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A Mass Spectroscopic Study of Organomercurials and Mercuric Halides

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The fragmentation of various mercury compounds of the types HgR_2, $HgXR$ and HgX_2 is reported where R = Me, C_6H_5, m–FC_6H_4, p-FC_6H_4, Me_3MCH_2 (M = Si, Ge) and X = halide. Their behaviour, especially that of the organomercury halides, varies considerably with the nature of the R group whilst changing the halide has little effect. For diarylmercurials and arylmercuric halides the base peak is the carbonium ion R^+ whereas in the methylmercury halides the base peak is $HgXMe^{+\cdot}$. In compounds containing the grouping Me_3MCH_2–Hg the fragmentation is dominated by cleavage of the Me–M rather than Hg–C bonds. For the mercury(II) dihalides variations in electron voltage give evidence for two routes to the X^+ ion. Attempts to prepare (o-$FC_6H_4)_2Hg$ resulted in the isolation of 2, 2'-(o-fluorophenyl)diphenylmercury. Some ionization and appearance potentials are reported.

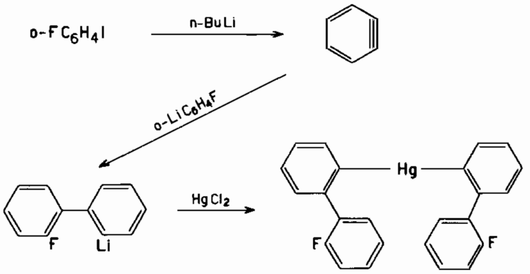
Introduction

Many studies have been reported on the mass spectra of main group organometallic compounds[1] and various generalizations appear to be justified: even-electron ions are more abundant than odd-electron ions; most of the ion current is carried by metal-containing species and spectra are dominated by the cleavage of those bonds which are probably the weakest in the neutral molecules[2]. We have extended earlier studies on a variety of organomercury compounds mainly to examine the extent to which these considerations apply.

Dibeler and Mohler[3] first reported the mass spectra of various mercury dialkyls and Gowenlock measured appearance and ionization potentials and correlated these with thermochemical data. The most relevant points in relation to the present work are that although $\bar{D}$(Hg–C) in $HgMe_2$ is low (~120 KJ mol^{-1}), D_1 corresponding to $HgMe_2 \rightarrow Me\cdot + HgMe\cdot$, is much stronger (~200 KJ mol^{-1}). In HgClMe D(Hg–C) is stronger than in $HgMe_2$ and $\bar{D}$ in $HgPh_2$ is stronger than in $HgMe_2$[4]. Recent studies[5–7] on the mass spectra of mercury diaryls and related compounds have demonstrated the dominance of 5 ions ($HgR_2^{+\cdot}$, HgR^+, Hg^+, $R_2^{+\cdot}$ and R^+); in the case of $HgPh_2$ the two hydrocarbon ions carried 67% of the charge. Mercury dialkyls fragment in a similar way except for the low abundance of the $R_2^{+\cdot}$ ion. It thus appears that mercury in its organo compounds is rather anomalous in the high proportion of charge carried by hydrocarbon ions, possibly reflecting the high first ionization potential of mercury.

Experimental

Analytically pure samples of the mercuric halides were commercially available, the purity being confirmed by analyses and Raman spectroscopy. The organomercuric halides were prepared from HgR_2 and HgX_2 in ethanol; HgR_2 compounds were prepared from $HgCl_2$ and the appropriate Grignard reagent. Attempts to prepare the orthofluorophenyl compound via either the Grignard or lithio derivatives of o-fluoroiodobenzene and $HgCl_2$ gave exclusively (I) as a white powder, m.p. 142° C (dec.) Found: C, 53.0; H, 2.9. $C_{24}H_{16}F_2Hg$ requires C, 53.1; H, 2.9%. This compound is presumably formed via benzyne by the addition of o-fluoroiodobenzene or o-lithiofluorobenzene *(Scheme I).*



(1)

The structure of 2,2'-(o-fluorophenyl)diphenylmercury (I) was confirmed by its hydrolysis using ethereal HCl to 2-fluorobiphenyl, m.p. and mixed m.p. 73° C; with $HgCl_2$ in ethanol (I) was converted into (2-fluorophenyl)phenylmercuric chloride, $C_{12}H_8ClFHg$ m.p. 150° C. Found: C, 35.4; H, 1.9; Hg, 49.3. $C_{12}H_8ClFHg$ requires C, 35.4; H, 2.0; Hg, 49.3%. ν(Hg–Cl) 334, 325 cm^{-1}. ν(Hg–C) 455 cm^{-1}. Silver fluoride gave $C_{12}H_8FHgF$, m.p. 142° C. Found: C, 36.9; H, 2.4. $C_{12}H_8F_2Hg$ requires C, 36.9; H, 2.1%. ν(Hg–F) 479, ν(Hg–C) 460 cm^{-1}.

