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General Scheme of Fragmentation of Monofunctional Organic Compounds under Electron Ionization

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Abstract—General scheme of fragmentation of monofunctional organic compounds RX (R, alkyl and X, functional group) has been elucidated basing on analysis of mass spectra under conditions of electron impact. The mass spectra have been considered as superposition of a few peaks of characteristic ions containing group X or its fragments and the peaks of hydrocarbon ions (hydrocarbon subspectra). The hydrocarbon subspectrum analysis has allowed interpretation of the fragmentation processes forming the RX compounds mass spectra and estimation of contribution of each process into the total ion current. The possibility of simulating the spectra of non-studied compounds RX via the transformation of available mass spectra of RX compounds with the same alkyl fragment is discussed .

Keywords: mass spectroscopy (EI), fragmentation, spectrum interpretation, hydrocarbon subspectrum

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Fragmentation processes of organic compounds under conditions of electron ionization mass spectroscopy have been classified in the reference literature according to the compounds classes or according to the decay type. The first approach is mainly presented in organic chemistry textbooks [1–8], whereas the second one is based on common classification of organic compounds decay [9–11] and has been developed in [12–14].

At the same time, assignment of the prevailing decay types to the classes of organic compounds has been scarcely studied. Hence, the qualitative similarity of fragmentation of compounds of different classes and its quantification has remained open issues so far. The related discussion will aid in better understanding the relationship between mass spectroscopy fragmentation of organic compounds and their properties, including electronic structure, and open the possibilities for prediction of the mass spectra.

This work addresses the above-mentioned issues using the monofunctional RX compounds as example [R being alkyl fragment and X being a heteroatom or functional group: OH, SH, Cl, F, Br, I, NO_2, CN, OCH_3, NH_2, $N(CH_3)_2$, $CH_3C(O)O$, $CH_3P(O)FO$, $CH_3P(O)(OCH_3)O$, etc]; as a first approximation, X may be considered an indivisible block (quasi atom) in the fragmentation processes. As seen from the above-listed series, monofunctional compounds include rather complex molecules consisting of a single functional group and an alkyl substituent.

In the previous works we have considered mass spectra of RX compounds as a superposition of the hydrocarbon and the characteristic subspectra [15–18]. The majority of mass spectral peaks of monofunctional compounds correspond to the hydrocarbon ions C_nH_{2n+m} (m = 1, 0, or –1) [1–3, 15–18]. Generally, organic compounds are ascribed to a class (homologous series) basing on the peaks of characteristic ions [3] containing the functional group X or its fragments; these peaks form characteristic subspectrum. Less attention is directed to the hydrocarbon subspectra; the structural features of alkyl chains are often elucidated from mass numbers and intensities of characteristic peaks rather than these of the hydrocarbon subspectrum [2, 3].

This work mainly considers the features of hydrocarbon subspectra of the monofunctional compounds; the characteristic subspectra will be discussed in the oncoming reports.

Basing on the analysis of mass spectra recorded under electron impact we suggested the general scheme of fragmentation of monofunctional compounds (see below), a set of decay pathways of the molecular ion, the latter being a source of both hydrocarbon and characteristic ions. A well studied class of the aliphatic alcohols was used as a basic homologous series.

$$RX]^{+\bullet} \rightarrow [R - H]^{+\bullet} + HX, \quad (1.1)$$

I

Decay of the alkene molecular ion $[R - H]^{+\bullet}$, (1.2)

$$[RX]^{+\bullet} \rightarrow (R^1)^{\bullet} + [R^2(CH{=}X)]^{+}, \quad (2.1)$$

II

$$[RX]^{+\bullet} \rightarrow [R^1]^{+} + [R^2(CH{=}X)]^{\bullet}, \quad (2.2)$$

III

$$[RX]^{+\bullet} \rightarrow [R^3 - H]^{+\bullet} + R^4X, \quad (3)$$

IV

$$[RX]^{+\bullet} \rightarrow [R]^{+} + X^{\bullet}, \quad (4.1)$$

V

Decay of alkyl ion $[R]^{+}$, (4.2)

Specific reactions. (5)

The first decay reaction (1.1) consists in the elimination of a neutral HX molecule from the molecular ion. It has been marked in the course of fragmentation of some of the above-listed monofunctional compounds [1–3, 6–7, 9] but not in all the cases. Our analysis of mass spectra revealed that the reaction was general; for the majority of the considered compounds it was a main source of hydrocarbon ions. However, the nature of the formed cation-radical $[R - H]^{+\bullet}$ (alkene or cycloalkane) has remained undefined. It has been stated in [1] that both structures are possible. Thermodynamic features determining the rearrangement process during fragmentation are fairly complex. Molecular and fragment ions can be isomerized into the more favorable form provided that the energy input is sufficient [14]. The isomerized ion can yield the products that are not the most favorable in view of the structure of the parent ion; therefore, the conclusions on the fragmentation mechanism have been cautious [1, 3]. Furthermore, the analysis is complicated by the similarity of mass spectra of certain cycloalkanes and alkenes with equal number of carbon atoms [19]. Some evidences in favor of alkenes formations have been found. In particular, we have attempted identification of the R' group in the molecules of *O*-alkylmethylfluorophosphonates $CH_3P(O)F(OR')$ via selection of subspectrum of the $[R' - H]^{+\bullet}$ cation-radical from mass spectra of these compounds [15]. In the case of highly branched R' fragments, the subspectrum has been reliably identified as the corresponding alkene spectrum using the NIST system [19]: the Match and R.Match parameters were sufficiently high. In the cases of less branched alkyl fragments, the assignment has been less reliable. Likely, the more branched R' fragments give the more characteristic spectrum of the [R' – H] alkene. Prediction of mass spectra of the $CH_3P(O)F(OR')$ compounds basing on mass spectra of the alkenes [R' – H] has also evidenced the prevailing formation of alkenes in the course of the general reaction (1) [15].

