Gas chromatographic identification of chlorination products of aliphatic ketones

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ABSTRACT

Chlorinated derivatives of aliphatic ketones are a class of organic compounds poorly characterized by both mass spectra and chromatographic retention indices up to present. It is caused by objective difficulties of isolation of individual products from reaction mixtures formed in the result of non-selective chlorination of parent carbonyl compounds. Nevertheless the differences of GC retention indices for structurally analogous chlorination products of different ketones and initial substrates indicate the constancy depending on the number and position of chlorine atoms in the molecules. This feature permits us to use the simplest kind of additive schemes in identification of such chlorinated derivatives, including diastereomeric α,α'-dichloro-k-alkanones ($k > 2$). Hence, the identification of chlorination products of aliphatic ketones becomes possible for any compounds of this class without using mass spectrometric data only in the result of accurate measurement of their GC retention indices.

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1. Introduction

The application of retention indices (RIs) in the identification of analytes in gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) techniques is well known. However, the reference values of these analytical parameters "dispersed" through numerous original publications and the advantages of this approach cannot be realized effectively without RI collection and systematization in comprehensive well-organized databases. The largest collection at present is RI database developed at the National Institute of Standards & Technology (NIST, USA) [1–3]. The last available version of this database (October 2008) includes 293,247 RI values for 44,008 organic compounds on standard non-polar and polar phases. The application of such represented collection simplifies strongly the solution of various analytical tasks.

On the other hand, the unification of experimental RI values published in original literature is the simplest way to reveal the classes (or sub-groups) of organic compounds which are still unsatisfactory characterized by chromatographic retention parameters such as the group of polyhalogenated (mostly, polychlorinated) derivatives. Usually such compounds are synthesized by radical chlorination – a low substrate and regioselective process which forms isomers and/or congeners of polychlorinated derivatives. Physicochemical properties of polychlorinated isomers can be

rather similar, that complicates the isolation of individual products from such mixtures. The difficulties in separation of products explains us the impossibility to determine their individual physicochemical constants and chromatographic retention parameters, especially to attribute these data to compounds with defined chemical structures. It leads to the lack of informational maintenance (including RIs) for identification of products of corresponding reactions. In general, this situation becomes similar to "vicious circle". Hence, the search of appropriate identification algorithms for products of non-selective chlorination remains to be an actual problem.

One of the criteria of effectiveness of contemporary methods of identification of organic compounds is the possibility of applying them for unknown analytes, namely compounds not characterized by any analytical parameters, including mass spectra and/or GC RIs. In gas chromatography this situation can be solved by comparison of experimental and theoretically calculated retention parameters, including RI evaluations obtained with the use of simplest additive schemes [4].

This approach requires no isolation of chlorination products from reaction mixtures and implies preliminary estimation of RI values for all theoretically possible structures. It was applied in identification of 839 congeners of polychlorinated hydroxybiphenyls (metabolites of polychlorinated biphenyls) [5], products of free-radical chlorination of cyclohexane [6], isomeric 4-nonyl phenols (total number of structural isomers is 211) [7], and so on. The commonly used alternative way to identify similar reaction products implies their syntheses followed by standard GC characterization. The examples of such approach are known in analytical practice, as well, namely, in the case of polychlorinated monoter-

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penes [8]. However, it occurs to be so work- and time-consuming (this group includes few thousand congeners) that permits us to doubt in its rationality.

Most of chlorinated derivatives of aliphatic carbonyl compounds remain uncharacterized up to present. However, the formation of these compounds was observed at the chlorination of portable water [9–12]. The alkaline destruction of 1,1,1-trichloro-2-ketones (so called haloform reaction) is considered to be the principal process that leads to appearance of the volatile chlorinated derivatives of methane series in the water [13–16], for example:

$$RCOCCl_3 \xrightarrow{OH^-} RCO_2^- + CHCl_3$$
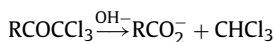
Some regularities of halogenation of aliphatic ketones are characterized well [17–25], namely kinetics parameters of reactions in a gas phase [24]. Surprisingly, only few literature sources contain reference data on physicochemical constants (which can be recalculated into GC RIs) even for simplest chloroderivatives (e.g. [17,18,20]). Mass spectra of only few chloroalkanones are included in the NIST/NIH/EPA MS database [3], while RI values on standard non-polar stationary phases are known only for 1-chloro-2-propanone (RI = 653 [26], 683 [27]) and 1,1-dichloro-2-propanone (707 [28]). Among the sub-group of chlorinated alkyl aryl ketones the simplest homologues and congeners are characterized, as well. One of them is 2-chloroacetophenone possessing the lachrymatory properties (RI values 1230 [29–31], 1231, 1241 [32]). Such insufficient level of characterization of highly important class of organic compounds cannot be accepted satisfactory. This fact determines the aim of our work that is the revealing of GC criteria for identification of chlorination products of aliphatic ketones directly in reaction mixtures.

2. Experimental

2.1. Initial substrates

Aliphatic ketones of "pure" grade with content of principal compounds not less than 98–99% (chromatographic control) were used as initial substrates for chlorination: acetone, 2-butanone, 2-pentanone, 2-hexanone, 4-methyl-2-pentanone, 3,3-dimethyl-2-butanone, and 2,6-dimethyl-4-heptanone (Reakhim, Moscow, Russia); 2-heptanone, 2-octanone, 2-nonanone, 5-nonanone, 6-undecanone, 2-dodecanone, 4-dodecanone, 3-methyl-2-butanone, 2-methyl-3-pentanone, and 5-methyl-2-hexanone (Fluka, Switzerland), 3-pentanone, 3-heptanone, and 4-heptanone (Lancaster, Great Britain), 3-hexanone and 3-nonanone (Merck, Germany). The single available reference sample of chlorinated carbonyl compound was 1,3-dichloro-2-propanone (Lancaster, Great Britain). Distilled sulfuryl chloride (Fluka, Germany) was used as chlorinating agent. The choice of this reagent is caused by regioselectivity of the reaction of ionic chlorination [18,22,33]: the substitution of hydrogen atoms only in α-positions relative to carbonyl group is observed:

$$RCH_2COCH_3 + SO_2Cl_2 \rightarrow RCHClCOCH_3 + RCH_2COCH_2Cl$$

$$+ \ldots + HCl + SO_2$$
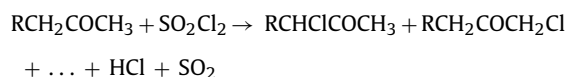
2.2. General procedure for chlorination of aliphatic ketones with sulfuryl chloride

