Gas-liquid chromatography of thioesters of perfluorocarboxylic acids
1. Characteristics of retention

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Retention of thioesters of perfluoropentanoic acid $C_4F_9C(O)SR$ was studied by GLC on packed and capillary columns using stationary phases SE-30, SKTFT-50X, XE-60, and Carbowax 20M. The retention indices of these compounds were calculated, and their relationship with the structure of the compounds and the conditions of the analysis were established.

Key words: gas-liquid chromatography; thioesters of perfluoropentanoic acid, retention indices.

Previously, we have studied the variation of retention parameters and thermodynamic functions for the sorption of esters (E) and amides of perfluorocarboxylic acids (PFA) on stationary phases (SP) of various polarities.[1–4] It was found that the contributions of methylene and difluoromethylene groups to retention indices (RI) largely depend on the remoteness of these groups from the functional group and the nature of the SP. The presence of perfluoroalkoxycarbonyl group enhances the nonadditivity of the contributions of methylene units to the sorption parameters compared to those in nonfluorinated esters.[1–3] The replacement of the carbonyl group by an amide group results in an increase in the RI, which is the larger, the more polar is SP, and in the enhancement of the nonadditivity of the contributions of difluoromethylene groups on polar SP.[4]

Although some thioesters of perfluorocarboxylic acids (TE PFA) have been synthesized previously and their physicochemical characteristics have been obtained,[5] the GC behavior and sorption properties of these compounds have not yet been studied. PFA thioesters are a convenient analytical form for the determination of small concentrations of thiols;[6] therefore, a more detailed study of these compounds is of practical interest.

Up to now, data on the RI for ~500 sulfur-containing organic compounds have been systematized. The GLC behavior of thiols and dithiols,[7] sulfides,[8] esters of thiocarboxylic acids,[9] and S-, N-, and O-analogs of heterocyclic compounds[10] have been studied, and thermodynamic functions of sorption of fragments of members of homologous and pseudohomologous series have been considered. Dispersion forces play a crucial role in the interaction of the compounds studied with nonpolar SP; in the case of polar SP, an additional contribution to retention is made by induction, orientation, and donor-acceptor interactions.[7–11] The replacement of the O atom by the S atom increases the differential molar free energy of sorption on SP of various polarities by 4.2—4.4 kJ mol^{-1} (see Ref. 11).

The purpose of this study is to follow the regularities of retention of thioesters of perfluoropentanoic acid (TE PFPA) on SP of various polarities, to elucidate the effects of the replacement of the O atom by the S atom and of the extension of the alkyl chain in the molecule on the retention parameters.

Experimental

GLC studies were carried out on a Tsvet-550M chromatograph with a FID and glass columns (3 m × 1.5 mm) packed with Chromaton N AW-HMDS (0.16—0.20 mm) with supported SP: 10% SKTFT-50X or 10% SE-30, or with Chromaton N AW-DMCS (0.16—0.20 mm) with 5% XE-60; argon was used as the carrier gas (flow rate 30 mL min^{-1}). In addition, a Shimadzu gas chromatograph with a micro-FID and quartz capillary columns (25 m × 0.25 mm) with supported SE-30 and Carbowax-20M SP was used; helium was used as the carrier gas (flow rate 30 mL min^{-1}), the flow rate of hydrogen was 30 mL min^{-1}, that of air was 300 mL min^{-1}; the flow was split in a ratio of 1 : 50. The temperature of the thermostat for the columns was 60—180 °C, that of the evaporating chamber was 120—220 °C, and that of the FID was 200 °C.

Solutions (0.01—0.1 mg mL^{-1}) of pure samples of TE and E PFPA ($C_4F_9C(O)SR$ and $C_4F_9C(O)OR$, R = Me, Et, ..., C_6H_{13}) in *n*-hexane were used for the measurements. The retention time for the non-sorbable gas (t_0) was calculated by the Peterson—Hirsch procedure:

$$t_0 = (t_1t_3 - t_2^2)/(t_1 + t_3 - 2t_2),$$

where t_1, t_2, and t_3 are retention times of three neighboring homologs of *n*-alkanes. The Kovats retention indices were calculated from the equation

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 984—986, May, 1997.

1066-5285/97/4605-0944 $18.00

$$I = 100(\log t'_x - \log t'_m)/(\log t'_{m+1} - \log t'_m) + 100m,$$

where t'_x, t'_m, and t'_{m+1} are corrected retention times of the analyzed compound and of the neighboring *n*-alkanes, $t'_m < t'_x < t'_{m+1}$.

The contributions of the methylene groups $\Delta I_i(CH_2)$ were calculated from the RI for two neighboring homologs: $\Delta I_i(CH_2) = I_i - I_{i-1}$.

