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GAS CHROMATOGRAPHY WITH PLASMA EMISSION SPECTROSCOPIC DETECTION OF FRIEDEL–CRAFTS CATALYZED ALKYL GROUP REDISTRIBUTION PRODUCTS AMONG Si, Ge, Sn AND Pb ATOMS

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SUMMARY

Specific element detection for silicon, germanium, tin and lead is employed in the gas chromatographic analysis of Friedel–Crafts catalyzed redistribution reactions among tetraalkyl compounds of these elements. Two plasma emission spectroscopic detection systems are employed, an atmospheric pressure d.c. argon plasma and a microwave induced and sustained atmospheric pressure helium plasma. These may be employed with packed or capillary columns. Selectivities for the elements noted are given. The relative degrees of alkyl group redistribution are compared for different pairs of elements. The formation of trialkyllead chlorides and trialkyltin chlorides by reaction with aluminum chloride during redistribution is also investigated.

INTRODUCTION

The similarity noted in gas chromatographic (GC) behavior between tetraalkyl compounds of Group IVA elements and hydrocarbons makes the technique very suitable for rapid assessment of scrambling between different substituents among silicon, germanium, tin and lead atoms. Calingaert and co-workers[1–7], Pollard *et al.*[8] and others studied these redistribution reactions extensively by various means. Pollard *et al.*[8] used GC with non-selective detection necessitating the availability of standard compounds for the conclusive identification of each redistribution product.

In the present work, redistribution mixtures from Friedel–Crafts catalyzed reactions of different alkyls on Group IVA elements are detected after GC separation by element specific plasma emission spectroscopic detection. The argon d.c. plasma emission detector (DCP)[9] and the microwave induced and sustained atmospheric pressure helium plasma emission detector (MED)[10] are employed in combination with flame ionization detection. Specific element detection provides absolute elemental content identification along with sensitivity equal to or exceeding that of the flame ionization system.

STATISTICAL ANALYSIS OF REDISTRIBUTION REACTIONS

If all chemical reactions involved in alkyl group redistribution are neglected, except that of the rapidly catalyzed reaction involving aluminum halide catalyst, and metal–carbon bond breaking and reforming, the completed reaction can be considered as a simple statistical redistribution of alkyl groups on the central element. The general expression of the concentration of any possible redistribution product is given[1] by

$$\text{Concentration} = \frac{n!\,(r_1)^a\,(r_2)^b \ldots \ldots \ldots (r_s)^j}{a!\,b!\,\ldots \ldots \ldots j!} \tag{1}$$

where $n = a + b \ldots \ldots + j$ is the number of equivalent valencies of the central metal atom M having s types of substituent group, R_1, $R_2 \ldots \ldots R_s$, with mole fractions r_1, $r_2 \ldots \ldots r_s$. This equation holds since the possibility of any particular M–R bond being formed depends both on the total number of M–R bonds already formed, and on the proportion of R groups remaining in the reaction mixture. The total number of possible redistribution compounds for a tetraalkyl species of type $R_1R_2R_3R_4M$ is given for each metal center by:

$$\frac{(n + s - 1)!}{n!\,(s - 1)!}$$

Where $n = 4$ and $s = 4$, the number of possible compounds is given as 35. Where two starting compounds of the form $(R_1)_4M_1$ and $(R_2)_4M_2$ are involved five redistribution products are produced for each metal center. For each metal the quantitative proportions are as follows: $(R_1)_4M$, 6.25%; $(R_1)_3R_2M$, 25%; $(R_1)_2(R_2)_2M$, 37.5%; $R_1(R_2)_3M$, 25%; $(R_2)_4M$, 6.25%.

There are three suggested mechanisms for redistribution reactions. The first[1-7] involves aluminum chloride as an active intermediate, thus:

(A) $A_3MA + Al_2Cl_6 \rightleftharpoons A_3MCl + AAl_2Cl_5$; $B_3ZB + AAl_2Cl_5 \rightleftharpoons B_3ZA + BAl_2Cl_5$

The second mechanism[11] involves a metallonium ion intermediate for subsequent scrambling of the mixture, thus:

(B) $A_2MCl_2 + Al_2Cl_6 \rightleftharpoons A_2MCl^+ + Al_2Cl_7^-$
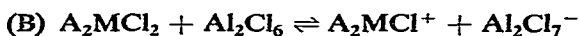
The third mechanism[12,13] involves electrophilic substitution on carbon and nucleophilic substitution on the metal, the Friedel-Crafts catalyst providing the means to attain this state:

(C) $A_3MA + AlCl_3 \rightleftharpoons [A_3MA^{\delta+} \ldots \ldots {}^{\delta-}AlCl_3]$,
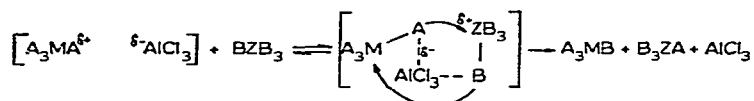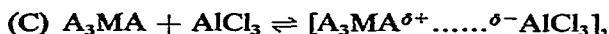
Mechanism C is believed to predominate with A and B making minor contributions[10,11].

