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RETENTION DATA OF CHROMIUM CHELATES WITH DIFFERENT β -DIKETONES AS LIGANDS

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SUMMARY

Relative retention data and relative heats of solution were determined for chromium chelates with five different ligands on eleven non-polar and moderately polar stationary phases in order to find the minimum retention times. It was found that minimum retention was observed for the second or third members of the homologous series of fluorinated chromium chelates. Partial fluorination of the ligands decreased the retention times of chromium chelates, particularly on stationary phases with a large number of phenyl groups in the molecule. The relative molar entropy of solution is the main factor that decreases the retention times of the fluorinated chelates.

INTRODUCTION

Mixtures of some metals can be analysed as chelates with extremely high sensitivity by gas chromatography (GC). Although the GC analysis of 46 metal chelates has been reported¹⁻⁷, quantitative results have been given for only nine metals on a level of 10^{-8} - 10^{-14} g. Poor reproducibility, chemical reactions occurring in the column and high interphase adsorption limit the quantitative analysis of chelates⁸⁻⁹. The appearance of many peaks due to decomposition products has been reported, and some attempts have been made to minimize the retention times of the chelates in the column.

The retention time can be decreased by (a) increasing the flow-rate of the carrier gas, (b) decreasing the amount of the stationary phase in the column, w_L , (c) increasing the column temperature, (d) choosing an appropriate stationary phase and (e) choosing appropriate ligands for the chelates. The carrier gas flow-rate is of limited use in achieving an acceptable column performance; decreasing w_L seems to be the most promising technique^{1,6}. However, interphase adsorption takes part in such changes and it is not desirable to use packings with $w_L < 3\%$ ⁹. When the column

temperature is increased, the decomposition rate is also increased. Hence, factors (d) and (e) seem to be the most promising for resolving the problem of chelate analysis.

Partial fluorination is a technique commonly used to increase the volatility of chelates^{1-4,7,10,11}; a decrease in the Van der Waals forces has been reported as the reason for this effect. However, the stability of the fluorinated chelates is lower than that of the corresponding non-fluorinated chelates^{12,13}. Trifluoroacetylacetone (HTFA) and hexafluoroacetylacetone (HHFA) are the most commonly used ligands (Table I); the latter is used less often because of its higher reactivity. It should be noted that the choice of the fluorinated ligands for metal chelates in previous work was arbitrary and no systematic reports have been published about the effect of the fluorination of different acetylacetone homologues on retention time. Moreover, some workers¹⁴⁻¹⁶ have reported that in some instances the fluorination of the ligands does not increase the volatility of the chelates obtained. The question of the choice of stationary phase has not been studied adequately: only a few examples of the reaction of chelates with polar stationary phases have been reported¹⁷. No attention has been paid to the thermodynamic properties of the stationary phases, selectivity or chelates with different ligands.

The aim of this work was to compare different fluorinated and non-fluorinated ligands and some non-polar and low-polarity stationary phases in order to determine conditions for obtaining minimal retention times of the chelates. Stable chromium chelates were chosen.

EXPERIMENTAL

Retention data were measured with Tsvet-104 gas chromatograph with a flame-ionization detector and a flow-rate of carrier gas (argon) of 25 ml/min. A glass-lined injector (heated to 250 °C) and glass columns (1 m × 3 mm I.D.) were used. The column temperature was maintained to within 0.15 °C. The contact time of the chelates with the stainless-steel capillary connecting the column exit with the detector was about 0.1 sec.

In order to prevent irreversible chelate adsorption on the glass-wool plug, the latter was treated with phosphorous acid and the amount of it was kept to the minimum.

Stationary phases (5%) were loaded on the support (Chromaton N AW HMDS, 0.125-0.16 mm; Lachema, Brno, Czechoslovakia) from chloroform solution. The following stationary phases were used (in order of increasing polarity): polyisobutylene (synthesized, average molecular weight 2000, polar impurities removed with silica gel), silicones E-301, OV-1, OV-101 (methylsilicones), SE-52 (5% of phenyl groups), SE-54 (5% of phenyl, 1% of vinyl groups), OV-17 (50% of phenyl groups), PPMS-6 (50% of phenyl groups, manufactured in the U.S.S.R.), 6-ring polyphenyl ether (PPE, manufactured in the U.S.S.R.), silicone elastomer SKTFT-50 (fluoro-silicone, manufactured in the U.S.S.R.) and silicone OV-225 (25% of phenyl, 25% of cyanopropyl groups).

