Positive and Negative Ion Mass Spectra of Some Pentafluorophenylmercurials

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Summary The positive and negative ion mass spectra of bis(pentafluorophenyl)mercury and pentafluorophenylmercuric chloride and bromide show both distinct similarities and differences.

RECENT studies[1,2] on electron impact of pentafluorophenyl derivatives of Groups IV and V indicated fluorine abstraction by the central atom, in addition to the normal mode of fragmentation. For comparative purposes, the positive and negative ion mass spectra of bis(pentafluorophenyl)mercury and pentafluorophenylmercuric chloride and bromide have been investigated.

The most abundant ion for all three compounds was $C_6F_5^+$, as in the fragmentation observed[3,4] for dialkylmercurials, but no species arising from elimination of HgF or HgF_2 were detected. The main fragmentations observed in the positive ion spectra:

$$\begin{tikzcd}
(C_6F_5)_2Hg^+ \arrow[dr, "-C_6F_5"] & & \\
 & C_6F_5Hg^+ \arrow[r, "-Hg"] & C_6F_5^+ \\
C_6F_5HgX^+ \arrow[ur, "X"'] & &
\end{tikzcd}$$

were supported by the appearance of metastable peaks. In addition, metastable peaks were observed for the processes:

$$C_6F_5^+ \xrightarrow[-CF_2]{} C_5F_3^+ \text{ and } C_6F_4^+ \xrightarrow[-CF_2]{} C_5F_2^+.$$

This metastable loss of CF_2 has been recently observed[5] in the mass spectrum of hexafluorobenzene. The corresponding metastable peaks for loss of CF_3 and F, reported for hexafluorobenzene[5] and perfluoropolyphenylenes,[6] were not, however, detected.

The most prominent peaks for the three mercurials are given in the Table. For bis(pentafluorophenyl)mercury, the relative abundances of the non-mercury containing ions are in close agreement with the values reported by Bruce,[7] but those for $(C_6F_5)_2Hg^+$ and $C_6F_5Hg^+$ are considerably higher. The formation of the ions, $C_6F_5Cl^+$, $C_6F_5Br^+$, and Hg^+ can be explained by the processes:

Relative abundances in the positive ion mass spectra of $(C_6F_5)_2Hg$ *and* C_6F_5HgX (X = Cl *and* Br)

Ion	$(C_6F_5)_2Hg$	C_6F_5HgCl	C_6F_5HgBr
$(C_6F_5)_2Hg^+$	36·9	—	—
$C_6F_5HgX^+$	—	77·0	60·3
$C_6F_5Hg^+$	35·3	32·0	36·8
HgX^+	—	4·4	7·4
Hg^+	2·0	26·5	13·0
$C_6F_5X^+$	—	5·0	1·7
$C_6F_5^+$	100·0	100·0	100·0
$C_6F_4^+$	4·8	10·3	9·9
$C_5F_3^+$	41·4	60·6	66·0
$C_5F_2^+$	9·2	19·7	19·5
$C_3F_3^+$	8·3	15·8	16·0
C_5F^+	5·4	14·1	14·3

$$C_6F_5HgX^+ \xrightarrow[-Hg]{} C_6F_5X^+ \text{ and}$$

$$C_6F_5HgX^+ \xrightarrow[-C_6F_5X]{} Hg^+$$

and account for the increase in the proportion of Hg^+ for C_6F_5HgX compared to $(C_6F_5)_2Hg$. In the latter, Hg^+ would only be formed by the process $C_6F_5Hg^+ \xrightarrow[-C_6F_5]{} Hg^+$ which also occurs for the pentafluorophenylmercuric halides. An unexpected observation is the different proportions of the ions arising from fragmentation of $C_6F_5^+$ in $(C_6F_5)_2Hg$ and C_6F_5HgX. This discrepancy is unlikely if $C_6F_5^+$ was formed only by the process indicated above, and formation of this ion in different excited states for one of the compounds is possible.

