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CHROMATOGRAPHIC ANALYSIS OF ELECTROPHILIC SUBSTITUTION REACTIONS OF METAL ACETYLACETONATES

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SUMMARY

Electrophilic bromination and nitration of rhodium(III), cobalt(III) and chromium(III) acetylacetonates under limiting conditions lead to the formation of mono-, bi- and tri-substituted derivatives. The individual complexes and mixtures of the complexes have been investigated to determine their suitability for analysis by gas chromatography (GC) and high-performance liquid chromatography (HPLC). The cobalt(III) complexes were found to be thermally unstable and hence unsuitable for GC, whereas the rhodium and chromium complexes were readily separated on an OV-101/Chromosorb W column. Analysis of reaction mixtures containing labile or thermally unstable complexes, especially the nitrated acetylacetonates of cobalt(III), have been carried out using normal-phase HPLC.

INTRODUCTION

Electrophilic substitution reactions of metal acetylacetonates have been shown to lead to substitution on the central (or γ) carbon of the chelate ring^{1,2}. The mixed-ligand complexes arising from electrophilic reactions of 2,4-pentanedionates of trivalent metals were isolated in those early studies by classical chromatographic techniques such as thin-layer chromatography and florisil column chromatography^{1,3}.

We have recently applied gas chromatography (GC) and high-performance liquid chromatography (HPLC) to the separation of the brominated products of chromium(III) and cobalt(III) acetylacetonates⁴ and HPLC was recommended for monitoring the electrophilic substitution reactions of these chelates.

In this paper, we wish to report the results of more extensive investigations on the application of modern chromatographic techniques to the separation of the products of bromination and nitration reactions of metal acetylacetonates.

EXPERIMENTAL

The metal acetylacetonates of cobalt(III), chromium(III) and rhodium(III)

were prepared by documented procedures⁵⁻⁸. Cobalt and chromium chelates were purified by recrystallisation from benzene-petroleum spirits, and the rhodium chelates by column chromatography on acid-washed alumina using chloroform as eluent. In all cases, the melting points agreed with those in the literature⁵⁻⁸ and the respective molecular ions were observed in the mass spectra of the chelates.

Mixtures of the brominated derivatives of metal acetylacetonates were obtained by mixing appropriate amounts of the metal chelate and N-bromosuccinimide in carbon tetrachloride, and the reaction mixture was stirred at ambient temperature for 4 h⁹. The solution was filtered and the solvent removed in a stream of nitrogen. The resulting solid was washed with aqueous sodium bisulfite and water, and then air dried.

Documented procedures for nitration of metal acetylacetonates were modified for the present work^{10,11}. The metal chelate and an appropriate quantity of copper nitrate in acetic anhydride were stirred at room temperature for 4 h. A solution of chilled sodium acetate was added and the mixture stirred for 1 h. The mixture of nitrated chelates was collected by filtration, washed with aqueous sodium bicarbonate, water and then air-dried.

GC was carried out using a Perkin-Elmer F11 gas chromatograph fitted with a flame ionization detector, however, any chromatograph with provision for on-column injection would be suitable. After packing, all columns were silanized with Silyl-8 before use. Experimental conditions are given elsewhere in this paper.

HPLC data were obtained using an Altex 420 liquid chromatograph and UV detection at a wavelength of 254 nm. Columns (150 × 4.6 mm I.D.) were slurry-packed with 7- μ m Zorbax silica using isopropanol as slurry solvent at a pressure of 4500 p.s.i. Preparative HPLC was performed on a Waters Prep LC-system 500 using a PrepPak-500 silica radial compression cartridge and refractive index detector.

Mass spectra of the chelates were recorded on a JEOL JMS D100 mass spectrometer using a direct insertion probe and an electron impact voltage of 70 eV.

RESULTS AND DISCUSSION

GC

In a previous paper⁴, conditions were established for GC analysis of mixtures arising from bromination of chromium(III) acetylacetonate, Cr(acac)₃. Using on-column injection into a glass column packed with 2.5% OV-101 on Chromosorb W, the three brominated chromium(III) complexes and Cr(acac)₃ were eluted at 160°C without decomposition and the order of elution was found to be: Cr(acac)₃ < Cr(acac)₂(Bracac) < Cr(acac)(Bracac)₂ < Cr(Bracac)₃, where Bracac is the brominated acetylacetonate ligand anion.

