## CONCLUSIONS

1. Fragmentation of the $[M + H]^+$ and $[M + C_2H_5]^+$ ions of the alkyl-substituted phenols is largely determined by the size of the substituent and its position in the benzene ring.

2. The $[M + H]^+$ ions of the spatially hindered phenols can eliminate a $H_2O$ molecule, even without participation of the gas-reagent proton in the cleavage process.

3. The presence of the functional substituents can affect the fragmentation of the compounds in question here, at least under chemical ionization in methane.

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# GAS CHROMATOGRAPHIC CHARACTERIZATION OF SULFUR-CONTAINING COMPOUNDS

## 4. THE EFFECT OF UNSATURATED RADICALS ON THE RETENTION INDICES OF THE VINYL, ALLYL, AND PROPARGYL ALKYL SULFIDES

R. V. Golovnya, T. A. Misharina,
and V. G. Garbuzov

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The unsaturated aliphatic sulfur-containing compounds are largely responsible for the odor attaching to plant and animal alimentary products [1-3]. Because there has been no gas chromatographic (GC) characterization of these compounds, their qualitative and quantitative determination in such products is a matter of difficulty.

The present work was a study of the gas-chromatographic behavior of 30 unsaturated vinyl, allyl, and propargyl alkyl sulfides on four columns of different polarities. Comparison was made of the retention indices of these compounds and of the corresponding saturated sulfides. Determination was made of differences in the differential molar free energies of solution, the factor characterizing the effect of the unsaturated radical on sulfide gas-chromatographic behavior.

## EXPERIMENTAL

The ethylvinyl and diallyl sulfides used here were pure grade materials. The remaining sulfides were synthesized by alkylation of the various potassium mercaptides [4].

Synthesis of the Vinyl and Allyl Sulfides. To 50 ml of a 2 N 1 : 1 alcohol—water solution of KOH there was added 0.1 mole of the alkyl mercaptan. The resulting mercaptide solution was transferred to a 100 ml ampule, and 0.12 mole of either allyl or vinyl bromide added to it.* The ampule was sealed and heated to 100°C, for 30 min in the case of the allyl sulfides and for 5-10 h in the case of the vinyl sulfides. The ampule was then cooled, broken

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*The ampule was cooled during addition of the vinyl bromide (bp, 15.8°C).

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TABLE 1. Retention Indices at 130°C (I), and Boiling Points ($t_{bp}$), for the Vinyl, Allyl, and Propargyl Alkyl sulfides

