Note

Behaviour of aromatic β-diketones and their metal chelates on silica gel layers

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Among its many applications, thin-layer chromatography (TLC) is useful as a rapid guide to anticipated column performance in gas chromatography (GC) and high-performance liquid chromatography (HPLC). The limited amount of data[1–5] available on the TLC of metal β-diketonates is, then, surprising considering that β-diketones are widely available and used chelating reagents in analytical chemistry.

Accordingly, an examination was undertaken of a number of aryl β-diketones and their chelates, including several novel ligands containing extensive substitution with fluorine. The metal ions and terminal substituents (R_1 and R_2, in the β-diketone $R_1COCH_2COR_2$) were chosen in an effort to highlight the effect of certain structural factors on behaviour during TLC and to compare these with the known GC behaviour. Thus, chromium(III) and iron(III) were included since their chelates exhibit the two extremes of chromatographic behaviour for neutral, non-hydrated species. On the other hand, cobalt(II) was included since its chelates are, as for the compounds examined here, normally solvated. Other metal ions examined were copper(II), vanadium(III) and oxovanadium(IV). With the exception of pentane-2,4-dione (Hacac), 2,2,6,6-tetramethylheptane-3,5-dione (Hdpm) and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione (Hhpm), the β-diketones can be regarded as derivatives of 1-phenylbutane-1,3-dione (Hba) or 4,4,4-trifluoro-1-phenylbutane-1,3-dione (Hbta).

EXPERIMENTAL

Syntheses

The ligands and chelates, with the exception of Hacac, were synthesised as previously described[6,7]. The compounds were: 4,4-dimethyl-1-phenylpentane-1,3-dione (Hbpm), 3,3-diphenylpropane-1,3-dione (Hdbm), 4,4,4-trifluoro-1-(2′-trifluoromethylphenyl)butane-1,3-dione (HoCF₃bta), 4,4,4-trifluoro-1-(4′-*tert.*-butylphenyl)butane-1,3-dione (HpBubta), 4,4,4-trifluoro-1-(4′-nitrophenyl)butane-1,3-dione (HpNO₂bta), 4,4,5,5,6,6,6-heptafluoro-1-(4′-fluorophenyl)hexane-1,3-dione (HpFbhp), 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione (HF₅bta), 1-

(pentafluorophenyl)butane-1,3-dione (HF$_5$ba) and the copper(II), iron(III) and chromium(III) chelates of each ligand. The cobalt(II), vanadium(III) and oxovanadium(IV) chelates of selected ligands were also included. Infrared spectra confirmed that, with the exception of the cobalt(II) chelates, all compounds were anhydrous.

Chromatographic solvents

Before use, benzene and methanol were subjected to distillation from an all-glass fractionating still and stored in amber-glass storage bottles.

Chromatographic procedure

Silica gel E (E. Merck, Darmstadt, F.R.G.) was used. To prepare the plates, a homogeneous slurry of the silica gel in distilled water was applied to clean glass plates adjusting the layer thickness to a nominal 500 μm. The coated layers were air-dried for 3 4 days before use. Plates were examined by applying a fluorinated β-diketone (0.5% Hbta in ethanol as a spray) to one from each batch of dry plates. Satisfactory silica gel gave no red coloration due to the presence of iron.

Activity of the layers was not monitored since the data are comparative only and were collected on the same day from the same batch of plates. β-Diketones were detected by spraying with an 0.5% (w/w) solution of copper(II) acetate in aqueous ethanol, while the metal chelates were obvious from their characteristic colours. For each solvent system, duplicate runs were made immediately following the application of each compound (10 20 μg) to the plate as a small compact spot.