TABLE I. Ion Abundances, HgR_2 at 70 eV.

	$HgR_2^{+\cdot}$	HgR^+	$Hg^{+\cdot}$	$R_2^{+\cdot}$	R^+	Other Hydrocarbons
$HgPh_2$	17.6	11.0	1.3	2.6	44.0	23.3
$Hg(p\text{-}FC_6H_4)_2$	22.2	16.7	2.9	1.8	36.4	20.0
$Hg(m\text{-}FC_6H_4)_2$	15.2	11.5	1.0	1.0	52.4	18.8
$Hg(C_{12}H_8F)_2$	7.8	1.8	1.1	3.5	35.3	50.5

Mass spectra were recorded on an MS902 instrument using a direct insertion probe at 100–200° C and an accelerating voltage of 6 kV. In deriving ion abundances the ion currents due to the combination of isotopes for each species have been summed and are expressed as a percentage of the total ion current. Ionization and appearance potentials (±0.2 eV) were evaluated by the Warren method[1].

Results and Discussion

Mercury Diaryls

Ion abundances are listed in Table I, the fragmentation scheme following that previously described[5,6]. Our values for $HgPh_2$ differ significantly from those previously reported, probably due to the use of a different type of mass spectrometer. The dominance of hydrocarbon ions R^+ is apparent for each compound (reactions 1–3) whilst the low abundance $R_2^{+\cdot}$ ions are formed by reaction 4. Our work does not support the conclusion of Druzhkov[8] that Hg^+ is formed exclusively by catalytic decomposition of $HgPh_2$ in the source.

$$HgR_2^{+\cdot} \rightarrow R^+ + HgR^\cdot \qquad 1$$

$$HgR^+ \rightarrow R^+ + Hg \qquad 2$$

$$R_2^{+\cdot} \rightarrow R^+ + R^\cdot \qquad 3$$

$$HgR_2^{+\cdot} \rightarrow R_2^{+\cdot} + Hg \qquad 4$$

Successive Hg–C bond cleavage also results in retention of charge by mercury (reaction 5)

$$\begin{tikzcd} HgR_2^{+\cdot} \arrow[r] \arrow[rr, bend right] & HgR^+ \arrow[r] & Hg^{+\cdot} \end{tikzcd} \qquad 5$$

In Table I ions listed as "other hydrocarbons" are mostly those resulting from successive elimination of acetylene from $C_6H_5^+$ or HF from $C_6H_4F^+$, as previously described[6]. Effects ascribable to the *m*- or *p*-fluorine atoms are insignificant allowing for the poor reproducibility of ion abundances when a solid insertion probe is used. Similarly the ionization and appearance potential data in Table II are extremely similar apart from $A(Hg^{+\cdot})$ derived from $Hg(m\text{-}C_6H_4F)_2$; this difference may be accounted for since either or both of two processes (reaction 5) produce $Hg^{+\cdot}$.

Aryl- and Methyl-mercuric Halides

Ion abundances (Table III) show surprisingly small differences between the first six compounds, rarely differing by more than a factor of 2. Hence inductive and electromeric effects of *m*- or *p*-fluorine are hardly evident. Parent ions are always of high abundance but hydrocarbon ions carry at least 50% of the ion current since cleavage of the R–HgX bond gives predominantly charge retention on carbon. Elimination of $RX^{+\cdot}$ was only apparent for three compounds. Metastable peaks were observed for the following transitions: $HgXR^{+\cdot} \rightarrow HgR^+$; $HgR^+ \rightarrow R^+$; $C_6H_5^+ \rightarrow C_4H_3^+$; $C_6H_4F^+ \rightarrow C_6H_3^+$.

The mass spectra of the methylmercuric halides (X = Cl, Br, I) contained no metastable peaks and the ions $HgXMe^{+\cdot}$, HgX^+, $HgMe^+$ and Hg^+ were the main charge carriers. The abundance of CH_3^+ and ions derived from it were far lower than has been observed both for aryl- and the higher alkyl-mercuric halides; this is to be expected because of the low stability of the methyl carbonium ion. The class b character of mercury is reflected in the high abundance of HgI^+ relative to $HgCl^+$ and $HgBr^+$, the abundance of $Hg^{+\cdot}$ consequentially showing the reverse relationship. For HgClMe and HgBrMe the Hg^{2+} ion carried 3.1 and 1.0% of the ion current respectively. Ionization potentials decrease between the chloride and iodide (HgCl Me, 11.3; HgBrMe, 10.6; HgIMe, 9.4 eV) as also do the appearance potentials of the HgX^+ ions ($HgCl^+$, 13.3; $HgBr^+$, 12.8; HgI^+, 12.2 eV).