To investigate the dependence of the retention data on fluorine in the molecule different ligands were synthesized (Table I). To compare the retention data of fluorinated and non-fluorinated ligands, ligand 3 (Table I) was also prepared. The

TABLE I
SOME β -DIKETONES USED AS LIGANDS FOR CHELATES

No.	Formula	Name	Abbreviation
1	CF ₃ -CO-CH ₂ -CO-CH ₃	1,1,1-Trifluoropentane-2,4-dione	HTFA
2	CF ₃ -CO-CH ₂ -CO-CF ₃	1,1,1,5,5,5-Hexafluoropentane-2,4-dione	HHFA
3	CH ₃ -CO-CH ₂ -CO-C(CH ₃) ₃	2,2-Dimethylhexane-3,5-dione	HPM
4	CF ₃ -CO-CH ₂ -CO-C(CH ₃) ₃	1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione	HTPM
5	C ₂ F ₅ -CO-CH ₂ -CO-C(CH ₃) ₃	1,1,1,2,2-Pentafluoro-6,6-dimethylheptane-3,5-dione	HPPM
6	C ₃ F ₇ -CO-CH ₂ -CO-C(CH ₃) ₃	1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctane-4,6-dione	HHPM
7	C ₄ F ₉ -CO-CH ₂ -CO-C(CH ₃) ₃	1,1,1,2,2,3,3,4,4-Nonafluoro-8,8-dimethylnonane-5,7-dione	HNPM

ligands were prepared by condensation of pinacolone with methyl esters of different acids in the presence of sodium methylate. Diketones were extracted as copper salts, which were then decomposed with sulphuric acid; free diketones were extracted with diethyl ether and distilled. GC analysis showed that the amount of impurities in the ligands was 1.5%. The identities of the ligands were confirmed by nuclear magnetic resonance spectroscopy.

Chromium(III) chelates were prepared by adding stoichiometric amounts of β -diketones to a boiling methanolic solution of chromium nitrate at *ca.* pH 6. Chromium chelates with HPM, HTPM and HNPM (for abbreviations see Table I) are dark-green greases; after distillation *in vacuo* they become dark red, slowly crystallized substances. The chromium chelate with HPPM is a dark-red grease, and that with HHPM a dark-brown solid.

The retention data were measured as the relative retentions, r , anthracene being the standard. In some instances when the retention time of anthracene was relatively large, naphthalene was used as the standard and then all relative retentions were re-calculated to anthracene as the standard. Relative retention data were determined at 3–5 different temperatures. Relative molar heats of solution, ΔH_s^0 , were calculated using the relationship $\log r$ versus $1/T$. Relative mean standard deviations were 0.2 and 5% for r and ΔH_s^0 , respectively.

To determine reproducible retention data, the dependence of retention time, t_N (the difference between the retention time of the solute and that of a non-sorbed gas, methane) on peak height, h , was established for the solutes. In many instances no such dependence was found; when a dependence of t_N on h was observed, the retention data were measured at a constant h value (so-called isobaric retention data). To calculate t_N at constant h the following empirical equation¹⁸ was used:

$$t_N = \frac{A_1}{\log h} + B \quad (1)$$

where A_1 and B are constants. This equation is valid for a restricted range of h (about 2–3 orders of magnitude) for the "adsorption" region of the relationship between t_N and h ; increasing t_N with decreasing h is observed in this region.

When a dependence of t_N on h was observed, the isobaric retention data were

calculated at $1/\log h = 0.4$ (h is measured in millimetres, using a 250-mm recorder chart, re-calculated to full-scale 10^{-11} A).

To evaluate the retention times of the chelates under the same conditions we used the t_N/t_0 ratio (where t_0 is dead retention volume) as the value proportional to retention volume because $1/t_0$ is proportional to flow-rate. If w_L , the column temperature and the flow-rate are kept constant, the t_N/t_0 ratio is the relative value of the retention time for the solute on different packings.

RESULTS AND DISCUSSION

Dependence of retention time on peak height

The dependence of t_N on h is a curve with a minimum¹⁸. Let us restrict the discussion to only the "adsorption" section of the relationship between t_N and h because large samples are required for other parts of the curve. To evaluate the non-linearity of the sorption isotherm one can use the slope of the relationship between t_N and $1/\log h$. A relative value of this slope can be calculated by using the retention times, t_N , measured at $1/\log h$ equal to 0.4 and 0.5 ($t_{N\ 0.4}$ and $t_{N\ 0.5}$, respectively):

$$A = \frac{t_{N0.5} - t_{N0.4}}{t_{N0.4}} \quad (2)$$

Table II shows that the dependence of t_N on h is observed only at low column temperatures and for CrPM₃ and CrNPM₃. When using column temperatures of 469–487 °K the A values are negligibly small on most of the stationary phases.