It should be kept in mind that processes of decay of molecular and fragment ions are nonequilibrium monomolecular reactions [1]. The relative amount of products of the competing reactions is strongly dependent on their relative formation rates [1, 20] (if their further decay can be neglected). According to the available data, $M^{+\bullet}$ ions of higher aliphatic alcohols eliminate water primarily involving the hydrogen atom in position 4 (~90%) [1, 3, 21, 22]. This reaction should yield the four-membered cycle, evidencing in favor of cycloalkanes formation. However, the four-membered cycles are known to be formed very slowly [23]. The presence of the branching at position 4 or at the neighbor carbon atoms will further decelerate the cycle formation due to the entropy factor. In view of this, the stepwise mechanism of HX elimination from molecular ions of RX compounds leading to the alkenes formation [3] seems most probable.

The NIST information system favors the alkenes formation, mainly these obeying the Zaitsev rule [24].

Reaction (2) can be viewed as the first and further cleavage of carbon-carbon bonds in RX molecules. The reaction can occur via two paths. The first one (2.1) leads to onium ions (**II**) $[R^2(CH{=}X)]^{+}$ along with alkyl radicals $(R^1)^{\bullet}$. The total number of carbon atoms in the ion $[R^2(CH{=}X)]^{+}$ and the radical $(R^1)^{\bullet}$ equals to that in the R part of the starting molecule. Some of the $[R^2(CH{=}X)]^{+}$ ions are formed via rearrangement reactions [1, 10, 14, 32], their mechanism being outside of the scope of this work. Reaction (2.1) is a main source of the characteristic ions in the cases of the majority of RX compounds.

However, the positive charge can be localized not only on the fragment **II** {$[R^2(CH=X)]^+$ (2.1)} but also on the hydrocarbon fragment to form the corresponding carbocations **III** (2.2). The process direction is determined by the ability of the group X to stabilize the onium ion due to its mesomeric and inductive effects [1, 9, 25]. In the spectra of RX compounds, the peaks at *m*/*z* 43 ($C_3H_7^+$), 57 ($C_4H_9^+$), and 71 ($C_5H_{11}^+$) are the strongest carbocation ones, likely due to the low ionization energy of the corresponding radicals (7.55, 6.93, and 6.94 eV [1]). To the best of our knowledge, the probability of the (2.2) decay for RX compounds other than alcohols has not been systematically studied.

Reaction (3) leads to alkene cation-radicals with less of carbon atoms than in the starting molecule. Possible mechanisms of such processes have been discussed in the case of alcohols [1–4]. The reactions are usually described as simultaneous elimination of ethylene (or other alkene) and water [2, 3]. Such mechanism seems unreasonably complex and sometimes contradicts the experimental data.

The general reaction path (3) consists in elimination of the R^4X molecule with R^4 being the alkyl fragment smaller than R part in the starting molecule. The (3) pathway is an important source of hydrocarbon ions in the cases of branched fragment R.

The last source of hydrocarbon ions is the molecular ion decay into the alkyl cation R^+ via elimination of $X^{\bullet}$ radical (4) [13, 26]. Thermochemical calculations [13, 26] have shown that halogen elimination in the radical form is the most probable in the cases of iodo and bromo derivatives. However, this process occurs to some extent in the course of fragmentation of most of the considered RX compounds.

The processes (1)–(4), except for the (2.1) reaction, result in hydrocarbon ions forming the hydrocarbon subspectrum of the monofunctional compounds. Note that the X fragment behaves as a quasi atom in these processes.

The specific reactions are listed under item (5) in the general scheme. They are the processes typical of the given class of compounds and leading to the formation of characteristic ions containing the X group or its fragment. Such processes include the McLafferty rearrangement [1, 2, 4], formation of protonated ion of the corresponding acid in the case of esters, phosphates, and phosphonates decay [4, 27–29], formation of $[RCO]^+$ and $[PO]^+$ (*m*/*z* 47) ions during the decay of the same compounds [4, 27–29], elimination of $[NO]^+$ (*m*/*z* 30) from nitroalkanes [3, 7], elimination of ethylene from nitriles [3, 7], and a few other decay reactions. As a whole, the peaks of ions formed via reactions (2.1) and (5) form the characteristic subspectrum of monofunctional compounds.

Evidently, the similarity of hydrocarbon subspectra of compounds RX required separation of those subspectra. To do so, the peaks with mass number exceeding that of the fragment R were removed, and then peaks of characteristic ions {$[R^2(CH=X)]^+$ and those formed via specific decay reactions (5)} were removed. As a result, we obtained the hydrocarbon subspectra of the full mass spectra. The subspectra were collected in the Carb base library included into the list of NIST system databases.

The Carb base library was built using mass spectra of the mainlib library of NIST system. Further, the NIST database was used to decompose the subspectra into the components corresponding to various reactions of the general scheme.

