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Stability and the gas chromatography of alkyl-substituted η^6-benzenetricarbonylchromium(0) complexes

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Abstract

Thermoanalytical and gas chromatographic data are reported for benzenetricarbonylchromium(0) and nine of its methyl- and t-butyl-substituted derivatives. The distinct trends found for the volatilities, thermal stabilities, air stabilities and gas chromatographic retentions with increasing alkyl substitution are interpreted in terms of Cr–ligand bond energies and polarity and steric effects. Satisfactory chromatographic behaviour was observed only when highly inert columns were used, and when the solutions were deaerated and stored in the dark.

Introduction

Gas chromatography (GC) and high pressure liquid chromatography (HPLC) are gaining wider acceptance in organometallic chemistry for analytical and preparative scale separations [1–5]. Advantages of these techniques include (i) the ability to separate complex organometallic mixtures with or without organic compounds present, (ii) an intrinsic inert atmosphere operation, and (iii) the availability of a wide range of techniques, columns, mobile phases, and detection systems. Molecular, ionic, or polymeric species can be determined [1–6]. Species not directly suitable for chromatography can be determined indirectly following pyrolysis, hydrolysis, or derivatisation [2].

Although certain organometallics, including many ferrocenes, alkylsilanes, and alkylgermanes, are well suited for chromatography [2], most organometallics are of low stability and are highly reactive. For these, precautions are necessary to minimise on-column decomposition and irreversible alteration of the characteristics of the chromatographic column. This is particularly important in GC, where temperatures above 100 °C are typically required for elution [1,2]. The removal of moisture, oxygen, and other reactive impurities [7] from the mobile and stationary phases are obvious precautions, but such precautions, surprisingly, seem to be mostly overlooked in this area [2].

As part of a continuing study of the chromatography of metal-containing compounds we have examined the GLC of the series of aryltricarbonylchromium(0) complexes I and II. An appreciable number of these species, and their Mo and W

$Cr(C_6H_{6-n}(CH_3)_n)$ $(I, n = 0–6)$ $Cr(C_6H_{6-n}(t\text{-}Bu)_n)$ $(II, n = 0–3)$

analogues have been eluted apparently intact [8–12]. However, there is evidence [12,13] that extensive decomposition can occur during the GC of such compounds. Since such complexes also undergo photo-oxidative decomposition in solution [14] it is not clear whether decomposition occurs in solution prior to GLC or within the column itself.

The aims of this paper are to examine and rationalise the effect of alkyl substitutions on the stability, volatility, and chromatographic behaviour of the complexes, and to identify conditions suitable for their GLC.

Experimental

Benzenetricarbonylchromium(0) was prepared from triamminetricarbonylchromium(0) as described by Aladjin and Sirotkin [15]. The corresponding complexes of toluene, 1,4-xylene, mesitylene, durene, pentamethylbenzene, hexamethylbenzene, t-butylbenzene, 1,4-di-t-butylbenzene and, 1,3,5-tri-t-butylbenzene, were prepared by refluxing chromium hexacarbonyl with an excess of the arene in trimethylpyridine or (in the case of tri-t-butylbenzene) n-butyl ether under nitrogen for 30 h [16–18]. The solvent and the excess of hexacarbonyl were removed under vacuum at 40–60 °C, and the residual yellow complexes purified by double vacuum sublimation at 70–120 °C (0.01 mmHg). Melting points were within 2 °C of the literature values [14]. The samples were then stored in vacuum-sealed borosilicate glass tubes. Solutions for GLC were prepared in purified, deaerated tetrahydrofuran. Such solutions were generally stable for at least four days in the dark, but rapidly decomposed on exposure to air and light.

Thermal analyses were performed on a Rigaku Thermoflex M8076 combined TG/DTA instrument with powdered samples (7.5 mg) in platinum cups and heating at 10 °/min in argon or air (100 ml/min). Identification of volatiles, where required, was obtained by cooling the exit tube of the furnace in a mixture of dry ice and acetone. Condensed material was dissolved in chloroform and analysed by GLC. Residues from thermal analyses were tested for reaction with 3 *M* sulphuric acid under argon.

