

## Electron Acceptor–Electron Donor Interactions. Part XX.<sup>1</sup> Charge-transfer Interactions of Some of the Highest-valency Halides, Oxyhalides, and Oxides with Aromatic Hydrocarbons and Fluorocarbons. Ball–Plane Interactions. Group VB

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We examine the species  $\text{NF}_3\text{O}$ ,  $\text{PF}_5$ ,  $\text{PF}_3\text{O}$ ,  $\text{PCl}_5$ ,  $\text{PCl}_3\text{O}$ ,  $\text{AsF}_5$ ,  $\text{SbCl}_5$ , and  $\text{SbF}_5$ . Both phosphorus and antimony pentachlorides, particularly the latter, are reactive and impose restrictions on the choice of donors for equilibrium studies. Nevertheless, phosphorus pentachloride with naphthalene and antimony pentachloride with benzene and octafluoronaphthalene demonstrate intermolecular spectra and exhibit extremely weak 1 : 1 interactions in a number of solvents; moreover the naphthalene–phosphorus pentachloride system is thermochromic. Phosphoryl chloride behaves like carbon tetrachloride in that it enhances markedly the spectra of hexamethylbenzene in solution (less so for benzene, naphthalene, anthracene, and pyrene) and this characterizes an extremely weak or just contact 1 : 1 interaction. The transition is assigned tentatively to a combined intensity-borrowing and electron-transfer process. Intermolecular charge-transfer spectra are not observed with other compounds of Group VB, although some of the materials are reactive chemically. Attempts at detecting arsenic and bismuth pentachlorides are unsuccessful. A spectrophotometric method for determining molecular self-association is suggested and it is pointed out that continuous-variation plots for a weakly interacting system do not provide information on molecularity.

WE are examining interactions of the tetra- and higher co-ordinate halides, oxyhalides, and oxides of the elements, in their highest oxidation states, towards the strictly  $\pi$ -electron donors, including the aromatic hydrocarbons and fluorocarbons. In this article we examine compounds for Group VB.

Prolonged reaction of phosphorus pentachloride with anthracene in benzene was reported to give an intense red colour.<sup>2</sup> Molecular-weight studies and i.r. and n.m.r. spectra indicated behaviour of  $\text{PCl}_5$  as the monomer in benzene solvent.<sup>3,4</sup> The molecular weight of phosphorus oxychloride in benzene did not change appreciably with the concentration of the solution, and its slightly high value (8%) was attributed either to an internal pressure difference between the solvent and solute or to a small association of the solute.<sup>5</sup> Parachors of the benzene mixture were a linear function in the mole fraction composition.<sup>6</sup> The effect of solvent (cyclohexane, carbon tetrachloride, benzene) on the  $\text{P=O}$  vibrational frequency of phosphoryl chloride showed

small frequency changes.<sup>7</sup> They were little greater than the corresponding changes for dimethyl hydrogen phosphonate or for changes in the  $\text{S=O}$  vibration in dimethyl sulphoxide, and do not appear to afford evidence for specific benzene– $\text{POCl}_3$  association. Preliminary measurements on a phosphorus pentafluoride interaction with 3,4-benzopyrene in 1,2-dichloroethane, under conditions where water had been rigorously excluded, showed small reversible spectral changes.<sup>8</sup> These were not affected by exposing the solution to a brief u.v. irradiation. A possible covalent hydrocarbon–acceptor bond was implied by analogy with a boron trifluoride adduct.

Coloured solutions of antimony pentachloride with hydrocarbons were described in early literature,<sup>9</sup> but many of these must be attributed to radicals or to further chemical reaction. Mixtures in dichloromethane solvent, for example, were shown to be excellent sources

<sup>1</sup> Part XIX, preceding paper. This is also considered as Part IX of a parallel series 'Studies on High Electron Affinity Molecules.'

<sup>2</sup> B. M. Mikhailov and M. S. Promyslov, *J. Gen. Chem. U.S.S.R.*, 1950, **20**, 359.

<sup>3</sup> V. P. Petro, 'Cryoscopic, Spectroscopic, and Conductimetric Study of Phosphorus Pentachloride in Selected Non-aqueous Solvent Systems,' Ph.D. dissertation, Ohio State University, 1964.

