

IR MATRIX ISOLATION STUDIES OF THE CONFORMATIONS OF 1,3-DICHLORO-2,2-DIMETHYLPROPANE AND 2-(CHLOROMETHYL)-2-METHYL-1,3-DICHLORO-PROPANE

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ABSTRACT

The IR spectra of the title compounds matrix isolated in argon and nitrogen at 14 K, were recorded with the hot nozzle method at temperatures of 300, 450, 700 and 900 K. In 1,3-Dichloro-2,2-dimethylpropane a third conformer (AA) with C_{2v} symmetry was detected in addition to those with C_2 (GG) and C_1 (AG) symmetries observed previously. The enthalpy differences were measured as $\Delta H^\circ(\text{AG-GG})$ equal to 4.0 and $\Delta H^\circ(\text{AA-GG})$ equal to 7.5 kJ mol⁻¹.

In 2-(Chloromethyl)-2-methyl-1,3-dichloropropane the spectra revealed the three conformers with symmetries C_s , C_1 and C_3 determined earlier, and the enthalpy differences were measured to be $\Delta H^\circ(\text{C}_1\text{-C}_s)=1.7$ and $\Delta H^\circ(\text{C}_3\text{-C}_s)=3.9$ kJ mol⁻¹.

INTRODUCTION

The two title compounds 1,3-dichloro-2,2-dimethylpropane ($\text{CH}_2\text{Cl-C}(\text{CH}_3)_2\text{-CH}_2\text{Cl}$) (DCDMP) and 2-(chloromethyl)-2-methyl-1,3-dichloropropane ($\text{CH}_2\text{Cl})_3\text{C}(\text{CH}_3)$ (CMDCP) have both been studied by gaseous electron diffraction (refs 1, 2) and by vibrational spectroscopy (refs. 3, 4) with special reference to the conformations in these molecules. They are examples of halogenated neopentanes with the general formula $\text{C}(\text{CH}_3)_{4-w}(\text{CH}_2\text{X})_w$ where $w=1,2,3,4$ and $\text{X}=\text{F,Cl,Br}$. Some of these have been studied in this laboratory, including 1-chloro-2,2-dimethylpropane (ref. 5), 1,3-dibromo-2,2-dimethylpropane (ref. 6), 2,2-di(chloromethyl)-1,3-dichloropropane (ref. 7), 2,2-di(bromomethyl)-1,3-dibromopropane (ref. 7) and 2,2-di(fluoromethyl)-1,3-difluoropropane (ref. 8) in addition to DCDMP (ref. 3) and (CMDCP (ref. 4).

Among the neopentanes with two halogens, only four conformers, among the nine staggered possibilities, are spectroscopically distinguishable. Their symmetry, notation and statistical weights are C_2 (GG, 2), C_1 (AG, 4), C_{2v} (AA, 1) and C_s (GG', 2). The symbols G (*gauche*) and A (*anti*) refer to the orientations of the C-X bonds around the two significant C-C(X) bonds. Conformer GG' of C_s symmetry has one parallel 1,3 interaction between the C-X bonds, which according to molecular mechanics (refs. 1,2) calculations reduces its stability to the extent that only the three conformers GG, AG and AA will be present. (refs. 1,3). According to the gaseous electron diffraction studies at

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333 K by Stølevik (ref. 1) DCDMP has the following abundance: 56 % (4) of GG, 37 % (6) of AG and 7 % (6) of AA. If we assume the same vibrational partition function and relates the entropy terms only to the statistical weights for all the conformers, the enthalpy differences between the conformers are the following: $\Delta H^{\circ}(\text{AG-GG}) = 3.07$ and $\Delta H^{\circ}(\text{AA-GG}) = 3.84 \text{ kJ mol}^{-1}$ from the composition. According to ^1H NMR measurements in solution at 110 K, DCDMP exists only as a GG conformer (ref. 9). The IR and Raman spectra were interpreted in terms of the two conformers GG and AG and an enthalpy difference between them equal to 4-5 kJ mol^{-1} were found in the plastic phase (ref. 3).

