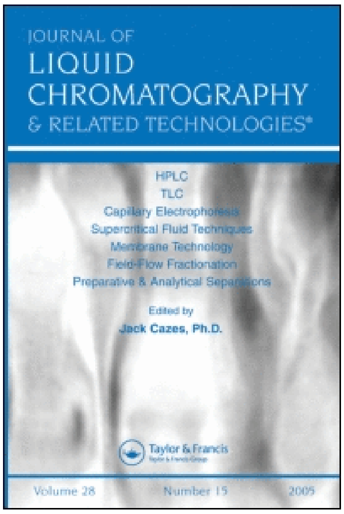

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RPLC RETENTION OF OXYGEN CONTAINING NON-IONIC ORGANIC SULFUR COMPOUNDS

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ABSTRACT

All formal oxidation products of alkylthioethers (alkyl sulfides) from alkanesulfenic acid ester through dialkylsulfate have been investigated via HPLC at an ODS phase. The possible bond states of oxygen-sulfur, >S=O and R-O-S, produce different retention effects. The former reduces retention strongly, the latter only little. In sulfoxides and sulfones, insertion of O between R and S leads to a pronounced retention increase. The observed retention changes can be coarsely related to solute dipole moments. The correlation between retention and solute size is good for different terminal groups R.

INTRODUCTION

The introduction of oxygen into organic molecules generally increases solute polarity and, consequently, reduces retention in reversed-phase LC (RPLC). Recently, it has been shown that oxygen atoms between sulfur chains and aliphatic terminal groups reduce retention less than they do, for example, in ethers or alcohols [1,2,3]. In terms of retention indices, replacing one CH_2 group by one O atom lowers retention by about 600 units. Upon replacing one CH_2 adjacent to a sulfur chain, an index decrease on the order of only 100 units is observed. It has been proposed that oxygen bonded to sulfur has a reduced ability to form hydrogen bridges [2], but a conclusive explanation of the observed effects has not yet been reached.

There is a remarkable variety of oxygen containing organic sulfur compounds which can formally be regarded as oxidation products of thioethers or di- and polysulfides. There is little information about the liquid chromatographic properties of these compounds. A separation method appears desirable because the species under consideration are frequently formed as mixtures, and many of them are easily converted into others , e.g. via oxidation reactions [4].

It will be of particular interest to investigate the influence on retention of oxygen in its different forms of being bonded to sulfur, namely >S=O and -S-O-R. Retention data shall be discussed in terms of retention indices and related to molecular properties such as solute molecular surface area and dipole moment.

EXPERIMENTAL

The apparatus was assembled using a Gynkotek 300 C pump, a helium driven Valco C6W injection valve, a Knauer 98.00 refractive index detector, and a Trio integrator. The column 250•4.6 mm SS Inertsil ODS II 5 µ (Melz-VDS) was kept in a thermostated water bath at 40°C. The eluent was 80% MeOH (Promochem Chrom AR) and 20% water purefied in a Millipore set. Composition was determined by weight. The eluent was helium-sparged.

Sulfides, Disulfides, dimethyl and diethyl sulfites, -sulfates and -sulfones are commercially available, also diphenyl and dibenzyl sulfoxide and -sulfone, dimethyl and dibutyl sulfone, dimethyl sulfoxide and methanesulfonic acid methyl ester.

The other sulfoxides [5] and sulfones [6] were prepared by oxidation of the respective sulfides with sodium periodate or hydrogen peroxide. The sulfites [7], sulfoxylates [8], dialkoxydisulfides [9], and dialkylsulfates [10,11] were synthesized according to the literature. Sulfenates [12], Sulfonates [13,14], and diphenylsulfate [15] were prepared by reacting the respective sulfenyl chlorides [16,17], sulfonyl chlorides (Lancaster or Aldrich) and chlorosulfonic acid phenyl ester [18] with the appropriate alcohols or alcoholates. The n-alkylsulfinic acid esters can be made according to the Wenschuh [19] method in the sense of a thio - Arbusow rearrangement from sulfoxylates and alkyl iodides. The isopropyl compound cannot be made this way. The formation of benzylsulfinic acid benzyl ester has been described by Thompson [4], that of methanethiosulfonic acid methyl ester by Douglas and Farah [20]. 1-Isopropoxy-ω-isopropyl disulfide and trisulfide were made, following the method of Kagami and Motoki [21], from diisopropylsulfoxylate or diisopropoxydisulfide, respectively, and isopropyl mercaptane. In the case of the sulfoxylate, the addition of catalytic amounts of the sodium thiolate was necessary.

