Aluminium(III) Chloride–Chlorohydrocarbon Chemistry. Fourier Transform Infra-red Spectroscopic Studies of the Reactions between Solid Aluminium(III) Chloride and 1,1,1-Trichloroethane or 1,1-Dichloroethene Vapours†

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The reactions of 1,1,1-trichloroethane and 1,1-dichloroethene vapours with solid aluminium(III) chloride have been studied using Fourier-transform i.r. spectroscopy to determine stoicheiometries as a function of time. Dehydrochlorination of 1,1,1-trichloroethane to give 1,1-dichloroethene and hydrogen chloride appears to be the only important process in the initial stage of the reaction, but the 1,1-dichloroethene formed reacts with the solid phase and the main product is a mixture of involatile chlorohydrocarbon species. The quantity of hydrogen chloride evolved indicates that the involatile material is highly unsaturated and in both reactions $AlCl_3$ becomes progressively coated with a strongly purple-coloured tar. Small quantities of carbon tetrachloride are also produced in both reactions.

A major use of 1,1,1-trichloroethane is in the large-scale vapour degreasing of metals, for example aluminium and its alloys. In this application inhibitors are added to CH_3CCl_3 in order to prevent unwanted degradation and corrosion. These processes have been attributed to aluminium(III) chloride-catalysed dehydrochlorination of CH_3CCl_3 followed by catalytic oligomerisation of the dehydrochlorinated product.[1] However, the catalytic action of $AlCl_3$ is not well understood for two main reasons. First, the solubility of $AlCl_3$ in non-complexing solvents is low and multi-phase reaction systems are normally observed. Secondly, it is difficult to study the reactions of $AlCl_3$ with organic compounds in the absence of trace quantities of water or hydrogen chloride, both of which are frequently reported to modify its catalytic properties.

The present work was undertaken to elucidate the role of $AlCl_3$ in its behaviour towards CH_3CCl_3. Although reactions between $AlCl_3$ and CH_3CCl_3 or related compounds have been well studied,[2,3] the main emphasis has been on product isolation, either from homogeneous solution-phase systems or from more complicated multi-phase systems. There is evidence that heterogeneous phenomena are important but apparently no studies have been reported of the reactions between gaseous CH_3CCl_3 or 1,1-dichloroethene and solid $AlCl_3$.

It is generally believed that $AlCl_3$-catalysed dehydrochlorination of CH_3CCl_3 produces $CH_2{=}CCl_2$ and HCl in a 1:1 molar ratio but this has apparently never been verified experimentally. In the present work Fourier-transform i.r. spectroscopy has been used to determine how the composition of the vapour above solid $AlCl_3$ varies during the dehydrochlorination and subsequent reactions and to obtain some information concerning the nature of the surface after exposure to CH_3CCl_3 or $CH_2{=}CCl_2$.

Results and Discussion

When 1,1,1-trichloroethane or 1,1-dichloroethene vapour was exposed to freshly sublimed, solid aluminium(III) chloride at room temperature the observed behaviour was the same in each case. Rapid reactions occur with the immediate formation of a purple material at the $AlCl_3$ surface. The observations made are summarised in the flow diagrams, Figures 1 and 2, and pressure *vs.* time relationships for CH_3CCl_3, $CH_2{=}CCl_2$, and HCl are illustrated in Figures 3 and 4. Selected vapour composition data are given in Tables 1 and 2.

The formation of the purple material is not unexpected in view of the results from previous studies carried out under multi-phase conditions,[1,2] However the large quantities of HCl produced from the reactions between CH_3CCl_3 and $AlCl_3$, Table 1, greater than can be accounted for solely from the dehydrochlorination of CH_3CCl_3 to give $CH_2{=}CCl_2$, are unexpected. Also unexpected is the observation of carbon tetrachloride, albeit as a minor product, from both reactions, Tables 1 and 2, indicating that C–C bond fission occurs. There is no evidence from i.r., g.c.–i.r., or g.c.–m.s. studies for the formation of methane, methyl chloride, or any other C–C fission product, suggesting that the species co-produced with CCl_4 is not volatile. Neither CCl_4 nor other C_1 species have been observed previously from reactions carried out in solution.[2]

In both reactions the major route for consumption of $CH_2{=}CCl_2$ leads to the formation of purple material which appears to be polymeric. Its formation is accompanied by HCl evolution; hydrochlorination of $CH_2{=}CCl_2$ to give CH_3CCl_3 is observed also but is relatively unimportant, Table 2. There is no evidence for monochloroethyne, indicating either that HCl is produced by dehydrochlorination of an involatile species derived from $CH_2{=}CCl_2$ or that $HC{\equiv}CCl$ undergoes further reaction very rapidly.