Coincidence of the spectra was evaluated applying an *identity* algorithm. Recent studies have revealed that using this algorithm in the NIST system gave the most reliable results of identification of compounds from their mass spectra [30, 31]. The values of Match and R.Match parameters above 670 (of 1000) were considered a satisfactory match, and their values above 750 pointed to a good coincidence.

Let us consider some examples.

Figure 1a shows mass spectrum of 2,3-dimethylpentanol-1. The spectrum contains the **I** ion peak at *m*/*z* 98 and the **II** ion peaks at *m*/*z* 31, 45, and 59. Deleting the characteristic peaks **II** of oxonium ions and the peaks with mass numbers exceeding 99 gave the hydrocarbon subspectrum. In Fig. 1b it is compared with the spectrum of the first alkene with the corresponding hydrocarbon backbone via library search using NIST system. The spectra coincidence was hardly satisfactory (Match 669 and R.Match 671). The spectrum contained the carbocation **III** peaks at *m*/*z* 57 and 85 expected in view of the alcohol structure; those peaks were absent in the alkene spectrum. The peak at *m*/*z* 43 was likely of the same sort; its intensity in the alkene spectrum was 6 times lower than in the alcohol spectrum. Moreover, the hydrocarbon subspectrum

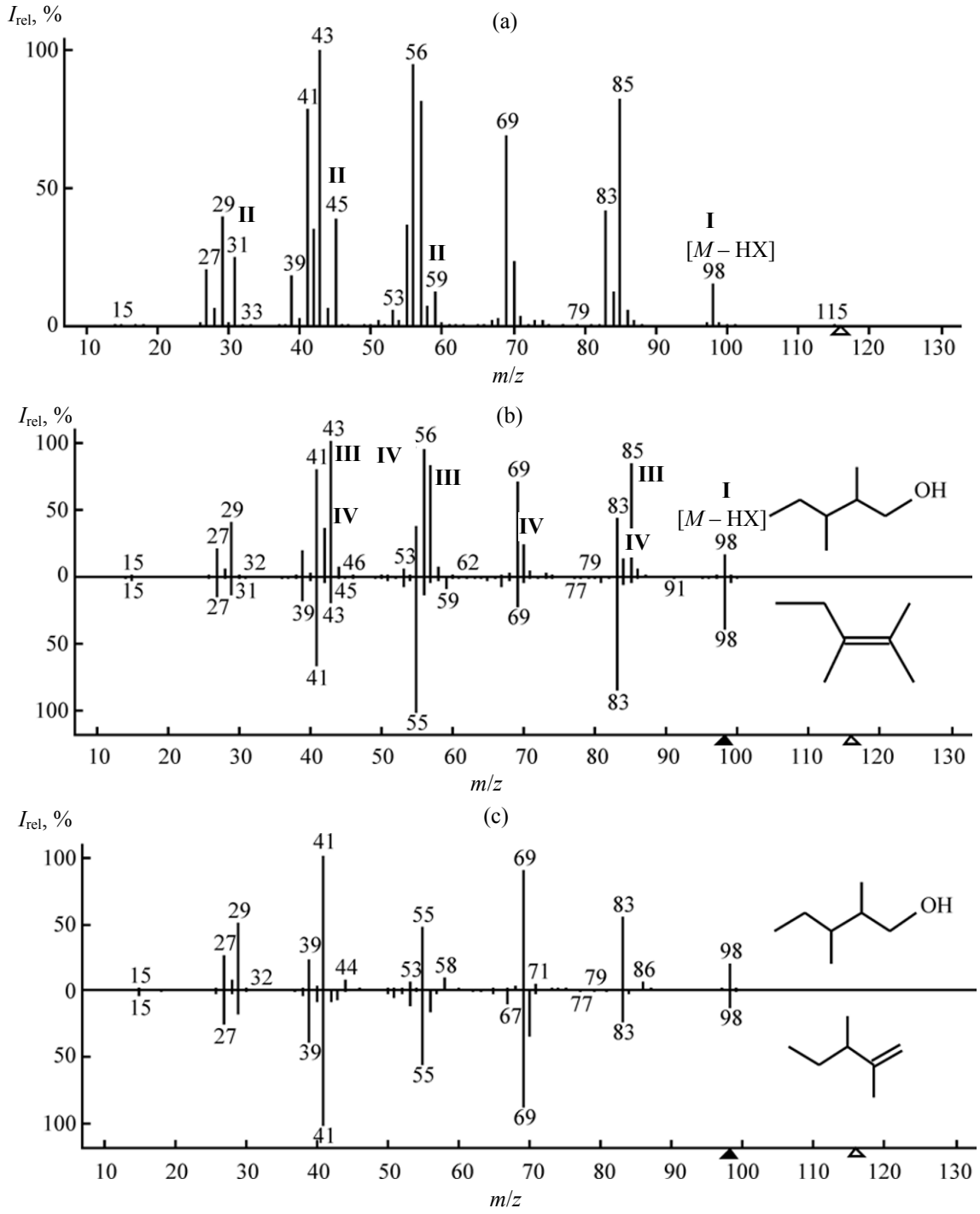

Fig. 1. Mass spectrum of 2,3-dimethylpentanol-1 (a) and comparison of its subspectrum (after removal of peaks **II**) with spectrum of 2,3-dimethylpentene-2 (b), and of its subspectrum (after removal of peaks **III** and **IV**) with spectrum of 2,3-dimethylpentene-1 (c).

contained ions **IV** peaks at *m*/*z* 42, 56, 70, and 84; they were observed only as isotope satellites in the alkene spectrum.

