

**1106.** *Antimony Halides as Solvents. Part IV.*<sup>1-3</sup> *The Ions produced by Perylene and the Effect of Oxidising Agents, Hydrogen Chloride, and Water.*

By J. R. ATKINSON, T. P. JONES, and E. C. BAUGHAN

In pure liquid antimony trichloride the hydrocarbon perylene ionises slightly as a 1:1 weak electrolyte. On addition of oxygen, or antimony pentachloride, one  $\text{SbCl}_4^-$  anion and one free-radical cation are produced per molecule of perylene; on addition of dry hydrogen chloride one  $\text{SbCl}_4^-$  anion and one protonated cation; the addition of water in equivalent proportions has no effect. These solutes produce very few ions in the absence of perylene.

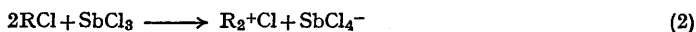
The evidence, from conductance, freezing-point, electron spin resonance, oxygen uptake, and colour, is presented and the stoichiometry worked out; the results are discussed and compared with the reactions of amines.

ANTIMONY TRICHLORIDE is a solvent of high dielectric constant (33 at 75°C) and convenient freezing-point (73.17°C) in which many inorganic chlorides and triphenylmethyl chloride are strong electrolytes and the chloride ion  $\text{SbCl}_4^-$  is abnormally mobile (cf. refs. 1, 2, and references therein). This Series is mainly concerned with the ionization of organic compounds caused by the peculiar chemistry of the solvent as well as by its dielectric properties. Thus  $\text{SbCl}_3$  is a strong chloride-ion acceptor<sup>1, 2, 4</sup>



and sometimes an electron-pair acceptor; it would therefore be classified as an acid in "solvent-system" classifications and in G. N. Lewis's scheme. But it is neither an acid nor a base in Brønsted's proton-classification; it has no protons to donate nor does it accept them, at least not from carbonium ions<sup>2</sup> or, as is shown here, from dry hydrogen chloride. Finally  $\text{SbCl}_3$  is not an oxidising agent, for it would itself have to be reduced to metallic antimony or possibly to sub-chloride.<sup>5</sup>

The chemistry of this ionising solvent is therefore in many ways simpler than that of sulphuric acid which is a proton-acid and base ( $\text{H}_3\text{SO}_4^+$ ), an oxidising agent, a sulphonating agent, and a dehydrating agent, and produces<sup>6</sup> about 0.10M of ions at 25° from its self-ionizations. Hence unusual reactions of ionization may be investigated in  $\text{SbCl}_3$ , e.g., from organic chlorides  $\text{RCl}$ , the reaction<sup>2</sup>



We now extend our work to aromatic hydrocarbons. Preliminary measurements<sup>7</sup> had shown a complicated picture. The more reactive hydrocarbons, such as tetracene and pentacene, showed intense colours, high degrees of ionization, and the e.s.r. signals of the free-radical cations,<sup>3</sup> but these results were sensitive to the presence of impurities. Less reactive hydrocarbons, e.g., naphthalene, do not show these phenomena clearly. It was therefore desirable to investigate systematically a hydrocarbon of intermediate reactivity in a more rigorously purified solvent.

For hydrocarbon we chose perylene, because of the important work of the Amsterdam school<sup>8</sup> on it in other solvents, and because its free-radical cation in  $\text{SbCl}_3$  is unusually stable;

<sup>1</sup> Part I, G. B. Porter and E. C. Baughan, *J.*, 1958, 744.

<sup>2</sup> Part II, A. G. Davies and E. C. Baughan, *J.*, 1961, 1711.

<sup>3</sup> Part III, E. C. Baughan, T. P. Jones, and L. Stoodley, *Proc. Chem. Soc.*, 1963, 274.

<sup>4</sup> Cf. for water solution, N. A. Bonner and W. Goishi, *J. Amer. Chem. Soc.*, 1961, **83**, 85.

