Fragmentation of alkylmercury halides under electron impact and the structure of the $C_2H_4HgX^+$ ion (X = Cl, Br, I) in the gas phase

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Abstract

Electron impact mass spectrometry was used to investigate the fragmentation of alkylmercury halides of the RHgX type (X = halogen, R = alkyl). The more common directions of molecular ion dissociation are manifested in the rupture of metal–ligand bonds, yielding R^+, RHg^+, XHg^+ and Hg^+ ions. The spectra of the linear alkyl derivatives show intense peaks for the $C_2H_4HgX^+$ ions. The factors which govern the formation of these ions and our quantum chemical calculations (MNDO method) indicate that the most probable structure of $C_2H_4HgX^+$ is a halogenmercurinium ion.

Mercurinium ions (I) were first detected by in situ NMR spectroscopy as intermediates in olefin oxymercuration [1]. The formation of these ions during this reaction determines the considerable stereospecificity of the process [2]. $C_2H_4HgX^+$ ions (X = CH_3, or X absent) and methylated analogs were also found as the products of gas-phase ion-molecule reactions [3–5]. Quantum chemical calculations
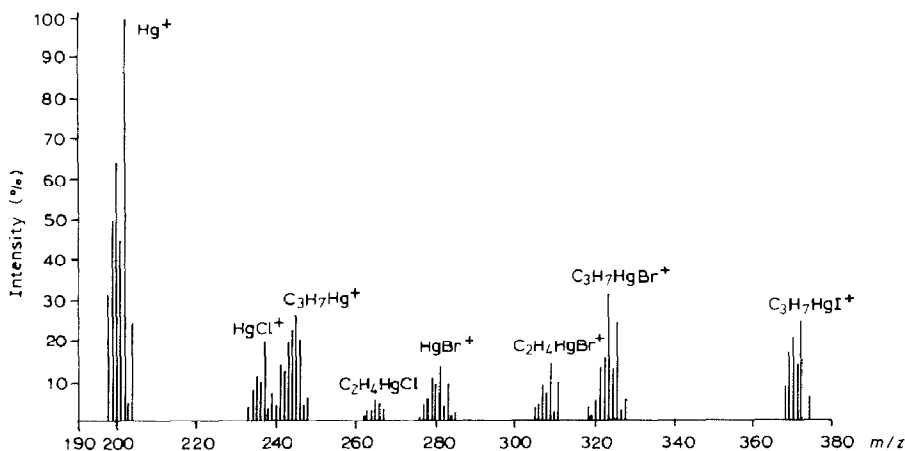
Fig. 1. Part of mass spectrum of n-PrHgCl.

led to them being assigned the structure I. At the same time, further calculations [6] showed that the I structure is not always the most thermodynamically stable.

Here we report on the fragmentation studies of alkylmercury halides RHgX (X = Cl, Br, I; R = Me, Et, Pr, i-Pr, Bu, i-Bu, t-Bu, C_5H_{11}, i-C_5H_{11}, C_6H_{13}, t-BuCH$_2$CH$_2$) under electron impact with formation of $C_2H_4HgX^+$ ions. MNDO was used to calculate their geometric and energy characteristics.
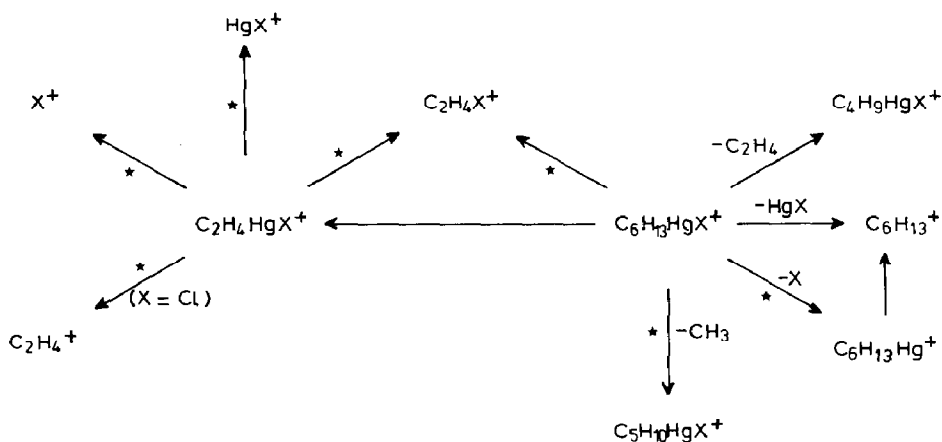
Mass spectra of lower alkylmercury halides are given in ref. 7 and 8. Figure 1 shows the relative intensities of the main mercury-containing ions in the spectrum of a studied alkylmercury halide, n-PrHgCl. It is shown that along with the Cl-containing ions, spectra include peaks corresponding to derivatives of Br and I. In a similar way, RHgBr mass spectra (Table 1) contained ions corresponding to RHgI fragmentation. The appearance of higher halogenide ions in RHgCl mass spectra are the result of secondary exchange processes of the halogen atoms on the wall of the mass spectrometer's ion source [9].

