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Note

Liquid chromatographic analysis of bromination reactions of metal trifluoroacetylacetonates

T. J. CARDWELL* and T. H. LORMAN

Analytical Chemistry Laboratories, Chemistry Department, La Trobe University, Bundoora, Victoria 3083 (Australia)

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Many of the electrophilic substitution reactions investigated by Singh and Sahai[1] and Joshi and Pathak[2] and some of those studied by Collman *et al.*[3,4] have included trivalent metal β-diketonates with unsymmetrical ligands. These octahedral metal complexes display geometrical isomerism yet it is surprising that there is only one brief reference to this type of isomerism in these early investigations: isomers were claimed for the substituted products of the formylacetone chromium(III) chelate[4] but no supporting evidence was given[5].

In two previous papers from these laboratories, it was demonstrated that gas chromatography (GC) was effective in separating the mono-, bi- and tri-substituted products in the bromination of the trifluoroacetylacetonates of chromium and rhodium[6,7]. In the separation of the rhodium compounds, the chromatogram clearly showed the presence of geometrical isomers in the bi- and tri-brominated derivatives[7] whereas the corresponding chromatogram for the chromium compounds showed that isomers seemed to be present only in the mono-substituted derivative[6].

The geometrical isomers of cobalt(III) and chromium(III) chelates of trifluoroacetylacetone, benzoylacetylacetone and 2,2-dimethylhexane-3,5-dione have been separated by high-performance liquid chromatography (HPLC) in the adsorption mode[8] and this technique has also been recommended for the analysis of electrophilic substitution reactions involving labile or thermally unstable metal β-diketonates[9]. In this paper, the effects of the presence of geometrical isomers in electrophilic substitution reactions is investigated and HPLC is applied to the separation of isomeric forms of the products in the bromination of some trivalent metal trifluoroacetylacetonates.

EXPERIMENTAL

The trifluoroacetylacetonates of chromium(III), rhodium(III) and cobalt(III) were prepared by the method of Fay and Piper[10] and samples were purified by column chromatography on acid-washed alumina using chloroform as eluent. As this eluent yields mixtures of isomers, the identities of the chelates were established by the presence of molecular ions in their mass spectra. Highly pure samples of the meridional isomers were isolated (i) after several recrystallisations from benzene–hexane

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(50:50) followed by column chromatography on acid-washed alumina using hexane–benzene (20:80) as eluent[10] or (ii) using preparative liquid chromatography with dichloromethane–hexane (20:80) as the mobile phase. The purity of the meridional isomer was confirmed by HPLC and its identity (for rhodium and cobalt chelates) was established by NMR.

Bromination of the metal chelates was performed in chloroform at room temperature using a 4:1 mole ratio of bromine to metal complex. The reaction mixture was analysed as follows: the solvent was rapidly removed in a stream of nitrogen, the residue was washed successively with aqueous sodium bicarbonate, aqueous sodium bisulphite and water, air-dried and then it was dissolved in hexane or the HPLC mobile phase to a concentration of 0.5–1.0%. The reaction time under these conditions is indicated in each of the figure legends.

HPLC was carried out by injecting 20 μl of sample solution into either an Altex 420 chromatograph fitted with an Hitachi 100-10 variable-wavelength detector or a Laboratory Data Control system consisting of a Constametric IIG pump and an LDC UV monitor set at 254 nm. Two analytical columns were used; a Phase Separations 5-μm Spherisorb silica column (250 × 4.6 mm I.D.) and a 7-μm Zorbax column (150 × 4.6 mm I.D.), slurry-packed using isopropanol as slurry solvent at a pressure of 4500 p.s.i. Preparative liquid chromatography of solutions containing 100–500 mg complex in hexane was performed on a Waters Prep LC-system 500 using a PrepPak-500 silica radical compression cartridge and a refractive index detector. Electron impact mass spectra of the chelates were recorded on a JEOL JMS D-100 mass spectrometer by direct insertion probe introduction of solid samples at 70 eV. NMR spectra were obtained on a JEOL JNM-FX200 Fourier transform NMR spectrometer and samples were made up in deuterochloroform with tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

Bromination of Cr(tfa)$_3$.

