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GAS CHROMATOGRAPHY OF VOLATILE METAL DIALKYL-DITHIOPHOSPHATES

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SUMMARY

Examination of a wide range of metal dialkyldithiophosphates has shown that the diethyl and diisopropyl derivatives of nickel, palladium, platinum, chromium and rhodium can be successfully eluted by gas chromatography on inert diatomaceous-earth supports such as Gas-Chrom Q or Chromosorb 750 coated with silicone stationary phases OV-101, SE-30 or PS-300. The corresponding zinc chelates, although volatile, display considerable tailing on all columns tested, and it is proposed that this phenomenon may be due to the presence of dimeric species in the gas phase. Thermal analysis of other metal dialkyldithiophosphates show them to be non-volatile and unsuitable for gas chromatography.

INTRODUCTION

During the 1960's, many of the reports on the gas chromatography (GC) of metal chelates were based on the β -diketonates and their fluorinated derivatives, and several reviews cover this area¹⁻⁵. In the last decade, there has been a distinct trend towards the investigation of other chelate systems; these include the monothioacetylacetonates, bidentate and tetradentate β -ketoamines, and dialkyldithiocarbamates; much of this work has been reviewed by Uden and Henderson⁶.

Metal complexes of O,O'-dialkyldithiophosphoric acids have been known for many years^{7,8} and extensive investigations on their solvent extraction have been reported⁹⁻¹¹. Cavell *et al.*^{12,13} claimed that some metal diethyldithiophosphates were volatile, and this prompted us to commence an examination of the suitability of these chelates for GC elution.

We have previously made a preliminary report on the GC of the dialkyldithiophosphates of zinc, nickel, palladium, platinum, rhodium and chromium using silanized glass microbeads as packing material¹⁴. In an attempt to improve the chromatography of these chelates, a more extensive investigation was undertaken, and we wish to report the results in this paper.

EXPERIMENTAL

Preparation of metal chelates

The metal dialkyldithiophosphates were prepared by methods similar to those used by Malatesta and Pizzotti⁷. A fresh ligand solution was generated by adding phosphorus pentasulphide to an excess of the appropriate alcohol, boiling gently for 10 min to expel hydrogen sulphide, filtering and cooling in an ice bath. The metal chelate was prepared by adding the appropriate metal salt (preferably the acetate) to the ligand solution; the mixture was heated gently for 5 min, then cooled, and the precipitated chelate was collected by filtration. The chelate was purified by passing its solution in chloroform through a column of acid-washed alumina, and was then recrystallized twice from acetone.

Thermal analyses

Thermal analyses of the purified chelates were performed under nitrogen, with use of a Stanton TR01 thermobalance at heating rates indicated in the text.

Vacuum sublimation of the chelates was performed in a sublimation apparatus immersed in an oil bath, and the sublimes were collected on a cold-finger condenser cooled by circulating water. The initial fraction was discarded, as mass spectrometry indicated that it was contaminated with volatile organic impurities.

Mass spectrometry

Mass spectra were recorded on a JEOL JMS D-100 mass spectrometer using a direct-insertion probe.

Gas chromatography

The GC studies were carried out on a Perkin-Elmer F30 gas chromatograph, with flame ionization detection. Various stationary liquid phases and solid supports were investigated in glass or stainless-steel packed columns of maximum length 2 m. The liquid phases included Apiezon L (Supelco, Bellefonte, Pa., U.S.A.), silicones OV-101, QF-1, PS-300 (Alltech Assoc., Arlington Heights, Ill., U.S.A.), SE-30 (Varian Aerograph, Walnut Creek, Calif., U.S.A.) and OV-1 (Hewlett-Packard, Avondale, Pa., U.S.A.). Solid supports included Gas-Chrom Q (100-120 mesh; Applied Science Labs., State College, Pa., U.S.A.), Chromosorb 750 (80-100), Chromosorb W (60-80) and Chromosorb W HP (80-100) (Supelco), and glass microbeads (60-80) (Applied Science Labs., Cat. No. 05476).