GC was carried out with a Pye Unicam PU 400 gas chromatograph equipped with an SGE direct splitless injector and flame ionisation detector. Vitreous silica WCOT columns obtained from SGE (Australia) were 25 m × 0.22 mm ID OV 101. High purity dry nitrogen ($<$ 10 ppm oxygen) was used as carrier gas together with on-line oxygen and moisture traps (Alltech Gas Purifier packed with 5 Å molecular sieve and Alltech oxy-trap. The latter is claimed to reduce oxygen to less than 1 ppm for a carrier gas containing 10 ppm oxygen).

Specific retention volumes and heats of solution in the stationary phase were calculated as previously described [19]. Rates for on-column decomposition of the complexes were measured by injecting a mixture of each organometallic compound (50 ng) and either n-$C_{18}H_{38}$ for the methyl derivatives or n-$C_{19}H_{40}$ (t-butyl derivatives) as internal standard at various carrier gas flow rates ranging from 2.0 to 4.0 ml/min at column temperatures of 160 or 175 ° C, respectively. First-order rate constants (k) for the decompositions were measured [19] from the decrease in relative peak area A_1/A_2 according to the equation:

$$k = \ln(A_1/A_2)/(t_{r2} - t_{r1})$$

and the half-life $t_{1/2} = \ln 2/k$
where
A_1 = area for the solute peak
A_2 = area for the internal standard
t_{r1} = adjusted retention time for the solute peak
t_{r2} = adjusted retention time for the internal standard

Results and discussion

Thermoanalytical properties

Thermal analyses of the aryltricarbonyl complexes show them to have only marginally suitable stability for GC. Thus in the thermogram for benzenetricarbonylchromium(0) (Fig. 1a) volatilisation begins near 100 ° C and decomposition occurs at about 210 ° C. Decomposition accompanying volatilisation for this complex is ascribed to the dissociation reaction in eq. 1, and gives metallic chromium. A

$$C_6H_6Cr(CO)_3 \rightarrow C_6H_6 + Cr + 3CO \qquad (1)$$

side reaction is the formation of chromium hexacarbonyl [16], but GC analysis of volatile collected from the exit tube of the furnace indicated that the main components were unchanged complex and benzene.

Thermoanalytical data for the methyl-substituted complexes, summarised in Table 1, indicates that the decomposition temperature increases regularly with the extent of methyl substitution. This trend parallels, and is probably a consequence of, the variations in Cr–arene bond energies, which also increase with the extent of methyl substitution [20,21].

The data in Fig. 2 reveal distinct trends also in the volatilities. In the methyl-substituted series, the drop in volatility with progressive methyl substitution is almost certainly due to the combined effects of increased polarity and polarisability [22]. In the t-butyl substituted series, a somewhat different trend is observed. Here, although volatility decreases with the number of t-butyl substituents, the significant steric effect of the t-butyl groups considerably reduces the volatility difference between the di- and tri-t-butyl-substituted complexes.

In air the thermal behaviour of the complexes, as expected, altered completely. Thus benzenetricarbonylchromium(0) decomposed at about 130 ° C without sublimation. The reaction, involving formation of chromous oxide, was highly ex-