<sup>4</sup> V. P. Petro, J. Howatson, and S. G. Shore, *Amer. Chem. Soc., Div. Inorg. Chem.*, No. 75, **33-o**, 150th Meeting, 1965; M. S. Newman, *J. Org. Chem.*, 1969, **34**, 741, footnote 4.

<sup>5</sup> A. R. Morgan and S. T. Bowden, *Trans. Faraday Soc.*, 1940, **36**, 394.

<sup>6</sup> H. Isikawa and T. Atoda, *Bull. Inst. Phys. Chem. Res.*, 1939, **18**, 150; *Chem. Abs.*, 1940, **34**, 2664<sup>7</sup>.

<sup>7</sup> L. J. Bellamy, C. P. Conduit, R. J. Pace, and R. L. Williams, *Trans. Faraday Soc.*, 1959, **55**, 1677.

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

<sup>9</sup> S. Hilpert and L. Wolf, *Ber.*, 1913, **46**, 2215.

of the hydrocarbon radical cations, where naphthalene, benzene, and *p*-xylene were among the few materials difficult to oxidize.<sup>10</sup> Unstable colours of solutions in chloroform were tentatively identified as the spectra of positive ions, although it is noteworthy that displacement of the spectra for bromobenzene, benzene, toluene, xylene, and mesitylene was as expected for electron-transfer transitions.<sup>11</sup> In contrast with the well-recognized Menshutkin adducts of antimony trichloride with aromatic hydrocarbons,<sup>12</sup> the pentachloride did not form complexes,<sup>13</sup> the pure mixed systems were unstable chemically,<sup>14a</sup> and if a  $\pi$ -halide complex precedes reaction it must have a very small association constant.<sup>14b</sup>

We examine materials described in the abstract omitting the known compounds  $\text{AsOF}_3$ ,  $\text{SbOF}_3$ ,  $\text{SbOCl}_3$ , and  $\text{BiF}_5$ , whereas attempts to prepare  $\text{AsCl}_5$  have been unsuccessful.<sup>15</sup> With the exception of antimony pentafluoride,<sup>16</sup> all molecules are the monomeric spherical structures in the vapour<sup>17-19</sup> and probably the liquid<sup>17,20a,21</sup> states, although phosphorus pentachloride dimerises in carbon tetrachloride but not in other solvents.<sup>3,4,22</sup> Information on the solids is lacking, although most species probably exist as monomers<sup>18,23</sup> with the likely exception of antimony pentafluoride and the certain exception of phosphorus pentachloride.<sup>20,24</sup>

## EXPERIMENTAL

Commercial materials were purified by sublimation (phosphorus pentachloride 100 °C, 4 mmHg) and distillation (phosphoryl chloride, Allied Chemical Corporation, quoted minimum purity 99%; antimony pentachloride, Research Organic/Inorganic Chemical Corporation, quoted minimum purity 99%). Failure to distil the phosphoryl chloride resulted in a low-intensity maximum at 270 nm which probably arises from impurities containing the pyrophosphoryl bond. With regard to the question of molecular-arity, the tail absorption of phosphorus pentachloride in carbon tetrachloride at 320, 330, and 340 nm and the

naphthalene absorption at 330 nm were found to obey Beer's law within the accuracy of measurement (0.2%) at room temperature. Similarly, absorptions of antimony pentachloride (0.5M) in carbon tetrachloride or cyclohexane obey Beer's law on dilution. The cyclohexane-antimony pentachloride mixture is unstable to keeping; it darkens and produces an oily deposit over three days.

## RESULTS AND DISCUSSION

Solutions of phosphorus pentachloride in cyclohexane, dichloromethane, or carbon tetrachloride with hexamethylbenzene, naphthalene, anthracene, and pyrene