For the synthesis of diethyl and diisopropyl trisulfides and tetrasulfides, 45 mmol freshly distilled thiole in 10 ml dry pentane were ice cooled and stirred. 15 mmol distilled SCl_2 (S_2Cl_2) in 5 ml dry pentane were added slowly. During the reaction (≈ 30 min), the HCl formed was removed by blowing argon through the mixture. The excess thiole and pentane were removed in vacuo at room temperature.

RESULTS

Table 1 shows the different compound classes which have been investigated and the terminal groups for each class. In most cases, homologous series CH_3-$(CH_2)_x$- [S,O] - $(CH_2)_x$-CH_3 were prepared because such series permit the separation of retention effects of the terminal groups from those of the functional group or substituent [22-26].

In tables 2 - 10, the experimental retention times t_{msr}, the natural logarithm of the capacity factors ln k′, and the retention indices I_K for the different solute classes are shown. The raw retention time t_{msr} as read from the integrator comprises the extra-column dead time of 0.123 min at a flow rate of 1.0 ml/min. For the calculation of ln k′ , the column dead time t_m must be known. t_m has been determined in three ways :

1) as the average of peak times of signals obtained from injection of samples of 85%MeOH/15%H_2O and of 75%MeOH/25%H_2O when running the RPLC system with an 80%MeOH/20%H_2O eluent. Raw dead time t_{mr} values between 2.553 min and 2.624 min were found over a time period of 2 weeks.

2) Application of the t(n+1)/ t(n) method according to Berendsen [27] to the series of sulfoxides yielded t_{mr} between 2.497 and 2.560 min.

3) Application of the same method to n-alkanes gave lower values around 2.3 min. It seems that the low polarity alkanes experience a smaller dead volume than the more polar solutes. Such a non-uniformity of dead volumes has been mentioned by Engelhardt [28].

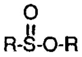
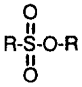
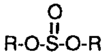
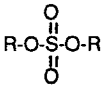
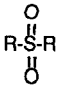
For further calculations, an average value of t_{mr} = 2.560 min and t_m = 2.437 min was used. This is only an approximation as it can be shown that for solutes of increasing chain length, the effective t_m decreases due to the solute size dependence of the accessibility of the pore volume [29].

The retention index quotes retention relative to that of n-alkanes, the ln k′of which is given by

$$(1) \qquad \ln k' = \mathbf{a} + \mathbf{b} \cdot n_C$$

TABLE 1

Investigated compounds. Names, structures and terminal groups.

Compound Class	Structure	Terminal Groups
Disulfides	R-S-S-R	Me-Pe, iPr, Bz, Ph
Tri-, Tetrasulfides	R-S-S-S-R R-S-S-S-S-R	Et, iPr
1-Alkoxy,ω-alkyl-di- and trisulfides	R-O-S-S-R R-O-S-S-S-R	iPr
1,w-Dialkoxy-Disulfides	R-O-S-S-O-R	Et, iPr, Npe, Bz
Sulfides	R-S-R	Me-Hx, iPr, Bz, Ph
Sulfenates	R-O-S-R	Et, iPr
Sulfoxylates	R-O-S-O-R	Me-Hx, iPr, iBu, Npe
Sulfinates	 $R-\overset{\overset{O}{\|}}{S}-O-R$	Me-Bu, iPr, Bz
Sulfonates	 $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-R$	Me-Pr, Bz, Ph
Sulfites	 $R-O-\overset{\overset{O}{\|}}{S}-O-R$	Me-Hx, iPr, Bz, Ph
Sulfates	 $R-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-R$	Me-Hx, iPr, Ph
Sulfoxides	 $R-\overset{\overset{O}{\|}}{S}-R$	Me-Hx, iPr, Bz, Ph
Sulfones	 $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-R$	Me-Hx, iPr, Bz, Ph

Abbreviations : Me - Hx = Methyl - n-Hexyl, iPr = isoPropyl, iBu = isoButyl, Npe = Neopentyl, Ph = Phenyl, Bz = Benzyl

TABLE 2
Retention Data of Sulfides
Column 250x4.6 mm Inertsil ODS 5μ, 40°C, 1 ml/min
MeOH/H_2O 80/20 v/v