RESULTS AND DISCUSSION

Several metal O,O'-dialkyldithiophosphates of general formula $M[S_2P(OR)_2]_n$ [where R = CH₃ or C₂H₅, M = Ni, Pd or Pt; R = n-C₃H₇, M = Ni or Pd; R = iso-C₃H₇, M = Zn, Ni, Pd, Pt, Cu, Hg, Cr(III), Rh(III), Co(III), Au(III), Ru(III) or Ir(III)] have been prepared. All the complexes are readily soluble in common organic solvents and, with the exception of the dimethyl derivatives, the solutions are stable for at least several days.

Thermal and mass spectral studies

Vacuum-sublimation studies showed that the diisopropyl dithiophosphates of Cu, Hg, Au, Ru and Ir were non-volatile and therefore unsuitable for inclusion in GC studies. In addition, the Co complex, although volatile, was excluded from further investigations, as a considerable portion of the sample remained unsublimed (black residue), strongly indicating that decomposition was taking place. All remaining complexes readily sublimed with only slight traces of residue in some instances, thus indicating that decomposition was negligible. It is interesting to note that Zn diisopropyl dithiophosphate was found to be volatile, contrary to earlier observations^{13,15}.

The thermal behaviour of those complexes shown to be volatile by sublimation studies was further investigated by thermogravimetric (TG) analysis. The di-isopropyl dithiophosphates were chosen as representative of the dialkyl dithiophosphates, and their thermograms at 20°/min are shown in Fig. 1. The most notable feature of these results is that the TG curves do not indicate the complete volatilization that one might have expected from the sublimation studies; weight losses vary from about 15% (Pt complex) to 40% (Ni complex). At a slower heating rate (4°/min), weight losses were greater in each instance and none of the complexes displayed complete volatilization. The effect of variation in the heating rate strongly suggests that the observed weight losses arise not from decomposition alone, but from volatilization and decomposition. It is proposed that complete volatilization of the complexes is hindered by decomposition to yield polymeric metallic species similar in composition to the products observed by Dickert and Rowe¹⁶. In their studies on the thermal decomposition of metal dialkyl dithiophosphates at 155°, analyses of the glass-like, insoluble solid (m.p. > 400°) led these workers to conclude that the substance was polymeric, with the general formula $[(RO)_2O_2P_2S_3M]_n$.

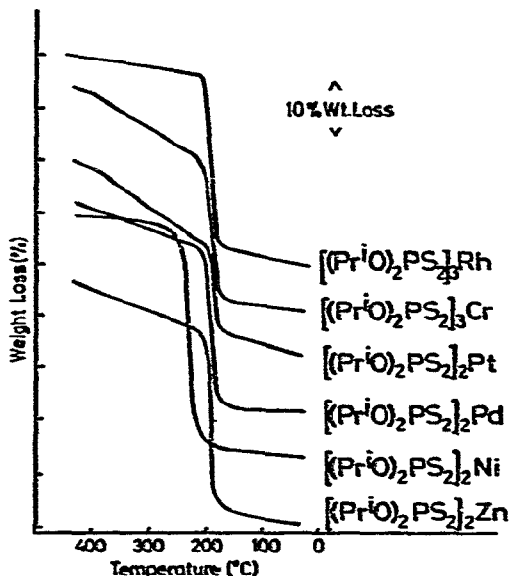


Fig. 1. Thermograms of metal diisopropyl dithiophosphates at a heating rate of 20° min⁻¹ in atmosphere of nitrogen.

In the literature on the GC of metal chelates, it is common practice to determine their thermal stabilities and volatilities by TG analysis, and frequently the order of volatilities observed in the latter technique is compared with the order of elution of the metal chelates in GC. However, it is clear from the present work that TG studies are not a useful guide to the suitability of metal dialkyldithiophosphates for GC, but vacuum sublimation studies indicate that some of these metal complexes might well be sufficiently volatile for and amenable to GC elution.

