# The Complex between Chloromethane and Benzene*

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$^{35}$Cl Nuclear Quadrupole Resonance, NQR, spectra of mixtures of Chloromethane and Benzene, with relative molar compositions in the range 1:3 to 3:1, and at temperatures in the range 77 K to 180 K, reveals the presence of a new crystalline phase, in addition to that of pure Chloromethane. The temperature-dependence and the deuterium isotope effect of this new resonance show that the chloromethane molecule is much more labile in the new crystalline phase than in pure chloromethane. The existence of the new crystalline phase is confirmed by Differential Thermal Approach, DTA, which in addition provides evidence that the complex has a 1:1 composition and that the enthalpy of fusion is ≈ 660 cal./mole. Raman spectroscopy provides further evidence of the existence of the complex.

## Introduction

It is well-known that both carbon tetrachloride and chloroform form loose complexes with a variety of organic bases, in particular with benzene, $C_6H_6$, and these complexes have been extensively studied by $^{35}$Cl NQR [1, 2]. One or two similar complexes of methylene chloride have likewise been observed [2], but we are not aware of any reports of such behaviour for the first member of this series: chloromethane, $CH_3Cl$.

NQR spectroscopy is a particularly useful technique in this context since the appearance of a new narrow resonance is diagnostic of the creation of a new crystalline phase, since NQR lines of solid solutions are almost always so broad as to be completely undetectable. In addition, the value of the NQR frequency together with its temperature dependence is a source of information as to the nature of the interaction responsible for the formation of the complex.

## Experimental

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802A digital thermometer and varied between 77 K and room temperature by using a cryostat controlled with an Artronix 5301-E temperature controller.

DTA was performed, either with a constant rate of warming as a function of temperature or simply as a function of time, on a Dupont de Nemours thermal analyser model 990*. Raman spectra were measured on a spectrometer constructed in this Department, using a Neon/Argon laser as the exciting source**.

## Results and Discussion

### *Nuclear Quadrupole Resonance*

Rapid cooling to 77 K of mixtures of $CH_3Cl$ in $C_6H_6$, whose relative molecular composition can be varied in the range 1:3 to 3:1, gives rise to a system whose NQR spectrum shows two lines in the 35 MHz region. One of the two lines is identical in frequency to that of pure $CH_3Cl$ (34.023 MHz) and the relative intensities of these two lines depends both on the composition of the mixture and the rate of cooling. A pair of less intense lines, due to the corresponding $^{37}$Cl nuclei, at 26.818 and 27.213 MHz confirm both the identity of the line at 34.203 MHz

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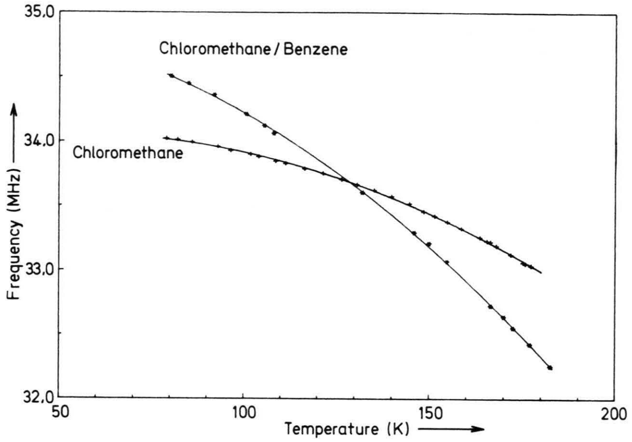

Fig. 1. The temperature dependence of the $^{35}$Cl resonance frequencies of Chloromethane and its complex with Benzene.

and that the line at 34.524 MHz is due to a resonance of the $^{35}$Cl nucleus. There is no reasonable doubt that this additional line arises from chloromethane associated in some way with the benzene molecules.

The temperature-dependence of both these lines can be followed up to 180 K, and is shown in Figure 1. The line at 34.023 MHz evolves identically to that of pure $CH_3Cl$; a further proof of the attribution of this resonance to chloromethane. The temperature-dependence of the other line is much more marked, and indeed at 180 K the resonance due to complexed $CH_3Cl$ is now much lower in frequency than that of pure $CH_3Cl$ when, 100 K lower, it was 0.5 MHz above it. The temperature-dependence of the complexed species is indeed remarkably high in that a change of 100 K decreases the frequency by 2.3 MHz. Pure $CH_3Cl$ itself, essentially no doubt because of its small dimensions, is already rather abnormal in this respect, for the majority of fairly rigid organochlorine molecules change by only 0.2 to 0.4 MHz in this temperature range.