The mentioned peaks were removed, and the library search was repeated; the results are given in Fig. 1c. The obtained score of coincidence between the edited alcohol spectrum and the alkene spectrum were very high (Match 809 and R.Match 827). Remarkably, the Zaitsev-type alkene was selected as the best match [24].

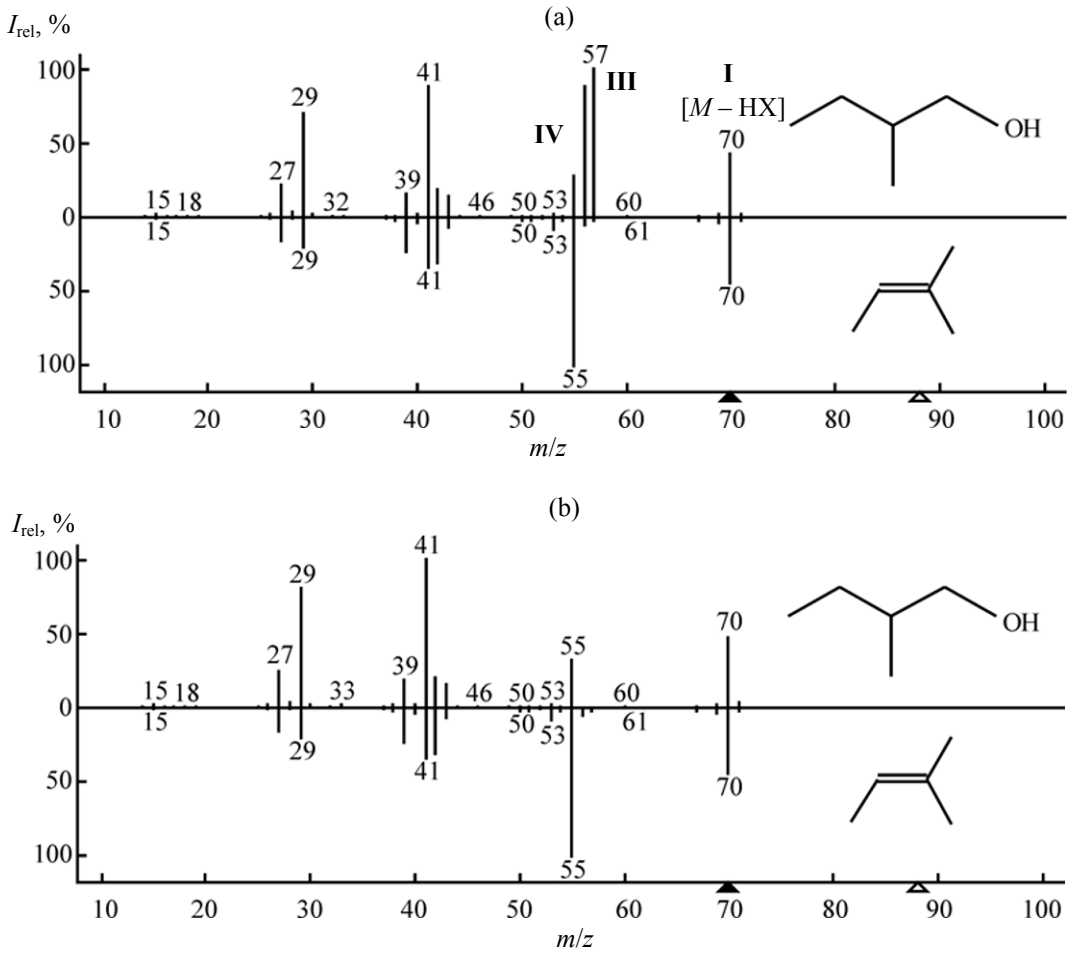

Fig. 2. Comparison of subspectrum of 2-methylbutanol-1 with that of 2-methylbutene-2 (a) and the same comparison after removal of peaks **III** and **IV** from 2-methylbutanol-1 subspectrum (b).

As another example, comparison of hydrocarbon subspectrum of 2-methylbutanol (above the central line) with the spectrum of the best matching alkene 2-methylbutene-2 is shown in Fig. 2a.

The spectra coincidence was hardly satisfactory (Match 670 and R.Match 672). Again, the expected strong carbocation **III** peak at *m*/*z* 57 was observed in the alcohol spectrum, being absent in the alkene spectrum. Furthermore, the hydrocarbon subspectrum showed a strong alkene **IV** peak at *m*/*z* 56. The presence of that peak could be likely explained by the formation of molecular ion of butene via reaction (3) accompanied by methanol elimination.

$$[CH_3CH_2CH(CH_3)CH_2(OH)]^{+\bullet} \rightarrow \underset{\textbf{IV}}{[C_4H_8]^{+\bullet}} + CH_3OH. \quad (3.1)$$

Table 1. Processes determining mass spectrum of 2-methylbutanol[a]

Decay process	Contribution to the total ion current, %
Elimination of water, formation of alkene ion $[C_5H_{10}]^{+\bullet}$ (1.1), and its partial decay (1.2)	59
Formation of CH_2OH^+ (*m*/*z* 31), $C_2H_4OH^+$, (*m*/*z* 45), and $C_3H_6OH^+$ (*m*/*z* 59) (2.1)	8
Formation of $C_4H_9^+$ (*m*/*z* 57) (2.2)	18
Formation of $[C_4H_8]^{+\bullet}$ (*m*/*z* 56) (3)	15

[a] According to [15] (NIST#: 233556).