The samples of aliphatic ketones (1 mmol) were placed into test-tube (10 mL volume) and dissolved in 1.2 mL of dry CCl_4. Sulfuryl chloride (1–2 mmol, usually 1.5 mmol) was added by stepwise dropping, followed by keeping reaction mixtures during 10–12 h under periodical shaking. After that reaction mixtures were washed in succession with 1 mL of water (twice), 1 mL of 5% water solution of $NaHCO_3$, and finally, with 1 mL of water (twice),

followed by drying over anhydrous $MgSO_4$ (0.2 g). Under these conditions the main reaction products are chlorinated derivatives containing not more than three chlorine atoms located in different α-positions relative to carbonyl groups. Only few samples contained detectable amounts of α,α,α′,α′-tetrachloroderivatives. Quantities of highly chlorinated products ($n_{Cl} > 4$), formed in the result of concurrent radical chlorination in remote positions, were less than 1–3% (estimation using relative areas of chromatographic peaks)

2.3. Gas chromatographic analysis of reaction mixtures

Gas chromatographic analysis of reaction mixtures was carried out with gas chromatograph Biokhrom-1 (Russia) with flame ionization detector and quartz WCOT column (25 m length, 0.20 mm i.d.) with OV-101 (film thickness 0.25 mkm) in temperature programming regime: initial temperature 40 °C, final temperature 240 °C, ramp 6° min⁻¹. Injector and detector temperatures were 240 and 250 °C, correspondingly. Carrier gas nitrogen, linear flow rate 21 cm s⁻¹. Sampling volumes were 0.3–0.5 mL, split ratio 1:30. For determination of retention indices all samples of reaction mixtures were co-analyzed with the mixture of reference n-alkanes C_6–C_{24} (homologues with even number of carbon atoms in the molecules only). Parameters of chromatographic peaks were measured using TR 2213 integrator (Japan) and UniChrom software (version 4.x-5, Minsk, Byelorussia). The calculation of linear–logarithmic retention indices was carried out using the simplest program (QBasic) [34].

2.4. GC–MS analysis

GC–MS analysis of chlorination products of 4-heptanone, 2-nonanone, and 4-dodecanone was carried out with gas-chromatograph–mass spectrometer DSQ II (Thermo Finnigan) with quartz WCOT column (60 m length, 0.25 mm i.d.) with TR-5 MS (film thickness 0.25 mkm) in the following temperature regime: isotherm 40 °C (2 min), ballistic heating (∼40° min⁻¹) until 75 °C, followed by linear temperature programming until 280 °C (ramp 5° min⁻¹), isotherm 280 °C (10 min). Carrier gas helium, flow rate 1.0 mL min⁻¹. Temperatures of injector, interface, and ion source were 270, 290, and 200 °C, correspondingly. Mass spectra were recorded at ionization energy 70 eV. If necessary, the chromatograms of the same reactions mixtures obtained with various instruments at different conditions were compared using the algorithm [35].

The calculation of intramolecular vibration and rotational energies required for interpretation of the order of chromatographic elution of diastereomers [36] was carried out by molecular dynamics simulation using HyperChem software (HyperCube Corp., Canada, version 6.0) at following parameters: simulation temperature 300 K, simulation time 20 ps, step 0.0005 ps, relaxation time 0.1 ps. Preliminary optimization of molecular geometry was carried out using MM+ molecular mechanics method.

3. Discussion

3.1. Some regularities in GC retention parameters of chlorinated alkanones

The principal difficulty of both GC and GC–MS identification of chlorinated derivatives of aliphatic ketones at the starting moment of this work was the strongly restricted analytical information about this group of compounds. It made impossible the identification of the components of reaction mixtures by direct comparison of both their experimental mass spectra and GC retention indices with reference data and requires the use of non-standard approaches in

Table 1
The constancy of differences in retention indices between some 2-alkanones and their chlorination products.

Parent 2-alkanone	ΔRI values for chlorination products in the order of their appearance on chromatograms				
	1	2	3	4	5
2-Pentanone	125	187	197	248	308
2-Hexanone	116	175	200	250	302
2-Heptanone	118	184	203	251	303
2-Octanone	112	177	189	244	296
2-Nonanone	108	179	191	249	301

data interpretation. In the most extent this situation looks similar to the identification of cyclohexane chlorination products with $2 \le n_{Cl} \le 5$ chlorine atoms in the molecule, where initial reference data were restricted by mass spectra and RIs of few simplest compounds only [7,37].

In such cases the importance of GC RIs increases strongly. Numerous methods of theoretical evaluations of these analytical parameters are known, including the simplest modes of additive schemes. The grounds of this approach is RI proportionality to free energies of sorbate–stationary phase interactions. Precalculation of GC RIs using additive schemes is considered often as obsolete concept, but it has no equivalents in the obviousness and simplicity. To confirm that it is noteworthy to mention the last version of "classical" additive scheme for RI evaluations used in the NIST/NIH/EPA MS/RI database [3], which was published in 2007 [38].

Like an objective reason for application of these algorithms in the case under discussion the following fact should be indicated: the differences of retention indices for most of chlorination products and parent alkanones ($\Delta RI = RI_{product} - RI_{initial}$) remain highly constant that can be illustrated in Table 1 on the example of 2-alkanones C_5–C_9. Their sample-to-sample variations are not exceeding 17 i.u. (index units) for product no. 1 and only 7 i.u. for product no. 5.

This constancy confirms the formation of structurally analogous chlorination products from different 2-alkanones and, hence, the possibility for the application of additive schemes. The most remarkable feature of interpretation of ΔRI values is not only the simplicity of this approach, but the possibility to use their values for any (known) analytes in the identification of chlorination products of other (unknown yet) compounds. For example, even available data for simplest ketone – acetone (average RI value is 472) – permit us to interpret the two from five ΔRI values for 2-alkanones mentioned in Table 1. If we evaluate the average RI values for 1-chloro-2-propanone using the data taken all available literature sources like 668, then the increment ΔRI, corresponding to the substitution H → Cl in the methyl group of 2-alkanones, is equal ca. $668 - 472 = 196$ that corresponds to the interval of ΔRI values for product no. 3 (189–203). Analogous evaluation can be obtained from RI of 1,3-dichloro-2-propanone (870), that gives $870 - 472 = 398 = 2 \times 199$, i.e. exceeds approximately twice the ΔRI

increment for single structure transformation $COCH_3 \rightarrow COCH_2Cl$. Evaluating the ΔRI value for transformation $COCH_3 \rightarrow COCHCl_2$ using the data for 1,1-dichloroacetone (707 [28]) gives the difference $707 - 472 = 235$, that is close to the ΔRI values for products no. 4. Thus, using the data for chlorination products of acetone only we can conclude that chlorination of any 2-alkanones leads to formation of 1-chloro- (no. 3) and 1,1-dichloro-2-alkanones (no. 4) together with other products. However, at this stage of data interpretation we have no sufficient information to reveal the structures of chlorination products nos. 2, 3, and 5.