| Alkyl | Sulfide | $t_{bp}$, °C |  | $I^{Ap}$ | $I^{OV}$ | $I^{Tr}$ | $I^{PEG}$ |
|---|---|---|---|---|---|---|---|
|  |  | Experimental | Calculated * |  |  |  |  |
|  | Vinylalkyl sulfides |  |  |  |  |  |  |
| Methyl | 2-Thia-3-butene | 68,0 [6] | 66,9 | 608 | 716 | 835 | 912 |
| Ethyl | 3-Thia-1-pentene | 91,5 [6] | 92,3 | 696 | 797 | 909 | 981 |
| n-Propyl | 3-Thia-1-hexene | – | 118,8 | 794 | 890 | 1000 | 1069 |
| n-Butyl | 3-Thia-1-heptene | 141,0 [6] | 143,8 | 893 | 989 | 1097 | 1163 |
| n-Amyl | 3-Thia-1-octene-1 | – | 167,2 | 992 | 1088 | 1196 | 1261 |
| Isopropyl | 4-Methyl-3-thia-1-pentene | – | 104,5 | 740 | 833 | 936 | 993 |
| sec-Butyl | 4-Methyl-3-thia-1-hexene | – | 131,9 | 845 | 936 | 1036 | 1098 |
|  | Allyl Alkyl Sulfides |  |  |  |  |  |  |
| Methyl | 2-Thia-4-pentene | 92,3 [6] | 92,6 | 697 | 799 | 921 | 1001 |
| Ethyl | 4-Thia-1-hexene | 115,5 [7] | 114,4 | 777 | 883 | 995 | 1067 |
| n-Propyl | 4-Thia-1-heptene | 139,0 [7] | 138,2 | 870 | 973 | 1081 | 1152 |
| n-Butyl | 4-Thia-1-octene-1 | – | 161,5 | 967 | 1070 | 1174 | 1246 |
| n-Amyl | 4-Thia-1-nonene | – | 183,5 | 1065 | 1169 | 1272 | 1343 |
| Isopropyl | 5-Methyl-4-thia-1-hexene | 126–127 | 126,1 | 822 | 921 | 1021 | 1089 |
| sec-Butyl | 5-Methyl-4-thia-1-heptene | – | 150,4 | 920 | 1019 | 1117 | 1184 |
| sec-Isoamyl | 5,6-Dimethyl-4-thia-1-heptene | 169,5 | 168,4 | 997 | 1090 | 1185 | 1248 |
| tert-Butyl | 5,5-Dimethyl-4-thia-1-hexene | – | 139,9 | 877 | 969 | 1066 | 1132 |
| tert-Amyl | 5,5-Dimethyl-4-thia-1-heptene | – | 167,7 | 994 | 1088 | 1186 | 1254 |
| Allyl | 4-Thia-1,6-heptadiene | 139,0 [6] | — | 854 | 972 | 1114 | 1191 |
|  | Propargyl Alkyl Sulfides |  |  |  |  |  |  |
| Methyl | 2-Thia-4-pentene | 108–109 | 107,4 | 705 | 859 | 1090 | 1204 |
| Ethyl | 4-Thia-1-hexyne | 129,0 | 127,4 | 782 | 939 | 1155 | 1270 |
| n-Propyl | 4-Thia-1-heptyne | 151,0 | 149,8 | 877 | 1032 | 1241 | 1352 |
| n-Butyl | 4-Thia-1-octyne | 172,0 | 170,8 | 974 | 1129 | 1337 | 1447 |
| n-Amyl | 4-Thia-1-nonyne | 191,5 | 190,3 | 1073 | 1228 | 1435 | 1544 |
| Isopropyl | 5-Methyl-4-thia-1-hexyne | 136,0 | 139,6 | 833 | 978 | 1184 | 1291 |
| sec-Butyl | 5-Methyl-4-thia-1-heptyne | 161–162 | 162,2 | 933 | 1083 | 1281 | 1386 |
| Isoamyl | 7-Methyl-4-thia-1-octyne. | 186,0 | 183,0 | 1035 | 1184 | 1388 | 1492 |
| tert-Butyl | 5,5-Dimethyl-4-thia-1-hexyne | 149,5 | 153,1 | 892 | 1036 | 1232 | 1338 |
| tert-Amyl | 5,5-Dimethyl-4-thia-1-heptyne | – | 178,0 | 1010 | 1155 | 1354 | 1460 |
| Allyl | 4-Thia-1-heptene-6-yne | – | — | 858 | 1026 | 1264 | 1380 |
| Propargyl | 4-Thia-1,6-heptadiyne | – | — | 862 | 1076 | 1436 | 1595 |

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*$t_{bp}$ values calculated from equations of the general form: $t_{bp} = \alpha + \beta(I^{Ap} + \gamma)$, the coefficients being determined from three measured values of $t_{bp}$ and $I^{Ap}$; for the vinylalkyl and alkylsulfides: $b_p = 687.7 - 2{,}147{,}000/(I^{Ap} + 2{,}073)$ ($\sigma = 1.5$), for the propargyl alkylsulfides $t_{bp} = 614.1 - 952{,}000/(I^{Ap} + 1{,}174)$ ($\sigma = 2.2$), $\sigma$ being the standard deviation of the calculated and experimental values.

open, its contents poured into 100 ml of cold water, and the product extracted with pentane (30 ml × 3). The extract was evaporated down in a current of $N_2$, and then chromatographed. In some cases the sulfide was subjected to microdistillation in $N_2$ at atmospheric pressure prior to chromatographing.

Synthesis of the Propargyl Alkyl sulfides. A solution containing 0.1 mole KOH dissolved in 20 ml of water was added to 0.1 mole of mercaptan under constant stirring, the resulting mixture cooled in an ice bath, and 0.15 mole of freshly prepared propargyl bromide added to it. The ice bath was removed after 15-20 min, and the mixture stirred for 1-3 h at ~ 20°C. The organic layer was separated off, washed with distilled water, dried over anhydrous $Na_2SO_4$, and then distilled in $N_2$ at atmospheric pressure. This procedure gave a 20-70% yield of sulfide. The following propargyl alkylsulfides were prepared in this way (alkyl, $n_D^{20}$ value): methyl, 1.4920; ethyl, 1.4849; n-propyl, 1,4796; n-butyl, 1.4772; n-amyl, 1.4750; isopropyl, 1.4840; sec-butyl, 1.4775; isoamyl, 1.4743; tert-butyl, 1.4755.

The GC measurements were carried out under the conditions described in [5]. Analyses were performed at 130°C using 210 × 0.4 cm glass columns packed with Chromosorb W, AW-DMCS, 80/100 mesh, with 5% Apiezon M (Ap), Silicone OV-17 (OV), Triton X-305 (Tr), and polyethylene glycol-1000 (PEG). Values of the retention index each the mean of 3-7 measurements, are listed in Table 1.

