

Fig. 3 : Comparison of potentiodynamic responses and open circuit potentials of Ni in electrolyte additive free (a) and containing N-methylthiourea (b).

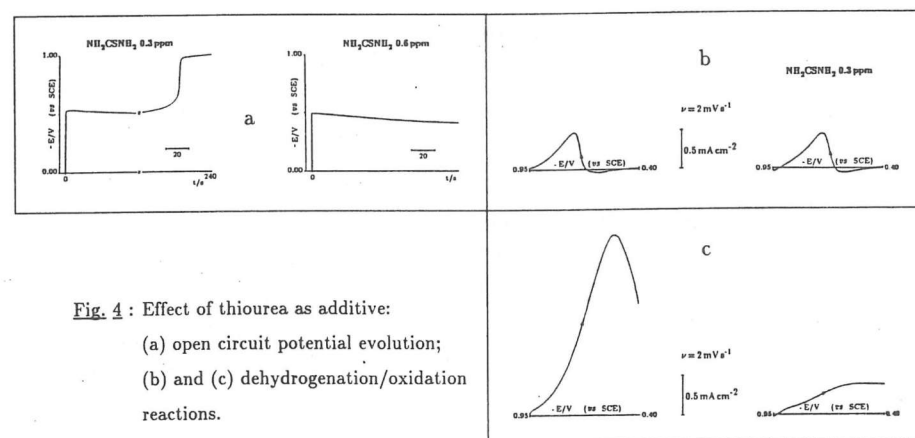


Fig. 4 : Effect of thiourea as additive:
(a) open circuit potential evolution;
(b) and (c) dehydrogenation/oxidation reactions.

(NaCH_3COO 0.50 M + DMAB 0.20 M + thiourea as indicated)

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Oxime-imine reduction in the liquid-gas interface in Fast Atom Bombardment Mass Spectrometry: an electrochemical analogy

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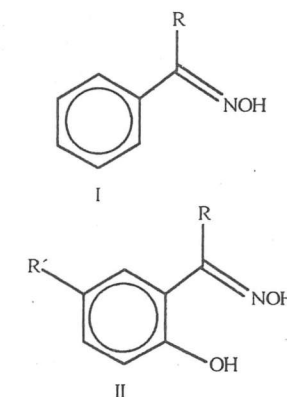
Introduction

The advent of the so-called "soft" ionization methods in Mass Spectrometry, such as Fast Atom Bombardment (FAB) and Liquid Secondary Ion Mass Spectrometry (LSIMS), where the samples under analysis are dissolved or suspended in liquid matrices, enlarged the field of the aforementioned technique from purely gas-phase chemistry to condensed-phase chemistry. Different types of reactions were shown to occur under FAB conditions in the liquid-gas interface: acid-base, substitution and addition, oxidation-reduction and others. Despite the large amount of data obtained since the discovery (1), or as some claim the rediscovery (2), of FAB, the first attempt to establish a systematic correlation between the formation of some ionic species in FAB and LSIMS and the half-wave potential of their neutral counterparts was not made until a later date (3).

As the oxime-imine reduction in the liquid-gas interface in FAB Mass Spectrometry has been found to be relevant in the elucidation of the mechanism of FAB ionization (4), the study of its relation with the electrochemical behaviour in solution of the same system was undertaken.

Results and discussion

FAB Mass Spectrometry was used in positive and in negative mode for aromatic oximes, I, and hydroxyoximes, II. The mass spectra of the two types of compounds show peaks at m/z values corresponding to $[\text{M}+\text{H}]^+$ and $[(\text{M}+\text{H})-\text{O}]^+$ ions, (M being the neutral oxime). We observed that the relative abundances of $[\text{M}+\text{H}]^+$ ions decrease whereas the relative abundances of the $[(\text{M}+\text{H})-\text{O}]^+$ ions increase with increasing time.



As shown elsewhere (4), this is part of the evidence that indicates that the $[(M+H)-O]^+$ ions are not formed in the gas phase. The elemental composition of the $[(M+H)-O]^+$ ions was checked by accurate mass measurements, and the aforementioned ions were identified as the corresponding protonated imines by mass spectrometric techniques (CAMIKE spectra). In Figure 1, the complete identity of the CAMIKE spectra of the $[(M+H)-O]^+$ species of benzophenone oxime (1A), and the protonated ion of benzophenone imine (1B), can be determined.

