Inorganica Chimica Acta, 21 (1977) L27–L28
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Mass Spectra of Saturated Organomercurials

L. SIMONOTTI* and C. TROMBINI**
Chemistry Division, JCR, Euratom, Ispra, Italy

Received December 13, 1976

The excess energy transferred to the ion in electronic and vibrational forms from a bombarding electron in a vertical ionisation process, or the thermal decomposition of the sample (*e.g.* when it is introduced through a hot inlet system such as a glc column), account for several classes of compounds showing insignificant molecular ion in 70 eV mass spectra.

Saturated organomercurials, not so extensively studied in the literature as the unsaturated and aromatic analogues [1], represent one of these classes of compounds.

We subjected some symmetrical dialkylmercury compounds to soft ionisation lowering the ionisation voltage (20, 15, 10 eV) in electron-impact experiments, and using ion–molecule reactions in a chemical ionisation ion chamber.

The investigated compounds, R_2Hg, synthesized by transmetalating the appropriate Grignard reagent, were: R = CH_3(I), C_2H_5(II), nC_3H_7(III), nC_4H_9(IV), iC_4H_9(V), sC_4H_9(VI), nC_5H_{11}(VII).

Electron Impact Spectra

Varian MAT CH7, direct inlet system, accelerating voltage 3kV, source temperature 100 °C.

With the exception of (I), whose mass spectrum is dominated by the ions $R_2Hg^{+\cdot}$ (45%), RHg^+ (100%) and CH_3^+ (41%), in the 70 eV mass spectra of all examined compounds, more than 90% of TIC (total ion current) is carried by mercury-free fragments which display an anonymous alkyl fragmentation pattern.

Lowering the ionisation voltage to 20 and 15 eV (Table I), the mercury-containing fragments gain authority, while the increased relative abundances of the odd-electron ions $R - 1^{+\cdot}$ and $R_2^{+\cdot}$ are in agreement with intramolecular rearrangements with typical low frequency factor compared to that of cleavage ion R^+. In particular the ion $R - 1^{+\cdot}$ comes from an intramolecular hydrogen transfer in $R_2Hg^{+\cdot}$ with loss of RHgH and charge retention in the alkene moiety, as confirmed by the appropriate metastable ion in the spectrum of (V).

Unfortunately we were unable to detect $RHgH^{+\cdot}$ ions because of their low abundance and the difficulty in separating their contribution from the isotopic peak series relative to RHg^+ ions.

Finally at 10 eV more than 95% of TIC is carried by the molecular ions.

TABLE I. Relative abundances at 20 eV (at 15 eV).

	$R_2Hg^{+\cdot}$	RHg^+	$R_2^{+\cdot}$	$R - 1^{+\cdot}$	R^+
(I)	100(100)	16(12)	9(5)	– (–)	15(12)
(II)	100(100)	6(5)	41(23)	6(1)	37(9)
(III)	100(100)	8(9)	3(8)	27(17)	48(21)
(IV)	100(100)	5(4)	– (–)	39(45)	60(48)
(V)	67(75)	6(6)	– (–)	95(100)	100(100)
(VI)	52(57)	3(2)	– (–)	82(89)	100(100)
(VII)	30(29)	4(2)	– (–)	90(100)	100(38)

Chemical Ionisation Spectra

(Du Pont 21492–B, source pressure 1 Torr, ionisation voltage 70 eV, emission current 300 μA, accelerating voltage 1.5 kV).

Reagent Gas: Methane ($P_{CH_4}/P_{R_2Hg} \simeq 10^3$)

The major ions in the CI spectrum of CH_4 at pressure above 0.1 Torr (about 90% of TIC) are CH_5^+ and $C_2H_5^+$ [2].

Collisions between CH_5^+ or $C_2H_5^+$ and the sample involve either electron transfer leading to molecular ions $R_2Hg^{+\cdot}$ or particle transfer. Table II collects the mercury-containing ion region of the CI spectra, and always refers to ^{202}Hg isotope.

