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# SALT EFFECTS AND CONSTITUTIONAL EFFECTS IN IODODEMETALLATION OF TETRAALKYLTINS IN METHANOL

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## Summary

Rate constants are reported for iodometallation by $I_2/I^-$ of a series of tetraalkyltins, $R_4Sn$, where R = Me, Et, $Pr^n$, $Bu^{iso}$, and $Pe^{neo}$. Together with previous literature results the present work shows that constitutional effects of the alkyl group, R, do not parallel those in typical $S_N2$ reactions of alkyl halides. Kinetic studies of the effect of added foreign nucleophiles on the iododemetallation revealed that the anions $N_3^-$, $ClO_4^-$, $Cl^-$ and $Br^-$ did not take part in any kinetically significant step, although small specific kinetic salt effects were noted. Product analyses showed also that neither $Br^-$ nor the solvent methanol were involved in any product determining step. The two-stage mechanism proposed by Mathieu can therefore definitely be excluded for the iododemetallation of tetraalkyltins in methanol and other alcoholic solvents.

## Introduction

Rate constants for the iododemetallation of tetraalkyltins in polar solvents such as methanol have been reported by several workers [1—9], especially by Gielen and Nasielski [7—9]. In their extensive investigations, the latter workers showed that in the iododemetallation of tetramethyltin by $I_2/I^-$ in methanol, there is no catalysis by iodide ion and that the iododemetallation follows a simple second-order rate eq. (1). Rate constants for the cleavage of a large number of symmetrical and unsymmetrical tetraalkyltins by $I_2/I^-$ in methanol were also obtained by Gielen and Nasielski [7,8], and later by Boué, Gielen and Nasielski [9].

$$v = k_2[Me_4Sn][I_2] \qquad (1)$$

In spite of all this work, it is still not possible to assign a definite mechanism to the iododemetallation of tetraalkyltins in polar solvents. Firstly, the stereochemical course of the iododemetallation is not known. It is now evident that in the related bomodemetallation of sec-butyltin compounds in methanol, the sec-butyl bromide product may be formed with either predominant inversion or predominant retention of configuration, depending on the size of the leaving $SnR_3$ group [10—12]. There seems to be such a fine balance between the energetics of the inversion and retention mechanisms of substitution that it is difficult, if not impossible, to predict the stereochemical course of the iododemetallation reaction. Furthermore, such a fine balance leads to the difficulty (unknown in $S_N2$ substitutions) that even if the stereochemical course of substitution is known for one particular member of the alkyl series, for example the sec-butyl- or PhCHDCHD- group, there is no guarantee that the same stereochemical course will obtain in general along the series of alkyl groups. Secondly, there are now known to be possible mechanisms of substitution that are compatible with the simple kinetic form (1) but which do not proceed by a single elementary reaction. Mathieu [13] has re-interpreted the work of Jensen and Davis [10] on the bromodemetallation of sec-butyltin compounds by $Br_2/Br^-$ in methanol, in terms of the two-step mechanism shown in eq. 2 and 3. Application of the steady-state theory to eq. 2 and 3 reveals that the observed kinetic

$$Bu^sSnR'_3 + Br_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Bu^sSn^+(Br)R'_3 \qquad (2)$$

$$Br^- + Bu^sSn^+(Br)R'_3 \xrightarrow[k_x]{S_N2} BrBu^s + R'_3SnBr \qquad (3)$$

form is the simple second-order equation $v = k_2^{obs}[Bu^sSnR'_3][Br_2]$ where $k_2^{obs} = k_f k_x/(k_b + k_x)$, and thus on simple kinetic grounds the mechanism cannot be distinguished from a simple elementary reaction between the tetraalkyltin and bromine. Mathieu [13] suggests that the observed inversion of configuration in the sec-butyl group is actually the result of the $S_N2$ substitution (3).

We now report a reinvestigation of the iododemetallation of tetraalkyltins in methanol, with particular reference to the possibility of the mechanism proposed by Mathieu [13], and to the effect of more complicated alkyl groups on the rate of iododemetallation. Recent structure-reactivity studies on successive methyl-for-hydrogen replacement in substrates of type RHgBr revealed that a rate-accelerating inductive (electronic) effect works in opposition to a rate-retarding steric effect [14]. Whereas the former dominates for $\alpha$-substitution, the latter dominates for $\beta$-substitution. It seemed therefore useful to obtain rate constants for the iododemetallation of several more tetraalkyltins, so that a more complete series of $\alpha$- and $\beta$-methylated alkyl groups would be covered.