EXPERIMENTAL

Tetravinylsilane, tetraethyltin, tetra-*n*-propyltin, tetra-*n*-butylgermane and tri-*n*-propyltin chloride were obtained from Ventron Corporation (Beverly, MA, U.S.A.), and tetraethyllead from ROC/RIC Chemical Corp. (Sun Valley, CA, U.S.A.). Triethyllead chloride samples were obtained from Ethyl Corp. (Ferndale, MI, U.S.A.), and anhydrous aluminum chloride, *n*-hexane, *n*-pentane, *n*-pentadecane and ethyl acetate from Fisher Scientific (Fairlawn, NJ, U.S.A.). Methylethyl-*n*-propyl-*n*-butylsilane and tetra-*n*-propylsilane were prepared by sequential Grignard reaction from chlorosilanes[8]. The argon used in the GC–DCP system was a commercial grade (99.995%) as was the helium for the GC–MED system. The latter was also purified by passage through a molecular sieve 3A trap[10,14].

Equipment

The d.c. argon plasma emission GC detection system has been described in detail elsewhere[9]. The prototype model Spectraspan III echelle spectrometer (Spectrametrics, Andover, MA, U.S.A.) was employed with the three-electrode Spectrajet plasma jet, instead of the two-electrode jet used previously. A Varian 1200 flame ionization detector gas chromatograph was interfaced to the plasma jet by a heated 1/16 in. I.D. stainless-steel transfer line of the design described previously[9]. Typical d.c. plasma operating conditions were: argon sheath gas flow-rate, 1.42–1.65 l/min; argon cathode gas flow-rate, 2.00 l/min; argon anode gas flow-rate, 1.30 l/min; current, 7 A; voltage, 40–60 V. The spectrometer entrance and exit slits were 100 × 200 μm (width × height).

The atmospheric pressure helium microwave emission detection system also utilized the prototype Spectraspan III echelle grating monochromator[10,14]. A Varian 2440 gas chromatograph was used interfaced with the microwave plasma as described by Quimby *et al.*[10]. The TM_{010} microwave cavity employed (RKB Products, Lexington, MA, U.S.A.) was constructed of copper after the description of Beenakker[15] except that the inner diameter was 92.7 mm and the UG-58 connector was mounted on the cavity without further modification. A valve oven was used to house the interface system; among other functions this allowed venting of solvent to preclude disruption of the plasma.

The helium plasma operating conditions for silicon were: helium carrier replacement gas flow-rate, 25–35 ml/min, added to replace helium carrier gas vented with the solvent; helium plasma gas flow-rate, 450 ml/min, a high flow-rate which was necessary to reduce silicon background from the quartz discharge tube[10]. The microwave input power was 75–80 W and the reflected power was tuned to a minimum *ca.* 0 W at 2.45 GHz. The spectrometer entrance slit width was 50 μm; entrance slit height, 500 μm; exit slit width, 100 μm; and exit slit height, 200 μm.

GC columns were made of 1/8 in. O.D. stainless-steel or nickel tubing. The OV-210 stationary phase coated on Ultrabond 20M was obtained from RFR Corp. (Hope, RI, U.S.A.). The glass capillary column (100 m × 1.0 mm O.D. × 0.25 mm I.D.) was prepared by a dynamic coating procedure on tubing drawn on a Shimadzu Model GDM 1 drawing machine.

Reaction procedure

A total volume of 100 μl of liquid samples (100 μl for single-component reactions and 50 μl each for two-component reactions) was placed in a 2-ml screw-capped glass vial. A 5–10 mg piece of resublimed anhydrous aluminum chloride was added and the vial immediately closed with an aluminum-foil-lined screw cap. The vial was placed on a hot plate at 100–120°C, its top being cooled by a forced air draft from a hood to prevent rupture while under reflux. After about 30 min, heating was stopped and the product liquid was diluted with *n*-pentane, *n*-hexane or *n*-pentadecane. Dilution ratios were 50:1 except for the methylethyl-*n*-propyl-*n*-butylsilane system where dilution was 1000:6. In the case of the reaction mixture of tetraethyllead with tetra-*n*-propyltin, a small quantity (*ca.* 1–5 mg) of a white precipitate (see Table II) produced was dissolved in *ca.* 200 μl of ethyl acetate. Volumes of the resulting dilutions of 3.7 μl and 0.5 μl were injected, yielding chromatographic peaks containing quantities of compounds from about 5–10 μg and 10–150 ng, for GC–DCP and GC–MED analysis, respectively.

Table I lists the operating conditions used for redistribution product analysis. All of the initial two-component redistribution mixtures were gas chromatographed on a packed OV-101 methyl silicone column. The methylethyl-*n*-propyl-*n*-butylsilane redistribution mixture was resolved on an OV-225 cyano silicone oil column and the trialkyllead and -tin chlorides were separated on an OV-210 fluoro silicone oil column.