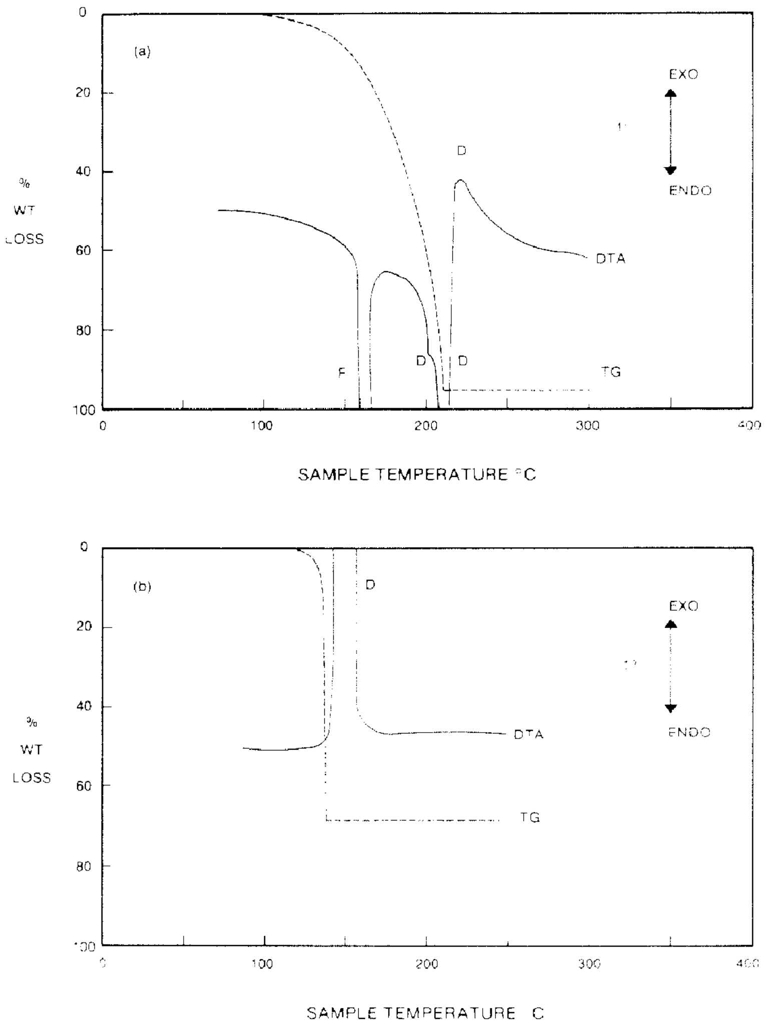

Fig. 1. Thermograms (DTA/TG) for benzenetricarbonylchromium(0) in (a) argon and (b) air. Conditions as described in Experimental section. Events identified are fusion (F) and decomposition (D).

othermic, as evident from Fig. 1b, and is ascribed to the selective oxidation shown in eq. 2. This conclusion was based on the appearance of the residue and its

$$C_6H_6Cr(CO)_3 + 2O_2 \rightarrow C_6H_6 + CrO + 3CO_2 \qquad (2)$$

reaction with dilute sulphuric acid *, and on the percentage weight of residue obtained (Found 29.7%; calculated for CrO, 31.8%; Cr, 24.4%; Cr_2O_3, 36.4%). Percentage residues obtained for the other complexes were also consistent with the formation of chromous oxide. The stability of the complexes, in this case to oxidation, is again enhanced by the extent of alkyl substitution (Table 1), with

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* A black powder was obtained as residue. This dissolved in dilute sulphuric acid under argon without gas evolution to give a clear blue solution, presumably of chromous sulphate.

Table 1

Decomposition temperatures (obtained by DTA) for the aryltricarbonyl complexes in argon and in air

No. of alkyl substituents	Decomposition temperatures (°C)	
	Argon	Air
(methyl)		
0	208, 216 (*exo*)	130 (highly *exo*)
1	200	168
2	221, 225	
3	> 230	170 (highly *exo*)
4	236	180
5	256	
6	274 (*exo*)	182 (highly *exo*)
(*t-butyl*)		
1	237 (*exo*)	172
2	254, 260 (*exo*)	190 (highly *exo*)
3	> 254	195 (highly *exo*)

tri-t-butylbenzenetricarbonylchromium(0) the most stable species. However, it is apparent that rapid oxidation of all the complexes will occur at 200 °C in air.

Retention times and enthalpies of solution

On non-polar fused-silica capillary columns the aryltricarbonyl complexes gave sharp, symmetrical peaks, without apparent decomposition (Fig. 3). In each series