Compound	tmsr [min]	ln k′	IK	ΔI
MeSMe	3.65	- 0.8086	20.7	-279.3
EtSEt	4.77	- 0.1027	195.9	- 304.1
PrSPr	7.73	0.7494	407.2	- 292.8
BuSBu	13.91	1.5370	602.5	- 297.5
PeSPe	27.39	2.3199	796.7	- 303.3
HxSHx	57.10	3.1068	991.8	- 308.2
iPrSiPr	6.47	0.4713	338.2	-361.2
BzSBz	10.72	1.2073	520.7	-979.3
PhSPh	10.20	1.1410	504.3	-795.7

which holds for C_5 to C_{17} in ODS/MeOH systems with sufficient accuracy [29,30]. The index is defined [31,32] as

$$(2) \qquad I_K(A) = (100/\mathbf{b}) \bullet [\ln k'(A) - \mathbf{a}]$$

The index change ΔI is the index of a particular compound, minus the index of an n-alkane having the same number of skeleton atoms :

$$(3) \qquad \Delta I(A) = I_K(A) - 100 \bullet n_{skeleton}$$

All atoms other than hydrogen are counted as skeleton atoms. It would have been more appropriate to subtract from I_K the retention index of a homomorphe alkane in Schomburg′s sense [33] (e.g. 4,4-dimethylheptane in the case of diethylsulfate), but these reference compounds were not available.

Many of the investigated compounds have very low retention. In order to obtain reasonably accurate retention indices under these circumstances, a set of n-alkanes was added to the sample solution, and all necessary calculations were carried out on the basis of this internal reference system. That is the reason why values obtained this way, and values calculated using the average dead time of 2.437 min show some difference in several cases.

The n-alkyl thioethers form a homologous series with a step width of 2 CH_2-groups. The ln k′ can be approximated as a linear function of carbon number n_C :

(4) $\ln k' = a + b \cdot n_C = -1.6296 + 0.3947 \cdot n_C$; r= 3N8 ; (C_2 - C_{12})
(4a) $\ln k' = -1.6065 + 0.3928 \cdot n_C$; r=6N4 ; (C_6 - C_{12})

r is the correlation coefficient, expressed as 3N8 = 0.9998. In parentheses is given the carbon number range included in the regression calculation.
Similarly, the retention indices I_K may be written as :

(5) $I_K = A + B \cdot n_C = -183.3 + 97.9 \cdot n_C$; r=3N8 ; (C_2 - C_{12})
(5a) $I_K = -177.1 + 97.4 \cdot n_C$; r=6N4 ; (C_6 - C_{12})

The di-n-propyl through di-n-hexyl sulfides are almost perfectly linear over n_C. Methyl and ethyl compounds deviate more strongly. There are two apparent reasons. First, the surface area of sulfides shows a linear dependence on n_C only for propyl and higher terminal groups. Second, the aliphatic groups closest to the hetero atom are influenced more strongly by inductive forces than the groups further away.
Obviously, the index contribution of CH_2 in thioethers is slightly influenced by the presence of the S atom, since, in n-alkanes, B would be 100. The reduction of CH_2 increments in sulfur compounds has already been described [34]. The A term comprises the difference between CH_3 and CH_2 increments, and the increment of the sulfur atom. The latter may be composed of several effects. The value of ΔI for, e.g., diethylsulfide, of - 303.6 shows, that replacing the central CH_2 group in n-pentane by S reduces retention to that of a hypothetical alkane having 1.96 C atoms. The ΔI is composed of 1) the loss of 1 CH_2 contributing ≈ -100 units, 2) the introduction of 1 S, which, in polysulfides, produces ≈ + 110 units at $MeOH/H_2O$ = 80/20, and 3) a remaining difference of ≈ - 300 units, which has been attributed to the formation and solvatization of local polar centres at the CH_2-S bonds [32]. The isopropyl sulfide exhibits less retention than the n-propyl sulfide which is in part due to its smaller surface area. The area ratio, however, is clearly lower than the index ratio which may indicate that the contact to the stationary phase is less for the branched compound [35]. The phenyl compound has relatively low retention, due to the presence of aromatic systems which have an increased interaction with the mobile phase. The methylene groups in the benzyl sulfide produce almost zero retention, although they increase the surface area of the molecule appreciably. It is obvious that the hydrogen atoms on these groups are activated and interact strongly with the eluent. This is a well known effect frequently observed with methylene groups bonded to electron withdrawing substituents, e.g. with diphenyl, diphenylmethane, triphenylmethane series.

Alkyl disulfides produce more retention than sulfides, which is attributed to the increased size. The index increase is on the order of 130. In the phenyl and benzyl compound, the index increase is only around 80 units. This may indicate that the sulfur electron density is disturbed by the aromatic rings, inducing an increased interaction with the eluent. In disulfides, the benzyl compound has less retention than the phenyl. It seems that the methylene hydrogen atoms get even more activated such that they destroy more retention via eluent interaction than they produce due to the increased cavity energy. It is tentatively suggested that electron density from the methylene C-H bonds can delocalize into sulfur atoms and chains, the more effectively the larger the sulfur system is.