Neopentanes with three identical halogens (CMDCP) classically have 27 staggered configurations of which 7 are spectroscopically distinguishable. Four of them have one or three parallel 1,3 interactions between the C-X bonds and are sterically very unfavourable (ref. 2). The remaining three conformers have symmetries and statistical weights C_s (3), C_1 (6) and C_3 (2). From the electron diffraction experiments Stølevik (ref. 4) gave the following composition at 361 K: 45 % (6) of C_s , 34 % (16) of C_1 and 21 % (14) of C_3 . In an ^1H NMR study of CMDCP in CBrF_3 at 102 K three conformers were found (ref. 10): 58 % of C_s , 34 % of C_1 and 8 % of C_3 . Again assuming the same vibrational partition functions for the conformers, the following data were calculated: $\Delta H^{\circ}(C_1-C_s) = 2.92$, $\Delta H^{\circ}(C_3-C_s) = 1.07 \text{ kJ mol}^{-1}$ from electron diffraction (ref. 2) and $\Delta H^{\circ}(C_1-C_s) = 1.04$ and $\Delta H^{\circ}(C_3-C_s) = 1.34 \text{ kJ mol}^{-1}$ from the NMR study (ref. 10). In the recent IR and Raman study (ref. 4) we determined the enthalpy difference between the C_s and C_1 conformer as 5 kJ mol^{-1} in the plastic and 3 kJ mol^{-1} in the liquid state.

We have recently published our results for the related 1,3-dibromo-2,2-dimethylpropane (ref. 5), and it was found that matrix isolation spectroscopy with the hot nozzle technique was an efficient method for studying the high energy conformers for this compound. Therefore, we have now remeasured the IR spectra of DCDMP and CMDCP in argon and nitrogen matrices at 14 K with nozzle temperatures in the range 300-900 K. The increased abundance at high temperatures made it possible to detect some bands characteristic of the high energy conformer and to determine the enthalpy differences ΔH° between the conformers.

EXPERIMENTAL

The samples of DCDMP and CMDCP were both commercial products, left over from the earlier investigations (refs. 3,4); gas chromatographic analyses revealed the purity to be better than 99 % in both cases. The IR spectra were recorded with a Perkin-Elmer model 225 dispersive model and on a Bruker IFS-114c Fourier transform spectrometer. Matrix isolation spectra were recorded in the ratio 1 : 500 (DCDMP) and 1 : 1000 (CMDCP) in argon and nitrogen matrices at ca. 14 K with a Displex model CSW-202 from Air Products. The inlet system consisted of a nozzle of quartz, which was

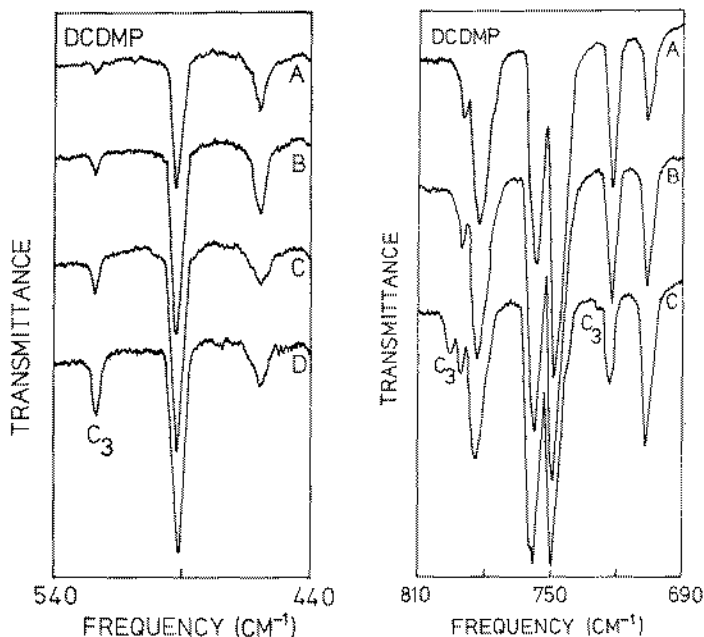


Fig. 1 (left) IR spectra of DCDMP in nitrogen matrices (1:500), recorded at 14 K; nozzle temperatures: 313 (curve A), 450 (B), 700 (C) and 900 K (D). Fig. 2 (right) IR spectra of DCDMP in nitrogen matrices (1 : 500) recorded at 14 K; nozzle temperatures 313 (A), 450 (B) and 900 K (C).

heated electrically to temperatures of 313, 450, 700 and 900 K, permitting the vapour mixture to reach these temperatures before being shock cooled on the cold window.