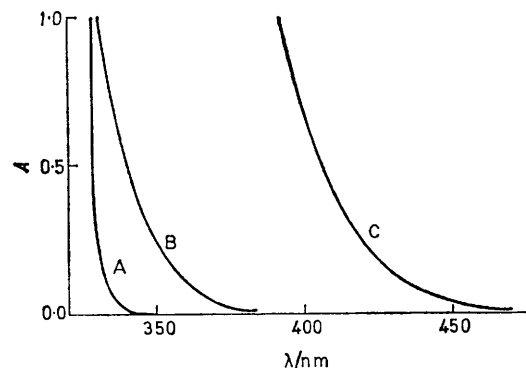


FIGURE 1 Charge-transfer absorption of phosphorus pentachloride with naphthalene in carbon tetrachloride, 2.0 cm cells; A, 0.30M-Naphthalene alone; B, 0.02M- $\text{PCl}_5$  alone; C, 0.02M- $\text{PCl}_5$  and 0.30M-naphthalene

produce yellow, yellow, orange, and orange solutions respectively, immediately on mixing. The pyrene, and to a lesser extent the anthracene and hexamethylbenzene, systems are unstable. Spectra of phosphorus pentachloride with naphthalene in dichloromethane or carbon tetrachloride are very similar, and show absorption tails, not maxima (Figure 1). Studies of this system according to the method of continuous variations for dichloromethane as solvent are in accord with 1 : 1 interactions. Similar comments apply for carbon tetrachloride (Figure 2) although the measurements are

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<sup>11</sup> M. Das and S. Basu, *Spectrochim. Acta*, 1961, **17**, 897.

<sup>12</sup> B. N. Menshutkin, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1275, 1303, 1329.

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<sup>19</sup> G. V. Romanov and V. P. Spiridonov, *J. Struct. Chem. (U.S.S.R.)*, 1967, **8**, 131; K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 1965, **4**, 1775; L. V. Vilkov, L. S. Khaikin, A. F. Vasil'ev, and T. F. Tulyakova, *J. Struct. Chem. (U.S.S.R.)*, 1968, **9**, 954; T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, 1971, **10**, 344; J. K. Wilmshurst, *J. Mol. Spectroscopy*, 1960, **5**, 343.

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<sup>23</sup> R. F. Schneider and J. V. DiLorenzo, *J. Chem. Phys.*, 1967, **47**, 2343; H. Chihara, N. Nakamura, H. Okuma, and S. Seki, *Bull. Chem. Soc. Japan*, 1968, **41**, 1809.

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difficult on account of limited solubility, whereas the solubility in cyclohexane is too low for convenient examination. The conclusions concerning stoichiometry are relevant even when one of the components,

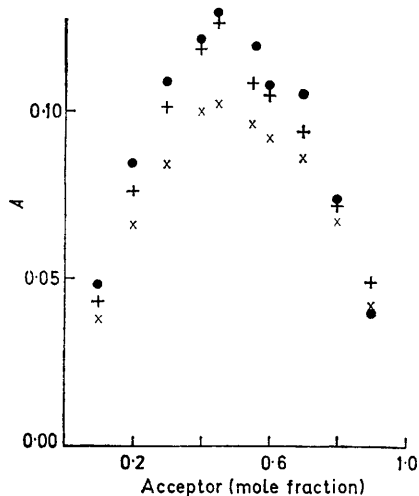
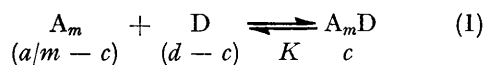


FIGURE 2 Continuous-variation curves (5.0 cm cells) for phosphorus pentachloride, naphthalene ( $[A] + [D] = 0.02M$ ) in carbon tetrachloride, corrected for  $PCl_5$  absorption ( $PCl_5$  assumed as monomer); ●, 340 nm; +, 350 nm; ×, 360 nm

introduced on the false assumption of monomeric species, polymerises.\* A few crystals of the chloride dispersed in molten naphthalene give an orange liquid which freezes to a practically colourless solid, and the process can be repeated many times. A yellow melt with hexamethylbenzene rapidly decomposes; nevertheless, reversible colour change can be demonstrated by immersing the sample in an oil-bath at 110 °C. An orange melt with anthracene is unstable and does not lose its colour when frozen. Apart from phase separation for the phosphorus pentachloride thermochromic systems, there is also a structural change from the covalent  $PCl_5$  liquid to the ionic  $PCl_4^+PCl_6^-$  solid.