Next step in the interpretation of chromatographic retention parameters at the absence of reference RI data is the literature search of raw retention time (t_R) values. These parameters possess no interlaboratory reproducibility, but they can be recalculated into RIs. Such data have been revealed for products of 2-butanone chlorination [39]. To provide recalculating the whole set of t_R values into RIs, the data for at least three compounds from this list should be selected as reference, which RI values should be known. Different modes of the recalculation (1–3) depend on the different selection of reference points. Results obtained are presented in Table 2 and are based on the selection of 2-butanone (RI = 578), 3,3-dichloro-2-butanone (RI = 741), and 1,3,3-trichloro-2-butanone (RI = 956) (mode 1). Mode 2 implies selecting the reference RI values for 3-chloro-2-butanone (RI = 704) instead of the data for non-chlorinated 2-butanone. Reference compounds for mode 3 are 3-chloro-2-butanone, 1,1-dichloro-2-butanone (RI = 820), and 1,3,3-trichloro-2-butanone. If the selection of these reference points was made correctly and the initial set of t_R values contains no errors, the results of RI evaluations by different modes should be close each other, as it is in Table 2. The RI values recalculated by this way permit us to identify components nos. 1, 2, and 5 (see set of data in Table 1) like 3-chloro- (no. 1), 3,3-dichloro- (no. 2), and 1,3-dichloroderivatives (no. 5) of 2-alkanones.

3.2. Mass spectrometric confirmation of the results of GC identification of chlorinated alkanones

Mentioned regularities in GC retention parameters of the chlorinated alkanones make it possible to restrict the number of reaction

Table 2
Recalculation of retention times of chloroderivatives of 2-butanone [39] into their retention indices on standard non-polar phases using three sets of reference compounds.

Compound	t_R, min	Mode 1	Mode 2	Mode 3	Averaged RI values	ΔRI
2-Butanone	1.95	**578**[a]				
3-Chloro-2-butanone	3.61	–	**704**	**704**	704	126
3,3-Dichloro-2-butanone	4.49	**741**	**741**	745	742	164
1-Chloro-2-butanone	4.72	757	753	758	756	178
1,1-Dichloro-2-butanone	5.72	825	814	**820**	820	242
1,3-Dichloro-2-butanone	6.52	881	872	876	876	298
1,3,3-Trichloro-2-butanone	7.59	**956**	**956**	**956**	956	378
1,1,3-Trichloro-2-butanone	7.59	956	956	956	956	378
1,1,3,3-Tetrachloro-2-butanone	8.35	1010	1020	1016	1015	437
1,1,1,3-Tetrachloro-2-butanone	8.54	1024	1037	1032	1031	453
1,3,3,4-Tetrachloro-2-butanone	9.31	1078	1105	1096	1093	615

[a] Experimental RI values selected as reference points are marked in bold.

Table 3
Mass spectra of chlorination products of some aliphatic ketones.