Compounds of the Types $(Me_3MCH_2)_2Hg$ and Me_3MCH_2HgX (M = Si, Ge, X = Br, Cl)

Compounds containing trimethylsilyl (or germyl) methyl groups bonded to main group and transition metals have been extensively studied in recent years[8]

TABLE II. Ionisation and Appearance Potentials for HgR_2,eV.

	Ph	$m\text{-}FC_6H_4$	$p\text{-}FC_6H_4$
$I(HgAr_2^{+\cdot})$	9.4	9.6	9.5
$A(HgAr^+)$	11.5	11.9	11.9
$A(Hg^+)$	10.0	11.3	10.5

TABLE III. Ion Abundances, HgXR at 70 eV.

	$HgXR^{+\cdot}$	HgR^{+}	HgX^{+}	Hg^{+}	R^{+}	$RX^{+\cdot}$	Others
$HgCl(C_6H_5)$	18.5	11.5	0.7	4.5	35.0	2.8	$C_4H_3^{+}$, 26.9
$HgBr(C_6H_5)$	16.6	6.1	1.1	4.5	55.9		$C_4H_3^{+}$, 15.6
$HgCl(m\text{-}FC_6H_4)$	34.1	7.0	1.1	7.7	35.2		$C_6H_3^{+}$, 14.7
$HgBr(m\text{-}FC_6H_4)$	34.2	7.3	2.7	3.8	38.5		$C_6H_3^{+}$, 13.5
$HgCl(p\text{-}FC_6H_4)$	25.9	7.9	1.9	5.4	37.6		$C_6H_3^{+}$, 21.1
$HgBr(p\text{-}FC_6H_4)$	33.2	8.1	2.2	5.5	36.9		$C_6H_3^{+}$, 14.0
$HgF(C_{12}H_8F)$	20.9	0.5	0.5	4.7	24.1	1.7	R^{+} fragments, 50.3
$HgCl(C_{12}H_8F)$	14.8	0.1	9.0	0.8	21.8	2.1	R^{+} fragments, 51.4
HgClMe	23.2	16.2	5.9	27.5	8.5[a]	0.3[a]	$HCl^{+\cdot}$, 13.4, Cl^{+}, 1.8
HgBrMe	37.9	17.2	17.6	15.6	6.0[a]	3.1[a]	$HBr^{+\cdot}$, 0.9, Br^{+}, 0.8
HgIMe	35.4	15.9	27.5	8.4	1.9[a]	8.8[a]	$HI^{+\cdot}$, 1.4, I^{+}, 0.6

[a] $R^{+} = CH_3^{+} + CH_2^{+} + CH^{+} + C^{+}$.

TABLE IV. Major Ion Abundances, $(Me_3MCH_2)_2Hg$ at 70 eV.

	M = Si	M = Ge
$(Me_3MCH_2)_2Hg^{+\cdot}$	5.5	4.3
$Me_3MCH_2HgCH_2MMe_2^{+}$	39.0	50.5
$Me_3Me_3MCH_2Hg^{+}$	0.4	1.2
$Hg^{+\cdot}$	1.3	3.1
$(Me_2MCH_2)_2Hg^{2+}$	2.2	3.3
Hg^{2+}	0.2	0.3
$Me_3Me_3MCH_2^{+}$	2.4	0.7
$m/e \leqq 86$	46.0	32.4

and are often of unusually high thermal stability. The mass spectra of the bis compounds $(Me_3MCH_2)_2Hg$ are complex and quite strikingly different from other mercury-dialkyls and -diaryls reported in this and earlier work. The spectra contain over 30 ions varying in abundance from <0.1–39% when M = Si to 0.2–50.5% when M = Ge (Table IV).

One of the most striking features of the spectra is the low abundance of the parent ions compared to those of ions resulting from cleavage of an M–Me bond. This might imply that in these compounds the Hg–C bond strength is not greatly weaker than Si–C or Ge–C. A strong metastable peak was present corresponding to the process:

$$(Me_3MCH_2)_2Hg^{+\cdot} \rightarrow Me^{\cdot} + Me_3MCH_2HgCH_2MMe_2^{+}$$

When mercury–carbon bonds are cleaved most of the charge is carried by mercury-free species. For example a metastable peak was observed for the decomposition:

$$Me_3MCH_2HgCH_2MMe_2^{+} \rightarrow Me_3MCH_2^{+} + Me_2MCH_2Hg^{\cdot}$$

The total ion current due to HgR^{+} ($R = Me_3MCH_2$, Me_2MCH_2, Me_3M *etc.*) is less than 2%. Four metastable supported transitions for ethylene loss from mercury-free ions follow routes well established for the decomposition of organo-silanes and -germanes[1].