## Discussion

Rate constants for iododemetallation of tetraalkyltins by $I_2/I^-$ in methanol were obtained using the spectrophotometric procedure outlined by Gielen and Nasielski [7,8]. In Table 1 are given results in terms of the alkyl reactivity constants, $-\log(k^R/k^{Me})$, for the iododemetallation of the symmetrical tetraalkyltins in methanol, together with literature values for the corresponding unsymmetrical compounds [9], for the bromodemetallation of $RSnPe_3^{neo}$ compounds in methanol [10], and for typical $S_N2$ reactions [15]. By comparison to the

TABLE 1

ALKYL REACTIVITY CONSTANTS, $-\log(k^{R}/k^{Me})$, FOR HALOGENODEMETALLATION IN METHANOL

| R | $S_N2$ [a] | $Br_2 + RSnPe^{neo}_3$ [b] | $I_2 + R_4Sn$ [c] | $I_2 + RSnMe_3$ [d] | $I_2 + RSnEt_3$ [d] |
|---|---|---|---|---|---|
| Me | 0 | 0 | 0 | 0 | 0 |
| Et | 1.31 | 0.84 | 0.90 | 0.84 | 1.21 |
| $Pr^n$ | 1.67 | 1.39 | 1.68 | 1.50 | 1.74 |
| $Bu^{iso}$ | 2.70 |  | 1.95 |  |  |
| $Pr^{iso}$ | 2.92 | 2.12 | 3.22 | 2.25 | 2.95 |
| $Pe^{neo}$ | 6.18 | 3.23 | 1.89 (2.34) | — | — |

[a] Values for typical $S_N2$ substitutions of alkyl halides [15]. [b] Ref. [10]. [c] This work (see Table 6 in the Experimental section). [d] Ref. [9].

values for the $S_N2$(Inv) reactions, the reactivity of the $Pe^{neo}$ (and $Bu^{iso}$) group in the halogenodemetallations is greater than expected; this is especially marked for the iododemetallation of the symmetrical compounds, and although there may be leaving-group effects, we feel that the heavily substituted β-methylated alkyl groups probably react by a mechanism involving retention of configuration at the carbon atom undergoing substitution. Calculations [16—18] suggest that for processes involving such retention of configuration, steric effects of β-methyl groups (as in the alkyl groups $Bu^{iso}$ and $Pe^{neo}$) are very much less than for related substitutions involving inversion of configuration. These calculations [16—18] also indicate that steric effects of α-methyl groups (as in the alkyl groups $Pr^{iso}$ and $Bu^{sec}$) are much larger for processes involving retention of configuration that those in which inversion of configuration takes place. It is therefore quite possible for $Pe^{neo}$ groups to react with retention of configuration and yet for $Pr^{iso}$ and $Bu^{sec}$ groups to react with inversion of configuration in the same series of substitutions. We therefore decided to test Mathieu's [13] mechanism in the case of iododemetallation of tetraethyltin by kinetic salt effects, and for iododemetallation of several tetraalkyltins by product analyses.

If iododemetallation of a tetraalkyltin is carried out in the presence of a nucleophile, $Y^-$, where $Y^-$ is not the common-ion, $I^-$, then Mathieu's mechanism may be expressed in terms of eq. 4—7.

$$R_4Sn + I_2 \xrightarrow{k_f} R_4Sn^+I + I^- \tag{4}$$

$$R_4Sn^+I + I^- \xrightarrow{k_b} R_4Sn + I_2 \tag{5}$$

$$R_4Sn^+I + I^- \xrightarrow{k_x} RI + R_3SnI \tag{6}$$

$$R_4Sn^+I + Y^- \xrightarrow{k_y} RY + R_3SnI \tag{7}$$

Application of the steady-state theory to the intermediate $R_4Sn^+I^-$ yields for the observed rate constant, defined by eq. 8, the expression 9.

$$v = k_2^{obs}[R_4Sn][I_2] \tag{8}$$

$$k_2^{obs} = k_f \frac{k_x + k_y[Y^-]/[I^-]}{k_b + k_x + k_y[Y^-]/[I^-]} \tag{9}$$