Similar GC conditions were applied to the analysis of nitration and bromination reaction mixtures of chromium(III), cobalt(III) and rhodium(III) acetylacetonates. The liquid phase loading was reduced from 2.5% to 1.0% OV-101 in order to decrease the total analysis time especially in the case of the chromium(III) complexes, which tend to be thermally unstable at temperatures above 170°C. For example, at 160°C Cr(Bracac)₃ is eluted in about 11 min using a 1.0% OV-101 loaded column compared to a retention of around 32 min using a 2.5% OV-101 loaded column.

The complete series of brominated and nitrated complexes of chromium and rhodium are eluted at 160°C without any evidence of decomposition whereas the substituted derivatives of cobalt(III) acetylacetonate are thermally unstable. The retention data for the chromium and rhodium complexes are listed in Table I and retention times are observed to increase with the extent of substitution consistent with that reported previously for the brominated chromium(III) complexes⁴. In each case, chromium elutes before rhodium and the brominated complexes elute before the corresponding nitrated complexes. The nitrated complexes tend to be less thermally stable than the brominated complexes and at temperatures above 160°C miscellaneous peaks, characteristic of decomposition of metal chelates, are observed in the chromatograms of the former. Furthermore, the brominated rhodium(III) complexes are the most stable in the series of metal complexes studied in this investigation and excellent resolution of the components of a composite mixture of Rh(acac)₃ and its brominated derivatives can be achieved at temperatures up to 200°C, as shown in the chromatogram presented in Fig. 1. GC may be used to monitor the course of these electrophilic substitution reactions as demonstrated in our previous paper⁴.

A linear relationship between the logarithm of the retention time (t_R) and the number of bromine substituents was satisfied by the brominated acetylacetonates of rhodium(III), an observation which has been reported for the brominated derivatives of Cr(acac)₃ and alkyl substituted metal β -diketonates^{4,12}. If the retention data in Table I including those for the unsubstituted metal acetylacetonates are used to construct log plots, then it is doubtful that a universal linear relationship exists between log t_R and the number of substituents on the γ -carbon of the metal chelate rings (see Fig. 2). The nitrated metal acetylacetonates, especially those of chromium(III), consistently give log plots which are non-linear. In view of the limited number of substituted metal acetylacetonates investigated, the reason for the anomalous behaviour of the nitrated derivatives is not obvious but it may be due to thermal instability of these complexes within the column. In support of this, thermogravimetric (TG) and differential thermal analysis (DTA) indicated that the tri-nitrated chromium chelate decomposes at a lower temperature than the corresponding rhodium chelate.

TABLE I

GC RETENTION DATA FOR CHROMIUM(III) AND RHODIUM(III) ACETYLACETONATES AND SUBSTITUTED DERIVATIVES AT 160°C

Other conditions as in Fig. 1.

Metal complex	Retention time (min)	
	<i>M</i> = Cr	<i>M</i> = Rh
M(acac) ₃	0.75 ± 0.05	1.5 ± 0.05
M(Bracac)(acac) ₂	1.75 ± 0.05	3.40 ± 0.10
M(Bracac) ₂ (acac)	4.45 ± 0.25	8.35 ± 0.15
M(Bracac) ₃	10.85 ± 0.35	19.80 ± 0.30
M(NO ₂ acac)(acac) ₂	2.35 ± 0.05	3.95 ± 0.10
M(NO ₂ acac) ₂ (acac)	6.65 ± 0.30	10.25 ± 0.25
M(NO ₃ acac) ₃	15.45 ± 0.35	23.50 ± 0.30

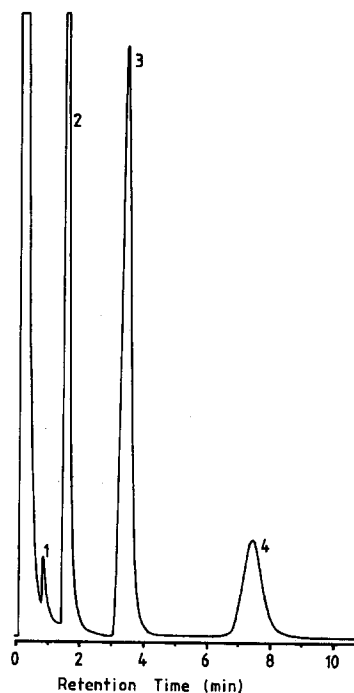


Fig. 1. Gas chromatogram of a synthetic mixture of brominated rhodium(III) acetylacetonates and $\text{Rh}(\text{acac})_3$. Column: glass (1 m \times 3 mm I.D.) packed with 1% OV-101 on Chromosorb W. Conditions: oven, 180°C; injector and detector, 220°C; carrier gas (N_2) flow-rate, 45 $\text{cm}^3 \text{min}^{-1}$. Peak identities: 1 = $\text{Rh}(\text{acac})_3$; 2 = $\text{Rh}(\text{Bracac})(\text{acac})_2$; 3 = $\text{Rh}(\text{Bracac})_2(\text{acac})$; 4 = $\text{Rh}(\text{Bracac})_3$.