Alkanone (MW, RI)	Chlorination product (RI)	Mass spectrum: m/z (I_{rel})
4-Heptanone (114, 851)	3-Chloro-4-heptanone (977)	150(3), 148(10)M, 77(4) $[C_3H_6Cl]$, 71(100) $[C_3H_7CO]$, 55(7), 43(51), 41(18)
	3,3-Dichloro-4-heptanone (1047)	182(0.4)M, 113(2), 111(3) $[C_3H_5Cl_2]$, 104(2), 77(3), 75(7) $[C_3H_4Cl]$, 71(100) $[C_3H_7CO]$, 61(2), 55(2), 49(2), 43(50), 41(14)
	(R,S)- and (S,R)-3,5-dichloro-4-heptanone (1072)	186(1), 184(6), 182(9)M, 156(4), 154(5) $[M-C_2H_4]$, 107(12), 105(40) $[C_3H_6ClCO]$, 79(31), 77(100) $[C_3H_6Cl]$, 70(5), 55(11), 51(2), 49(3), 41(27)
	(R,R)- and (S,S)-3,5-dichloro-4-heptanone (1104)	186(1), 184(5), 182(8)M, 156(4), 154(6) $[M-C_2H_4]$, 107(12), 105(37) $[C_3H_6ClCO]$, 79(32), 77(100) $[C_3H_6Cl]$, 70(6), 55(11), 51(2), 49(3), 41(28)
	3,3,5-Trichloro-4-heptanone (1180)	220 (0.2), 218(0.8), 216(0.8)M, 113(16), 112(2), 111(26) $[C_3H_5Cl_2]$, 110(2), 107(16), 105(53) $[C_3H_6ClCO]$, 104(3), 103(3), 89(3), 83(2), 79(29), 77(100) $[C_3H_6Cl]$, 76(4), 75(27) $[C_3H_4Cl]$, 72(2), 70(8), 69(2), 63(2), 61(3), 55(5), 53(2), 51(3), 49(4), 41(21)
2-Nonanone (142, 1077)	3-Chloro-2-nonanone (1187)	178(1), 176(2)M, 97(2), 94(15), 92(43) $[M-C_6H_{12}]$, 84(2), 71(3), 69(3), 57(2), 55(15), 54(2), 43(100) $[CH_3CO]$, 41(10)
	3,3-Dichloro-2-nonanone (1258)	210(0)M, 128(2), 126(3) $[M-C_6H_{12}]$, 105(2), 95(2), 55(3), 53(2), 43(100) $[CH_3CO]$, 41(7)
	1-Chloro-2-nonanone (1279)	176(0.6)M, 128(5), 127(99) $[M-CH_2Cl]$, 109(10), 105(3), 94(4), 93(3), 92(15) $[M-C_6H_{12}]$, 85(2), 84(3), 83(3), 82(3), 81(2), 79(4), 77(11) $[ClCH_2CO]$, 71(3), 69(5), 67(5), 57(100) $[M-CH_2Cl-C_5H_{10}]$, 55(23), 53(4), 51(4), 49(9) $[CH_2Cl]$, 43(37), 41(28).
	1,1-Dichloro-2-nonanone (1326)	210(0)M, 128(6), 127(96) $[M-CHCl_2]$, 125(6), 109(11), 85(6), 83(11) $[CHCl_2]$, 77(2), 76(5), 71(2), 69(4), 67(4), 57(100) $[M-CHCl_2-C_5H_{10}]$, 55(22), 53(3), 43(34), 41(26).
	1,3-Dichloro-2-nonanone (1378)	212(0.4), 210(0.6)M, 161(4) $[M-CH_2Cl]$, 139(2), 133(3), 130(11), 128(65), 126(100) $[M-C_6H_{12}]$, 119(2), 107(5), 105(9), 98(4), 97(75) $[C_7H_{13}]$, 95(3), 94(2), 93(4), 92(5), 91(12), 85(6), 84(24), 83(3), 82(6), 81(3), 79(12), 77(34) $[ClCH_2CO]$, 75(2), 71(4), 70(3), 69(14), 67(5), 65(3), 63(2), 62(3), 57(16), 56(4), 55(73) $[C_4H_7]$, 53(6), 51(5), 49(10) $[CH_2Cl]$, 43(29), 42(4), 41(20)
	Unidentified component (1466)	163(6), 162(3), 161(19) $[C_7H_{14}ClCO]$, 160(2), 133(2), 125(3), 98(5), 97(100), 95(2), 93(4), 91(10) $[C_4H_8Cl]$, 89(2), 87(2), 85(9), 83(13), 81(2), 79(2), 78(2), 77(5), 76(7), 75(2), 71(6), 69(12), 67(3), 62(2), 57(19), 55(67), 53(5), 51(2), 48(2), 43(47), 41(21)
	1,3,3-Trichloro-2-nonanone (1479)	244(0.1)M, 166(3), 164(6), 162(19) $[M-C_6H_{12}]$, 156(8), 155(100), 141(2), 139(4), 137(5), 133(10), 131(24), 127(2), 119(2), 112(2), 111(2), 110(3), 109(2), 107(3), 105(8), 103(3), 99(2), 98(3), 97(5), 96(9), 95(98), 94(2), 93(6), 92(16), 91(6), 89(20), 87(2), 86(2), 85(26), 83(9), 82(3), 81(14), 79(28), 77(84) $[ClCH_2CO]$, 75(4), 74(4), 72(2), 71(51), 70(4), 69(35), 68(3), 67(11), 65(3), 63(3), 61(4), 58(2), 57(41), 55(44), 53(9), 51(9), 49(17) $[CH_2Cl]$, 43(85), 42(5), 41(43)
	1,1,3-Trichloro-2-nonanone (1582)	244(0)M, 189(3), 181(2), 168(2), 153(3), 135(6), 133(2), 131(2), 130(10), 129(4), 128(62), 126(100) $[M-C_6H_{11}Cl]$, 123(2), 121(3), 119(11), 113(3), 112(42), 111(2), 110(5), 107(7), 105(19), 98(2), 97(4), 95(4), 93(3), 92(2), 91(5), 85(2), 84(3), 83(26) $[CHCl_2]$, 81(7), 79(14), 77(35), 75(2), 71(25), 70(5), 69(46), 67(6), 57(27), 56(3), 55(31), 53(5), 51(4), 49(9), 43(25), 42(5), 41(22)
4-Dodecanone (184, 1367)	5-Chloro-4-dodecanone (1477)	220(2), 218(6)M, 162(2), 139(2), 122(6), 120(18) $[M-C_7H_{14}]$, 92(3), 71(100) $[C_3H_7CO]$, 69(4), 55(8), 53(2), 43(11), 41(2)
	3-Chloro-4-dodecanone (1493)	220(0.4), 218(1.2)M, 142(8), 141(100) $[C_8H_{17}CO]$, 123(5), 92(2), 81(6), 77(2), 71(20), 69(3), 67(3), 57(29), 55(10), 43(6), 41(6)
	5,5-Dichloro-4-dodecanone (1547)	252(0)M, 96(2), 89(2), 71(100) $[C_3H_7CO]$, 43(57)
	3,3-Dichloro-4-dodecanone (1563)	252(0)M, 142(7), 141(100) $[C_8H_{17}CO]$, 123(3), 118(2), 113(4), 111(4), 111(3), 104(2), 97(2), 85(2), 84(2), 83(5), 81(9), 77(3), 76(3), 75(7), 74(6), 72(2), 71(17), 70(30), 69(7), 67(4), 58(2), 57(21), 56(27), 55(21), 53(2), 49(2), 43(26), 42(5), 41(17)
	(R,S)- and (S,R)-3,5-dichloro-4-dodecanone (1576)	254(3), 252(4)M, 177(3), 175(10) $[M-C_3H_6Cl]$, 158(10), 157(4), 156(65), 154(100) $[M-C_7H_{14}]$, 147(2), 139(4), 133(3), 128(6), 126(10), 121(5), 120(2), 119(3), 112(3), 111(35), 107(17), 105(52) $[C_3H_6ClCO]$, 98(11), 97(2), 96(4), 95(3), 93(4), 91(8), 89(2), 83(5), 79(22), 78(2), 77(68) $[C_3H_6Cl]$, 75(3), 70(10), 69(88), 67(3), 65(2), 62(2), 57(19), 56(2), 55(46), 53(5), 43(13), 42(3), 41(27)
	(R,R)- and (S,S)-3,5-dichloro-4-dodecanone (1600)	254(2), 252(4)M, 177(3), 175(10) $[M-C_3H_6Cl]$, 158(10), 157(4), 156(64), 155(2), 154(100) $[M-C_7H_{14}]$, 147(2), 139(4), 133(3), 128(6), 126(9), 121(5), 119(3), 112(2), 111(37), 107(17), 106(2), 105(53) $[C_3H_6ClCO]$, 98(10), 97(2), 96(4), 95(2), 93(4), 91(8), 89(2), 83(4), 79(22), 78(2), 77(66) $[C_3H_6Cl]$, 75(2), 70(9), 69(82), 67(3), 65(2), 62(2), 57(21), 55(43), 53(5), 43(9), 42(3), 41(24)
	3,5,5-Trichloro-4-dodecanone (1687)	286(0.1)M, 192(2), 190(5), 188(5) $[M-C_7H_{14}]$, 175(5), 113(2), 111(9), 109(13), 107(31), 106(2), 105(100) $[C_3H_6ClCO]$, 103(6), 98(2), 97(3), 96(2), 93(2), 91(5), 89(3), 88(4), 83(4), 81(3), 79(31), 77(96), 75(6), 71(11), 70(9), 69(33), 67(7), 63(2), 61(3), 57(17), 55(21), 54(3), 53(4), 43(15), 42(7), 41(27)
	3,3,5-Trichloro-4-dodecanone (1689)	286(0)M, 177(6), 175(16) $[M-C_3H_5Cl_2]$, 153(2), 147(2), 113(3), 112(5), 111(43), 109(2), 107(6), 105(21), 104(4), 103(2), 98(4), 97(2), 93(3), 91(6), 89(2), 85(3), 83(4), 81(3), 75(19), 71(11), 69(100), 67(4), 57(40), 56(16), 55(37), 53(5), 43(38), 41(23)

mixtures which require a detailed interpretation of mass spectrometric data. Thus, in our case, GC–MS analysis was carried out for the chlorinated products of 4-heptanone, 2-nonanone, and 4-dodecanone only. Mass spectra of chlorination products of these alkanones ($m/z \geq 41$, $I_{rel} \geq 2\%$, the signals of molecular ions are indicated even at less intensities) were recorded for components of reaction mixtures and presented in Table 3 in the order of their chromatographic elution. For each of them the chemical name, molecular weight of initial ketone (MW), retention index (RI), and interpretation of most characteristic signals are indicated.