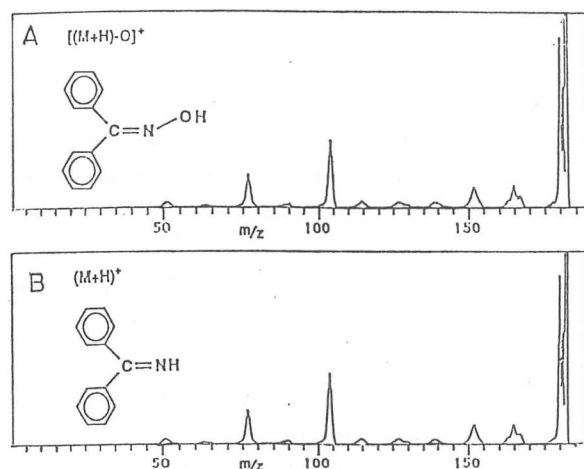


Figure 1 - CAMIKE Spectra of : A - $[(M+H)-O]^+$ ion of benzophenone oxime
B - $[M+H]^+$ ion of benzophenone imine

Reduction is also observed under FAB in negative mode for some types of oximes. The hydroxyoximes, II, are reduced as it can be ascertained by the presence of the $[(M-H)-O]^-$ species in the mass spectra, Figure 2, while the aromatic oximes, I, are not, the $[(M-H)-O]^-$ species being absent from the mass spectra (Figure 3).

Evidence from polarographic studies (5,6) show that oximes are reduced to amines *via* the imines and that protonated

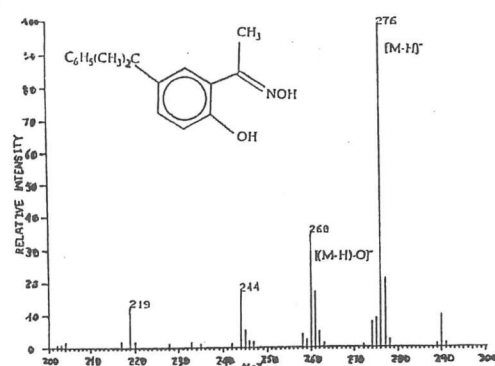


Figure 2 - FAB mass spectra of a hydroxyoxime

oximes, $[M+H]^+$, are reduced at a less negative potential than the corresponding conjugate bases, M. Also, electrochemical reduction of oximes was found to occur only in slightly basic media, because in strong basic media the corresponding conjugated bases $>CNO^-$ are formed.

From the analysis of our results, it can be seen that in FAB positive mode reduction occurs from the protonated oximes, $[M+H]^+$ for all the types of oximes studied, whereas in FAB negative mode, reduction occurs only for hydroxyoximes or other type of oximes having a more acidic proton than the oximic. So, reduction from the $[M-H]^-$ ion occurs only when the oximic group $>C=NOH$ remains intact or, in another words, when the $[M-H]^-$ ion is the $>CNO^-$ ion reduction does not occur.

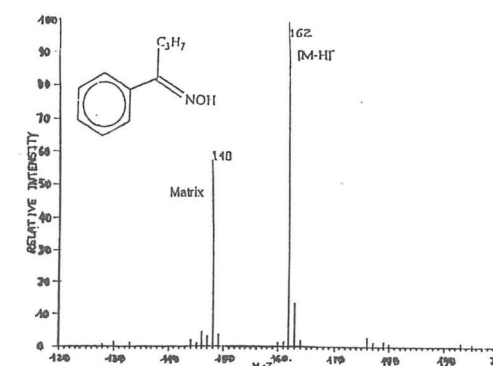


Figure 3 - FAB mass spectra of an oxime

From the comparison of our data with the polarographic data published, we can conclude that the electrochemical behaviour of oximes in acidic media is the same that can be found when they are subjected to positive mode FAB. Also, the electrochemical behaviour of oximes in slightly basic media parallels the behaviour of hydroxyoximes (or other type of oximes having a more acidic proton than the oximic one) under negative mode FAB and finally, the electrochemical behaviour of oximes in strong basic media is analogous to the behaviour of oximes that do not possess a more acidic proton than the oximic one, under negative mode FAB.

