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XPS STUDY OF SURFACE CHANGES IN MAGNESIUM SUBJECTED TO ATTACK BY AN ALKYL HALIDE

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Summary : Metal-solution interfacial phenomena occuring when magnesium is attacked by a halogen derivative are studied by XPS analysis of the state of the surface formed during this reaction.

Although many studies[1] deal with the mechanism of organomagnesium compound formation in solution, we are not aware of any concerning the physico-chemical phenomena occurring at the metal-solution interface when the metal is attacked by a halogen derivative. This is due to the fact that, generally, this type of attack does not cause an observable surface change that would allow this type of study to be conducted. In synthesizing 1-adamantyl magnesium bromide[2] from 1-bromoadamantane, we succeeded in obtaining, on the metal surface, a black layer with a thickness of up to 7 μ. The elements present at different depths of the layer were detected and analyzed using XPS[3] and ion bombardment,[4] thereby establishing the relationship between the characteristic signals of C_{1s}, Mg_{2s} and Br_{3d} electrons. These results, together with chemical analysis of the black layer, made it possible to reconstitute the phenomena involved in this surface change and in the synthesis of the organometallic compound.

RESULTS

Spectroscopic recordings of the metal were taken

1) before reaction,
2) after the reaction was initiated with dibromoethane,[5]
3) at the end of the reaction when the metal was covered with the black layer.

1) The XPS spectrum of the metal recorded before reaction (spectrum 1, Fig.1) indicates surface contamination by oxides (O_{1s} : 720 eV), aliphatic carbons (C_{1s} : 285 eV) and carbonate or acid carbons (C_{1s} : 289 eV). The value found for the oxidized magnesium[6] is 90.1 eV for Mg_{2s} (as compared to 89.5-89.95 eV reported in literature[7]).

2) The XPS spectrum recorded after the addition of dibromoethane to the medium (spectrum 2, Fig.1) indicates a strong decrease in the intensity of the peak of the contamination carbon and the appearance of low intensity peaks due to the 3s, 3p and 3d electrons of the bromine. Scouring a commercial magnesium turning by ion bombardment also shows a marked decreased in the contamination carbon peak.

3) The XPS spectrum of the Mg turning covered with a black deposit indicates that the signal intensity ratio R_1 of the C_{1s} and Mg_{2s} electrons ($R_1 = C_{1s}/Mg_{2s}$) is 15, whereas the signal intensity ratio R_2 for the Br_{3d} and Mg_{2s} electrons ($R_2 = Br_{3d}/Mg_{2s}$) is 8.

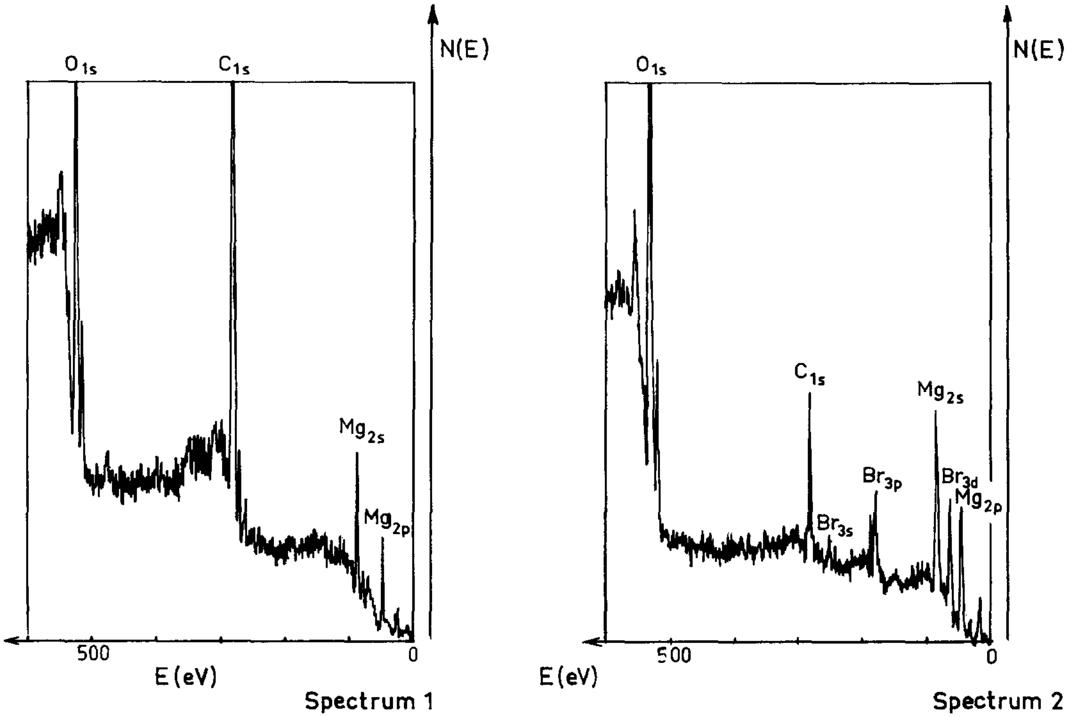


Figure 1: XPS spectra of a Mg turning: 1) before and 2) after the reaction was initiated with dibromoethane.

