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THE FORMATION AND REACTIONS OF ORGANOMERCURIC CATIONS IN THE GAS PHASE UTILIZING CHEMICAL IONIZATION MASS SPECTROMETRY

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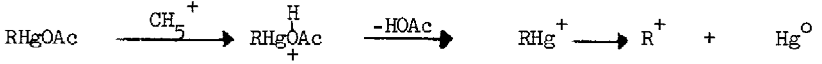
Organomercuric cations, RHg^+, have been generated and studied extensively in acidic solutions[1a-d], while similar studies under protonolysis conditions in the gas phase have not been attempted. The recent successful use of chemical ionization mass spectrometry (CIMS) in studying the gas phase protonolysis reactions of organotin compounds[2] and some organometallic transition metal complexes[3a,b] would make a similar study of organomercuric acetates particularly interesting in light of the solution results[1a-d].

We wish, therefore, to communicate our preliminary results on the methane CIMS of a variety of organomercuric acetates that will illustrate how this technique can be used to generate RHg^+ ions as well as study their fate in a solvent free environment.

When compounds of the general formula RHgOAc were subjected to methane CIMS the following logical sequence of reactions is postulated to occur (eq 1).



$$RHgOAc \xrightarrow{CH_5^+} RHg\underset{+}{\overset{H}{O}}Ac \xrightarrow{-HOAc} RHg^+ \longrightarrow R^+ + Hg^0 \qquad (1)$$

Table 1 summarizes the results as the R group is varied (eq 1).

Table 1. Methane CIMS of RHgOAc Compounds

		Relative Intensities %[a,b]					
Compound	R	$RHg\overset{+}{O}Ac\cdot H$	(m/e)	RHg^+	(m/e)	R^+	(m/e)
1	ϕ	42	(339)	29	(279)	14	(77)
2	CH_3	7	(277)	6	(217)	c	
3	$CH_3(CH_2)_3CH_2$	1.3	(333)	-		2	(71)
4	$CH_3CH_2\underset{CH_3}{CH}$	-		-		100	(57)
5	$(CH_3)_3C$	-		-		100	(57)
6	$ϕCH_2$	-		-		100	(91)

[a] The Hg containing ions represent a summation of all Hg isotopes: 202 Hg arbitrarily reported.
[b] The base peak in 1-3 is m/e 61 $[HOAc\cdot H]^+$.
[c] We cannot observe this ion with methane CIMS

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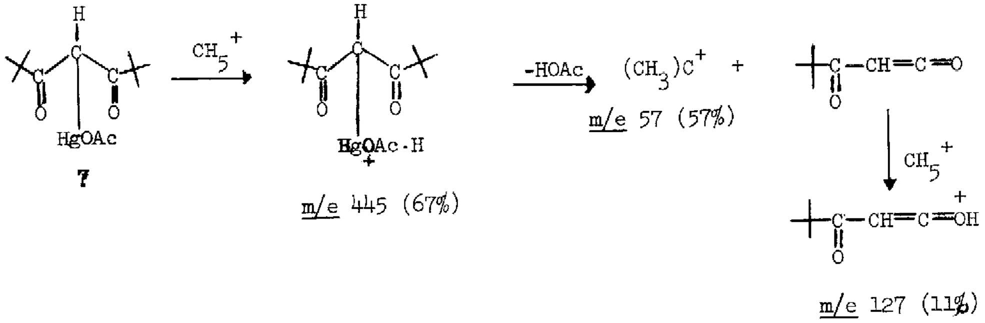
It is clear from Table 1 that after the formation of RHg^+ the subsequent demercuration to the carbonium ion is dependent on carbonium ion stability. Thus compounds 4-6 show only the carbonium ion (R^+) and no mercury containing ions, while phenylmercuric acetate, 1, has a large M+1 ion and a relatively large phenylmercuric ion. Further supportive evidence for the reaction sequence in eq 1 and the demercuration ($RHg^+ \longrightarrow R^+ + Hg^o$) dependency on the stability of R^+ comes from use of the weaker Bronsted acid $C_4H_9{}^+$ (isobutane reagent gas), which shows predominently M+1 ions with 1-3 and only the R^+ ions with 4-6.

It is interesting to point out that electron impact (EI) mass spectral studies[4,5] on aryl and alkyl organomercurials do not indicate differences in carbonium ion stability, since under the higher energy EI conditions phenyl cation is formed (base ion) as readily as an alkyl cation.

We also wanted to generate a RHg^+ cation in a system that could not directly demercurate to a stable carbonium ion. Thus dipivaloylmethylmercuric acetate, 7[6], was studied and found to give the following results (eq 2).