TABLE 3
Retention Data of Disulfides
Conditions as in table 2

Compound	tmsr [min]	ln k′	IK	ΔI
MeSSMe	4.45	-0.2593	157.4	-242.6
EtSSEt	6.55	0.4915	343.4	-256.6
PrSSPr	11.33	1.2790	538.5	-261.5
BuSSBu	21.45	2.0469	728.8	-271.2
PeSSPe	43.12	2.8111	918.2	-281.8
iPrSSiPr	9.87	1.0972	493.5	-306.5
BzSSBz	13.07	1.4600	583.4	-1016.6
PhSSPh	14.16	1.5592	608.0	-792.0

TABLE 4
Retention Data of Sulfoxylates
Conditions as in table 2

Compound	tmsr [min]	ln k′	IK	ΔI
MeOSOMe	3.51	- 0.9406	- 10.5	- 510.5
EtOSOEt	4.52	- 0.2169	168.6	- 531.4
PrOSOPr	7.11	0.6250	377.0	- 523.0
BuOSOBu	12.49	1.4048	570.0	- 530.0
PeOSOPe	23.92	2.1710	759.7	- 540.3
HxOSOHx	48.26	2.9318	948.0	-552.0
iPrOSOiPr	6.37	0.4462	332.8	-567.2
iBuOSOiBu	12.23	1.3788	563.6	-536.4
nePOSOneP	21.22	2.0361	726.3	-573.7

(6) $\ln k' = -1.0350 + 0.3848 \cdot n_C$; r=4N8 ; (C_2 - C_{10})
(6a) $\ln k' = -1.0185 + 0.3830 \cdot n_C$; r=6N0 ; (C_6 - C_{10})
(7) $I_K = -34.8 + 95.4 \cdot n_C$; r=4N8 ; (C_2 - C_{10})
(7a) $I_K = -30.9 + 94.9 \cdot nC$; r=4N8 ; (C_6 - C_{10})
(8) $\ln k' = -1.7347 + 0.3901 \cdot n_C$; r=3N8 ; (C_2 - C_{12})
(8a) $\ln k' = -1.6758 + 0.3843 \cdot n_C$; r=4N8 ; (C_6 - C_{12})
(9) $I_K = -207.1 + 96.6 \cdot n_C$; r=3N8 ; (C_2 - C_{12})
(9a) $I_K = -192.5 + 95.1 \cdot n_C$; r=4N8 ; (C_6 - C_{12})

It is seen that the introduction of 2 oxygen atoms into a sulfide molecule does not change retention very much. The ΔI is more negative, because the reference alkanes now have 2 more C-atoms.

(10) $\ln k' = -3.322 + 0.395 \cdot n_C$
(11) $I_K = -602.6 + 98.0 \cdot n_C$

Both sulfinate equations are crude estimates because only propyl and butyl data was used. The methyl and ethyl compounds elute too close to the dead time. If ethyl data is included, B in eq. 11 goes up to 105.4. Such a high value is very unlikely to be real because in all homologous series we have investigated so far, a methylene increment exceeding that in alkanes by more that the average data scatter has never been observed.
Nevertheless, it is obvious that, in these solutes which are isomers of the sulfoxylates, the retention change ΔI is much more negative.

TABLE 5
Retention Data of Sulfinates
Conditions as in table 2

Compound	tmsr [min]	ln k´	IK	ΔI
Me(SO)OMe	2.69	- 2.8495	- 485.7	- 985.7
Et(SO)OEt	2.93	-1.8532	- 238.6	- 938.6
Pr(SO)OPr	3.50	- 0.9402	- 12.2	- 912.2
Bu(SO)OBu	4.64	-0.1541	182.8	-917.2
iPr(SO)OiPr	3.37	-1.0900	-49.3	-949.3
Bz(SO)OBz	4.27	-0.3459	135.3	-1564.7

TABLE 6
Retention Data of Sulfites
Conditions as in table 2

Compound	tmsr [min]	ln k′	IK	ΔI
MeO(SO)OMe	2.90	-1.9729	- 268.1	- 868.1
EtO(SO)OEt	3.30	- 1.1936	- 74.9	- 874.9
PrO(SO)OPr	4.30	- 0.3379	137.3	- 862.7
BuO(SO)OBu	6.40	0.4527	333.4	- 866.6
PeO(SO)OPe	10.68	1.2030	519.4	- 880.6
HxO(SO)OHx	19.80	1.9557	706.1	- 893.9
iPrO(SO)OiPr	3.95	-0.5626	81.6	-918.4
BzO(SO)OBz	5.90	0.3130	298.7	-1501.3
PhO(SO)OPh	5.50	0.1869	267.5	-1332.5

