MOLTEN ANTIMONY TRICHLORIDE AS A SOLVENT FOR ELECTROCHEMICAL STUDIES. II.* ELECTROCHEMICAL OXIDATION OF SOME AMINES. APPLICATION TO THE pHCl MEASUREMENT

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The electrochemical oxidation of 8 aromatic amines in molten antimony trichloride at 100°C is shown to proceed through a one-electron step. Two types of amines were found to exist: in the first the half-wave potential of the anodic curve increases with increasing pCl while in the second it remains unchanged. Due to the ability of these compounds to fix a proton, the pHCl of the solution can be determined through $E_{1/2}$ measurements of the protonated species. The acidity constant of water is evaluated through this technique.

The electrochemical oxidation of amines has been studied in a number of solvents, and it has been shown in most cases, to proceed through a complicated pathway. Antimony trichloride, in which organic cation radicals seem to be more stable than in organic solvents (such as acetonitrile), was used as a solvent for such a study. It was expected that electrochemical reactions proceed through simpler mechanisms in such a medium.

The purpose of our work was to determine the nature of the various redox species of amines in antimony trichloride, and to study their formal potential changes against various factors. According to these results we suggest a scheme for their electrochemical oxidation.

EXPERIMENTAL

Chemicals: Amines are commercial products of highest purity. Antimony trichloride was purified by distillation on antimony under a nitrogen atmosphere. Distillate purity was checked conductometrically according to Baughan's technique[1]. Potassium chloride was dried several days at 200°C. Aluminum trichloride was kept in a sealed flask.

Apparatus: The conductometric measurements were performed according to Desbarres and Texier[2]. The curves were recorded using a Tacussel three-electrode polarographic set type PRG 2.

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The potential differences were measured by means of Tacussel electronic millivoltmeter type S6P. The cell, with thermostated jacket, allowed to work in an inert atmosphere under nitrogen circulation, at 100°C. The auxiliary electrode (platinum wire) and the reference electrode (antimony wire immersed in KCl saturated antimony trichloride) were separated from the solution by frit glass plugs. The working disk electrode was made of a vitreous carbon rod (diameter 2 mm) sealed in a pyrex tube which was rotated 600 r.p.m. (velocity was checked with a stroboscope).

Measurements: Measurements were carried out in antimony trichloride solutions containing: for low pCl ($= -\log [SbCl_4^-]$) values (pCl = O) potassium chloride in concentration 1 mol/l, for high pCl values (pCl = 8) aluminum trichloride in concentration 1 mol/l. In both cases, the amine concentration was $5 \cdot 10^{-3}$ mol/l. Oxygen was removed by a stream of pure nitrogen.

RESULTS

Dissolution of Amines

In aprotic medium. The conductometric study of the dissolution of some amines shows that they fall into two classes. The abnormaly high electrical conductance of "class A" compounds (Fig. 1) suggests that they are 1 : 1 electrolytes, giving the $SbCl_4^-$ anion. These results can be explained by the reaction:

$$A + 2\,SbCl_3 \rightarrow A{,}SbCl_2^+ + SbCl_4^- . \qquad (A)$$

On the other hand, the electrical conductance of the solvent is not modified by dissolution of "class B" amines.

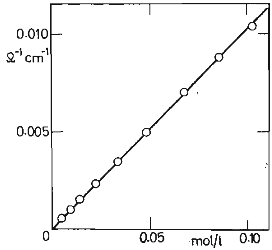

FIG. 1

Dissolution of Antipyrine in Antimony Trichloride

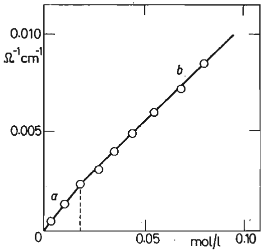

FIG. 2

Conductometric Titration of Residual Water Using 1-Aminoanthracene in Antimony Trichloride

In protic medium (H_2O or HCl-containing $SbCl_3$). The protonation of basic amines can be studied by conductometry. Results are given on Fig. 2. In the conductometric titration of residual water by 1-aminoanthracene (Am), a change in the slope is observed for a stoichiometric ratio 1-aminoanthracene/water equal to 2. Before the end point (part *a* of the curve), the reaction with water is:

$$H_2O + 2\,Am + 3\,SbCl_3 \rightarrow 2\,AmH^+ + SbOCl + 2\,SbCl_4^- .$$

When all water has been neutralized, the reaction of the amine with $SbCl_2^+$ leads to $SbCl_4^-$ (part *b*), according to (*A*). In analogous manner, water can be titrated using "class B" amines as conductometric indicators. The end point determination is more accurate, since part *b* of the titration curve is a horizontal line.

