113. *The Liquid Hydrogen Chloride Solvent System. Part IV.*[1] *Reactions of Some Compounds Containing Multiple Bonds.*

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The reactions and conductivities of some compounds containing olefin, acetylene, nitrile, carbonyl, and azo-groups have been studied. These compounds act as solvobases, and some reactions with the solvoacid boron trichloride have been investigated. Evidence for the formation of the carbonium ions Ph_2MeC^+ and $PhMeC^{2+}$ has been found, as well as for the protonation of other species.

This paper concerns, first, compounds in which carbon forms a double or triple bond with carbon, nitrogen, or oxygen and, secondly, compounds containing a nitrogen–nitrogen double bond. Singly charged carbonium ions of the type Ph_2MeC^+ have previously been reported in concentrated sulphuric acid solutions of 1,1-diphenylethylene.[2] The doubly charged ion $(C_6Me_5)ClC^{2+}$ has also been prepared from pentamethyltrichloromethylbenzene in concentrated sulphuric acid.[3] Extensive investigations of the phase diagrams of hydrogen chloride with olefins, acetylenes, aromatic hydrocarbons,[4] and nitriles[5] reveal that all these compounds form addition products with hydrogen chloride; many of these can be formulated in terms of protonated species and solvated chloride ions, $Cl(HCl)_x^-$. The infrared spectra of hydrogen halides in acetonitrile indicate that the compounds MeCN,2HHal have two distinct structures, $Me{\cdot}C{\equiv}NH^+HCl_2^-$ and $MeBrC{=}NH_2^+Br^-$.[6] In sulphuric acid, carbonyl compounds act as strong bases, forming, by protonation, ions of the type $RR'C{=}OH^+$.[7] The same basic properties have been found in acids and esters, although the latter usually undergo solvolysis; from amides, the hydrochlorides[8] are formed by protonation of the nitrogen, not the oxygen, *e.g.*, $Me{\cdot}CO{\cdot}NH_3^+Cl^-$. Conductivity measurements in liquid hydrogen chloride reported in this paper show that these doubly bonded compounds are invariably protonated in

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[1] Part III, Peach and Waddington, *J.*, 1961, 1238.

[2] Gold and Tye, *J.*, 1952, 2172.

[3] Hart and Fish, *J. Amer. Chem. Soc.*, 1958, **80**, 5894.

[4] Cook, Lupien, and Schneider, *Canad. J. Chem.*, 1956, **34**, 957, 964.

[5] Murray and Schneider, *Canad. J. Chem.*, 1955, **33**, 797.

[6] Janz and Danyluk, *J. Amer. Chem. Soc.*, 1959, **81**, 3846, 3850, 3854.

[7] Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 58.

[8] Kahovec and Knollmüller, *Z. phys. Chem.*, 1941, *B*, **51**, 49.

solution. However, reaction with boron trichloride in the solvent often produces, not the tetrachloroborate, but the adduct, a proton being expelled from the compound. The exceptions are 1,1-diphenylethylene, which is protonated to give Ph_2MeC^+, and phenylacetylene, which is doubly protonated to give $PhMeC^{2+}$; neither of these gives adducts with boron trichloride.

The reactions of various compounds containing azo-bonds are also discussed below. These compounds again contain π-bond systems, which might be protonated. Azobenzene is known to form a yellow compound with hydrogen chloride.[9] These protonated azo-compounds have been stabilised as tetrachloroborates, and their infrared spectra examined.

EXPERIMENTAL

The apparatus and techniques used have been described previously.[1] The main technique used was conductimetric titration: after titration of the materials with boron trichloride the solvent and the excess of boron trichloride were removed at $-80°$. The residue was then allowed to warm to room temperature and the amount of gas evolved measured: this is expressed in moles per mole of starting material.

Chloride was determined by the Volhard method or gravimetrically, and boron acidimetrically as the mannitol–borate complex: carbon, hydrogen, and nitrogen were determined by combustion. Molecular weights of involatile materials were determined by the lowering of the vapour pressure of methylene dichloride.

Infrared measurements were made on a Perkin–Elmer 21 double-beam continuously recording spectrophotometer with rock salt, fluorite, or potassium bromide optics.

Conductivities.—These results are shown in Table 1.

TABLE 1.

Specific and molar conductances of compounds in liquid hydrogen chloride at $-95°$.