RESULTS AND DISCUSSION

The results, presented in Table I, divide the free ligands into compounds migrating as uniform ellipsoidal spots and those giving very diffuse tailing spots. The

TABLE I

TLC DATA FOR THE AROMATIC LIGANDS AND CHELATES

N.E. = Not examined. Solvents: A, benzene; B, benzene methanol (92:8).

| β-Diketone anion	R_F						
	Ligand		Cu(II)		Co(II)		Fe(III)
	A	B	A	B	A	B	A
ba	0.72	0.88	0.13	0.67	0.0	0.78	0.08
bpm	0.91	0.93	0.80	0.96	N.E.	N.E.	0.85
dbm	0.86	0.90	0.0	0.0	N.E.	N.E.	N.E.
bta	0.24 0.72	0.21 0.78	0.60	0.76	0.0	0.30	0.0 0.38
oCF$_3$bta	0.68	0.0 0.70	0.20 0.36	0.73	N.E.	N.E.	0.13
pBubta	0.24 0.66	0.26 0.70	0.78	0.60 0.86	0.0	0.33	0.0 0.36
pNO$_2$bta	0.0 0.35	0.0 0.34	0.14	0.29 0.59	0.0	0.27	0.10
pFbhp	0.0 0.60	0.0 0.56	0.31 0.73	0.29 0.80	N.E.	N.E.	N.E.
F$_5$bta	0.0 0.63	0.0 0.62	0.60	0.74	0.0	0.29	0.08
F$_5$ba	N.E.	N.E.	0.59	0.80	N.E.	N.E.	N.E.

presence of a fluoroalkyl group in the molecule has been associated with the latter type of behaviour and attributed[2,8,9] to the greater tendency of the fluorinated ligands to form hydrates, due to a higher Lewis acidity. The R_F values of the β-diketones increase in the following order and are independent of the solvent: HpNO$_2$bta < HpFbhp < HF$_5$bta < HpBubta $\simeq$ HoCF$_3$bta < Hbta < Hba < Hdbm < Hbpm.

Considering the chelates, the trend in R_F values varied considerably for the different metal ions and a parallel between the TLC and GC behaviour[10] of the chelates is immediately apparent. The compounds migrate either as compact spots with somewhat diffuse tails or, in several instances, tailing was so severe that it became necessary to assign a range to the R_F values. The chromium(III) chelates were an exception, migrating as uniform, ellipsoidal spots. Evidently, under the influence of the nitro group, Cr(pNO$_2$bta)$_3$ migrates, however, as a very diffuse band. For each β-diketone, the chromium(III) chelate was the most mobile and, hence, least strongly adsorbed. It is interesting that, with the exception of Cr(ba)$_3$, the *cis trans* isomers were not resolved. This may be due to the low concentration of the more polar isomer which, as a result, remained undetected on the TLC plate. Again, the behaviour of the chromium chelates is in contrast to that of iron(III). The iron(III) β-diketonates migrated as diffuse bands rather than distinct spots, although Fe(bpm)$_3$ and Fe(dbm)$_3$ in migrating as spots, were exceptions.

A plausible explanation for the difference in adsorptive behaviour of the iron and chromium chelates involves the extent of interaction of the compounds[11,12] with the bound water in the silica gel layers. It appears likely that such an interaction will involve the octahedral faces of a tris-chelate and, since the 3d^5 electrons of iron(III) have spherical symmetry not concentrated in the octahedral faces[12], the degree of interaction will be greater for iron(III) chelates than for chromium(III) chelates. A second important distinction between the chelates of chromium and iron is the dif-

	V(III)		Cr(III)		V(IV)	
B	A	B	A	B	A	B
0.54 0.95	0.48	0.90	0.29, 0.15	0.95	0.0 0.13	0.48–0.91
0.97	N.E.	N.E.	0.91	0.95	N.E.	N.E.
0.98	0.0 0.75	0.94	0.89	0.95	N.E.	N.E.
0.16–0.81	0.0 0.70	0.94	0.96	0.96	0.0 0.06	0.18 0.32
0.13 0.50	0.0–0.90	0.83	0.92	0.92	0.0–0.11	0.19 0.32
0.14–0.65	N.E.	N.E.	0.97	0.95	N.E.	N.E.
0.0 0.19	N.E.	N.E.	0.15 0.78	0.33–0.95	N.E.	N.E.
0.11 0.70	N.E.	N.E.	0.96	0.95	N.E.	N.E.
0.08–0.34	0.0 0.25	0.18 0.35	0.97	0.95	0.0 0.13	0.18 0.42
0.85	N.E.	N.E.	0.87	0.93	N.E.	N.E.