Using dichloromethane–hexane (20:80), resolution of the geometrical isomers of chromium trifluoroacetylacetonate, $Cr(tfa)_3$, was readily achieved by normal-phase adsorption HPLC in good agreement with the previous results of Uden *et al.*[8]. It was confirmed that the meridional (*mer*) isomer was eluted ahead of the facial (*fac*) isomer by injecting samples enriched in one isomer according to the method of Fay and Piper[10]. In the bromination of a mixture of isomers of $Cr(tfa)_3$, one would expect each of the brominated products to display geometrical isomerism but the HPLC analysis in Fig. 1C indicates that there are more components in the reaction mixture than could be explained simply by geometrical isomerism. The last two peaks, identified on the basis of their retention volumes (V_R) of 9.9 and 16.0 cm^3, are the geometrical isomers of the unreacted chromium chelate, $Cr(tfa)_3$. In a previous paper, the authors used mass spectral evidence to identify the major peaks in the gas chromatogram of the above reaction mixture to be the mono-, bi- and tri-brominated derivatives of $Cr(tfa)_3$, eluted in the order[6] $Cr(tfa)_3 < Cr(tfa)_2(Brtfa) < Cr(tfa)(Brtfa)_2 < Cr(Brtfa)_3$, where Brtfa represents the brominated trifluoroacetylacetonate anion. In an attempt to identify the components giving rise to the peaks in Fig. 1C, samples of the individual GC peaks were collected in small quantities for analysis by HPLC.