The silicon, germanium, tin and lead emissions were observed at 251.6 nm, 265.1 nm, 286.3 nm and 368.3 nm, respectively. The selectivity ratios for silicon,

TABLE I

OPERATING PARAMETERS FOR THE GAS CHROMATOGRAPHY–d.c. ARGON PLASMA (GC–DCP) AND THE GAS CHROMATOGRAPHY–ATMOSPHERIC PRESSURE MICROWAVE PLASMA (GC–MED)

	GC–DCP		GC–MED
	1	*2*	
Column			
Packing	5% OV-101 on 100–120 mesh Chromosorb 750	3% OV-210 on 100–120 mesh Ultrabond 20M	OV-225 support-coated open tubular
Material and dimensions	Stainless steel, 6 ft. × 1/8 in. O.D.	Nickel tubing, 1 m × 1/8 in. O.D.	Glass capillary, 100 m × 1.0 mm O.D. × 0.25 mm I.D.
Carrier gas (helium) flow-rate	40 ml/min	40 ml/min	4 ml/min
Temperature program	From 80°C at 6 or 8°C/min	From 80°C at 8°C/min	From 40°C at 4°C/min
Injector temperature	210°C	210°C	210°C
Interface temperature	220°C	220°C	250°C
Plasma gas	Argon	Argon	Helium
Observed wavelengths (nm)	Si 251.6 Ge 265.1 Sn 286.3 Pb 368.3	Si 251.6 Ge 265.1 Sn 286.3 Pb 368.3	Si 251.6

germanium, tin and lead over carbon at these wavelengths are $8.8 \cdot 10^5$, $1.7 \cdot 10^5$, $1.3 \cdot 10^6$ and $1.1 \cdot 10^4$, respectively. Selectivity ratios are defined as the peak area response of an element per mole of the element divided by the peak response of carbon per mole of carbon (*e.g.*, 880,000 moles of carbon are required to give the same response as 1 mole of silicon).

RESULTS AND DISCUSSION

Observation of the reaction mixtures

All mixtures were clear liquids before refluxing, with the aluminum chloride as a solid yellow-white particle. Table II lists the appearance of the mixtures after reflux. In each case, the change in color or state of the aluminum chloride indicated reaction to have occurred. The catalyst either became a yellow oil in a separate lower layer from the redistribution products or it turned a rust brown. When lead compounds were present, copious amounts of a white precipitate formed, which obscured the aluminum chloride.

TABLE II

APPEARANCE OF THE REDISTRIBUTION REACTION MIXTURE AFTER REFLUX

Et = Ethyl; Pr* = *n*-propyl; Bu* = *n*-butyl; Vn = vinyl.

Mixture	Appearance
1 Pr*₄Sn + Et₄Pb	Colorless solution, white precipitate, obscuring AlCl₃
2 Et₄Sn + Bu*₄Ge	Colorless solution, AlCl₃ appears in lower layer of yellow oil
3 Pr*₄Si + Bu*₄Ge	Colorless solution, AlCl₃ appears as rust colored solid
4 Bu*₄Ge + Et₄Pb	As 1
5 Vn₄Si + Et₄Sn	As 2
6 Vn₄Si + Bu*₄Ge	As 3

Analysis of redistribution reaction mixtures

Earlier work has shown that redistribution of alkyl groups between two adjacent elements in Group IV, *i.e.*, Si–Ge, Ge–Sn and Sn–Pb, proceeds readily under the catalytic conditions employed here[8]. Redistribution between other element pairs was not generally seen, however. Figs. 1 and 2 show clearly the utility of specific element plasma emission spectroscopic detection for qualitative and quantitative analysis of an adjacent element redistribution. In Fig. 1 is seen a dual response chromatogram of the equilibrium products from tetraethyllead and tetra-*n*-propyltin. While the lower trace shows the overall redistribution as detected by flame ionization, the upper lead specific chromatogram obtained with the d.c. argon plasma system, monitored at 368.3 nm, shows the theoretical sequential pattern of tetraalkyllead compounds from tetraethyllead to tetra-*n*-propyllead.

Fig. 2 shows a similar pair of chromatograms, the d.c. plasma trace now monitored at 286.3 nm to show tin specific detection.