Standard mass spectra of most chlorinated alkanones excluding acetone derivatives remain to be unknown up to present [3]. Hence, they can be interpreted using general rules of fragmentation of organic compounds under electron impact [40]. Some of the chlorinated alkylketones indicate signals of molecular ions of very low ($I_{rel} \sim 0.1\%$) or zero intensity, but the lack of this information is exhaustively compensated by revealing of isotopic patterns and easily interpreted signals of ions $[C_nH_{2n+1}CO]^+ \rightarrow [C_nH_{2n+1}]^+$, $[ClC_mH_{2m}CO]^+ \rightarrow [ClC_mH_{2m}]^+$, $[C_kH_{2k-1}Cl_2]^+$, $[M-C_nH_{2n}]^+$ (McLafferty rearrangement), and so on. Thus, the results of the

Table 4

Increments of GC retention indices on standard non-polar stationary phases for chlorine atom(s) in α-positions relative to carbonyl group in chlorinated derivatives of aliphatic ketones.

| Path of chlorination	Position(s) of chlorine atom(s)	ΔRI
2-Alkanones		
$RCOCH_3 \rightarrow RCOCH_2Cl$	1-Cl	197 ± 9
$RCOCH_3 \rightarrow RCOCHCl_2$	$1,1-Cl_2$	241 ± 13
$RCH_2COCH_3 \rightarrow RCHClCOCH_2Cl$	$1,3-Cl_2$	300 ± 6
$RCH_2COCH_3 \rightarrow RCCl_2COCH_2Cl$	$1,3,3-Cl_3$	386 ± 9
$RCH_2COCH_3 \rightarrow RCHClCOCHCl_2$	$1,1,3-Cl_3$	396 ± 5
$RCH_2COCH_3 \rightarrow RCCl_2COCHCl_2$	$1,1,3,3-Cl_4$	431 ± 10
k-Alkanones ($k > 2$)		
$RCH_2COCH_2R' \rightarrow RCH_2COCHClR'$	α-Cl	117 ± 8
$RCH_2COCHR'R'' \rightarrow RCH_2COCClR'R''$	α-Cl[a]	90 ± 7
$RCH_2COCH_2R' \rightarrow RCH_2COCCl_2R'$	$\alpha,\alpha-Cl_2$	174 ± 15
$RCH_2COCH_2R' \rightarrow$ (R,S and S,R)-RCHClCOCHClR'	$\alpha,\alpha'-Cl_2$	203 ± 11
$RCH_2COCH_2R' \rightarrow$ (R,R and S,S)-RCHClCOCHClR'	$\alpha,\alpha'-Cl_2$	234 ± 12
$RCH_2COCH_2R' \rightarrow RCHClCOCCl_2R'$	$\alpha,\alpha,\alpha'-Cl_3$	306 ± 15

[a] Chlorine is located at tertiary carbon atom.

interpretation of mass spectra do not contradict with interpretation of GC RIs in all cases. Finally, the joint statistical processing of the whole set of ΔRI increments for every type of the chlorination products gives their reliable average values, presented in Table 4. This set of increments permits us both to predict the retention indices of chlorination products for other carbonyl compounds, and to identify them in the reaction mixtures. The obligatory conditions for application of this identification algorithm are to carry out GC analysis using standard non-polar polydimethylsiloxane stationary phases and to know RI values for initial carbonyl compounds. Both these conditions seem to be easily fulfilled in analytical practice.

3.3. The features of RI increments for chlorinated alkanones

The content in Table 4 merits additional comments. At first, a small chemometrics remark should be done. It is easy to evaluate that the average RI difference between neighbor GC peaks of chlorinated derivatives of aliphatic ketones is 45 ± 23 i.u. (index units), while average standard deviation of all the ΔRI increments is only 10 ± 4 i.u. Thus, unambiguous GC identification of the chlorination products using additive evaluations is possible in all cases.

Secondly, an important structural feature of chlorinated compounds formed in the reaction should be taken into account. The use of selective chlorination agent (sulfuryl chloride) explains us the primary formation of α-monochloroderivatives. Next step of chlorination leads to the formation of α,α-dichloro- and α,α'-dichloroderivatives. In the case of k-alkanones ($k > 2$) the molecules of α,α'-dichloroderivatives contain two asymmetric carbon atoms, so that they are formed as the racemic mixture of two diastereomers; each of them is a pair of enantiomers, i.e. α-(S),α'-(R) + α-(R),α'-(S) and α-(S),α'-(S) + α-(R),α'-(R):
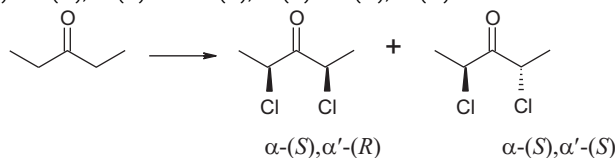
If the reaction of chlorination is not stereoselective (like it is in our case), such diastereomers form in a ratio close to 1:1, but usually possess a different retention parameters and practically identical mass spectra. The presence of diastereomers we can expect among the chlorination products of 3-pentanone, 3-hexanone, 3-heptanone, 4-heptanone, 5-methyl-3-hexanone, 3-nonanone, 5-nonanone, 6-undecanone, and 4-dodecanone. The data of Table 3 confirm the presence of the products with identical mass spectra for 4-heptanone and 4-dodecanone. In other reaction mixtures such pairs of diastereomers can be easily revealed using the criterion

of close intensities of their chromatographic peaks. Obviously, 2-alkanones cannot form diastereomeric products of α-chlorination.

It is noteworthy that α,α'-dichloroderivatives of aliphatic k-alkanones ($k > 2$) are characterized by highly large RI differences between diastereomers. Their values vary from 24 (4-dodecanone) up to 43 (3-pentanone); the average value of these differences is 32 ± 6 i.u.

The evaluation of chromatographic elution order of diastereomers is coupled with the structural assignment of every chromatographic peak, a still remaining problem. If their isolation as individual compounds is unreliable, the obviously available way is to indicate "isomer no. 1", "isomer no. 2" (usually in the order of their elution) without attribution of the chemical structures for them. A solution of this problem seems to be possible by calculating the total intramolecular energies (vibration and rotational) by molecular dynamics simulations obtained with HyperChem software; the algorithm is proposed and discussed in [36]. This approach is applicable to both structural isomers and diastereomers. Those isomers with higher intramolecular energies (E) usually eluted earlier than isomers with less intramolecular energies. This regularity was established first empirically by correlation E vs. RI values, but its sense can be explained by following hypothesis. Retention of analytes on non-polar phases depends in most extent on dispersion (Van der Waals) energies; for isomers of the same homologous series they are almost equal to one another. However, resulting interaction of sorbates with stationary phase is less for isomers having higher intramolecular energies. The same regularity is observed for boiling points of isomers.

This modeling for stereoisomeric α,α'-dichloroderivatives of k-alkanones ($k > 2$) indicates that ΔE values for diastereomers α-(S),α'-(R) slightly exceed ΔE values for diastereomers α-(S),α'-(S), that can be illustrated on the example of diastereomeric 3,5-dichloro-4-heptanones:

	(3S,5R)	(3S,5S)
E_0, kcal/mol	4.9	5.8
E_{din}, kcal/mol	45.0	45.2
ΔE	40.1 > 39.4	

Here E_0 is a static contribution on intramolecular energy, evaluated by methods of molecular mechanics, E_{din} is a total inner-molecular energy (result of modeling), and $\Delta E = E_{din} - E_0$ – the dynamics contribution of intramolecular energy.