Polymerisation of an acceptor (or donor) species in a solution prepared according to the false assumption of monomers can, in principle, be determined from the equilibrium equation (1). This was attempted for the carbon tetrachloride solvent system, in which phosphorus pentachloride is reported to dimerise,<sup>3,4,22</sup> and was



compared with the dichloromethane system. After substitution of  $A/\epsilon l$  for  $c$ , the expanded equation, without approximations, becomes (2). For typical large

$$\frac{ad}{A} = \frac{m}{K\epsilon l} + \frac{md}{\epsilon l} + \frac{a}{\epsilon l} - \frac{mA}{\epsilon^2 l^2} \quad (2)$$

$\epsilon$  values, the last term on the right-hand side can be neglected. Gradients of plots of  $ad/A$  against  $d$  (for constant  $a$ ), and against  $a$  (for constant  $d$ ) are in the

\* This is discussed in the Appendix.

ratio  $m$ , the molecularity. In both dichloromethane and carbon tetrachloride, however, the system is very slowly reacting (1% decrease in 1.5 h) and although for the experimental arrangement this is not critical for conditions of varying  $d$ , it markedly affects the measurements for varying  $a$ , particularly at the low concentrations in carbon tetrachloride. Also, equilibrium measurements for dichloromethane and carbon tetrachloride solvents, shown below, give very similar results whether for constant or for varying  $PCl_5$  concentrations. If dimerization occurs in carbon tetrachloride, it is not readily distinguishable under our conditions of examination.

Equilibrium values for the naphthalene interaction according to customary dilution plots are shown in Table 1, and measurements according to equation (2) for constant  $a$  are also tabulated. They characterise extremely weak interactions. The order of magnitude of the compensated  $\epsilon'$  values for the benzene two-component system (*ca.*  $10^3$ ) can be seen in Figure 3, and these are implied for the naphthalene. Such spectra are presented with reservation, owing to the sensitivity of phosphorus pentachloride to impurities. The effect of temperature on the 370–450 nm absorption edge in dichloromethane produces a uniform and reversible decrease (18%) for increasing temperature (–30 to 31 °C), although most of this (14%) can be attributed to solvent expansion. For the doubtful assumption that

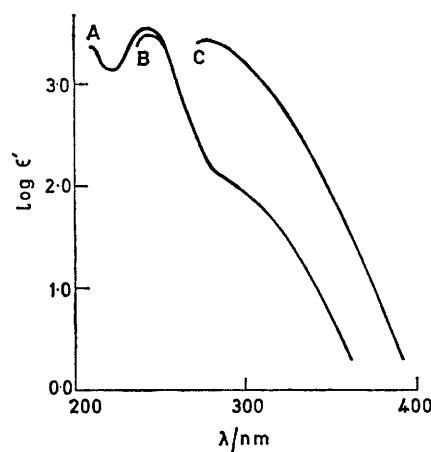


FIGURE 3 Molar absorptivities for some phosphorus pentachloride solutions determined at  $10^{-2}M$  concentrations with different path-length cells; A, dichloromethane; B, carbon tetrachloride; and C, benzene

the change arises entirely from an enthalpy effect, this requires a very small  $\Delta H$  of *ca.*  $-110 \text{ cal mol}^{-1}$ . Similarly, a small, fairly uniform decrease of the absorption edge of Figure 1 is found, although an irreversible 2% loss of absorbance occurs at the higher temperature as a result of chemical reaction. Correction for this and for solvent expansion indicates a very small enthalpy of  $-70 \text{ cal mol}^{-1}$  (Table 2).

Aromatic hydrocarbons do not produce coloured

TABLE 1  
Equilibria and spectral data for some aromatic donor-Group Vb acceptor interactions at 26 °C

