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IDENTIFICATION OF ORGANIC REACTION PRODUCTS IN THE ABSENCE OF ADDITIVITY OF CHROMATOGRAPHIC RETENTION INDICES. CHLORO DERIVATIVES OF METHYL-*tert*-BUTYL KETONE

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As a result of a joint interpretation of mass spectra and gas chromatographic retention indices more than ten products of free radical chlorination of methyl-*tert*-butyl ketone are identified. They contain from one to six chlorine atoms in the molecule and were not previously characterized either by mass spectrometric or chromatographic reference data. It is found that retention index increments corresponding to a gradual increase in the number of chlorine atoms in the molecule per unit are non-additive and vary in wide ranges (from 53 i.u. to 219 i.u.), which does not hinder the use of separate elements of additive schemes for the estimation of the indices of products of such non-regioselective reactions.

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One of the most important conditions for increasing the efficiency of chromato-mass-spectrometric identification of traces of organic compounds in complex mixtures without their preparative separation is the extension and improvement of information support of this method. Thus, the latest version (2011) of the database of the National Institute of Standards and Technology (NIST, US) [1] contains 243,893 mass spectra of 212,961 compounds. Starting from 2005, this database was supplemented with chromatographic retention indices (RIs), whose number reached 346,757 for 70,835 compounds in version 2011. A combination of simultaneously determined different analytic parameters improves the uniqueness of identification results and increases the number of correct answers, substantially decreasing the number of both first and second order errors.

However, the creation of all-embracing databases containing information on all theoretically possible organic compounds is principally impossible. Therefore, another not less important requirement to the improvement of interpretation algorithms for chromato-mass-spectrometric data is their application for the identification of such compounds that have not been characterized either by mass-spectra or RIs by the time of analysis. A solution of these problems is based on the use of the most general rules for the interpretation of mass spectra and the obligatory comparison of experimental RIs of analytes with theoretical estimations of these parameters. Due to a combination of simplicity and sufficient accuracy, various types of additive schemes seem to be one of the most preferred out of numerous methods of RI estimation [2].

The most detailed variant of additive schemes (I) implies the summation of increments ΔRI_i of separate atoms or

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structural fragments, which is based on atomic, group or bond increments [3], by analogy with the known methods of calculating molar refractions, i.e.

$$RI = \sum \Delta RI_i. \quad (1)$$

Limitations of this approach consist in the necessity of a preliminary calculation of a large number of increments and difficulties of taking into account steric factors affecting RI values. Nonetheless, the latter variant of such additive schemes was proposed in 2007 [4] and used for the estimation of RIs in the database [1].

The most popular is variant (II) based on the use of RI increments of separate structural fragments (functional groups). If the RI value of some basic compound AX is known and it is required to estimate the RI value of a structurally related compound AY, then the structure transformation increment $\Delta RI(X \rightarrow Y)$ is applied[5]

$$RI(AY) = RI(AX) + \Delta RI(X \rightarrow Y). \quad (2)$$

Another way to write down this relation involves the summation of RI of some basic (unsubstituted) compound RI_0 with increments of functional groups Y, which is equivalent to the substitution $H \rightarrow Y$

$$RI(BY) = RI_0 + \Delta RI(Y). \quad (3)$$

From the latest examples illustrating the possibilities of this approach it is possible to note the derivation of RI estimates for chloro derivatives of carbonyl compounds [6, 7] and ethers [8] ($H \rightarrow Cl$ substitution at different sites of molecules). In principle, it is possible to propose scheme (2) that is equivalent to the synthesis scheme of complex compounds from simpler ones and to assign the meaning increments of RI variation in different chemical reactions to $\Delta RI(X \rightarrow Y)$ increments [9]. Limitations of this approach are also related to the effect of steric factors, whose taking into account may lead to inefficient detailing of a system of increments.

Relatively recently [10] a variant of additive schemes (III) has been proposed, which excluded the necessity of a preliminary calculation of increments. The structure of any organic compound can be assembled from the structures of simpler analogues by virtue of formal addition and subtraction operations, such an assembling being performed in several ways. The scheme of calculating chromatographic RIs of complex molecules from simpler ones immediately follows the selected ways of assembling molecular structures, i.e. if

$$ABCD = ABC + BCD - BC,$$

then

$$RI(ABCD) = RI(ABC) + RI(BCD) - RI(BC). \quad (4)$$

The efficiency of this approach was exemplified by the identification of 839 congeners of polychlorinated hydroxybiphenyls [10], isomeric alkylbenzenes [11, 12], 211 isomeric 4-nonylphenols [13], cyclohexane chlorination products [14, 15], condensation of carbonyl compounds [16, 17], and so on. In order to exclude possible contradictions of schemes of type (3) a special system of linear coding of the structural features of organic molecules affecting their chromatographic retention parameters was proposed [18]. Method (III) implies the availability of reference RIs of the selected precursors; here it is necessary to avoid multistage assembling schemes because this causes a decrease in the reliability of estimates obtained.