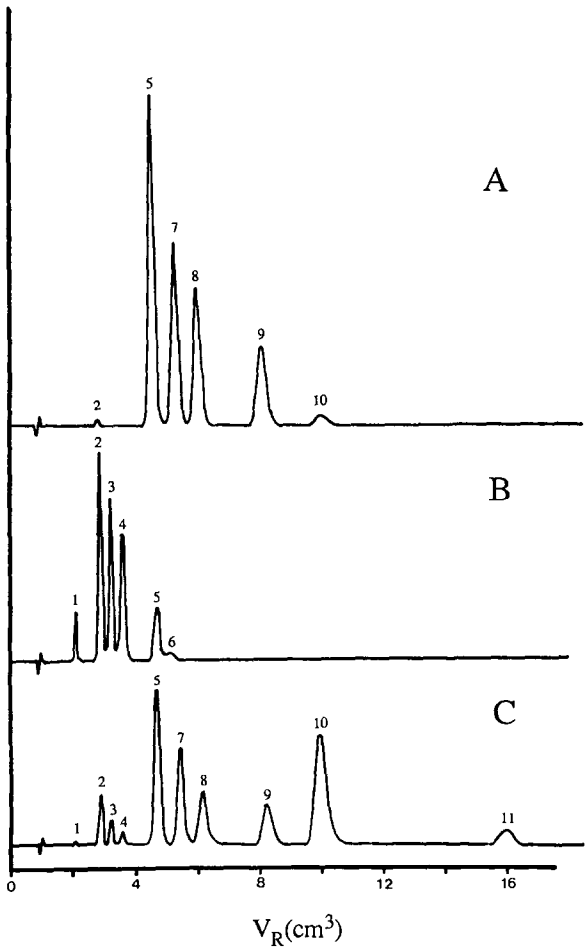

Fig. 1. Liquid chromatograms of samples of (A) the mono- and (B) the bi-brominated chromium trifluoroacetylacetonate, as collected by GC, and (C) of the reaction mixture of brominated $Cr(tfa)_3$ sampled after 45 min. Column: 5-μm Spherisorb silica, 250 × 4.6 mm I.D.; mobile phase: dichloromethane–hexane (20:80) at 1 cm^3 min^{-1}. Peaks: 1 = *mer*-$Cr(Brtfa)_3$; 2,3,4 = *mer*-$Cr(Brtfa)_2(tfa)$; 6 = *fac*-$Cr(Brtfa)_2(tfa)$; 5,7,8 = *mer*-$Cr(Brtfa)(tfa)_2$; 9 = *fac*-$Cr(Brtfa)(tfa)_2$; 10 = *mer*-$Cr(tfa)_3$; 11 = *fac*-$Cr(tfa)_3$.

The last eluting GC peak corresponds to the first LC peak (V_R = 2.1 cm^3 in Fig. 1) and hence its identity is the tri-brominated chromium chelate. The liquid chromatograms for the samples of mono- and bi-brominated chelates are shown in Figs. 1A and 1B. The last peak in Fig. 1A (V_R = 9.9 cm^3) is clearly due to traces of the *mer* isomer of $Cr(tfa)_3$ in the collected sample of the mono-brominated species. The latter appears to give rise to four major peaks with retention volumes ranging from 4.4 to 8.6 cm^3 under these conditions yet only two components were observed in the gas chromatogram of this sample. Mass spectral data for collected fractions of each of the four HPLC peaks are practically identical and the spectra show parent ions at m/z = 591 and 589 in an intensity ratio of 1:1, indicating that the four components corre-

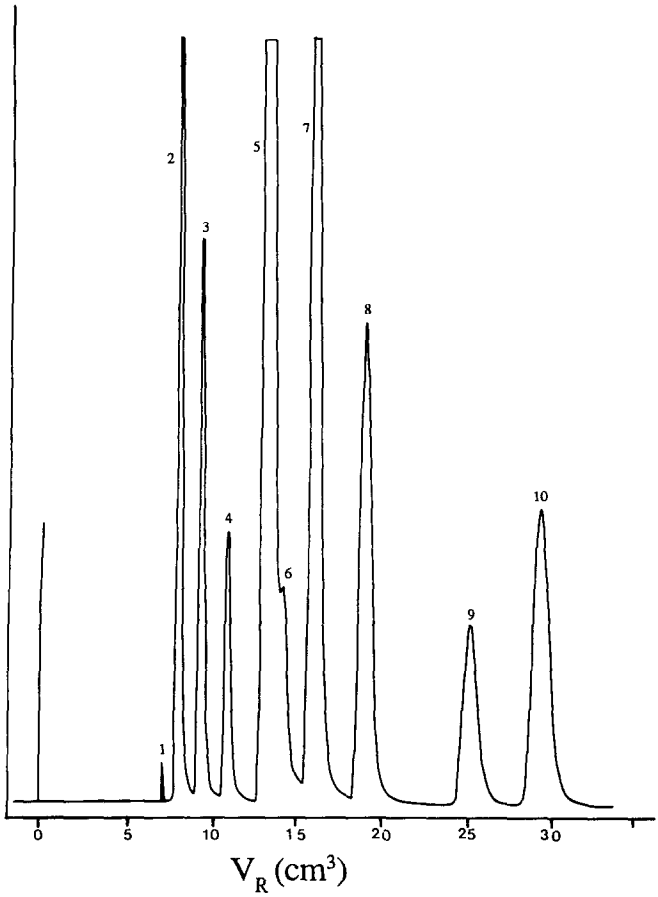

Fig. 2. Liquid chromatogram of the bromination reaction mixture of $Co(tfa)_3$ sampled after 90 min. Column: 7-μm Zorbax silica, 150 × 4.6 mm I.D.; mobile phase: dichloromethane–hexane (8:92) at 1 cm^3 min^{-1}. Peaks: 1 = *mer*-$Co(Brtfa)_3$; 2,3,4 = *mer*-$Co(Brtfa)_2(tfa)$; 6 = *fac*-$Co(Brtfa)_2(tfa)$; 5,7,8 = *mer*-$Co(Brtfa)(tfa)_2$; 9 = *fac*-$Co(Brtfa)(tfa)_2$; 10 = *mer*-$Cr(tfa)_3$.