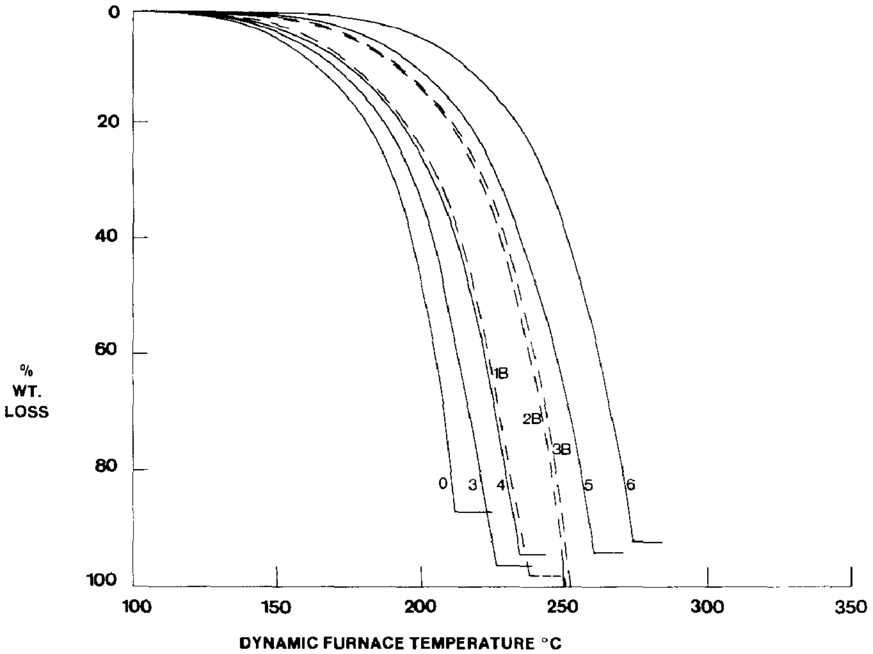

Fig. 2. Thermograms (TG) for aryltricarbonylchromium(0) complexes in argon. 0–6 and 1B, 2B and 3B identify the number of methyl and t-butyl substituents, respectively in the complex (see Experimental section for identification of the aryl ligands).

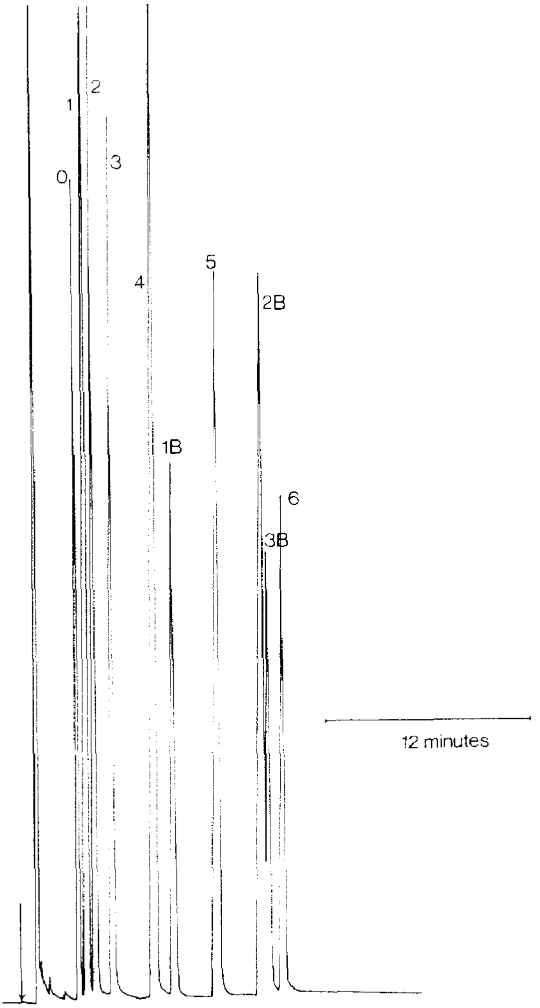

Fig. 3. Chromatogram of a mixture of the complexes (100–200 ng each on the OV 101 column). Temperature programming: 150 °C (8 min) to 190 °C (3 °C/min). Nitrogen gas flow 0.9 ml/min. Injection port and detector temperatures 200 °C. 0–6 and 1B, 2B and 3B refer to the aryl ligands indicated in Fig. 2.

the elution order paralleled the volatilities, as seen in Fig. 2. However, plots of log $t_{R'}$ against the number of alkyl substituents were non-linear, and pronounced deviations were observed with series II *. Similarly, non-linear plots were obtained for the free energy of solution, ΔG_s, against the incremental free energy of solution, $\Delta G_s'$ (eq. 3) [23], again with pronounced deviation for series II.

$$\Delta G_s = \Delta G_R + n\ \Delta G_s' = RT\ \ln V_g - \ln 273R/M \qquad (3)$$

where

V_g = specific retention volume

M = mean molecular weight of stationary phase

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[*] Linear plots have been obtained for the homologous series of n-alkylbenzenetricarbonylchromium(0) complexes [11].