Donor	Acceptor	Solvent	nm	<i>a</i>	<i>d</i>	Points per run	<i>K</i> / l mol <sup>-1</sup>	<i>σ</i>	10 <sup>-3</sup> <i>ε</i>
Naphthalene	Phosphorus penta- chloride	Dichloromethane	350	0.0094	0.80	8	0.04	0.02	2.8
Naphthalene	Phosphorus penta- chloride	Dichloromethane	360	0.0094	0.80	8	0.02	0.01	0.43
Naphthalene	Phosphorus penta- chloride	Dichloromethane	370	0.0094	0.80	8	0.02	0.01	1.8
Naphthalene	Phosphorus penta- chloride	Dichloromethane	380	0.0094	0.80	8	0.07	0.01	0.78
Naphthalene	Phosphorus penta- chloride	Carbon tetrachloride	390	0.0125	0.80	8	0.07	0.04	1.25
Naphthalene	Phosphorus penta- chloride	Carbon tetrachloride	400	0.0125	0.80	8	0.08	0.04	0.64
Naphthalene	Phosphorus penta- chloride	Carbon tetrachloride	410	0.0125	0.80	8	0.08	0.03	0.40
Naphthalene	Phosphorus penta- chloride	Dichloromethane	390	0.10 constant	0.20	6	0.17	0.05	0.40
Naphthalene	Phosphorus penta- chloride	Dichloromethane	400	0.10 constant	0.20	6	0.20	0.06	0.24
Naphthalene	Phosphorus penta- chloride	Dichloromethane	410	0.10 constant	0.20	6	0.21	0.07	0.16
Naphthalene	Phosphorus penta- chloride	Carbon tetrachloride	350	0.016 constant	0.20	11	0.17	0.05	1.26
Naphthalene	Phosphorus penta- chloride	Carbon tetrachloride	360	0.016 constant	0.20	11	0.23	0.04	0.96
Naphthalene	Phosphorus penta- chloride	Carbon tetrachloride	370	0.016 constant	0.20	11	0.24	0.07	0.76
Hexamethylbenzene	Phosphoryl chloride	Cyclohexane	310	1.00	0.10 constant	6	-0.02	0.01	-0.42
Hexamethylbenzene	Phosphoryl chloride	Cyclohexane	315	1.00	0.10 constant	6	0.04	0.02	0.16
Hexamethylbenzene	Phosphoryl chloride	Cyclohexane	320	1.00	0.10 constant	6	0.07	0.02	0.05
Benzene	Antimony penta- chloride	Cyclohexane	430	0.01	1.25	8	-0.05	0.02	-1.25
Benzene	Antimony penta- chloride	Cyclohexane	440	0.01	1.25	8	0.07	0.02	0.56
Benzene	Antimony penta- chloride	Cyclohexane	450	0.01	1.25	8	0.08	0.02	0.27
Benzene	Antimony penta- chloride	Carbon tetrachloride	430	0.01	1.25	8	-0.09	0.03	-0.51
Benzene	Antimony penta- chloride	Carbon tetrachloride	440	0.01	1.25	8	-0.09	0.02	-0.36
Benzene	Antimony penta- chloride	Carbon tetrachloride	450	0.01	1.25	8	-0.11	0.03	-0.18
Benzene	Antimony penta- chloride	Carbon tetrachloride	460	0.031	1.25	8	-0.06	0.02	-0.26
Benzene	Antimony penta- chloride	Carbon tetrachloride	470	0.031	1.25	8	-0.08	0.04	-0.12
Benzene	Antimony penta- chloride	Carbon tetrachloride	480	0.031	1.25	8	-0.07	0.02	-0.08
Octafluoronaphthalene	Antimony penta- chloride	Carbon tetrachloride	430	0.10	0.10	8	0.17	0.07	0.27
Octafluoronaphthalene	Antimony penta- chloride	Carbon tetrachloride	440	0.10	0.10	8	0.11	0.06	0.35
Octafluoronaphthalene	Antimony penta- chloride	Carbon tetrachloride	450	0.10	0.10	8	0.11	0.05	0.31

TABLE 2  
Enthalpies for some Group Vb charge-transfer interactions

Acceptor	Donor	Solvent	Position of absorption measurement	-Δ <i>H</i> /cal mol <sup>-1</sup>
Phosphorus pentachloride	Naphthalene	Dichloromethane	Absorption tail	110
Phosphorus pentachloride	Naphthalene	Carbon tetrachloride	Absorption tail	70
Phosphoryl chloride	Hexamethylbenzene	Cyclohexane	Absorption tail	-590
Antimony pentachloride	Octafluoronaphthalene	Carbon tetrachloride	Absorption tail	-110



solutions in phosphoryl chloride although their spectra are stable and show changes reminiscent of the carbon tetrachloride solvent system (Figure 4). There is some