Electrochemical Oxidation

The electrochemical oxidation of 8 aromatic amines proceeds through a reversible one-electron step. However, the cation-radical is not stable, due to chemical reactions following the electron transfer. The plot of the half-wave potential of the anodic curve *versus* the pCl indicates a different behavior of the amines according to the class they belong to:

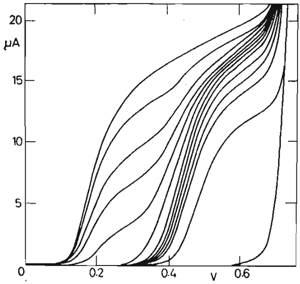

FIG. 3

i–E Curves during the Titration of 0·12M Water in Antimony Trichloride +1M-KCl (pCl = 0) by Pyridine

pHCl Potentiometric indicator: α-naphthylamine ($5 \cdot 10^{-3}$ mol/l).

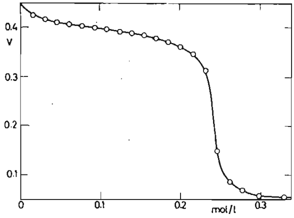

FIG. 4

Plot of the Oxidation Half-Wave Potential (from Fig. 3)

The anodic half-wave potential of the "*class A*" *amines* (Table I) increases by 0·074 V ($= 2{\cdot}3\boldsymbol{RT}/\boldsymbol{F}$ at 100°C) with a 1-unit increase of the pCl, suggesting the following reaction to occur:

$$\text{A,SbCl}_2^+ + \text{SbCl}_4^- \rightarrow \text{A}^+ + 2\,\text{SbCl}_3\,. \qquad (B)$$

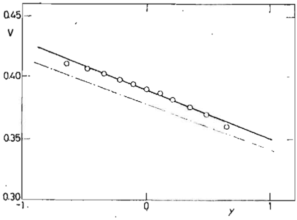

FIG. 5

Plot of $y = \log [x]/[(C_0 - x)]$ *versus* the Oxidation Half-Wave Potential (from Fig. 3) of α-Naphthylamine

TABLE I

Oxidation Half-Wave Potentials[a] and Acidity Constants of Amines in Molten Antimony Trichloride at 100°C

Compound	$E_{1/2}$[b]	pK[e]
"Class A" amines		
1-Aminoanthracene	0·05	7·8
2-Aminoanthracene	0·20	7
Aniline	0·52	5·3
p-Chloroaniline	0·51	5·7
m-Chloroaniline	0·50	6
Pyridine	[c]	>8
Diphenylguanidine	[c]	>8
Antipyrine	[c]	<1·5[d]
"Class B" amines		
α-Naphthylamine	0·18	6·7[f]
β-Naphthylamine	0·34	7·5
Diphenylamine	0·27	6

[a] *vs.* Sb/SbCl$_3$, sat. KCl electrode; [b] $E_{1/2}$ at pCl = 0; [c] not oxidizable; [d] cannot be protonated even by HCl; [e] pK at pCl = 0; [f] first acidity constant.

The "class B" amines are oxidized at a potential which does not depend on the pCl (Table I). This result can be explained by the simpler scheme:

$$\mathrm{B - e \rightarrow B^+} . \qquad (C)$$

Oxidation of *the protonated species*: According to conductometric results, both types of compounds can fix a proton, leading to AH^+ and BH^+ respectively. In both cases, the oxidation half-wave potential is pCl dependent, according to:

$$\mathrm{AH^+ + SbCl_4^- - e \rightarrow A^+ + SbCl_3 + HCl} , \qquad (D)$$

$$\mathrm{BH^+ + SbCl_4^- - e \rightarrow B^+ + SbCl_3 + HCl} . \qquad (E)$$

Thus, the half-wave potential of the redox system AH^+/A^+ is:

$$E_{1/2} = E^0 + 0{\cdot}074\,\mathrm{pCl} - 0{\cdot}74\,\mathrm{pHCl} , \qquad (1)$$

where E^0 is the standard potential of the system AH^+/A^+. Therefore, the pHCl of antimony trichloride solutions is easily determined through $E_{1/2}$ measurements.

Application to the pHCl *Measurement*

Determination of the acidity constant of water. The acidity constant of water has been evaluated by titration with pyridine using α-naphtylamine as pHCl potentiometric indicator. In antimony trichloride, water exhibits acidic properties[4] according to:

$$\mathrm{H_2O + SbCl_3 \rightleftarrows SbOCl + 2\,HCl} \qquad (F)$$

with an equilibrium constant $K = [\mathrm{HCl}]^2[\mathrm{SbOCl}]/[\mathrm{H_2O}]$, the pHCl of a water + + antimony oxychloride solution is given by:

$$\mathrm{pHCl} = \tfrac{1}{2}\mathrm{p}K + \tfrac{1}{2}\log([\mathrm{SbOCl}]/[\mathrm{H_2O}]) . \qquad (2)$$

Water is neutralized by the added pyridine:

$$\mathrm{H_2O + 2\,Py + 3\,SbCl_3 \rightarrow 2\,PyH^+ + SbOCl + 2\,SbCl_4^-} .$$