Compound	Concn. (mole/l.)	Spec. conductance (ohm^{-1} cm.$^{-1}$)	Molar conductance (ohm^{-1} cm.$^{-1}$)	Compound	Concn. (mole/l.)	Spec. conductance (ohm^{-1} cm.$^{-1}$)	Molar conductance (ohm^{-1} cm.$^{-1}$)
$PhHC{=}CH_2$	0·36	$1{\cdot}65 \times 10^{-5}$	0·046	Me·CHO ...	Satd.	$1{\cdot}6 \times 10^{-6}$	—
$Ph_2C{=}CH_2$	0·37	$0{\cdot}65 \times 10^{-3}$	1·77	Ph·CHO ...	,,	$1{\cdot}81 \times 10^{-3}$	—
$PhC{\equiv}CH$	0·37	$0{\cdot}28 \times 10^{-3}$	0·74	$Ph{\cdot}CO_2H$...	,,	$0{\cdot}37 \times 10^{-5}$	—
$PhC{\equiv}CPh$	Satd.	$0{\cdot}19 \times 10^{-4}$	—	$Ph{\cdot}CO_2Et$	0·33	$0{\cdot}32 \times 10^{-2}$	9·74
Anthracene......	,,	$0{\cdot}46 \times 10^{-4}$	—	Me_2CO ...	0·41	$0{\cdot}43 \times 10^{-2}$	10·4
MeCN	0·42	$1{\cdot}22 \times 10^{-3}$	2·94	Ph_2CO ...	0·25	$1{\cdot}81 \times 10^{-3}$	7·15
PhCN	0·30	$0{\cdot}43 \times 10^{-3}$	1·43	$Me{\cdot}CO{\cdot}NH_2$	Satd.	$1{\cdot}64 \times 10^{-3}$	—
PhN=NPh	Satd.	$0{\cdot}37 \times 10^{-3}$	—	$Ph{\cdot}CO{\cdot}NH_2$	0·23	$0{\cdot}80 \times 10^{-3}$	3·48
$(m\text{-}Me{\cdot}C_6H_4)_2N_2$	,,	$0{\cdot}22 \times 10^{-3}$	—	Ph·COCl ...	0·33	$1{\cdot}50 \times 10^{-5}$	0·046
PhN(O)=NPh ...	0·15	$0{\cdot}30 \times 10^{-3}$	1·97	Me·COCl ...	0·30	$0{\cdot}29 \times 10^{-5}$	0·0097
PhN(O)=N(O)Ph	Satd.	$1{\cdot}44 \times 10^{-3}$	—				

Olefins and Acetylenes.—Styrene was soluble, giving a colourless solution from which a colourless liquid was isolated at $-95°$. This gave analyses for a phenylethyl chloride (Found: C, 70·3; H, 6·4. Calc. for C_8H_9Cl: C, 68·4; H, 6·4%). The infrared spectrum, when compared with that of phenethyl bromide, showed it to be α-methylbenzyl chloride; this is known to lose hydrogen chloride fairly readily with the formation of styrene and polymerised styrene. Titration with boron trichloride was valueless as the conductivity was low and time-variable: however the solution became increasingly yellow as the boron trichloride was added. A yellow liquid product was obtained at $-80°$ which changed to red on warming to room temperature, giving off less than 0·1 mol. of boron trichloride; the product was shown by its infrared spectrum to be α-methylbenzyl chloride.

1,1-Diphenylethylene was fairly soluble in liquid hydrogen chloride, giving a moderately conducting red-brown solution. In a titration with boron trichloride (Fig. 1) a sharp break was observed when the molar ratio was 1·0 : 1·0, suggesting that the reactions occurring are:

$$Ph_2C{=}CH_2 + 2HCl \longrightarrow Ph_2MeC^+ + HCl_2^-$$

$$Ph_2MeC^+ + HCl_2^- + BCl_3 \longrightarrow Ph_2MeC^+ + BCl_4^- + HCl$$

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[9] Rodd, "Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1954, Vol. IIIA, p. 330.

After titration a red solid was obtained on removal of the solvent and excess of boron trichloride at $-95°$, but this decomposed at room temperature, evolving hydrogen chloride and boron trichloride and leaving a trace of green liquid.