There are two extreme cases that lead to a simplification of eq. 9:

(a) If $k_b >> k_x$, $k_y$ and if $[Y^-]/[I^-]$ is not too large, then

$$k_2^{obs} = \frac{k_f k_x}{k_b} + \frac{k_f k_y}{k_b} \times \frac{[Y^-]}{[I^-]} \tag{10}$$

This situation corresponds to a rapid equilibrium (4 and 5) followed by rate-determining $S_N2$ processes (6 and 7). Therefore, the constitutional effects of R on the observed rate constant $k_2^{obs}$ will be a combination of effects on the equilibrium constant, $k_f/k_b$, and on the rate constant $k_x$ or $k_y$. More importantly from the present point of view, if the ratio $[Y^-]/[I^-]$ is altered, then the rate constant, $k_2^{obs}$, should vary and a plot of $k_2^{obs}$ against $[Y^-]/[I^-]$ should yield a straight line of slope $k_f k_y/k_b$ and intercept $k_f k_x/k_b$. Furthermore, the product should contain both RY and RI in the ratio $[RY]/[RI] = k_y[Y^-]/k_x[I^-]$. The intermediate $R_4Sn^+I$ could also react with the solvent to yield the corresponding methyl ether, ROMe; although eqs. 9 and 10 can be modified to incorporate this process, such modification does not affect the general form of eq. 10.

(b) If $k_b << k_x$, $k_y$ then eq. 9 collapses to yield the simple expression $k_2^{obs} = k_f$. This corresponds to a rate-determining initial reaction (4), followed by rapid reactions (6 and 7). Constitutional effects of R should therefore be apparent only as regards the initial step 4. There should be no effect of $[Y^-]$ on the observed rate constant, but since the intermediate $R_4Sn^+I$ now reacts rapidly with any nucleophile in the system, both RI and RY should be formed as products, as well as the product of solvolysis of $R_4Sn^+I$, that is the ether ROMe.

We first studied the effect of added azide ion on the rate constant, adjusting the ratio $[N_3^-]/[I^-]$ and holding the ionic strength constant, Table 2. There seems to be a slight effect of increase in $k_2^{obs}$ with increase in the ratio $[N_3^-]/[I^-]$, as required by eq. 10, but we tested the equation further by a set of experiments in which the ionic strength was held constant by perchlorate ion, Table 3. Again, there are small variations in $k_2^{obs}$, but no really definite trend as expected on replacing $ClO_4^-$ by the very nucleophilic $N_3^-$ in an $S_N2$ reaction at a carbon centre in methanol. In an effort to understand the reason for the small variations of $k_2^{obs}$ at constant ionic strength, Tables 2 and 3, we also carried out experiments in which the ionic strength was allowed to vary, Table 4.

TABLE 2

RATE CONSTANTS [a] FOR IODODEMETALLATION OF $Et_4Sn$ IN PRESENCE OF $N_3^-$

| $10^3$[KI] (mol dm$^{-3}$) | $10^3$[NaN$_3$] (mol dm$^{-3}$) | $k_2^{obs}$ (dm$^3$ mol$^{-1}$ s$^{-1}$) |
|---|---|---|
| 12.13 | 0.00 | 1.22 |
| 9.71 | 2.44 | 1.35 |
| 7.28 | 4.85 | 1.31 |
| 4.85 | 7.28 | 1.42 |
| 2.43 | 9.71 | 1.56 |
| 1.21 | 10.92 | 1.33 |

[a] In methanol at 293 K. Initial concentrations were $Et_4Sn$ ($9.1 \times 10^{-2}$ mol dm$^{-3}$), iodine ($3.1 \times 10^{-5}$ mol dm$^{-3}$).

