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Note

Gas chromatographic monitoring of the reaction of beryllium oxyacetate and beryllium oxypropionate in acetone solution

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Wynne and Bauder¹ have used proton magnetic resonance spectrometry to demonstrate that mixed beryllium oxycarboxylates undergo carboxylate scrambling in solution. Earlier claims to the preparation of pure mixed ligand beryllium oxycarboxylates by a number of investigators^{2,3} were shown by Marvel and Martin⁴ and Hardt⁵ to be mixtures of mixed carboxylate complexes of general formula $\text{Be}_4\text{O}(\text{RCO}_2)_n(\text{R}'\text{CO}_2)_{6-n}$, where $0 < n < 6$, resulting from ligand-exchange reactions in solution.

We have established the optimum conditions for gas chromatographic (GC) elution of beryllium oxyacetate, oxypropionate, oxypivalate and oxyisobutyrate⁶; use of exhaustively silanized supports coated with 5% Apiezon L yielded more satisfactory chromatographic behaviour for beryllium oxyacetate and oxypropionate than that previously described by Barratt *et al.*⁷. Beryllium oxyacetate is eluted at 140° with a much shorter retention time than the other three beryllium oxycarboxylates.

Although GC has been used widely in the measurement of reaction kinetics and equilibrium constants for organic systems, this technique has rarely been used for kinetic studies in metal complex systems. Linck and Sievers⁸ reported the use of GC to study the formation of mixed-ligand complexes in mixtures of aluminium acetylacetonate and aluminium hexafluoroacetylacetonate; however, as this work was never published in the scientific literature, kinetic data for this system are not readily available.

In view of the lack of GC investigations in the areas of kinetics and equilibria in metal complex systems, we have been interested in investigating the feasibility of monitoring ligand-exchange reactions in mixtures of beryllium oxyacetate and oxypropionate by GC. In addition, it may be possible to use GC to separate and isolate mixed-ligand complexes and thus overcome the problems outlined by previous workers¹ in the separation of complexes with similar properties.

EXPERIMENTAL

Beryllium oxyacetate and oxypropionate were prepared by the method of Moeller⁹ and purified by vacuum sublimation.

GC was carried out on a Perkin-Elmer F11 gas chromatograph using flame

ionization detection. Pyrex glass columns (1 m \times 0.4 mm I.D.) were packed with 5% Apiezon L on DMCS-treated Universal B (60–80 mesh). The column temperature was set at 140°, injector and detector at 200° and nitrogen flow-rate at 60 ml/min.

Ligand exchange reactions were performed by mixing beryllium oxyacetate and oxypropionate in the molar ratio of 1:2 at 90° in acetone (0.01 *M* solutions). The reaction mixture was sampled (1–2 μ l) using a 5- μ l syringe and injected immediately into the chromatograph.

Identification of eluted samples was carried out by mass spectrometry (MS) using a Jeol JMS D-100 mass spectrometer and a direct solids probe.

RESULTS AND DISCUSSION

Separate injections of the pure reactants, beryllium oxyacetate and beryllium oxypropionate, yielded retention times of 4.2 and 24.2 min, respectively, at 140°. MS analysis of the eluted samples confirmed that the complexes were eluted without decomposition⁶.

Ligand-exchange reactions were carried out at 90° because it was found that exchange was very slow at room temperature. Typical chromatograms for sampling of the reaction at 90° in acetone are shown in Fig. 1. As expected for ligand exchange of two beryllium carboxylates of formula Be_4OAc_6 and Be_4OPr_6 (where Ac = acetate and Pr = propionate), seven peaks are observed corresponding to the species $\text{Be}_4\text{OX}_n\text{Y}_{6-n}$, where $0 < n < 6$. The retention times of the first and seventh peaks are identical to those obtained for the reactants. Although it could well be assumed that the remaining peaks are due to the mixed-ligand complexes generated in the reaction, confirmation of their composition was obtained by MS analysis.