spond to the mono-brominated species[6]. For the bi-brominated chelate sample (Fig. 1B), the peaks at V_R = 2.1 and 4.5 cm^3 arise from the tri- and mono-brominated species, respectively, which are present as impurities; hence, there appears to be four components in the bi-brominated sample also although the fourth component (V_R = 5.0 cm^3) is often difficult to detect in the chromatogram of the reaction mixture because of overlap with early eluting peaks attributed to the mono-brominated complex.

The peak area ratios of the four components for the bi-brominated chelate are relatively constant for all reactions, regardless of the reaction time or the initial isomeric ratio of $Cr(tfa)_3$; this is not unexpected as the bi-brominated species appear late in a reaction and by that stage, isomerisation would have occurred already so that an equilibrium isomeric mixture would be observed. On the otherhand, bromination reactions of $Cr(tfa)_3$ enriched with the *fac* isomer produce greater proportions of the

fourth component (V_R = 8.1 cm^3) for the mono-brominated species and if left in solution, this component decreases while the other three species increase in total peak area implying that isomerisation may be taking place on standing. This is not unusual as it has been found that the *fac* isomers of trifluoroacetylacetonates of trivalent metals isomerise to the more stable *mer* isomers in solution[10]. As the *mer* isomer is eluted before the *fac* isomer, these observations also suggest that the *mer* isomer of the partially brominated metal trifluoroacetylacetonates accounts for three peaks and the *fac* isomer one peak in the HPLC chromatogram. Only one peak is detected for the tri-brominated species by HPLC and this is in agreement with the observations in GC[6].

Bromination of Co(tfa)$_3$ and Rh(tfa)$_3$.

Analyses of reaction mixtures from the bromination of cobalt and rhodium trifluoroacetylacetonates, shown in Figs. 2 and 3, yield remarkably similar results to those observed for the chromium system. Samples of the individual rhodium complexes collected in GC again show that four well resolved peaks are observed in HPLC for the mono- and bi-brominated derivatives (Fig. 3). Confirmation of the identity of each peak in the liquid chromatography of the rhodium complexes was made by mass spectral analysis of a fraction of the peak collected from the exit line of the LC detector. All four peaks with retention volumes in the range 19–33 cm^3 in Fig. 3 had similar spectra; the fragmentation patterns (Table I) and the 1:1 intensity ratio