The third remark about ΔRI increments presented in Table 4 is their dependence on the branching of carbon skeleton at the atoms where the substitution H → Cl takes place. Namely, if the value of

Table 5
Results of GC identification of aliphatic ketones chlorination products and their chromatographic parameters.

Parent carbonyl compound (molecular mass; reference RI value)	RI of reaction product	ΔRI	Identification
Acetone (58; 472 ± 12)	677 ± 6	205	1-Chloro-2-propanone
	714 ± 2	242	**1,1-Dichloro-2-propanone**[a]
	870 ± 5	398	1,3-Dichloro-2-propanone
2-Butanone (72; 578 ± 12)	**704 ± 3**	126	**3-Chloro-2-butanone (704)**[b]
	741 ± 3	163	3,3-Dichloro-2-butanone (742)
	820 ± 2	242	1,1-Dichloro-2-butanone (820)
	881 ± 2	303	**1,3-Dichloro-2-butanone (876)**
	956 ± 3	378	1,3,3-Trichloro-2-butanone (956)
	971 ± 3	393	1,1,3-Trichloro-2-butanone (956)
2-Pentanone (86; 670 ± 8)	**795 ± 2**	125	**3-Chloro-2-pentanone**
	857 ± 2	187	3,3-Dichloro-2-pentanone
	867 ± 4	197	1-Chloro-2-pentanone
	918 ± 2	248	1,1-Dichloro-2-pentanone
	978 ± 2	308	**1,3-Dichloro-2-pentanone**
3-Methyl-2-butanone (86; 641 ± 11)	**725 ± 4**	84	**3-Chloro-3-methyl-2-butanone**
	820 ± 2	179	1-Chloro-3-methyl-2-butanone
	866 ± 4	225	1,1-Dichloro-3-methyl-2-butanone
	932 ± 3	291	**1,3-Dichloro-3-methyl-2-butanone**
2-Hexanone (100; 768 ± 9)	**884 ± 4**	116	**3-Chloro-2-hexanone**
	929 ± 3	161	Not identified
	943 ± 3	175	3,3-Dichloro-2-hexanone
	968 ± 2	200	1-Chloro-2-hexanone
	1018 ± 2	250	1,1-Dichloro-2-hexanone
	1070 ± 3	302	**1,3-Dichloro-2-hexanone**
	1104 ± 2	336	1,3,3-Trichloro-2-hexanone
	1110 ± 4	342	1,1,3-Trichloro-2-hexanone
	1187 ± 2	419	1,1,3,3-Tetrachloro-2-hexanone
	1326 ± 2	558	Not identified ($n_{Cl} \geq 4$)
4-Methyl-2-pentanone (100; 753 ± 2)	**850 ± 3**	97	**3-Chloro-4-methyl-2-pentanone**
	907 ± 3	154	3,3-Dichloro-4-methyl-2-pentanone
	942 ± 2	189	1-Chloro-4-methyl-2-pentanone
	966 ± 2	213	1,1-Dichloro-4-methyl-2-pentanone
	1047 ± 3	294	**1,3-Dichloro-4-methyl-2-pentanone**
	1134 ± 2	381	1,3,3-Trichloro-4-methyl-2-pentanone
3,3-Dimethyl-2-butanone (100; 705 ± 13)	904 ± 4	199	4-Chloro-3,3-dimethyl-2-butanone
	915 ± 3	210	**1-Chloro-3,3-dimethyl-2-butanone**
	983 ± 2	278	**1,4-Dichloro-3,3-dimethyl-2-butanone**
3-Hexanone (100; 771 ± 7)	**888 ± 3**	117	4-Chloro-3-hexanone
	892 ± 3	121	2-Chloro-3-hexanone
	935 ± 2	164	4,4-Dichloro-3-hexanone
	957 ± 2	186	2,2-Dichloro-3-hexanone
	976 ± 3	205	**(R,S)- and (S,R)-2,4-dichloro-3-hexanone**
	1011 ± 3	240	**(R,R)- and (S,S)-2,4-dichloro-3-hexanone**
	1080 ± 4	309	2,4,4-Trichloro-3-hexanone and 2,2,4-trichloro-3-hexanone
2-Methyl-3-pentanone (100; 737 ± 9)	**828 ± 3**	91	**2-Chloro-2-methyl-3-pentanone**
	847 ± 2	110	4-Chloro-2-methyl-3-pentanone
	870 ± 2	133	Not identified
	886 ± 2	149	4,4-Dichloro-2-methyl-3-pentanone
	942 ± 2	205	**2,4-Dichloro-2-methyl-3-pentanone**
	1014 ± 3	277	2,4,4-Trichloro-2-methyl-3-pentanone
2-Heptanone (114; 869 ± 4)	**987 ± 2**	118	**3-Chloro-2-heptanone**
	1040 ± 2	171	3,3-Dichloro-2-heptanone
	1053 ± 2	184	Not identified
	1072 ± 2	203	1-Chloro-2-heptanone
	1120 ± 2	251	1,1-Dichloro-2-heptanone
	1172 ± 2	303	1,3-Dichloro-2-heptanone
	1262 ± 3	393	1,3,3-Trichloro-2-heptanone
3-Heptanone (114; 871 ± 8)	982 ± 2	111	4-Chloro-3-heptanone
	988 ± 3	117	2-Chloro-3-heptanone
	1032 ± 3	161	4,4-Dichloro-3-heptanone
	1042 ± 4	171	2,2-Dichloro-3-heptanone
	1068 ± 3	197	**(R,S)- and (S,R)-2,4-dichloro-3-heptanone**
	1102 ± 2	231	**(R,R)- and (S,S)-2,4-dichloro-3-heptanone**
	1165 ± 3	294	2,4,4-Trichloro-3-heptanone and 2,2,4-trichloro-3-heptanone
4-Heptanone[c] (114; 851 ± 4)	**977 ± 2**	126	**3-Chloro-4-heptanone**
	1047 ± 2	196	3,3-Dichloro-4-heptanone
	1072 ± 2	221	**(R,S)- and (S,R)-3,5-dichloro-4-heptanone**
	1104 ± 2	253	**(R,R)- and (S,S)-3,5-dichloro-4-heptanone**
	1180 ± 2	329	3,3,5-Trichloro-4-heptanone
4-Methyl-2-hexanone (114; 828 ± 7)	**940 ± 2**	112	**3-Chloro-4-methyl-2-hexanone**
	1014 ± 2	186	3,3-Dichloro-4-methyl-2-hexanone
	1031 ± 5	203	1-Chloro-4-methyl-2-hexanone
	1080 ± 4	252	1,1-Dichloro-4-methyl-2-hexanone
	1120 ± 2	292	**1,3-Dichloro-4methyl-2-hexanone**