TABLE 3

RATE CONSTANTS [a] FOR IODODEMETALLATION OF $Et_4Sn$ IN PRESENCE OF $N_3^-$ AND $ClO_4^-$

| $10^2$ [$Bu_4NI$] (mol dm$^{-3}$) | $10^2$ [$NaClO_4$] (mol dm$^{-3}$) | $10^2$ [$NaN_3$] (mol dm$^{-3}$) | $k_2^{\text{obs}}$ (dm$^3$ mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|
| 0.115 | 10.0 | 0 | 1.54 |
| 0.115 | 9.0 | 1.0 | 1.58 |
| 0.115 | 8.0 | 2.0 | 1.55 |
| 0.115 | 7.0 | 3.0 | 1.54 |
| 0.115 | 5.0 | 5.0 | 1.64 |
| 0.115 | 4.0 | 4.0 | 1.67 |
| 0.115 | 3.0 | 7.0 | 1.62 |
| 0.115 | 2.0 | 8.0 | 1.55 |
| 0.115 | 1.0 | 9.0 | 1.65 |
| 0.115 | 0 | 10.0 | 1.46 |

[a] In methanol at 298 K. Initial concentrations were $Et_4Sn$ ($8.0 \times 10^{-2}$ mol dm$^{-3}$), and iodine ($3.0 \times 10^{-5}$ mol dm$^{-3}$).

It can be seen from Table 4 that there are specific salt effects on the values of $k_2^{\text{obs}}$. These are sufficient to explain the small variations in $k_2^{\text{obs}}$ shown in Tables 2 and 3, and our conclusion is that added foreign anions do not affect the observed rate constant in the sense of eq. (10). Thus case (a), above, can be excluded on the basis of the overall results given in Tables 2, 3, and 4.

Product analyses were also carried out to test both case (a) and case (b). An iododemetallation was carried out in the presence of iodide ion ($1.0 \times 10^{-3}$ mol dm$^{-3}$) and bromide ion ($1.0 \times 10^{-1}$ mol dm$^{3}$) together, Examination of the reaction products by GLC revealed that the maximum possible concentration of bromoethane was less than 2% of the formed iodoethane. Taking into account the 100-fold excess of initial bromide ion over iodide ion, it can be deduced that reaction 7 ($Y^- = Br^-$) takes place to an extent not greater than 0.02% of reaction 6. We also examined a number of iododemetallations, both in the presence and the absence of iodide ion, for the ether that would be obtained by an $S_N2$ attack of the solvent on the intermediate $R_4Sn^+I$. For analytical reasons we used a number of alcohol solvents with the various tetraalkyltins. As can be seen from Table 5, in no case was any substantial quantity of ether formed; indeed, no ether was ever detected. The product analyses both for bromoethane and for the ethers again confirms that the mechanism of Mathieu [13] does not

TABLE 4

EFFECT OF ADDED SALTS ON RATE CONSTANTS [a] FOR THE IODODEMETALLATION OF $Et_4Sn$

| Added salt (mol dm$^{-3}$) | $k_2^{\text{obs}}/k_2^{\circ}$ | | | |
|---|---|---|---|---|
| | $NaClO_4$ | NaCl | NaBr | $NaN_3$ |
| 0 | 1 | 1 | 1 | 1 |
| 0.005 | 0.95 | 1.02 | 0.86 | |
| 0.010 | 0.93 | 1.07 | 0.81 | |
| 0.050 | 1.01 | 1.23 | 0.95 | |
| 0.100 | 1.12 | 1.25 | 0.84 | 1.07 |

[a] In methanol at 298 K; initial concentrations as in Table 3, [$Bu_4NI$] = $1.15 \times 10^{-3}$ mol dm$^{-3}$.