TABLE 7
Retention Data of Sulfonates
Conditions as in table 2

Compound	tmsr [min]	ln k′	IK	ΔI
Me(SO$_2$)OMe	2.62	- 3.5562	-661.0	-1261.0
Et(SO$_2$)OEt	2.80	- 2.2966	- 348.6	-1148.6
Pr(SO$_2$)OPr	3.22	- 1.316	- 101.5	- 1101.5
Me(SO$_2$)OMe	-	- 2.904*	- 498.5*	- 1098.5*
Et(SO$_2$)OEt	-	- 1.742*	- 210.6*	- 1010.6*
iPr(SO$_2$)OiPr	3.14	-1.4292	-133.4	-1133.4
Bz(SO$_2$)OBz	3.82	-0.6493	60.0	-1740.0
Ph(SO$_2$)OPh	3.97	-0.5411	86.9	-1513.1

(12) $\ln k' = -2.7445 + 0.3946 \cdot n_C$; r=3N7 ; ($C_2 - C_{12}$)
(12a) $\ln k' = -2.6156 + 0.3816 \cdot n_C$; r=4N2 ; ($C_6 - C_{12}$)
(13) $I_K = -459.5 + 97.9 \cdot n_C$; r=3N7 ; ($C_2 - C_{12}$)
(13a) $I_K = -427.5 + 94.6 \cdot n_C$; r=4N2 ; ($C_6 - C_{12}$)

Comparing these data with table 4, it is seen that the insertion of an O atom between R and the -(SO)- group increases the retention index by about 140 units.

(14) $\ln k' = -3.698^{*} + 0.397^{*} \cdot n_C$
(15) $I_K = 695^{*} + 98.5^{*} \cdot n_C$

The retention times of the methyl and ethyl compound are so close to the dead time that the error is probably very high. The values marked with an asterisk were obtained by taking the average of the b data from sulfates and sulfones which have one more and one less oxygen atom, respectively, in correspondig positions, as an approximate b value for sulfonates, and subtracting the appropriate multiples from ln k′ of propanesulfonic acid propyl ester. This data should be regarded as a crude estimate.

(16) $\ln k' = -3.3134 + 0.4043 \cdot n_C$; r=3N6 ; ($C_2 - C_{12}$)
(16a) $\ln k' = -3.1435 + 0.3869 \cdot n_C$; r=4N1 ; ($C_6 - C_{12}$)
(17) $I_K = -593.8 + 99.8 \cdot n_C$; r=3N6 ; ($C_2 - C_{12}$)
(17a) $I_K = -552.0 + 95.6 \cdot n_C$; r=4N1 ; ($C_6 - C_{12}$)
(18) $\ln k' = -4.0913 + 0.3798 \cdot n_C$ (r=0.9997)
(19) $I_K = -793.0 + 94.1 \cdot n_C$

Calculation of eq. 18 and 19 was done with propyl to hexyl data only.

(20) $\ln k' = -4.3644 + 0.3957 \cdot n_C$ (r=0.9996)
(21) $I_K = -861.2 + 98.1 \cdot n_C$

TABLE 8
Retention Data of Sulfates
Conditions as in table 2

Compound	tmsr [min]	ln k′	IK	ΔI
$MeO(SO_2)OMe$	2.75	-2.5393	-402.7	-1102.7
$EtO(SO_2)OEt$	3.00	- 1.7175	- 199.7	- 1099.7
$PrO(SO_2)OPr$	3.62	-0.8348	18.2	- 1081.8
$BuO(SO_2)OBu$	4.92	-0.0320	216.4	- 1083.6
$PeO(SO_2)OPe$	7.63	0.7322	405.1	- 1094.9
$HxO(SO_2)OHx$	13.37	1.4900	592.3	- 1107.7
$iPrO(SO_2)OiPr$	3.41	-1.0485	-34.5	-1134.5
$PhO(SO_2)OPh$	4.98	-0.0086	222.2	-1477.8