For $2x$ of added pyridine to a pCl = 0 solution, and with a given initial concentration of water C_0, equations (*1*) and (*2*) lead to

$$E_{1/2} = E^0 + 0{\cdot}037\,\mathrm{p}K - 0{\cdot}037\log[x/(C_0 - x)] \qquad (3)$$

Current–potential curves of α-naphtylamine during water titration by pyridine are given in Fig. 3. The αNapH$^+$ wave height, increase during titration. That is probably due to diacid αNapH$_2^{2+}$ formation in acidic medium; then pyridine can react either on water or on αNapH$_2^{2+}$ leading to αNapH$^+$. After the end point, the base takes a proton from the indicator, and a new wave appears at a lower potential. Fig. 4 and. Fig. 5 show the plots of $E_{1/2}$ *versus* x and $\log [x/(C_0 - x)]$, respectively. When [SbOCl] = [H$_2$O], $E_{1/2}$ (αNapH$^+$) = 0·39 V, *i.e.* pHCl = 3·75, and $K =$ = 7·5.

Solubility of HCl: HCl solubility in antimony trichloride has been found to be $6 \cdot 10^{-2}$ mol/l (ref.[1]) (cryometry), and $3 \cdot 10^{-2}$ mol/l (ref.[3]) using 1-aminoanthracene as indicator.

Dependence of Amines Acidity Constants upon pCl:

Potential measurements allow determination of the acidity constants of amines, through equation

$$\mathrm{p}K = 1{\cdot}5 + (E_2 - E_1)/0{\cdot}074\,, \qquad (4)$$

where E_1 is the [A]/[A$^+$] formal potential and E_2 the formal [AH$^+$]/[A$^+$] potential in a saturated HCl solution.

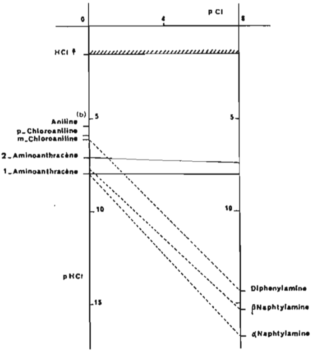

FIG. 6

Variation of the Acidity Constants of Some Amines *versus* pCl in Antimony Trichloride Solutions

"*Class A*" *compounds*: $E_2 - E_1$ does not depend on the pCl. Therefore, the acidity constants of such compounds remain unchanged at every pCl value (Fig. 6, Table I).

"*Class B*" *compounds*: According to (*C*) and (*E*), the acidity constants of BH^+/B systems increase by 1 unit increase of the pCl (Fig. 6, Table I).

In the Fig. 6 the acidity constants of the "Class B" amines are evaluated in 1M-$AlCl_3$ medium (pCl =8), supposing that the oxidation half-wave potential E_1 is the same as in low pCl medium (at pCl = 8, E_1 is lower that Sb/Sb (III) potential). The protonated species AH^+ of aniline, *p*-chloroaniline and *m*-chloroaniline are electroinactive, at any pCl in saturated HCl solutions. The acidity constants of these amines have been measured using another indicator.

It is to note that in low pCl media (pCl = 0), 1-aminoanthracene and α-naphthylamine have the same acidity constant, whereas in high pCl media (pCl = 8), a eight-unit difference of their p*K* on the pHCl scale makes their simultaneous titration easy.

DISCUSSION

Hydrogen electrode operation is not possible in antimony trichloride, due to solvent reduction by hydrogen. The potentiometric indicator method thus offers an attractive technique for acidity determinations. However, practical limitations to this method are to be considered:

The range of accessible potentials is small[4]. Theoretically, a maximum of only 9 pHCl units can be covered with one amine.

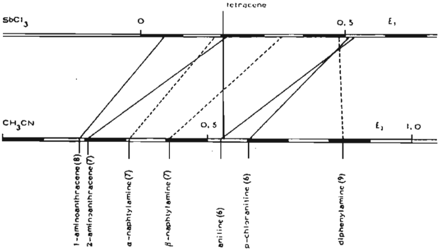

FIG. 7

Comparison of the Oxidation Half-Wave Potentials of Amines in Antimony Trichloride and in Acetonitrile

Oxidation potential of tetracene has been taken as a common potential reference. The values in acetonitrile are taken from ref.[6-9] for E_1 the reference electrode $Sb/SbCl_3$, sat. KCl and for E_2 the reference electrode Ag/0·1M-Ag^+ was used.

Cation radical unstability precludes conventional potentiometric measurements. Acidity constant determination thus requires the plot of a number of voltammetric curves.

$E_{1/2}$ correlations in antimony trichloride and acetonitrile (Fig. 7), based on tetracene[5], show that the amines are less oxidizable in antimony trichloride. This can be ascribed to stronger solvation in $SbCl_3$, and also to complexation of $SbCl_2^+$ by "class A" amines.

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