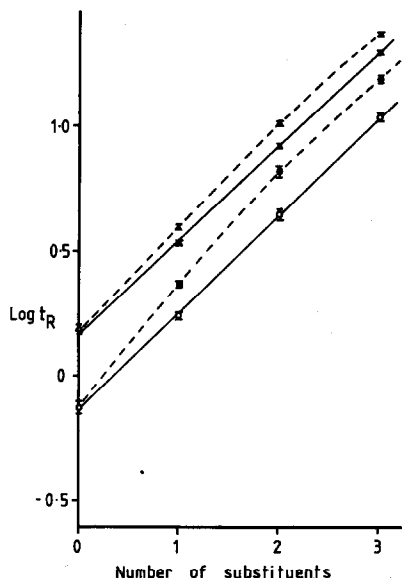


Fig. 2. Plots of logarithm of retention time, $\log t_R$, against the number of substituents in brominated and nitrated acetylacetonates of rhodium and chromium (\circ = brominated Cr complexes; \bullet = nitrated Cr complexes; \triangle = brominated Rh complexes; \blacktriangle = nitrated Rh complexes).

HPLC

Using dichloromethane as eluent, normal-phase HPLC was applied to the separation of mixtures of brominated or nitrated acetylacetonates of all three metals. Excellent resolution of each series of complexes was achieved and the tri-substituted complex was eluted with the lowest retention volume. If the unsubstituted parent metal acetylacetonate is included in the mixture of its substituted derivatives, the former is strongly retained by the column using pure dichloromethane as eluent. A typical chromatogram for the mixture of nitrated cobalt(III) acetylacetonates and $\text{Co}(\text{acac})_3$ is presented in Fig. 3. An independent thermoanalytical study of these nitrated complexes shows that they are extremely unstable and hence Fig. 3 is a good example of the applicability of HPLC to the analysis of labile or thermally unstable metal complexes.

Capacity factors for the complete series of rhodium, chromium and cobalt(III) complexes are listed in Table II. The identity of each chromatographic peak was established by fraction collection followed by mass spectral analysis. The order of elution of the nitrated derivatives is in agreement with that previously established for

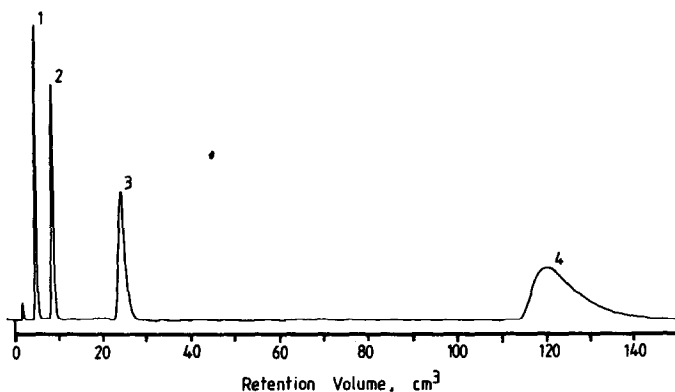


Fig. 3. Liquid chromatogram of a synthetic mixture of nitrated cobalt(III) acetylacetonates and $\text{Co}(\text{acac})_3$. Column: 7- μm Zorbax silica, 150×4.6 mm I.D. Eluent: dichloromethane at $2.1 \text{ cm}^3 \text{ min}^{-1}$. Detector wavelength, 254 nm. Peak identities: 1 = $\text{Co}(\text{NO}_2\text{acac})_3$; 2 = $\text{Co}(\text{NO}_2\text{acac})_2(\text{acac})$; 3 = $\text{Co}(\text{NO}_2\text{acac})(\text{acac})_2$; 4 = $\text{Co}(\text{acac})_3$.

the brominated species⁴, however, each nitrated complex is retained more strongly than its corresponding brominated analogue. For complexes of the same stoichiometry, the cobalt complex is more strongly retained and the rhodium complex less strongly retained than the corresponding chromium complex, *i.e.*, $\text{Rh} < \text{Cr} < \text{Co}$; this result is consistent with previous observations on symmetrical metal β -diketonates in normal-phase HPLC¹³.