<sup>5</sup> J. B. Corbett, S. v. Winbush, and F. C. Albers, *J. Amer. Chem. Soc.*, 1957, **79**, 3020.

<sup>6</sup> B. J. Kirkbride and P. A. H. Wyatt, *Trans. Faraday Soc.*, 1958, **54**, 483; S. J. Bass, R. J. Gillespie, and E. A. Robinson, *J.*, 1960, 821.

<sup>7</sup> A. C. M. Finch, unpublished work in these laboratories.

<sup>8</sup> W. I. Aalbersberg, G. J. Hoijsink, E. L. Mackor, and W. P. Weijland, *J.*, 1959, 3049, 3055.

no change was detected in the e.s.r. signal of a sample kept for eighteen months in a sealed tube at 80°C. For the solvent we replaced the "previous" nitrogen-technique of Part II by a "vacuum-line" technique.

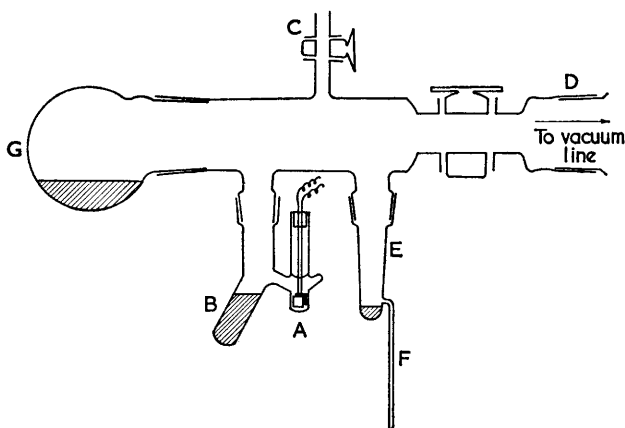
Solutions were investigated by conductance, which measures ionic concentrations; by freezing-point, which measures the total of solute particle concentrations; and by e.s.r. which detects free-radicals and identifies them, but only measures their concentrations very roughly. Qualitative observations of colour proved of diagnostic value.

The work started with perylene in the pure solvent and then considered the effects of adding separately oxygen, antimony pentachloride, hydrogen chloride, and water to such solutions; the absorption of oxygen was measured volumetrically. Blank experiments were made on the addition of these compounds to antimony trichloride *without* any perylene; very few, if any, ions were produced (cf. also Klemensiewicz and Zebrówska<sup>9</sup>).

#### EXPERIMENTAL

*Materials and Technique.*—Oxygen and nitrogen ("white-spot" purity) from B.O.C. cylinders and hydrogen chloride (from AnalaR sulphuric acid and AnalaR ammonium chloride) were dried first with sulphuric acid, and finally by passage through long spirals cooled to -78°C. Antimony pentachloride was prepared from chlorine and AnalaR trichloride and distilled in nitrogen; additions of this (and of water) were made by calibrated micrometer syringes.

Two samples of perylene were used. Most of the work was done with a sample (Messrs. Lights) sublimed *in vacuo*, the "previous technique" conductance and one of the "vacuum-line" technique runs with a sample from the Aldrich Chemical Co. crystallised from toluene and dried *in vacuo*.



Conductance and freezing point were measured as previously;<sup>1,2</sup> the cryoscope was modified for magnetic stirring. In the later experiments with hydrogen chloride conductances were measured in a side-arm sealed to the cryoscope.

Antimony trichloride for "previous technique" conductance measurements and for cryoscopy was prepared as before.<sup>1,2</sup> The "vacuum-line" technique was as follows: AnalaR antimony trichloride distilled three times in dry nitrogen at reduced pressure was distilled into the 500 c.c. flask G. At  $10^{-5}$  cm. or less it was then sublimed into the conductance cell B, which contained a known amount of perylene, by cooling B with liquid nitrogen. Pure nitrogen was then admitted through tap C, the solvent melted, the hydrocarbon dissolved, and the conductance measured. For e.s.r. measurements the hydrocarbon was placed in tube E and the solvent sublimed into there. By rotating the ground joints solutions could be poured into cell A or the 2-mm. diameter tube F which was then sealed and taken to the e.s.r. apparatus, where the spectra were measured at 75°.

