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MINIMIZING THE RETENTION OF CHROMIUM CHELATES WITH SOME FLUORINATED β-DIKETONES

V. P. MIKHAYLENKO and I. P. SEREDA

Kiev State University, Chemical Department, Vladimirskaya 60, Kiev 252017 (U.S.S.R.)

and

A. N. KOROL

Institute of Physical Chemistry, pr. Nauki 31, Kiev 252028 (U.S.S.R.)

SUMMARY

   The influence of the branched and fluorinated groups, containing an oxygen atom, in the terminal positions of β-diketones on retention data and thermogravimetric properties of chromium chelates was investigated. The *tert.*-butyl group was found to have the optimal properties for decreasing the retention and increasing the chelate stability in chromatographic columns. The new fluorinated oxygen-containing ligands are proposed for gas–liquid chromatography of chelates in order to achieve the minimal retention.

INTRODUCTION

   In our previous paper[1] on chromium chelates with homologous series of fluorinated β-diketones we made some suggestions concerning the synthesis of new chromium chelates with minimal retention to provide the best conditions for quantitative analysis of chelates: the shorter the contact time of the chelate with the packing the lower is the probability of decomposition of the chelate in the column. The principal aim of the present paper is to test our conclusions with the use of both traditional and newly synthesized ligands. As before, we have chosen chromium chelates.

   Since data on the volatility of these chromium chelates were not available, the thermogravimetric technique was applied in order to estimate volatility and to compare the volatility data with those of retention.

EXPERIMENTAL

   The synthesis of the chromium chelates was performed in methanolic solutions by boiling the stoichiometric amounts of chromium(III) nitrate with the corresponding diketone for 12–24 h. The purity of the chelates was evaluated by determining fluorine. The diketones were prepared as in ref. 1 by using Claisen condensation. The ligands are

TABLE I

DIKETONES INVESTIGATED

No.	Formula	Name	Abbreviation
1	$CF_3OCF_2COCH_2COC(CH_3)_3$	1-Trifluoromethoxy-1,1-difluoro-5,5-dimethyl-hexanedione-2,4	H OPPM
2	$CF_3OCF_2CF_2COCH_2COC(CH_3)_3$	1-Trifluoromethoxy-1,1,2,2-tetrafluoro-6,6-dimethylheptanedione-3,5	H OHPM
3	[furyl]—$CF_2COCH_2COC(CH_3)_3$	1-Perfluorofuryl-1,1-difluoro-5,5-dimethylhex-anedione-2,4	H FFPM
4	$CF_3OCF_2COCH_2COCH(C_2H_5)_2$	1-Trifluoromethoxy-1,1-difluoro-5-ethylhep-tanedione-2,4	H OPEM
5	$CF_3COCH_2COC(CH_3)_3$	1,1,1-Trifluoro-5,5-dimethylhexanedione-2,4	H TPM
6	$C_2F_5COCH_2COC(CH_3)_3$	1,1,1,2,2-Pentafluoro-6,6-dimethylheptane-dione-3,5	H PPM
7	$C_3F_7COCH_2COC(CH_3)_3$	1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctane-dione-4,6	H HPM
8	$C_4F_9COCH_2COC(CH_3)_3$	1,1,1,2,2,3,3,4,4-Nonafluoro-8,8-dimethyl-nonanedione-5,7	H NPM
9	$CF_3COCH_2COCH_2CH(CH_3)_2$	1,1,1-Trifluoro-6-methylheptanedione-2,4	H i-TPM
10	$CF_3COCH_2COCH_3$	1,1,1-Trifluoropentanedione-2,4	H TFA
11	$C_3F_7COCH_2COCH_3$	1,1,1,2,2,3,3-Heptafluoroheptanedione-4,6	H HAM

listed in Table I. Substances 1–4 were kindly provided by Professor L. M. Yagupolskii and Dr. Yu. A. Fialkov (Institute of Organic Chemistry, Kiev).

