2836 *J. Phys. Chem.* **1994,** *98,* 2836-2843

Infrared Spectra and Relative Stability of Hydrogen Chloride van der Waals Complexes with Various Alkyl Chlorides in Liquefied Noble Gases

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Received: October 13, 1993; In Final Form: January 3, 1994[●]

Mid-infrared spectra (4000–400 cm^{-1}) of mixtures of HCl with ethyl-d_5, *n*-propyl, isopropyl-d_7, or *tert*-butyl chloride, dissolved in liquefied argon (95–117 K) and liquefied krypton (122–148 K) have been investigated. In all cases the formation of a 1:1 van der Waals molecule between HCl and the alkyl chloride was observed. At higher concentrations, a new absorption band, due to a 1:2 complex (RCl)•(HCl)$_2$ was found. The association enthalpy in liquefied argon was determined to be −9.8 ± 0.6 kJ mol^{-1} for $C_2D_5Cl{\cdot}HCl$, −10.0 ± 0.5 kJ mol^{-1} for *gauche*-*n*-$C_3H_7Cl{\cdot}HCl$ and −10.8 ± 0.5 kJ mol^{-1} for *iso*-$C_3D_7Cl{\cdot}HCl$. The ΔH_0 for the $C_2D_5Cl{\cdot}HCl$ species in liquefied krypton was determined to be −9.4 ± 0.5 kJ mol^{-1}. For the formation of the 1:2 complex from the 1:1 complex and hydrogen chloride, the ΔH_0 was determined to be −3.7 ± 0.4 kJ mol^{-1} for the ethyl-d_5 chloride complex and −4.5 ± 0.3 kJ mol^{-1} for the isopropyl-d_7 chloride complex.

Introduction

Recently the mid- and far-IR spectra of several liquefied argon solutions containing both CD_3Cl and HCl were described.[1] In all spectra, evidence was found for the existence of a 1:1 hydrogen-bonded complex, the relative stability of which was determined to be −7.8 ± 0.4 kJ mol^{-1}. At higher concentrations of HCl, evidence was also found for the existence of another complex, having a different stoichiometry. The formation of these species has also been observed in matrix-isolation experiments.[2,3] In the mid-IR spectra of argon matrices containing mixtures of a higher alkyl chloride with HCl, similar associations were observed. Unfortunately, since the solid matrices are not in thermodynamical equilibrium, no value for the relative stability of the observed species could be obtained. Furthermore, the mid-IR spectra of the argon matrices were mainly studied in the hydrogen chloride stretching region[2-4] while experimental evidence for the existence of molecular associations can also be found in other regions of the infrared spectra.[1] To get a more complete description of the hydrogen-bonded species formed between higher alkyl chloride (RCl) and hydrogen chloride molecules, a detailed investigation was initiated. In this study we report on solutions in liquefied argon and krypton of ethyl, *n*-propyl, isopropyl, and *tert*-butyl chloride mixed with HCl. In addition to collecting their vibrational frequencies, evidence was gathered on the stoichiometry and on the stability of the complexes, mainly by undertaking temperature and concentration studies. To simplify the quantitative analysis, for ethyl chloride and isopropyl chloride the totally deuterated isotopomers C_2D_5Cl and $(CD_3)_2CDCl$ were used.

Experimental Section

The samples of *n*-propyl chloride, *tert*-butyl chloride, and isopropyl-d_7 chloride were synthesized by mixing the corresponding alcohol with a small amount of PCl_3 at room temperature. The ethyl-d_5 chloride was synthesized by adding an amount of ethyl-d_5 iodide (MSD isotopes MD-211) to an excess of dry, fresh AgCl. After 48 h, the reaction product was collected by bulb-to-bulb distillation. The hydrogen chloride was made in small amounts by hydrolyzing PCl_3 with water and was purified afterward by pumping the reaction mixture through an isopropyl alcohol slush (180 K). All compounds were purified on a low-temperature, low-pressure fractionating column. The argon and krypton used have stated purities of 99.9999% and 99.998%, respectively, and were therefore used without further purification.

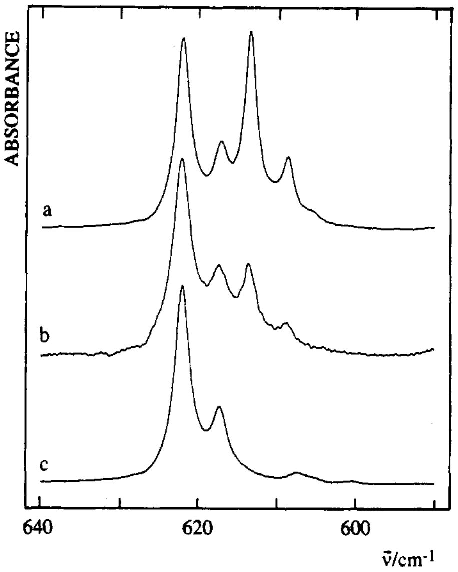

Figure 1. Comparison of the ν(C–Cl) region observed in the spectra of C_2D_5Cl dissolved in liquefied argon at 108.2 K (c) and of a C_2D_5Cl/HCl mixture dissolved in liquefied argon at 105.6 K (a) and at 115.6 K (b).

Infrared spectra were recorded on a Bruker IFS 113v Fourier transform spectrometer. For all spectra, a Globar source, a Ge/KBr beam splitter and a LN2 cooled broad-band MCT detector were used. The interferograms, recorded at a resolution of 0.5 cm^{-1}, were averaged over 200 scans, Happ Genzel apodized, and Fourier transformed using a zero-filling factor of 4.

A description of the liquid noble gas setup was given in a previous study[1] and will not be repeated here. To be able to distinguish the spectra of dissolved from undissolved alkyl chloride, the solid-state spectra of the latter were obtained by condensing a small amount of the compound onto a liquid nitrogen cooled CsI window, followed by annealing until no further changes were observed in the infrared spectrum.

The solid state experiments on $(CH_3)_3CCl/HCl$ mixtures were performed using a Leybold ROK 10-300 double-stage cryostat with closed-cycle helium cooling.