XPS spectra of this Mg turning recorded at different times after ion bombardment (1 μA at 1000 eV[8]) show that, in the first 500 Å of the layer, the ratio R_1 increases, while the ratio R_2 decreases. Both ratios then become constant up to a depth of 3 μ, then gradually decrease until they reach zero at 7 μ,[9] when the metal surface is reached. The XPS spectrum recorded after reaching the surface is identical to that of a scoured Mg turning. These spectra are interpreted by following the ratios R_1 and R_2.

The 4 μ thick lower region of the layer (Fig.2) is heterogeneous, as indicated by the increase in R_1 and R_2 ; the bromide content is low and the main constituents are Mg, and organic compounds detected by the C_{1s} electron signals. Above 4 μ, in the intermediate region, the two ratios are constant, thereby indicating that the layer is homogeneous and made up of the same components.[10]

In the upper region which is 500 Å, R_2 increases and reaches a value very near the one obtained by XPS analysis of a magnesium bromide sample.[11] This upper region is mostly composed of this salt. Rinsing the black-layer Mg sample with ether causes the R_2 ratio in the upper layer to drop from 8 to 1.5, which can be explained by the very high solubility of this salt in this solvent (50 g/l).[12]

GPC analysis, after the metal has been dissolved in an aqueous medium of 30 % nitric acid, and after extraction, indicates that 1-diadamantane is the only organic compound present in the layer. No trace of adamantane is detected, thereby revealing the absence of adamantyl magnesium bromide in the layer.

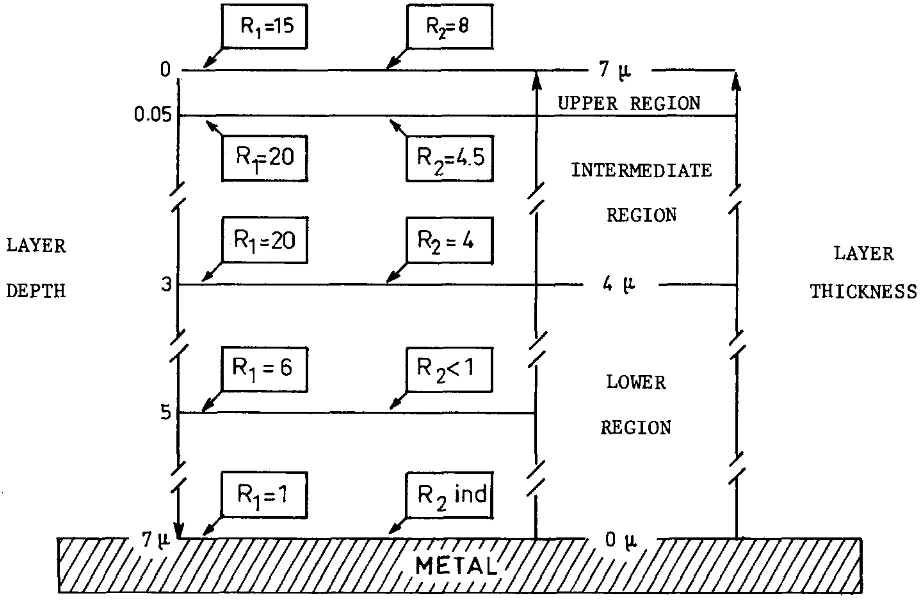
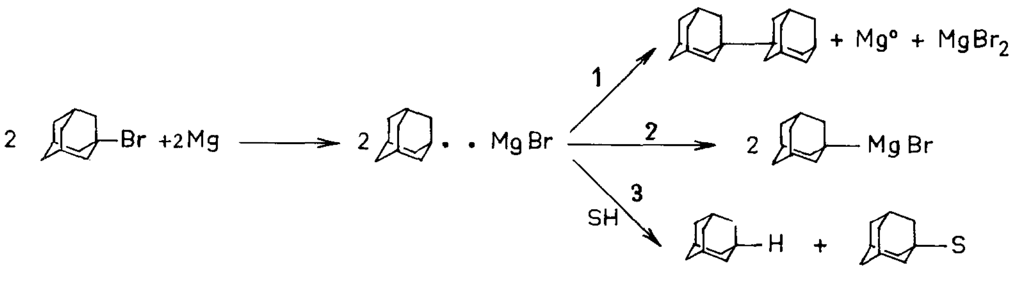


Figure 2: XPS analysis of the layer at differents depths ($R_1 = C_{1s}/Mg_{2s}$; $R_2 = Br_{3d}/Mg_{2s}$)

DISCUSSION

The lower and intermediate regions of the deposited layer (Fig.2) are made up of Mg and diadamantane. In all likelihood these products result from the dismutation (pathway 1) of radical complex I adsorbed at the Mg surface.