TABLE 9

Retention Data of Sulfoxides

Conditions as in table 2

Compound	tmsr [min]	ln k′	IK	ΔI
Me(SO)Me	2.60			
Et(SO)Et	2.70			
Pr(SO)Pr	2.95	- 1.8356	- 233.8	- 1033.8
Bu(SO)Bu	3.44	-1.0202	- 31.8	- 1031.8
Pe(SO)Pe	4.38	- 0.2911	148.9	- 1051.1
Hx(SO)Hx	6.40	0.4536	333.5	- 1066.5
iPr(SO)iPr	2.91	-1.9536	-263.3	-1063.3
Bz(SO)Bz	3.45	-1.0088	-29.0	-1629.0
Ph(SO)Ph	3.33	-1.1538	-65.0	-1465.0

TABLE 10

Retention Data of Sulfones

Conditions as in table 2

Compound	tmsr [min]	ln k′	IK	ΔI
Me(SO_2)Me	2.56			
Et(SO_2)Et	2.65			
Pr(SO_2)Pr	2.89	- 2.0183	- 279.4	- 1179.4
Bu(SO_2)Bu	3.32	- 1.1669	- 68.2	- 1168.2
Pe(SO_2)Pe	4.22	- 0.3880	124.9	- 1175.1
Hx(SO_2)Hx	6.06	0.3599	310.4	- 1189.6
iPr(SO_2)iPr	2.81	-2.2823	-344.8	-1244.8
Bz(SO_2)Bz	3.30	-1.1982	-76.0	-1776.0
Ph(SO_2)Ph	3.30	-1.1982	-76.0	-1576.0

TABLE 11
Retention Data of Various Compounds
Conditions as in table 2

Compound	tmsr [min]	ln k´	IK	ΔI
Et-SSS-Et	9.21	1.0015	469.7	-230.3
Et-SSSS-Et	12.28	1.3819	564.0	-236.0
iPr-SSS-iPr	14.81	1.6135	621.5	-278.5
iPr-SSSS-iPr	20.18	1.9769	711.6	-288.4
Et-S-O-Et	4.24	-0.3710	130.5	-469.5
iPr-S-O-iPr	5.80	0.2845	292.7	-507.3
Et-O-SS-O-Et	5.91	0.3165	300.0	-500.0
iPr-O-SS-O-iPr	8.37	0.8669	436.4	-563.6
Npe-O-SS-O-Npe	34.76	2.5803	861.7	-538.3
Bz-O-SS-O-Bz	14.13	1.5562	607.2	-1192.8
iPr-O-SS-iPr	9.69	1.0719	487.1	-412.9
iPr-O-SSS-iPr	12.60	1.4143	572.1	-527.9
$Me(SO_2)SMe$	2.72	-2.7650	-463.7	-1063.7

DISCUSSION

Data presented in the results section show that the retention effects caused by insertion of up to four oxygen atoms into a thioether vary over an unexpectedly broad range.This is schematically illustrated in figure1 for the diethyl compounds. The sulfide has a retention index of 195.9. Insertion of 1 oxygen between Et and S with sp^3 σ–bonds yields the sulfenate which has a somewhat lower index of 130.5. If, however, the O atom is $\sigma + d\pi$ bonded only to sulfur, yielding the sulfoxide, there is a hughe retention loss of 680 units which is similar to the effect observed with the formation of an alcohole or an amine [2]

A second O atom can be placed into either one of the positions just mentioned. If it is located "in chain", yielding the sulfoxylate, it increases retention slightly with respect to the sulfenic acid ester, up to 168.6, which is still a little less than in the thioether. Attached to the sulfur atom, it produces the sulfone which has even lower retention than the sulfoxide (I_K = - 593.9). The diethyl sulfone retention corresponds to a sorption free enthalpy of about + 4.3 kJ / mole which shows that the sulfone group is extremely solvophilic.

Now it is interesting to observe the changes occuring upon insertion of purely σ bonded O atoms into the sulfoxide and sulfone. One oxygen atom added to the