To measure oxygen uptake the trichloride was sublimed into a Warburg flask with some perylene in a side-arm; the flask was then equilibrated with oxygen at 75°, cooled, and detached in a dry-box. It was then attached to the manometer, reheated to 75°, and allowed to equilibrate

<sup>9</sup> Z. Klemensiewicz and A. Zebrówska, *Roczniki Chem.*, 1934, 14.

with oxygen once more. Finally the antimony trichloride and perylene were mixed and the oxygen uptake measured.

All manipulations involving opening of ground joints, etc., were done in a dry-box in an atmosphere of purified nitrogen. All conductance measurements were made at 75°.

The specific conductance  $\kappa_0$  of such  $\text{SbCl}_3$  varied from 2 to 4 micromhos/c.c. It had been argued<sup>2</sup> that  $\kappa_0$  was principally due to a strong electrolyte impurity with  $\text{SbCl}_4^-$  anion. If so, the temperature coefficient of  $\kappa_0$  should be entirely due to the effect of temperature on mobilities, while a weak electrolyte would also show the larger effect of temperature on ionic concentrations. Table 1

TABLE 1.

Temp.	$\kappa_0$ (micromhos/c.c.)	$\Lambda_{\text{KCl}}$	100 $\kappa_0/\Lambda$
75·1°	3·29	98	3·36
79·9	3·71	104	3·56
80·2	3·75	105	3·56
85·1	4·01	111	3·61
94·9	4·74	126	3·75
100·0	5·07	133	3·78

shows that  $\kappa_0$  for one solvent sample varies with temperature roughly proportionally to  $\Lambda$  for the strong electrolyte KCl (data for 0·02M-KCl interpolated from Klemensiewicz<sup>10</sup>). Most of the self-conductance is therefore due to a strong-electrolyte  $\text{SbCl}_4^-$  impurity; the concentration implied ( $3 \cdot 10^{-5}N$ ) is reasonable.

## RESULTS

I. *Perylene in the Pure Solvent.*—Solutions of perylene in the antimony trichloride thus prepared showed no e.s.r. signals and were greenish in dilute and yellow in more concentrated solutions. They showed a specific conductance  $\kappa_c$  considerably higher than that  $\kappa_0$  of the pure solvent. The results are in Table 2, and compared with those of Finch<sup>7</sup> by the "previous technique." The Table gives the equivalent conductance  $\Lambda$  both uncorrected and corrected by

TABLE 2.

$10^3 C$	Present vacuum-line technique					Previous technique <sup>7</sup>					
	0·268	1·08	4·2	2·05	21·6	0·71	3·11	10·85	27·6	50·3	71·7
$\kappa_0$	2·45	2·45	2·45	3·38	2·68	3·17	3·17	3·17	3·17	3·17	3·17
$\kappa_c$	8·35	17·9	40·9	28·9	86·0	14·9	29·7	55·6	100	140	192
$\Lambda_{\text{uncorr.}}$	31·1	16·5	9·7 <sub>3</sub>	14·1	3·98	20·8	9·5 <sub>3</sub>	5·13	3·64	2·78	2·68
$\Lambda_{\text{corr.}}$	22·0	14·3	9·1 <sub>5</sub>	12·4	3·88	16·5	8·5 <sub>3</sub>	4·83	3·51	2·72	2·63
$\Lambda_{\text{uncorr.}}^2 C$	0·258	0·295	0·395	0·406	0·343	0·310	0·285	0·287	0·363	0·390	0·515
$\Lambda_{\text{corr.}}^2 C$	0·130	0·220	0·352	0·317	0·325	0·194	0·226	0·253	0·340	0·372	0·496
$-\log_{10} K_{\text{th}}$	4·53	4·44	4·32	4·30	4·43	4·44	4·49	4·48	4·45	4·39	4·28

Mean  $-\log_{10} K_{\text{th}} = 4·4_1$ ;  $K_{\text{th}} = 3·9 \times 10^{-5}$ .