Table III shows the measured compositions for the ten tetraalkyl compounds in comparison with the expected values. Peak areas are computed from the lead and tin specific peak responses and thus do not require correction for response factors for
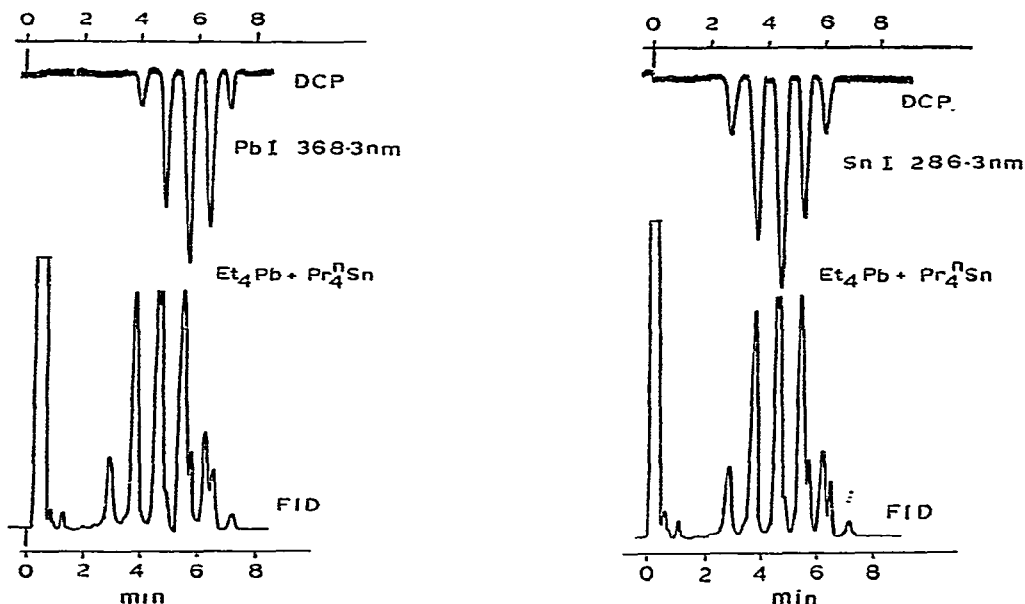
Fig. 1. Dual-detection gas chromatogram of the redistribution products between tetraethyllead and tetra-n-propyltin. Column: 5% OV-101 on 100–120 mesh Chromosorb 750, 6 ft. × 1/8 in. I.D. stainless steel. Temperature program: from 80°C at 8°C/min. Lower chromatogram, flame ionization detection (FID); upper chromatogram, d.c. argon plasma emission detection (DCP) for lead at 368.3 nm.

Fig. 2. Dual-detection gas chromatogram of the redistribution products between tetraethyllead and tetra-n-propyltin. Column and conditions as in Fig. 1. Lower chromatogram, flame ionization detection; upper chromatogram, d.c. argon plasma emission detection for tin at 286.3 nm.

TABLE III

CALCULATED AND EXPERIMENTAL VALUES FOR THE PROPORTIONS OF TETRA-ALKYLTIN AND -LEAD COMPOUNDS FORMED FROM THE FRIEDEL–CRAFTS CATALYZED ALKYL GROUP REDISTRIBUTION BETWEEN TETRAETHYLLEAD AND TETRA-n-PROPYLTIN

Compound	$(R_1)_4M$	$(R_1)_3R_2M$	$(R_1)_2(R_2)_2M$	$R_1(R_2)_3M$	$(R_2)_4M$
Theor. (%)	6.25	25.00	37.50	25.00	6.25
Lead alkyls	Et_4Pb	Et_3Pr^nPb	$Et_2Pr^n_2Pb$	$EtPr^n_3Pb$	Pr^n_4Pb
Exptl. (%)	6.3	22.6	35.6	28.4	7.1
Tin alkyls	Et_4Sn	Et_3Pr^nSn	$Et_2Pr^n_2Sn$	$EtPr^n_3Sn$	Pr^n_4Sn
Exptl. (%)	10.0	25.1	33.9	21.9	9.2

individual compounds. Both the lead and tin series show values close to those predicted for complete statistical scrambling of alkyl groups. There is a small departure from completely symmetrical distribution in the instance given, showing a bias towards propyl groups favoring lead atoms and ethyl groups favoring tin atoms, but this may be a result of experimental variation for this particular sample, especially since equal volume rather than equal molar quantities were employed; calculation shows that of 400 ethyl and propyl groups, lead has 193 ethyl and 207 propyl, while tin has 205 ethyl

and 195 propyl, figures well within quantitative experimental error limits. It may also be noted that the symmetrical tetraalkyltin species are slightly favored over the mixed alkyl compound.