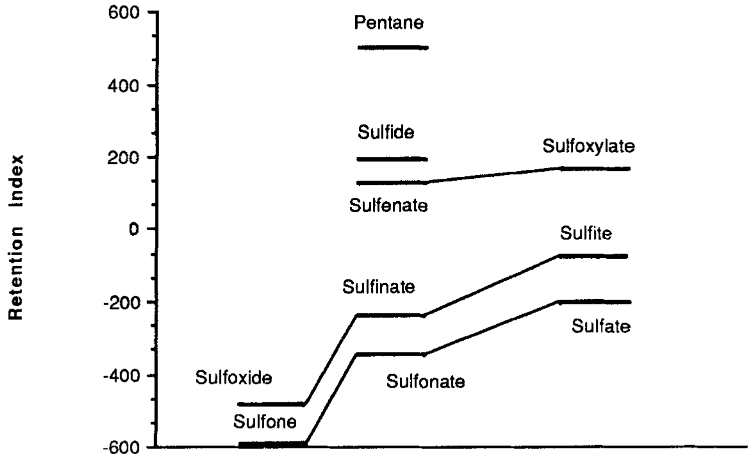


FIGURE 1

sulfoxide yields the sulfinate with a retention index increase of non less than 246.3 units. One more O leads to the sulfite, and the index goes up by another 163.7 units. In the case of diethyl sulfone, the effects are similar. The first step to the sulfonate increases retention by 245.3 index units, the second to the sulfate by another 148.9 units. It has to be mentioned that a similar effect has been observed in ion pair chromatography of dodecyl sulfonate and dodecyl sulfate where the latter has clearly higher retention than the former [36].

Data from table 8 show that the sorption free enthalpy of diethyl sulfate is +1 kJ / mole, that of dipropyl sulfate - 1.3 kJ / mole. If it is assumed that a formal coefficient of solute partition between stationary and mobile phase, $K > 1$, indicates solvophobicity, dipropyl sulfate can already be regarded as solvophobic, while diethyl sulfate is solvophilic.

The difference ΔI between the retention index of the solute under consideration and an n-alkane having the same number of skeleton atoms, varies, in the case of ethyl compounds, from zero for the alkane itself to -1300 for the sulfone. Figure 2 shows ΔI versus dipole moment μ as taken from the literature [37,38]. The correlation is obvious, although not perfect. One possible reason for the deviations might be the different size of the solutes. Another could be a change of dipole moment with eluent polarity.

The dependence of retention on the length of the alkyl groups is pooled in table 13 which gives the parameters of the ln k′ and I_K equations.

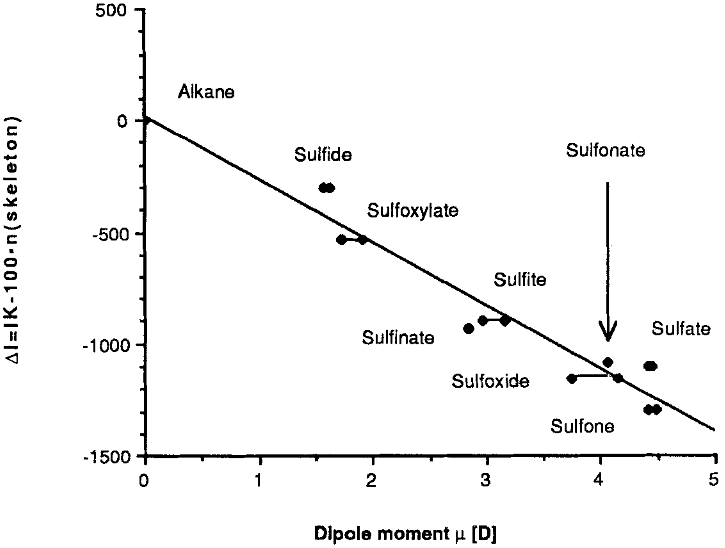


FIGURE 2

TABLE 13

Parameters of equations ln k′ = a + b•n_C and IK = A + B•n_C

na and ne carbon number of first and last member used for regression, r = correlation coefficient, expressed as 4N4 = 0.99994. Values * for sulfonates are tentative, see text.

Series	na	ne	a	b	r	A	B
Sulfides	2	12	-1.6296	0.3947	4N4	-183.3	97.9
Sulfides	6	12	-1.6065	0.3928	6N4	-177.1	97.4
Disulfides	2	10	-1.0350	0.3848	4N8	-34.8	95.4
Disulfides	6	10	-1.0185	0.3830	6N0	-30.9	94.9
Sulfoxylates	2	12	-1.7347	0.3901	3N8	-207.1	96.6
Sulfoxylates	6	12	-1.6758	0.3843	4N8	-192.5	95.1
Sulfinates	6	8	-3.32	0.40	----	-600	98
Sulfites	2	12	-2.7445	0.3946	3N8	-459.5	97.9
Sulfites	6	12	-2.6156	0.3816	4N2	-427.5	94.6
Sulfonates*	2	6	-3.70	0.40	----	-695	99
Sulfates	2	12	-3.3134	0.4043	3N6	-593.8	99.8
Sulfates	6	12	-3.1435	0.3869	4N1	552.0	95.6
Sulfoxides	6	12	-4.0913	0.3798	3N7	-793.0	94.1
Sulfones	6	12	-4.3644	0.3957	3N6	-861.2	98.1

Slopes B are slightly lower than the alkane value of 100, possibly reflecting the size increase caused by the hetero atoms, which, in turn, lowers the pore volume accessibility by at few percent. In addition, there appears to be an influence of hetero atoms on the intrinsic retention production of methylene groups. This effect is generally observed with substituents having the ability to withdraw some electon density from alkyl groups, e.g. S, O, Cl, Br, etc.