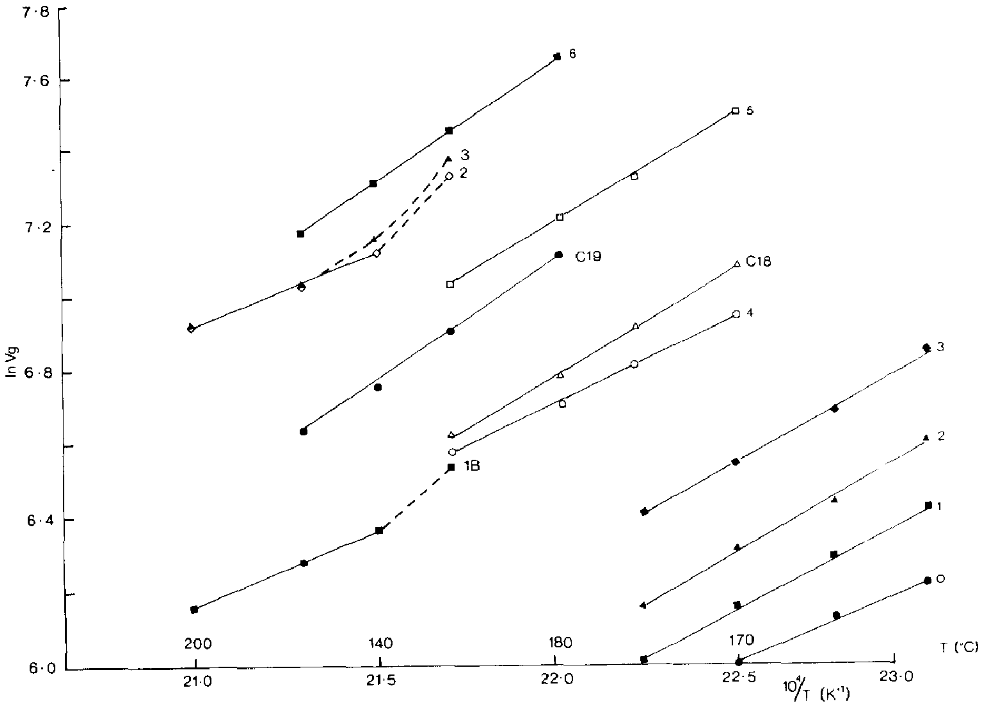

Fig. 4. Plot of ln V_g versus $10^4/T$ for the aryltricarbonyl complexes on the OV 101 column.

ΔG_s, ΔG_R, $\Delta G_s'$ = free energy of solution for the solute, reference solute [benzenetricarbonylchromium(0)], and incremental substituent ($ArCH_3$–ArH or Ar(t-Bu)–ArH)g, respectively.

n = number of alkyl substituents per molecule

These deviations again reflect mainly steric and electronic (polarity and polarisability) effects arising from the direct attachment of the alkyl groups to the benzene ring. The properties of these complexes thus do not fit the pattern observed for a homologous series of n-alkylbenzenetricarbonylchromium(0) complexes [11].

Enthalpies for the heats of solution (ΔH_s) in OV 101 (a non-polar methylpolysiloxane stationary phase) were evaluated from the temperature-dependence of V_g (Fig. 4) in the equation

$$-\Delta H_s = \frac{R\mathrm{d}\ln V_g}{\mathrm{d}(1/t)}$$

by use of a linear least-square fit of ln V_g versus $10^4/T$, as previously described [21]. The data, summarised in Table 2 show a general decrease in the enthalpy term for series I. This effect also is attributed to the increasing polarity and polarisability along the series.