The mass spectra of the volatile metal chelates were studied in order to confirm the identities of samples eluted in GC. All the complexes show a parent ion corresponding to the monomeric form of the chelate, and no ions of mass greater than that of the parent are observed.

Livingstone and Mihkelson¹⁷ have thoroughly investigated the mass spectrum of Ni diethyldithiophosphate, and the presence of metastable peaks indicated the occurrence of electron-ion reactions involving the stepwise loss of four molecules of ethylene and a free ethoxy radical. In the present work, similar fragmentation patterns have been observed for the bis-chelates of zinc, palladium and platinum. With the tris-chelates of chromium and rhodium, the mass spectra show the loss of one ligand in addition to the successive elimination of four alkene molecules and an ethoxy radical.

Gas chromatography

Successful GC elution of some metal diisopropyldithiophosphates was previously carried out by using a glass column (1 m × 4 mm I.D.) packed with silanized glass micro-beads¹⁴. The packing material was prepared by direct addition of dichlorodimethylsilane (DCMS) to the beads in an open vessel, with thorough mixing for 30 min before washing sparingly with methanol and drying briefly in an oven at 150°.

Since that earlier report, further investigations with this packing material have shown that it is difficult to pack glass columns of I.D. < 4 mm and almost impossible to pack metal columns. This handling problem arises from the tackiness of the support after treatment with the silane. In addition, the silanization procedure lacks reproducibility and occasionally gives a batch of packing that does not generate the chromatographic data observed with other batches.

In order to overcome the above-mentioned problems, a wide range of packing materials has been examined and tested for elution of metal dialkyldithiophosphates.

With Chromosorb W as support in glass columns, various liquid phases ranging in polarity from moderately polar QF-1 to non-polar Apiezon L were investigated at column temperatures up to 190°. Elution of diethyl- or diisopropyldithiophosphates could only be achieved on an OV-101 column at temperatures around 160° after several large injections of metal chelate, a phenomenon previously observed for some β -diketonates by Uden and Jenkins¹⁸ and attributed to adsorption. Discolouration of the column packing below the point of injection provided further evidence for strong adsorption. De-activation of the support with DCMS marginally improved the chromatographic characteristics of the OV-101 column; a tailing peak was observed for the first injection of any of the nickel chelates, but the detector response increased on subsequent injections until it reached a maximum, thus indicating that the DCMS treatment was not completely effective¹⁸. Typical results for the separation of zinc and nickel diisopropyldithiophosphates on DCMS-treated Chromosorb W coated with 2.5% of OV-101 are shown in Fig. 2¹⁹.

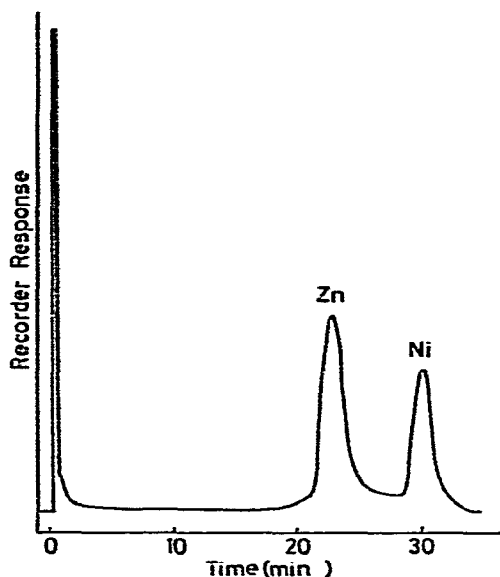


Fig. 2. Gas chromatogram of a mixture of zinc and nickel diisopropyldithiophosphates¹⁹. Conditions: column temp., 165°; injector and detector, 200°; Pyrex-glass column (1 m × 4 mm I.D.) packed with 2.5% of OV-101 on DCMS-treated Chromosorb W (60–80 mesh); nitrogen flow-rate, 70 cm³ min⁻¹.