This greater degree of motional liberty in the complex is likewise reflected in the deuterium isotope effect. The isotope effect on nuclear quadrupole coupling constants and on NQR frequencies has recently been discussed in some detail [3]. As far as resonance frequencies are concerned the isotope effect is due to the sum of an intramolecular effect – which can be directly observed via one or other of the methods of determining quadrupole coupling constants in the gas phase – and a lattice effect which is essentially due to the effect of isotopic substitution on the various librational modes. The isotope effect in pure chloromethane has been extensively studied both in the gaseous and solid phases [3]. If it is assumed that the intramolecular isotope effect is the same in gaseous $CH_3Cl$, in solid $CH_3Cl$ and in the $CH_3Cl/C_6H_6$ complex the resonance frequencies shown in Table 1 yield a lattice isotope effect which is noticeably higher for the complex than the pure halide. This is again consistent with a greater degree of motional liberty for the complex compared to the pure compound.

## *Differential Thermal Analysis*

DTA showed in general the existence of four phases. In order of decreasing temperature these are: benzene; a solid solution whose melting point stretches from 0 °C to −70 °C; a phase melting sharply at −75 °C and, finally, chloromethane. The mixture containing ≈ 77 mole% of $CH_3Cl$ showed, however, only two phases; that of pure $CH_3Cl$ and that of the phase melting at −75 °C which we assume is the complex. By following the warning-up curve of this mixture from −120 °C to room-temperature and comparing the heat evolved for a sample of pure $CH_3Cl$ in the same way, we were able to show that the complex has the composition 1 : 1 and that the enthalpy of fusion of the complex is ≈ 2760 J · mol$^{-1}$. This rather small enthalpy of fusion is consistent with the complex being only rather weakly bound.

Table 1. Isotope effects at 80 K.

| | Frequency | Isotope shift | |
|---|---|---|---|
| | | Total | Lattice |
| $CH_3Cl_{gas}$ | 37.376 | | |
| $CD_3Cl_{gas}$ | 37.286 | −0.090 | – |
| $CH_3Cl$ | 34.023 | | |
| $CD_3Cl$ | 33.970 | −0.053 | +0.037 |
| $CH_3Cl/C_6H_6$ | 34.505 | | |
| $CD_3Cl/C_6H_6$ | 34.465 | −0.040 | +0.050 |
| $CH_3Cl/C_6D_6$ | 34.514 | – | +0.009 |
| $CD_3Cl/C_6D_6$ | 34.472 | −0.033 | +0.057 |

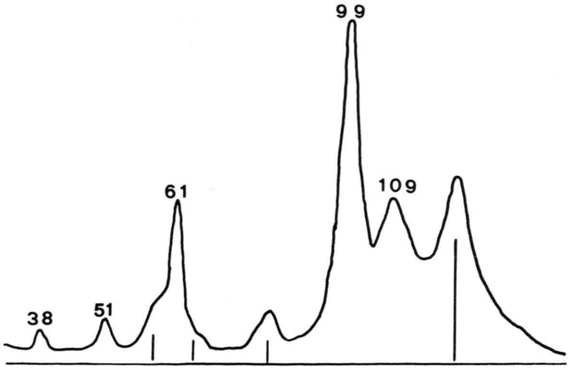

Fig. 2. The Raman spectrum, measured at 70 K, of a 77 mole% solution of Chloromethane in Benzene. The numbers show the frequencies ($\mathrm{cm}^{-1}$) of the lines attributed to the complex, the stick diagram shows the positions and approximate intensities of the lines of pure chloromethane at the same temperature.

## Raman Spectroscopy

The Raman spectrum of the 77 mole% chloromethane mixture – shown above to contain only the complex and pure $CH_3Cl$ – was measured at various temperatures below 150 K. At the higher end of the temperature range the lines are rather broad but sharpen noticeably as the temperature is lowered. The spectrum at 70 K is shown in Figure 2. The lines for chloromethane – due to translational and librational lattice modes [4] – are clearly visible, but the remaining sharp lines must be assigned to lattice modes of the complex. No attempt has been made to assign these lines but, in the present context, they serve as a further demonstration of the existence of the chloromethane/benzene complex.

## Conclusion

The formation of a loose 1:1 complex between chloromethane and benzene at low temperatures has been demonstrated by a combination of NQR, DTA and Raman spectroscopy. The structure of this complex may well be similar to that formed between benzene and chloroform; alternatively the high degree of motional freedom of the chloromethane molecule in the complex may imply that the structure more ressembles that of a clathrate.

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