Indeed, the fact that highly reactive[13] magnesium, Mg°, and highly soluble magnesium bromide are trapped in the layer indicates that the reaction (pathway 1) occurs at the metal surface. As soon as it begins to form, the barely soluble diadamantane constitutes a compact deposit which partially protects the Mg° from attack by 1-bromoadamantane, and the $MgBr_2$ from solvent influence. The existence of 0-order kinetics[2] for magnesium compound formation (pathway 2) and for solvent attack (pathway 3) fits the theory that these reactions are also caused by the formation of radical complex I at the metal surface (the rate-determining step of the general mechanism).

This exceptional experimental situation has made it possible to analyze the surface state in such a way that the true chronology of the reactions occurring when the magnesium is attacked by the halide is clearly established.

NOTES AND REFERENCES

1. H.M. Walborsky and A.E. Young, J.Am.Chem.Soc., 86, 3288 (1964) ; H.M. Walborsky and M.S. Aronoff, J.Organomet.Chem., 51, 31 (1973) ; H.W.J. Bodewitz, C. Blomberg and F. Bickelhaupt, Tetrahedron Lett., 281 (1972) ; Ibid., 2003 (1975) ; Idem., Tetrahedron, 29, 719 (1973) ; Ibid., 31, 1053 (1975).
2. J.E. Dubois, P. Bauer, G. Molle and J. Daza, C.R.Acad.Sci., Ser. C, 284, 145 (1977).
3. X-ray photoelectron spectroscopy : an AEI ES 200 apparatus with an FRR adaptation and a magnesium anticathode was used.
4. C.R. Brundle, J.Vac.Sci.Technol., 11, 212 (1974).
5. 1-Adamantyl magnesium bromide formation is initiated over a relatively long period of time after being triggered by the addition of a few drops of dibromoethane.
6. It is very hard to obtain XPS spectra of alkaline or alkaline-earth metals, because they very readily combine with residual oxygen in the vacuum chamber to yield the corresponding oxides. Previous studies[4] indicate that vacuums of $5 \cdot 10^{-10}$–10^{-11} T are needed in order to keep magnesium in its metallic form after ion bombardment.
7. J.C. Fuggle, L.M. Watson, D.J. Fabian and S. Afarssman, J.Phys. F, 5, 375 (1975).
8. Thicknesses were determined according to the time at which ion bombardment starts, t = 0, and the time needed to reach the metal, while assuming that the rate of abrasion is constant at about 50 Å/mn (value found for $MgBr_2$).
9. The same results are observed whether scouring is by ion bombardment or mechanical. The different ratios are identical in value. Therefore, the changes in ratio are due to the variable chemical composition of the layer at different depths, and not to decomposition phenomena during ion bombardment.
10. The heterogeneous character of the layer in the lower region can be explained by the fact that, as the layer spreads, the magnesium detected by analysis tends to be only Mg° from the radical complex, without any trace of the subjacent magnesium from the turning (thereby explaining the increase in R_1 and R_2). In this theory, the constant character of R_1 and R_2 can be explained by the formation of a quasi-continuous layer at the metal surface.
11. An additional XPS analysis of magnesium bromide spectra indicates that the ratio of intensity peaks for Br_{3d} and Mg_{2s} electrons is between 8 and 10 (which is in good agreement with the theoretical value reported in B. Barbaray's 3rd cycle thesis, Université Paris 7, 1977). When this bromide is subjected to ion bombardment, the ratio decreases slightly, but then remains constant during scouring. This indicates that, in the case of a homogeneous substance such as $MgBr_2$, there is no noteworthy chemical decomposition at the ion beam intensity used, and that the Br_{3d} and Mg_{2s} electron emission is constant, regardless of how long scouring lasts.
12. The surface deposit of $MgBr_2$ probably results from evaporation of the film of ether containing this salt when the turning to be analyzed is extracted from the medium.
13. The black powder taken from the turning and cleansed of diadamantane by boiling under argon in deoxigenated ether, used previously to make another magnesium compound, is rapidly attacked by 1-bromoadamantane.

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