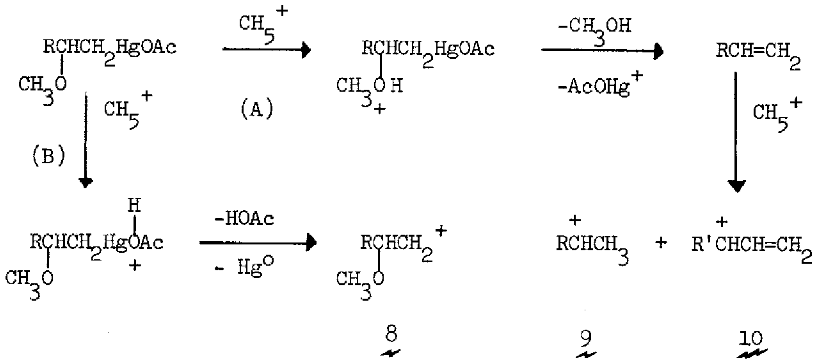


(2)

Since compound 7 cannot directly give a stable carbonium upon demercuration, we propose that it undergoes a β elimination reaction to give the stable t-butyl cation.

One of the most widely studied solution (acidic) reactions in organomercury chemistry is deoxymercuration[7]. A perusal of this reaction in the gas phase would be informative since solvent effects are known to be important in stabilization of the intermediate mercurinium ions[7]. More importantly, it was imperative to see if RHg^+ formation and its subsequent demercuration[8] could compete with deoxymercuration in the gas phase.

The following general reaction scheme (eq 3) is presented to show how deoxymercuration (A) and demercuration (B) are affected by structural changes (Table 2).



(3)

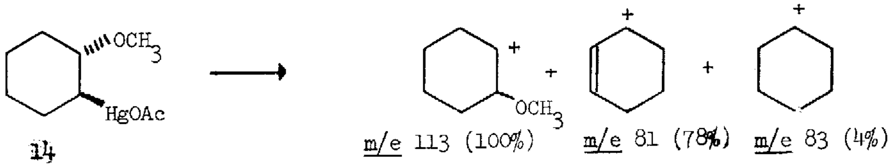
Table 2. Relative Ratios of Pathways A and B as a Function of R

Compound	R	R'	% Demercuration (B)[a]	% Deoxymercuration[b] (A)	B/A
11	ϕ	-	96	4	24
12	$CH_3CH_2^-$	CH_3^-	76	24	3.2
13	$CH_3(CH_2)_6^-$	$CH_3(CH_2)_5^-$	59	41	1.4

[a] Based on ion intensity of 8.

[b] Based on ion intensity of both 9 and 10. Control experiments with the known olefins confirm the formation of 9 and 10. We assume that the rate of reaction of CH_5^+ with the olefins is comparable to pathways A and B.

A cyclic oxymercuration derivative, 14, also shows a similar trend (eq 4).



14

(4)

The ratio of pathways B to A in 14 is 1.2.

These results with compounds 11-14 point out that protonation by CH_5^+ on acetate is favored over methoxyl in the absence of solvent, thus causing demercuration (B) to predominate over deoxymercuration (A).Pertinently, substitution of a good stabilizing group i.e., phenyl, (Table 2) almost eliminates the deoxymercuration reaction (A). Thus neighboring group stabilization by oxygen or phenyl seems to compete favorably with carbon-mercury sigma electrons (σ-π conjugation) in stabilizing incipient carbonium ions in the gas phase. The EI spectra of several oxymercuration products were reported by Bryant and Kinstle[4], however, under those conditions more complex fragmentation occurs and comparisons between CIMS and EIMS are not obvious[9,10].

In summary, our CIMS study demonstrates in a solvent free gas phase environment that RHg^+ ions readily demercurate to carbonium ions and that this pathway is predominantly followed even though others (eg. deoxymercuration) can occur. It is also worth noting that in the CIMS if the RHg^+ ion contains a direct bond to an aromatic ring (i.e. phenyl) then there is less tendency to demercurate. The gas phase results parallel those found in solution[1a-d] in that demercuration from RHg^+ depends on carbonium ion stabilization including neighboring group effects.

We are continuing our studies in order to further define the relationship between solution and gas phase chemistry of organomercurials[†]

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9. The CIMS were recorded on a Finnigan 1015D instrument (methane ~ 1 Torr) coupled with a Systems Industries Model 150 Computer with plotter. The temperature was varied from 50-100° depending on compound volitility.

10. Compounds used in this study were obtained commercially or prepared as indicated in the literature (Ref. 7).

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