By contrast, the reaction between tetraethyltin and tetra-n-butylgermane, as illustrated in Figs. 3 and 4, proceeds to a lesser degree after a similar reaction time. All possible redistribution products are noted by tin-specific detection in Fig. 3 (at 286.3 nm) and by germanium-specific detection in Fig. 4 (at 265.1 nm). The percentages of each product calculated again by peak area measurement are given in
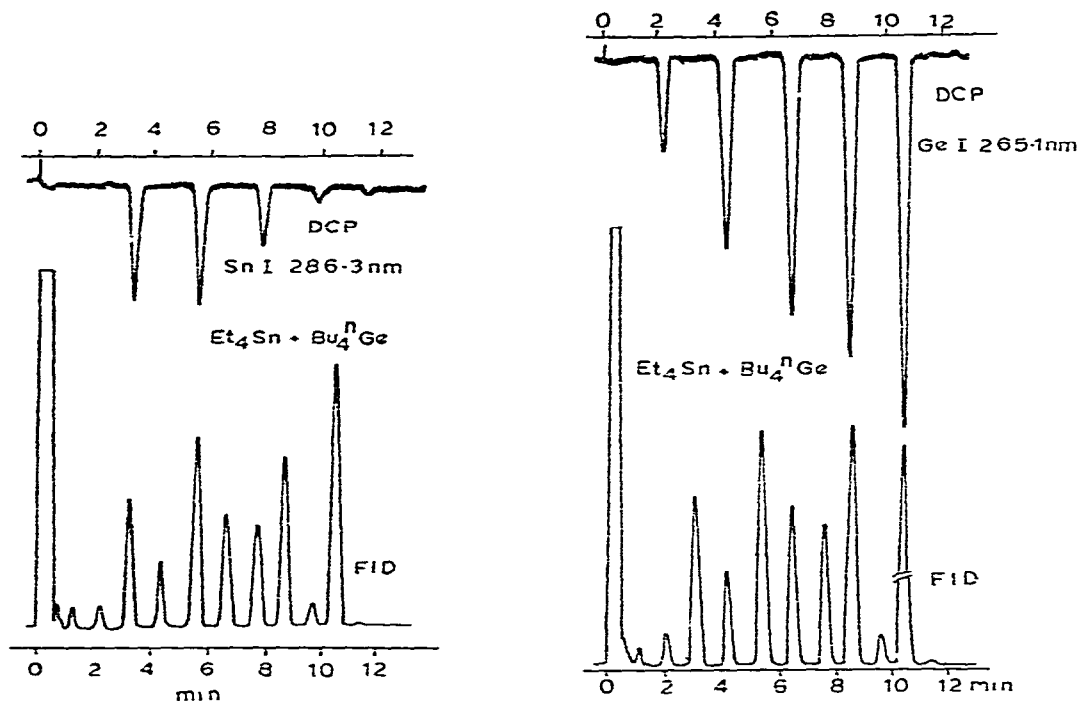

Fig. 3. Dual-detection gas chromatogram of the redistribution products between tetraethyltin and tetra-n-butylgermane. Column and conditions as in Fig. 1. Detection as in Fig. 2.

Fig. 4. Dual-detection gas chromatogram of the redistribution products between tetraethyltin and tetra-n-butylgermane. Column and conditions as in Fig. 1. Lower chromatogram, flame ionization detection; upper chromatogram, d.c. argon plasma emission detection for germanium at 265.1 nm.

Table IVa. Clearly this redistribution is moving towards statistical scrambling at the time of analysis and if required the reaction could be monitored to determine reaction rates and completeness. In Table IVb is shown the redistribution extent attained in a similar experiment between tetra-n-butylgermane and tetra-n-propylsilane. A somewhat lesser degree of reaction is seen to that noted in Table IVa. Illustrated effectively is the observation that for redistributions between adjacent elements in Group IV the overall reaction rate sequence shows Pb–Sn greater than Sn–Ge, greater than Ge–Si, in agreement with increased element reactivity on descending Group IVA.

TABLE IV

CALCULATED AND EXPERIMENTAL VALUES FOR THE PROPORTIONS OF REDISTRIBUTION PRODUCTS FROM THE FRIEDEL-CRAFTS CATALYZED REACTIONS

Compound	$(R_1)_4M$	$(R_1)_3R_2M$	$(R_1)_2(R_2)_2M$	$R_1(R_2)_3M$	$(R_2)_4M$
Theor. (%)	6.25	25.00	37.50	25.00	6.25
(a) Reaction between tetraethyltin and tetra-n-butylgermane					
Germanium alkyls	Et_4Ge	Et_3Bu^nGe	$Et_2Bu^n_2Ge$	$EtBu^n_3Ge$	Bu^n_4Ge
Exptl. (%)	5.1	15.1	22.0	26.1	31.2
Tin alkyls	Et_4Sn	Et_3Bu^nSn	$Et_2Bu^n_2Sn$	$EtBu^n_3Sn$	Bu^n_4Sn
Exptl. (%)	34.1	38.0	19.4	6.2	2.3
(b) Reaction between tetra-n-butylgermane and tetra-n-propylsilane					
Germanium alkyls	Pr^n_4Ge	$Pr^n_3Bu^nGe$	$Pr^n_2Bu^n_2Ge$	$Pr^nBu^n_3Ge$	Bu^n_4Ge
Exptl. (%)	—	2.0	12.0	37.2	48.8
Silanes	Pr^n_4Si	$Pr^n_3Bu^nSi$	$Pr^n_2Bu^n_2Si$	$Pr^nBu^n_3Si$	Bu^n_4Si
Exptl. (%)	37.9	44.5	15.2	2.5	—

