

MOLTEN ANTIMONY TRICHLORIDE  
AS A SOLVENT FOR ELECTROCHEMICAL STUDIES. I.  
ELECTROCHEMICAL OXIDATION  
OF SOME POLYNUCLEAR AROMATIC HYDROCARBONS

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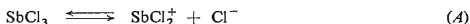
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In order to compare the properties of solutes in different solvents, it is interesting to correlate the standard potential scale, established in a given solvent, with those established in other solvents. The choice of a common reference potential is closely related to solvation problems. Several hypotheses have been suggested and among them the following one is frequently used: When both species of a redox system are solvated in the same way, the standard potential of this system does not depend on the nature of the solvent. Positive and negative ions of an aromatic hydrocarbon (Ar) can often be formed in an inert aprotic solvent; Peover and coworkers<sup>1</sup> studied such ions in acetonitrile and showed that species  $\text{Ar}^-$ , and  $\text{Ar}^+$  are solvated in the same way according to their big size and the delocalization of their electric charge. Therefore we shall discuss here the study of polynuclear aromatic hydrocarbons redox systems in antimony trichloride, fused at 99°C.

EXPERIMENTAL AND RESULTS

The Solvent

Molten antimony trichloride (m.p. 73.2°C) is an inorganic halide solvent which exhibits a low electrical conductivity. The following self-ionisation scheme can be considered:



or

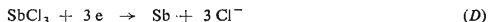


The ionic product<sup>2</sup> is  $K_1 = [\text{SbCl}_2^+][\text{Cl}^-] = 10^{-7.8} \text{ mol}^2 \text{ l}^{-2}$ . The chloride ion behaviour has a particular importance in this solvent; its concentration is determined by the value of the parameter  $\text{pCl} = -\log [\text{Cl}^-]$ . The neutrality of the medium is defined by  $[\text{Cl}^-] = [\text{SbCl}_2^+]$  and corresponds to pure  $\text{SbCl}_3$ , or  $\text{SbCl}_3$  containing an electrolyte such as  $(\text{AlCl}_4^-, \text{K}^+)^3$  which does not show any chloride ion donor or acceptor property. In such a medium the potential range is about 1.5 V. With a (Sb/SbCl<sub>3</sub>, sat. KCl) reference electrode, this potential range extends from -0.00 V to +1.50 V. The following reactions occur at the potential limits, with a vitreous carbon working electrode:

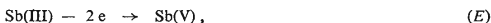
cathodic process



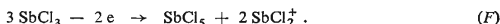
or



anodic process



or



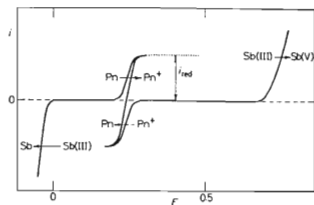


FIG. 1

Voltammetric Curves in  $\text{SbCl}_3$  Low pCl Medium (0.1M-KCl as electrolyte)

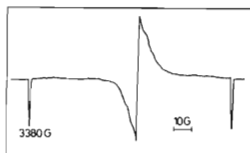


FIG. 2

ESR Spectra of  $\text{Pn}^+$  in Solid Antimony Trichloride (registered on Varian 4508)

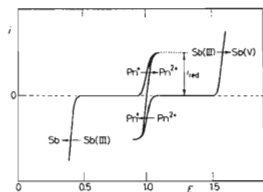


FIG. 3

Voltammetric Curves in Antimony Trichloride High pCl Medium (0.1M- $\text{AlCl}_4^-$ ,  $\text{SbCl}_2^+$  as electrolyte)

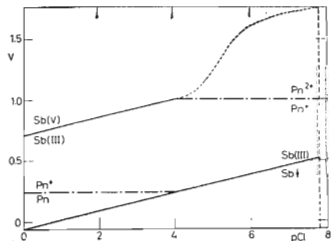


FIG. 4

Potential-pCl Diagram:  $\text{Pn}/\text{Pn}^+$ ,  $\text{Pn}^+/\text{Pn}^{2+}$  Systems in Molten Antimony Trichloride

The potential range limits depend on the pCl of the solution: *In low pCl medium*, or chloride rich medium (0.1M-KCl as electrolyte for instance), the potential range extends from 0.00 V to +0.65 V (Fig. 1). The upper reactions occur at the limits: reduction and oxidation of Sb(III). *In high pCl medium*, or chloride poor medium (0.1M-AlCl<sub>3</sub>), the supporting electrolyte is AlCl<sub>4</sub><sup>-</sup>, SbCl<sub>2</sub><sup>+</sup>; the solvent becomes more oxidizing because the conditional redox potential of the system Sb(III)/Sb(O) increases with the pCl of the solution. Concomitantly SbCl<sub>3</sub> is less oxidizable because the conditional redox potential of the system Sb(V)/Sb(III) increases. Then, the potential range extends from +0.45 V to +1.50 V (Fig. 3, curve 4).

#### Redox Behaviour of Perylene

In fused antimony trichloride, solutions containing the cation Ar<sup>+</sup> are quite stable<sup>4,5</sup>, provided that water and oxidizing agents are rigorously excluded. Therefore, measurements of the standard potential corresponding to the oxidation step:



can be made, using voltammetric techniques. The electrochemical reduction of Ar cannot be made in antimony trichloride according to the oxidizing power of this solvent and to its small potential range.

*In low pCl media*, perylene solutions are yellow and do not exhibit any ESR signal. Perylene (Pn) is oxidized at a vitreous carbon electrode (Fig. 1), in a one-electron step:



The value of the half-wave potential is 0.24 V (see ref.<sup>4,5</sup>). The redox system is reversible. A complete electrochemical oxidation of Pn forms quantitatively the purple monocationic species Pn<sup>+</sup> which exhibits a characteristic ESR signal (Fig. 2); it can be reduced coulometrically (Fig. 1).