TABLE 5

PRODUCT ANALYSES FOR IODODEMETALLATION OF TETRAALKYLTINS

| $R_4Sn$ | Reagent | Solvent | RI [a] | Ether (%) [a] |
|---|---|---|---|---|
| $Me_4Sn$ | $I_2$ | $Bu^nOH$ | MeI | $MeOBu^n(<1)$ |
| $Me_4Sn$ | $I_2/I^-$ | $Bu^nOH$ | MeI | $MeOBu^n(<1)$ |
| $Et_4Sn$ | $I_2$ | $Bu^nOH$ | EtI | $EtOBu^n(<1)$ |
| $Et_4Sn$ | $I_2/I^-$ | $Bu^nOH$ | EtI | $EtOBu^n(<1)$ |
| $Pr_4^nSn$ | $I_2$ | $Pr^nOH$ | $Pr^nI$ | $Pr^nOPr^n(<1)$ |
| $Pr_4^nSn$ | $I_2/I^-$ | $Pr^nOH$ | $Pr^nI$ | $Pr^nOPr^n(<1)$ |
| $Bu_4^nSn$ | $I_2$ | $Bu^nOH$ | $Bu^nI$ | $Bu^nOBu^n(<1)$ |
| $Bu_4^nSn$ | $I_2/I^-$ | $Bu^nOH$ | $Bu^nI$ | $Bu^nOBu^n(<1)$ |
| $Pr_4^{iso}Sn$ | $I_2$ | $Pr^{iso}OH$ | $Pr^{iso}I$ | $Pr^{iso}OPr^{iso}(<1)$ |
| $Pr_4^{iso}Sn$ | $I_2/I^-$ | $Pr^{iso}OH$ | $Pr^{iso}I$ | $Pr^{iso}OPr^{iso}(<1)$ |
| $Bu_4^{sec}Sn$ | $I_2$ | $Bu^{sec}OH$ | $Bu^{sec}I$ | $Bu^{sec}OBu^{sec}(<1)$ |
| $Bu_4^{sec}Sn$ | $I_2/I^-$ | $Bu^{sec}OH$ | $Bu^{sec}I$ | $Bu^{sec}OBu^{sec}(<1)$ |

[a] Yields of RI based on the amount of iodine ranged from 50—100%, no attempt being made to optimise these yields by varying the reaction time, etc.

apply to the iododemetallation of tetraalkyltins in the alcohols.

Having disposed of the possibility of the mechanism shown in 4—7, we briefly discuss the charge-transfer (CT) mechanism proposed by Fukuzumi and Kochi [19]. These workers observed transient charge-transfer complexes between tetraalkyltins and iodine in nonpolar solvents, and suggested that such complexes were intermediates in the iododemetallation reaction, the latter proceeding through, eventually, an ion-pair species $[R_4Sn^{+\cdot}I_2^{-\cdot}]$. Although the CT complexes cannot be observed in polar solvents, Fukuzumi and Kochi generalised their CT mechanism to include iododemetallation in polar solvents as well as nonpolar solvents. It is known [1,19] that the relative reactivity of a series of $R_4Sn$ compounds towards an electrophile such as iodine depends markedly on the solvent. In polar solvents such as acetonitrile and methanol (Table 1) the sequence of reactivity is $Me_4Sn > Et_4Sn > Pr_4^nSn > Bu_4^{iso}Sn > Pr_4^{iso}Sn$, but in dichloromethane the sequence is [19] $Et_4Sn > Pr_4^nSn > Bu_4^{iso}Sn > Me_4Sn > Pr_4^{iso}Sn$, and in chlorobenzene [1] the tetraisopropyltin is more reactive than tetramethyltin: $Et_4Sn > Pr_4^{iso}Sn > Me_4Sn > Pr_4^nSn$. Fukuzumi and Kochi suggest that the rate-limiting step in iododemetallation is the electron transfer step $[R_4SnI_2] \rightarrow [R_4Sn^{+\cdot}I_2^{-\cdot}]$ that follows the initial CT formation, $R_4Sn + I_2 \rightleftharpoons [R_4SnI_2]$. Thus the relative reactivity of a series of $R_4Sn$ compounds will depend not only on the CT equilibrium constant (related to the $R_4Sn$ ionisation potential) but also to the interaction energy in the ion pair, the relative proportions of these two 'driving forces' being solvent dependent *. However, for polar solvents the CT mechanism seems [19] to merge with the mechanism of electrophilic substitution; on the CT mechanism, the sequence of reactivity in polar solvents is due to effects such as steric effects in the interaction energy term, whilst on the $S_E2$ mechanism, the reactivity sequence is due to steric effects in a generalised transition state [16—18]. Thus at the moment we conclude that

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* But note also our previous comment that in any given series of $R_4Sn$ compounds, the same stereochemical course may not be followed along the series.

the iododemetallation of the simple tetraalkyltins in the alcohols we have studied proceeds by either an $S_E2$ mechanism or by a CT mechanism that is close to the simple $S_E2$ mechanism. From our comparison of rate constants with those for $S_N2$ substitutions, it seems probable that (at least) the β-substituted compounds react on iodometallation in methanol with retention of configuration at the carbon atom undergoing substitution.