Previous studies had indicated that scrambling reactions of alkyl groups occurred only between adjacent Group IV atom pairs[8]. In the present work, however, it was observed that a limited degree of redistribution did occur under the relatively mild conditions employed between atoms separated by one other Group IV element, *i.e.*, Si–Sn and Ge–Pb. While surprising in view of reactivity and kinetic considerations, this observation may be the result of high catalyst concentrations. Fig. 5 depicts the germanium-specific chromatogram of the redistribution between tetraethyllead and tetra-*n*-butylgermane. While the starting germanium compound still predominates,
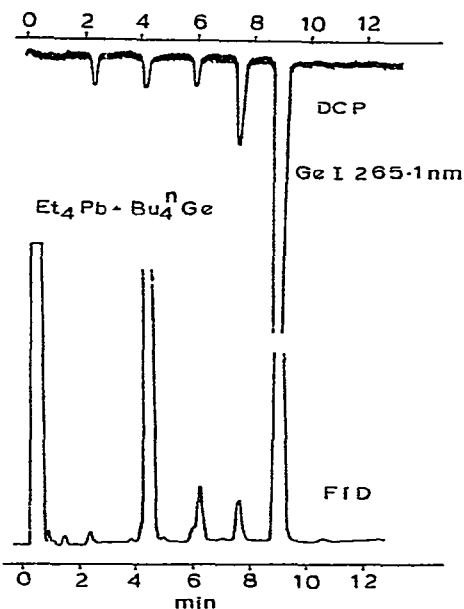

Fig. 5. Dual-detection gas chromatogram of the redistribution products between tetraethyllead and tetra-*n*-butylgermane. Column and conditions as in Fig. 1. Detection as in Fig. 4.

the other possible products are present. Table V gives redistribution product proportions for germanium and lead. Only triethyl-*n*-butyllead was observed from redistribution and thus proportions are given for two lead compounds only. It appears possible however that small quantities of higher butyllead species may have been formed but reacted to give higher butyllead chlorides, as indicated by the formation of quantities of white precipitate in the reaction mixture.

TABLE V

CALCULATED AND EXPERIMENTAL VALUES FOR THE PROPORTIONS OF REDIS-TRIBUTION PRODUCTS FROM THE FRIEDEL–CRAFTS CATALYZED REACTIONS BETWEEN TETRA-*n*-BUTYLGERMANE AND TETRAETHYLLEAD

Compound	$(R_1)_4M$	$(R_1)_3R_2M$	$(R_1)_2(R_2)_2M$	$R_1(R_2)_3M$	$(R_2)_4M$
Theor. (%)	6.25	25.00	37.50	25.00	6.25
Germanium alkyls	Et_4Ge	Et_3Bu^nGe	$Et_2Bu^n_2Ge$	$EtBu^n_3Ge$	Bu^n_4Ge
Exptl. (%)	3.1	3.1	3.1	6.6	84.2
Lead alkyls	Et_4Pb	Et_3Bu^nPb	$Et_2Bu^n_2Pb$	$EtBu^n_3Pb$	Bu^n_4Pb
Exptl. (%)	82.3	17.7	—	—	—

A reaction between tetraethyltin and tetra-*n*-propylsilane carried out under the same conditions gave only a small indication of the formation of one redistribution product, ethyltri-*n*-propylsilane.

When an unsaturated tetra-substituted silane, tetravinylsilane, was investigated for redistribution reaction with either tetra-*n*-butylgermane or tetraethyltin, no detectable redistribution products were observed. It is postulated that tetravinylsilane inhibits redistribution by reacting with aluminum chloride to produce an unreactive species.