Retention data were measured by using a Model Tsvet-104 gas chromatograph with a flame-ionization detector (F.I.D.). Pyrex glass columns (1 m × 3 mm I.D.) were used, their inner walls being treated with phosphorous acid before filling[2]; injection of samples was made by an on-column technique. Plugs of glass wool in the column inlet were not used in order to prevent chelate adsorption[2,3].

The following stationary phases (5 %) were loaded on the support (Chromaton N AW HMDS, 0.125–0.16 mm; Lachema, Brno, Czechoslovakia): OV-225 (25 % of phenyl, 25 % of cyanopropyl groups); OV-17 (50 % of phenyl groups); six-ring poly-phenyl ether (PPE, manufactured in the U.S.S.R.) and PEF-240 (perfluoropropylene oxide, manufactured in the U.S.S.R.). The first three phases allow us to achieve the minimal retention time[1], and PEF-240 is of great interest for comparison with the nonfluorinated phases.

Anthracene was used as a standard in the calculation of relative retention data. Naphthalene was used as an intermediate standard for some solutes and the data were recalculated relative to anthracene. All other chromatographic conditions were as in ref. 1.

The thermogravimetric studies were carried out by using the F. Paulik, J. Paulik, L. Erdey model derivatograph[4] (MOM, Budapest, Hungary) in air. Heating was applied at a rate of 10°/min up to 600°. Measured amounts of the chelates (0.08–0.2 g) were placed into the open platinum crucible with the support of the inert Al_2O_3.

In order to illustrate our discussion it was desirable to compare the retention data with the geometric structure of the chelates under study. These structures were constructed by using the space-filling atomic models[5]. The coordination sphere of the models is considered to have a radius of 3.2 Å, which was calculated as the sum of the

C–O (1.29 Å) and Cr–O (1.93 Å) bond lengths[6]. Photographs of the above models of the chelates are shown in Fig. 1.

The model of the tris(2,2,6,6-tetramethylheptane-3,5-dionato)chromium chelate has been chosen as the basis, because this can be approximated as a sphere of radius 9.2 Å (R). The fluorinated fragment of the chelate which protrudes from this sphere (R_F) (Fig. 1a) is characterized by the value Δ. Measurements of the Δ values have been made for three or four cases of different turnings of the fluorinated radical around the basic β-diketone structure in the chelate model (for one β-diketone ligand) within an error of 0.2 Å.
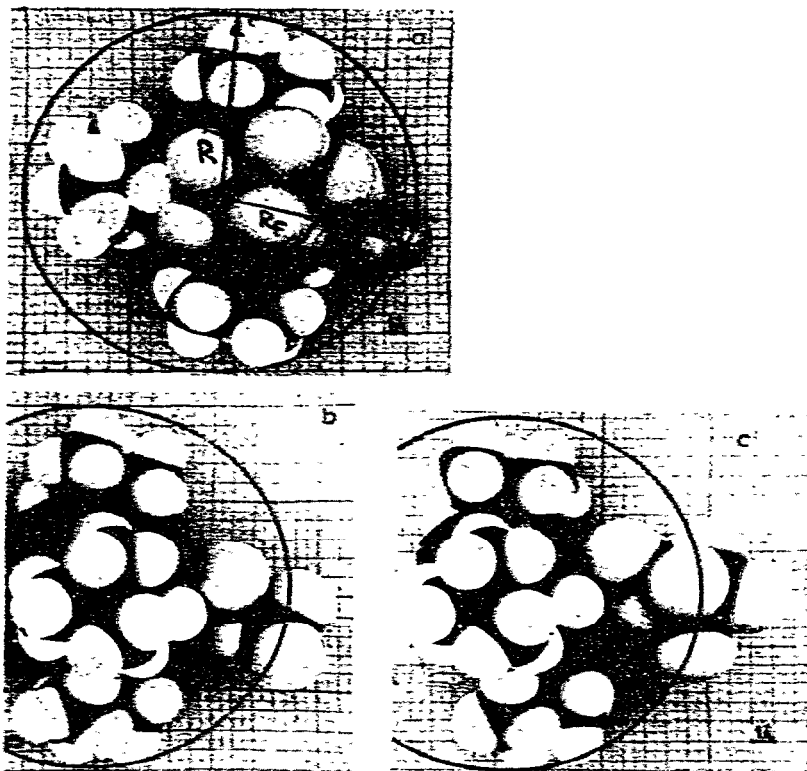

Fig. 1. Photographs of the molecular models of Cr HPM$_3$ (a), Cr OPPM$_3$ (b) and Cr OHPM$_3$ (c).