Apart from the above mentioned there is a variant of converted additive schemes (IV), which is the most efficient especially in a joint interpretation of chromato-mass-spectrometric data. In this case, RIs of complex analytes are used to estimate RIs of simpler compounds presented in detail in databases [19, 20]. If in a molecule (*U–K*) it becomes possible to reveal (suppose) from the mass spectrum the presence of a structural fragment (*K*), then hypothetically it can be substituted by a simpler fragment (***S***). This leads to analogs of unknown analytes with molecular masses smaller by a value $\Delta M = M(UK) - M(US)$. If these transformations are characterized by the corresponding increments of gas chromatographic retention indices (ΔRI), then it is possible to estimate RIs of structural analogs $RI(US) \approx RI(UK) - \Delta RI$. Hence, we obtain an additional possibility to identify simpler analogs of initial analytes, which significantly increases the probability of getting correct answers. The capabilities of such an approach are illustrated by the identification of strongly branched compounds containing *tert*-butyl groups ($(CH_3)_3C \rightarrow CH_3$ transformation) [21], destruction products of VX chemical warfare [22, 23], and so on.

The main condition of the application of all mentioned variants of additive schemes is the permanence of ΔRI values within some groups of organic compounds. In all cases, the definition of applicability domains of additive relations needs special verification because such combinations of homologs or congeners not always can be theoretically predicted. In the general case, especially in groups of congeners, only some additivity elements are held (for limited subgroups of compounds), whereas the general rule is its absence. Consequently, one of the relevant problems in the development of the concept of additive estimations of RI should be considered to be the determination of ways of its application in complex cases.

The aim of this work is to consider the possible application of additive estimations of RI by the example of chromato-mass-spectrometric identification of 3,3-dimethylbutane-2-one (methyl-*tert*-butyl ketone, pinacolone, MTBK) chlorination products.

EXPERIMENTAL

Ionic chlorination of methyl-*tert*-butyl ketone by sulfuryl chloride was performed by the general chlorination procedure for aliphatic ketones [6, 7]. Into a 10-ml tube 0.15 g of MTBK (1.5 mmol) (Fluka, Switzerland, main substance content not less than 99%) was placed and 2.7 ml of dry CCl_4, 0.27 g of sulfuryl chloride (2 mmol; Fluka) was added dropwise; a molar excess of sulfuryl chloride was 1.3:1 and the reaction mixture was kept at room temperature for 10-12 h with periodic stirring. It was successively washed two times with 1 ml of water, 1 ml of 5% aqueous solution of sodium bicarbonate, 1 ml of water (twice) and dried by calcined sodium sulfate (0.2 g). The choice of this reagent for the chlorination of alkanones was determined by reaction regioselctivity: in accordance with the literature data [24-26], by the ionic mechanism only hydrogen atoms at α-positions relative to the carbonyl group are substituted

$$XH + SO_2Cl_2 \rightarrow XCl + HCl + SO_2.$$

Free radical chlorination of methyl-*tert*-butyl ketone by an excess of molecular chlorine. Through a ~2.5 mmol MTBK (0.25 g) solution in 3.8 g of CCl_4 gaseous chlorine was bubbled (5-7 ml·min^{-1}) at common light until the solution became colored because of unreacted chlorine. Then bubbling of a low chlorine flow (2-3 ml·min^{-1}) was continued for 1 h under the DRL-400 lamp light at a distance of 40 cm from the reaction system. After the chlorination was completed dry argon was bubbled through the reaction mixture for 5-7 min (10-15 ml·min^{-1}) to remove main amounts of HCl.

Gas chromatographic analysis of reaction mixtures was performed on a Biokhrom-1 chromatograph with a flame-ionization detector and a quartz WCOT column with a length of 25 m and an inner diameter of 0.20 mm with a OV-101 stationary phase (a 0.25 μm thick phase layer) in linear temperature programming mode from 40°C to 240°C with a rate of 6 deg/min. The injector temperature was 240°C; detector temperature was 250°C; carrier gas was nitrogen with a linear velocity of 21 cm·s^{-1}. For injection the Gazokhrom-101 syringe was used; sample volume was 0.3-0.5 μl; flow ratio was 1:30. Parameters of chromatographic peaks were measured by a TR 2213 integrator. In order to determine retention indices a mixture of reference *n*-alkanes C_6–C_{16} or C_6–C_{24} (homologs only with an even number of carbon atoms in molecules) were added to the samples. Linearly logarithmic indices were calculated using the QBasic program given in [27].

Chromato-mass-spectrometric analysis of MTBK chlorination products was conducted on two instruments in different division modes.

A. On a QP 2010+ chromato-mass-spectrometer with a MS WCOT column with a length of 25 m and an inner diameter of 0.20 mm with a HP-5 stationary phase (0.33 μm thick layer) in temperature programming mode from 45°C (1 min) to 280°C (2 min) with a rate of 5 deg/min. Carrier gas was helium with a volume velocity of 1.0 ml/min. The injector temperature was 250°C; interface temperature was 280°C; the ion source temperature was 200°C. Ionization energy was 70 eV. The solvent cut time was 4 min.

B. On a DSQ II (Thermo Finnigan) spectrometer with a WCOT column with a length of 60 m, an inner diameter of 0.25 mm with a MS TR-5 stationary phase (0.25 μm thick layer) in temperature programming mode from 40°C (2 min); ballistic heating (~40 deg/min) to 75°C; linear programming with a rate of 5 deg/min to 280°C (10 min isotherm) and then

5 deg/min to 290°C (10 min isotherm). Carrier gas was helium with a volume velocity of 1.0 ml/min. The injector temperature was 270°C; the interface temperature was 290°C; the ion source temperature was 200°C. Ionization energy was 70 eV.

Components of reaction mixtures on chromatograms measured by different instuments under different conditions were compared by their RI values.