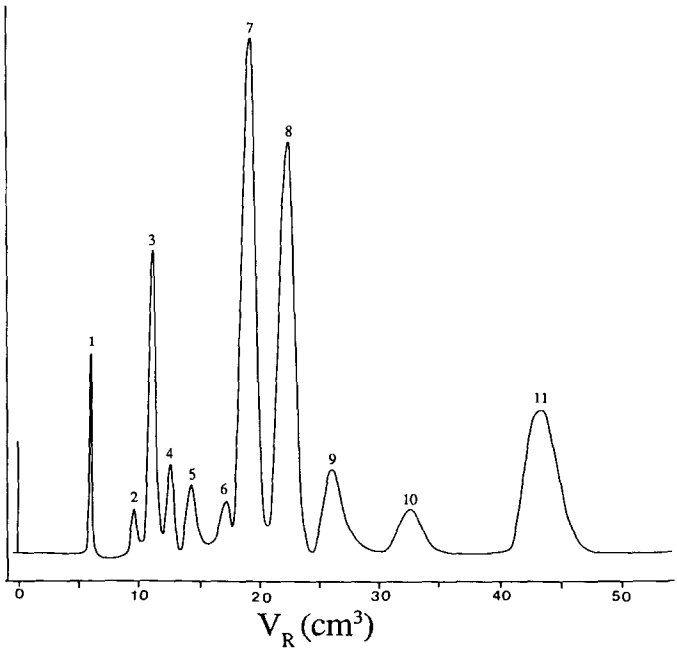

Fig. 3. Liquid chromatogram of the bromination reaction mixture of Rh(tfa)$_3$ sampled after 2 h. Columns as in Fig. 2; mobile phase: dichloromethane–hexane (6:94) at 1 cm^3 min^{-1}. Peaks: 1 = *mer*-Rh(Brtfa)$_3$; 2 = *fac*-Rh(Brtfa)$_3$; 3,4,5 = *mer*-Rh(Brtfa)$_2$(tfa); 6 = *fac*-Rh(Brtfa)$_2$(tfa); 7,8,9 = *mer*-Rh(Brtfa)(tfa)$_2$; 10 = *fac*-Rh(Brtfa)(tfa)$_2$; 11 = *mer*-Rh(tfa)$_3$.

TABLE I

RELATIVE INTENSITIES OF FRAGMENT IONS IN THE MASS SPECTRA OF $Rh(tfa)_3$ AND ITS BROMINATED DERIVATIVES

Ion	*Rh(tfa)$_3$*	*Rh(Brtfa)(tfa)$_2$*	*Rh(Brtfa)$_2$(tfa)*	*Rh(Brtfa)$_3$*
M^+	50	38	43	40
$[M-(tfa)]^+$	100	12	26	–
$[M-(Brtfa)]^+$	–	100	100	100
$[M-(Brtfa)-CF_2]^+$	–	15	6	1
$[M-(Brtfa)-CF_3]^+$	–	28	23	13
$[M-(Brtfa)-2CF_3]^+$	–	17	14	7
$[M-(Brtfa)-(tfa)]^+$	–	23	9	–
$[M-2(tfa)]^+$	9	–	–	–
$[M-2(Brtfa)]^+$	–	–	43	80
$[M-2(tfa)-CF_3]^+$	4	–	–	–
$[M-2(Brtfa)-CF_3]^+$	–	–	13	7

of the parent ions at m/e = 642 and 640 indicate that all components in this group of LC peaks are mono-brominated species. The four peaks with V_R = 11.0–17.2 cm^3 are bi-brominated species which give parent ions at m/e = 722, 720 and 718 in a ratio of 1:2:1. The tri-brominated rhodium complex displays two isomers in GC and HPLC, the first eluting in each case being the *mer* isomer as shown later. The *fac* and *mer* isomers of the tri-brominated complexes gave similar spectra with parent ions at m/e = 802, 800, 798 and 796 in an intensity ratio of 1:3:3:1. Table I lists the data for the major fragments in the mass spectra of brominated derivatives of $Rh(tfa)_3$

As the HPLC results provide very strong evidence that there are three components for the *mer* isomer of each of the partially brominated chelates, it was of interest to carry out bromination reactions on the *mer* isomer only. Pure samples of the *mer* isomers of $M(tfa)_3$ were isolated by fractional recrystallisation[10] or preparative LC and bromination reactions were performed as described above for mixtures of isomers. HPLC analysis of the rhodium reaction mixture yielded a similar chromatogram to that in Fig. 3 and the peak due to the *fac* isomer of the initial rhodium reactant was absent. In all three metal systems, four peaks and not three were observed for the partially brominated chelates.

NMR spectroscopy

In order to characterize all of the components giving rise to the various liquid chromatographic peaks by NMR spectroscopy, attempts were made to isolate sufficient quantities of each of the species. Although fractional recrystallization was found to be suitable in the isolation of the chromium compounds[6], separation of the brominated rhodium chelates requires preparative LC using dichloromethane–hexane (10:90) and it was only possible to isolate *mer*-$Rh(tfa)_3$ and $Rh(Brtfa)_2(tfa)$. Two samples of the bi-brominated derivative were isolated; analytical HPLC showed that one of these samples contained only the first eluting component (V_R = 11.0 cm^3, Fig. 3) whereas the other sample contained the first three of the four components attributed to the bi-brominated complex.

