

THE IR MATRIX ISOLATION SPECTRA AND CONFORMATIONAL ENERGIES OF EIGHT HALOACETYLHALIDES ($\text{CH}_2\text{X-COY}$; X, Y = F, Cl, Br)

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ABSTRACT

The nine possible haloacetylhalides ($\text{CH}_2\text{X-COY}$; X, Y = F, Cl, Br) except fluoroacetylfluoride were studied by matrix isolation spectroscopy in the IR region $4000\text{-}200\text{ cm}^{-1}$ (1:500 ratio) in argon and nitrogen matrices. With an electrically heated quartz nozzle, vapour mixtures at different temperatures between 300 and 900 K were deposited on the window at 14 K. Assuming the thermodynamic equilibrium between the conformers to be maintained in the matrix at the window, $\Delta H^\circ(\textit{gauche-anti})$ were calculated from van't Hoff plots of several pairs of *anti* and *gauche* bands. By annealing the matrices to 30-36 K, the *gauche* bands nearly vanished, indicating barriers of the order $6\text{-}7\text{ kJ mol}^{-1}$, except for fluoroacetylchloride and fluoroacetyl bromide for which the barrier must be above $11\text{-}12\text{ kJ mol}^{-1}$ since the thermodynamic equilibrium was not achieved at the annealing temperature. The ΔH° values were determined independently in the liquid state from Raman measurements.

INTRODUCTION

The conformational equilibria in the haloacetylhalides ($\text{CH}_2\text{X-COY}$) have been studied by various methods, including IR and Raman (refs. 1,2), NMR (ref. 3), microwave (refs. 4,5) and electron diffraction (ref. 6). It is well established from these studies that all the haloacetylhalides studied have two conformers in the vapour, liquid and in solution. The more stable conformer is invariably *anti*, which is also present in the crystals. The second conformer is generally *gauche*, and e.g. in chloroacetylchloride a dihedral angle of 116.4° from *anti* was measured from electron diffraction (ref. 6). In fluoroacetylfluoride, however, the second conformer appears to be *syn*, based upon results from microwave spectroscopy (ref. 4,5).

Since most of the vibrational spectroscopic work on the haloacetylhalides was fairly old, we planned to make a thorough investigation of these molecules by IR and Raman spectroscopy with the purpose of making complete assignments of the *anti* and *gauche* (or *syn*) conformations and to determine the enthalpy difference (ΔH°) between the conformers with good accuracy. In this work, complete IR matrix isolation spectroscopy in two matrices with the hot nozzle technique was included, since this technique has not previously been applied to the haloacetylhalides. With the narrow bands obtained in the matrices, we hoped to detect overlapping bands better than in the vapour and condensed phases. With the hot nozzle technique we assumed that the large temperature span (310-900 K) should make an accurate determination of the ΔH° feasible.

After this work was in progress, we became aware of extensive spectroscopic work on nine of the haloacetylhalides carried out by Durig and coworkers, of which three papers have so far been published (refs. 7,8) and other articles are in press (ref. 9). For this reason, we decided to restrict our studies mostly to the matrix work and to the variable temperature studies of the liquid. A preliminary account of these results will be given here.

EXPERIMENTAL

Four of the compounds $\text{CH}_2\text{X-COY}$, abbreviated (FCI), (ClCl), (BrCl), and (BrBr), were commercial products, the remaining compounds (FBr), (ClBr), (ClF) and (BrF) were synthesized. All the compounds were purified by distillation under vacuum and at the end by one or two times preparative gas chromatography, but in some of the spectra impurity peaks could not be avoided.

The IR spectra were recorded on FTIR spectrometers model 88 ($4000-400\text{ cm}^{-1}$) and an evacuable 114c ($600-50\text{ cm}^{-1}$) from Bruker and on a Perkin-Elmer model 225. The samples were mixed with argon or nitrogen in the ratio 1:500 and sprayed on a CsI window kept at ca. 14 K, cooled by a closed cycle cryostat (Air Products CSW-202). The inlet system consisted of a nozzle of quartz which could be heated electrically to more than 900 K. IR spectra of samples having different thicknesses were recorded, and subsequently the samples were annealed to temperatures between 14 and 38 K (34 for nitrogen) for periods between 1/2 h and 16 h, before new spectra were recorded. Additional IR spectra of the liquids at ambient temperature and of unannealed and annealed solids were recorded at 85 K.

Raman spectra were obtained with a triple monochromator spectrometer (Dilor RTI 30), connected to an Aspect 2000 computer and illuminated by an argon ion laser model 2000 from Spectra Physics. The samples were sealed into ampoules, surrounded by a Dewar and cooled by gaseous nitrogen. Raman spectra of the liquids at various temperatures and of the crystals were obtained, and amorphous and crystalline solids were independently recorded on a cold finger of copper, cooled by liquid nitrogen.