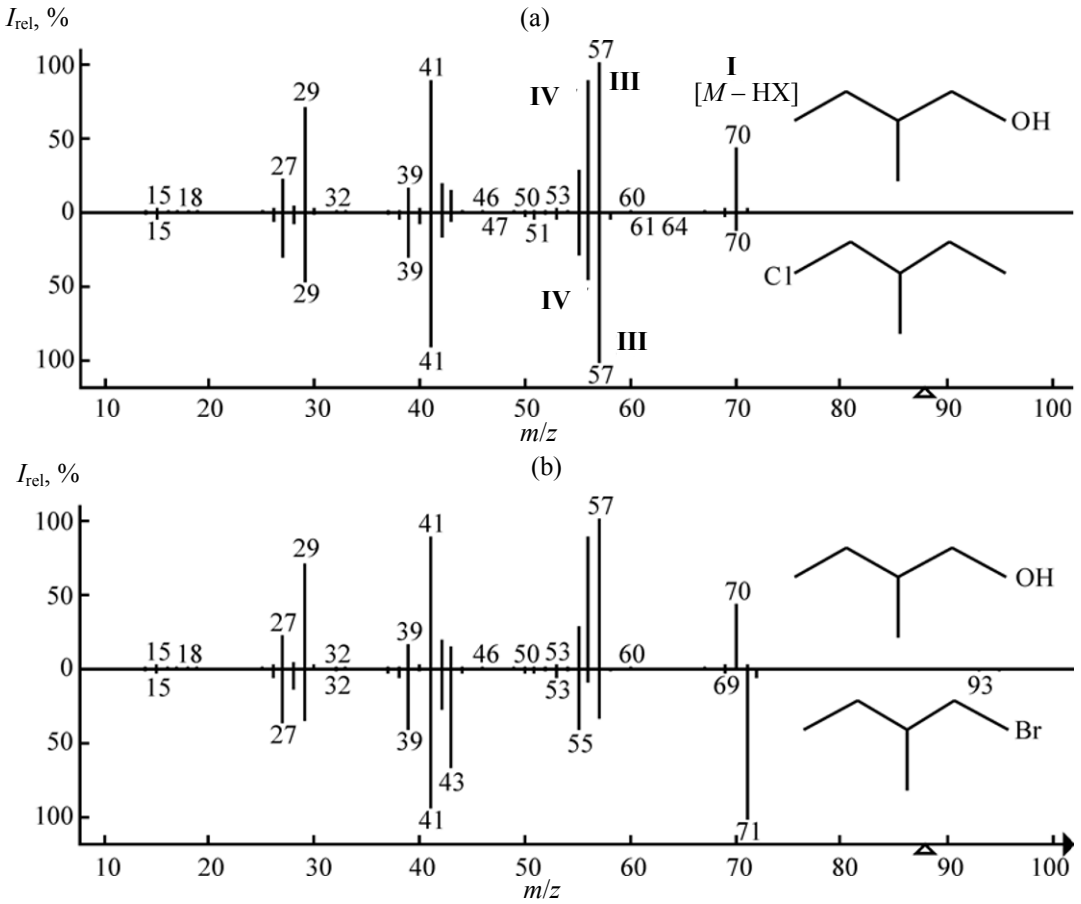

Fig. 3. Comparison of hydrocarbon subspectra of 2-methylbutanol with those of 2-methyl-1-chlorobutane (a) and 2-methyl-1-bromobutane (b).

After removal of peaks **III** and **IV** from hydrocarbon subspectrum, the library search was repeated; the result is given in Fig. 2b.

The spectra coincidence was good (Match 791 and R.Match 795). Hence, the alcohol spectrum was a superposition of the corresponding alkene spectrum, a few peaks of ions **III** and **IV**, and the characteristic ion **II** peaks.

Basing on the demonstrated results we concluded that the proposed analysis scheme using the NIST system simplified interpretation of spectra of many monofunctional compounds (both qualitative and quantitative). That revealed the processes forming the spectrum according to the general scheme and estimated their contribution into the total ion current. The results of the analysis in the case of 2-methylbutanol are collected in Table 1.

The analysis uncertainty primarily resulted from the discrepancy of the spectra of the same compounds extracted from various references leading to the noticeable inaccuracy of the peak intensity determination. Therefore, the fragmentation schemes of the particular compounds derived during our analysis were inevitably simplified. In particular, the processes of decay of cation-radicals **IV** could not be reliably elucidated.

On top of that, analysis of mass spectra of alkene differed in the double bond location revealed that being rather similar they sometimes show different intensity of peaks corresponding to ions **III** (43, 57, 71, and 85 Da) [9]. Consequently, with more than 5 carbon atoms in the R group of RX two or even three possible variations existed of the general decay scheme; however, the differences between them were minor.