^1H NMR spectroscopy has been found to be extremely useful in the character-

ization of the configurations of isomers of trivalent metal trifluoroacetylacetonates. The *fac* isomer of $Rh(tfa)_3$ was reported to give single resonances for the methyl and methine protons at 2.36 and 5.99 ppm, respectively, whereas the *mer* isomer gave three methyl resonances at 2.35–2.40 ppm and three methine resonances at 5.98–6.03 ppm[10,11]. The sample corresponding to the peak with V_R = 6.1 cm^3 in Fig. 3 has three methyl group resonances at 2.72–2.75 ppm and no methine proton resonance; this is consistent with non-equivalent methyl groups in a *mer* configuration and bromination of all three chelate rings, as in $Rh(Brtfa)_3$. A mixture of the isomers of the tri-brominated complex shows four methyl groups resonances at 2.72–2.76 ppm.

The spectra of the two isolated samples of the bi-brominated rhodium chelate were identical and had three methyl resonances at 2.30–2.32 ppm indicative of a *mer* configuration and in each case, a single methine resonance was observed at 5.96 ppm arising from one unbrominated ligand. As there is no evidence of another methyl resonance peak in the ^1H NMR spectrum of the sample which displays three HPLC peaks, this indicates that the *mer* isomer of this compound consists of three components and hence the *fac* isomer gives one HPLC peak. This supports the earlier suggestions of solution isomerisation for the mono-brominated species observed in the HPLC monitoring of the bromination of $Cr(tfa)_3$ initially enriched in the *fac* isomer.

^{13}C NMR spectra were also run on the above rhodium samples collected by preparative LC. As these data confirm the assignment of *mer* configurations already derived from the ^1H NMR spectral data but provide no additional structural information, they are not presented in this paper. ^1H and ^{13}C NMR spectra were both unsuccessful in differentiating the individual components of the *mer* isomers of the partially brominated chelates.

On the basis of the NMR and mass spectral data for the brominated rhodium chelates and the close similarities of the elution profiles of bromination reaction mixtures of all three trifluoroacetylacetonates, it is concluded that the *mer* isomers of the partially brominated trifluoroacetylacetonates of chromium(III), rhodium(III)

TABLE II

CHROMATOGRAPHIC RETENTION DATA FOR METAL TRIFLUOROACETYLACETONATES AND THEIR BROMINATED DERIVATIVES

Column: 7-μm Zorbax silica, 150 × 4.6 mm I.D.; mobile phase: dichloromethane–hexane (10:90); column dead volume: 1.9 cm^3. *mer* (1/2/3) = Three components of the *mer* partially brominated derivatives.

Metal complex	*Isomer*	*Capacity factors for individual components*		
		M = Cr	*M = Rh*	*M = Co*
$M(Brtfa)_3$	*mer*	1.95	1.2	2.3
	fac	–	1.9	–
$M(Brtfa)_2(tfa)$	*mer* (1/2/3)	2.65/2.95/3.25	2.05/2.3/2.6	2.6/3.05/3.5
	fac	4.3	3.15	4.6
$M(Brtfa)(tfa)_2$	*mer*(1/2/3)	4.1/4.6/5.2	3.6/4.05/4.7	4.3/5.1/6.0
	fac	7.25	6.05	7.8
$M(tfa)_3$	*mer*	7.8	7.95	8.9
	fac	12.95	12.7	14.1

and cobalt(III) consist of three components which are readily separated by normal-phase HPLC. The chromatographic capacity factors for the parent metal chelates and their brominated derivatives have been determined under identical chromatographic conditions and the data are listed in Table II.

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