The negative ion mass spectrum of bis(pentafluorophenyl)mercury consisted of the ions $(C_6F_5)_2Hg^-$, $C_6F_5^-$,

$C_6F_4^-$, and F^-. The molecular anion appeared at electron energies of 20—70 ev, with maximum intensity at about 40 ev, too high for the ion's formation by a resonance electron capture mechanism[8] $(C_6F_5)_2Hg + e \rightarrow (C_6F_5)_2Hg^-$. Hence, formation is by secondary electron capture, analogous to the formation[9] of the negative molecular ion, $(CF_3)_2CO^-$. The only other examples of parent negative ions derived from organometallic compounds are the polyorganosilanes, reported by Gohlke:[10] the ion $(C_6F_5)_2Hg^-$ represents the first negative molecular ion of its type.

Both the $C_6F_5^-$ and $C_6F_4^-$ ions derived from $(C_6F_5)_2Hg$ have maximum intensities at *ca.* 12·5 ev, with ionisation efficiency curves as shown in the Figure. The anion $C_6F_5^-$ cannot arise in the way described[11] for its formation from hexafluorobenzene, but can be explained by a dissociative electron capture mechanism[8] (1) or ion-pair formation[8] (2)

$$(C_6F_5)_2Hg + e \rightarrow C_6F_5^- + C_6F_5Hg \qquad (1)$$

$$(C_6F_5)_2Hg + e \rightarrow C_6F_5^- + C_6F_5Hg^+ + e \qquad (2)$$

The ion $C_6F_5^-$ fragments in an analogous manner to the dissociation[11] of $C_6F_6^-$:

$$C_6F_5^- \begin{array}{l} \nearrow C_6F_4^- + F \\ \searrow C_6F_4 + F^- \end{array}$$

For the pentafluorophenylmercuric halides, the predominant negative ions observed were $C_6F_5X^-$, $C_6F_5^-$, and X^-. The highest intensities for $C_6F_5Cl^-$ and $C_6F_5Br^-$ were obtained at about 35 and 40 ev, respectively, and the ionisation efficiency curves exhibited by these ions were considerably broader than that for $C_6F_5^-$ (see Figure). The formation of $C_6F_5X^-$ can be explained by means of a partially dissociative electron capture mechanism (3) or an unusual type of ion-pair formation (4):

$$C_6F_5HgX + e \rightarrow C_6F_5X^- + Hg \qquad (3)$$

$$C_6F_5HgX + e \rightarrow C_6F_5X^- + Hg^+ + e \qquad (4)$$

the latter being more likely for the electron-energy region involved. This type of mechanism for the formation of a negative ion has not been previously described, but has a certain similarity to the formation of the corresponding positive ion above. Dissociative resonance of the $C_6F_5X^-$ ion produces the other ions observed:

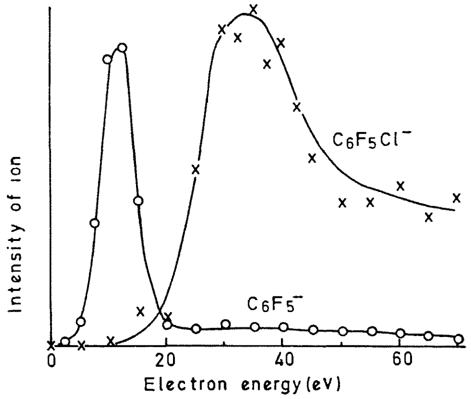

FIGURE. *Ionisation efficiency curves for the anions* $C_6F_5^-$ *and* $C_6F_5Cl^-$.

$$C_6F_5X^- \begin{array}{l} \nearrow C_6F_5^- + X \\ \searrow C_6F_5 + X^- \end{array}$$

These results indicate the usefulness of examining both the positive and negative ions formed by electron impact.

We thank the Petroleum Research Fund for partial support of this work, and the National Science Foundation for a fellowship (to E. C. T.).

(*Received, December 29th,* 1969; *Com.* 1957.)

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