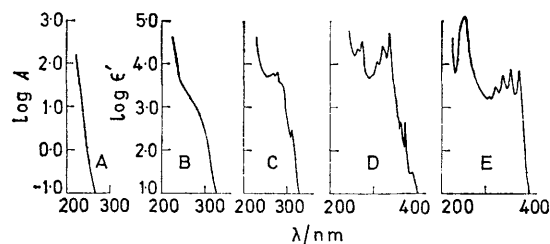


FIGURE 4 Hydrocarbon spectra in phosphoryl chloride compensated for solvent absorptions; A, Solvent absorption (1.0 cm) alone; B, hexamethylbenzene; C, naphthalene; D, pyrene; and E, anthracene

loss of fine structure although little enhancement over the cyclohexane spectra occurs except for the wells between the maxima. The benzene absorption behaves similarly. Again, hexamethylbenzene shows the most pronounced changes in the 300–350 nm region. Concentrations of materials necessary to produce a measurable effect are large compared with the  $[A][D] = ca. 0.01$  rule;<sup>25</sup> moreover phosphoryl chloride has a strong, neighbouring local absorption. We tentatively assign the spectral changes to a combined intensity-borrowing and intermolecular electron-transfer process. Continuous-variation curves ( $[A] + [D] = 0.2M$  in cyclohexane at 310, 320 nm) and the equilibrium studies reported in Table 1 are in accord with extremely weak 1:1 interactions. The effect of increasing temperature produces an uneven gain in the steep absorption edge which, corrected for the solvent expansion, is equivalent to a positive enthalpy varying from 430 to 750 cal mol<sup>-1</sup> for increasing wavelength. Change of band shape must be occurring.

Although naphthalene and stronger donors produce coloured radical species with antimony pentachloride

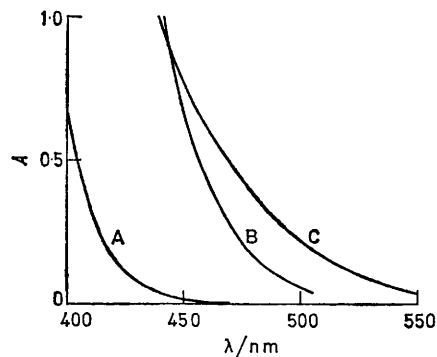


FIGURE 5 Charge-transfer absorptions of antimony pentachloride systems in carbon tetrachloride, 2.0 cm cells; A, 0.025M-SbCl<sub>5</sub> alone; B, 0.025M-SbCl<sub>5</sub> and 0.50M-benzene; C, 0.10M-SbCl<sub>5</sub> and 0.10M-octafluoronaphthalene

particularly in appropriate solvents, the weaker, less reactive donors benzene and octafluoronaphthalene show fairly stable intermolecular spectra, whereas transient

absorptions are seen for some of the methylbenzenes. Carbon tetrachloride and cyclohexane solutions produce similar tail absorptions (Figure 5) although the benzene in cyclohexane shows faint turbidity within  $\frac{1}{2}$  h. Two-component mixtures of antimony pentachloride with hexafluorobenzene, benzene, octafluoronaphthalene, and mesitylene are pale yellow, orange, orange, and red-orange respectively. The benzene and mesitylene are unstable, and even the octafluoronaphthalene darkens slightly on several hours' standing. None of the colours vanish on freezing, although for mixtures low in octafluoronaphthalene, a marked diminution, close to the pale yellow of the antimony chloride, can be achieved. Frozen specimens of the pentachloride at -40 and -50 °C and mixtures with octafluoronaphthalene show

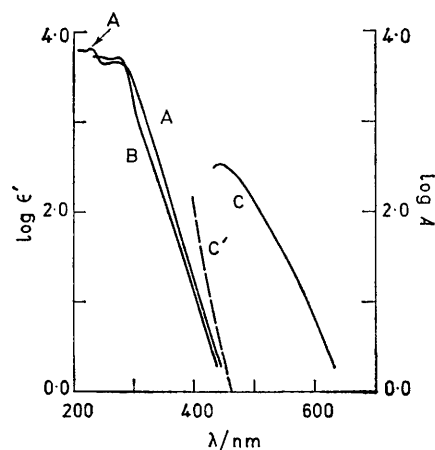


FIGURE 6 Molar absorptivities for some two component mixtures, determined at 10<sup>-2</sup>M of the minor component with different path-length cells. Antimony pentachloride in A, cyclohexane; B, carbon tetrachloride; C, octafluoronaphthalene in antimony pentachloride compensated for the acceptor absorption, C'

extremely diffuse X-ray diffraction patterns, in contrast with the sharp pattern for the pure naphthalene system.