$$Me_3MCH_2^{+} \rightarrow C_2H_4 + H_2M(Me)CH_2^{+}$$
$$Me_2MCH_2^{+} \rightarrow C_2H_4 + H_2MCH_2^{+}$$
$$Me_3M^{+} \rightarrow C_2H_4 + H_2MMe^{+}$$
$$Me_2MH^{+} \rightarrow C_2H_4 + H_3M^{+}$$

For the halide compounds, Me_3MCH_2HgX (Table V) parent ions are of low abundance, by far the most abundant mercury-containing ions resulting from methyl radical elimination from the parent.

In marked contrast to other types of organomercury halides elimination of $X^{\cdot}$ does not occur to any signi-

TABLE V. Major Ion Abundances, Me_3MCH_2HgX at 70 eV.

	Me_3SiCH_2HgCl	Me_3SiCH_2HgBr	Me_3GeCH_2HgCl	Me_3GeCH_2HgBr
$Me_3MCH_2HgX^{+\cdot}$	1.8	2.6	0.8	0.8
$Me_2MCH_2HgX^{+}$	24.1	17.8	14.4	18.3
HgX^{+}	0.4	0.6	0.9	0.3
Hg^{+}	2.0	2.0	1.8	2.6
$Me_2MCH_2X^{+}$	10.3	13.0	17.4	19.0
$H_2MCH_2X^{+}$	24.1	21.3	14.8	13.8
Other Fragments from $Me_2MCH_2X^{+}$	33.8	32.8	44.6	40.1

ficant extent and some 65% of the charge is carried by three ions formed by the following metastable-supported processes:

$$Me_3MCH_2HgX^{+\cdot} \xrightarrow{-Me^{\cdot}} Me_2MCH_2HgX^{+} \xrightarrow{-Hg}$$

$$Me_2MCH_2X^{+} \xrightarrow{-C_2H_4} H_2MCH_2X^{+}$$

Thus the main process involved in Hg–X bond cleavage is the elimination of mercury from the even-electron ion $Me_2MCH_2HgX^+$ and the distinction from the behaviour of other organomercury halides can be ascribed to the facile elimination of a methyl radical from the parent ion so that subsequent decompositions maintain even-electron ions throughout. Between 25 and 15 eV the abundances of $H_2MCH_2X^+$ ions fall by a factor of ~10 whilst $Me_2MCH_2HgX^+$ and $Me_2MCH_2X^+$ are relatively unaffected. This is the effect to be expected since the elimination–recombination reaction resulting in the formation of $H_2MCH_2X^+$ would have a low frequency factor.

Mercuric Halides

Analytically pure $HgCl_2$ produced a spectrum grossly contaminated with the parent ions, $HgI_2^{+\cdot}$, $HgBrI^{+\cdot}$, $HgClI^{+\cdot}$, $HgBr_2^{+\cdot}$, $HgBrCl^{+\cdot}$ and their fragment ions, between them carrying 90% of the total charge. The abundance of these ions, which must be derived from halide impurities in the source, diminished rapidly with time and after 30 minutes a satisfactory spectrum of $HgCl_2$ could be recorded[10]. Mercuric bromide likewise gave, initially, the high abundance ions $HgI_2^{+\cdot}$, $HgBrI^{+\cdot}$ and $HgI^{+\cdot}$. Ion abundances are listed in Table VI.

TABLE VI. Ion Abundances, HgX_2 at 70 eV.

	$HgCl_2$	$HgBr_2$	HgI_2
$HgX_2^{+\cdot}$	49.6	48.1	58.0
HgX^+	3.9	6.1	10.9
Hg^+	37.3	37.4	13.2
HgX_2^{2+}	2.8	2.1	5.2
HgX^{2+}	0.4	0.04	–
Hg^{2+}	5.8	5.1	1.2
$X_2^{+\cdot}$	–	0.2	3.8
X^+	3.3	2.4	6.4

Most of the charge is carried by the parent ions and the $Hg^{+\cdot}$ ion; an unusual feature being the abundance of doubly charged ions which were absent from the spectra at 25 eV. For HgI_2 the abundances of HgI^+ and I^+ decreased markedly between 15 and 12 eV whereas the abundance of $I_2^{+\cdot}$ remained constant, as expected for the rearrangement process: $HgI_2^{+\cdot} \rightarrow Hg + I_2^{+\cdot}$.

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