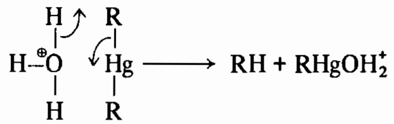
Quasi-molecular ions $(R_2Hg - 1)^+$ can originate by hydride transfer from R_2Hg to $C_2H_5^+$ to give C_2H_6 or by dissociative proton transfer from CH_5^+ or $C_2H_5^+$ to give CH_4 or C_2H_4 and H_2.

Similarly the unstable ion $(R_2Hg + 1)^+$ can collapse to more stable ions undergoing a loss of alkane.

Reagent Gas: Methane/Water (8/2)

Near the ions reported in Table II, in almost the same relative ratios a new group of ions appears, the oxocations $RHgOH_2^+$.

Probably they come from a four-center reaction between hydronium ion and R_2Hg:



---

*To whom correspondence should be addressed. Present address: ISF, Italseber, via Leonardo da Vinci 1, 20090 Trezzano sul Naviglio, Milano, Italy.

**Present address: Istituto Chimico "Giacomo Ciamician", Università di Bologna, Bologna, Italy.

TABLE II. Relative Abundances.

	$R_2Hg^{+\bullet}$	$(R_2HgH - H_2)^+$	$(R_2HgH - RH)^+$	$(R_2HgH - RCH_3)^+$
(I)	4	5	100	–
(II)	34	21	100	5
(III)	36	27	100	12
(IV)	100	32	38	10
(V)	100	37	18	5
(VI)	100	65	22	8
(VII)	100	42	37	9

TABLE III. Relative Abundances. A corresponds to the addition ion R_2HgBu^+.

	$R_2Hg^{+\bullet}$	$(A - RH)^+$	$(A - RCH_3)^+$	$(A - RBu)^+$	Others
(I)	88	72	19	65	$(A - CH_2)^+100$
(II)	88	25	5	100	$(A - C_4H_{10})^+50$, $(A - CH_2)^+4$, $(A - C_2H_4)^+20$
(III)	43	17	100	16	$(A - C_3H_6)^+7$
(IV)	40	100	5	–	$(A - C_6H_{14})^+13$, $(A - C_5H_{10})^+3$
(V)	39	100	29	–	$(A - C_6H_{14})^+27$
(VI)	60	100	4	–	
(VII)	100	–	–	–	$(A - C_4H_8)^+36$, $(A - C_5H_{10})^+5$, $(A - C_6H_{12})^+8$

The relative abundances of ions $RHgOH_2^+$ are: (I) 20%, (II) 14%, (III) 18%, (V) 13%, (VI) 26%.

Reagent Gas: Isobutane ($P_{iC_4H_{10}}/P_{R_2Hg} \simeq 10^3$)

About 85% of TIC of high pressure isobutane mass spectrum is represented by tert-butyl cation (Bu), which can act both as Brönsted and Lewis acid [2].

The most important features of the mercury-containing ion region of CI mass spectra are shown in Table III and all relative abundance values refer to ^{202}Hg isotope.

The short-lived addition ion $(R_2HgBu)^+$, detected in traces in the (I) spectrum, follows two decomposition pathways. In the first it loses an alkene with formation of the ions group $(R_2HgBu - C_nH_{2n})^+$, in the second it loses an alkane with formation of the ions group $(R_2HgBu - C_nH_{2n+2})^+$.

Such behaviour is very similar to that of the paraffins. Moreover, in these experiments molecular ions $R_2Hg^{+\bullet}$ coming from electron transfer reactions are also present.

References

1 W. F. Bryant and T. H. Kirstle, *J. Organometal. Chem., 24,* 573 (1970). S. W. Breuer, T. E. Fear, P. H. Lindsay and F. G. Thorpe, *J. Chem. Soc. C,* 3519 (1971). N. A. Bell and S. W. Breuer, *J. Chem. Soc. Perkin II,* 717 (1974). A. Casalini, C. Trombini and L. Simonotti, *Ann. Chim., 66,* 67 (1976). F. Glockling, J. G. Irwin, R. J. Morrison and J. J. Sweeney, *Inorg. Chim. Acta, 19,* 267 (1976).
2 F. H. Field, in "Mass Spectrometry", ed. A. Maccoll, M.T.P. International Review of Science, Series 1, Vol. 5, Butterworths, London (1972).