RESULTS AND DISCUSSION

1,3-Dichloro-2,2-dimethylpropane (DCDMP)

As representative examples, the matrix spectra of DCDMP in characteristic regions are given in Fig. 1 (nitrogen) at temperatures 313 (A), 450 (B), 700 (C) and 900 K (D) and in Fig. 2 (argon) at temperatures 313 (A), 450 (B) and 900 K (C). It is immediately seen from the spectra that the bands at 524, 726 and 795 cm^{-1} which are hardly noticed at 313 K are strongly enhanced at the higher temperatures compared to their neighbouring bands. Together with another enhanced band at 1313 cm^{-1} they are attributed to the AA conformer. The remaining bands are from the GG conformer (460, 721, and 748 cm^{-1}) and from the AG conformer (492, 705 and 756 cm^{-1}) while the bands at 783 and 790 cm^{-1} belong to both conformers. From Fig. 2 it appears that the AG band at 705 is enhanced at higher temperatures compared to the GG band at 721 cm^{-1} , demonstrating that the low energy conformer is GG (ref. 1,3).

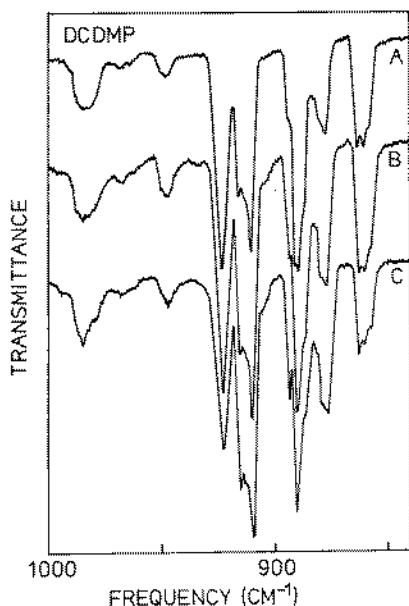


Fig. 3. IR spectra of DCDMP in nitrogen matrices (1:500), nozzle temp.: 313 K (A), 450 K (B) and 900 K (C).

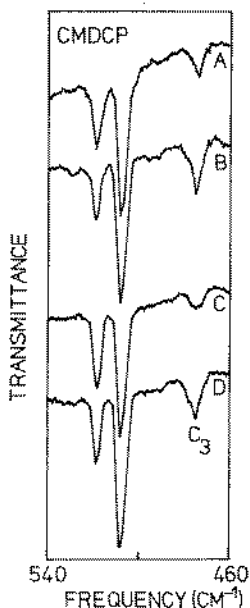
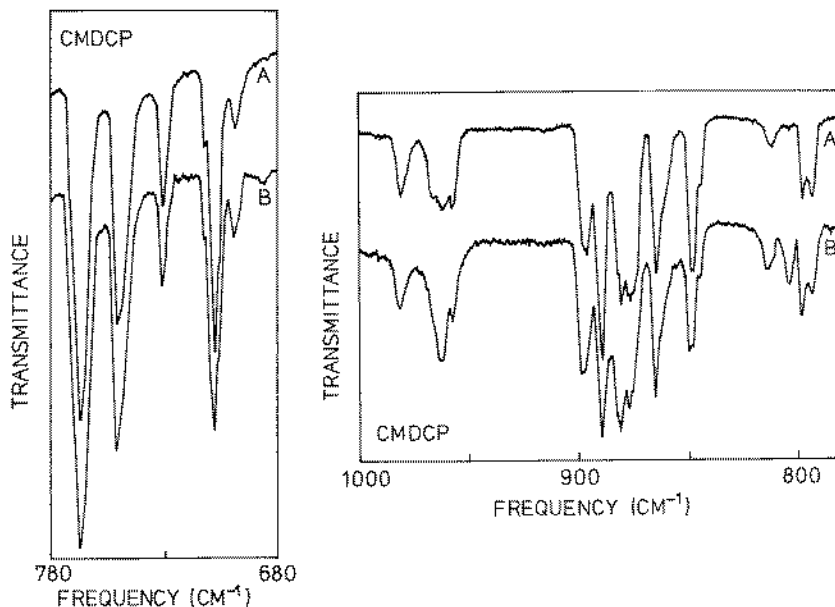


Fig. 4. IR spectra of CMDCP in Ar (A,B) and N₂ (C,D) matrices. Nozzle temperatures 313 (A,C) and 900 K (B,D).

The enthalpy difference between the conformers were determined from intensity variations of suitable pairs of "pure" GG, AG and AA bands in the matrix spectra. Thus, the band pairs 492/460, 705/721, 756/748, 877/863, 910/923, 1240/1255 and 1289/1277 cm⁻¹, representing the AG/GG ratio in the nitrogen (and correspondingly in the argon) matrix were employed in the van't Hoff plots, giving the value $\Delta H^{\circ}(\text{AG-GG}) = 4.0 \pm 0.6$ kJ mol⁻¹. For the determination of $\Delta H^{\circ}(\text{AA-GG})$ we could only employ the AA band at 524 cm⁻¹ which is well separated in the spectra and seen as a weak band even at 313 K. It was used in combination with the GG bands mentioned above, giving a value of 7.5 ± 0.8 kJ mol⁻¹. These results are in good agreement with those of the earlier vibrational study (ref. 3) and with the NMR investigation (ref. 6) since at 110 K the abundance of the

GG conformer is nearly 98%. Compared with the results from electron diffraction it appears that the abundance of the less stable conformers are somewhat overestimated (ref. 1).

