eV	Compound	W_M (70 eV)	IE±0.1 eV	E_{CI}±0.1 eV
Ia	1,2	9,5	0,2	IIa	15	8,8	0,6
Id	0,1	9,1	0,1	IId	12	8,7	0,4
Ie	0,2	8,9	0,1	IIe	0,1	8,7	0,2
If	16	8,2	1,7	IIf	15	8,2	1,0

Scheme 1

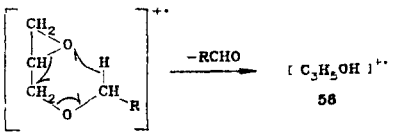


of glycidyl and, in particular, thioglycidyl ethers consists in the existence of a large number of processes that are specific only for individual homologs (which are manifested by the formation in the mass spectra of ions that are not observed in the fragmentation of other members of the series).

The principal pathways of the fragmentation of the glycidyl ethers (A-E) can be represented by scheme 1* (see above.)

The ions indicated in the scheme together constitute from 44% to 70% of the overall ion current. Only secondary processes are included in the fragmentation pathways confirmed by peaks of metastable ions, since $W_M \simeq 0$ for the aliphatic compounds of the I series. Fragmentation pathways A-C, which do not have analogies with the fragmentation of the precursors (see the experimental section) of ethers I with a similar carbon skeleton — alkoxy chlorohydrins [8] — and are due to cleavage of the C–O bond in the α position relative to the exocyclic oxygen atom, are the most interesting. In fact, this combination of atypical processes (α cleavage relative to one oxygen atom, γ cleavage relative to the other, and β cleavage relative to the ring) is due to the specific effect of the heteroring. Processes D and E are two variants of "traditional" β cleavage of the C–C bonds relative to the oxygen atom that predominates in the molecular ions of alkoxy chlorohydrins [8].

If process A is simple cleavage of the C–O bond, migration of a hydrogen atom from the RCH_2 fragment is required for the formation of odd-electron ions with m/z 58. According to modern concepts, the mass-spectrometric behavior of compounds that contain three-membered heterorings is similar in many respects to the fragmentation of compounds with a C=X bond (X = O, NR) [1]. In particular, this pertains to a McLafferty rearrangement of the *inside* type with the participation of an oxirane ring [1], which explains the appearance of ions with m/z 58 in the mass spectra of ethers I:

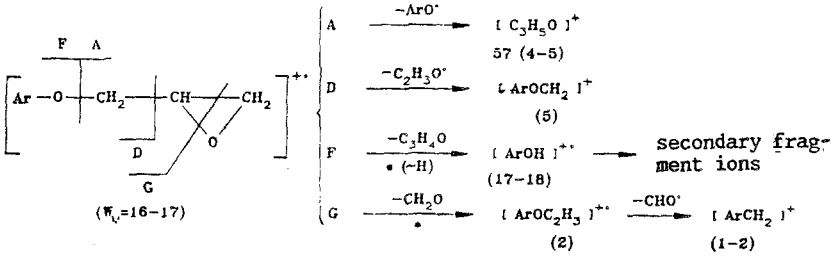


*Here and subsequently, the m/z values are presented under the formulas of the ions; the ranges of the intensities of the peaks of these ions for the different homologs at 70 eV in percent of the overall ion current Σ_{27} are given in parentheses.

The rearranged character of the ions with m/z 58 is indicated by the sharp increase in their intensities (to 50-60% Σ_{27}) with a decrease in the ionization energy to 12 eV.

The ion peaks with m/z 59, which vary markedly in intensity (from 1% in the spectrum of Ia to 15% Σ_{27} for ether Ib), may be due to the so-called "double" migration of hydrogen, a structural prerequisite for which is the presence of several heteroatoms in the molecule [5, 9].

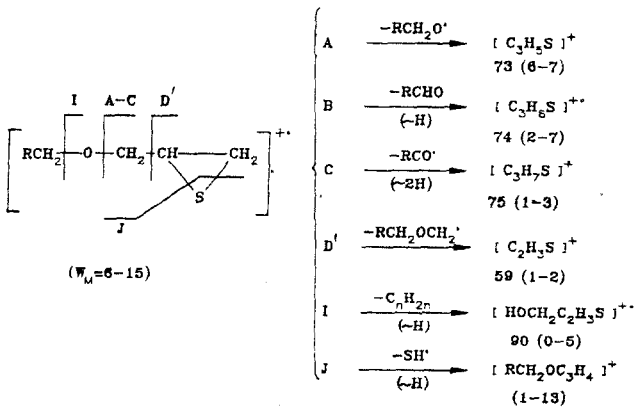
If one introduces the concept of the average ratio of the intensities of peaks of ions that are formed as a result of processes that assume the presence of a charge on the exocyclic oxygen atom to the intensities of the peaks of ions associated with charge localization on the ring heteroatom (the y coefficient), it can be used as a measure of the distribution of the charge of the molecular ions on two centers. In the case of alkylglycidyl ethers the ratio of the overall contributions of processes **D** and **E** to ions of the **A-C** type is ~0.9. This parameter differs substantially for arylglycidyl ethers, when processes **B**, **C**, and **E** are forbidden by the structure of the investigated substances, but two new types of fragmentation appear:



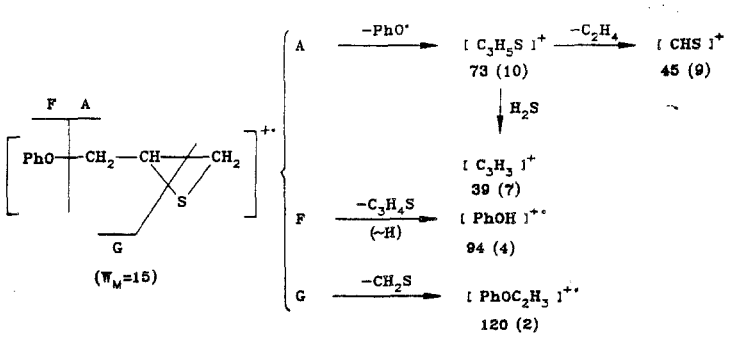
The ions formed in processes **A** and **D-G** constitute more than 50% of the overall ion current (process **F**, which is associated with the migration of a hydrogen atom and is common to all compounds with aryloxy groups, is the principle process). The ratio of the intensities of the ion peaks of the processes **(A + G)/(F + D)** (the y coefficient) is six, which corresponds to predominant localization of the charge of the molecular ions on the oxygen atom conjugated with the π system of the aryl substituent.

The mass spectra of the thioglycidyl ethers is considerably more complex. The scheme presented below reflects the principal pathways of their fragmentation.

The overall intensities of the peaks of the ions presented in this scheme is 38-45% Σ_{27}, while the estimate of the y factor from these data (<0.1) is in agreement with primary localization of the charge on the sulfur atom and corresponds to the photoelectronic spectral data. The loss of an SH· radical is a nonspecific process in the fragmentation of most aliphatic sulfur-containing compounds [9], just like the formation of $[CHS]^+$ (m/z 45) and $[CH_2SH]^+$ (m/z 47) ions, the specific mechanism of the formation of which cannot be established.



A peculiarity of the fragmentation of the only representative of arylthioglycidyl ethers IIf is also the low selectivity of the fragmentation of the molecular ions:



The overall intensity of the peaks of the ions presented in the scheme is ~47%, and the y factor is ~0.15. The consequences of a marked change in the character of the fragmentation as a result of replacement of the oxygen atom by a sulfur atom show up most distinctly when one compares the mass spectra of phenyglycidyl and phenylthioglycidyl ethers. This primarily pertains to the change in the ratio of the peaks of the ions formed during processes A and F and, as a consequence of this, the change in the y factor from 6 to less than 0.15.

All of the investigated series, which are represented by several homologs, can be characterized by ionic-series spectra [5]. In this way of representing mass-spectrometric information the above-noted complexity and ambiguity of the fragmentation processes of the investigated compounds are not an obstacle to the group identification of representatives of these series.

1. Alkylglycidyl ethers (homologous group $y_M = 4$)

$$C_nH_{2n}O_2,\ M_1=88;$$

6_2, 34_4, 17_6, 22_4, 1_1, 0, 0, 0, 0, 0, 0, 5_3, 1_1, 14_6, $\Sigma S = 27$, major peaks of 1, 2, 3, and 13 groups.

2. Arylglycidyl ethers (y_M - 10), evaluation with respect to two homologs

$$C_nH_{2n-8}O_2,\ M_1=150;$$

0, 11_2, 1_1, 6_2, 0, 0, 1_1, 15_2, 4_1, 18_3, 34_3, 6_1, 0, 4_1, $\Sigma S = 17$, major peaks of 1, 3, 7, 9, and 10 groups.

3. Alkylthioglycidyl ethers ($y_M = 6$)

$$C_nH_{2n}OS,\ M_1=104;$$

2_1, 24_3, 6_2, 18_2, 9_3, 5_1, 16_4, 3_1, 1_1, 0, 0, 3_1, 1_1, 12_3, $\Sigma S = 23$, major peaks of 1, 3, 4, 6, and 13 groups.