A marked effect of h on r is seen only when using the non-polar stationary phase polyisobutylene. The A value increases with increasing length of the fluorinated functional group in the ligand. A similar effect is seen for the packings with PPE and OV-225, but in this instance interphase adsorption acts on the solid surface.

TABLE II

A VALUES OF CHROMIUM(III) CHELATES AT DIFFERENT COLUMN TEMPERATURES ON VARIOUS PACKINGS

Chelate	OV-225, 420° K	PIB			PPE, 420° K
		416° K	424° K	431° K	
Cr(PM) ₃	Decomp.	0.026	0.015	0.009	Decomp.
Cr(TPM) ₃	0.000	0.000	0.000	0.000	0.000
Cr(PPM) ₃	0.000	0.000	0.000	0.000	0.002
Cr(HPM) ₃	0.009	0.006	0.008	0.000	0.100
Cr(NPM) ₃	0.029	0.022	0.018	0.011	0.120

When using low column temperatures (about 140 °C) partial decomposition of the non-fluorinated chelates on PPMS-6, PPE, OV-225 and SKTFT-50 was observed: four peaks appeared on the chromatogram instead of only one. This is additional proof of chelate decomposition with long contact times with the packing.

Taking into account these effects, the following determinations of retention data were carried out under conditions such that t_N does not depend on h and no decomposition is observed.

Retention data for homologous series of fluorinated ligands

Ligands 3–7 (Table I) differ in the number of CF_2 groups in the molecule, and therefore the chromium chelates with these ligands differ in the number of these groups (C_F). A linear relationship between $\log r$ and the number of carbon atoms in homologous molecules has often been reported, except for the first members of the series; only in rare instances have some minima been observed (for example, *n*-alcohols on glycerol¹⁹). Fig. 1 shows the non-linear relationship between $\log r$ and C_F and the minimum is observed for the chelates with $C_F = 6-9$. A marked minimum is noted for the stationary phases with a large number of phenyl groups in the molecule. The polarity of the stationary phase does not seem to be an important factor for the depth of the minimum.

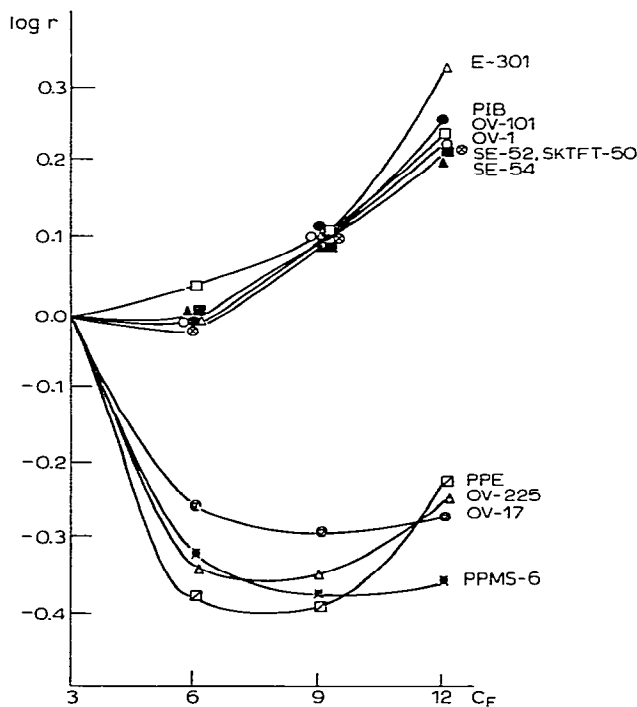


Fig. 1. Relationship between $\log r$ and number of fluorinated carbon groups in molecule of chelate, C_F .