Units:  $C$  in moles/l.  $\kappa$  in micromhos/c.c.  $K$  in moles/l.

subtracting  $\kappa_0$  from  $\kappa_c$ . It can be seen (a) that  $\Lambda$  decreases with  $C$  and is always considerably less than that for a 1:1 strong electrolyte chloride ( $\Lambda \simeq 90$ ); (b) that  $\Lambda^2 C$  is roughly constant; perylene is a 1:1 weak electrolyte; (c) that the two sets of results by different workers, with different samples of perylene and with different techniques of solvent purification, are in substantial agreement. The ionization is reproducible; such reproducibility is also shown by anthracene.<sup>7</sup> The nature of those ions, however, remains unknown but the cation *cannot* be the free-radical cation produced by oxygen (cf. next section) since this would, at the concentrations inferred from  $\Lambda$ , give a deep purple colour and strong e.s.r. signals; neither was observed.

We later speculate as to the nature of these ions; if the anion be  $\text{SbCl}_4^-$  ( $\Lambda \sim 90$ ) the appropriate Ostwald dissociation constant from  $\Lambda^2 C \sim 0·350$  would be  $0·350 \div 8100 = 4·3 \times 10^{-5}$ . The full treatment, allowing for effects of ionic strength on mobility and activity coefficients, and assuming the common ion  $\text{SbCl}_4^-$  for  $\kappa_c$  and  $\kappa_0$ , has been carried out (Part II<sup>2</sup>); the last line of Table 2 gives the thermodynamic dissociation constants  $K_{\text{th}}$  so deduced (mean  $3·8 \times 10^{-5}$ ). The fact that  $K_{\text{th}}$  varies less than  $\Lambda^2 C$  provides some support for the idea that the anion is  $\text{SbCl}_4^-$ .

<sup>10</sup> Z. Klemensiewicz, *Z. physik. Chem.*, 1924, **113**, 28.

II. *Effect of Oxygen.*—(a) Blank experiments on the pure solvent showed no change in  $\kappa_0$  when the nitrogen atmosphere was replaced by dry oxygen and the cells shaken. The f. p. fell only by about  $0.1^\circ\text{C}$ ; this could well be due to small differences in solubility of oxygen and nitrogen as the "ideal solubilities" predicted imply depressions of about this magnitude ( $0.1^\circ \simeq 0.004$  mole/kg.). Hence, no reaction was detected between oxygen and pure solvent.

(b) On thus adding dry oxygen to perylene in pure antimony trichloride, the solution became deep purple, a strong signal of the free radical cation appeared, and  $\Lambda$  values for perylene were obtained, as shown in Table 3. These  $\Lambda$  values agree closely with those<sup>2</sup> for 1:1 electrolytes giving

TABLE 3.

	Run 1: $\kappa_0 = 7.4 \times 10^{-6}$						Run 2: $\kappa_0 = 5.0 \times 10^{-6}$					
$10^3 C$	1.36	3.98	8.51	12.9	19.4	33.0	2.05	3.95	8.92	13.2	20.4	29.2
$\Lambda_{\text{corr.}}$	94.2	83.0	84.4	84.8	82.0	80.5	91.0	85.3	87.0	84.9	80.1	76.5
$\Lambda_{\text{calc.}}$	88.9	87.0	85.0	84.4	82.4	80.2	88.3	87.0	84.9	83.7	82.1	80.8

the  $\text{SbCl}_4^-$  anion (triphenylmethyl chloride  $\Lambda_0 = 89.4$ , tetramethylammonium chloride  $\Lambda_0 = 96.9$ ) and fall with concentration in the same way; the last line of Table 3 gives  $\Lambda_{\text{calc.}}$  from

$$\Lambda_{\text{calc.}} = \Lambda_0 - X\sqrt{\mu}/(1 + Y\sqrt{\mu}) \quad (3)$$

with  $\Lambda_0 = 92$ ,  $X = 90.6$  (theoretical),  $Y = 2.2$ , an equation intermediate between those<sup>2</sup> for the two strong electrolytes quoted.