Phenylacetylene dissolved to a deep-red conducting solution. In a conductimetric tiration against boron trichloride (Fig. 2) a break was observed when the molar ratio was 2·1 : 1·0 (BCl_3:Ph·C≡CH), suggesting that the following reactions occur:

$$\mathrm{PhC{\equiv}CH} + 4\mathrm{HCl} \longrightarrow \mathrm{PhMeC}^{2+} + 2\mathrm{HCl_2}^-$$

$$\mathrm{PhMeC}^{2+} + 2\mathrm{HCl_2}^- + 2\mathrm{BCl_3} \longrightarrow \mathrm{PhMeC}^{2+} + 2\mathrm{BCl_4}^- + 2\mathrm{HCl}$$

The red solid product obtained on removal of the solvent decomposed at room temperature to a tar, with evolution of hydrogen chloride and boron trichloride. Evaporating a solution of phenylacetylene afforded an unstable monomeric liquid at room temperature, probably 1,1-dichloro-2-phenylethane, which slowly became tarry (Found: *M*, 185. Calc. for $C_8H_8Cl_2$: *M*, 174). The infrared spectrum showed loss of the C≡C frequency at 2100 cm.$^{-1}$ and new peaks in the C–Cl stretching region (800—700 cm.$^{-1}$).

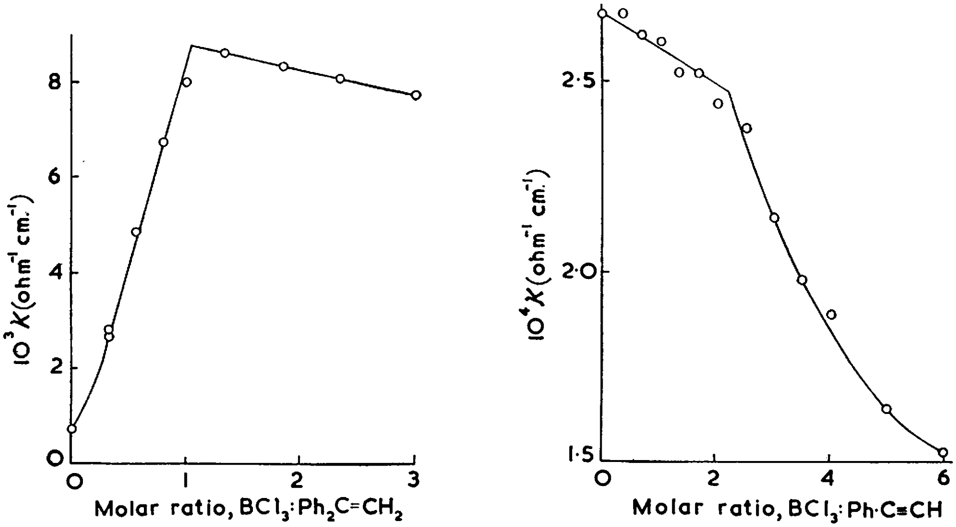

FIG. 1.

FIG. 2.

FIGS. 1 AND 2. Conductimetric titration of (Fig. 1) 0·37M-$Ph_2C{:}CH_2$ and (Fig. 2) 0·37M-Ph·C⋮CH with BCl_3.

Diphenylacetylene was sparingly soluble. Initially a yellow solution was formed, but this gradually became deep red. Analysis of the liquid product indicated a mixture of unchanged starting material and a chloro-olefin.

Nitriles.—Acetonitrile, when freshly distilled from phosphorus pentoxide, dissolved to a colourless solution. In a titration against boron trichloride precipitation occurred as the acid was added; however, the curve showed a sharp break when the molar ratio was 1·0 : 1·0. The white solid product was the acetonitrile–boron trichloride adduct (Found: B, 6·7; Cl, 66·7. Calc. for $C_2H_3BCl_3N$: B, 6·8; Cl, 67·2%). The infrared spectrum showed that the C≡N frequency had been modified from 2250 to 2400 cm.$^{-1}$.

Benzonitrile was reasonably soluble, giving a faintly purple solution. A conductimetric titration with boron trichloride showed a break when the molar ratio was 1·0 : 1·0 (Fig. 3). The solid product was the benzonitrile–boron trichloride adduct (Found: B, 4·7; Cl, 47·7. Calc. for $C_8H_5BCl_3N$: B, 4·9; Cl, 48·3%). The infrared spectrum showed a modified C≡N frequency at 2320 cm.$^{-1}$ (2220 cm.$^{-1}$ in benzonitrile), which is characteristic of the adduct.[10]

Compounds Containing Carbonyl Groups.—Acetaldehyde behaved as a fully ionised base in sulphuric acid.[7] It was insoluble in hydrogen chloride.

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[10] Gerrard, Lappert, Pysora, and Wallis, *J.*, 1960, 2182.