A comparison of these series with series that were previously characterized by ionic-series spectra [5] makes it possible to solve the problem regarding the distinctive character of their fragmentation and to uncover series with similar mass-spectrometric features. Using $D = \Sigma|I_1 - I_2|$ and $D = \Sigma(S_1 + S_2)$ [10] as the criterion for comparing the ionic-series spectra one can, for example, establish that of the isomeric alkylthioglycidyl ethers of the series with the general formula $C_nH_{2n}OS$, heterocyclic compounds that contain S and O atoms in the same ring (oxathianes, oxathiolanes), $D = 74 < \Sigma(S_1 + S_2) = 81$, and acyclic oxathiaalkenes with the general formula $ROCH_2CH_2SCH_2CH{=}CH_2$, which were characterized in [11], $D = 48 < \Sigma(S_1 + S_2) = 56$, have the most similar ionic-series spectra. The ionic-series spectrum of oxathiaalkenes has the form: 1_1, 17_{10}, 22_2, 26_{11}, 6_1, 4_1, 7_2, 1_1, 0, 0, 0, 3_1, 1_1, 12_2, $\Sigma S = 33$, major peaks of 1, 2, 3, and 13 groups.

However, even in the indicated cases the differences in the intensities of the individual components of the ionic-series spectra make it possible to reliably distinguish these series. Alkylthioglycidyl ethers and oxathiaalkenes, in particular, are characterized by noncoinciding values of the sums of the intensities of the peaks of the homologous group y = 2 (6 ± 2% and 22 ± 2% of the overall ion current).

EXPERIMENTAL

The purity of the preparations was monitored by means of GLC with an LKhM-72 chromatograph using a 3 m by 5 mm column packed with 5% XE-60 on Chromaton N-AW at 120-210°C and a catharometer as the detector. The mass spectra were recorded as follows: with an MKh-1320 spectrometer with introduction of the samples through a chromatographic column and through

TABLE 3. Physiochemical Constants of Thioglycidyl Ethers IIa, c-e

Compound	bp, °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D		Calculated, %			Empirical formula	Calculated, %			Yield, %
				found	calc.	C	H	S		C	H	S	
IIa	61 (17)	1,0369	1,4788	28,49	28,48	46,3	7,6	30,7	C_4H_8OS	46,1	7,7	30,8	91
IIc	74—75 (15)	0,9530	1,4668	42,44	42,57	57,2	9,3	22,3	$C_7H_{14}OS$	57,5	9,6	21,9	87
IId	73 (17)	0,9880	1,4786	37,31	37,35	55,3	7,8	24,6	$C_6H_{10}OS$	55,3	7,7	24,6	90
IIe	76—78 (1)	1,1310	1,5716	47,97	48,34	65,4	6,6	19,3	$C_9H_{10}OS$	65,0	6,1	19,3	77

the SVP-3 system (ionization energies 70, 40, 20, and 12 eV, inlet-cylinder temperature 120°C, and source temperature 120°C), with an HP-5995 chromatographic mass spectrometer with introduction of the samples through a glass capillary column packed with OV-101 at 50°C, and with an LKB-2091 chromatographic mass spectrometer using a 2 m by 2 mm column packed with OV-225 under conditions of temperature programming from 50°C to 150°C. The recording of the photoelectronic spectra and the determination of the ionization energies and the development of fragment ions were carried out with an MKh-1302 spectrometer (Scientific-Research Institute of Physics, A. A. Zhdanov Leningrad State Univerisity) by the method described in [13].

Compounds Ia, d-f were synthesized by a modified method [12]; the physicochemical constants of the described substances were in agreement with the literature data. Preparations Ib, c, g were obtained in 0.01-mole amounts, and their mass spectra were recorded without preparative isolation of the compounds during the chromatographic mass-spectrometric analysis.

Thioglycidyl Ethers (Table 3). These compounds were synthesized by a general method. A 0.3-mole sample of the glycidyl ether was added dropwise to 100 ml of an aqueous solution of KCNS (4 M), the reaction mixture was stirred for 1.5 h, and a second portion of the ether (0.1 mole) was added. Stirring was continued for 2 h, after which the aqueous layer was separated and treated with a solution of KCNS (0.2 M) with stirring in the course of 4 h. The aqueous layer was extracted with three 25-ml portions of ether, the extract was combined with the organic layer, and the mixture was dried with anhydrous $MgSO_4$. The ether was removed by distillation, and the reaction product was distilled in vacuo. The mass spectrum of IIc was recorded without isolating the substance from the reaction mixture.

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