Table 5 (*Continued*)

Parent carbonyl compound (molecular mass; reference RI value)	RI of reaction product	ΔRI	Identification
2-Octanone (128; 978 ± 3)	**1090 ± 2**	112	**3-Chloro-2-octanone**
	1155 ± 2	177	3,3-Dichloro-2-octanone
	1167 ± 2	189	1-Chloro-2-octanone
	1222 ± 2	244	1,1-Dichloro-2-octanone
	1274 ± 3	296	**1,3-Dichloro-2-octanone**
	1358 ± 5	380	1,3,3-Trichloro-2-octanone
5-Methyl-3-heptanone (128; 931 ± 3)	1022 ± 3	91	5-Chloro-5-methyl-3-heptanone
	1047 ± 2	116	**4-Chloro-5-methyl-3-heptanone**
	1063 ± 3	132	**2-Chloro-5-methyl-3-heptanone**
	1101 ± 3	170	4,4-Dichloro-5-methyl-3-heptanone and 2,2-dichloro-5-methyl-3-heptanone
	1150 ± 2	219	**(R,S)- and (S,R)-2,4-dichloro-5-methyl-3-heptanone**
	1180 ± 3	249	**(R,R)- and (S,S)-2,4-dichloro-5-methyl-3-heptanone**
2-Nonanone[c] (142; 1077 ± 11)	**1186 ± 2**	109	**3-Chloro-2-nonanone**
	1256 ± 3	179	3,3-Dichloro-2-nonanone
	1268 ± 2	191	1-Chloro-2-nonanone
	1276 ± 3	199	Not identified
	1326 ± 2	249	1,1-Dichloro-2-nonanone
	1378 ± 2	301	**1,3-Dichloro-2-nonanone**
	1464 ± 2	387	1,3,3-Trichloro-2-nonanone
	1477 ± 3	400	1,1,3-Trichloro-2-nonanone
	1582 ± 3	505	Not identified ($n_{Cl} \geq 4$)
	1780 ± 3	703	Not identified ($n_{Cl} \geq 4$)
3-Nonanone (142; 1082 ± 4)	**1184 ± 2**	102	**4-Chloro-3-nonanone**
	1192 ± 2	110	**2-Chloro-3-nonanone**
	1239 ± 2	157	4,4-Dichloro-3-nonanone
	1250 ± 2	168	2,2-Dichloro-2-nonanone
	1272 ± 2	190	**(R,S)- and (S,R)-2,4-dichloro-3-nonanone**
	1308 ± 6	226	**(R,R)- and (S,S)-2,4-dichloro-3-nonanone**
	1368 ± 2	286	2,4,4-Trichloro-3-nonanone and 2,2,4-trichloro-3-nonanone
5-Nonanone (142; 1060 ± 8)	**1171 ± 2**	111	**4-Chloro-5-nonanone**
	1244 ± 2	184	4,4-Dichloro-5-nonanone
	1256 ± 2	196	**(R,S)- and (S,R)-4,6-dichloro-5-nonanone**
	1283 ± 2	223	**(R,R)- and (S,S)-4,6-dichloro-5-nonanone**
	1359 ± 2	299	4,4,6-Trichloro-5-nonanone
6-Undecanone (170; 1261 ± 4)	**1370 ± 2**	109	**5-Chloro-6-undecanone**
	1440 ± 2	179	5,5-Dichloro-6-undecanone
	1460 ± 2	199	**(R,S)- and (S,R)-5,7-dichloro-6-undecanone**
	1484 ± 2	223	**(R,R)- and (S,S)-5,7-dichloro-6-undecanone**
	1564 ± 2	303	5,5,7-Trichloro-6-undecanone
2-Dodecanone (184; 1379 ± 5)	**1504 ± 3**	125	**3-Chloro-2-dodecanone**
	1584 ± 2	205	3,3-Dichloro-2-dodecanone
	1614 ± 2	235	1-Chloro-2-dodecanone
	1623 ± 2	244	1,1-Dichloro-2-dodecanone
	1640 ± 2	261	Not identified
	1688 ± 3	309	**1,3-Dichloro-2-dodecanone**
	1816 ± 3	437	1,1,3,3-Tetrachloro-2-dodecanone
4-Dodecanone[c] (184; 1367 ± 2)	**1477 ± 2**	110	**5-Chloro-4-dodecanone**
	1493 ± 2	126	**3-Chloro-4-dodecanone**
	1547 ± 2	180	5,5-Dichloro-4-dodecanone
	1563 ± 3	196	3,3-Dichloro-4-dodecanone
	1576 ± 2	209	**(R,S)- and (S,R)-3,5-dichloro-4-dodecanone**
	1600 ± 3	233	**(R,R)- and (S,S)-3,5-dichloro-4-dodecanone**
	1687 ± 2	320	3,5,5-Trichloro-4-dodecanone
	1689 ± 2	322	3,3,5-Trichloro-4-dodecanone
	1973 ± 3	606	Not identified ($n_{Cl} \geq 4$)
Cyclohexanone[d] (98; 864 ± 5)	**1026 ± 2**	162	**2-Chlorocyclohexanone**
	1147 ± 3	283	2,2-Dichlorocyclohexanone
	1206 ± 2	342	2,6-Dichlorocyclohexanone
	1337 ± 5	473	2,2,6-Trichlorocyclohexanone

[a] The data for principal reaction products are marked in bold.
[b] Precalculated RI values for chlorination products of 2-butanone (see Table 1) are indicated in parentheses.
[c] For these compounds GC identification of products was confirmed by results of GC–MS identification.
[d] The single example of cyclic ketone (cyclohexanone) is presented for comparison.

ΔRI increment for methyl group of 2-alkanones, $COCH_3 \rightarrow COCH_2Cl$ (substitution at the primary carbon atom), is 197 ± 9. The RI increment for a methylene group of *k*-alkanones (*k* > 2), $RCH_2COCH_2R' \rightarrow RCH_2COCHClR'$ (substitution at the secondary carbon atom), is clearly smaller, at 117 ± 8. If the molecule of carbonyl compounds contains the branching of carbon skeleton at α-position to carbonyl group like $RCH_2COCHR'R'' \rightarrow RCH_2COCClR'R''$ (substitution at the tertiary carbon atom), the value of corresponding

increment becomes less again (90 ± 7). This feature of additive schemes explains to us the need to use 12 different values of increments (all of them are listed in Table 4), namely six for 2-alkanones and six for *k*-alkanones (*k* > 2).

The values of ΔRI increments determined for the substitution H → Cl in α-positions of aliphatic ketones are typical for compounds of this class only and cannot be used for substrates of other chemical origin. In accordance with data from

Table 6
Prediction of retention indices for 3-pentanone (compound not included into the training set of data) using the additive scheme discussed.