*In high pCl media*, perylene solutions are purple and exhibit the same ESR signal (Fig. 2) as Pn<sup>+</sup> solutions: in such high pCl media, Pn is oxidized by the solvent

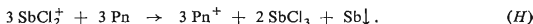


TABLE I

Half-Wave Potentials of Some Aromatic Hydrocarbons in Molten Antimony Trichloride

Compound	$E_{1/2}$ , V	Compound	$E$ , V
Tetracene	0.21	Anthracene	0.51
Perylene	0.24	Pyrene	0.59
9,10-Dimethylantracene	0.31	1,2-Benzanthracene	0.63
3-Methylcholanthrene	0.34	Acenaphthene	0.64
9,10-Diphenylantracene	0.39	Coronene	0.64
3,4-Benzpyrene	0.44	1,2-Benzpyrene	0.66

$\text{Pn}^+$  is oxidized at a vitreous carbon electrode (Fig. 3), in a one electron step:



The value of the half-wave potential is 1.0 V. The redox system is reversible. A complete electrochemical oxidation of  $\text{Pn}^+$  forms quantitatively the blue dicationic species  $\text{Pn}^{2+}$  which does not exhibit any paramagnetism; it can be reduced coulometrically (Fig. 3). The previous results are summarized in a potential-pCl diagram (Fig. 4). It appears that  $\text{Pn}^{2+}$  cannot exist in low pCl media: in such conditions it is reduced by the solvent.

#### Redox Behaviour of Some Aromatic Hydrocarbons

Eleven hydrocarbons were studied by voltammetry, as perylene was: in low pCl media, they are all oxidized in one electron steps. The redox systems are reversible, therefore we shall set the measured half-wave potentials (Table I) equal to the standard potentials, we estimate the error involved in this approximation to be  $< 0.005$  V. The anodic half-wave potentials do not depend on the pCl of the solution. In high pCl media hydrocarbons which potentials are lower than 0.5 V exist only as the charged radicals  $\text{Ar}^+$ . Radicals of 9,10-diphenylanthracene and coronene can be oxidized into dicationic species.

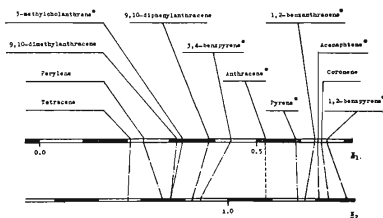


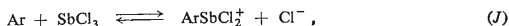
FIG. 5

Comparison of Standard Potential Scales in Fused  $\text{SbCl}_3$  ( $E_1$ ) and in Acetonitrile ( $E_2$ )

Conventionally potentials of anthracene are placed in front. ● unstable  $\text{Ar}^+$ . Reference electrodes:  $\text{Sb}/\text{SbCl}_3$ , sat.  $\text{KCl}$  in molten  $\text{SbCl}_3$ , s.c.e. in acetonitrile.

#### DISCUSSION

The previous results are presented on Fig. 5. The two potential scales established respectively in acetonitrile and in antimony trichloride are very close. There is no inversion in the order of the potentials and differences between two consecutive potentials are kept in the error range of  $\pm 0.05$  V. We consider that these deviations do not contradict the above hypothesis; they must probably be imputed to reactions of the type



because antimony trichloride is a complexing agent. Such reactions have been studied by Baughan and Johnson<sup>6</sup>; the equilibrium constant for perylene is about  $4 \cdot 10^{-5} \text{ mol l}^{-1}$ . But in the pCl range between 0 and 4 this equilibrium does not noticeably occur. Nevertheless, the results presented here let us expect the possibility of establishing correlations between organic solvents and antimony trichloride.

#### REFERENCES

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### ELEKTROKATALYTISCHE OXYDATION UND REDUKTION VON WASSERSTOFF AN CARBIDEN, SILICIDEN UND NITRIDEN VERSCHIEDENER ÜBERGANGS-METALLE

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Für Brennstoffzellen mit sauren Elektrolyten ist die Suche nach platinmetallfreien Elektroden besonders schwierig, da diese neben der Preiswürdigkeit vier, oft schwer miteinander vereinbare Forderungen erfüllen müssen:

Hohe Säurefestigkeit, gute Leitfähigkeit, große innere Oberfläche und ausreichende katalytische Aktivität. Säurefest und elektrisch leitfähig sind viele sog. Hartstoffe, d.h. Boride, Nitride, Carbide und Silicide von Übergangselementen der 4.—6. Gruppe des Periodensystems.

Die vorliegende Arbeit hatte zwei Ziele: Erstens sollte die katalytische Aktivität für die anodische Oxydation von Brennstoffen, hier des Wasserstoffs, bestimmt werden. Zweitens wurde nach Gesetzmäßigkeiten gesucht, die eine Voraussage der katalytischen Aktivität aus der chemischen Zusammensetzung ermöglichen könnten. Als Anhaltspunkte wurden Überlegungen herangezogen, wie sie z.B. Samsonov<sup>1</sup> für die heterogene Katalyse bei Dehydrierungsreaktionen angestellt hat.

#### EXPERIMENTELLER TEIL

Einige der untersuchten Hartstoffe konnten im Handel bezogen werden. Der überwiegende Teil mußte selber hergestellt werden. Dabei erfolgte die Präparation auf möglichst ähnliche Weise, um große Unterschiede in der Aktivität aufgrund der Herstellungsbedingungen weitgehend zu vermeiden. Silicide und Carbide gewannen wir aus den Elementen durch Festkörperreaktion