## Experimental

Methanol was distilled under nitrogen; a large fore-run was rejected and the middle fraction retained. Iodine was resublimed Analar grade, and the various inorganic salts were also Analar grade materials. The tetraalkyltins were prepared and purified as described in refs. 20—22 except for tetraneopentyltin which was a kind gift from Professor H. Zimmer.

Rate constants for the iododemetallation of the tetraalkyltins at 293 K were determined spectrophotometrically by the procedure described in detail by Gielen and Nasielski [7,8] using a Cary 17 recording spectrophotometer. Kinetic experiments were carried out using a large excess of the $R_4Sn$ compound and a large excess of $I^-$, and the first-order rate constants thus obtained converted in the usual way to the observed second-order rate constants; the equilibrium constant for $I_3^-$ formation at 293 K in methanol was taken as $2.04 \times 10^4$ $dm^3$ $mol^{-1}$ [7,8]. Details of the kinetic procedures and results are in Table 6. The salt effect studies reported in Table 2 were obtained in exactly the same way.

The rate constants and data at 298 K shown in Tables 3 and 4 were obtained from experiments carried out at lower concentrations of $I^-$ in the form of $Bu_4NI$, $1.15 \times 10^{-3}$ mol $dm^{-3}$. At these concentrations of $I^-$, the iododemetallation proceeds very rapidly, and kinetic data were obtained using an on-line computer coupled to a spectrophotometer [23]; the computer was programmed to calculate rate constants using Guggenheim's method for a first-order reaction,

TABLE 6

KINETIC RESULTS ON THE IODODEMETALLATION OF TETRAALKYLTINS IN METHANOL AT 293 K

| $R_4Sn$ | Initial concentration ($10^2$ mol $dm^{-3}$) | | $k_1^{obs}$ ($s^{-1}$) | $k_2^{obs}$ ($dm^3$ $mol^{-1}$ $s^{-1}$) |
|---|---|---|---|---|
| | $[R_4Sn]$ | [KI] | | |
| $Me_4Sn$ | 9.150 | 2.225 | 13.14 | 6.52 |
| | 9.084 | 2.730 | 10.71 | 6.57 |
| $Et_4Sn$ | 9.301 | 2.594 | 1.485 | 0.845 |
| | 9.160 | 2.730 | 1.349 | 0.820 |
| $Pr^n_4Sn$ | 9.106 | 2.730 | 0.2364 | 0.145 |
| | 8.943 | 3.233 | 0.1732 | 0.127 |
| $Bu^{iso}_4Sn$ | 9.106 | 2.728 | 0.0986 | 0.060 |
| | 9.064 | 2.728 | 0.1204 | 0.074 |
| | 9.099 | 2.722 | 0.1281 | 0.078 |
| $Pe^{neo}_4Sn$ | 0.1998 | 2.728 | 0.00309 | 0.086 [b] |

[b] Another set of experiments gave $k_2^{obs} = 0.021$ with $[Bu_4NI] = 0.0026$ mol $dm^{-3}$ and $k_2^{obs} = 0.026$ with $[Bu_4NI] = 0.0158$ mol $dm^{-3}$. These values correspond to $k_2^{obs} = 0.03$ $dm^3$ $mol^{-1}$ $s^{-1}$ at $\mu = 0.027$ mol $dm^{-3}$.

and the first-order rate constants were converted to values of $k_2^{obs}$ using $K(I_3^-) = 1.57 \times 10^4$ at 298 K.

Product analyses were carried out by GLC using a Perkin-Elmer flame ionisation gas chromatograph. The column used for all the analyses was a 1.5 m long column packed with O.P.N. Porasil bonded to a solid support of Porasil C, and operated at 383 K. All the possible haloalkanes and ethers were either obtained commercially or were prepared, and retention times of the compounds were determined relative to bromobenzene as an internal standard. For quantitative analyses, standard solutions containing the haloalkanes and ethers as well as the internal standard were prepared and calibration factors relating peak height to concentration were obtained for all the haloalkanes and ethers. For the analysis of the solutions after iododemetallation, the reaction mixture was made up to a standard volume after the addition of a known weight of the internal standard, and samples of the mixture injected directly onto the column. Measurement of the peak heights of the haloalkanes, ethers, and bromobenzene, together with a knowledge of the calibration factors and the (known) concentration of the internal standard, enabled the concentration of the haloalkanes and ethers to be obtained, Table 5.

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