In an effort to overcome the adsorption phenomena observed with Chromosorb W, more inert supports such as Gas-Chrom Q and Chromosorbs 750 and WHP were investigated, with nickel diisopropyldithiophosphate as test sample. In general, columns were varied in length from 40 cm to 2 m, the stationary phases included the silicones OV-101, SE-30 and Ailtech PS-300 (a phenyl silicone polymer), and their loading was varied from 1–5%.

After testing a number of columns, those shown in Table I were selected, as their efficiencies and the symmetry of the peak for the eluted nickel chelate were superior to those observed for the silanized Chromosorb W column.

TABLE I

COLUMNS SUITABLE FOR ELUTION OF METAL DIALKYL DITHIOPHOSPHATES

Column efficiencies ($N_{eff.}$) were measured at the minimum ($\mu_{opt.}$) of the Van Deemter curve with use of nitrogen as carrier gas, injector and detector temperatures of 250° and a column temperature of 160°.

Column No.	Packing material	Column dimensions and material	Value of $N_{eff.}$ at $\mu_{opt.}$	
			Ni(dtp) ₂	C ₂₃ n-alkane
1	2.5% of OV-101 on Gas-Chrom Q	1 m × 2.2 mm; stainless steel	~ 800	~1050
2	2.5% of OV-101 on Chromosorb 750	1 m × 2.2 mm; stainless steel	~ 850	~1000
3	2.5% of SE-30 on Chromosorb 750	1 m × 3.0 mm; glass	~ 900	~1000
4	1% of PS-300 on Chromosorb 750	1 m × 3.0 mm; glass	~1200	~1250

In all instances, the nickel chelate was eluted without evidence of decomposition in the column-temperature range 150–180°, although retention times were long at 150°, even at high carrier-gas flow-rates. Within this temperature range, both stainless-steel and glass columns gave comparable results. At temperatures above 190°, there was a tendency for the nickel chelate to decompose within the column, especially with stainless-steel columns; this showed up as an increase in background response of the baseline between the solvent tail and the chelate peak, with subsequent return to normal baseline after emergence of the latter peak.

All volatile metal dialkyldithiophosphates, except the zinc chelates, showed excellent chromatographic behaviour on the above columns under conditions similar to those for nickel diisopropyldithiophosphate. The peak for zinc diisopropyldithiophosphate showed considerable tailing on all columns, similar to the chromatogram shown in Fig. 2; this may be attributed to strong adsorption of the zinc chelate or it may arise from the presence of species other than the monomeric zinc chelate in the gas phase. In the solid state, zinc diisopropyldithiophosphate has been shown to be dimeric²⁰, and, if the dimer is volatile, it may give rise to the persistent tailing observed for this complex. Analogous claims have been made previously for zinc and cadmium diethyldithiocarbamates, the chromatograms of both complexes showing two peaks, one of which was attributed to the dimer²¹.

Fig. 3 shows an example of the chromatography of a mixture of nickel, palladium and platinum diisopropyldithiophosphates at 170°; it is clear that, under these conditions, resolution of palladium and platinum is poor. With the same column, if the column temperature is set at the upper limit of thermal stability of these chelates

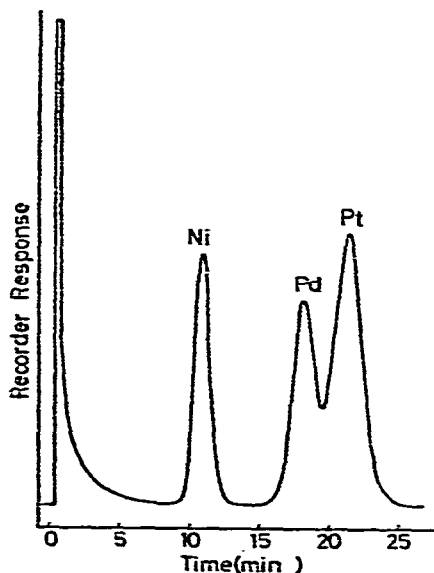


Fig. 3. Gas chromatogram of a mixture of nickel, palladium and platinum diisopropyldithiophosphates. Conditions: column temperature, 170°; injector and detector, 200°; stainless-steel column (1 m × 2.2 mm I.D.) packed with 2.5% of OV-101 on Chromosorb 750 (80–100 mesh); nitrogen flow-rate, 35 cm³ min⁻¹.