TABLE 2. Parameter Values Used in Calculating Retention Indices for the Unsaturated Sulfides through Eq. (1), and Differences in the Retention Indices (δI) and Free Energies of Solution [δ(ΔG)] for the Analogous Saturated and Unsaturated Sulfides

| Stationary phase | Calculated quantity | | Allyl sulfides | | |
|---|---|---|---|---|---|
| | | | VinSR | AllSR | PgSR |
| Apiezon M | Parameters of Eq. (1) | $A$ | 484,8 | 555,6 | 558,7 |
| | | $B$ | 100,5 | 100,3 | 101,0 |
| | | $C$ | 23 | 41 | 45 |
| | | $\sigma$ | 0,6 | 0,2 | 0,6 |
| | Difference in the retention indices, calculated through Eq. (2) | $\delta I$ | −3 | −16 | −10 |
| | | $\sigma'$ | 3,3 | 2,4 | 2,3 |
| | Value of $-\delta(\Delta G)$, calculated through Eq. (3), cal/mole | | −15 | −80 | −50 |
| OV-17 | Parameters of Eq. (1) | $A$ | 569,4 | 657,8 | 715,0 |
| | | $B$ | 102,0 | 100,8 | 100,9 |
| | | $C$ | 45 | 41 | 43 |
| | | $\sigma$ | 0,3 | 1,7 | 0,4 |
| | Difference in the retention indices, calculated through Eq. (2) | $\delta I$ | 7 | −1 | 57 |
| | | $\sigma'$ | 3,9 | 1,2 | 3,0 |
| | Value of $-\delta(\Delta G)$, calculated through Eq. (3), cal/mole | | 30 | ~0 | 260 |
| Triton X-305 | Parameters of Eq. (1) | $A$ | 675,2 | 763,9 | 907,6 |
| | | $B$ | 101,9 | 99,4 | 102,4 |
| | | $C$ | 58 | 58 | 81 |
| | | $\sigma$ | 0,5 | 1,9 | 1,3 |
| | Difference in the retention indices, calculated through Eq. (2) | $\delta I$ | 35 | 29 | 192 |
| | | $\sigma'$ | 2,6 | 2,7 | 1,1 |
| | Value of $-\delta(\Delta G)$, calculated through Eq. (3), cal/mole | | 140 | 120 | 790 |
| PEG-1000 | Parameters of Eq. (1) | $A$ | 745,9 | 826,0 | 1021,2 |
| | | $B$ | 100,4 | 100,5 | 101,5 |
| | | $C$ | 66 | 75 | 82 |
| | | $\sigma$ | 0,5 | 1,1 | 2,5 |
| | Difference in the retention indices, calculated through Eq. (2) | $\delta I$ | 47 | 47 | 249 |
| | | $\sigma'$ | 8,3 | 3,2 | 3,9 |
| | Value of $-\delta(\Delta G)$, calculated through Eq. (3), cal/mole | | 180 | 180 | 970 |

## DISCUSSION OF RESULTS

The data (see Table 1) showed that the retention indices and the number of carbon atoms in the n-alkyl chain (n) were related by an equation of the form:

$$I = A + Bn + C/n \tag{1}$$

for each of the vinyl, allyl, and propargyl alkyl sulfides, and with each of the different types of stationary phases. Here A, B, and C are constants whose values depend on the conditions of the GC analysis and the nature of the homologous series to which the compound under analysis belongs. The values of the B and C coefficients were determined from measured I values for the methyl, n-propyl, and n-amyl sulfides; each value of A was an average of values for all five members of the homologous series. It can be seen from Table 2 that the standard deviation* was, in general, no more than two index units (i.u.). This made it possible to identify higher members of a given homologous series from the calculated values of their retention indices. The effect of replacing the saturated ethyl and propyl groups of the sulfide molecule with the unsaturated vinyl (Vin), allyl (All), and propagaryl (Pg) radicals was described by equations of the following form, one set being developed for each of the four types of stationary phases δI

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*The standard deviation was calculated from the equation: $\sigma = \sqrt{\dfrac{\sum_{1}^{K}(X_c - X_e)^2}{K-1}}$, $X_c$ being the calculated, and $X_e$ the experimentally determined, value, and K the number of compounds involved in the comparison.