In order to obtain spectroscopic information about the nature of the purple material *in situ* techniques are necessary since it cannot be obtained free of $AlCl_3$ and exposure of the supported material to moist air leads to the colour being discharged. A secondary ion mass spectrometry (s.i.m.s.) analysis of $AlCl_3$ whose surface has been exposed to CH_3CCl_3 vapour shows the presence of the fragment ions CCl^+, C_3H^+, $C_4H_3{}^+$, $C_6H_2{}^+$, and $C_6H_3{}^+$, consistent with the presence of organic species. Fragment ions detected from $AlCl_3$ under comparable conditions are $Al(OH)^+$, Al_2O^+, $Al_2O_2H^+$, Al_2OCl^+, and $Al_2OCl_2{}^+$.

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† *Non. S.I. unit employed:* Torr ≈ 133 Pa.

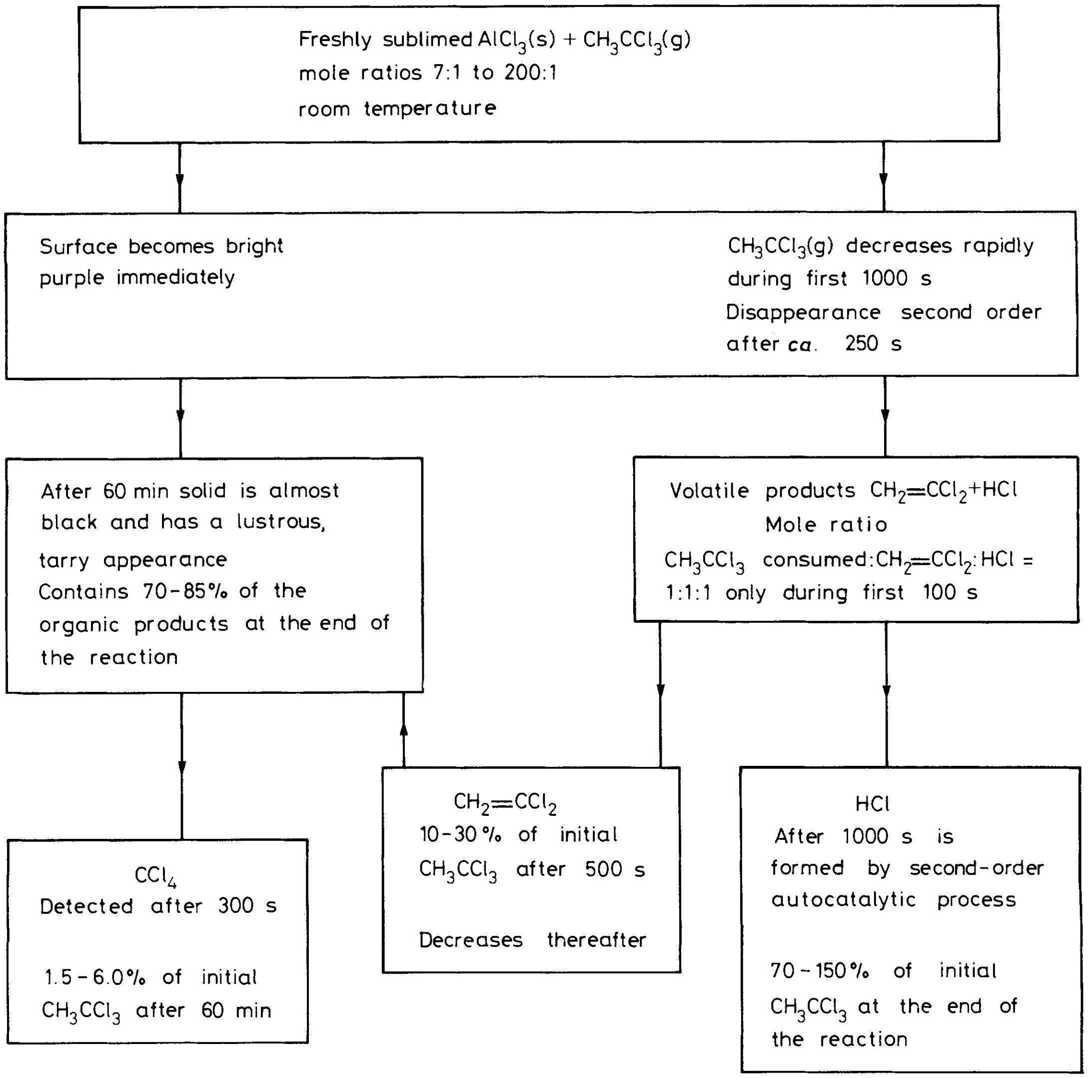

Figure 1. The reaction of 1,1,1-trichloroethane vapour with solid aluminium(III) chloride at room temperature