Discussion

Ethyl-d_5 Chloride. In Figure 1 the C–Cl stretching region of a spectrum of a solution of C_2D_5Cl in liquefied argon, recorded

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[●] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

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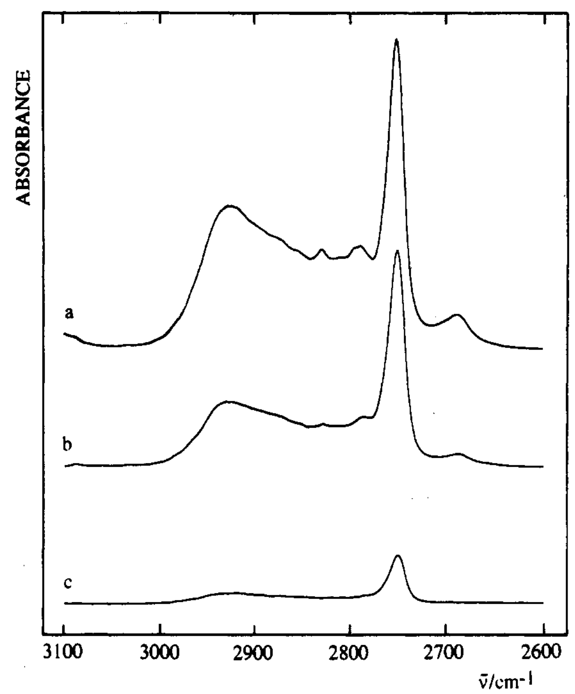

Figure 2. H–Cl stretch region for mixtures of C_2D_5Cl and different amounts of hydrogen chloride, in liquefied argon at 108.0 K. From top to bottom, decreasing amounts of HCl are present in the solution.

at 108.0 K, is compared with spectra of a C_2D_5Cl/HCl mixture in the same solvent, recorded at 105.6 and 115.1 K. In the spectrum of the solution of C_2D_5Cl, Figure 1c, the C–Cl stretching at 622 cm^{-1} shows the expected isotopic sideband at 617 cm^{-1}. Furthermore, on the low-frequency side of this band another weak doublet, with maxima at 607 and 602 cm^{-1}, can be seen. These bands are due to undissolved compound. When hydrogen chloride is added to the solution, new bands are observed at 613 and 608 cm^{-1}. As can be seen in Figure 1a,b, the relative intensity of these bands decreases with the temperature of the solution. The frequency difference between these bands and their relative intensity are similar to those in the C–Cl stretch doublet in the spectra of the pure C_2D_5Cl solution. These bands are similar to the new bands observed for CD_3Cl/HCl mixtures[1] and therefore are regarded as evidence that also between ethyl-d_5 chloride and HCl a van der Waals complex is formed.

In the H–Cl stretching region of the spectra of a C_2D_5Cl/HCl mixture in liquefied argon, next to the broad monomer HCl band, a sharp band is observed at 2752 cm^{-1}, which must be assigned to the van der Waals complex between both species.

The intensities of the bands due to the complex exhibit a pronounced dependence on the concentrations of the constituent molecules. This is illustrated in Figure 2, where the influence of the HCl concentration is demonstrated. At low relative concentrations of HCl, 0.1×10^{-3} M HCl versus 1.0×10^{-3} M C_2D_5Cl, Figure 2c, the relative intensity of the band due to monomer HCl is much smaller than that of the complex band at 2751 cm^{-1}, showing that the greater part of the HCl molecules is hydrogen bonded to ethyl chloride.

At higher HCl concentrations, Figure 2b, the relative intensity of the monomer HCl band increases. At the same time new, weak bands become apparent at 2789 and 2690 cm^{-1}. Since these bands do not appear in the spectra of solutions containing only ethyl chloride or HCl, also these bands must be due to species formed between C_2D_5Cl and HCl. At still higher concentrations of HCl, Figure 2a, weak absorption bands at 2830 and 2797 cm^{-1} can be observed. These are attributed to dimer and trimer HCl, respectively.[5]

As argued below, the bands near 2752 and 2789 cm^{-1} have to be assigned to the same molecular complex. However, the relative intensities of the bands at 2752 and 2690 cm^{-1} depend in different ways on temperature and monomer concentration. Therefore, they have to be assigned to two different molecular complexes which, until their stoichiometry is discussed, will be named type A (2752 cm^{-1}) and type B (2690 cm^{-1}) complexes.

With one exception, the fundamentals localized in the CD_3-CD_2 group show no measurable frequency shift upon complexation. The exception is the CD_2 wagging fundamental, for which a new band, red shifted by 2 cm^{-1}, is observed upon complexation.

At high concentrations of C_2D_5Cl and HCl, bands similar to those described above can also be observed in the spectra of the liquefied krypton solutions. Next to the 2861 cm^{-1} monomer HCl band, a weak band at 2782 cm^{-1} and a strong band at 2744 cm^{-1}, both due to the type A complex, are observed. Even at the highest concentration of HCl no absorption band due to a type B complex was detected for these solutions. In liquefied krypton also a small red shift is observed for the ν(C–Cl) fundamentals: the bands due to $\nu(C–{}^{35}Cl)$ and $\nu(C–{}^{37}Cl)$ in nonassociated and in hydrogen-bonded ethyl-d_5 chloride are observed at 620.5 and 615.5 cm^{-1} and at 615 and 607 cm^{-1}, respectively.

***n*-Propyl Chloride.** The behavior of *n*-propyl chloride dissolved in liquefied noble gases will be described in detail elsewhere,[7] and therefore only the more important characteristics will be given here. *n*-Propyl chloride exists as a mixture of a *trans* and a slightly more stable *gauche* conformer,[7,8] leading to C–Cl stretches in two different regions: the bands near 743 cm^{-1} are assigned to the trans while the bands near 664 cm^{-1} are assigned to the gauche conformer.[8] In the same region two other bands are observed, at 748 and 791 cm^{-1}, which have been assigned as the (C)CH_2(C) rocking fundamentals in the trans and gauche conformer, respectively.[7] When HCl is added to the liquid argon solution, new bands with a red shift of approximately 13 cm^{-1} occur for all C–Cl stretch fundamentals, proving the formation of a van der Waals complex by each of the conformers. Furthermore, the (C)CH_2(C) rocking fundamental of the gauche conformer also gives rise to a new, red shifted band. Due to its weakness and to the overlap with more intense absorption bands, no new band was observed for the trans conformer.

When HCl is added to solutions of *n*-propyl chloride, new absorption bands occur in the ν(H–Cl) region at 2748 and 2683 cm^{-1}. These we assign to a type A and a type B hydrogen bonded species, respectively. It must be observed that while both trans and gauche *n*-propyl chloride form a hydrogen-bonded species, only one absorption band due to the type A and one due to the type B species can be observed in the ν(H–Cl) region. Because of the linear relationship between the H–Cl stretching frequency of the complex and the complexation enthalpy, which will be discussed below, this observation shows that for *n*-propyl chloride the conformation of the alkyl group has no observable influence on the strength of the hydrogen bond.

Isopropyl-d_7 Chloride. Phenomena as those described above can also be observed for $(CD_3)_2CDCl$/HCl mixtures. When HCl is added to a solution of $(CD_3)_2CDCl$, new bands emerge at 565.5 and 561.0 cm^{-1}, which we assign to the complex formed between HCl and $(CD_3)_2CD^{35}Cl$ and $(CD_3)_2CD^{37}Cl$, respectively.