The following example demonstrates applicability of the proposed scheme for compounds other than alcohols. Figure 3 compared complete hydrocarbon

Table 2. Reasons for similarity and difference of hydrocarbon subspectra of compounds (n-C_5H_{11})X and pentanol-1

X	Coincidence with hydrocarbon subspectrum of pentanol-1 (Match)		Coincidence with mass spectrum of pentene-1 (Match)	Intensity of the peak (m/z)	
	for spectra from our Carb base library	averaged over all the references (number of references)		**I** (70)	**V** (71)
OH	999	934 (6)	808	509	39
Cl	857	846 (5)	862	809	47
SH	830	826 (5)	808	429	41
NO_2	652	636 (2)	633	64	198
CN	673	649 (4)	<588	37	13
Br	625	600 (5)	691	50	839
I	485	510 (4)	583	5	731

subspectra of 2-methylbutanol and 2-methyl-1-chlorobutane as well as 2-methylbutanol and 2-methyl-1-bromobutane from the Carb base library.

The hydrocarbon subspectra of the compounds belonging to different classes (alcohols and chloroalkanes) were remarkably close, Match and R.Match being 837 and 840, respectively. Evidently, the fragmentation of those compounds involved similar reactions with close relative rates.

For instance, the formation of alkene cation-radical **IV** with m/z 56 in the course of 2-methyl-1-chlorobutane fragmentation occurred via reaction (3.2), similar to reaction (3.1) with elimination of chloromethane.

$$CH_3CH_2CH(CH_3)CH_2Cl]^{+\bullet} \rightarrow [C_4H_8]^{+\bullet} + CH_3Cl. \quad (3.2)$$

After removal of peaks **III** and **IV**, the hydrocarbon subspectrum of 2-methyl-1-chlorobutane perfectly matched mass spectrum of 2-methylbutene-1 (Match and R.Match of 770).

The situation was different in the case of structurally similar 2-methyl-1-bromobutane. Its hydrocarbon subspectrum was different from that of 2-methylbutanol (Match 633 and R.Match 678). In contrast to the spectra of the alcohol and the chloroalkane, the considered spectrum contained a strong peak of carbocation **V** with m/z 71 (Fig. 3b) formed via elimination of $X^{\bullet}$ from the molecular ion. Moreover, the alkene molecular ion peak (m/z 70) was absent in the spectrum of the bromoalkane; the formation of the alkene ion **IV** with m/z 56 was not observed for the brominated derivative as well.

Note that the intensity of the peaks of carbocations with m/z 57 and 43 in the spectra of the alcohol and the bromoalkane were reversed. The mean ratio of intensities of the m/z 43 and 57 peaks was 2.08 (standard deviation 0.80, 9 references) for 2-methyl-1-bromobutane and of 0.16 (standard deviation 0.03, 7 references) for 2-methylbutanol. The stronger peak at m/z 57 as compared to the peak at m/z 43 was expected taking into account the carbon scaffold structure containing a branching at position 2. The reason for the reversed intensities ratio in the case of the bromoalkane was likely a different source of those ions. In the case of 2-bromobutane the ion with m/z 43 was formed via decay of carbocation **V** [reaction (4.2) of the general scheme] rather than via reaction (2.2); more specifically, the process involved elimination of the olefin from the alkyl ion, typical of many organic compounds decay [3].

$$[CH_3CH_2CH(CH_3)_2]^+ \rightarrow \underset{m/z\ 43}{[C_3H_7]^+} + C_2H_4. \quad (4.2)$$

The ion with m/z 57 could not be directly formed in that reaction, and its peak was weaker.

The presented results confirmed applicability of the proposed general scheme for interpretation of mass spectral fragmentation of monofunctional compounds. In particular, the similarity of hydrocarbon subspectra of the monofunctional compounds was determined by the contribution of the fragmentation reactions [except for the processes (2.1) and (5)] into the total ion current.

If the processes of decay of the structural analogs belonging to different classes of compounds were the same and their contributions into the ion current were similar, the resulting hydrocarbon subspectra were similar as well. If at least one of the conditions was not held, the hydrocarbon subspectra were substantially different.