The marked decrease in the relative retentions for PPE, OV-225, OV-17 and PPMS-6 for $C_F \approx 6-9$ is of great interest in attempts to reduce the retention times of the chelates, and the reason for this effect therefore has to be established. The dependence of ΔH_s^0 for chromium chelates on C_F is shown in Fig. 2. An almost linear

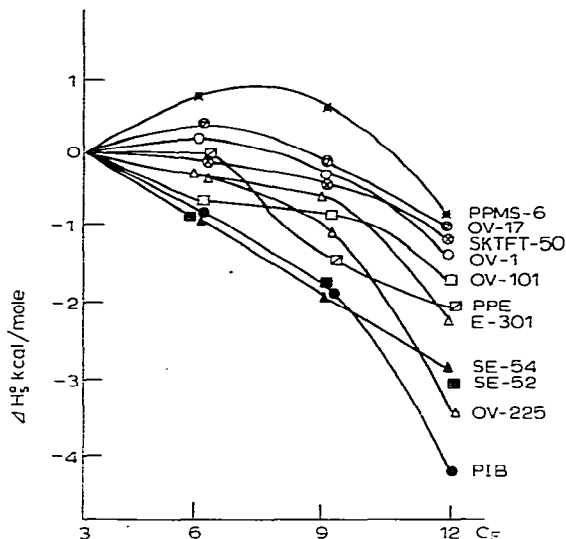


Fig. 2. Relationship between relative molar heats of solution, ΔH_s^0 , and number of fluorinated carbon groups, C_F .

relationship between ΔH_s^0 and C_F is observed for PIB, E-301, SE-52 and SE-54; a slight maximum at $C_F = 6$ is found for PPMS-6 and OV-1.

The non-linear relationship between ΔH_s^0 and C_F may be explained as follows. It was reported²⁰ that for aromatic hydrocarbons and olefins hyperconjugation of methyl groups with π -electrons increases the intermolecular forces for the solutes. When a methylene group is inserted between a methyl group and a system with double bonds (for example, in passing from toluene to ethylbenzene), the effect of hyperconjugation disappears. By analogy with alkylbenzenes it is reasonable to assume that the same effect will occur for the fluorinated ligands where, in passing from $-\text{CF}_3$ to $-\text{CF}_2-\text{CF}_3$, the intermolecular interaction decreases.

On comparing Figs. 1 and 2 it can be seen that only in a few instances do the minima in Fig. 1 coincide with the maxima in Fig. 2; therefore, some other factor must determine the minimum value for chromium chelates. The only remaining term is the relative molar entropy of solution, ΔS_s^0 . Using the basic thermodynamic relationships we can write the following equation for the distribution coefficient, K :

$$-RT \ln K = \Delta H_s - T \Delta S_s \quad (3)$$

where ΔS_s is the molar entropy of solution.

Taking into account that $r = K_x/K_{st}$ (the subscripts x and st refer to the solute and the standard solute, respectively), eqn. 3 can be rewritten in terms of relative molar heat of solution and relative molar entropy of solution:

$$-RT \ln r = \Delta H_s^0 - T \Delta S_s^0 \quad (4)$$

Because of the compensation effect between ΔH_s and ΔS_s , the entropic selectivity

term, F^0 , has been proposed²¹, which relates to the loss of rotational entropy during solution:

$$F^0 = \Delta S_s^0 - \frac{0.435}{T} \cdot \Delta H_s^0 \quad (5)$$

where ΔH_s^0 is measured in calories per mole.

The variation of F^0 with C_F is shown in Fig. 3. The stationary phases with a large decrease in F^0 in the homologous series (PPE, OV-17, PPMS-6 and OV-225), which is not compensated for by the corresponding variation in ΔH_s^0 , show a marked minimum in the relationship between $\log r$ and C_F .