In Figure 3, the ν(H–Cl) region is shown for two $(CD_3)_2CDCl$/HCl solutions that have a different HCl concentration (3.2×10^{-3} M vs 4.1×10^{-3} M HCl). Two complex bands can be seen to be present, near 2740 and 2670 cm^{-1}. These again are assigned to type A and a type B species. In contrast with the spectra discussed above, the band at 2740 cm^{-1} exhibits a weak high-frequency shoulder, at 2755 cm^{-1}. A possible explanation for this shoulder will be discussed below.

***tert*-Butyl Chloride.** In Figure 4, parts of the spectrum of a solution in liquefied argon of $(CH_3)_3CCl$, recorded at 120 K, are compared with those of a solution of a $(CH_3)_3CCl$/HCl mixture, recorded at 120 and 105 K, respectively. The C–Cl stretching region of the solution of pure $(CH_3)_3CCl$ shows two distinct

TABLE 1: ν(C–Cl) and ν(H–Cl) Vibrational Frequencies of Several Alkyl Chloride Monomers and Their Corresponding Hydrogen-Bonded Species

	liquefied argon solution				solid argon matrices[a]	
		associated			ν(H–Cl)[c]	
	nonassociated		ν(H–Cl)[b]			
base molecule	ν(C–Cl)	ν(C–Cl)	type A	type B	type A	type B
CD_3Cl	697	690	2765	2713	2745	2730
	691	684				
C_2D_5Cl	622	613	2751	2690	2740	2728/2715
	617	608				
gauche-n-C_3H_7Cl	664	651	2749	2683	2735	
	657	643				
trans-n-C_3H_7Cl	742	732	2749	2683	2735	
	738	727				
i-C_3D_7Cl	575	565.5	2740[d]	2670	2734	2725/2715
	570.5	561				
t-C_4H_9Cl	581	569	2728[e]		2724	2718

[a] References 2 and 3. [b] Monomer frequencies at 2869 cm^{-1}. [c] Monomer frequency at 2861 cm^{-1}. [d] Shoulder at 2755 cm^{-1}. [e] Shoulder at 2742 cm^{-1}.

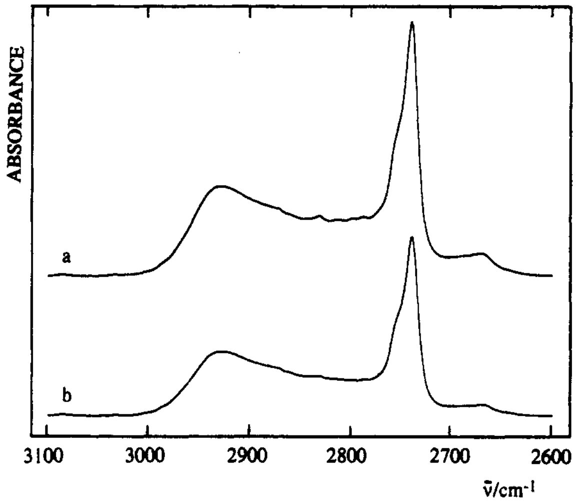

Figure 3. H–Cl stretch region for mixtures of *iso*-C_3D_7Cl and different amounts of hydrogen chloride (a, 4.1 × 10^{-3} M HCl; b, 3.2 × 10^{-4} M HCl) dissolved in liquefied argon at 108.0 K.

absorptions, at 581 and 556 cm^{-1}, each having a weak low-frequency shoulder, at 578.5 and 554 cm^{-1}, respectively. The relative intensity of the 556-cm^{-1} band increases when the temperature is lowered. This can be correlated to the low solubility of *tert*-butyl chloride in liquefied argon, since an identical band at 556 cm^{-1} is present in the spectra of crystalline $(CH_3)_3CCl$. Therefore, the bands near 581 and 556 cm^{-1} have to be assigned to dissolved and crystalline *tert*-butyl chloride, respectively.

In Figure 4b,c the same regions of the spectrum of a $(CH_3)_3CCl/HCl$ mixture, dissolved in liquefied argon, recorded at 120 and 105 K, respectively, are shown. At 120 K C–Cl stretches can be observed at 581, 569, 556, and 544 cm^{-1}. When the solution is cooled to 105 K, only the bands at 556 and 544 cm^{-1} persist. A similar effect is observed in the ν(H–Cl) region, which is also shown in Figure 4. In the spectrum recorded at 120 K, two bands due to the H–Cl stretch in associated species occur, at 2728 and 2701 cm^{-1}, the former showing a relatively weak shoulder near 2746 cm^{-1}. At 105 K, only the band at 2701 cm^{-1} remains. This behavior suggests that two different associated species are present, a first one giving rise to the bands at 2728 and 569 cm^{-1}, the other belonging to the bands at 2701 and 544 cm^{-1}.

For all other complexes studied, the C–Cl stretch in the hydrogen-bonded species is observed between the bands due to nonassociated alkyl chloride and those due to crystalline alkyl chloride. Therefore, in analogy with the results obtained for the other alkyl chloride/hydrogen chloride mixtures, the absorption bands at 569 and 2728 cm^{-1} can be assigned to a type A hydrogen-bonded species present in the liquefied argon solution.

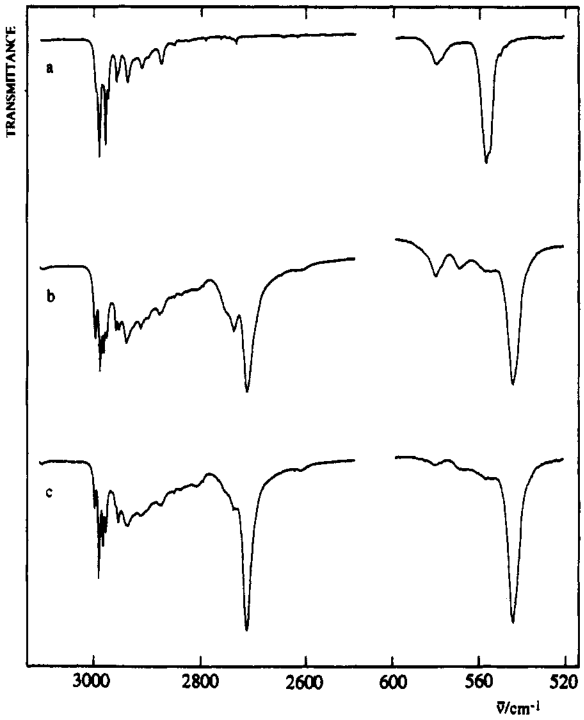

Figure 4. Characteristic regions for the spectra of *tert*-butyl chloride dissolved in liquefied argon at 120 K (a) and a *tert*-butyl chloride/HCl mixture dissolved in liquefied argon at 120 (b) and at 105 K (c).

For all alkyl chlorides investigated it was found that the C–Cl stretch is red shifted by approximately 24 cm^{-1} when passing from solution to the crystalline phase. An analogous frequency shift is shown by the bands at 569 and 544 cm^{-1}. This suggests that the absorption bands at 544 and 2701 cm^{-1} are due to a crystalline phase containing the species formed between HCl and *tert*-butyl chloride. The occurrence of such a new, crystalline phase containing both molecules was confirmed by solid-state experiments, to be discussed below.