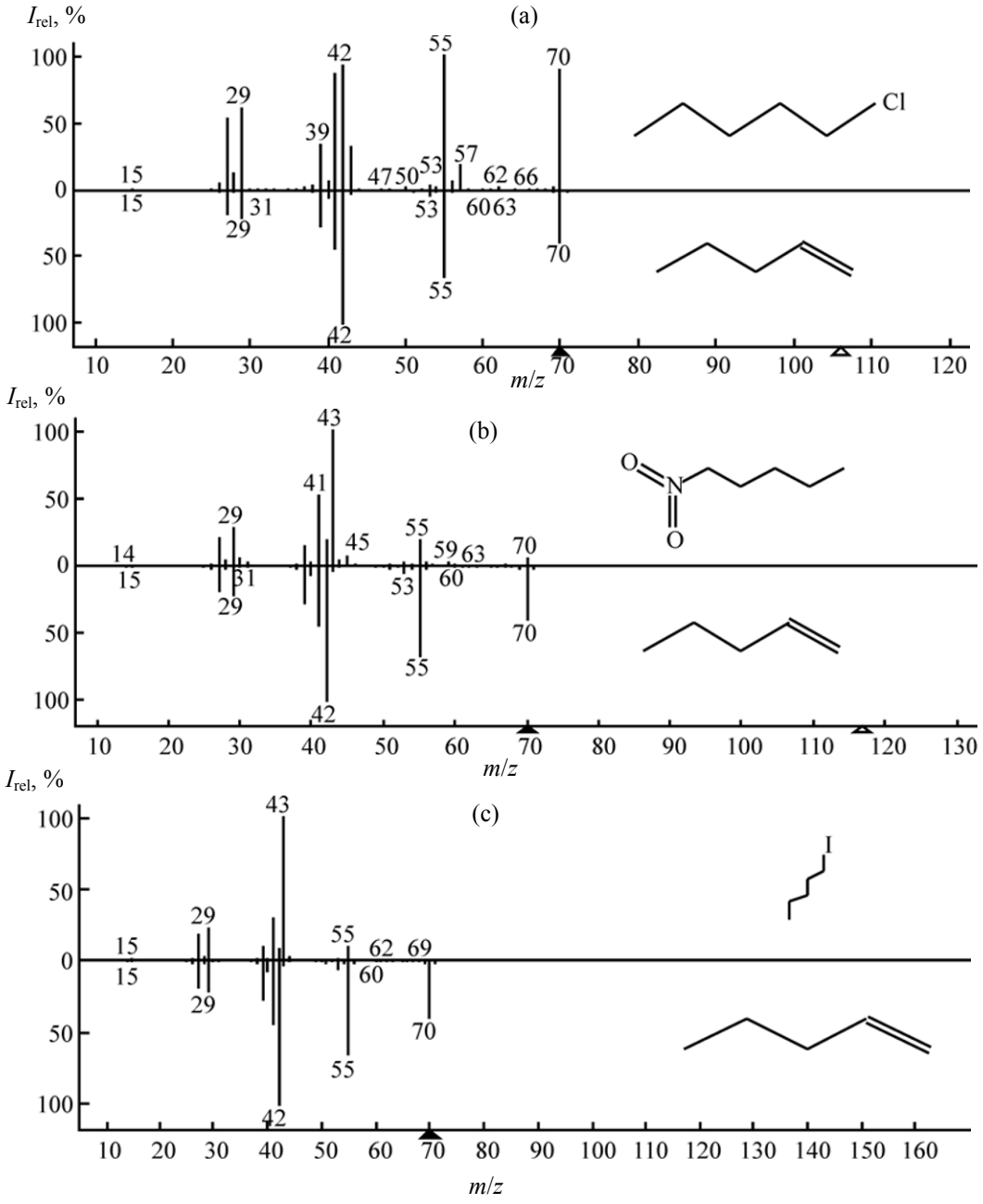

Fig. 4. Comparison of truncated hydrocarbon subspectra of *n*-$C_5H_{11}X$ compounds: 1-chloropentane (a), 1-nitropentane (b), and 1-iodopentane (c) with pentene-1 spectrum.

In order to find the reason for the differences, we analyzed hydrocarbon subspectra of primary derivatives of *n*-pentyl $C_5H_{11}X$ and calculated parameters of their coincidence with hydrocarbon subspectra of pentanol-1 from the Carb base library (the raw data: NIST 230531). The results are given in Table 2.

Statistical processing demonstrated that using the spectra from our Carb base library (Table 2, column 2) gave practically identical results as when using the data averaged over the available data from mainlib and replib libraries of NIST system (Table 2, column 3).

The data in Table 2 shows that good agreement of carbon subspectra with that of pentanol-1 were observed in the cases of the thiol and chloro derivatives; the largest difference was found in the case of the iodo derivative.

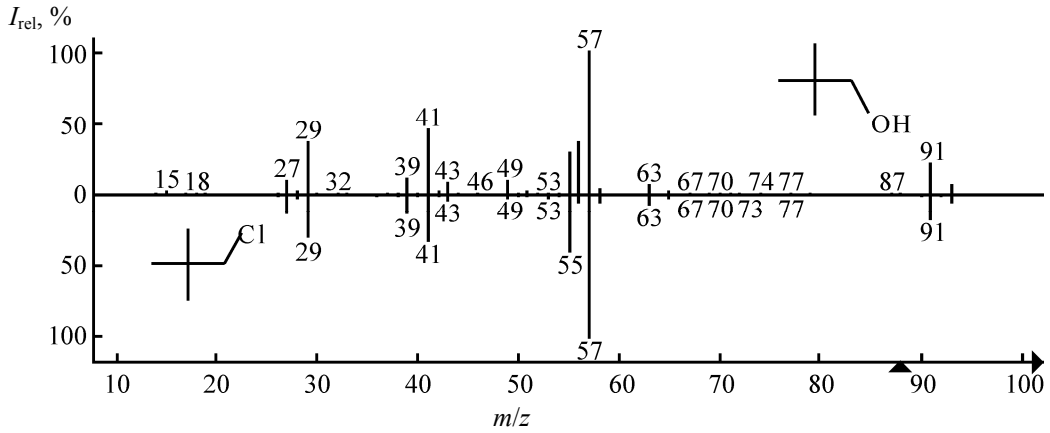

Fig. 5. Comparison of transformed mass spectrum of 2,2-dimethylpropanol with experimental spectrum of 2,2-dimethyl-1-chloropropane.

The data in Table 2 and Fig. 4 give the main reasons for similarity and diversity of the RX compounds hydrocarbon subspectra. In particular, Fig. 4 compares the truncated (with the peak **V** removed) hydrocarbon subspectra of the $C_5H_{11}X$ compounds from our library with the spectrum of pentene-1.

The spectral similarity was very high in the cases of pentanol-1,1-chloropentane, and 1-thiopentane; their hydrocarbon subspectra being weakly perturbed spectrum of pentene-1 (Fig. 4a; Table 2, column 4), containing strong peaks of the molecular pentene cation at *m*/*z* 70.