ference in lability. Whereas the chromium β-diketonates are relatively inert, those of iron(III) are labile implying the existence of equilibria[13] of the type depicted below (where L stands for ligand molecule):
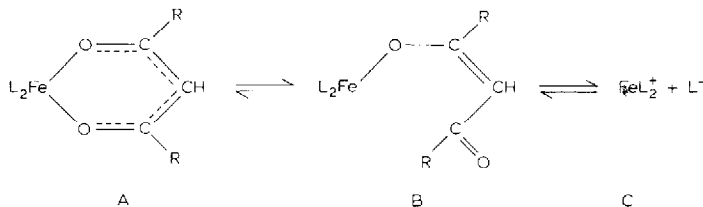
The species B and C are susceptible to severe interaction with the adsorbent, so that the extent of dissociation, and hence chelate lability, will determine the degree of tailing.

Of these two explanations, the first implies a susceptibility to steric effects. Indeed, tailing was reduced significantly in Fe(dbm)$_3$, Fe(bpm)$_3$ and Fe(dpm)$_3$ (see Tables I and II) consistent with the ability of the bulky substituents in these compounds to shield the octahedral faces of the chelate. On the other hand, a dissociative mechanism requires that the extent of tailing depend on the degree of dissociation so that in the presence of free β-diketone dissociation ought to be suppressed in favour of the undissociated chelate (A). This is supported by the results for the iron(III) β-diketonates in a solvent consisting of benzene and a β-diketone (see Table II). Although not suppressed by the incorporation of Hacac in the solvent system, tailing was eliminated below the ligand front when other β-diketones were used. The results suggest that both mechanisms are important in causing the tailing of β-diketonates.

TABLE II

TLC DATA FOR IRON(III) β-DIKETONATES

β-Diketone anion	R_F value in developing solvent				
	Benzene	1% Hacac in benzene	0.5% Hba + 0.5% Hbta in benzene	1% Htfa* in benzene	1% Hhfa** in benzene
acac	0.0 0.08	0.05 0.13	0.42 0.48	0.46 0.56	0.22 0.45
dpm	0.84	0.80	0.43 0.46	0.68 0.73	0.72–0.87
hpm	0.0–0.75	0.0 0.80	0.44–0.52	0.71 0.83	0.25–0.84
ba	0.0 0.08	0.05–0.10	0.42 0.46	0.43 0.53	0.21–0.50
bpm	0.28 0.85	0.08–0.40	0.40 0.46	0.45–0.86	0.40 0.86
bta	0.0 0.38	0.0–0.75	0.44 0.47	0.45 0.80	0.23–0.63
oCF$_3$bta	0.0–0.13	0.12 0.44	0.44 0.48	0.45–0.50	0.25–0.43
pBubta	0.0 0.36	0.0–0.70	0.44–0.53	0.45 0.82	0.25 0.86
pNO$_2$bta	0.0–0.10	0.0 0.40	0.44–0.48	0.43 0.48	0.25–0.32
pBrbta	0.0–0.27	0.0–0.68	0.44 0.51	0.45 0.61	0.25–0.50
F$_5$bta	0.0–0.08	0.10 0.25	0.44	0.47	0.25–0.37
Second solvent front	—	0.40	0.44	0.45	0.25

* 1,1,1-Trifluoropentane-2,4-dione.
** 1,1,1,5,5,5-Hexafluoropentane-2,4-dione.

The behaviour of the copper(II), vanadium(III) and oxovanadium(IV) chelates was unexceptional and confirms the ability of TLC to separate various mixtures of the cations. As expected, the hydrated cobalt(II) chelates failed to migrate in benzene. When methanol was introduced into the developing solvent however, the cobalt chelates migrated as reasonably compact ellipsoidal spots. This behaviour is in contrast to that of the non-hydrated iron(III) chelates. As is the case in GC[14,15], the presence of iron(III) presents difficulties in any separation by TLC and seems predictable, also, in HPLC, especially in the normal-phase mode.

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