The results of d.r.i.f.t.s. (diffuse-reflectance i.r. Fourier-transform spectroscopy) studies on an $AlCl_3$ surface before and after treatment with CH_3CCl_3 or $CH_2{=}CCl_2$ are given in Table 3. It is clear from the spectrum, *cf.* ref. 4, that the $AlCl_3$ surface is partially hydrated, presumably due to incomplete removal of adsorbed water from the cell walls. Subsequent formation of the purple material is still rapid. The striking feature of the spectra of $AlCl_3$ surfaces that have been exposed to CH_3CCl_3 or $CH_2{=}CCl_2$ is that they are rather similar to those of the free molecules,[5,6] suggesting that these species are adsorbed on the surface. Removal of the purple surface layer formed after prolonged exposure of $AlCl_3$ to $CH_2{=}CCl_2$ exposes a black, tarry material. Its i.r. spectrum, Table 3, suggests that the new surface exposed is highly unsaturated and its spectrum is similar to that of black, dehydrochlorinated poly(1,1-dichloroethene).[7]

The transmission i.r. spectrum of purple material obtained by exposure of $AlCl_3$ to CH_3CCl_3 and blown onto a KBr window during the reaction is very similar to those in Table 3 but contains additional bands in the region 800—400 cm^{-1}. Five bands between 690 and 580 cm^{-1} are in the region expected for ν(Al–C) and CH_2 modes by analogy with the spectrum of solid triethylaluminium[8] and a band at 480 cm^{-1} may be due to the $AlCl_4^-$ anion.[9]

The reaction of $AlCl_3$ with $CH_2{=}CCl_2$ has been studied previously under conditions where liquid $CH_2{=}CCl_2$ and both solid and dissolved $AlCl_3$ were present.[2] A bright violet colour was observed at −50 to −80 °C after 30—60 h. The products detected were 1,1,3,3,5,5-hexachlorocyclohexane and a species claimed to be $CCl_2{=}CHCCl_2CH_3$. Formation of 2,4,4,4-tetrachlorobut-1-ene has been reported from a mixture of $AlCl_3$ and $CH_2{=}CCl_2$ that was allowed to react at −23 °C for 8 h.[3] In this instance the results can be accounted for by assuming that $AlCl_3$ in solution exists as dimeric Al_2Cl_6 molecules in equilibrium with small concentrations of the ions $AlCl_2^+$ and $AlCl_4^-$. The cation reacts with $CH_2{=}CCl_2$ to generate a carbocation, $Cl_2AlCH_2CCl_2^+$, which undergoes reaction with further $CH_2{=}CCl_2$. This hypothesis is consistent both with the known behaviour of $AlCl_3$ in alkyl halide solution, and with the mechanism suggested for the $AlCl_3$-catalysed polymerisation of isobutene in isobutyl chloride.[10]

The same hypothesis accounts for the observations made in the present work, assuming also that adsorption of $CH_2{=}CCl_2$ at a co-ordinatively unsaturated surface aluminium(III) site of $AlCl_3$ is followed by reconstruction of the surface to form a carbocation leading to polymerisation of $CH_2{=}CCl_2$. Depending on the degree of surface coverage by $CH_2{=}CCl_2$, the overall order of the reaction could, in principle, have any value between