On-column decomposition and other column effects

The limited stabilities of the complexes revealed by thermal analysis were confirmed in the GLC studies. However, the purely thermal behaviour of the

Table 2

Decomposition rate constants, half-lives and heats of solution for the complexes on a metal-contaminated OV 101 column

No. of alkyl substituents	Adjusted retention time (min) [a]	Decomposition rate constant (s^{-1}) [b]	Half-life (min) [b]	Heat soln. (kJ mol^{-1})
(methyl)				
0	1.14	0.0029	4.0	−34.9
1	1.27	0.0017	6.7	−43.2
2	1.45	0.0014	8.4	−46.6
3	1.86	0.0014	8.4	−44.9
4	2.7	0.0013	9.1	−39.9
5	4.5	0.0010	11.9	−49.9
6	7.4	0.0008	14.3	−59.9
(t-butyl)				
1	2.8	– [c]	– [c]	−33.3
2	6.2	– [c]	– [c]	−33.3
3	6.4	– [c]	– [c]	−33.3

[a] Methyl series at 182°C, t-butyl series 191°C. [b] Determined at 160°C. [c] No decomposition detected for these compounds within determination limit of 10^{-6} s^{-1}.

complexes was complicated by their instability in solution and catalytic, and/or oxidative, decomposition in the column.

Solutions of complexes prepared without precautions were found to decompose fairly rapidly, but solutions in de-aerated solvent in the absence of light were completely stable for at least four days. When the solutions were stored in the dark but not de-aerated, much slower decomposition rates were observed, implying that photoxidation is the primary mechanism of decomposition for these complexes.

Although on-column decomposition of the complexes was not observed on new columns, such decomposition was observed on columns repeatedly exposed to the complexes or other metal compounds [19]. This is evident from Fig. 5 for the case of series I complexes. At a fixed temperature (160°C) these complexes underwent pseudo first order on-column decomposition with half lives of 4 to 14 min (Table 2) on the "active" columns. Half-lives increased in a regular manner with the extent of methyl substitution. No significant decomposition was obtained for the t-butyl-substituted complexes up to 200°C even on "active" columns. In series I complexes, decomposition probably proceeds as shown in eq. 1, catalysed by traces of Cr metal or other Lewis acid sites in the column.

The propensity of the complexes to on-column oxidative decomposition at elevated temperatures was confirmed with air as the carrier gas. In such experiments, very small peaks corresponding to the starting complexes were still observed at 160°C, but earlier peaks corresponding to free arene were the main components identified in each case. From these observations it is evident that the level of oxygen in the carrier gas must be kept as low as possible *. Commercial gas purifiers with indicating tubes can now assure levels of oxygen below 10 ppb [24].

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* In principle there is sufficient oxygen in 10 ml of nitrogen carrier gas containing 1 ppm oxygen to oxidise about 50% of 1 μg of benzenetricarbonylchromium(0) according to eq. 2.