Since resolution was best in the later stages of the chromatogram, fractions of the last two mixed-ligand species in the series were collected by restricting sampling

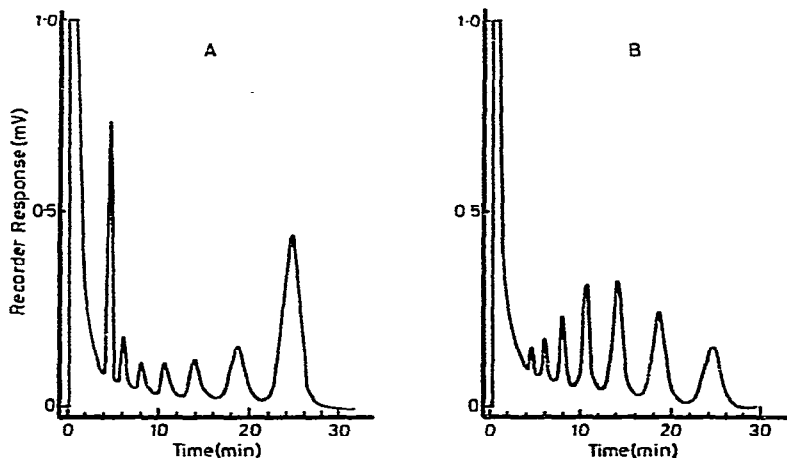


Fig. 1. Chromatograms for the reaction of beryllium oxyacetate and oxypropionate at 90° in acetone for an initial molar ratio of 1:2. Conditions: column temp., 140°; injector and detector, 200°; Pyrex glass column, 1 m \times 0.4 mm I.D., packed with 5% Apiezon L on silanized Universal B (60–80 mesh); nitrogen flow-rate, 60 ml/min. Sampling time (A) 36 min, (B) 200 min.

TABLE I

MASS SPECTRAL DATA FOR SAMPLES COLLECTED FROM CHROMATOGRAPHIC PEAKS WITH RETENTION TIMES 13.7 min ($\text{Be}_4\text{OAc}_2\text{Pr}_4$) AND 18.2 min ($\text{Be}_4\text{OAcPr}_5$)
 N.D. = Not detected.

<i>m/e</i>	Ion	Relative intensity (%)	
		$\text{Be}_4\text{OAc}_2\text{Pr}_4$	$\text{Be}_4\text{OAcPr}_5$
417	$\text{Be}_4\text{OPr}_5^+$	2	100
403	$\text{Be}_3\text{OAcPr}_4^+$	37	95
389	$\text{Be}_2\text{OAc}_3\text{Pr}_3^+$	100	N.D.
375	$\text{Be}_4\text{OAc}_3\text{Pr}_2^+$	6	6
287	$\text{Be}_4\text{OPr}_3\text{O}^+$	2	30
273	$\text{Be}_3\text{OAcPr}_2\text{O}^+$	9	22
262	$\text{Be}_3\text{OPr}_3^+$	9	88
259	$\text{Be}_2\text{OAc}_2\text{PrO}^+$	6	N.D.
248	$\text{Be}_3\text{OAcPr}_2^+$	27	44
234	$\text{Be}_3\text{OAc}_2\text{Pr}^+$	11	11
231	$\text{Be}_3\text{OPr}_2(\text{OH})\text{O}^+$	2	25
217	$\text{Be}_4\text{OAcPr}(\text{OH})\text{O}^+$	6	13

to coincide with the top portions of the peaks of retention times 13.7 and 18.2 min; collection times were 13.2–14.2 min and 17.6–18.8 min, respectively. The major ions observed in the mass spectra of both samples are listed in Table I.

The mass spectrum of the sample eluted at 13.7 min reveals that the high intensity peaks at $m/e = 403$ and 389 arise from the predicted fragmentation pattern of the mixed-ligand complex, $\text{Be}_4\text{OAc}_2\text{Pr}_4$ (refs. 1, 7 and 10). The peaks from m/e 287 to 217 result from further fragmentation of the ions $\text{Be}_4\text{OAcPr}_4^+$ and $\text{Be}_4\text{OAc}_2\text{Pr}_3^+$. The low intensity peaks at m/e 417 and 375 are due to minor impurities from neighbouring mixed-ligand complexes in the chromatogram, *viz.* $\text{Be}_3\text{OAcPr}_5$ and $\text{Be}_4\text{OAc}_3\text{Pr}_3$. Absence of peaks at m/e 245 and 220, which would result from fragmentation of $\text{Be}_4\text{OAc}_3\text{Pr}_2^+$ (m/e 375), suggests that the level of impurity from $\text{Be}_4\text{OAc}_3\text{Pr}_3$ is small. Although the peak at m/e 403 is intense in the spectra of both samples, the peak at m/e 417 is weak in the spectrum of $\text{Be}_4\text{OAc}_2\text{Pr}_4$ and most intense for $\text{Be}_4\text{OAcPr}_5$ (see Table I), thus suggesting that $\text{Be}_4\text{OAcPr}_5$ is only a trace contaminant in the complex eluted at 13.7 min.