Table 3. Test for normal distribution of the Match parameter of hydrocarbon subspectra of RX compounds with hydrocarbon subspectra from Carb base library

X	Number of compounds	p[a]		
		Shapiro–Wilk test	D'Agostino's test	Anscomb-Glynn test
OH	21	0.097	0.756	0.080
Cl	18	0.219	0.502	0.763
SH	15	0.184	0.536	0.347
F	5	–	–	–
Br	18	0.636	0.640	0.304
NO_2	8	0.310	0.771	0.191
CN	8	–	–	–
I	10	0.303	0.252	0.078

[a] The distribution was considered normal at $p > 0.05$.

Table 4. Parameters of normal distribution of the Match values of hydrocarbon subspectra of RX compounds with subspectra of alcohols from Carb base library

X	Average Match value	Standard deviation	Confidence interval[a]
OH	934	32	±15
Cl	789	49	±24
SH	786	64	±36
F	824	33	±41
Br	695	77	±38
NO_2	653	49	±41
CN	685	42	±35
I	562	86	±61

[a] Reliability 0.95.

The second group of compounds included 1-bromopentane, 1-nitropentane, and hexanenitrile; their hydrocarbon subspectra (Fig. 4b) showing several times weaker peak of the molecular pentene ion and a strong peak at *m*/*z* 43. The similarity parameters were at the edge of satisfactory ones.

Finally, the 1-iodopentane showed no pentene molecular ion peak in the subspectrum (Fig. 4c), and the spectral similarity parameters were very low.

The obtained results indicated two main decay pathways in the cases of the considered monosubstituted pentanes: the reaction of formation and further decay of the pentene ion **I** (1.1) and the formation and further decay of the carbocation **V** via reaction (4). The first path was the main one for the first group of the compounds, the second path was governing for 1-iodopentane, and the compounds of the intermediate group underwent both reactions with comparable rates.

We further determined the coincidence parameters (Match) of hydrocarbon subspectra of the RX compounds (X = OH, Cl, SH, F, Br, NO_2, CN, and I) from the mainlib and replib NIST libraries [15] with the hydrocarbon subspectra of the corresponding alcohols from our Carb base library. The Match parameter was averaged over all the available references for each of the compounds.

Processing of the data in Table 2 assumed normal distribution of the Match parameter. In order to test the hypothesis, we used several statistical tests (Table 3), the threshold significance value being p 0.05.

The distribution of Match parameter for the six examined series was normal. Normal distribution of that parameter for the non-studied compounds (fluoroalkanes and alkylnitriles) was a reasonable assumption. Therefore, the Student's t-statistics could be used to obtain the standard deviation and the confidence interval of the Match values.

Table 4 lists the mean values of Match parameters for hydrocarbon subspectra from our Carb base library and the corresponding standard deviations. Interestingly, they were close to the corresponding parameters obtained via averaging over all the sources listed in mainlib and replib libraries, thus giving the representative results in shorter time.

As seen from Table 4, the confidence intervals of Match values for chloroalkanes, thiols, and fluoroalkanes were above 750, and the coincidence between hydrocarbon subspectra of those compounds with the subspectra of the corresponding alcohols was good; those classes formed the first group of the examined compounds. In the cases of bromoalkanes, nitrocompounds, and nitriles the confidence interval of the Match values corresponded to satisfactory or somewhat below satisfactory spectral similarity; those classes formed the second group of compounds. Finally, the third group of the examined compounds contained iodoalkanes with the Match values below satisfactory.

The obtained results marked a way to predict mass spectra of chloroalkanes, thiols, and fluoroalkanes based on the spectra of alcohols or other compounds of the first group. The general approach consists of the addition of characteristic peaks of the RX compound with the corresponding intensities to the hydrocarbon subspectrum of the alcohol. To do so, the knowledge of relationship between the characteristic subspectra of those classes of compounds is required. This falls out of the scope of this report; let us limit the discussion with a single example of simulation of 2,2-dimethyl-1-cloropropane mass spectrum basing on the spectrum of the corresponding alcohol.

To simulate the chloroalkane mass spectrum, we removed the specific peaks **II** ($C_nH_{2n}OH^+$) from the alcohol spectrum; that were the peaks with *m*/*z* 31, 45, and 73. Instead, the peaks **II** of chloroalkane ($C_nH_{2n}Cl^+$) were introduced with the same intensity, their masses being increased by 18 as compared to the alcohol peaks: *m*/*z* 49 (103), 63 (69), 91 (221). On top of that, the peaks corresponding to the Cl^{37} isotope with the intensity of 35% of the above-listed values were introduced into the simulated spectrum. The so corrected spectrum of 2,2-dimethylpropanol is given in Fig. 5.

The simulated spectrum was further input into the NIST base for identification. The expected structure of 2,2-dimethyl-1-chloropropane was recognized as the most probable. As seen from Fig. 5, the simulated and the experimental spectra of the chloroalkane were similar (Match 831, R.Match 837).

To conclude, besides fundamental interest of reasons for similarity of the mass spectra of monofunctional compounds, its investigation opens the possibility to simulate mass spectra of the non-characterized compounds RY via transformation of the

spectra of the RX compounds with R being the identical alkyl fragment, and X(Y) being a functional group.

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