Comparison with Matrix Isolation. It is interesting to compare the spectra of the solutions in liquefied argon with those of the corresponding matrices.[2-4] In Table 1, the H–Cl stretching frequency of the molecular complexes in argon matrices and in liquefied argon solutions are compared with each other. It can be seen that when passing from the matrix to the solution, the electron acceptor HCl molecule increases its ν(H–Cl) frequency. This effect can be correlated to the density change in the environment when passing from liquid to solid.[5]

As can be seen in Table 1, the frequency shifts for the H–Cl and the C–Cl stretch frequencies, described as Δν(H–Cl) and Δν(C–Cl), were found to systematically increase from −104 and

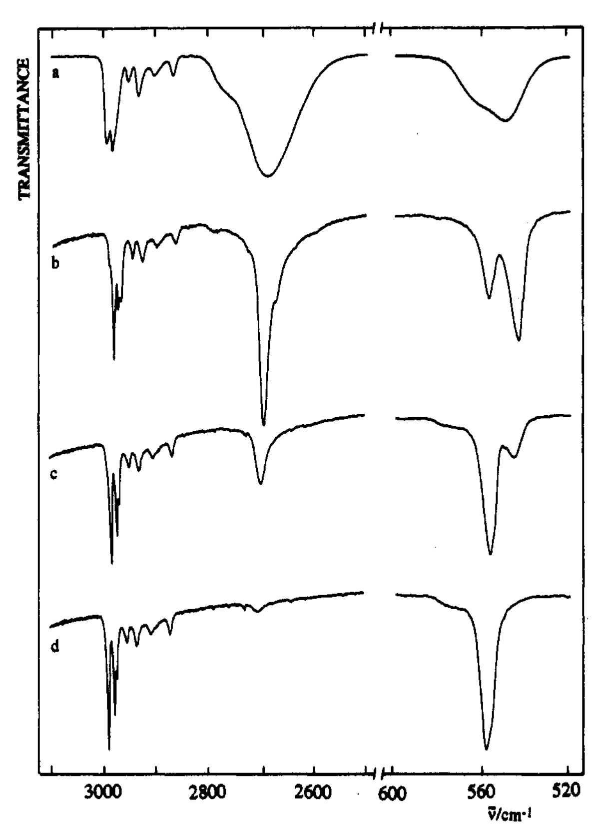

Figure 5. Solid-phase spectra observed after condensing a *tert*-butyl chloride/hydrogen chloride mixture onto a cooled window at 10 K (a) and after anealing to 85 (b), 120 (c), and 150 K (d), respectively.

-7 cm^{-1} ($\Delta\nu$(C–Cl)/ν(C–Cl) = -0.010) for the methyl-d_3 chloride type A complex to -141 and -12 cm^{-1} ($\Delta\nu$(C–Cl)/ν(C–Cl) = -0.020) for the *tert*-butyl chloride type A complex. An analogous effect can be seen in Table 1 for the type B complexes. The reason for these different increases must be attributed to a different stability of the observed complexes

Solid State Experiments

To confirm the nature of the bands at 544 and 2701 cm^{-1} in the spectra of liquefied argon solutions of *tert*-butyl chloride/hydrogen chloride mixtures, solid-state experiments were performed. A gas mixture that contained equal fractions of *tert*-butyl chloride and hydrogen chloride and that had been left to homogenize during 24 h was slowly deposited on a cold window held at 10 K. In Figure 5a, a part of the mid-infrared spectrum of the amorphous phase, obtained immediately after deposition, is shown. As can be seen, the C–Cl stretching region is characterized by a broad band near 548 cm^{-1}, having a shoulder near 562 cm^{-1}. In the ν(H–Cl) region a broad band can be observed near 2780 cm^{-1}, having a less intense shoulder near 2850 cm^{-1}.

Subsequently, the amorphous phase was slowly annealed, while at regular intervals of time infrared spectra were recorded. At a temperature of approximately 85 K the spectrum changes, indicating crystallization of the solid film. As can be seen in Figure 5b, the spectrum of the emerging crystalline solid is characterized by two rather intense bands in the C–Cl stretching region, at 558 and 544 cm^{-1}, and an intense band in the HCl stretching region at 2701 cm^{-1}. The band at 558 cm^{-1} is also found in the spectra of crystalline $(CH_3)_3CCl$ and therefore has to be assigned to this species. The bands at 2701 and 544 cm^{-1}, however, cannot be found in the spectra of crystalline *tert*-butyl chloride or in the spectra of crystalline hydrogen chloride,[9] and therefore they have to be assigned to a crystalline phase containing both kinds of molecules.

At still higher temperatures, the pressure in the cryostat suddenly increased from its normal value of 1×10^{-7} to 5×10^{-6} mbar, suggesting the evaporation of HCl from the solid phase. At the same time the infrared spectrum changed dramatically, as is illustrated by Figure 5c,d: the bands assigned to the solid containing both *tert*-butyl chloride and hydrogen chloride decrease in relative intensity, confirming the evaporation of the HCl. At about 150 K, the bands due to the $(CH_3)_3CCl$/HCl phase have disappeared almost completely, and the resulting spectrum is identical to that of pure solid $(CH_3)_3CCl$.

The bands at 2701 and 544 cm^{-1} in the spectra of the solutions in liquefied argon correspond exactly to those assigned to the $(CH_3)_3CCl$/HCl phase in the solid-state experiment, and the latter experiment therefore confirms their assignment.

Stoichiometry of the Observed Species

Although it appears logical that the type A complex is a 1:1 complex in which the alkyl chloride is the electron donor and HCl is the electron acceptor,[1] matters for the type B complex are somewhat more complex. Since the chlorine atom in HCl on its term can act as an electron donor, with a second HCl molecule a 1:2 complex of the type RCl·HCl·HCl can be formed. In an analogous way higher molecular complexes, with 1:3, 1:4, etc., stoichiometry may be envisaged. In contrast, in the matrix spectra of several RI/HI mixtures bands were identified that had to be assigned to the species $(RI)_2\cdot(HI)$.[10] Analogous complexes can also be envisaged between alkyl chlorides and HCl. Therefore, to establish the correct stoichiometry of the species observed in this study, an analysis of the intensities in concentration series was undertaken for both ethyl-d_5 and isopropyl-d_7 chloride. To this end, infrared spectra of several solutions containing different concentrations of the appropriate alkyl chloride, varying from 0.5×10^{-3} to 2.3×10^{-3} M, and of HCl, varying from 0.2×10^{-3} to 4.5×10^{-3} M, were recorded at a constant temperature of 108.0 ± 0.3 K.