Hence, oxygen produces one  $\text{SbCl}_4^-$  ion for one perylene molecule; the anion cannot be  $\text{SbCl}_6^-$  which is much less mobile.<sup>2, 11</sup>

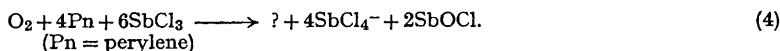
(c) The oxygen taken up was measured, with the results in Table 4, supporting the idea that one

TABLE 4.

Perylene (mg.)	14.2	3.26	4.07	8.62
$\text{O}_2$ uptake (c.c. at $75^\circ/760$ mm.)	0.35	0.08	0.11	0.21
Moles $\text{O}_2$ /moles perylene	0.22	0.22	0.24	0.22

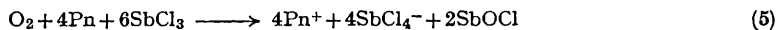
oxygen can oxidise four perylenes (0.25 oxygen per perylene).

(d) From (b) and (c), if we suppose the oxygen and chlorine to remain in known inorganic compounds, we infer



(e) Since four perylenes thus give up four electrons it is possible that *all* the perylene is converted into the singly-charged free-radical cation which was unambiguously identified by e.s.r.,<sup>3</sup> but the apparatus used could hardly<sup>12</sup> estimate concentrations to better than  $\pm 30\%$ .

(f) We checked the total number of particles by cryoscopy; in  $\text{SbCl}_3$ ,  $\text{SbOCl}$  gives a normal freezing-point<sup>13</sup> and ionises very little.<sup>9</sup> Table 5 shows the results for perylene.  $\theta_N$  is the depression caused by perylene at  $m$  moles/kg. in solvent saturated with dry nitrogen; the value calculated is from the cryoscopic constant (15.6) of Part I. Perylene is mainly a normal solute—we have already shown that its ionization is small.  $\theta_0$  gives the steady depression after adding oxygen; the mean ratio  $\theta_0/\theta_N$  is  $2.30 \pm 0.10$ . If all the solutes behaved ideally, this would be the number  $\gamma$  of particles. At these concentrations<sup>1</sup> covalent solutes are likely to be ideal, univalent ions with osmotic coefficients between 0.85 and 0.95, say 0.90. Supposing the process to be



we would expect  $\theta_0/\theta_N = 0.50 + 2 \times 0.90 = 2.30$ , as found. This indirectly verifies the scheme of eqn. (5).

(g) So complex a stoichiometry could not occur in one step; an experiment in simultaneous measurement of oxygen uptake and conductance showed the two rates to be about the same, so the slow step is probably oxygen diffusion. It is probable that antimony pentachloride is involved

<sup>11</sup> G. Jander and K. H. Swart, *Z. anorg. Chem.*, 1959, **301**, 65.

<sup>12</sup> L. Stodley, personal communication.

<sup>13</sup> B. Dacre and J. R. Atkinson, unpublished work in these laboratories.

TABLE 5. Depressions.

$10^3 m^*$	$\theta_N$		$\theta_O$	$\theta_O/\theta_N$
	Calc.	Obs.		
5.39	0.084°	0.066°	—	—
6.46	0.101	0.087	0.22	2.56
8.78	0.137	0.132	0.29	2.18
9.93	0.155	0.113	—	—
10.85	0.169	0.189	—	—
13.68	0.213	0.200†	0.44 <sub>5</sub>	2.23
16.11	0.251	0.237	0.63	2.66
16.75	0.261	0.235	—	—
18.35	0.286	0.314	—	—
20.81	0.325	0.316	0.64 <sub>4</sub>	2.04
22.90	0.357	0.334†	0.720	2.16
23.92	0.373	0.336	—	—
30.18	0.471	0.420	—	—
31.40	0.490	0.458	1.04 <sub>7</sub>	2.28