Chlorination product	RI_{calcd}	$RI_{experim}$	Difference ($RI_{calcd} - RI_{experim}$)
2-Chloro-3-pentanone	796 ± 13	802 ± 2	-6
2,2-Dichloro-3-pentanone	853 ± 18	834 ± 12	19
(R,S)- and (S,R)-2,4-dichloro-3-pentanone	882 ± 15	872 ± 3	10
(R,R)- and (S,S)-2,4-dichloro-3-pentanone	913 ± 16	915 ± 3	-2
2,2,4-Trichloro-3-pentanone	985 ± 18	972 ± 3	13
Average RI difference			± 10

Table 7
Restrictions in RI evaluations for chlorination products of branched aliphatic ketones (on the example of 2,6-dimethyl-4-heptanone).

Chlorination product	$RI_{experim}$	RI_{calcd}	Difference ($RI_{calcd} - RI_{experim}$)
3-Chloro-2,6-dimethyl-4-heptanone	1096 ± 2	1071 ± 9	25
3,3-Dichloro-2,6-dimethyl-4-heptanone	1180 ± 3	1128 ± 15	52
(R,S)- and (S,R)-3,5-dichloro-2,6-dimethyl-4-heptanone	1204 ± 2	1157 ± 11	47
(R,R)- and (S,S)-3,5-dichloro-2,6-dimethyl-4-heptanone	1240 ± 2	1188 ± 12	52
3,3,5-Trichloro-2,6-dimethyl-4-heptanone	1334 ± 3	1260 ± 15	74

[41] the values $\Delta RI\,(H \to Cl)$ for hydrocarbons are 228 ± 14 (at primary carbon atoms, compare with 197 ± 9 for alkanones), 182 ± 22 (at secondary carbon atoms, compare with 117 ± 8), and 175 ± 10 (at tertiary carbon atoms, compare with 90 ± 7), i.e. significantly more. Analogously, the values of ΔRI increments for acyclic ketones cannot be used for cyclic ketones like it is illustrated by the example of cyclohexanone (see Table 5 below). On the other hand, if necessary, ΔRI values presented in Table 4 can be "expanded" onto chlorination products of acyclic alkyl aryl ketones. Namely, the value $\Delta RI\,(H \to Cl)$ for 2-chloroacetophenone $C_6H_5COCH_2Cl$ is $(1237 \pm 8) - (1041 \pm 9) = 196$ agrees well to the value for 2-alkanones, 197 ± 9, for 2,2-dichloroacetophenone $C_6H_5COCHCl_2$ it is $(1295 \pm 6) - (1041 \pm 9) = 254$ (compare with close value 241 ± 13), and for 2-chloropropiophenone $C_6H_5COCHClCH_3$ it is $(1271 \pm 3) - (1144 \pm 15) = 127$ (close to 117 ± 8).

Table 5 includes the results of identification of the chlorination products of 21 aliphatic ketones treated with sulfuryl chloride. The data for cyclohexanone are included in the last line for the comparison. All carbonyl compounds are listed in the order of increasing of their molecular weights; RI values are indicated for each of them. Some reaction products with higher ΔRIs remain unidentified. They contain more than four chlorine atoms in the molecule which can be located not only at $\alpha-$, but at a more remote positions from carbonyl group as result of the radical chlorination process. The discussed version of additive scheme includes no data for the identification of such products, but its further development is possible. Another part of unidentified components (small chromatographic peaks) can be explained by presenting of the impurities in the initial carbonyl compounds.

The approach proposed allows the prediction of RI values for chlorination products of various carbonyl compounds not included in Table 5 yet. For instance, in the case of 3-pentanone (diethyl ketone, reference RI value is 697 ± 10) the results of comparing the RI evaluations for principal components of reaction mixture with experimental data are presented in Table 6. In this table the values RI_{calcd} are calculated by summarizing RI of diethyl ketone with ΔRI increments in Table 4; $RI_{experim}$ are measured experimentally at the same conditions as those for all other compounds.

The average RI difference between additive evaluations and experimental values is ± 10 i.u., which is comparable with contemporary interlaboratory RI reproducibility on standard non-polar phases. At the same time, additive schemes as any other methods of RI evaluations are characterized by some restrictions which should be taken into account.

3.4. Restriction of additive RI evaluations for chlorinated carbonyl compounds

The ΔRI increments presented in Table 4 characterize the replacements $H \to Cl$ in α-positions of molecules of aliphatic ketones having no branchings of carbon skeleton in β-positions relative to carbonyl group. The presence of such branchings is the structural feature which influences remarkably on RIs of chlorination products due to steric hindrance between different groups located in vicinal positions one relative to others:
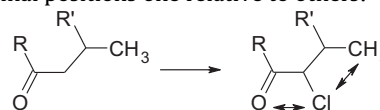
These steric interactions restrict the intramolecular rotations and vibrations that decrease the intramolecular energies (can be confirmed molecular dynamics modeling using HyperChem software); the consequence of that is increasing both boiling points of such isomers and their GC retention indices [36].

This feature should be specially illustrated on the example of 2,6-dimethyl-4-heptanone (diisobutyl ketone, RI 953 ± 2). The reaction mixture of its chlorination contains five principal products which can be identified by analogy with other samples using the order of their elution, which remains the same in all cases under consideration. However, the ΔRI values for these products exceed strongly the values presented in Table 4. The values RI_{calcd} are calculated by summarizing RI of diisobutyl ketone with ΔRI increments in Table 4; $RI_{experim}$ are measured experimentally. The differences $RI_{calcd} - RI_{experim}$ are 25 i.u. for mono-chlorinated product, 47–52 i.u. for bis-chlorinated products, and 75 i.u. for tris-chloro derivative, i.e. they depend approximately additively on the number of chlorine atoms in the molecules (deviations are about $\sim 25 \times n_{Cl}$). It means the inapplicability of evaluation presented in Table 4 to an additionally branched carbonyl compounds, or the necessity to use extra RI increments, like it is illustrated in Table 7.

The large number of such additional increments depending on the presence of different structural fragments in a molecule of organic compounds is the known feature of various additives schemes used in chemistry. Very often this fact is classified as a restriction of such approach, so that such unnecessary complicated additive schemes are not recommended for practical using.

4. Conclusion

The results discussed in this paper suggest that the simplest additive schemes in their different modifications should

be recognized as a useful approach in the interpretation of gas chromatographic retention indices. One of the most important examples of their application is the identification of products of chemical reactions. It is just the reason to apply the additive scheme for evaluation of retention indices of chlorinated aliphatic ketones and identification of these compounds without their isolation from reaction mixtures.

It is shown that chlorination of the aliphatic carbonyl compounds with sulfuryl chloride occurs preferably in α-positions to the carbonyl group. It leads to the formation of α-mono-, α,α-di-, two diastereomeric α,α'-di-, tri-, and, sometimes, tetra-chloroderivatives. In all cases the mode of calculation includes the summation of retention indices of initial carbonyl compounds with preliminary determined set of increments.

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