The difference between the retention indices of TE PFA and E PFA were calculated as $\Delta I_i(s—o) = I_s - I_o$, where I_s and I_o are the retention indices for S- and O-analogs having identical alkyl and perfluoroalkyl substituents.

The difference between the differential molar free energies for sorption of S-esters and the corresponding O-esters, $\Delta G_i(s—o)$, was calculated from the equation

$$-\Delta G_i(s—o) = RT \ln t'_s/t'_o,$$

where t'_s and t'_o are corrected retention times for the two analogs, $R_FC(O)SR$ and $R_FC(O)OR$.

The errors of determination of $\Delta I_i(s—o)$ were 1—3 index units (iu) on the SE-30 and SKTFT-50X phases and 1—2 iu on XE-60; the error of determination of $\Delta G_i(s—o)$ did not exceed 0.05 kJ mol^{-1} on the SE-30 and SKTFT-50X phases and 0.02 kJ mol^{-1} on XE-60.

Results and Discussion

The effect of the structure of TE PFA on the retention in the GLC analysis was estimated based on the RI of $C_4F_9C(O)S(CH_2)_iMe$ homologs (Table 1). We have chosen TE PFPA for this study, because this series of compounds makes it possible to estimate the effect of the S atom and the $C_4F_9C(O)S$ fragment on the retention of TE and on the variation of the contribution of a CH_2 group to the retention as a function of the length of the alkyl chain.

The retention indices and the $\Delta I(CH_2)_i$ contributions for TE PFPA were calculated with respect to the standard series of C_6—C_{14} *n*-alkanes and are listed in Table 1. The RI values found for packed and capillary columns with SE-30 were identical within the error of the determination (1—5 iu).

For all compounds in the homologous series of TE PFPA, the relation $I_{SKTFT-50X} > I_{XE-60} > I_{CW-20M} > I_{SE-30}$ holds in the temperature range studied (see Table 1). The fact that retention of TE PFPA on polar phases, XE-60 and CW-20M, is stronger than that on SE-30 implies that the orientation interaction of TE molecules makes a marked contribution to the retention.

The plots of RI against the number of CH_2 groups in the alkyl chain for the TE PFPA series are nonlinear, the largest deviations being observed for the first members of the homologous series (i = 1, 2).

As the temperature of the analysis (T_a) increases, the RI values decrease; the character of dependence of the RI on the structure of the molecule does not change. The effect of T_a on the values of RI is more pronounced in the case of more polar phases, XE-60 and CW-20M, than in the case of SE-30 and SKTFT-50X.

Table 1. Retention indices, I (iu), and contributions of the methylene groups, $\Delta I_i(CH_2)$, for thioesters $C_4F_9C(O)S(CH_2)_iMe$ on SP of various polarities at various temperatures

i	80 °C		100 °C		120 °C		140 °C		160 °C	
	I	ΔI	I	ΔI	I	ΔI	I	ΔI	I	ΔI
SE-30 (10%)										
0	708		697		689		688			
1	773	65	766	68	757	68	752	64		
2	851	87	854	88	847	89	838	85		
3	953	92	946	91	941	92	931	92		
4			1041	95	1034	95	1026	95		
5			1138	96	1131	96	1124	97		
SKTFT-50X (10%)										
0	849		841		836		825			
1	915	65	909	68	905	69	896	71	878	
2	1004	88	997	88	993	87	986	89	971	92
3	1099	95	1093	95	1086	93	1079	93	1070	99
4			1192	99	1182	96	1175	96	1169	99
5			1290	98	1279	97	1273	97	1267	97
XE-60 (5%)										
0	831		811		795					
1	878	46	855	44	840	45				
2	955	77	936	80	920	80				
3	1041	86	1024	88	1010	89				
4	1134	92	1118	94	1104	94				
5	1230	95	1214	96	1198	93				
CW-20M (capillary column)										
0	861		835		802		785			
1	880	18	855	20	821	19	797	12		
2	952	71	923	68	897	75	869	71		
3	1041	89.	1008	85	983	86	957	88	945	
4			1109	100	1080	97	1055	98	1050	104
5			1207	98	1180	99	1154	98	1150	99

The $\Delta I_i(CH_2)$ values on the SP studied increase as the alkyl chain becomes longer. For homologs with $i > 4$, the $\Delta I_i(CH_2)$ values approach the standard contributions (100 iu). In the case of polar SP, the deviation of the contributions of the first members of the homologous series $\Delta I_i(CH_2)$ from the standard value is more marked. For example, for SE-30 at 120 °C, $\Delta I_1(CH_2)$ = 68.5 iu and $\Delta I_2(CH_2)$ = 89.6 iu, whereas for CW-20M, $\Delta I_1(CH_2)$ = 19 iu and $\Delta I_2(CH_2)$ = 75 iu (see Table 1). The change in T_a has no substantial effect on $\Delta I_i(CH_2)$. Thus, the contributions of the methylene groups to RI are non-additive and are higher for the methylene groups located farther from the functional group.