Mean 2.30 ± 0.10

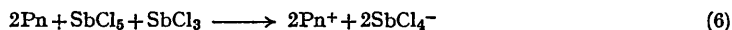
\*  $m$  = moles of perylene/kg. of  $SbCl_3$ . † Interpolated. Reproducibility (mean):  $\theta_N$  about 0.006°;  $\theta_O$  about 0.02<sub>0</sub>.

since this was known, from e.s.r., to give radicals,<sup>14</sup> and from conductance to give at least some ions.<sup>15</sup> Although oxygen does not react much with the pure solvent [cf. (a)], a balanced reaction



is likely which could go to completion with an oxidisable substrate.

On this view one oxygen molecule gives two of antimony pentachloride. Since, in fact, one oxygen with four perylenes gives four  $Pn^+$  and four  $SbCl_4^-$ , then two antimony pentachlorides should do the same; the reaction should be



The next section shows this. The conductance produced by oxygen can, to some extent, be reduced by pumping off the oxygen (reversible oxidation<sup>8</sup>).

III. *Effect of Antimony Pentachloride.*—When antimony pentachloride was added to a solution of perylene in the trichloride under nitrogen an immediate purple colour was observed and the electron spin resonance spectrum of the perylene radical cation identified. This was accompanied by an immediate large increase in conductance.

Table 6 shows conductance data for three runs, one with  $SbCl_5$  in concentration  $x$  in excess of that ( $C$ ) of perylene, the other two with approximately one mole of  $SbCl_5$  to two moles of perylene. In the first,  $x_0$  was measured,  $SbCl_5$  added giving conductance  $x_x$ , and then perylene giving  $x_C$ .

TABLE 6. Effect of  $SbCl_5$ .

	Run 1			Run 2	Run 3
	17	17	17		
$x_0$	17	17	17	4.37	5.81
$x_x$	25.6	25.6	25.6	—	—
$x_C$	—	679	1470	1456	1106
$10^3 x$ ( $SbCl_5$ )	32.8	32.8	32.8	10.9	8.7
$10^3 C$ (Perylene)	0	7.43	16.4	21.6	17.3
$\Delta x$	0.57	—	—	—	—
$\Delta c$	—	92	90	69	64
$\Delta c, calc.$	—	85	83	82	83

Units as before; no correction for solvent conductance in  $\Delta$ .

In the second two the perylene was added first so that  $x_x$  is not known; this was to look at the *speed* of the ionization which was complete within a few minutes. It can be seen ( $\Delta_x$ ) that the  $SbCl_5$  itself does not ionize much. For perylene  $\Delta_C$  is, for  $SbCl_5$  in excess, roughly equal to that ( $\Delta_{calc.}$ ) from eqn. (3); if  $SbCl_5$  is at one mole per two perylenes,  $\Delta_C$  is slightly smaller (incomplete reaction, loss of chlorine from  $SbCl_5$ ; this point needs further investigation).

<sup>14</sup> M. C. R. Symons in "Advances in Physical Organic Chemistry," ed. Gold, Academic Press, New York, 1963.

<sup>15</sup> G. E. Blomgren and J. Kommandeur, *J. Chem. Phys.*, 1961, **35**, 1636.

It is however clear that, as expected, *one*  $\text{SbCl}_5$  reacts with *two* perylenes to give *two*  $\text{SbCl}_4^-$  ions and some  $\text{Pn}^+$  free-radical ions (from colour and e.s.r.).

The addition of ferric chloride also produced the free-radical colour and conductance from perylene in  $\text{SbCl}_3$ .

IV. *Effect of Hydrogen Chloride.*—If *dry* hydrogen chloride be added to antimony trichloride as before, very little ionization occurs (Table 7); Klemensiewicz and Zebrówska<sup>9</sup> obtained still lower values of  $\Lambda_x$  at 98°. But the f. p. is significantly lowered corresponding to about 0.06M of an ideal solute (cryoscopic constant<sup>1</sup> 15.6). Hydrogen chloride presumably exists as the normal covalent molecule; extrapolation from the high-pressure data<sup>16</sup> would give the v.p. of anhydrous hydrogen chloride as 125 atm. at 75°, hence an "ideal solubility" of 0.09M.