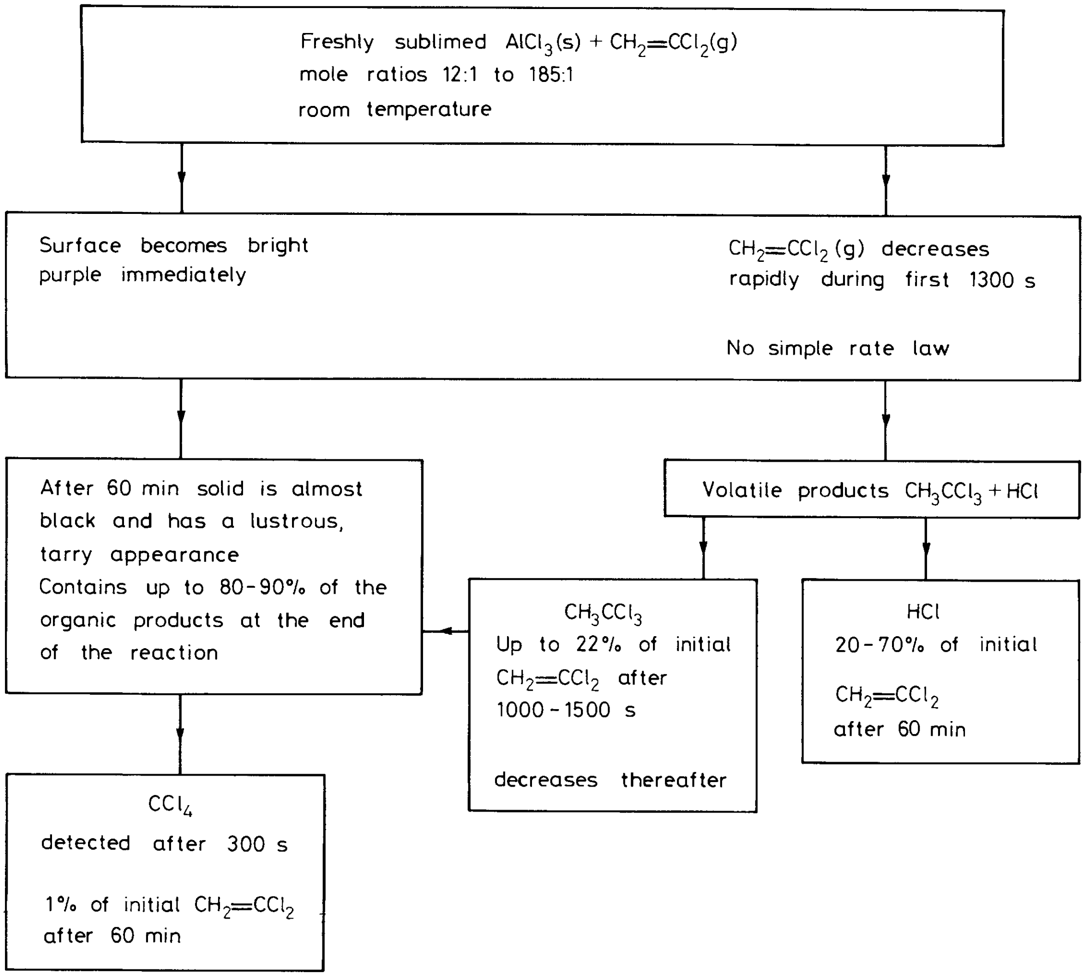

Figure 2. The reaction of 1,1-dichloroethene vapour with solid aluminium(III) chloride at room temperature

zero and two. This appears to be the situation in the reaction of $CH_2=CCl_2$, Figure 2, for which the kinetics will be further complicated by the hydrochlorination of $CH_2=CCl_2$. In the reactions derived from CH_3CCl_3 it is likely that CH_3CCl_3 and $CH_2=CCl_2$ compete for the same surface site, and since the pressure of the former is greater the surface coverage of $CH_2=CCl_2$ might be very small. Under these circumstances the expected overall second-order kinetics for the reaction is observed, Figure 1.

Carbon tetrachloride is formed following the formation of the purple material, presumably by dealkylation of oligomers derived from $CH_2=CCl_2$. The $AlCl_3$-catalysed alkylation of 1,1,2,3,4,5,5-heptachloropropene is known to be reversible[11] and C–C bond fission is a minor reaction in alkane isomerisations[12] and oligomer polymerisation,[13] catalysed by $AlCl_3$. The addition of CCl_4 to polybuta-1,2-dienes, which is catalysed by tris(triphenylphosphine)ruthenium(II) chloride,[14] also indicates that it is possible to alkylate long-chain, unsaturated polymers. In the present case the nature of the catalyst is not known but it is likely to be $AlCl_2^+$ or a co-ordinatively unsaturated aluminium(III) site.

The behaviour of CH_3CCl_3 and $CH_2=CCl_2$ towards $AlCl_3$ is affected markedly by the pretreatment given to the latter; in particular freshly sublimed $AlCl_3$ is required to produce reactions that have the short time-scale shown in Figures 3 and 4. The d.r.i.f.t.s. (Table 3) and s.i.m.s. experiments indicate that an $AlCl_3$ surface is hydrated readily; even minimal manipulation of a sample in contact with Pyrex or stainless steel results in a partially hydrated surface.