The formation of a complex species $(RCl)_n\cdot(HCl)_m$ between n RCl molecules and m HCl molecules is described by the equilibrium reaction:

$$n\mathrm{RCl} + m\mathrm{HCl} \rightleftharpoons (\mathrm{RCl})_n\cdot(\mathrm{HCl})_m$$

This equilibrium is characterized by the overall equilibrium constant K_{eq}:

$$K_{eq} = \frac{[(\mathrm{RCl})_n\cdot(\mathrm{HCl})_m]}{[\mathrm{RCl}]^n[\mathrm{HCl}]^m}$$

Assuming constant extinction coefficients throughout the concentration series, this expression can be rewritten as

$$K'_{eq} = \frac{I_{(\mathrm{RCl})_n\cdot(\mathrm{HCl})_m}}{(I_{\mathrm{RCl}})^n(I_{\mathrm{HCl}})^m}$$

In this expression I_{RCl}, I_{HCl}, and $I_{(RCl)_n\cdot(HCl)_m}$ are the integrated intensities of an absorption band of the RCl monomer, the HCl monomer and of the complex species, respectively. This equation shows that, at constant temperature, the intensity of a band of the $(RCl)_n\cdot(HCl)_m$ species must vary linearly with the product of the monomer intensities, $(I_{RCl})^n(I_{HCl})^m$. By plotting for a concentration series the successive integrated intensities of the complex band, $I_{(RCl)_n\cdot(HCl)_m}$, against the respective products of intensities $(I_{RCl})^p(I_{HCl})^q$, a linear plot will be obtained only when p and q equal n and m, respectively. Hence, from such plots for different p and q, the correct stoichiometry of the complex can be established.

From the expression for K'_{eq} it follows that integrated intensities of a band of each of the species involved must be known accurately. It can be seen in Figures 2 and 3 that the broad band due to free

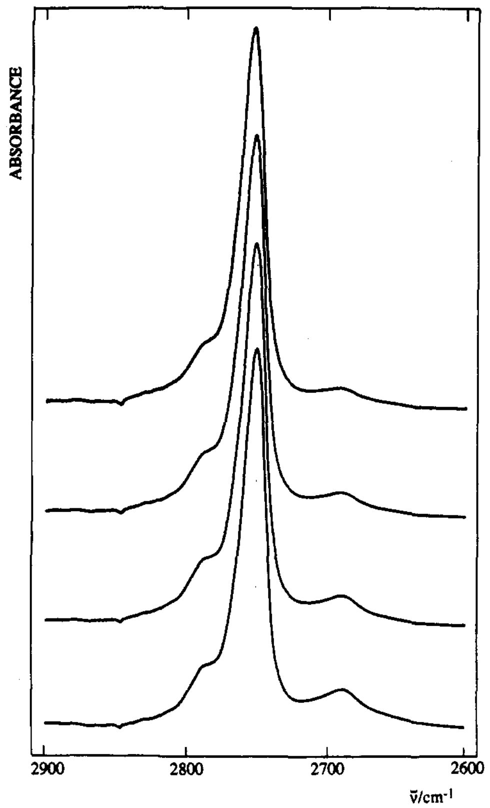

Figure 6. Calculated contribution of the $(C_2D_5Cl)\cdot(HCl)_y$ species for several solutions containing ethyl-d_5 chloride and different amounts of HCl, in liquefied argon at 108.0 K. From top to bottom, increasing amounts of hydrogen chloride were dissolved.

HCl in the solution strongly overlaps with the bands due to the complexes. In such cases the contributions of the HCl monomer species and the hydrogen-bonded species can be separated by fitting the experimental spectra obtained for the RCl/HCl mixtures with those obtained for a pure hydrogen chloride solution.[1] Furthermore, for all the bands observed in the ν(C–Cl) region, the integrated intensities were obtained from a least-squares band profile analysis.[1]

In Figure 6, some resulting spectra obtained by subtracting the corresponding spectra of several C_2D_5Cl/HCl mixtures and those of a pure hydrogen chloride solution are shown. For each spectrum, three different bands can be observed, at 2789, 2751, and 2690 cm^{-1}. A least-squares band profile analysis of this region was performed using a three-band combination. This yielded the intensity of the type A band at 2751 cm^{-1}. It was found, however, that the agreement between calculated and experimental spectrum in the region around 2690 cm^{-1} was less than could be desired. The reason for this presumably is the presence in this region of weak spectral features due to HCl oligomers,[5] incorrectly accounted for in the subtraction process. Therefore, as intensity of the type B band at 2690 cm^{-1} the absorbance at the band maximum was preferred above the integrated intensity obtained from the profile analysis. As all spectra for this analysis were recorded at the same temperature, this approximation was regarded as acceptable. As can also be seen in Figure 6, throughout the concentration series the intensity ratio of the bands at 2789 and 2751 cm^{-1} is constant. Therefore, these bands have to originate in the same species. On the other hand, the intensity ratio of the bands at 2751 and 2690 cm^{-1} is not constant, which confirms that the type B band at 2690 cm^{-1} must be due to a different species.

For the isopropyl-d_7 chloride/HCl concentration series, the intensities of the bands were obtained in a similar way.

Both for ethyl-d_5 chloride and isopropyl-d_7 chloride, when using the intensities of the type A band, a linear behavior of the intensity of the type A band was obtained only by plotting it against the product $I_{RCl}I_{HCl}$. Therefore, as anticipated, the type A band in both cases must be due to the 1:1 complex RCl·HCl. Again for both alkyl chlorides, the type B band shows a linear behavior only by plotting its intensity against the product $I_{RCl}(I_{HCl})^2$, showing that the type B band must be due to the 1:2 complex $RCl\cdot(HCl)_2$.

In addition to the bands in the H–Cl stretching region, the complex species also give rise to well-separated bands in the C–Cl stretching region. The band profile analysis of this region used to obtain I_{RCl} also yields integrated intensities of the C–Cl stretches of the complex species. Therefore, the above analysis can be repeated, using as $I_{(RCl)_n\cdot(HCl)_m}$ the intensity of the C–Cl stretches due to the complex. While it was discussed above that some difficulties arose with the profile analysis of the H–Cl stretches of the complexes, also the analysis of the 600–540-cm^{-1} region is not without problems. Upon formation of the 1:1 complex RCl·HCl, the C–Cl stretch is substantially lowered, leading to well-separated C–Cl stretches for the complex. The 1:2 complex, however, is thought to be of the type R–Cl·HCl·HCl. Therefore, the addition of a second HCl molecule is expected to have far less influence on the C–Cl stretch. As no separate C–Cl stretching doublet for the type B complex was observed, it must be concluded that its ν(C–Cl) doublet is superposed by that of the type A complex. As can be deduced from Figure 6, the concentration of the 1:2 complex is always much lower than that of the 1:1 complex, and therefore the intensity of the complex C–Cl stretches in the first place must be due to the 1:1 species. This is confirmed by the results in Figure 7 for the ethyl-d_5 chloride/HCl concentration series, where the integrated intensity of the bands at 618 and 613 cm^{-1} has been plot against several $(I_{RCl})^p(I_{HCl})^q$ combinations. It can be seen that only the plot against $I_{RCl}I_{HCl}$ is linear, and it is so over the entire concentration range. It follows that the influence of the 1:2 complex on the intensity is negligible. Unfortunately then, the lack of separate C–Cl stretches for the type B complex prevents the stoichiometry of this complex to be confirmed from its C–Cl stretch intensities.