The probability of a given configuration for the four-carbon chain was evaluated by the use of diketone models. There are two reasonable configurations for the chain (Fig. 2a, b): *cis* and *trans*. The most compact packing of the atoms takes place in the *cis*-form and we have therefore used this configuration for the chelate models. When the C_3 atom of the chain is replaced by oxygen, the *trans*-disposition is preferable because of repulsion between two oxygen atoms (Fig. 2b, c); also the C–O–C angle is not the same as the C–C–C angle.
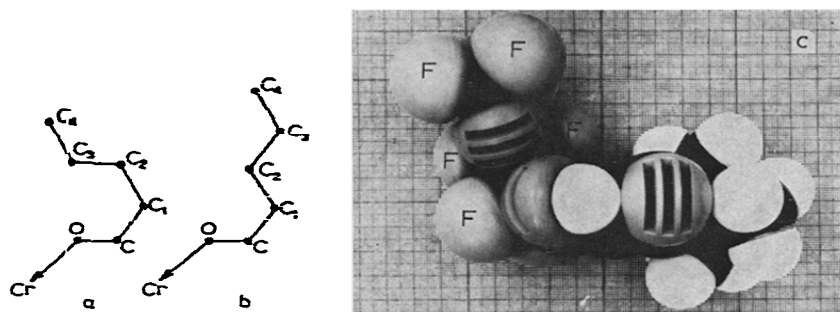
Fig. 2. The molecular model of H OHPM (c) and two reasonable conformations (a,b) for the fluorinated radical.

RESULTS AND DISCUSSION

Thermogravimetric analysis

The experimental data are presented in Table II. Weight loss from the samples in many cases occurs in two steps. The first step corresponds to the maximum losses and is accompanied by endothermic effects. The temperatures at which the maximum losses occur, as determined by the differential curve (DTG), are similar, which is an evidence for a common sublimation process with similar sublimation heats ΔH_v. Degree of fluorination of the chelate had no effect on decreasing the sublimation temperature. The most likely process for the second step, which is sometimes accompanied by exothermic effects, is oxidative decomposition of the chelates. The losses for the second step sometimes reach 10% and these must be taken into account for quantitative measurements of the chromium chelates.

Gas chromatography

The experimental retention data are listed in Tables III and IV. In accordance

TABLE II

THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (DTA) DATA OF CHROMIUM(III) CHELATES

Abbreviation	Reaction step	T, initial (°C)	T, final (°C)	ΔT, reaction interval (°C)	T for max. sample loss (°C)	T of DTA peak (°C)		Sample loss (%)
Cr TPM₃	I	140	300	160	290	290	endotherm	86.2
	II	300	420	120	—	400	exotherm	97.8
Cr PPM₃	I	140	300	160	280	280	endotherm	96.4
Cr HPM₃	I	160	320	160	300	300	endotherm	95.1
Cr NPM₃	I	140	340	200	320	wash out endotherm		89.0
	II	340	440	100	—	—		99.7
Cr TFA₃	I	150	280	130		160	endotherm	
					280	280	endotherm	95.3
	II	280	320	40	—	—		98.0
Cr FFPM₃	I	200	360	160	320	320	endotherm	83.0
	II	360	420	60	—	410	exotherm	94.7