The strong retention of the parent metal acetylacetonates results in long analysis times for mixtures arising from their electrophilic substitution reactions. This may be overcome by adding a polar modifier to the eluent; 3–5% acetonitrile in dichloromethane has proved to be satisfactory. For example, using 3% acetonitrile in dichloromethane, capacity factors for the unsubstituted metal acetylacetonates decrease to values in the range 6.9–9.2 while maintaining excellent resolution of the substituted derivatives. The more polar eluent has no effect on the order of elution within a series of substituted complexes of a particular metal or across the complete series for metal complexes of the same stoichiometry.

HPLC has been recommended for monitoring the bromination of metal acetylacetonates especially those which are labile or thermally unstable⁴. This may now be extended to include nitration reactions of these chelates using copper(II) nitrate in acetic anhydride as the electrophilic reagent. As the nitrated acetylacetonates of cobalt(III) are unsuitable for GC analysis, nitration of cobalt(III) acetylacetonate was chosen here to demonstrate the feasibility of determining the composition of this reaction mixture by HPLC. Using varying mole ratios of copper nitrate and $\text{Co}(\text{acac})_3$, the reactions were allowed to reach equilibrium before analysis of the isolated mixture of metal complexes. Equilibrium is achieved in about 2 h at room temperature (22°C); the resulting analytical data is presented in Table III. As in the case of the bromination reaction⁴, it is concluded from the data in Table III that a mole ratio of initial reactants greater than the stoichiometric 3:1 ratio is required to ensure complete nitration of the parent metal acetylacetonate. HPLC analysis has also

TABLE II

HPLC DATA FOR BROMINATED AND NITRATED ACETYLACETONATES OF RHODIUM, CHROMIUM AND COBALT(III)

Conditions as in Fig. 3; measured column dead volume, 1.9 cm³.

Metal complex	Capacity factor		
	<i>M</i> = Rh	<i>M</i> = Cr	<i>M</i> = Co
M(Bracac) ₃	0.4	0.5	0.7
M(Bracac) ₂ (acac)	1.8	2.3	3.0
M(Bracac)(acac) ₂	8.0	9.8	12.6
M(NO ₂ acac) ₃	1.1	1.4	1.7
M(NO ₂ acac) ₂ (acac)	2.8	3.2	3.9
M(NO ₂ acac)(acac) ₂	10.1	10.6	13.2
M(acac) ₃	39.3	48.7	64.7

shown that all substituted cobalt(III) acetylacetonates are unstable in solution and fresh solutions should be prepared daily; even in the solid state, there are strong indications that the cobalt complexes are unstable after about 30 days in storage and miscellaneous peaks appear in the chromatograms.

Preparative HPLC was developed in order to isolate sufficient quantities of pure samples of the individual substituted metal acetylacetonates. Using the equipment described earlier in this paper and 5% ethyl acetate in dichloromethane as eluent at a flow-rate of 100 cm³ min⁻¹, excellent resolution of all components in electrophilic substitution reaction mixtures was achieved. The purity of each mixed-ligand complex was determined using analytical HPLC.

CONCLUSIONS

HPLC is recommended for monitoring the electrophilic substitutions of acetylacetonates of trivalent metals mainly because of the thermal instability of the chelates of cobalt(III). In all of the cases included in this investigation, the order of

TABLE III

EFFECT OF MOLE RATIO OF REACTANTS ON THE DISTRIBUTION OF PRODUCTS IN THE NITRATION OF COBALT(III) ACETYLACETONATE

Column: as in Fig. 3. Eluent: 3% acetonitrile in dichloromethane.

Mole ratio <i>Cu(NO₃)₂/Co(acac)₃</i>	Percent distribution			
	<i>Co(acac)₃</i>	<i>Co(NO₂acac)(acac)₂</i>	<i>Co(NO₂acac)₂(acac)</i>	<i>Co(NO₂acac)₃</i>
1:1	0.7	65.0	34.3	
2:1		6.1	70.9	23.0
3:1			2.4	97.6
4:1				100.0

elution in normal-phase HPLC is: $M(X\text{-acac})_3 < M(X\text{-acac})_2(\text{acac}) < M(X\text{-acac})(\text{acac})_2 < M(\text{acac})_3$, where X = Br or NO₂, and this order is the reverse of that observed for elution in GC.

All of the substituted acetylacetonates of chromium and rhodium are extremely inert and are eluted quantitatively in HPLC. In the case of cobalt(III) complexes, quantitative elution can only be achieved when freshly prepared samples and solutions are analysed.

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