Benzaldehyde, again a strong base in sulphuric acid,[7] was sparingly soluble, probably forming an unstable hydrochloride: 1·3 moles of hydrogen chloride were given off when the product was warmed from −95° to 20°, leaving benzaldehyde. Owing to its complex reaction with boron trichloride giving $3Ph{\cdot}CHO,2BCl_3$, which pyrolyses to benzylidene dichloride,[11] this reaction was not studied in the solvent.

Acetone, another strong solvobase in sulphuric acid,[7] was readily soluble. In a titration with boron trichloride a sharp break was observed at molar ratio 1·0 : 1·0. The white solid obtained after removal of the solvent was the unstable boron trichloride adduct, Me_2CO,BCl_3, which is known to decompose readily [12] (Found: B, 6·1; Cl, 59·4. Calc. for $C_3H_6BCl_3O$: B, 6·1; Cl, 60·7%).

Benzophenone acted as a strong solvobase, as it does in sulphuric acid,[7] giving a colourless solution. After reaction with boron trichloride the adduct, Ph_2CO,BCl_3, was isolated (Found: B, 3·3; Cl, 34·0. Calc. for $C_{13}H_{10}BCl_3O$: B, 3·7; Cl, 35·5%). The product probably has the structure, $Ph_2ClC{\cdot}O{\cdot}BCl_2$, as this is obtained from the reaction of benzophenone and boron trichloride.[11]

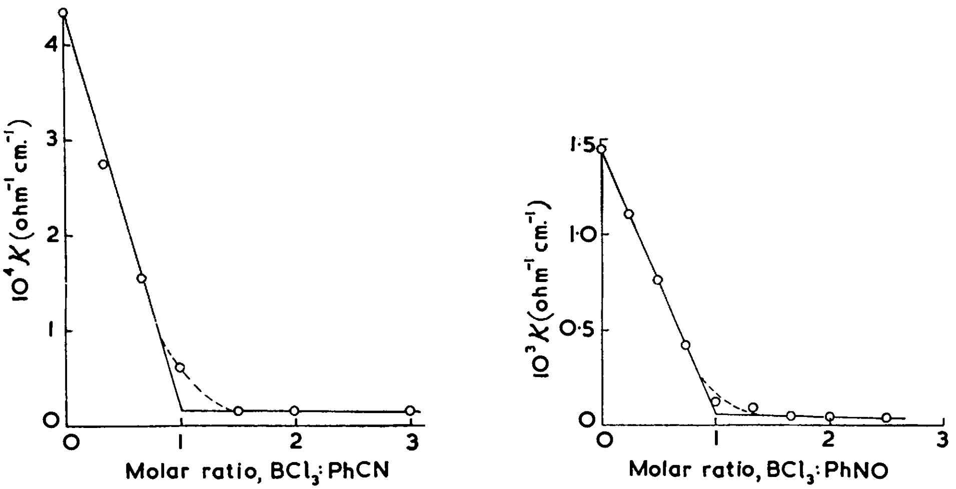

FIG. 3. FIG. 4.

FIGS. 3 AND 4. Conductimetric titration of (Fig. 3) 0·30M-PhCN and (Fig. 4) 0·29M-PhNO with BCl_3.

Benzoic acid has been reported [13] to have a high conductivity in liquid hydrogen chloride, but the present work showed it to be a poor conductor. There was no indication of solvolysis to benzoyl chloride; there might be some hydrochloride formation in the solvent, as 0·8 mol. of hydrogen chloride was given off when the solid obtained was warmed from −95° to 20°, and benzoic acid was recovered.

Acetamide, reported [14] to be a good conductor in liquid hydrogen chloride, was sparingly soluble, giving a white precipitate and a colourless solution. In a titration with boron trichloride further precipitation occurred, but there was a break when the molar ratio was 1·0 : 1·0. The white solid product was the acetamide–boron trichloride adduct [15] (Found: B, 5·6; Cl, 60·1. Calc. for $C_2H_5BCl_3NO$: B, 6·1; Cl, 60·4%). The infrared spectrum in the potassium bromide region had new peaks at 731, 775, and 802 cm.$^{-1}$; these have been assigned as B–Cl frequencies in the adduct.[16]

Benzamide dissolved to a colourless, highly conducting solution.