Relative Stability of the 1:1 Complexes

To establish the relative stability of the 1:1 and the 1:2 hydrogen-bonded species, temperature studies were carried out. The complexation enthalpy ΔH_0 of the hydrogen-bonded species was obtained from the van't Hoff isochore. Infrared spectra of ethyl-d_5 chloride/HCl and isopropyl-d_7 chloride/HCl solutions were recorded at several temperatures between 105.3 and 114.6 K and between 101.2 and 115.2 K, respectively. At lower temperatures, an important fraction of the alkyl chloride molecules crystallized, hampering accurate intensity determinations. Using the intensities of both monomer and hydrogen-bonded species, calculated by the methods as described above, for each alkyl chloride a van't Hoff plot was constructed. The resulting plots are shown in Figure 8. From the least squares straight line through the experimental points, an enthalpy difference ΔH_0 of -10.8 ± 0.5 kJ mol^{-1} for $(CD_3)_2CDCl\cdot HCl$ and of -9.8 ± 0.6 kJ mol^{-1} for $C_2D_5Cl\cdot HCl$ was calculated.

Due to the overlap between the ν(HCl) band of monomer HCl and the C–H stretches in trans and gauche *n*-propyl chloride, a similar analysis for this species is obstructed. A reliable value for the ΔH_0 can then be obtained only by introducing an approximation. When using an excess of hydrogen chloride, the total concentration of hydrogen chloride

$$C_{HCl} = [HCl] + [RCl\cdot HCl] + ...$$

can be approximated as

$$C_{HCl} \approx [HCl]$$

Therefore, the integrated intensity of the monomer HCl band can be assumed to be a constant during the whole temperature

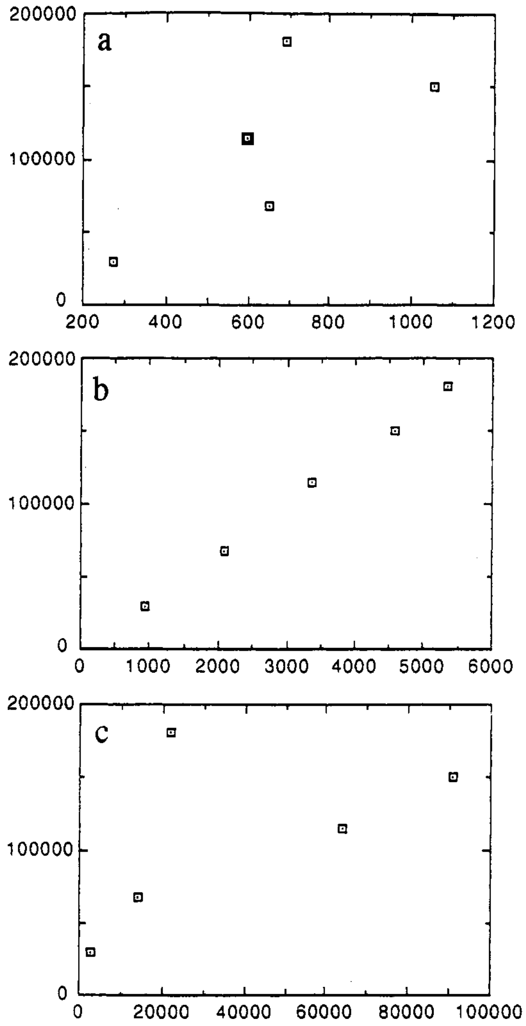

Figure 7. Intensity of the 618- and 613-cm^{-1} absorption bands observed in the spectra of C_2D_5Cl/HCl mixtures in liquefied argon at 108.0 K as a function of products of monomer intensities. The 618- and 613-cm^{-1} band intensity is given in the ordinate in arbitrary units. The abscissa gives the values obtained by multiplying the monomer intensities in arbitrary units for a proposed $(RCl)_2(HCl)$ (a), $(RCl)(HCl)$ (b), and $(RCl(HCl)_2$ (c) stoichiometry.

study. Then, the van't Hoff isochore can be written as

$$\ln \frac{I_{\mathrm{RCl\cdot HCl}}}{I_{\mathrm{RCl}}} \approx -\frac{\Delta H_0}{RT} + c^{\mathrm{st}}$$

As observed above, the conformation of the alkyl group does not appear to influence the relative stability of the hydrogen-bonded species. Therefore, in this study attention is paid only to the association between gauche *n*-propyl chloride and hydrogen chloride. From the ν(C–Cl) intensities of nonassociated and associated *n*-propyl chloride, and using the approximate equation given above, also for this species a van't Hoff plot was constructed, which is also given in Figure 8. Here a complexation enthalpy equal to −10.0 ± 0.5 kJ mol^{-1} was found.

Because of the low solubilities of t-butyl chloride and of the *tert*-butyl chloride/hydrogen chloride complex, no complexation enthalpy could be obtained.

A temperature study was also carried out for $C_2D_5Cl{\cdot}HCl$ in liquefied krypton. As described above, the complex can be observed with sufficient intensity only when higher concentrations of HCl and alkyl chloride are used. Then, due to the high absorbances, a reliable integration of bands due to the C_2D_5Cl monomer becomes difficult. The ΔH_0 was therefore approximated by using an excess of C_2D_5Cl, so that the intensity I_{RCl} could be assumed to be constant. Again, the intensities of the free and the associated HCl stretching bands were determined by fitting the spectra of the C_2D_5Cl/HCl mixtures with those of pure hydrogen chloride. Using these, the van't Hoff plot also shown in Figure 8 was obtained. The enthalpy difference ΔH_0 calculated from this plot is −9.4 ± 0.5 kJ mol^{-1}. Within the error limits, this value is identical to the one obtained for the liquid argon solution. Therefore, the influence of the noble-gas solvent on the relative stability of the $C_2D_5Cl{\cdot}HCl$ species appears to be negligible. This is similar to the behavior of the $CH_3F{\cdot}HCl$ and $CH_3F{\cdot}HBr$ complexes.[11,12] Also for these species, only small differences were found between the ΔH_0 in liquefied argon and in liquefied krypton solutions. In contrast, a relatively large difference was found between the relative stability of the HCl dimer in liquefied argon and that in liquefied krypton.[5] The behavior of the HCl dimer therefore seems to be somewhat different from that of the species described in this study.