TABLE 3. Retention Indices for the Ethers, and Values of $\delta I_{S-O}$

| Ether | $I^{Ap}$ | $I^{OV}$ | $I^{Tr}$ | $I^{PEG}$ | $\delta I_{S-O}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Ap | OV | Tr | PEG |
| Vinylethyl | 484 | 556 | 642 | 684 | 212 | 241 | 267 | 297 |
| Allylethyl | 567 | 650 | 731 | 780 | 210 | 233 | 264 | 287 |
| Propargylethyl | 571 | 702 | 884 | 962 | 211 | 237 | 271 | 308 |
| | | | Mean | | 211±1 | 237±4 | 267±4 | 297±10 |

$$\left.\begin{aligned}\delta I &= I_{\mathrm{VinSR}} - I_{\mathrm{EtSR}}\\ \delta I &= I_{\mathrm{AllSR}} - I_{\mathrm{PrSR}}\\ \delta I &= I_{\mathrm{PgSR}} - I_{\mathrm{PrSR}}\end{aligned}\right\} \qquad (2)$$

Values of the retention indices for ethyl and propyl alkyl sulfides, measured under the same conditions and reported in [5, 8], were used in the calculations. With exception of the tert-butyl and tert-amyl compounds, the values of δI for the normal and branched alkyl sulfides of any one series were constant on each stationary phase. Values of δI averaged over 7-10 determinations, and standard deviation of the experimentally determined values and of their mean (σ'), are given in Table 2. In general, the value of the standard deviation σ' was less than 4 i.u. The δI values could be used for calculating retention indices for unsaturated sulfides from data on the corresponding saturated compounds, and the results obtained then used for preliminary GC identification. Table 2 also shows values of the difference in the differential molar free energies of solution of the saturated and unsaturated sulfides [δ(ΔG)] as calculated from the expression [9].

$$\delta\,(\Delta G) = -\,0.023\,RTb\,\delta I \qquad (3)$$

in which R is the molar gas constant, T is the temperature of analysis, in °K, and b is the slope of a graph showing the logarithm of the corrected retention time plotted against the number of C atoms in the n-alkane molecule. The value of δ(ΔG) is the alteration in the differential molar free energy of solution resulting from replacement of a saturated radical by an unsaturated radical in the sulfide molecule (in the present case, replacement of a vinyl radical by an ethyl or allyl group, and a propargyl radical by an n-propyl group). On the nonpolar Ap phase, the absolute differential molar free energy of solution was 15-80 cal/mole higher for the saturated sulfides than for the unsaturated. Increasing the phase polarity altered the situation, the unsaturated sulfides being retained more firmly than the saturated on the PEG. The value of δ(ΔG) for the propargyl group is almost 1 kcal/mole, the contribution of the C≡C bond of the propargyl alkyl sulfide to the free energy of solution being almost equal to that of a single functional group, an S atom, for example [10]. It is obvious that this strong interaction between the PEG and the propargyl alkyl sulfide must trace back to the formation of hydrogen bonds between the propargyl radical and the oxygen atoms of the stationary phase. Such an assumption would be supported by the following facts. It is well-known that acetylene can form H bonds with the oxygen atoms of ethereal or carbonyl groups [11]. The IR spectra of mixtures of propargyl n-propyl sulfide with the dimethyl ether of diethylene glycol, a model compound, shows that H bonds must be formed between the acetyl hydrogen of the sulfide and the ether groups of the compound.

We have already observed [12] a certain similarity in the gas chromatographic behavior of the sulfur- and oxygen-containing compounds. In fact we showed in our earlier work that there was a linear correlation between the retention indices, of the aliphatic sulfides, on the one hand, and of similarly structured ethers, on the other, determination being made under identical conditions. To check the applicability of this same approach to the unsaturated compounds, we have synthesized the vinylethyl, allylethyl, and propargylethyl ethers, and compared the retention indices of the sulfides, on the one hand ($I_S$), and the ethers of analogous structure ($I_O$), on the other: $\delta I_{S-O} = I_S - I_O$. Values of the retention indices and $\delta I_{S-O}$ are shown in Table 3.

The values of this table indicate that $\delta I_{S-O}$ was essentially constant for each of the stationary phases. It is reasonable to assume that a similar relation would also apply to the other members of the various homologous series, in which case the $\delta I_{S-O}$ values could be used to calculate retention indices for the unsaturated sulfides from retention data on the oxygen-containing analogs.

## CONCLUSIONS

1. Retention indices have been determined for 30 vinyl, allyl, and propargyl alkyl sulfides, working with columns packed with Apiezon M, Silicone OV-17, Triton X-305, and Polyethylene glycol-1000 at 130°C.

2. Equations have been developed relating the retention indices for these sulfides with the number of carbon atoms in the n-alkyl radical chain, and with the retention indices of the analogous saturated sulfides.

3. The earlier reported analogy between the gas-chromatographic behavior of the sulfur- and oxygen-containing compounds has been shown to extend to the unsaturated sulfides and ethers of the same homologous series.

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