In order to estimate the boiling point (T_{boil}) of chlorination products, which are required for the characterization of the chromatographic elution sequence of isomers, the ACD software (1994-1996 version) was used.

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DISCUSSION

Ionic chlorination of MTBK with sulfuryl chloride under mild conditions result in the formation of only two α-monochloro derivatives with RIs of 904±3 and 915±3 on standard nonpolar polydimethylsiloxane stationary phases. Reaction mixtures of the products of free radical chlorination with molecular chlorine under harder conditions may contain several tens of components with RIs up to 2000. The total number of congeners in the group of MTBK chloro derivatives containing from 1 to 12 chlorine atoms in the molecule is 79, however, mass spectra have been known only for two of them: *tert*-$C_4H_9COCH_2Cl$ and *tert*-$C_4H_9COCHCl_2$ [1]. Estimates of RIs of these compounds made with the use of the algorithm [4] are 894 and 1015 respectively. Experimental RI values of MTBK chlorination products by the time of analysis were completely unknown. Hence, the problem being considered is a typical example of chromato-mass-spectrometric identification under conditions of practically complete absence of data support.

Table 1 presents analytic data for main MTBK chlorination products containing from one to six chlorine atoms in molecules, which were obtained by a combination of analysis results of several samples. For each of 13 mostly often found components listed in the order of their chromatographic elution standard mass spectra are given in modes **A** (for the first six) and **B** (for all except some simplest). The symbol **M** marks molecular ion peaks; for the most intense signals their assignment is given. Minor differences in the mass spectra measured on different devices do not affect the results of their interpretation.

Low intensities of molecular ion signals are a common sign of aliphatic polychloro derivatives, however, for the determination of their molecular masses $[M–Cl]^+ = [M-35]$ or $[M–CH_2Cl]^+ = [M-49]$ ion signals are informative. The determination of the total number of chlorine atoms in the molecule is possible based on the intensity ratios of isotopic peaks of fragment ions. Moreover, from the mass spectra of MTBK chlorination products with the general formula $C_4H_{9–x}COCH_{3–y}Cl_y$ ($0 \le x \le 9$, $0 \le y \le 3$) it is possible to determine the number of chlorine atoms (y) in the $COCH_{3–y}Cl_y$ fragment because $[CH_{3–y}Cl_y]^+$, $[M–CH_{3–y}Cl_y]^+$, and $[COCH_{3–y}Cl_y]^+$ ion signals are reliably measured in mass spectra. However, based on only mass spectrometric data it is impossible to determine the positions of chlorine atoms in the $C_4H_{9–x}Cl_x$ fragment. In order to solve this problem we need to estimate the chromatographic elution sequence of isomers, for example, based on estimates of their normal boiling temperatures obtained with the use of the ACD software (listed in Table 1 for all compounds). However, this technique yield reliable results only within a group of isomers and cannot be applied to compounds with different molecular formulas.

The assignment of all MTBK chlorination products in Table 1 corresponds to this criterion. For example, for two $C_6H_7OCl_5$ isomers the sequence of their chromatographic elution corresponds to 1,1,1,4-tetrachloro-3-methyl-3-(chloromethyl)butane-2-one (T_{boil} 272.2±25°C, RI 1373±7) and 1,1,4-trichloro-3,3-*bis*-(chloromethyl)butane-2-one (T_{boil} 314.6±27°C, RI 1420±2). Two simplest monochloro MTBK derivatives (4-chloro-3,3-dimethylbutane-2-one (RI 904±3) and 1-chloro-3,3-dimethylbutane-2-one (RI 915±3)) must be identified just in the sequence mentioned because their T_{boil} are 163.7±23°C (ACD estimate) and 171.5°C (experimental value) respectively. Moreover, the mass spectrum of the second contains signals of $[C_4H_9]^+$ (m/z 57), $[ClCH_2CO]^+$ (m/z 77, 79), and $[CH_2Cl]^+$ (m/z 49, 51) ions whereas such signals are absent in the mass spectrum of the first, but there is an intense signal of $[CH_3CO]^+$ ions with m/z 43.

TABLE 1. Retention Indices, Mass Spectra and Structures of Main Products of MTBK Chlorination