Continuous-variation measurements for both carbon tetrachloride and cyclohexane solvents show curves for the benzene and octafluoronaphthalene systems in accordance with 1:1 interactions. On dilution, all produce linear plots, although the benzene-antimony pentachloride in carbon tetrachloride system deviates slightly above the line (absorbance lower than expected) at high dilutions, and this must account for the negative sign of the small  $K$  values in Table 1. The only spectrum of a two-component acceptor-donor system sufficiently stable for examination is that of octafluoronaphthalene in antimony pentachloride (Figure 6), although even this shows some deterioration within  $\frac{1}{2}$  h. The  $\epsilon'$  value at 450 nm is 330 and 10<sup>2</sup> $f'$  for wavelengths longer than this is 0.27. The spectra of antimony pentachloride in cyclohexane and carbon tetrachloride are presented in Figure 6 with the usual reservations concerning sensitivity to impurities. The effect of increasing tem-

<sup>25</sup> L. A. Burkardt, P. R. Hammond, R. H. Knipe, and R. R. Lake, *J. Chem. Soc. (A)*, 1971, 3789.

perature (−30 to 30 °C) on the benzene–SbCl<sub>5</sub> spectrum in carbon tetrachloride produces a small absorption decrease comparable to the expected change caused by solvent expansion. The change is not completely reversible, however, implying slight chemical reaction under the conditions of measurement. Similarly the octafluoronaphthalene system in carbon tetrachloride shows a fairly uniform, reversible decrease of 9.7%, which is more than compensated by the solvent expansion of 13.3% for a 0–56 °C temperature range. A net positive enthalpy of 110 cal mol<sup>−1</sup> is indicated.

Arsenic pentachloride, if it were to exist, should behave similarly to phosphorus and antimony pentachlorides in forming coloured solutions with donors, and could well be intermediate in acceptor properties. Moreover this should be a sensitive test for the compound. Thus according to the  $[A]/[D] = 0.01$  criterion<sup>25</sup> applied to 1.0M-hydrocarbon dissolved in pure arsenic trichloride, 0.04% conversion into AsCl<sub>5</sub> could be detected. Bubbling dry chlorine into arsenic trichloride solutions produces blue-violet and blue-green colours with naphthalene and 1-chloronaphthalene respectively. However the absorptions do not develop immediately, the mixtures are weakly exothermic, and maxima for unstable solutions in carbon tetrachloride at 575 nm for naphthalene and 635 nm for 1-chloronaphthalene are not in the order expected of the donor ionization potentials or in the order of their maxima with other acceptors. Behaviour of the arsenic trichloride solution of the AsCl<sub>5</sub>, PCl<sub>5</sub> adduct<sup>15a</sup> in giving yellow and orange solutions with naphthalene and anthracene respectively is identical to that of phosphorus pentachloride dissolved in AsCl<sub>3</sub>, whereas the reported behaviour of the AsCl<sub>5</sub>, SbCl<sub>5</sub> adduct towards benzene<sup>15a</sup> is the same as for free antimony pentachloride. We prefer to interpret our results as unstable chemical intermediates rather than as evidence for the existence of arsenic pentachloride. Bismuth pentachloride, if it were to exist, should be reactive chemically; moreover it should be a strong acceptor; even the trichloride interactions with aromatic donors are coloured.<sup>26</sup> Bismuth trichloride suspensions in dry benzene, hexafluorobenzene, or octafluorotoluene, in which it has limited solubility, produce no colour change with chlorine at ambient, elevated, or reduced temperatures.

Intermolecular charge-transfer spectra cannot be established with the other Group VB species, namely trifluoramine oxide, phosphoryl fluoride, phosphorus pentafluoride, arsenic pentafluoride, and antimony pentafluoride. All are reactive towards  $\pi$ -donors, particularly the compounds of the heavier elements, and one product of reaction of antimony pentafluoride with octafluoronaphthalene is the green radical cation.<sup>27</sup> In terms of vertical electron affinities, antimony pentachloride is a stronger acceptor than phosphorus pentachloride; also, the chlorine acceptors are stronger than the fluorine.