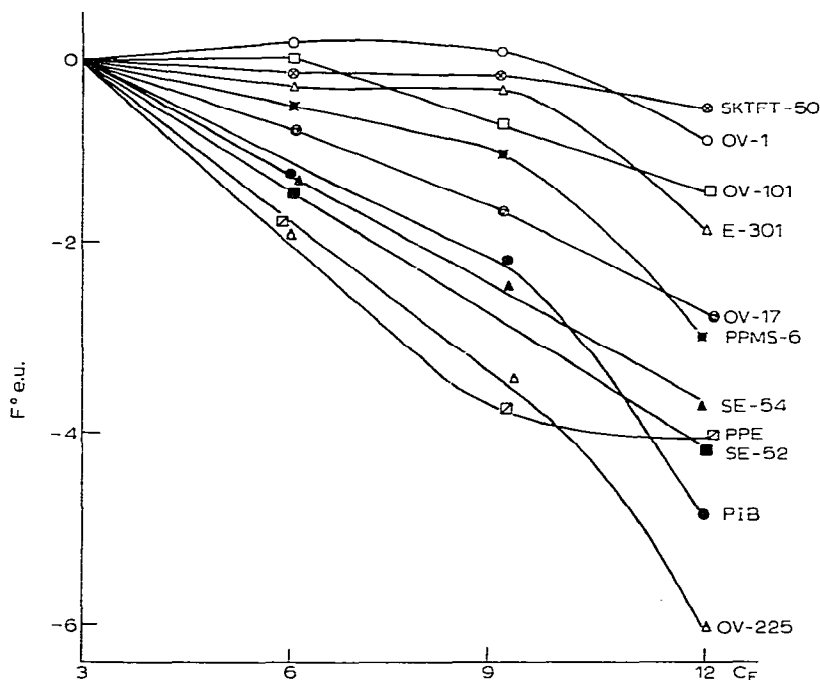


Fig. 3. Relationship between entropic selectivity of stationary phase, F^0 , and number of fluorinated carbon groups, C_F .

Comparing the results in Figs. 1-3, one can conclude that the appearance of a minimum in the relationship between $\log r$ and C_F relates mainly to an entropic factor of selectivity of the stationary phases. The presence of phenyl groups in the stationary phase molecules is the main reason for achieving a minimum in the retention time for members of homologous series with $C_F \approx 6-9$.

Effect of fluorination of methyl group on retention time of chelates

As a rule, the vapour pressure of a compound increases on fluorination. In spite of this rule, the ratio of the relative retention of a fluorinated chelate (ligand 4, Table I) to the corresponding non-fluorinated chelate (ligand 3, Table I), r^* , is greater

than unity for many stationary phases (Table III). This shows that fluorination of the methyl group reduces the retention times of the chelates in only a few instances (stationary phases OV-225 and PIB). The determination of ΔH_s^0 shows that after fluorination the relative molar heats of solution increase from 1.6 to 3.5 kcal/mole, which leads to an increase in the relative retentions of the fluorinated chelates. These results are in good agreement with the increase in the polarity of substances after partial fluorination: solutes with a CF_3 group are more polar than the corresponding hydrocarbon chelates.

TABLE III
RETENTION PARAMETERS OF CHROMIUM(III) CHELATES

The first three columns refer to comparison of non-fluorinated and fluorinated chelates.

Stationary	r^*	ΔH_s^0 (kcal/mole)	F^0 (e.u.)	r_1	t_s/t_0	Minimum relative retention time
PIB-2000	0.95	-1.6	-4.08	0.92	21.0	2.15
E-301	2.95	-2.16	-1.46	2.95	22.0	13.6
OV-1	3.03	-3.45	-2.12	2.98	21.8	13.2
OV-101	2.98	-2.4	-1.13	2.93	15.7	9.9
SE-52	2.85	-2.95	-1.96	2.81	26.1	13.2
SE-54	2.65	-2.2	-1.06	2.58	24.5	11.9
OV-17	1.47	-2.35	-2.42	0.74	64.4	4.9
OV-225	0.78	-3.5	-14.55	0.36	59.8	3.1
PPMS-6	1.31	-3.5	-12.9	0.55	66.6	59.2
SKTFT-50	2.70	-2.35	-1.31	2.59	17.5	13.4
PPE					7.14	1.7

On only two stationary phases (PIB and OV-225) is the relative retention of the fluorinated chelate lower than that of the corresponding non-fluorinated chelate, in accordance with the relative molar entropies of solution.

To make the effect of fluorination on relative retention more evident, let us compare the minimum values of the relative retentions of fluorinated chromium chelates (see Fig. 1) with the relative retentions of the corresponding non-fluorinated chelates; this ratio is represented by r_1 (Table III). The r_1 data show that the relative retentions of the fluorinated chelates are lower than those of the non-fluorinated chelates on four stationary phases (OV-225, PIB, OV-17 and PPMS-6). Two other stationary phases (OV-17 and PPMS-6) can be added because of the large decrease in the relative retentions for homologous series of fluorinated chelates.

The calculated minimum retention times for fluorinated chelates on different stationary phases are listed in the last column in Table III, and have a relative mean standard deviation of about 4%. On comparing the minimum retention times, one can conclude that these values depend markedly on the choice of the stationary phase, for example, the retention time of the chelate on PPMS-6 is 35 times greater than that on PPE. There are four stationary phases on which the retention times of the chelates have minimum values, PPE, PIB, OV-225 and OV-17; three of these have phenyl groups in the molecules. On comparing the retention data for fluorinated and non-fluorinated chelates, it can be seen that fluorination does not always decrease the retention times of chelates.

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