The enthalpies obtained for DCDMP can be compared with those calculated for the corresponding dibromo compound (1,3-dibromo-2,2-dimethylpropane) (ref. 5): $\Delta H^{\circ}(\text{AG-GG}) = 4.2 \pm 0.4$ (matrix) and 5.6 ± 0.6 kJ mol⁻¹ (liquid) and $\Delta H^{\circ}(\text{AA-GG}) = 6.5 \pm 1.0$ (vapour) and 6.4 ± 0.8 (liquid) kJ mol⁻¹. Thus, the dichloro and dibromo compounds not only have the same conformers present in the low temperature (GG) and high pressure crystals (AG), but the enthalpy differences between the three main conformers are within the experimental uncertainties. Also, the vibrational spectra of these two molecules were surprisingly similar (ref. 6), taking the heavier bromo substituents of the latter compound into account.



Figs. 5 (left) and 6 (right). IR spectra of CMDCP in nitrogen matrices (1:1000) recorded at 14 K; nozzle temperature 313 K (A) and 900 K (B).

2-(Chloromethyl)-2-methyl-1,3-dichloropropane (CMDCP)

Three matrix spectra for CMDCP are given in Figs. 4, 5 and 6 showing the region 540-460 cm^{-1} in nitrogen and argon matrices, and the 780-680 and the 1000-780 cm^{-1} ranges both in nitrogen matrices. For the sake of clarity, only the extreme temperatures 313 K (curve A) and 900 K (curve B) are shown in Figs 4-6. From the spectral curves in the 540-460 cm^{-1} region, one can see that the three bands change their intensities differently with temperature.

In agreement with our earlier interpretations (ref. 4) the band at 519 cm^{-1} belongs to the most stable C_S conformer, the band at 508 cm^{-1} comes from a less stable C_1 conformer whereas the 474 cm^{-1} line belongs to the least stable C_3 conformer (Fig. 4). This supports the conclusion that even at room temperature all the three conformers are present in detectable amounts. In Figs. 5 and 6 there are no well isolated bands belonging to the C_3 conformer, but rather bands at 962, 877, 766 and 708 cm^{-1} (in nitrogen) representing overlapping bands of conformers C_S and C_1 . To determine the enthalpy difference between them it is essential to find "pure" bands of each conformer.

The band pairs at 508/519, 750/730, 864/848 cm^{-1} , representing C_1/C_S (in the argon matrix) and the corresponding band pairs in nitrogen were employed for determining the enthalpy differences, since in this part of the spectrum the force constant calculations suggest no bands from the C_3 conformer. Values between 1.4 and 1.9 were obtained from the van't Hoff plots, giving $\Delta H^0(C_1-C_S) = 1.7 \pm 0.4 \text{ kJ mol}^{-1}$. Only the

separated C₃ band at 474 cm⁻¹ were used for determining the C₃-C_S enthalpy difference with the C_S bands mentioned above. A value of $\Delta H^{\circ}(\text{C}_3\text{-C}_S) = 3.9 \pm 0.6 \text{ kJ mol}^{-1}$ was obtained.

In the liquid and plastic phases of CMDCP, larger values of 3 ± 1 and $5 \pm 1 \text{ kJ mol}^{-1}$, respectively, for $\Delta H^{\circ}(\text{C}_1\text{-C}_S)$ were obtained (ref. 4), suggesting smaller enthalpy differences in the vapour (matrix) than in the condensed phases. If the entropy terms (beside those pertaining to the statistical weights of the various conformers) are neglected, the ΔG° and the ΔH° values can be equaled and our results compared to the equilibrium values from gaseous electron diffraction (ref. 2) or NMR in solution (ref. 6). The relative stabilities of the conformers C_S and C₁ were determined in the opposite order by gaseous electron diffraction (ref. 2), and in the ¹H NMR study the stability of conformer C₃ seemed to be overestimated (ref. 6).

When the matrices of both compounds were annealed to 34-36 K the matrix splitting varied, but no conformational changes were detected. Accordingly, the barriers between the conformers must be higher than 11-12 kJ mol⁻¹, when embedded in the matrices, since C₁ and C₃ did not convert to the low energy conformer (C_S) at these temperatures.

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