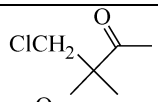
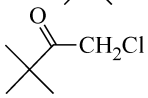
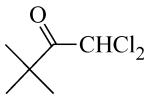
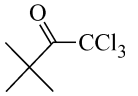
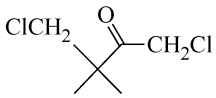
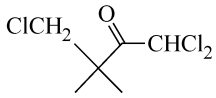
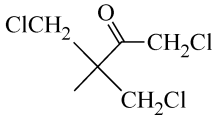
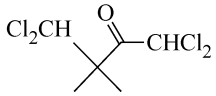
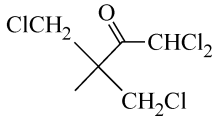
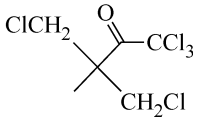
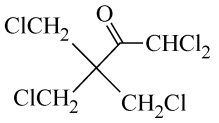
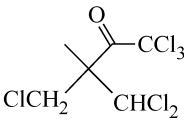
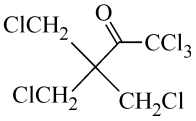
Retention indices	Mass spectra [$m/z \geq 40$ (**A**), ≥ 35 (**B**) $I_{rel} \geq 2\%$]	T_{boil} estimates (ACD) and the number of chlorine atoms in the molecule	Structure of the chlorination product
1	2	3	4
904±3 930±4*	**A.** 134(0,8)**M**, 63(2), 57(5), 56(100) [M–CH_3CO–Cl], 55(17), 53(2), 43(45) [CH_3CO], 42(2), 41(24)	163.7(1)	
915±3 942±1*	**A.** 134(0,6)**M**, 85(26) [C_4H_9CO], 77(4) [$ClCH_2CO$], 58(4), 57(100) [C_4H_9], 56(4), 55(7), 51(2), 49(5) [CH_2Cl], 43(2), 42(4), 41(43)	171.5(1)**	
983±2 1005±1*	**A.** 168(-)**M**, 89(2), 85(21) [C_4H_9CO], 83(13) [$CHCl_2$], 58(4), 57(100) [C_4H_9], 56(2), 55(3), 53(2), 42(2), 41(37), **B.** 168(-)**M**, 89(3), 85(30), 83(18), 78(2), 77(2), 76(6), 58(2), 57(100), 55(6), 53(4), 51(2), 50(3), 49(2), 48(5), 42(2), 41(30), 39(13)	173.8(2)	
1034±2 1060±1*	**A.** 202(-)**M**, 121(3), 119(4), 117(4) [CCl_3], 95(3), 93(10), 85(10) [C_4H_9CO], 82(2), 77(2), 58(6), 57(100) [C_4H_9], 55(3), 47(2), 44(2), 43(4), 42(2), 41(35)	179.8(3)	
1117±3 1140±1*	**A.** 168(0,8)**M**, 121(9), 119(28) [M–CH_2Cl], 93(29), 92(5), 91(96) [C_4H_8Cl], 90(3), 83(2), 82(6), 79(4), 77(12) [$ClCH_2CO$], 65(4), 63(12), 56(32), 55(100) [C_4H_8Cl–HCl], 54(2), 53(6), 51(6), 49(15) [CH_2Cl], 43(6), 42(8), 41(21), **B.** 168(1,2)**M**, 121(11), 119(31), 93(34), 91(100), 79(4), 77(13), 65(3), 63(9), 56(18), 55(84), 53(6), 51(10), 49(20), 43(2), 42(7), 41(18), 40(2), 39(18),	206.8(2)	
1187±1 1214±1*	**A.** 202(0,2)**M**, 121(7), 120(2), 119(20) [M–$CHCl_2$], 117(2), 105(2), 103(3), 93(30), 92(3), 91(98) [C_4H_8Cl], 85(4), 83(6), 76(2), 65(4), 63(12), 56(7), 55(100) [C_4H_8Cl–HCl], 54(2), 53(7), 52(2), 51(4), 50(2), 49(4), 48(3), 44(4), 42(3), 41(10), **B.** 202(-)**M**, 121(7), 119(19), 93(33), 92(2), 91(100), 89(2), 85(6), 83(9), 76(4), 65(3), 63(10), 56(2), 55(73), 53(6), 51(3), 50(2), 49(4), 48(3), 41(7), 39(9)	224.3(3)	
1226±5	**B.** 202(0,4)**M**, 157(3), 155(18), 153(25) [M–CH_2Cl], 129(11), 127(68), 125(100) [$C_4H_7Cl_2$], 119(4), 99(2), 97(2), 93(2), 92(16), 91(16), 90(55) [C_4H_7Cl], 89(44) [C_4H_6Cl], 85(4), 83(5), 79(9), 77(30) [$ClCH_2CO$], 75(7), 73(2), 65(4), 63(12), 61(2), 55(33), 54(8), 53(35) [C_4H_6Cl–HCl], 51(12), 49(19) [CH_2Cl], 43(2), 42(5), 41(7), 39(11)	254.3(3)	
1288±2	**B.** 236(-)**M**, 157(3), 155(17), 153(25) [M–$CHCl_2$], 129(11), 127(68), 125(100) [$C_4H_7Cl_2$], 117(2), 111(3), 97(2), 92(4), 91(15), 90(11) [C_4H_7Cl], 89(50) [C_4H_6Cl], 87(2), 85(9), 83(14), 77(4), 76(4), 75(4), 65(5), 63(13), 61(2), 55(15), 54(3), 53(33), 51(5), 50(2), 49(5), 48(3), 42(2), 41(5), 39(8),	250.1(4)	
1299±3	**B.** 236(-)**M**, 157(4), 155(29), 153(42) [M–$CHCl_2$], 129(11),127(69), 125(100) [$C_4H_7Cl_2$], 119(2), 117(7), 111(2), 92(15), 91(21), 90(49) [C_4H_7Cl], 89(72) [C_4H_6Cl], 87(2), 85(2), 83(3), 79(6), 77(20), 76(2), 75(8), 73(2), 69(2), 65(10), 63(25), 62(2), 61(2), 55(45), 54(8), 53(44) [C_4H_6Cl–HCl], 51(13), 49(19), 42(3), 41(7), 39(10)	271.3(4)	
1373±7	**B.** 270(-)**M**, 157(3), 155(17), 153(25) [M–CCl_3], 129(15), 127(67), 125(100) [$C_4H_7Cl_2$], 91(29), 90(4), 89(90) [C_4H_6Cl], 87(4), 85(9), 83(14), 78(3), 76(9), 75(3), 73(2), 69(2), 65(10), 63(28), 61(2), 55(11), 54(2), 53(43) [C_4H_6Cl–HCl], 51(7), 50(3), 49(9), 48(2), 47(2), 41(5), 39(8)	272.2(5)	