The main pathways of RHgX$^+$ dissociation determined by the direct analysis of daughter ions (DADI technique) the $C_6H_{13}HgX$ isomers are related to breaking of the Hg–R and Hg–X bonds (Scheme 1), as was the case for the alkylmercury

Table 1

Relative intensities (%) of ion peaks in RHgBr mass spectra

R	Et	Pr	i-Pr	Bu	s-Bu	C_5H_{11}	CH$_2$CMe$_3$	CH$_2$C$_5$H$_9$
RHgBr$^+$	11.4	5.1	1.4	0.8	0.6	1.4	7.9	0.2
HgBr$^+$	10.9	5.1	3.2	3.2	2.1	3.2	1.2	3.2
RHg$^+$	10.6	1.5	0.6	0.2	0.2	0.6	1.5	–
$C_2H_4HgBr^+$	–	2.1	0.2	3.6	–	6.6	–	0.1
$C_2H_4Hg^+$	–	0.2	–	0.4	–	0.6	–	0.1
CH$_2$Hg$^+$	1.1	0.6	–	0.1	0.1	0.1	0.2	0.1
Hg$^+$	12.3	6.6	6.0	6.4	3.8	4.4	3.1	3.1
R$^+$	53.5	76.6	88.0	85.4	92.4	82.2	87.5	91.5
RHgI$^+$	–	0.8	–	–	0.4	0.3	–	
HgI$^+$	–	0.7	–	–	0.4	0.3	–	
$C_2H_4HgI^+$	–	0.3	–	–	–	0.2	–	

HgX$^+$

X$^+$ C$_2$H$_4$X$^+$ C$_4$H$_9$HgX$^+$

$-$C$_2$H$_4$

C$_2$H$_4$HgX$^+$ ⟵——————— C$_6$H$_{13}$HgX$^+$ ——$-$HgX⟶ C$_6$H$_{13}^+$

(X = Cl)

C$_2$H$_4^+$

$-$X

$-$CH$_3$ C$_6$H$_{13}$Hg$^+$

C$_5$H$_{10}$HgX$^+$

Scheme 1

halides previously studied [7,8]. RHg$^+$, XHg$^+$, Hg$^+$ and among the ions that are formed in the process.

Presence of the ion peaks for RHgI and RHgBr in the mass spectra in relation to the alkylmercury chlorides does not provide a quantitative method to compare the various fragmentation pathway, since the RHg$^+$, Hg$^+$ and R$^+$ type ions that do not contain halogen could also result from the decomposition of any RHgX alkylmercury halogenide (X = Cl, Br, I). On the basis of data obtained for RHgCl and RHgBr (Table 1), the following trends become apparent: (1) alkylmercury halide stability to electron impact falls on going from EtHgBr to BuHgBr, and increases when the length of the alkyl chain is extended; (2) the net contribution of R$^+$ ions and its decomposition products increases, and the intensity of Hg$^+$ ions declines upon extension of the alkyl chain and on going from primary to secondary and tertiary alkyl radicals, indicating preferable charge localization on heavier alkyl radicals.

A characteristic feature of the mass spectra of the higher alkylmercury halides starting with PrHgX, is the presence of the C$_2$H$_4$HgX$^+$ peak. Formally, the C–C bond breaks and the alkyl radical splits off.

A decrease in the ionisation energy to 12 eV has no apparent effect on the C$_2$H$_4$HgX$^+$ peak intensity, but the HgX$^+$ and RHg$^+$ ions, which are generated when the Hg–X and R–Hg bonds are broken, are absent in low-voltage mass spectra. In accordance with the Cook–Williams Rule [10], this testifies to the rearrangement nature and relatively high stability of C$_2$H$_4$HgX$^+$ ions. Hence, of the two possible structures I and II, the mercurinium ion I is the more likely one.

That the cation of halogenmercurium is formed is supported by our quantum chemical calculations by the MNDO method. At surface potential energy for C$_2$H$_4$HgCl$^+$, two minima corresponding to isomers I and II were discovered upon full optimization of geometry. Final calculations for all molecules studied were carried out with optimization of geometry on preservation of C$_{2v}$ symmetry for I and C$_s$ for II. Enthalpies of formation for both isomers, as well as main internuclear distances are listed in Table 2, which points to structure I as the energetically more favourable form.