TABLE III

RETENTION PARAMETERS OF CHROMIUM(III) CHELATES

Abbrevia-tion	PPE			OV-17			OV-225		
	r^*	ΔH_s° (kcal/mole)	F° (e.u.)	r	ΔH_s° (kcal/mole)	F° (e.u.)	r	ΔH_s° (kcal/mole)	F° (e.u.)
Cr OPPM$_3$	0.00873	−1.60	−11.57	0.0764	−5.80	− 9.65	0.0399	−2.60	− 9.88
Cr OHPM$_3$	0.00849	−2.05	−12.22	0.0670	−5.75	− 9.85	0.0409	−3.30	−10.81
Cr OPEM$_3$	0.06490	−3.80	−10.51	0.4310	−6.45	− 7.08	0.2230	−4.85	− 9.46
Cr TPM$_3$	0.03110	0.35	− 6.43	0.1770	−5.00	− 6.91	0.2280	−2.70	− 6.59
Cr i-TPM$_3$	0.19600	−2.65	− 6.78	0.7890	−6.70	− 6.21	0.5770	−5.95	− 9.03
Cr TFA$_3$	0.05600	−0.60	− 6.53	0.2540	−7.15	− 9.07	0.2130	−4.15	− 8.61
Cr HAM$_3$	0.01370	−1.40	−10.40	0.1110	−6.80	−10.25	0.0618	−2.65	− 9.08
Cr HPM$_3$	0.00916	−0.85	−10.47	0.0948	−5.85	− 9.25	0.0493	−3.20	−10.26

* r = relative retention.

TABLE IV

RETENTION PARAMETERS OF CHROMIUM(III) CHELATES ON PEF-240

Abbreviation	r	ΔH_s° (kcal/mole)	F° (e.u.)
Cr OPPM$_3$	2.999	− 7.80	−8.23
Cr OHPM$_3$	6.982	− 9.40	−8.69
Cr OPEM$_3$	8.770	−10.50	−9.70
Cr TPM$_3$	1.660	− 6.80	−8.07
Cr PPM$_3$	3.266	− 8.05	−8.40
Cr HPM$_3$	6.792	− 9.45	−8.81
Cr NPM$_3$	13.00	−10.90	−9.31
Cr i-TPM$_3$	3.199	− 6.50	−6.37
Cr TFA$_3$	0.729	− 4.30	−6.37
Cr HAM$_3$	3.050	− 8.65	−9.33

with the previous paper[1], we used the ligands which showed the greatest entropic effects upon solution in the aromatic stationary phases. Some ligands (1–4, Table I) have a rigid fluorinated group, and some were selected as having different stereochemistries (4,5, 9–11, Table I). Ligands 6 and 7 appeared to be most promising for gas–liquid chromatography (GLC).

The data in Table III show that the minimal retention is achieved by using ligand 2 (Table I). The decrease in retention for Cr OHPM$_3$ compared with that for Cr HPM$_3$ amounts to 7% when the column with PPE is used, 17% with OV-225 and 30% with OV-17. The Cr FFPM$_3$ chelate is not stable under the chromatographic conditions, as shown in Fig. 3. However the thermogravimetric behaviour of this chelate is similar to other chelates. This confirms the low stability to GLC of the chelates with cyclic groups[7–9].

We now discuss the reasons for the change in retention data when a stationary phase with a regular coplanar structure, i.e., PPE, is used. The retention data (r) are correlated with the entropic selectivity, F°: the chelate with the minimal retention (Cr OHPM$_3$) also has the minimal value of F°. The entropy changes may be explained in terms of the models in Fig. 1a,b,c. The chelate Cr OHPM$_3$ has the largest Δ value,
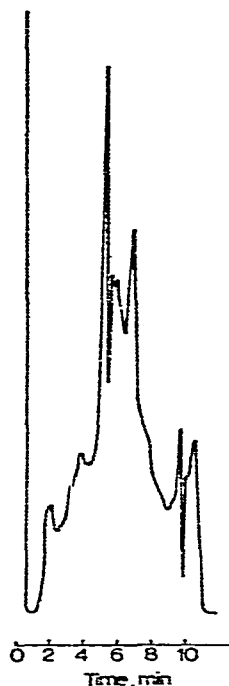
Fig. 3. Chromatogram of Cr FFPM$_3$. Column, 5% OV-17; column temperature, 172°; inlet temperature, 250°; argon carrier gas flow-rate, 22 ml/min.

which accounts for the great hindrance of the chelate molecules to rotation in the liquid media (this causes the decrease in rotational entropy, F^0). The fluorinated group of the Cr HPM$_3$ chelate is flexible and surrounds the molecule (Fig. 1a), causing the Δ value to decrease to 1.3 Å (Table V). It should be noted that the rigidity of the oxygen-containing group influences the entropic selectivity, but this group does not necessarily cause a decrease in the vapour pressure of the chelate.