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[11] Fraser, Gerrard, and Lappert, *J.*, 1957, 739.
[12] Massey, *J.*, 1961, 1103.
[13] Archibald, *J. Amer. Chem. Soc.*, 1907, **29**, 1421.
[14] Walker, McIntosh, and Archibald, *J.*, 1904, **85**, 1098.
[15] Gerrard, Lappert, and Wallis, *J.*, 1960, 2141.
[16] Gerrard, Lappert, Pysora, and Wallis, *J.*, 1960, 2144.

Ethyl benzoate, previously found to be a fairly good conductor,[14] formed a colourless solution. In a reaction with boron trichloride the unstable adduct was isolated, which fumed in a dry box (Found: increase in wt., 75. Calc. for $C_9H_{10}BCl_3O$: increase in wt., 79%). The adduct is known to decompose readily.[17]

Acetyl chloride was readily soluble, acting as a weak base. With boron trichloride a white solid was obtained; this was almost certainly the adduct $Me{\cdot}COCl,BCl_3$, of unknown structure, m. p. −54°.[18]

Benzoyl chloride dissolved, to form a very poorly conducting colourless solution: as no reaction has been observed with boron trichloride,[18] this was not tried in the solvent.

Azo-compounds.—Azobenzene was incompletely soluble, giving a yellow solution and a similarly coloured precipitate. A conductimetric titration against boron trichloride showed a break at molar ratio 1·0 : 1·0; the yellow solid product isolated was *azobenzenium tetrachloroborate*, $Ph_2N_2H^+BCl_4^-$ (Found: B, 3·0; Cl, 41·6, 42·6; N, 9·1. $C_{12}H_{11}BCl_4N_2$ requires B, 3·2; Cl, 42·2; N, 8·4%). Its structure was confirmed by its infrared spectrum which showed BCl_4^- frequencies at 711 and 667 cm.$^{-1}$ (ref. 19) and $N-H^+$ frequencies at 3175 and 1399 cm.$^{-1}$.

m-Azotoluene (bright orange) was sparingly soluble, forming a yellow solution and an orange-yellow precipitate. The compound reacted with the solvent, to form a hydrochloride which fairly readily decomposed at room temperature. With boron trichloride in a titration a break was found when the molar ratio was 1·0 : 1·0. The yellow solid product was m-*azotoluenium tetrachloroborate* (Found: B, 2·6; Cl, 38·6; N, 8·2. $C_{14}H_{15}BCl_4N_2$ requires B, 3·0; Cl, 39·0; N, 7·7%). This very slowly lost hydrogen chloride, forming the adduct. The infrared spectrum showed BCl_4^- peaks at 706 and 673 cm.$^{-1}$ and a weak $N-H^+$ peak at 3175 cm.$^{-1}$.

Azoxybenzene was completely soluble, forming a brown yellow solution. The solid recovered on evaporation of the solvent was azoxybenzene (m. p. and infrared spectrum). No Wallach rearrangement, therefore, to *p*-hydroxyazobenzene has occurred, as it does in concentrated sulphuric acid. In a titration with boron trichloride precipitation started as soon as the solvoacid was added. The bright yellow, solid product was the *azoxybenzene–boron trichloride adduct* (Found: C, 47·0; B, 2·9; Cl, 33·7, 33·1. $C_{12}H_{10}BCl_3NO$ requires C, 45·7; H, 3·2; B, 3·4; Cl, 33·7%). The infrared spectrum showed B–Cl peaks at 799, 720, and 670 cm.$^{-1}$, but it was difficult to assign a B–O or a B–N frequency with certainty.

Nitrosobenzene was sparingly soluble, giving a yellow solution and yellow precipitate. After removal of the solvent a yellow solid was obtained: at room temperature 1·0 mol. of hydrogen chloride was evolved and the residue was a tar. This material was probably the hydrochloride $(PhNO,HCl)_x$ (Found: C, 47·8; H, 3·8; N, 10·2. Calc. for $C_6H_6ClN_2O$: C, 50·2; H, 4·2; N, 9·8%). In a titration with boron trichloride (Fig. 4) a red precipitate was formed and a sharp break observed when the molar ratio was 1·0 : 1·0. A yellow-orange product was obtained at −80°, but it was not possible to analyse this as it exploded just below room temperature.

DISCUSSION

Use of Conductimetric Titrations.—In Part III[1] it was shown that the ratio of the molar conductivity of the pure base and that at the equivalence point will indicate whether ions are present at the equivalence point or not. This can be extended to some of the present series of compounds, the conductivities of which are shown in Table 2; unfortunately precipitation occurred in many titrations, so little information can be obtained about the products in solution by this technique. It is again observed that when an adduct is formed in solution the curve is smooth in the 1 : 1 molar ratio region, as in Fig. 3.