Hence from the f. p. lowering one can obtain the concentration,  $x$ , of hydrogen chloride. On addition of a concentration  $C$  of perylene ( $C < x$ ) there is a very large rise in conductance and the  $\Lambda_C$  values correspond once more to those predicted from eqn. (3) for *one*  $\text{SbCl}_4^-$  per perylene.

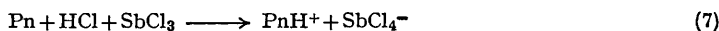
TABLE 7. Effect of HCl.

$x_0$	$x_x$	$x_C$	$10^3x$ (HCl)	$10^3C$ (Perylene)	$\Lambda_x$	$\Lambda_C$	$\Lambda_C$ , calc.
82	108	5210	61.7	56.6	0.43	90	78
71	73	2750	64.5	33.6	0.04	80	80

Units as before; no solvent correction.

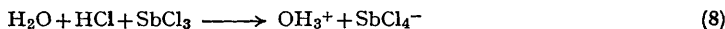
The results are given in Table 7 in the same form as in Table 6. These results were obtained in a cryoscope with conductance side-arm; in this apparatus  $x_0$  is much higher, supporting our view that the principal cause of  $x_0$  is impurity (probably from the glass, as in water).

E.s.r. observations showed in some cases no signal whatever, in others a very faint signal due to the free-radical ion (such signals we attribute to traces of oxygen). And the solutions were *green*, not purple, and therefore did not contain the free-radical cation. We interpret these results as due to a practically quantitative reaction

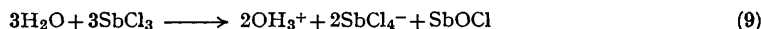


When oxygen is admitted, the colour immediately changes to purple and the e.s.r. signal becomes very marked. Oxygen produces therefore the free-radical cation both from solutions where most of the hydrocarbon exists as such and from those where most of it is protonated.

V. *Effect of Water.*—(a) In pure antimony trichloride water is a normal solute (from f. p.<sup>13</sup>) and conductance is very small<sup>9</sup> ( $\Lambda \sim 0.01$  at 98°). If water reacted with the solvent, it would produce HCl, and hence ions:



Thus when a few drops of concentrated hydrochloric acid (3.5 moles of  $\text{H}_2\text{O}$  per mole of HCl) were added to the solvent, a conductance was observed corresponding to one  $\text{SbCl}_4^-$  per HCl. The complete hydrolysis would presumably be



with  $\Lambda_{\text{H}_2\text{O}} \sim 60$ , and  $\nu = 5/3$ . Clearly this reaction does not happen.

(b) It would not be made to go by the presence of perylene for  $\text{H}_2\text{O}$  is a stronger base than the hydrocarbon.

(c) It is therefore not surprising that when water, in roughly equivalent proportions, was added to perylene in pure  $\text{SbCl}_3$  no change in conductance was observed during several hours; a noticeable change was observed only when the water was in about forty-fold excess.

## DISCUSSION

(a) *Results with Hydrogen Chloride.*—Since antimony trichloride is *not* a proton-base (e.g., carbonium ions do not give olefins<sup>2</sup>) hydrogen chloride should not ionise. Nor should hydrogen chloride and antimony trichloride give a stable *covalent* addition compound.<sup>17</sup>

<sup>16</sup> E. Cardoso and A. F. Germann, *J. Chim. phys.*, 1913, **11**, 632.

<sup>17</sup> L. Olah, "Friedel-Crafts and Related Reactions," Interscience Publishers, New York and London, 1963, vol. 1, p. 210—212.