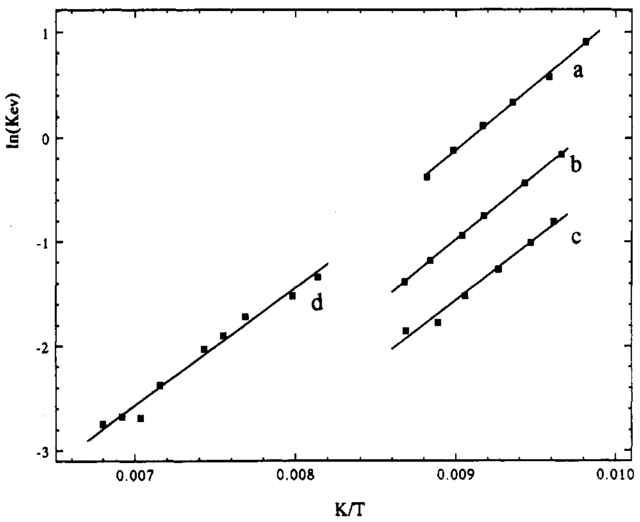

Figure 8. van't Hoff plots for the *n*-$C_3H_7Cl{\cdot}HCl$ (a), *iso*-$C_3D_7Cl{\cdot}HCl$ (b), $C_2D_5Cl{\cdot}HCl$ (c) complexes in liquefied argon and the $C_2D_5Cl{\cdot}HCl$ complex in liquefied krypton (d).

TABLE 2: Comparison of Some Characteristic Properties of Base···HCl Species, Observed in Liquefied Argon Solutions

base molecule	proton affinity/ kJ mol^{-1}	$\Delta\nu$(H–Cl)/ cm^{-1}	complexation enthalpy/ kJ mol^{-1}	ref
HCl	565	41	−3.8 ± 0.4	5
CH_3F	640	70	−4.6 ± 0.4	11, 12
CD_3Cl	669	104	−7.8 ± 0.4	1
C_2D_5Cl	715	118	−9.8 ± 0.6	this study
n-C_3H_7Cl		120	−10.0 ± 0.5	this study
i-C_3H_7Cl		129	−10.8 ± 0.5	this study
t-C_4H_9Cl	787	141		this study

In Table 2, the proton affinities as defined by Barnes,[3] the ν(H–Cl) stretching frequencies in liquefied argon (108 K), and the complexation enthalpies of the $RCl{\cdot}HCl$ complexes are compared with those for $HCl{\cdot}HCl$, $CH_3F{\cdot}HCl$, etc. Since all the complexes are the result of an electron transfer from the base molecule to the σ^* orbital of the hydrogen chloride, the complexation enthalpy must be correlated to the proton affinity of the base molecules involved. As can be seen in Table 2, both the proton affinity and the complexation enthalpy increase when more alkyl substituents are added to the α-carbon atom, which shows they must be correlated. Furthermore, for $C_2D_5Cl{\cdot}HCl$ and *n*-$C_3H_7Cl{\cdot}HCl$, only minor differences are observed between the respective properties. Therefore, adding more alkyl groups to the β-carbon atom appears to have a very small influence only on the hydrogen bond.

As described by Arlinghaus and Andrews,[13] the complexation enthalpy can be related to the frequency shift of the HCl stretching fundamental, $\Delta\nu$(H–Cl). In Figure 9, the value of $-\Delta H_0$ for several $RCl{\cdot}HCl$ species in liquefied argon is plot against the

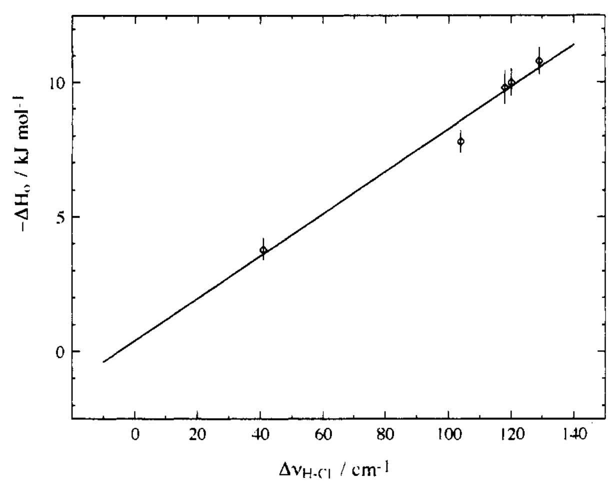

Figure 9. Enthalpy of complexation for several B·H–Cl species (B = HCl, CD_3Cl, C_2D_5Cl, *n*-C_3H_7Cl, and *iso*-C_3D_7Cl) as a function of the shift $\Delta\nu_{H-Cl}$, observed in the spectra of liquefied argon solutions at 108.0 K.

frequency difference $\Delta\nu$(HCl). As can be seen, these quantities are linearly related:

$$-\Delta H_0 = a + b\Delta\nu(\text{HCl})$$

Using a least-squares procedure, the parameters *a* and *b* were calculated to be 0.39 ± 0.75 kJ mol^{-1} and 0.0785 ± 0.0070 kJ cm mol^{-1}, respectively. It is clear that the calculated value of the increment *a*, within the error limits, equals the theoretically expected value of 0.0 kJ mol^{-1}. Furthermore, using the above relation, the $-\Delta H_0$ of the CH_3CN·HCl species, for which $\Delta\nu$(HCl) equals 216 cm^{-1},[14] was calculated to be −17.4 kJ mol^{-1}. This is in very good agreement with the experimental value of −17.0 kJ mol^{-1} obtained from liquefied xenon solutions.[14]

In the spectra of C_2D_5Cl/HCl mixtures dissolved in argon or in krypton, on the high-frequency side of the ν(H–Cl) fundamental of C_2D_5Cl·HCl, a weak absorption band can be observed. This band, in agreement with the results described for methyl-d_3 chloride,[1] is assigned to the combination band ν(H–Cl) + ν(Cl···H). As a consequence, the intermolecular stretching fundamental must be situated near 2789 − 2751 = 37 cm^{-1}, which is somewhat higher than the value of 31 cm^{-1} observed for the CD_3Cl·HCl species.[1] Since C_2D_5Cl·HCl is determined to be more stable than CD_3Cl·HCl, this is not surprising.