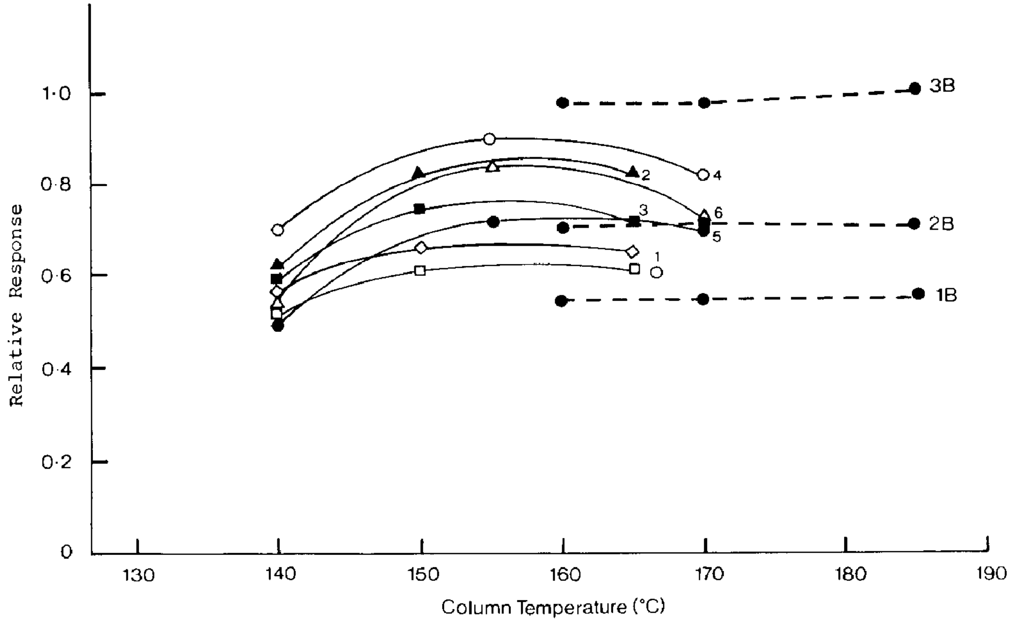

Fig. 5. Relative peak area for organometallics (100 ng) versus column temperature. Flow-rate was varied to maintain constant retention times. Other conditions as in Fig. 3.

In addition to the above problems, GC columns, even highly inert fused silica columns exhibit non-ideal effects which may be important in quantitative applications. Such effects are evident from peak distortion reversible and irreversible adsorption, and catalytic decomposition. Furthermore, they become more pronounced with column usage, particularly when reactive compounds such as organometallics are introduced into the column. These effects can be monitored by standard procedures such as those described by Grob [25]. For the complexes studied, changes produced in the capacity factor (retention), skewness (peak asymmetry), and relative response for a fixed set of organic test compounds were measured on a new column before and after repeated introduction of benzenetricarbonylchromium(0) comprising 100 injections of 1 μg of complex in tetrahydrofuran. The pure solvent, used first as a control, produced no changes in column parameters. Changes observed after the introduction of the complex were small but significant (Table 3), and led to enhanced retention and tailing for the organic test compounds. Relative responses based on peak area altered significantly only for the basic test solution containing 2,6-dimethylaniline. This implies an increase in acidic sites within the column following the introduction of complex. These sites may involve chromium or chromous oxide deposits.

The above effects were partially reversed by repeated injection (25×0.2 μl) of trifluoroacetylacetone (Htfa) on to the column. The effectiveness of this reagent is attributed to scavenging reactions (eq. 4 and 5) which lead to volatile chelate species that come off from the column.

$$2Cr(s) + 6Htfa(g) \rightarrow 2Cr(tfa)_3(g) + H_2(g) \tag{4}$$

$$2CrO(s) + 6Htfa(g) \rightarrow 2Cr(tfa)_3(g) + 2H_2O(g) + H_2(g) \tag{5}$$

Table 3

Data for test solutes on a new OV 101 column before and after introduction of 100×1 μg benzenetricarbonylchromium(0) onto the column. Capacity factors were determined at 90°C. Skew and relative response were calculated from chromatograms involving temperature programming (60–105°C at 2°/min)

Compound	Capacity factor [a]		Skew [b]		Relative response [b]	
	New	Used	New	Used	New	Used
octan-2-one	0.67	0.80	1.44	1.64	0.43	0.38
octan-1-ol	1.24	1.43	1.49	1.73	0.30	0.29
2,6-dimethylphenol	1.54	1.75	1.37	1.53	0.52	0.53
2,4-dimethylaniline	2.26	2.48	1.44	1.61	0.90	0.64
naphthalene	2.65	2.86	1.25	1.21	1.14	1.16
n-dodecane	3.39	3.65	1.00	1.01	1.00	1.00
n-tridecane	6.50	6.81	0.98	1.02	1.32	1.41

[a] Measured isothermally at 95°C. [b] Measured with temp. programming 60–105°C at 2°/min. Relative responses were measured relative to n-dodecane taken as 1.00.

Metals, oxides, and carbonyls are known [26,27] to react with Htfa in this manner, but rates are relatively slow. A more effective column treatment may involves passage of ligand vapour continuously through the column. Complete recovery of the column characteristics was achieved in this way. A problem with this approach, the so called ligand vapor gas chromatography (LVGC) method [28], is the possibility of actually adding metallic impurities to the column by reaction of ligand vapor with metallic components from the syringe and/or injection system [29], and so a system in which the ligand vapor does not come into contact with metal prior to passing through the column may be required.