Capillary column separation and detection with the MED

Where there are more than two different alkyl groups present in a redistributing sample, the GC separation becomes more difficult and capillary column methods are helpful. An example of such a separation is shown in Fig. 6. In this case, the microwave induced and sustained atmospheric pressure helium plasma emission detector was employed together with the flame ionization detector. The redistribution reaction involved is that of methylethyl-*n*-propyl-*n*-butylsilane, which on statistical scrambling produces 35 alkylsilane products as was noted earlier. The lower chromatogram shows the *n*-pentane solution of the redistributed mixture, the earlier low-molecular-weight products such as tetramethylsilane (b.p. 28°C) being obscured by the solvent. In the MED trace (top) no solvent peak is evident, however the operation of the MED[9,10] requires that solvent be vented prior to entry of the detected components into the detector to preclude extinguishing the plasma. Thus in order to quantitate the lowest boiling peaks a parallel chromatogram was run after taking up reaction products in *n*-pentadecane rather than *n*-pentane. This solvent elutes after the highest boiling silane (tetra-*n*-butylsilane). The start of this chromatogram is shown in the second MED trace, where the two earliest silanes are well separated (tetramethylsilane and trimethylethylsilane). Thirty-five major peaks are noted, the few low level additional silicon containing peaks being attributed to alkylchlorosilane by-products of reaction.
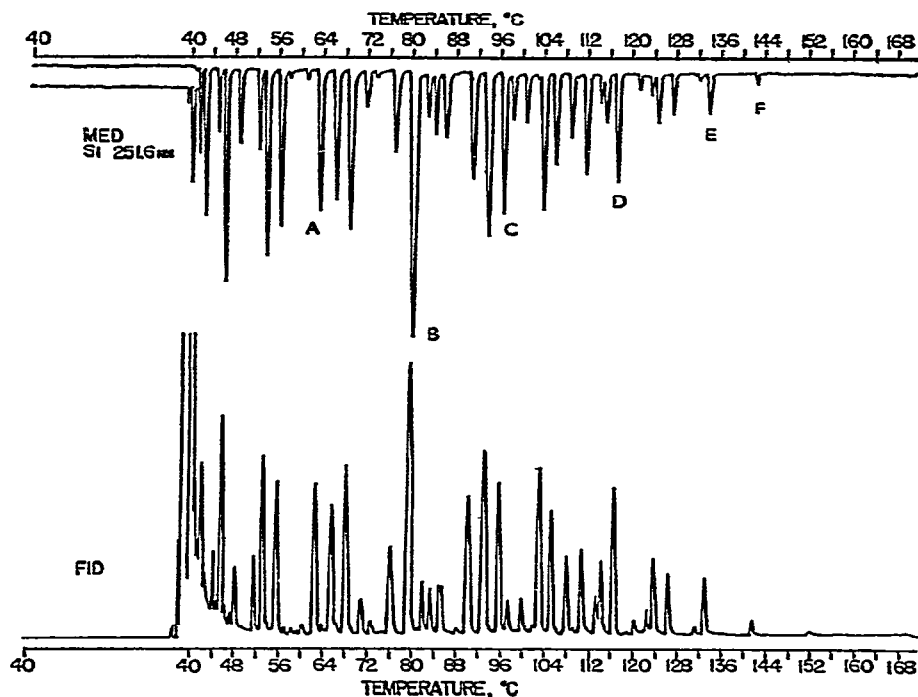
Fig. 6. Dual-detection gas chromatogram of the redistribution products of methylethyl-*n*-propyl-*n*-butylsilane. Column: OV-225 glass capillary support-coated open tubular column; 100 m × 0.25 mm I.D. Temperature program: from 40°C to 170°C at 4°C/min. Lower chromatogram, flame ionization detection; upper chromatogram, microwave plasma emission detection (MED) for silicon at 251.6 nm.

It appears that this reaction has proceeded close to the theoretical scrambling limit. Thus peaks labelled A–F, respectively attributable to methylethyldi-*n*-propyl-silane (A), methylethyl-*n*-propyl-*n*-butylsilane (B), methylethyldi-*n*-butylsilane (C), ethyl-*n*-propyldi-*n*-butylsilane (D), *n*-propyltri-*n*-butylsilane (E) and tetra-*n*-butyl-silane (F), should show the following relative peak intensities, based on silicon content, 12, 24, 12, 12, 4, 1. The observed peak areas for these components are clearly close to these values.

Redistribution products involving chlorination of the Group IV atom

It has previously been noted that alkyl group redistribution on mixed $R_1R_2R_3SiCl$ compounds is markedly hindered[8], no type of statistical scrambling occurring under mild conditions as employed in this study. Investigation of the white precipitate produced during the redistribution reaction of tetraethyllead and tetra-*n*-propyltin indicated that mixed alkyltin and -lead chlorides were produced. Fig. 7 depicts a dual flame ionization detection, d.c. argon plasma lead specific detection chromatogram of the ethyl acetate solution of the white precipitate. The early group of peaks correspond to the mixed tetraalkyltin compounds which have already been shown to be produced in the redistribution reaction in approximately statistical pro-
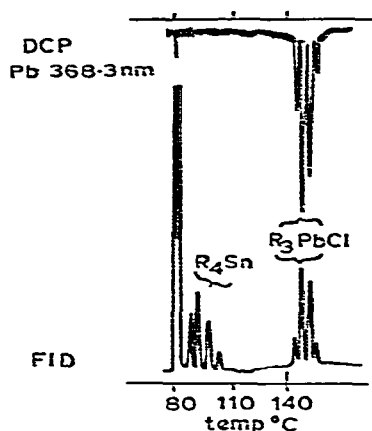
Fig. 7. Dual-column gas chromatogram of redissolved solid precipitate from redistribution reaction between tetraethyllead and tetra-*n*-propyltin. Column: 3% OV-210 on 100–120 mesh Ultrabond 20M™ 1 m × 1/8 in. I.D. nickel tubing. Temperature program: from 80°C at 8°C/min. Lower chromatogram, flame ionization detection; upper chromatogram, d.c. argon plasma emission detection for lead at 368.3 nm.

portions. In the precipitate these appear to be concentrated much more than the tetraalkyllead compounds. At higher detector sensitivities the latter are observed in the same part of the chromatogram. As is shown clearly by the lead specific chromatogram, the later group of peaks all contain lead and were suspected to be trialkyllead chlorides. The GC of trialkyllead chlorides has previously been reported only in one study[16] which has been subsequently shown to be suspect in view of their high polarity and reactivity[17]. For packed column GC of these compounds we have shown that a highly inert stationary phase–support combination is necessary and a non-reactive column material is needed. A suitable column has been shown to consist of Ultrabond 20M™, a support–stationary phase combination comprising Carbowax 20M bonded to diatomite, coated with the fluorosilicone oil OV-210. Trialkyllead chlorides elute from this column without degradation to the microgram level and slightly below.

