Inorganica Chimica Acta, 32 (1979) L75–L76

HSAB Theory Applied to Rearrangements in the Mass Spectra of Organometallic Compounds

JACK M. MILLER and TIMOTHY R. B. JONES
Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1
GLEN B. DEACON
Department of Chemistry, Monash University, Clayton, Victoria, Australia

Received November 6, 1978

The phenomenon of halogen transfer from a halocarbon ligand to the central atom in the normal 70 eV electron impact mass spectra of organometallic or organometalloid compounds is well established and has been discussed in a recent review [1]. In particular, fluorine transfer from fluoroaromatic ligands has been extensively studied. The requirement for observation of fluorine migration in the mass spectrometer appears to be the presence of an empty orbital on the central atom, substantiated by the absence of these rearrangement ions in the mass spectra of the corresponding carbon, oxygen or nitrogen compounds. Boron, however, with its vacant 2p orbital undergoes this rearrangement as the spectra of $(C_6F_5)_3B$ indicates. Here BF_3 is expelled from the molecular ion with the formation of $C_{18}F_{12}^{+\cdot}$ ions. For the heavier elements of Groups IV (Si → Pb) and V (P → Sb), evidence from studies of heterocyclic compounds suggests an expansion of co-ordination of the central atom involving vacant orbitals precedes expulsion of MF_n neutral species [1]. A similar pattern is observed for transition elements where compounds of iron and titanium give spectral evidence for M–F bond formation. For all the above systems, metastable ions confirm that these rearrangements occur as unimolecular gas phase reactions and are not thermolysis or source surface exchange products.

Some of these fluorine migrations can be summarized from work done in our laboratory for simple C_6F_5 derivatives of groups IV [2] and V [3] elements – all reasonably "hard" acids with respect to halide as the base.

$(C_6F_5)_4M$ (M = Si, Ge, Sn, Pb)
MF^+ is maximized for M = Sn
MF_3^+ is maximized for M = Si
$(C_6F_5)_2MF^+$ is maximized for M = Sn
$C_6F_5MF_2^+$ is maximized for M = Sn
MF_n neutral species are maximized for Si and Ge.

Similarly, for
$(C_6F_5)_3M$ (M = P, As, Sb):
M^+, MF^+, MF_2^+ and RMF^+ species are maximized for M = Sb while MF_n neutral species are maximized for M = P or Sb.

When we examined the spectrum of $(C_6H_5)_2Hg$ [4], no HgF species (charged, or neutral inferred by metastable ion evidence) were observed or could be inferred from daughter ions. When we looked at the whole series $(C_6X_5)_2Hg$ (X = F, Cl, Br) [4–7] the following observations were made:

Molecule	*Rearrangement Ions*	
$(C_6F_5)_2Hg$	*NO* HgF^+ or $C_6F_5HgF^+$	
$(C_6Cl_5)_2Hg$	*NO* $HgCl^+$ or $C_6Cl_5HgCl^+$	
$(C_6Br_5)_2Hg$	$C_6Br_5HgBr^+$	8.2%
	$HgBr_2^+$	1.2%
	$HgBr^+$	0.7%

Glockling [8, 9] has shown that preferential formation of HgBr and HgI species occur with exchange in mass spectrometer ion sources, consistent with behaviour of mercury as a class b metal. Although the relative influence of solid metal halides in the source reacting with metal containing ions *versus* gas phase rearrangements are difficult to estimate, it is clear that mercury shows a preference for the softer halides. For C_6X_5 derivatives, metastable ion and abundance measurements suggest that gas phase rearrangements play a significant role.

If we treat halide as the base and the central atom as the acid, these data make sense in terms of hard/soft acid base (HSAB) theory: mercury, being particularly soft, will be prone to favour bromide or iodide ligands in preference to fluoride or chloride. If we look at most of the other central metals for which we observe fluoride transfer, we see that they fall into the hard category and similarly, although phosphines are "soft" bases, with respect to the halide ion, phosphorus is a "hard" acid. This is seen in the spectra of $C_6F_5P(CH_3)_2 \cdot AuX$ (X = Cl, Br, I) where X migrates from gold to phosphorus with P–Cl species favoured over P–I species [10]. The same data show that "soft" gold does not form any AuF species. Similarly, we have looked at a series of C_6F_5Pt derivatives, and for none of these is any Pt–F species observed [4]. However, for the slightly softer chloride from Pt systems containing aromatic chlorides, slight traces of Pt–Cl species were observed [11]. Nickel, a borderline "soft" acid, does not exhibit Ni–F bond formation either. The original work on HSAB relationships in solution [12] suggested that solution factors might be critical, preventing any predictions concerning behaviour in the gas phase. The results cited here suggest that these interactions may indeed persist, even in the gas phase, although the expectation based on M–X bond strengths would have been that M–F should be favoured over M–Br formation. Pearson does, however, note [13] that in the Ca/Hg/F/I system CaF_2 and HgI_2 are favoured in the gas phase.

References

1 J. M. Miller and G. L. Wilson, 'Some Applications of Mass Spectroscopy in Inorganic and Organometallic Chemistry', in *Adv. Inorg. Chem. & Radiochem.*, eds. H. J. Emeléus and A. G. Sharpe, and references contained therein, vol. 18, Academic Press (1976).

2 J. M. Miller, *Can. J. Chem.*, *47,* 1613 (1969).

3 A. T. Rake and J. M. Miller, *J. Chem. Soc. A,* 1881 (1970).

4 J. M. Miller, unpublished observations.

5 S. C. Cohen, *J. Chem. Soc. A,* 632 (1971).

6 G. B. Deacon, G. J. Farquharson and J. M. Miller, *J. Organomet. Chem.*, *94,* C33 (1975).

7 G. B. Deacon, G. J. Farquharson and J. M. Miller, *Austr. J. Chem.*, *30,* 1013 (1977).

8 F. Glockling, J. G. Irwin, R. J. Morrison and J. J. Sweeney, *Inorg. Chim. Acta, 19,* 267 (1976).

9 F. Glockling, in 'Mass Spectrometry of Metal Containing Compounds', ed. J. Charalambous, Butterworths (1975).

10 T. R. B. Jones, J. M. Miller, J. L. Peterson and D. W. Meek, *Can. J. Chem.*, *54,* 1478 (1976).

11 Private communication from Dr. R. J. Pudderphatt, University of Liverpool to J. M. Miller (1977).

12 R. G. Pearson, *J. Chem. Ed.*, *45,* 581 (1968).

13 *Ibid.*, p. 643.