Water vapour has an inhibiting effect on the reactions judging from the different behaviour observed when the reaction of $CH_2=CCl_2$ vapour with $AlCl_3$ was studied by monitoring the change in the total vapour pressure with time. In these experiments $AlCl_3$ was contained in Pyrex and was pumped *in situ* overnight before admission of $CH_2=CCl_2$. In all cases the reactions were relatively slow and were preceded by an induction period, 13—350 min, the length of which was unrelated to the initial pressure, and during which the surface became pale purple. There was little change in pressure over this period. The onset of reaction resulted in a rapid pressure decrease followed by a rapid increase, pressure changes thereafter being less marked. When no further change in pressure was observed, normally after 3—5 h, the solid was dark purple. The vapour above the solid at this stage was predominantly HCl and all $CH_2=CCl_2$ appeared to have been consumed.

In conclusion, the purple material which is the main visual feature of these reactions, is unlikely to be a single species as has often been assumed in previous work. One constituent is a mixture of highly unsaturated oligomers, formally derived from $CH_2=CCl_2$, together with adsorbed CH_3CCl_3 or $CH_2=CCl_2$. Aluminium(III) chloride is present as solid particles coated with organic material. The formation of a carbocation containing an Al–C bond can account for the

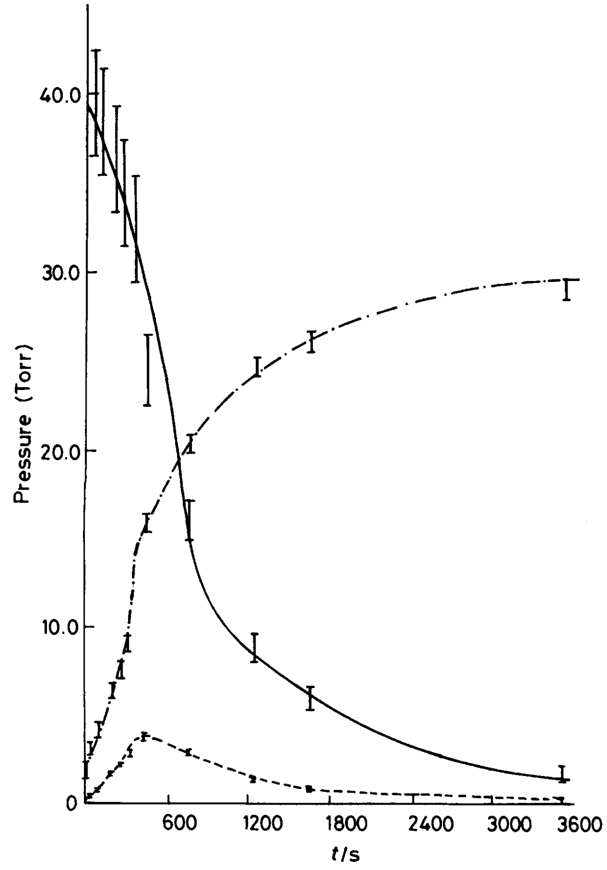

Figure 3. Variations in partial pressures of 1,1,1-trichloroethane(——), 1,1-dichloroethene (– – – –), and hydrogen chloride (— · — · —) with time in the reaction of 1,1,1-trichloroethane at solid aluminium(III) chloride