TABLE 1. (Continued)

1	2	3	4
1420±2	**B.** 270(-)**M**, 191(5), 189(15), 187(16) [M–$CHCl_2$], 163(13), 161(39), 159(41) [$C_4H_6Cl_3$], 128(10), 126(66), 124(100) [$C_4H_6Cl_2$], 123(48) [$C_4H_5Cl_2$], 111(3), 109(4), 103(2), 99(3), 97(6), 91(25), 89(85) [C_4H_6Cl], 87(26) [$C_4H_5Cl_2$–HCl], 85(7), 83(9), 79(12), 77(41), 75(7), 73(6), 69(3), 63(2), 61(3), 53(10), 51(23) [$C_4H_5Cl_2$–2HCl], 49(30), 47(2), 42(6), 41(2), 39(3)	314.6(5)	
1475±3	**B.** 304(-)**M**, 191(6), 189(30), 187(30) [M–CCl_3], 163(16), 161(52), 159(54) [$C_4H_6Cl_3$], 126(25), 124(45) [$C_4H_6Cl_2$], 123(59) [$C_4H_5Cl_2$], 103(2), 99(5), 97(7), 93(3), 90(29), 88(100) [C_4H_5Cl], 87(31) [C_4H_4Cl], 79(12), 75(12), 62(4), 52(2), 49(15), 47(2), 42(10), 38(2)	294.1(6)	
1494±5	**B.** 304(-)**M**, 191(6), 189(20), 187(21) [M–CCl_3], 163(16), 161(50), 159(51) [$C_4H_6Cl_3$], 127(2), 123(100) [$C_4H_5Cl_2$], 111(2), 109(2), 99(5), 97(8), 87(26) [$C_4H_5Cl_2$–HCl], 85(16), 83(25), 76(4), 75(2), 73(3), 69(2), 65(3), 63(9), 51(8), 49(3), 47(2)	313.7(6)	

*Retention indices on polydimethylsiloxane phases containing 5% of phenyl groups.
**Example of the structure characterized by the experimental value T_{boil} in the ACD software.

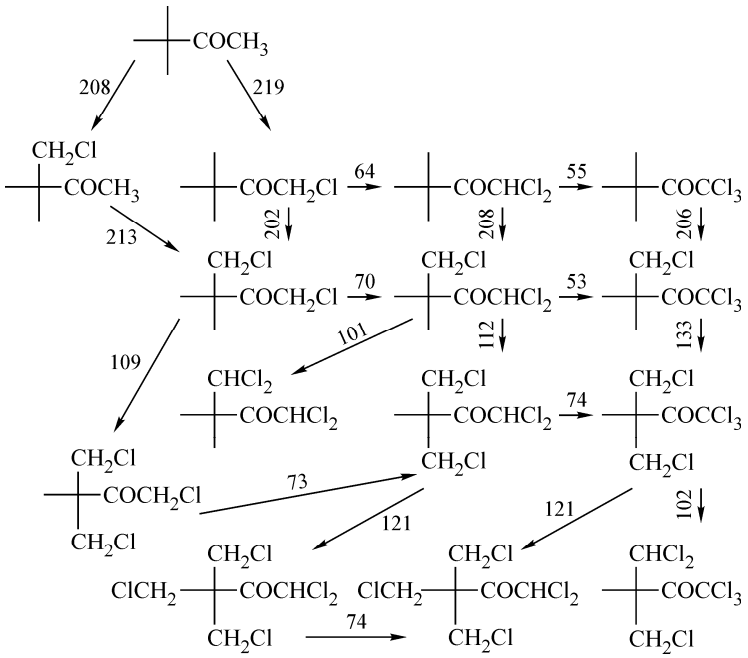
Mass spectra and RIs of the whole set of identified polychloro derivatives of aliphatic ketone are an essential supplementation of the existing databases.

Gas chromatographic and chromato-mass-spectrometric analysis of MTBK chlorination products was performed with the use of capillary columns with the standard nonpolar polydimethylsiloxane phase OV-101 and a few somewhat more polar phases containing 5% of phenyl groups (HP-5 and TR-5 MS). According to the classification accepted in the database [1], second type phases are assigned to the group of semi-standard non-polar phases, on which RIs of the same compounds are insignificantly larger than those on the standard nonpolar ones. Therefore, for the first six compounds Table 1 gives two RIs for each, whose mean difference is 26±2 i. u. Apart from the chlorination products mentioned in Table 1, in the course of the chromatographic analysis of separate samples the presence of components with the number of chlorine atoms more than six in the molecules, and correspondingly, with larger RIs, are revealed, namely 1551±4, 1577±4, 1592±5, 1626±4, 1667±5, 1740±5, 1971±6, and so on.

A comparison of RIs of all identified MTBK chlorination products does not allow us to characterize them by one additive scheme, but it makes it possible to reveal separate additivity elements with the estimation of the corresponding increments. The general product formation sequence and RI differences corresponding to them can be illustrated by scheme 1. In order to calculate all ΔRI values we used RIs on the standard nonpolar phase OV-101.