Arlinghaus and Andrews[13] have observed two distinct bands belonging to a 1:1 hydrogen-bonded species in the ν(H–F) region of the infrared spectra of solid argon matrices containing C_2H_5Cl/HF or $(CH_3)_2CHCl$/HF mixtures. These doublets show a frequency difference of 15 and 27 cm^{-1}, respectively. The splittings were attributed[13] to the presence of two different rotational isomers of the hydrogen-bonded species. Using the empirical rules proposed by Legon and Millen,[15] also for C_2D_5Cl·HCl and $(CD_3)_2CDCl$·HCl two rotational isomers, having a different orientation of the HCl molecule, can be considered. These are shown in Figure 10. In the spectra of C_2D_5Cl·HCl in liquefied argon, even at the lowest temperatures investigated, no splitting of the ν(H–Cl) fundamental was observed. Hence, there is no indication that C_2D_5Cl·HCl occurs as two different conformers. In contrast, in the spectra of $(CD_3)_2CDCl$·HCl in liquefied argon, two distinct bands belonging to the fundamental are observed, at 2740 and 2755 cm^{-1}, respectively. These bands in principle could be assigned to *trans*- and *gauche*-$(CD_3)_2CDCl$·HCl being present in the solutions. However, as can be seen in Figure 4, a similar splitting of the ν(H–Cl) absorption band was observed in the spectra of $(CH_3)_3CCl$·HCl, while this species cannot give rise to more than one rotational isomer. The assignment of the 2740- and 2755-cm^{-1} absorption bands to two different conformers in $(CD_3)_2CDCl$·HCl therefore must be doubted.

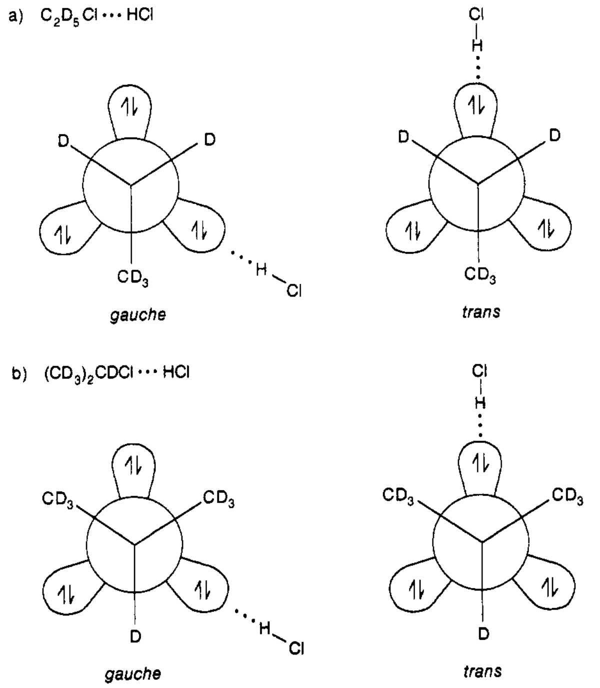

Figure 10. Possible orientations of the HCl molecule in C_2D_5Cl·HCl (a) and $(CD_3)_2CDCl$·HCl (b) hydrogen-bonded species.

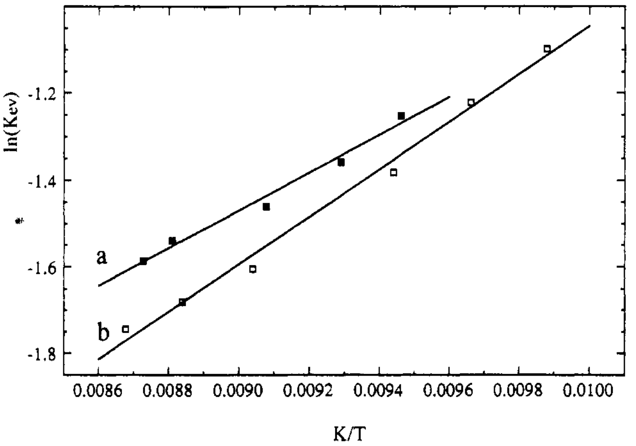

Figure 11. van't Hoff plot for the $(C_2D_5Cl)\cdot(HCl)_2$ (a) and $(iso\text{-}C_3D_7Cl)\cdot(HCl)_2$ (b) species in liquefied argon.

As described above, for CD_3Cl·HCl and C_2D_5Cl·HCl in liquefied argon, intermolecular stretching frequencies of 31 and 38 cm^{-1} are calculated from the observed ν(H–Cl) + ν(Cl···H) combination band. Unfortunately, no such combination band was observed in the spectra of $(CD_3)_2CDCl$·HCl or in those of $(CH_3)_3CCl$·HCl. Furthermore, the frequency difference of 15 cm^{-1} between the HCl stretching and the high-frequency shoulder observed in the spectra of $(CD_3)_3CDCl$·HCl compares well with the difference between the bands in the spectra of $(CH_3)_3CCl$·HCl (14 cm^{-1}). Therefore, we suggest that the high-frequency shoulder on the H–Cl stretching in the spectra of $(CD_3)_2CDCl$·HCl and $(CH_3)_3CCl$·HCl is due to another combination band, involving the ν(H–Cl) fundamental and another, as yet unidentified, low-energy deformation mode of the species.

Relative Stability of the 1:2 Complexes

To establish the relative stability of $C_2D_5Cl\cdot(HCl)_2$ and $(CD_3)_2CDCl\cdot(HCl)_2$, temperature studies were carried out between 105 and 115 K and between 100 and 116 K, respectively. Since the absorption band belonging to the 1:2 complex is rather weak, for both temperature studies solutions containing a higher concentration of HCl were used. As discussed above, the weakness of the 1:2 complex band also prevents an accurate determination of its integrated intensity. Therefore, the ΔH_0 for the formation of the 1:2 species from the 1:1 species was estimated using the height of the band maxima. The resulting van't Hoff plots are shown in Figure 11. From the least-squares fit, the complexation enthalpy ΔH_0 was calculated to be -3.7 ± 0.4 kJ mol^{-1} for $C_2D_5Cl\cdot(HCl)_2$ and -4.5 ± 0.3 kJ mol^{-1} for $(CD_3)_2CDCl\cdot(HCl)_2$.

The 1:2 complexes $(RCl)\cdot(HCl)_2$ are expected to have a chain structure in which the second HCl molecule is hydrogen bonded to the chlorine atom of the first HCl molecule: R–Cl···H–Cl···H–Cl. Therefore, in a first approximation, the enthalpy difference for the association of a second HCl molecule to the 1:1 species could be expected to be of the same magnitude as that for the formation of the HCl dimer, which was determined to be -3.78 ± 0.55 kJ mol^{-1}.[5] However, in molecular complexes containing more than one hydrogen bond, the so-called cooperative effect[16] can be active. This would lead to a complexation enthalpy for the reaction

$$RCl\cdot HCl + HCl \rightleftharpoons RCl\cdot HCl\cdot HCl$$

which is somewhat larger than the complexation enthalpy for the HCl dimer. The complexation enthalpy obtained in this study for the 1:2 complex of isopropyl-d_7 chloride indeed is somewhat larger than that for the HCl dimer, but for the 1:2 complex of ethyl-d_5 chloride, a value identical to that for the HCl dimer is found. These values at least confirm that the strength of the second hydrogen bond is similar to that of the bond in $(HCl)_2$, but, also taking into consideration the approximations used to obtain the experimental values, in our opinion they do not show the presence of a cooperative effect.

Acknowledgment. The NFWO is thanked for financial help toward the spectroscopic equipment used in this study and for a grant toward one of us (W.A.H.)

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