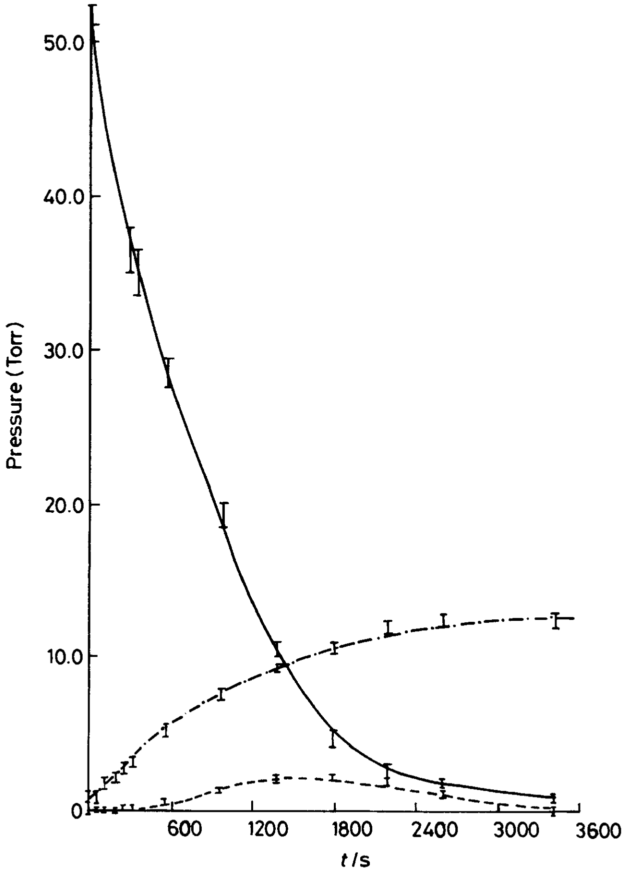

Figure 4. Variations in partial pressures of 1,1-dichloroethene (——), 1,1,1-trichloroethane (— — —), and hydrogen chloride (— · — · —) with time in the reaction of 1,1-dichloroethene at solid aluminium(III) chloride

Table 1. Stoicheiometries of the vapour phase[a] at various points in the reaction of 1,1,1-trichloroethane at solid aluminium(III) chloride

		Experiment			
		1	2	3	4
Initial CH_3CCl_3[b]	Torr	8.0 ± 0.5	39.8 ± 0.5	52.6 ± 0.5	65.3 ± 0.5
	mmol	0.023 ± 0.002	0.115 ± 0.002	0.152 ± 0.002	0.189 ± 0.002
First observation CH_2=CCl_2	Torr	1.2 ± 0.3	0.14 ± 0.01	6.9 ± 0.2	4.4 ± 0.2
	mmol	0.003 ± 0.001	0.0004 ± 0.0003	0.020 ± 0.0006	0.013 ± 0.0006
First observation HCl	Torr	1.2 ± 0.3	2.0 ± 0.5	6.3 ± 0.6	2.0 ± 0.5
	mmol	0.003 ± 0.001	0.006 ± 0.002	0.018 ± 0.002	0.006 ± 0.002
Maximum CH_2=CCl_2	Torr	3.1 ± 0.3	3.8 ± 0.2	10.3 ± 0.3	6.6 ± 0.2
	mmol	0.009 ± 0.0009	0.011 ± 0.0005	0.030 ± 0.001	0.019 ± 0.0006
CH_3CCl_3 at max. CH_2=CCl_2	Torr	1.7 ± 0.2	24.4 ± 1.9	27.5 ± 2.6	28.2 ± 2.6
	mmol	0.005 ± 0.0006	0.071 ± 0.006	0.080 ± 0.008	0.082 ± 0.008
HCl at max. CH_2=CCl_2	Torr	Not	15.9 ± 0.5	42.2 ± 0.5	25.2 ± 0.6
	mmol	obtained	0.046 ± 0.002	0.122 ± 0.002	0.073 ± 0.002
Final CH_3CCl_3	Torr	1.2 ± 0.2	1.8 ± 0.2	5.9 ± 0.5	17.8 ± 1.7
	mmol	0.003 ± 0.0005	0.005 ± 0.0006	0.017 ± 0.002	0.052 ± 0.005
Final HCl	Torr	8.0 ± 0.2	28.8 ± 0.5	83.3 ± 0.5	72.3 ± 0.5
	mmol	0.023 ± 0.0006	0.084 ± 0.002	0.242 ± 0.002	0.210 ± 0.002
Final CH_2=CCl_2	Torr	2.9 ± 0.3	0.26 ± 0.01	7.0 ± 0.2	5.4 ± 0.2
	mmol	0.008 ± 0.0008	0.0007 ± 0.0001	0.020 ± 0.0006	0.016 ± 0.0006
Final CCl_4	Torr	<0.5	<1.0	<1.5	<1.0
	mmol	<0.0015	<0.0029	<0.0043	<0.0029

[a] Determined by Fourier-transform i.r. spectroscopy. [b] Before admission of aluminium(III) chloride.