(180°), the best resolution factor obtained is 1.45 at low carrier-gas flow-rate (5 cm³ min⁻¹); however, baseline separation is not achieved because of tailing of the palladium peak. Column temperatures of *ca.* 200° are required to elute the chromium and rhodium analogues with retention times similar to those in Fig. 3 for palladium and platinum; similarly, under these conditions, complete resolution of the chromium and rhodium complexes is not achieved.

In general, the diethyl-derivatives give results similar to those obtained for the diisopropyl derivatives, but the dimethyl derivatives (except that of nickel) decompose, giving rise to spurious peaks (decomposition products) and noisy baselines; Fig. 4 illustrates the effect of the substituent on the order of elution of nickel dialkyldithiophosphates. The general instability of the dimethyl derivatives and the long retention times of the di-*n*-propyl and di-*sec.*-butyl derivatives narrow the choice of dialkyldithiophosphoric acids as derivatization reagents for the GC analysis of metals to the diethyl and diisopropyl derivatives.

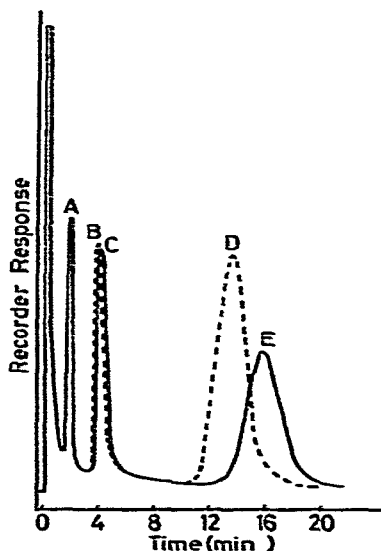


Fig. 4. Composite chromatogram of a mixture of nickel dialkyldithiophosphates. Peaks: A = Ni(dmdtp)₂; B = Ni(dedtp)₂; C = Ni(dpr'dtp)₂; D = Ni(dprdtp)₂; E = Ni(dbu'dtp)₂. Conditions: column temperature, 170°; injector and detector, 200°; stainless-steel column (35 cm × 2.2 mm I.D.) packed with 2.5% of OV-101 on Chromosorb 750; nitrogen flow-rate, 40 cm³ min⁻¹.

Many successfully eluted metal complexes do not have high column efficiencies because of undesirable interactions with the column packing or the column material. Table I lists the efficiencies measured at the minimum on the Van Deemter curve for the four columns found to be most suitable for the elution of metal dialkyldithiophosphates. In comparison, marginally higher column efficiencies were obtained for C₂₃ *n*-alkane on these columns under identical chromatographic conditions (Table I), indicating minimal interaction of the complex within the column. Detection limits were found to be of the order of 5–8 ng of metal using either the diisopropyl- or the diethyldithiophosphate complex.

In spite of the fact that the chromatography of the diethyl and diisopropyl derivatives appears to be reasonably good, the thermal instability of these chelates above 180° imposes serious limitations on the chromatographic conditions that can be used for the development of rapid analytical procedures. The marginal thermal stability at these temperatures would surely lead to slight decomposition on the metal surfaces within the injector and detector regions of the chromatographic system. Further, as shown in Fig. 3, analysis times for nickel, palladium and platinum are long even at 180° and at carrier gas flow-rates where there is lower column efficiency, resulting in poor resolution of palladium and platinum. Ideally, high volatility of the metal chelates, low solubility in the stationary phase or a long column operated at low carrier gas flow-rate and a temperature above 180° would seem to be required for rapid analysis of metal dialkyldithiophosphates. The use of capillary columns may provide a solution to the difficulties associated with the thermal instability of metal dialkyldithiophosphates at high GC operating temperatures, and we are currently investigating wall-coated open-tubular columns in the development of analytical procedures for these chelates.

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