TABLE V

STRUCTURE PARAMETERS OF CHROMIUM(III) CHELATES

For the meaning of R and R$_F$ see Fig. 1a.

Abbreviation	R (Å)	R$_F$ (Å)	Δ (Å)
Cr TPM$_3$	9.2	8.0	−1.2
Cr PPM$_3$	9.2	9.3	0.1
Cr HPM$_3$	9.1	10.4	1.3
Cr NPM$_3$	9.3	11.6	2.5
Cr OPPM$_3$	9.2	11.8	2.4
Cr OHPM$_3$	9.2	13.3	4.1
Cr TFA$_3$	7.5	8.1	0.6
Cr HAM$_3$	7.5	12.0	4.5
Cr i-TPM$_3$	10.3	8.1	−2.2

Some other trends may be seen in the chelate retentions. Replacing a methyl group by a *tert.*-butyl group (see Table III) decreases the *r* value because of steric hindrance to intermolecular interaction. When substituting a *tert.*-butyl group by an isoamyl one (ligand 4, Table I) the *r* value increases due to increases in the ΔH_s^0 and F^0 terms. Hence, the presence of the *tert.*-butyl group is preferable for the minimal *r* value of the chelate.

The Cr TPM$_3$ and Cr i-TPM$_3$ chelates are geometric isomers. The terminal nonfluorinated atoms of Cr i-TPM$_3$ lie at a greater distance from the centre of symmetry, than those of Cr TPM$_3$ (see Table V). This causes an increase in the *r* values through the ΔH_s^0 term. The aliphatic group in Cr i-TPM$_3$ blocks the electron acceptor group –CF$_3$, which "shuts-off" the interaction of the CF$_3$ group (see Tables III and V).

When using OV-17 the Cr OPPM$_3$ and Cr OHPM$_3$ chelates also have minimal retentions, but the intermolecular forces (ΔH_s^0) are of greater importance than for PPE. This relates to the decreasing of the intermolecular regularity of packing molecules when passing from PPE to the silicone stationary phase. When comparing two liquids with different regularities (the more polar OV-225 has greater regularity than OV-17) the F^0 term has the main effect on the retention data.

The sign and magnitude of ΔH_s^0 on PPE for Cr OHPM$_3$ and Cr HPM$_3$ show that the difference in retention of the chelates increases with decreasing column temperature; this is an advantage of the new type of chelates at low column temperatures. When using OV-17 and OV-225 the selectivity of the stationary phases undergoes no changes with column temperature.

PEF-240 has quite a different selectivity compared with other stationary phases (Table IV). The absolute values of retention are much higher for fluorinated chelates on PEF-240 than nonfluorinated stationary phases. The traditional relationships (for example, see Fig. 4) are observed on the fluorinated stationary phase in contrast to corresponding relationships for other classes of stationary phases[1]. The energy of the intermolecular forces (ΔH_s^0) is of greatest importance for the fluorinated stationary phase, affecting the relations between the chelate structures and retention values. The comparison of PEF-240 with the other stationary phases allows the conclusion that only the interaction between hydrocarbon and fluorinated groups affects the specific retention properties for chelates on the hydrocarbon-containing stationary phases.
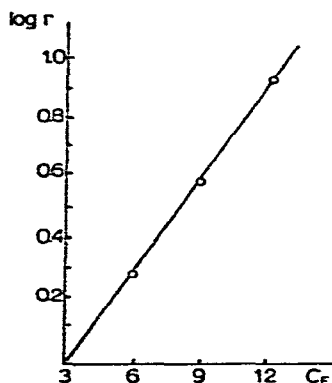

Fig. 4. The relationship between log *r* and the number of fluorinated carbon groups (C_F) obtained on PEF-240.

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