Table 2. Stoicheiometries of the vapour phase[a] at various points in the reaction of 1,1-dichloroethene at solid aluminium(III) chloride

		Experiment			
		1	2	3	4
Initial $CH_2{=}CCl_2$[b]	Torr	8.3 ± 0.5	24.5 ± 0.5	49.5 ± 0.5	51.6 ± 0.5
	mmol	0.024 ± 0.002	0.071 ± 0.002	0.144 ± 0.002	0.150 ± 0.002
First observation CH_3CCl_3	Torr	0.05 ± 0.01	0.6 ± 0.05	0.8 ± 0.07	0 ± 0.01
	mmol	0.0001 ± 0.0002	0.002 ± 0.0002	0.002 ± 0.0002	0 ± 0.0002
First observation HCl	Torr	0 ± 0.2	2.8 ± 0.6	0 ± 0.5	0.6 ± 0.5
	mmol	0 ± 0.0006	0.008 ± 0.001	0 ± 0.001	0.002 ± 0.001
Maximum CH_3CCl_3	Torr	1.9 ± 0.2	1.8 ± 0.2	2.6 ± 0.2	2.3 ± 0.2
	mmol	0.006 ± 0.0006	0.005 ± 0.0006	0.008 ± 0.0006	0.007 ± 0.0006
$CH_2{=}CCl_2$ at max. CH_3CCl_3	Torr	2.2 ± 0.2	5.8 ± 0.2	10.0 ± 1.0	6.5 ± 0.2
	mmol	0.006 ± 0.0006	0.017 ± 0.001	0.029 ± 0.003	0.019 ± 0.001
HCl at max. CH_3CCl_3	Torr	1.8 ± 0.4	8.5 ± 0.5	Not	11.0 ± 1.1
	mmol	0.005 ± 0.001	0.025 ± 0.001	obtained	0.032 ± 0.003
Final $CH_2{=}CCl_2$	Torr	1.0 ± 0.2	4.3 ± 0.2	4.4 ± 0.2	1.1 ± 0.04
	mmol	0.003 ± 0.0006	0.012 ± 0.0006	0.013 ± 0.0006	0.012 ± 0.0001
Final HCl	Torr	3.6 ± 0.2	10.1 ± 0.5	35.1 ± 0.5	12.3 ± 0.7
	mmol	0.010 ± 0.0006	0.029 ± 0.001	0.102 ± 0.001	0.036 ± 0.001
Final CH_3CCl_3	Torr	1.4 ± 0.2	1.5 ± 0.2	1.0 ± 0.1	1.0 ± 0.1
	mmol	0.004 ± 0.0005	0.004 ± 0.0005	0.003 ± 0.0003	0.003 ± 0.0003
Final CCl_4	Torr	<0.25	<0.25	<0.25	<0.25
	mmol	<0.0007	<0.0007	<0.0007	<0.0007

[a] Determined by Fourier-transform i.r. spectroscopy. [b] Before admission of aluminium(III) chloride.

Table 3. Diffuse-reflectance i.r. Fourier-transform spectroscopy (d.r.i.f.t.s.) ($\nu_{max.}$/cm^{-1})[a] of aluminium(III) chloride surfaces treated with CH_3CCl_3(g) or $CH_2{=}CCl_2$(g)

Untreated $AlCl_3$[b]	After treatment with CH_3CCl_3(g)[c]	After treatment with $CH_2{=}CCl_2$(g)[c]	Black layer[d]	Assignments
3 400vs, br				ν(OH)
			2 940vs	ν(CH)
			2 430m	ν(C≡C)?
2 260m, br				ν(O–H ••• O)
		1 630s	1 648vs	ν(C=C)
1 613s				δ(HOH)
	1 490m	1 490w	1 483w	δ_{asym}(CH)
	1 318w			δ_{sym}(CH)
	1 265w			CH_3 rock
1 116vs				δ(AlOH)
994(sh)				δ(AlOH)
		800s	816s	$\nu_{asym}(CCl_2)$
	750w			$\nu_{asym}(CCl_3)$

[a] Relative intensities: v = very, s = strong, m = medium, w = weak, br = broad, and sh = shoulder. [b] Treatment of the surface with ^2H_2O(g) resulted in additional bands $\nu_{max.}$ 2 480s, br, 1 441m, 1 063s, and 988(sh) cm^{-1}. [c] Spectrum of untreated $AlCl_3$ subtracted. [d] Exposed by removal of surface layer from the $CH_2{=}CCl_2$ reaction.

polymerisation of $CH_2{=}CCl_2$ although the evidence is not definitive.

Experimental

All operations involving aluminium(III) chloride were carried out using a Pyrex vacuum system (10^{-4} Torr) with a minimum of greased joints and stopcocks to facilitate baking-out. Transfers of solid were made in an inert-atmosphere box (< 10 p.p.m. water).