Olefins and Acetylenes.—The colour of the solutions produced by these compounds is characteristic of the corresponding carbonium ions: yellow solutions are formed in sulphuric acid by the ions Ph_2MeC^+ and 9,10-dihydro-9-anthryl, and a red one by $(C_6Me_5)ClC^{2+}$. The conductimetric titrations indicate that the ions Ph_2MeC^+ and $PhMeC^{2+}$

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[17] Gerrard and Wheelans, *J.*, 1956, 4299.
[18] Greenwood and Wade, *J.*, 1956, 1527.
[19] Kynaston, Larcombe, and Turner, *J.* 1960, 1772.

are formed in the solvent from 1,1-diphenylethylene and phenylacetylene respectively: although there is only slight evidence that the ion $PhMeHC^+$ is formed from styrene, which does not appear to have been studied in sulphuric acid. Unfortunately these ions could not be isolated as solids at room temperature after reaction with boron trichloride.

TABLE 2.

Conductivities at 1 : 1 molar ratio for boron trichloride titrations.

Base	Λ of base (cm.² ohm⁻¹ mole⁻¹)	Λ at 1 : 1 ratio (cm.² ohm⁻¹ mole⁻¹)	Ratio Λ (base)/Λ (1 : 1)	Product in solution
$Ph{\cdot}C{\equiv}CH$ ...	0·72	0·68	1·06	$PhMeC^{2+},2BCl_4^-$
$Ph_2C{=}CH_2$ ...	1·77	23·8	0·074	Ph_2MeC^+,BCl_4^-
PhCN	1·43	0·052	27·5	$PhCN,BCl_3$
Me_2CO	10·4	1·83	5·7	Me_2COH^+,BCl_4^-

Nitriles.—As the hydrochloride of acetonitrile is well known,[6] it was hoped to be able to isolate the ion $Me{\cdot}C{=}NH^+$ as a tetrachloroborate, and further to investigate the structure. The nitriles were found to be strong solvobases and must undoubtedly form the ions $R{\cdot}C{=}NH^+$ in solution, but as soon as boron trichloride is added the adduct is formed:

$$RCN + 2HCl \longrightarrow R{\cdot}C{=}NH^+ + HCl_2^-$$

$$R{\cdot}C{=}NH^+ + HCl_2^- + BCl_3 \longrightarrow RCN,BCl_3 + 2HCl$$

This difficulty had previously been encountered with ethers, thiols., etc.[1].

Carbonyl Compounds.—It was not possible to isolate a solid compound containing a protonated carbonyl group, $RR'C{=}OH^+$. The high conductivity of benzaldehyde, acetone, benzophenone, and ethyl benzoate indicates that ions of this type must be formed in solution. The amides also form highly conducting solutions and have been shown to form hydrochlorides by protonation of the nitrogen [8] but to react with boron trichloride to give adducts with structures $H_2N{\cdot}CR{=}O,BCl_3$.[16]

Acetyl chloride can function as a volatile weak base by loss of a chloride ion to give the acetylium ion, $Me{\cdot}CO^+$. The absence of solvolysis of benzoic acid to benzoyl chloride is not surprising as it is readily protonated in sulphuric acid.[7]

Azo-compounds.—The simple azo-compounds are known to form somewhat unstable hydrochlorides,[9] and the protonated species has been stabilised as the tetrachloroborate. The infrared spectra of these compounds have been examined, but it is impossible to say whether the proton is attached to one nitrogen atom or to the π-bond system. Azoxy-compounds form adducts with boron trichloride, presumably with a B–O bond, and not tetrachloroborates, so further extension of the azo-system is impossible.

Nitrosobenzene exists in the solid state as the *cis*-dimer and with concentrated sulphuric acid gives *p*-nitrosodiphenylhydroxylamine.[20] A hydrochloride of nitrosomethane of empirical formula MeNO,HCl is known, but its structure is not.[21] The reactions of nitrosobenzene in the solvent are uncertain; it forms a hydrochloride and, with boron trichloride, a compound of empirical formula $PhNO,BCl_3(HCl)_x$. Whether these are derivatives of the monomer or the dimer is not known.

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[20] Gowenlock and Lüttke, *Quart. Rev.*, 1958, **12**, 321.
[21] Kharasch, Meltzer, and Nudenberg, *J. Org. Chem.*, 1957, **22**, 37.