Results from time dependent studies of oximes under FAB positive mode (with and without the presence of an anionic surfactant) show that reduction is strongly dependent on the concentration of the $[M+H]^+$ ion at the matrix surface. This behaviour is illustrated in Figure 4 where the plots of the ratio of the relative abundances of $[M+H]^+$ and $[(M+H)-O]^+$ ions over their sum *versus* elapsed time, for dodecanophenone oxime, without and with added surfactant (lithium dodecyl sulfate) are presented.

The reduction mechanism proposed for the electrochemical reduction of oximes to amines *via* the imines is a two step, four electron process (5,6). In view of the data obtained we propose a two electron process for the reduction of the oxime to the imine. Further reduction to the amine is, in our case, prevented by the rapid desorption of the protonated imine to the gas phase.

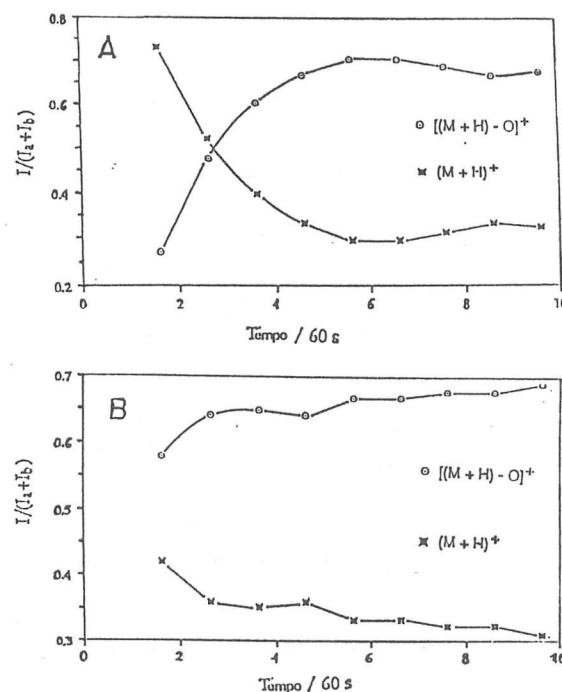


Figure 4 Time dependent plots of $[M+H]^+ / ([M+H]^+ + [(M+H)-O]^+)$ and $[(M+H)-O]^+ / ([M+H]^+ + [(M+H)-O]^+)$
 A - in the absence of surfactant
 B - in the presence of surfactant

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ADSORPTION AND ELECTROCHEMICAL ACTIVITY OF IMIDAZOLE DERIVATIVES ON Pt/Pt, Au AND Hg ELECTRODES.

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ABSTRACT.

Adsorption of 1-hydroxy-2,4,5-trimethylimidazole-3-oxide (HOTMI) on Pt/Pt, Au and Hg electrodes was studied using the methods potentiodynamic and differential charge capacity. It is shown that adsorption depends on the medium nature and on the ionic state of the compound in solution. Electrooxidation products were characterized by HPLC, IR spectroscopy, NMR and H-MS.

EXPERIMENTAL.

Synthesis of HOTMI was carried out by the method (1). Dichloromethane was purified according to (2). Quaternary salts were Merck spectral grade as were the inorganic salts.

The measurements of the differential capacity of the polycrystalline gold electrode and of the mercury electrode were carried out using an automatic equipment (3). Adsorption measurements and potentiodynamic curves on Pt/Pt were performed with a P-5827 potentiostat.

Oxidation of HOTMI was performed in CH_2Cl_2 (E vs Ag/Ag) and in aqueous media (E vs SCE) under potentiostatic conditions on Au and Pt electrodes at different potentials (0,6-0,95 V).

RESULTS AND DISCUSSION.

When the Pt/Pt was immersed in a 0,024 M HOTMI aqueous in 1 N H_2SO_4 solution at open circuit, a shift of the preestablished potential was observed with time indicating the adsorption of HOTMI on Pt/Pt. By choosing the E_p values in the capacitive and of hydrogen adsorption regions, the potential was shifted in the