The ΔRI values corresponding to a step-by-step increase in the number of chlorine atoms in the molecule per unit vary from 53 to 219 (four times), which illustrates the degree of non-additivity of the corresponding structural transformations. Similar non-additivity of RIs of polychloro derivatives is also observed in other groups of congeners.

Mean values of RI increments of different structural transformations are given in Table 2. The use of these data for the estimation of RIs of other chloro derivatives is related to the variant of type II additive schemes (see Introduction). The only structural fragment not presented among the identified products is the result of complete chlorine substitution for three hydrogen atoms of one methyl group in the composition of the *tert*-butyl moiety, i.e. the transformation of the form $C–CHCl_2 \rightarrow C–CCl_3$. The presence of similar products in reaction mixtures is quite possible at a high degree of MTBK chlorination, but their identification remains difficult because it is impossible to estimate the increments ΔRI. Attempts to estimate the corresponding increments by the data for other classes of chloro derivatives (e.g., polychloroalkanes) are possible, but they are less reliable.



Scheme 1. Formation sequence of pinacolone chloro derivatives and the corresponding differences in their retention indices.

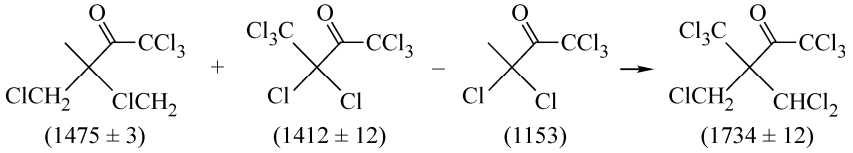
TABLE 2. Retention Index Increments of MTBK Chloro Derivatives

Structural transformation	Number of ΔRI values	Mean ΔRI
$COCH_3 \rightarrow COCH_2Cl$	2	216±4
$COCH_3 \rightarrow COCHCl_2$	2	283±2
$COCH_2Cl \rightarrow COCHCl_2$	3	69±4
$COCH_3 \rightarrow COCCl_3$	2	337±2
$COCHCl_2 \rightarrow COCCl_3$	3	61±12
$(CH_3)_2C–CH_3 \rightarrow (CH_3)_2–CH_2Cl$	4	206±3
$(CH_3)_2C–CH_2Cl \rightarrow (CH_3)_2C–CHCl_2$	2	102±2
$(ClCH_2)_x(CH_3)_{2–x}C–CH_3 \rightarrow (ClCH_2)_x(CH_3)_{2–x}C–CH_2Cl$ (x = 1.2)	5	119±9

The ΔRI estimates obtained are close but do not coincide with the estimates of these parameters obtained for chloro derivatives of other aliphatic ketones. For example, for 2-alkanones the ΔRI values for transformations $COCH_3 \rightarrow COCH_2Cl$ and $COCH_3 \rightarrow COCHCl_2$ are 197±9 and 241±13 [6, 7], which is smaller than those in the case of similar transformations of the MTBK structure (216±5 and 283±1, Table 2). An increase in ΔRI values corresponds to an increase in the effect of steric factors due to the presence of a branched *tert*-butyl group in the molecule. Thus, the whole series of MTBK chloro derivatives cannot be characterized by a minimum set of RI increments which provides the estimation of RIs of any chlorination products, however, separate structural transformations well meet the additivity condition.

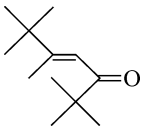
The increment estimates obtained enable the identification of a part of MTBK chlorination products not characterized by mass spectra and containing more than six chlorine atoms in the molecule (their RIs are given above). For example, based on RI of 1,1,1,4-tetrachloro-3,3-*bis*(chloromethyl)butane-2-one (1494±5) it is possible to estimate RI of 1,1,1,4,4-pentachloro-3,3-*bis*(chloromethyl)butane-2-one (1494±5) + (102±1) ≈ 1596±5, which corresponds to a product with RI of 1592±5. Similarly, based on RI of 1,1,4-trichloro-3,3-*bis*(chloromethyl)butane-2-one (1420±2), it is possible to estimate RI of 1,1,4,4-tetrachloro-3-(dichloromethyl)-3-(chloromethyl)butane-2-one (1420±2) + 2×(102±1) ≈ (1624±3), which is well consistent with a value of 1626±4 (see above).

For the estimation of RIs of highly chlorinated products the variant of additive schemes III (see Introduction), based on assembling complex structures from the structures of simpler analogs is also of apparent interest. For example, the structure of the 1,1,1,4,4,4-hexachloro-3-(dichloromethyl)-3-(chloromethyl)butane-2-one compound can be presented as a superposition of the structures of identified 1,1,1,4,4-pentachloro-3-methyl-3-(chloromethyl)butane-2-one (RI 1475±3) and octachloro-2-butanone (1412±12) minus the structure of 1,1,1,3,3-pentachloro-2-butanone (1153). The choice of the second structure is caused by the necessity to at least approximately take into account the effect of steric factors due to the presence of substituents at the α-position relative to the carbonyl group



Scheme 2

TABLE 3. Mass Spectra and Retention Indices of Minor Components of Reaction Mixtures of MTBK Chlorination, Not Belonging to a Series of Chloroalkanones