The identification of these peaks as trialkyllead chlorides was substantiated by co-elution of the mixture with triethyllead chloride added as an internal reference. Fig. 8a shows the chromatogram of the mixture with flame ionization detection; Fig. 8b shows the mixture with added triethyllead chloride, and tri-*n*-propyltin chloride. The latter reference compound indicates that trialkyltin chlorides are also present at low levels in the central region of the chromatogram. The trialkyllead chloride peaks correspond in order of elution to triethyllead chloride, diethyl-*n*-propyllead chloride, ethyldi-*n*-propyllead chloride, and tri-*n*-propyllead chloride. It is noteworthy that trialkyllead chlorides are formed in much higher proportions than trialkyltin chlorides. A separate quantitative study of trimethyl- and triethyllead chlorides is reported elsewhere[17], for these compounds of notable toxicological importance. Clearly aluminum chloride acts both to transfer chloride to the Group IVA atoms and to catalyze redistribution, as postulated in the Calingaert[1–7] and Whitmore[11] mechanisms. In view of the previously observed inhibition of alkyl group scrambling
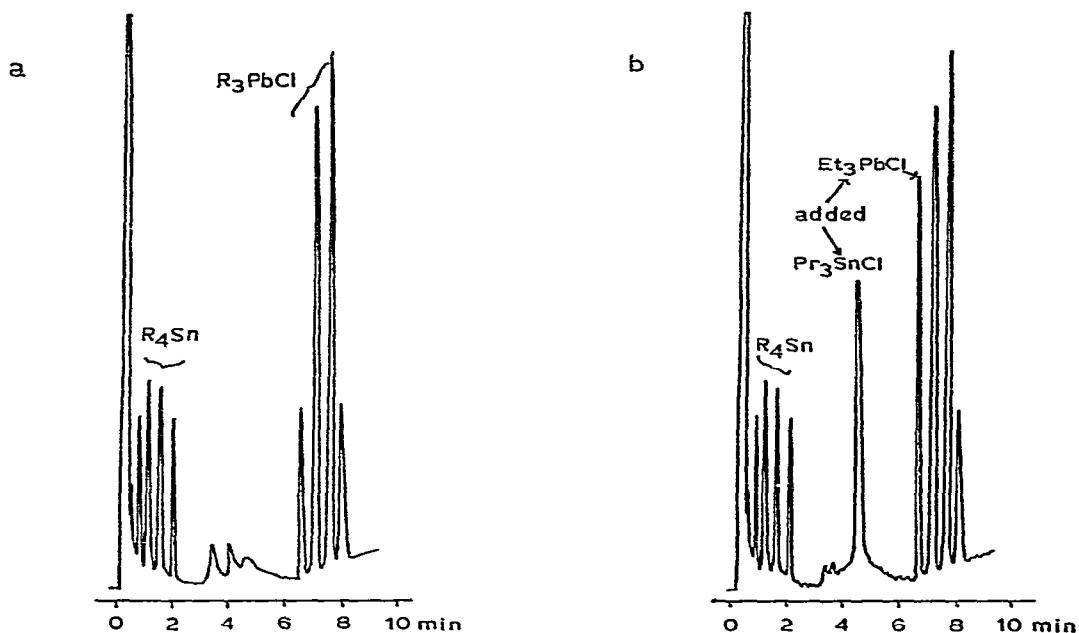
Fig. 8. Flame ionization detection gas chromatograms of redissolved solid precipitate from redistribution reaction between tetraethyllead and tetra-*n*-propyltin. Column and conditions as in Fig. 7. a, Mixture comprising primarily tetraalkyltin compounds and trialkyllead chlorides; b, reaction mixture with added triethyllead chloride and tri-*n*-propyltin as internal references.

on chloro-substituted compounds[8], it is probable that trialkyllead chlorides are formed from reaction of redistributed tetraalkyllead species with aluminum chloride.

A more detailed study of the relative rates of formation of tetraalkyllead and trialkyllead chlorides could substantiate this supposition.

CONCLUSIONS

Element-specific GC detection proves a useful technique for both qualitative and quantitative analysis of complex mixtures of volatile sigma-bonded metallic and metalloid compounds. Alkyl group redistributions on Group IV elements and side reactions with aluminum chloride catalyst are readily followed by either d.c. argon plasma emission spectroscopy or microwave induced and sustained atmospheric pressure helium plasma emission spectroscopy. Their use enables conclusions on peak identity to be drawn with a high degree of confidence without the need for pure standards or for extensive identification facilities such as GC–mass spectrometer combinations.

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