(I)   (II)
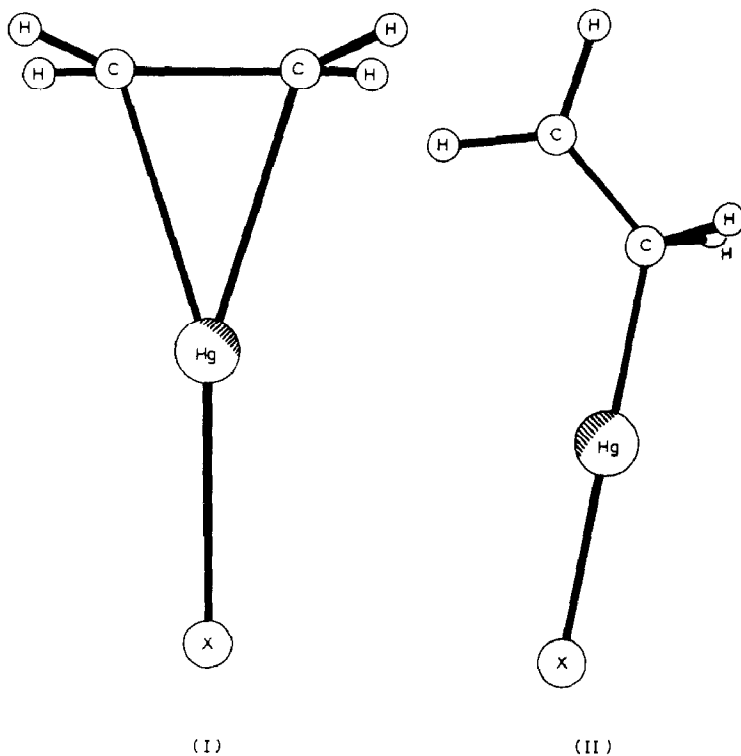
Unfortunately, the material obtained from the literature on MNDO calculations for organomercurials [6] cannot be used to judge the adequacy of our calculations, since the reference does not contain calculations for mercury π-complexes. We presume that the formation energies of $C_2H_4HgCl^+$ are too low, and those of $C_2H_4HgI^+$ too high, since Dewar observed similar trends [6]. Consequently, the difference between the energies of isomers I and II may be less.

Two degenerate high occupied molecular orbitals, filled with undivided non-binding pairs of halogen p-electrons are indicated by the calculations. Examination of bond orders (Table 3) shows mercurinium cations I to have stronger C–C and Hg–X bonds, but a weaker mercury to C_2H_4 π-bond than in II. Moreover, consolidation of the C–C bond in I on substitution of Cl for Br and I is evidently of

Table 2

Main internuclear distances (Å) and heats of formation (kcal mole^{-1}) of isomers I and II calculated with MNDO

	I				II			
	C–Hg	C–C	C–X	ΔH_f^0	C–Hg	C–C	C–X	ΔH_f^0
X = Cl	2.28	1.39	2.24	208.6	2.02	1.45	2.25	219.1
X = Br	2.29	1.39	2.33	226.2	2.03	1.45	2.34	238.3
X = I	2.30	1.39	2.45	230.6	2.04	1.45	2.45	246.0

Table 3

Bond orders in isomers I and II calculated with MNDO

	I			II		
	C–C	Hg–C	Hg–X	C–C	Hg–C	Hg–X
X = Cl	1.52	0.79	1.08	1.13	0.85	1.01
X = Br	1.54	0.76	1.10	1.13	0.83	1.04
X = I	1.58	0.69	1.11	1.13	0.78	1.09

decisive significance for the improvement of stability of I as compared to II, for X = Br and I.

Thus the experimental and calculated data show that the most probable structure of $C_2H_4HgX^+$ cations (X = Cl, Br, I) in the gas phase is the mercurinium ions I structure.

Experimental

Synthesis of the studied compounds was by a published procedure [11]. Electron impact mass spectra were recorded on an MS-30 mass spectrometer, equipped with a system enabling direct introduction of the sample into the ion source at 40°C. Ionizing energies were 12–70 eV, and the temperature of the ion source was 250°C.

DADI spectra were recorded with a modified Varian MAT 112 mass spectrometer; with an ionizing energy of 70 eV.

Automatic processing of averaged mass spectra (from 3 to 10 measurements) was carried out with the AELITA Programme [12] on Nova 2/10 and CM-3 computers. MNDO quantum chemical calculations with standard parameters for mercury [13] were carried out on an EC-1055M computer.

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