<sup>25</sup> S. Buffagni, I. M. Veyzosi, and G. Peyronel, *Gazzetta*, 1968, 98, 156.

## APPENDIX

*Influence of Molecularity and Concentration Inequality of the Components on Continuous-variation Curves.*—Job showed<sup>28</sup> that for the equilibrium (3), where the com-



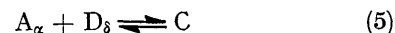
ponents A and D prepared in separate solutions at concentrations  $a$  and  $d$  of simple species associate to  $A_\alpha$  and  $D_\delta$ , the condition that the maximum of the continuous-variation curve should be independent of  $a$  and  $d$  is that  $[A_\alpha] = [D_\delta]$ . First the concentrations should be considered only in terms of the associated species present, and secondly these concentrations should be equal.

For weakly interacting non-self-associating components (the major interest of these papers) continuous-variation curves for 1:1 systems obey equation (4)

$$A = \frac{K\epsilon b^2 m(1-m)}{(1+Kb)} \quad (4)$$

where  $b$  is the combined acceptor plus donor concentration ( $a_0 = d_0 = b$  the concentrations at the extremes of the composition axis), and where  $m$  volumes of  $a_0$  are mixed with  $(1-m)$  volumes of  $d_0$ .

We examine deviations from the curve under the conditions of self-association and concentration inequality for small  $K$ . For a self-associating, weakly interacting system we obtain equation (5); contact of



one molecular aggregate of the acceptor with one donor aggregate should be sufficient to permit an intermolecular transition, and this will be the species monitored. Here  $a = mb$  and  $d = (1-m)b$  are prepared under the false assumption that A and D are monomeric in solution and where no further complication of the form  $A_\alpha \rightleftharpoons \alpha A$  apply, leading to equation (6) where  $c$

$$K_1 = \frac{c}{(mb/\alpha - c)[(1-m)b/\delta - c]} \quad (6)$$

is the concentration of complex. Neglecting terms in  $c^2$ , and substituting  $A_1/\epsilon_1$  for  $c$  (or, when the pathlength  $l$  is greater than 1 cm,  $\epsilon_1 l$  for  $\epsilon_1$ ), we obtain equation (7).

$$A_1 = \frac{K_1 \epsilon_1 m(1-m)b^2}{\alpha \delta [1 + K_1 b(m/\alpha + (1-m)/\delta)]} \quad (7)$$

Apart from the constants in equation (7), deviations from a parabolic curve are in the form (8). Alternatively

$$\frac{A_1}{A} = \frac{(1+Kb)}{[1 + K_1 b(m/\alpha + (1-m)/\delta)]} \quad (8)$$

for a 1:1 monomeric system prepared by mixing a volume  $m$  of concentration  $a_0$  with  $(1-m)$  of unequal concentration  $d_0$ , where  $d_0 = \rho a_0$ , we obtain equation (9)

<sup>27</sup> N. M. Bazhin, N. E. Akmetova, L. V. Orlova, V. D. Shteingarts, L. N. Shchegoleva, and G. G. Yakobson, *Tetrahedron Letters*, 1968, 4449.

<sup>28</sup> P. Job, *Ann. Chim. (Paris)*, 1928, 9, 113.

$$K = \frac{c}{(ma_0 - c)[(1 - m)\rho a_0 - c]} \quad (9)$$

and in a similar manner, equating  $a_0 = b_2$ , equation (10).

$$A_2 = \frac{K\epsilon m(1 - m)\rho b_2^2}{\{1 + Kb_2[(1 - m)\rho + m]\}} \quad (10)$$

Apart from constants in equation (10), deviations from a parabolic curve are in the form (11). For the

$$\frac{A_2}{A} = \frac{(1 + Kb)}{\{1 + Kb_2[(1 - m)\rho + m]\}} \quad (11)$$

very weak interactions studied here, where the conditions  $K = 0.2 \text{ l mol}^{-1}$ ,  $b = 0.02\text{M}$  are typical, or even for much larger  $K$  values, deviations of equations (8) and (11) from unity are very small so that the curves (7) and (10) are hardly distinguishable from (4). Thus even if there is self-association or concentration inequality in a weakly interacting 1 : 1 system examined on the false assumption of monomeric species or of equality, there will be little detectable variation from a 1 : 1 parabolic curve.

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