Anhydrous aluminium(III) chloride (> 99% pure, Fluka AG) was purified by sublimation under vacuum (10^{-4} Torr) at 393 K in the presence of aluminium wire (99.99% pure, Fluka AG/Balzers) to reduce any iron chloride impurities. The sublimate was collected at 77 K in a flamed-out Pyrex U-tube which was then sealed. The sublimate was transferred to several small ampoules equipped with poly(tetrafluoroethylene) p.t.f.e., Pyrex stopcocks (Rotaflo or J. Young). The samples were degassed and stored under vacuum. 1,1,1-Trichloroethane (Analar, Hopkin and Williams) was stored *in vacuo* over activated 3A molecular sieves and degassed before use. 1,1-Dichloroethene (99%, Aldrich Chemical Co) was stored *in vacuo* over activated 3A molecular sieves under subdued light to inhibit photopolymerisation and was vacuum distilled, to remove the stabiliser, before use.

Kinetic i.r. spectroscopic analyses of the vapour phase in the gas/solid reactions were carried out using a Nicolet 20SXB Fourier-transform i.r. system, resolution 4 cm^{-1}, and a purpose-built Pyrex gas cell equipped with KBr windows and a depression along the bottom to contain the solid. The cell was mounted in a holder to ensure reproducible positioning in the spectrometer beam. Before each reaction an ampoule containing $AlCl_3$ was attached to the cell. The cell was evacuated and a desired pressure of vapour added *via* a gas-handling manifold equipped with a constant-volume manometer. The cell was placed in the spectrometer, the stopcock on the ampoule was opened, and spectra were collected and stored at one per 18 s for the first 30 min of reaction and subsequently one per min until 60 min had elapsed. For appropriate bands, plots of absorbance or band area *vs.* time and first- and second-order kinetic plots were constructed. Compositions of the gas phase were determined using experimentally determined calibration relationships.

The $\nu_{max.}$ band of CCl_4 at 794 cm^{-1}, the only strong band in the region 4 000—600 cm^{-1} for this species, had limited analytical utility due to the close proximity of a band, $\nu_{max.}$ 796 cm^{-1}, in the spectrum of 1,1-dichloroethene. When both compounds were present, pressures of each were estimated by comparison with standard spectra.

When possible, g.c.–i.r. and g.c.–m.s. were used to confirm assignments and to search for species whose spectra were masked by the strong bands of the reactant vapours. In g.c.–i.r. investigations the components were separated on a BP1 (OV1) column (length 25 m, internal diameter 530 μm) in a Perkin-Elmer 8 310 gas chromatograph, using a Nicolet 20SXB Fourier-transform i.r. system as detector.

Reflectance i.r. spectra were obtained using a d.r.i.f.t.s. cell and evacuable stage (Spectra-Tech Inc.) in conjunction with Nicolet MX1 and 5DXC Fourier-transform i.r. spectrometers, resolution 4 cm^{-1}. Samples of $AlCl_3$ were loaded onto the stage in the glove-box and subsequent exposures of the surface to ^2H_2O, CH_3CCl_3, or $CH_2{=}CCl_2$ were made *in vacuo*. Spectra were collected after each operation and were subtracted as appropriate. Multiple exposures were normally performed to establish the growth of spectral bands. The s.i.m.s. investigations employed a surface-ionisation mass spectrometer (Riber Instruments). The sample cup was loaded in the glove-box with $AlCl_3$ and transferred to the sample compartment under dry N_2. Exposures to CH_3CCl_3 vapour were performed *in situ*.

Pressure-measurement studies were carried out using a Pyrex reaction vessel, which was designed so that, when connected to the vacuum system, the enclosed 'dead space' formed between the vessel and the manifold had an identical volume to that of the vessel below the p.t.f.e., Pyrex stopcock. Temperature readings were obtained from a thermocouple attached to the outside of the vessel and pressure readings from a pressure transducer inside the dead space. The reaction vessel was weighed, loaded with $AlCl_3$, reweighed, attached to the vacuum system, and pumped overnight. A desired pressure of gas was admitted to the dead space and data collection (microprocessor controlled) was initiated at the maximum rate (one reading per 3 s). Hard copy was obtained in the form time, temperature, pressure, and pressure increment. The stopcock on the vessel was opened and data were collected at the maximum rate for 10 min, then at one per min for a further 30 min, and finally at one per 5 min until no further change in pressure was detectable. Normally a reaction was followed for 5 h.

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