Conclusion

Great care is required in quantitative studies of aryltricarbonylchromium(0) complexes, and by implication other organometallics, by GC. De-aerated solvents, inert columns, and injection systems, low column temperature, and purification of the carrier gas stream are particularly important. Irreversible changes in column characteristic are to be expected for most organometallics, and can be monitored as described. Regeneration of columns used in such work may be effected by treatment with trifluoroacetylacetone.

References

1 G. Guichon and C. Pommier, Gas Chromatography in Inorganics and Organometallics, Ann Arbor Science Publishers, Ann Arbor, Michigan, (1973).

2 T.R. Crompton, Gas Chromatography of Organometrallic Compounds, Plenum Press, New York (1982).

3 G. Schwedt, Chromatographic Methods in Inorganic Analysis, Huthig, Heidelberg, 1981.

4 P.C. Uden, J. Chromatogr., 313 (1984) 3.

5 Y.S. Drugov, Zh. Anal. Khim., 40 (1984) 3.

6 E.J. Parks, W.F. Manders, R.B. Johannesen and F.E. Brinkman, J. Chromatogr., 351 (1986) 475.

7 R.J. Boyles and R.B. Denyszyn, Research and Development, March (1986) 98.

8 H. Veening, N.J. Graver, D.B. Clark and B.R. Willeford, Anal. Chem., 41 (1969) 1655.

9 W.R. Jackson and W.B. Jennings, J. Chem. Soc., B (1969) 1221.

10 D.E.F. Gracey, W.R. Jackson, C.H. Mcullen and N. Thompson, J. Chem. Soc., B (1969) 1197.
11 C. Sergard, B. Roques, C. Pommier and G. Guichon, Anal. Chem., 43 (1971) 1146.
12 J.S. Keller, H. Veening and B.R. Willeford, Anal. Chem., 43 (1971) 1146.
13 C. Segard, C. Pommier, B.P. Roques and G. Guichon, J. Organomet. Chem., 77 (1974) 49.
14 R. Davis and L.A.P. Kane-Maguire in G. Wilkinson, F.G.A. Stone and E.W. Abel, Comprehensive Organometallic Chemistry, Vol. 3, Pergamon Press, Oxford, 1982.
15 A.A. Aladjin and N.I. Sirotkin, J. Organomet. Chem., 111 (1976) 131.
16 B. Nicholls and M.C. Whiting. J. Chem. Soc., (1959) 551.
17 M.D. Rausch, J. Org. Chem., 39 (1974) 1787.
18 W. Strohmeier, Chem. Ber., 94 (1961) 2490.
19 E. Patsalides and K. Robards, J. Chromatogr., 357 (1986) 49.
20 J.A. Conner, H.A. Skinner and Y. Virmani, J. Chem. Soc., Faraday Trans. I, 69 (1973) 1218.
21 F.A. Adedeji, D.L.S. Brown, J.A. Connor, M.L. Leung, M.I. Paz-Andrade and H.A. Skinner, J. Organomet. Chem., 97 (1975) 221.
22 M.J. Aroney, M.K. Cooper, R.K. Pierens and S.J. Pratten, J. Organomet. Chem., 295 (1985) 333.
23 D.A. Leathard and B.C. Shurlock, Identification Techniques in Gas Chromatography, Wiley-Interscience London (1970).
24 The Supelco Reporter, International, Vol. VII (1) (1988), 1.
25 K. Grob, G. Grob and K. Grob Jr., J. Chromatogr., 219 (1981) 13.
26 R.E. Sievers, J.W. Connolly and W.D. Ross, J. Gas Chrom., 5 (1967 241.
27 M.L. Larson and F.W. Moore, Inorg. Chem., 1 (1962) 886.
28 T. Fuginaga, T. Kuwamoto and K. Sugiura, Bull. Inst. Chem. Res., Kyoto Univ., 58 (1980) 201 and refs. 8–12 therein.
29 S. Dilli, private communication.