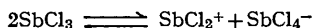


But the mixture should be a very strong Brönsted acid (proton-donor), as it is. The present facts are exactly paralleled by results on HCl-AlCl<sub>3</sub> mixtures; equally hydrogen fluoride will protonate aromatic substances (giving F<sup>-</sup>), the protonation being enhanced by BF<sub>3</sub><sup>18</sup> although there is no stable covalent addition compound.<sup>17</sup>

(b) *Results with Oxygen and Antimony Pentachloride.*—Aalbersberg and his co-workers first showed<sup>8</sup> that molecular oxygen could give the free-radical cation from perylene (in hydrogen fluoride and in trifluoroacetic acid); many authors have reported<sup>14</sup> e.s.r. spectra and colour from the reaction with antimony pentachloride.

Our results confirm these but go further, for we have worked out the stoichiometry and identified the anion SbCl<sub>4</sub><sup>-</sup> through its abnormally high mobility. The formation of SbCl<sub>4</sub><sup>-</sup> is, of course, enhanced by the excess of antimony trichloride. But one previous observation on the analogous reaction of some aromatic amines, suggests the same mechanism even in other solvents; Kainer and Hausser<sup>19</sup> obtained from 4,4'-dimethoxydiphenylamine with antimony pentachloride in carbon tetrachloride a black precipitate whose magnetic susceptibility proved the free radical and whose analysis repeatedly gave *one* antimony to *four* chlorines; we ourselves found that triphenylamine in antimony trichloride gives with oxygen the blue colour of the free-radical ion.

(c) *Ionisation in Pure Antimony Trichloride.*—This small but reproducible ionization is observed<sup>7</sup> with other aromatic hydrocarbons which are also 1:1 weak electrolytes. We offer the following hypothesis. In many reactions, aromatic hydrocarbons behave like nitrogen bases; the π-electrons act like the lone pair. Thus, both can be protonated; both can donate a *pair* of electrons to such reagents as Ag<sup>+</sup>; perylene can lose *one* electron to antimony pentachloride, and so can some aromatic amines. It is known<sup>20</sup> that pyridine is a 1:1 weak electrolyte in the similar solvent arsenic trichloride; compare our observations with perylene. Now antimony trichloride should tend to ionise



(although this has not yet been observed above the impurity-conductance). And the cation SbCl<sub>2</sub><sup>+</sup>, which has a sextet of electrons, should act as an electron-acceptor. Any electron-donor, such as pyridine or perylene, might therefore possibly enhance this ionization.

The results show the chemical advantages of this good ionising solvent many of whose physical advantages have not yet been much exploited. By itself, it is a chloro-anion acceptor and probably can be ionised by electron donors; the addition of hydrogen chloride produces a strong acid; the addition of oxygen (or antimony pentachloride) produces ions by oxidation.

This ability to separate, by controlled addition of covalent compounds, essentially different modes of ionisation in the *same* solvent seems of considerable value. Already we have separated three distinct ionization reactions of a hydrocarbon, obtained high concentrations of carbonium ions,<sup>2</sup> and observed previously unknown free-radical ions.<sup>3</sup> This separation of chemical functions, which is impossible with sulphuric acid, has to a less extent been effected with hydrogen fluoride;<sup>8,18</sup> from the purely practical standpoint, antimony trichloride is rather less convenient than sulphuric acid, but much more convenient than hydrogen fluoride.

We thank Dr. L. G. Stoodley for e.s.r. measurements and advice, and acknowledge a Government Research Fellowship (T. P. J.) and a D.S.I.R. Grant (J. R. A.).

DEPARTMENT OF CHEMISTRY AND METALLURGY, ROYAL MILITARY COLLEGE OF SCIENCE,  
SHRIVENHAM, SWINDON, WILTS. [Received, July 1st, 1964.]

<sup>18</sup> M. Kilpatrick and F. E. Luborsky, *J. Amer. Chem. Soc.*, 1953, **75**, 577.

<sup>19</sup> H. Kainer and K. H. Hausser, *Chem. Ber.*, 1953, **86**, 1563.

<sup>20</sup> V. Gutmann, *Monatsh.*, 1954, **85**, 491.