Retention indices	Mass spectra [$m/z \geq 40$ (**A**), ≥ 35 (**B**), $I_{rel} \geq 2\%$]	Interpretation
1074±2*	**A.** 156(3), 154(17), 153(2), 152(26)**M**, 137(8), 124(2), 120(2), 119(24), 118(7), 117(95) [M–Cl], 116(6), 109(2), 103(4), 98(2), 96(2), 89(7), 83(2), 82(8), 81(100) [M–Cl–HCl=C_6H_9], 80(6), 79(61), 77(5), 76(2), 75(7), 73(3), 70(2), 67(16), 66(5), 65(16), 63(3), 57(2), 56(6), 55(13), 54(6), 53(38), 52(4), 51(8), 50(3), 49(2), 44(3), 43(25), 42(3), 41(40), 40(5)	$C_6H_{10}Cl_2$
1076±2*	**A.** 154(-)**M**, 123(7), 121(24), 120(2), 119(64) [M–Cl], 112(3), 110(2), 95(2), 94(3), 93(18), 92(7), 91(63) [M–C_2H_4Cl], 85(2), 84(13), 83(42), 82(5), 79(30), 78(4), 77(100) [M–C_3H_6Cl], 69(9), 63(6), 57(7), 56(11), 55(72), 53(3), 51(9), 49(20), 47(2), 44(5), 43(6), 42(7), 41(33)	$C_6H_{12}Cl_2$
1106±2 1132±1*	**A.** 202(-)**M**, 169(3), 167(7) [M–Cl], 131(2), 125(3), 121(29), 120(5), 119(90) [M–$CHCl_2$], 117(2), 113(6), 112(2), 111(10), 109(2), 108(2), 105(2), 103(4), 94(2), 92(30), 92(4), 91(93) [C_4H_8Cl], 87(3), 85(15), 84(5), 83(61) [$CHCl_2$], 79(21), 78(4), 77(68) [C_3H_6Cl], 76(6), 75(3), 70(4), 69(2), 67(7), 65(4), 63(7), 57(8), 56(15), 55(100), 54(3), 53(7), 51(5), 50(3), 49(4), 48(5), 44(2), 43(19), 42(4), 41(51), 40(3); **B.** 202(-)**M**, 189(2), 187(2), 169(9), 167(14), 131(3), 121(35), 120(2), 119(100), 115(2), 113(8), 111(10), 105(2), 103(7), 95(2), 93(31), 91(89), 89(2), 87(5), 85(27), 83(70), 79(15), 78(3), 77(50), 76(14), 75(3), 67(5), 65(3), 63(7), 61(2), 56(10), 55(59), 53(8), 51(6), 50(6), 49(4), 48(7), 47(2), 43(3), 42(3), 41(30), 39(21), 38(2)	$C_7H_{13}Cl_3$
1138±2*	**A.** 182(2)**M**, 167(6), 126(9), 125(100) [M–C_4H_9], 124(16), 123(2), 111(3), 109(16), 107(4), 97(2), 95(6), 84(2), 83(13), 82(25), 81(5), 79(2), 69(6), 68(2), 67(9), 59(5), 57(3), 55(11), 53(3), 43(6), 41(11)	
1154±3*	**A.** 190(2), 188(6), 186(7)**M**, 167(4), 155(10), 154(5), 153(62), 152(8), 151(100) [M–Cl], 150(3), 139(2), 137(5), 135(5), 125(3), 124(8), 123(4), 122(6), 117(17), 116(4), 115(43) [M–Cl–HCl], 112(3), 111(4), 110(2), 109(10), 107(6), 101(8), 100(3), 99(14), 98(2), 97(3), 95(3), 91(2), 89(6), 87(5), 85(2), 83(8), 82(10), 81(9), 80(7), 79(72) [M–Cl–2HCl], 78(4), 77(39), 76(2), 75(12), 74(2), 73(7), 69(4), 68(2), 67(6), 66(2), 65(14), 63(5), 62(2), 61(2), 58(2), 57(7), 6\56(4), 55(6), 54(4), 53(19), 52(4), 51(15), 50(6), 49(6), 43(13), 42(3), 41(24), 40(5)	$C_6H_9Cl_3$
1213±3*	**A.** 168(0.2)**M**, 121(7), 119(21), 93(31), 92(4), 91(100) [M–Cl], 85(4), 83(6), 76(3), 75(2), 65(5), 63(12), 56(7), 55(99) [M–Cl–HCl], 53(6), 51(3), 50(2), 49(4), 48(2), 42(2), 41(11)	$C_7H_{14}Cl_2$

*Retention indices on polydimethylsiloxane phases containing 5% of phenyl groups.

The obtained estimate of RI coincides with RI of one of the unidentified products of MTBK chlorination, namely 1740±5 (see above).

Reaction mixtures of MTBK chlorination with molecular chlorine under hard conditions contain not only chloro derivatives of this ketone, but also a series of other products, in particular, di- and trichloro derivatives of C_6–C_7 hydrocarbons. Mass spectra and retention indices of some of most often occurring components are summarized in Table 3. A detailed determination of their structures from the analytic data used is inexpedient due to a large number of possible isomers, but the storage of this information provides a basis for the identification of these compounds in the future. Thus, RI of the product with the molecular formula $C_7H_{13}Cl_3$ (1106±2) is close to RIs of some isomers characterized by now. A possible mechanism of the formation of chloro derivatives of C_7 hydrocarbons must involve the interaction of C_6 substrates with trichloromethyl radicals generated from the solvent (CCl_4) under conditions of free radical chlorination. An alternative method of generation $CCl_3^{\bullet}$ radicals may involve the splitting of polychloro derivatives containing the $–COCCl_3$ fragment. Both versions are confirmed by the absence of such products in reaction mixtures obtained with the use of sulfuryl chloride.