Intercepts A vary strongly from one compound class to the other. Fig. 3 shows how intercepts A depend on the dipole moment μ. There seem to be two groups of solutes, each of which forms a reasonably good straigth line. Alkanes, sulfides, sulfoxylates, sulfites and sulfates have either no oxygen at all, or two R-O-S groups. Sulfinates, sulfoxides and sulfones have >S=O groups and no or only one R-O-group bonded to sulfur. The index difference between sulfone and sulfate, 394.2 units, is large, while dipole moments are almost identical. This indicates that the overall dipole moment as measured in the gas phase or in nonpolar solvents is not a very good descriptor for the polar effects influencing the retention of the compounds under consideration.

The remarkably low retention change after inserting oxygen between sulfur and alkyl group of thioethers has also been found with disulfides and trisulfides :

iPr-S-iPr → iPr-S-O-iPr ∴ - 45.5 index units
iPr-SS-iPr → iPr-SS-O-iPr ∴ - 51.5 "
iPr-SSS-iPr → iPr-SSS-O-iPr ∴ - 49.4 "
iPr-SS-iPr → iPr-O-SS-O-iPr ∴ - 57.1 "

Naturally, retention decreases more strongly if S atoms are <u>replaced</u> by O atoms :

iPr-SSSS-iPr ——→ iPr-SSSO-iPr ——→ iPr-OSSO-iPr
(- 139.5) (- 135.7)
or
iPr-SSS-iPr ----→ iPr-SSO-iPr ——→ iPr-OSO-iPr
(- 134.4) (- 154.3)

The retention index changes comprise a retention loss of about -100 to - 120 index units caused by the leaving S atom and a contribution of - 25 to -50 units caused by the O atom itself. The substantial scatter in these values occurs because the ln k′ and I_K of sulfides and polysulfides vary nonlinearly with sulfur rank in the range from S_1 to S_4. This has been attributed to an alternating dipole moment [32,39]. Recent low temperature NMR measurements indicate a conformational change of polysulfides at S_4, which seems to be an important factor contributing to non-linearity [40].

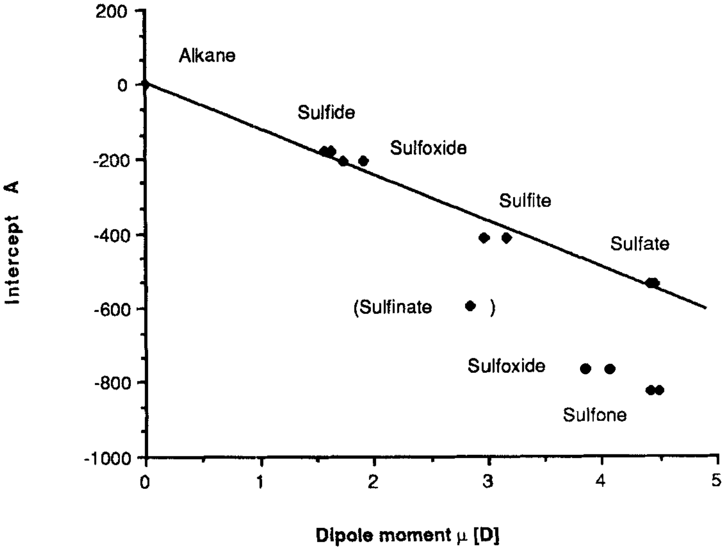


FIGURE 3

CONCLUSION

Oxygen atoms bonded to sulfur in organic compounds produce retention effects which depend strongly on the status of the oxygen - sulfur bond. In a sp^3 - σ - bonded R-O-S- or R-O-S-O-R, a small retention decrease is observed. In a bond with high $d\pi$ - content >S=O , the retention loss is similar to that in an alcohol or amine. If sp^3 - σ - bonded O is introduced into sulfoxides or sulfones, which have >S=O groups, it increases retention substantially.

There is a good correlation of retention of organic O - S - molecules with hydrocarbonaceous surface area, and a crude correlation with molecular dipole moment. The former has a positiv, the latter a negative coefficient. The actual reasons which govern retention on a molecular basis have not yet been identified.

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