A comparison with the RI values found previously for E PFA,[1—4] indicate that retention indices for the TE PFPA series on the SP studied are larger than those for their O-analogs (Table 2). There is no clear correlation between $\Delta I_i(s—o)$ and the length of the alkyl substituent for SE-30 and SKTFT-50X SP. The increase in T_a by 20 °C is accompanied by an increase in $\Delta I_i(s—o)$ by 1—6 iu. In the case of XE-60 SP, the $\Delta I_i(s—o)$ value decreases nonlinearly as the alkyl chain is lengthened; an increase in T_a is accompanied by a slight (by 1—2 iu) decrease in $\Delta I_i(s—o)$. For the first compound in the homologous series, the relation $\Delta I_i(s—o)_{XE-60}$ >

Table 2. Difference in the retention indices, ΔI_i(s—o), in the series $C_4F_9C(O)X(CH_2)_iMe$ (X = S, O) on SP of various polarities as a function of temperature

i	ΔI_i(s—o) (iu)							
	SE-30			SKTFT-50X			XE-60	
	80 °C	100 °C	120 °C	80 °C	100 °C	120 °C	80 °C	100 °C
0	161	162	—	134	137	139	171	—
1	154	157	161	129	132	138	163	—
2	152	156	162	129	134	140	160	—
3	154	157	161	134	137	140	158	156
4	—	158	162	—	140	140	157	155
5	—	159	163	—	141	139	156	154

$\Delta I_i(\text{s—o})_{\text{SE-30}} > \Delta I_i(\text{s—o})_{\text{SKTFT-50X}}$ holds at any T_a. At *i* > 3, the ΔI_i(s—o) values come closer to one another. The least difference between the retention of E PFPA and TE PFPA (130 iu) is observed in the case of the SKTFT-50X SP.

The increase in the retention of TE PFA with respect to that of E PFA was also described by calculations of $-\Delta G_i$(s—o), *i.e.*, the difference between the differential molar free energies of sorption of an S-derivative and its O-analog (Table 3). The highest ΔG_i(s—o) values (-3.2 kJ mol^{-1}) are typical of the SE-30 SP; they almost do not depend on the length of the alkyl chain. The values of ΔG_i(s—o) on the XE-60 SP range from -2.7 to -3.0 kJ mol^{-1} and decrease as the length of the alkyl chain increases. The smallest ΔG_i(s—o) were found for SKTFT-50X (from -2.3 to -2.6 kJ mol^{-1}); they do not depend on the length of the alkyl chain.

In a number of studies,[7—11] parameters of retention of esters and esters of thiocarboxylic acids containing a —C(S)O functional group have been determined. The $-\Delta G_i$(s—o) values amount to 3.9—4.1 kJ mol^{-1} and decrease as the alkyl chain is lengthened. An increase in the polarity of the SP leads to a decrease ΔG_i(s—o), which has been explained[7—11] by the fact that the contribution of the orientation interaction of the thionyl group becomes lower than that in the case of the carbonyl group.

Thus, on going from E PFA to TE PFA, the RI increase; this increase is more pronounced in the case of nonpolar SP. In the presence of perfluoroalkyl group, the ΔG_i(s—o) values are lower than those for other systems.[11] The ΔG_i(s—o) values in the series under consideration almost do not depend on the length of the alkyl chain in the series under consideration.

Table 3. Difference between the differential molar free energies of sorption, $-\Delta G_i$(s—o), in the series $C_4F_9C(O)X(CH_2)_iMe$ (X = O, S) on SP of various polarities at 100 °C

i	$-\Delta G_i$(s—o)/kJ mol^{-1}		
	SE-30	SKTFT-50X	XE-60
0	3.23	2.43	2.93
1	3.14	2.34	2.87
2	3.11	2.37	2.80
3	3.14	2.43	2.75
4	3.16	2.48	2.74
5	3.18	2.49	2.73

It has been found previously that on going from E PFA to dialkylamides of a similar structure, the energy of sorption increases by 4.1 kJ mol^{-1} for the OV-101 SP and by 6.7 kJ mol^{-1} for XE-60. This has been attributed to enhancement of the orientation interaction.[4] The increase in the energy of interaction of TE PFA molecules with the SP with respect to this energy for E PFA is smaller than that for amides, and, apparently, is caused to a greater extent by the increase in the dispersion interaction. At the same time, the perfluorocarbonyl group in all the homologous series considered exerts a crucial effect on the retention mechanism. The values of the difference between the RI of TE PFA and E PFA as well as the ΔG_i(s—o) values on nonpolar SP can be used as analytical characteristics in the identification of sulfur-containing compounds.

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Received June 19, 1996;
in revised form December 10, 1996