Yet another unexpected component is 2,2,5,6,6-pentamethylhept-4-en-3-one — the product of crotonic condensation of two MTBK molecules. Since its chloro derivatives are not found in reaction mixtures, then this compound is most likely to form after chlorination is completed in the acid medium from an excess of unreacted initial ketone.

Thus, an example of the chromato-mass-spectrometric identification of MTBK chlorination products based on a joint interpretation of mass spectrometric and chromatographic data indicates significant inadditivity of IRs corresponding to a gradual increase in the number of chlorine atoms in the molecule. Nevertheless, this inadditivity does not hinder the use of separate elements of additive schemes for the estimation of RIs of congeners and the verification of their correct identification.

REFERENCES

1. *The NIST 11 Mass Spectral Library* (NIST11/2011/EPA/NIH). *Software/Data Version* (NIST08); *NIST Standard Reference Database*, Number 69, August 2011. National Institute of Standards and Technology, Gaithersburg, MD 20899; http://webbook.nist.gov (April, 2012).
2. I. G. Zenkevich, in: *100 Years of Chromatography* [in Russian], Nauka, Moscow (2003), pp. 311-336.
3. F. Eisenlohr, *Spektrochemie Organischer Verbindungen, Molekularrefraktion und Dispersion*, Verlag von F. Enke, Stuttgart (1912).
4. S. E. Stein, V. I. Babushok, and R. L. Brown, *J. Chem. Inf. Model*, **47**, No. 3, 975-980 (2007).
5. J. Oszczapowic, J. Osek, and E. Dolecka, *J. Chromatogr. A*, **315**, 95-100 (1984).
6. I. G. Zenkevich, E. V. Eliseenkov, A. N. Kasatochkin, Z. A. Zhakovskaya, and L. O. Khoroshko, *Rus. J. Analyt. Chem*., **66**, No. 4, 396-406 (2011).
7. I. G. Zenkevich, E. V. Eliseenkov, A. N. Kasatochkin, Z. A. Zhakovskaya, and L. O. Khoroshko, *J. Chromatogr. A*, **1218**, 3291-3299 (2011).
8. I. G. Zenkevich, E. V. Eliseenkov, A. N. Kasatochkin, and A. I. Ukolov, *Mass Spectrometry*, **8**, No. 2, 119-128 (2011).
9. I. G. Zenkevich, Zh. Org. Khim., **29**, No. 9, 1827-1840 (1992).
10. I. G. Zenkevich, M. Moeder, G. Koeller, and S. Schrader, *J. Chromatogr. A*, **1025**, 227-236 (2004).
11. I. G. Zenkevich, A. I. Ukolov, A. S. Kushakova, and L. K. Gustyleva, *Rus. J. Anal. Chem*., **66**, No. 12, 1165-1172 (2011).
12. A. I. Ukolov and I. G. Zenkevich, *Vestn. SPbGU. Ser. Fiz. Khim*., Vyp. 1, 80-90 (2011).
13. I. G. Zenkevich, A. A. Makarov, S. Schrader, and M. Moeder, *J. Chromatogr. A*, **1216**, 4097-4106 (2009).
14. I. G. Zenkevich, E. V. Eliseenkov, and A. N. Kasatochkin, *Mass Spectrometry*, **6**, No. 2, 137-148 (2009).
15. I. G. Zenkevich, E. V. Eliseenkov, and A. N. Kasatochkin, *Chromatographia*, **70**, Nos. 5/6, 839-843 (2009).
16. I. G. Zenkevich and A. I. Ukolov, *Rus. J. General Chem*., **81**, No. 9, 1818-1828 (2011).
17. A. I. Ukolov and I. G. Zenkevich, *Mass Spectrometry*, **8**, No. 4, 264-272 (2011).

18. I. G. Zenkevich and A. I. Ukolov, *J. Struct. Chem*., **51**, No. 4, 642-651 (2010).
19. I. G. Zenkevich, *Mass Spectrometry*, **1**, No. 1, 45-52 (2004).
20. I. G. Zenkevich, *Chemometr. Intel. Lab. Systems*, **72**, 233-240 (2004).
21. I. G. Zenkevich, *J. Struct. Chem*., **50**, No. 5, 895-909 (2009).
22. E. I. Savelieva, I. G. Zenkevich, and A. S. Radilov, *Rus. J. Anal. Chem*., **58**, No. 2, 135-145 (2003).
23. E. I. Savelieva and I. G. Zenkevich, *Shimadzu News*, No. 1, 6/7 (2003).
24. D. P. Wyman and P. R. Kaufman, *J. Org. Chem*., **29**, No. 7,1956-1960 (1964).
25. D. Masilamani and M. M. Rogic, *J. Org. Chem*., **46**, No. 22, 4486-4489 (1981).
26. J. Dalluge, L. L. P. van Stee, X. Xu, J. Williams, J. Beens, R. J. J. Vreuls, and U. A. Th. Brinkman, *J. Chromatogr. A*, **974**, 169-184 (2002).
27. B. V. Stolyarov, I. M. Savinov, A. G. Vitenberg, et al., *Practical Gas and Liquid Chromatography* [in Russian], Izd. SPb. Univ., SPb (2002).