The mass spectrum of the eluent at 18.2 min identifies it as $\text{Be}_4\text{OAcPr}_5$ with high intensity peaks occurring at m/e 417, 403, 273, 262 and 248. The absence of peaks at m/e 389 and 259 indicates that $\text{Be}_4\text{OAc}_2\text{Pr}_4$ is not an impurity, however, it is interesting to note that peaks at m/e 375 and 234 suggest that $\text{Be}_4\text{OAc}_3\text{Pr}_3$ is present as a trace impurity. Contamination from Be_4OPr_6 is difficult to determine since peaks arising from its fragmentation (m/e 417, 287, 262 and 231) are also observed for the mixed-ligand complex, $\text{Be}_4\text{OAcPr}_5$.

MS identification of two of the mixed-ligand complexes shows that the order of elution is Be_4OAc_6 (4.2) < $\text{Be}_4\text{OAc}_5\text{Pr}$ (5.8) < $\text{Be}_4\text{OAc}_4\text{Pr}_2$ (7.8) < $\text{Be}_4\text{OAc}_3\text{Pr}_3$ (10.2) < $\text{Be}_4\text{OAc}_2\text{Pr}_4$ (13.7) < $\text{Be}_4\text{OAcPr}_5$ (18.2) < Be_4OPr_6 (24.2), with the respective retention times (min) given in parentheses.

The chromatograms in Fig. 1 show clearly that it is possible to monitor the ligand-exchange reactions of metal complex systems using GC. Fig. 1A represents

the reaction after 36 min and clearly shows that the reactants are still the predominant species in the reaction mixture while the mixed-ligand complexes are continuing to be produced. On the other hand, Fig. 1B represents the state of the reaction at equilibrium which occurs after about 200 min.

As it is possible that ligand-exchange reactions may also occur in the gas phase at the column temperature employed, it was considered important to test for such behaviour. Two simple tests were performed: (i) 1- μ l samples of beryllium oxyacetate and oxypropionate (as 0.01 M solutions) were collected into different syringes, the oxypropionate was injected first followed immediately by the oxyacetate so that the samples would mix in the injection port and in the column; (ii) a similar procedure was used allowing a 1-min delay between injections, so that the acetate would overtake the propionate on the column because of the much shorter retention time of the former. The resulting chromatograms for both tests were similar (Fig. 2) and, in addition to peaks for beryllium oxyacetate and oxypropionate, showed the appearance of insignificant peaks due to $\text{Be}_4\text{OAc}_3\text{Pr}$ and $\text{Be}_4\text{OAcPr}_3$, thus indicating negligible reaction in the column.

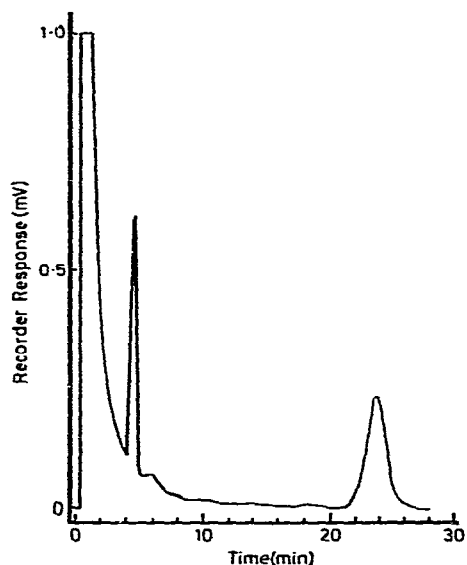


Fig. 2. Chromatogram illustrating the extent of interaction of beryllium oxyacetate and oxypropionate within the column. Column and conditions are identical to those in Fig. 1.

During the course of the present investigations, attempts were made to prepare and isolate pure samples of mixed-ligand beryllium oxycarboxylates, as described previously in the literature^{2,3}. The products were analysed by GC using the conditions outlined above; chromatograms similar to Fig. 1B were obtained, showing conclusively that the products were mixtures of mixed-ligand oxycarboxylates in agreement with the findings of Marvel and Martin⁴ and Hardt⁵. Fractional recrystallizations and/or column chromatography only marginally affected the chromatograms of the products.

The results presented in this paper demonstrate that GC can be used to separate mixtures of mixed-ligand beryllium oxycarboxylates of similar properties and to monitor ligand exchange reactions in these systems. An extensive investigation of the beryllium oxyacetate-oxypropionate system is currently being carried out in order to extract kinetic and equilibrium data for the ligand-exchange processes.

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