RESULTS AND DISCUSSION

Spectral assignments

As two representative examples, the Raman spectra of (FCI) as a liquid at ambient temperatures and as a crystalline solid at ca. 180 K are given to the left, those of (BrF) are shown to the right in Fig. 1. It is clearly seen from the spectra that a number of Raman bands of medium or weak intensities, present in the liquid spectra vanish in those of the crystals. They are attributed to the unstable conformer, being *gauche* or possibly *syn* in the fluorocompound (FF) (ref. 4,5). The bands remaining in the crystalline solids are due to the more stable conformer, in all the compounds this conformer

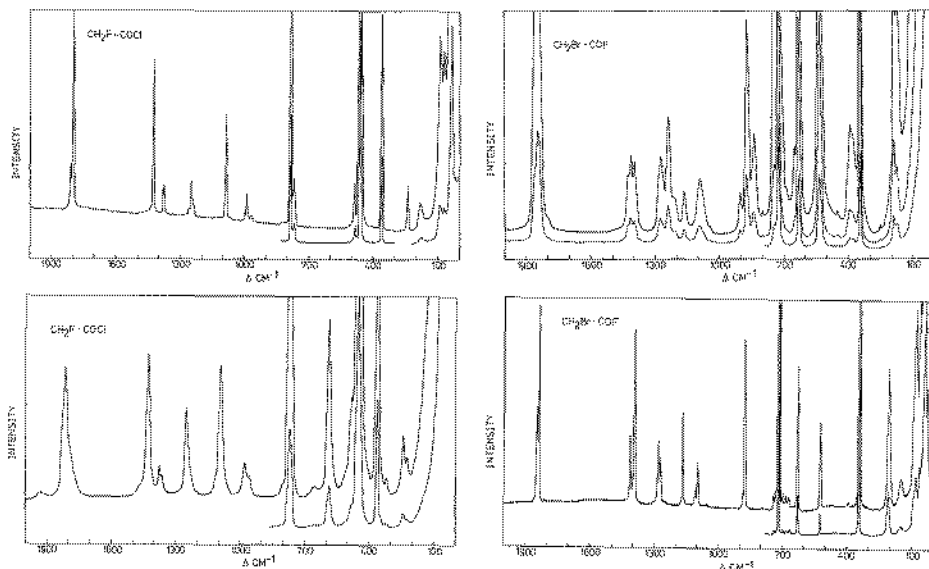


Fig. 1. Raman spectra of fluoroacetyl chloride (left) as a liquid (top) and crystal at 193 K (bottom); Raman spectra of bromoacetyl fluoride (right) as a liquid (top) and crystal at 198 K (bottom).

apparently has C_S symmetry with the halogens oriented *anti* (refs. 4-6). These Raman data as well as the corresponding results from IR have been used by all the earlier workers (refs. 1,2,7-9) to assign the vibrational spectra of both conformers, in some cases aided by normal coordinate analyses. It generally turns out, however, that there are many uncertainties since the *gauche* (eventually *syn*) conformer is never isolated in the spectra and many questions arise if the *anti* and *gauche* bands overlap or not.

In Fig. 2 an IR spectrum of (ClBr) isolated in nitrogen matrix at a nozzle temperature of 450 K is shown. The solid line represents a spectrum of the unannealed sample, containing bands both of *anti* and *gauche*. The dotted line, however, gives the IR spectrum after the sample was heated to ca. 34 K for 1/2 h. As is apparent certain bands

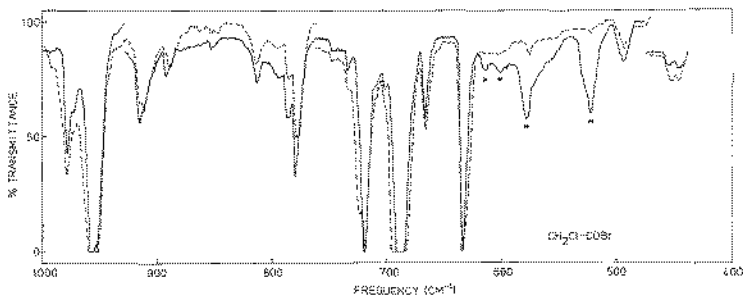


Fig. 2. IR matrix isolation spectra of chloroacetyl bromide in nitrogen at 14 K (1:500), nozzle temperature 450 K; solid line, unannealed; dotted, annealed to 34 K for 1/2 h.

vanish or are drastically reduced in intensities (equipped with asterisks in Fig. 2). They are generally the same bands which vanish in the crystal spectra and belong to the *gauche* conformer. In other bands, small shifts are observed or shoulders appear or disappear, interpreted as matrix effects caused by reorientation of the (ClBr) molecules in the matrix. From the conventional IR and Raman spectra the 583 cm^{-1} band in (ClBr) is hardly seen and two *gauche* bands were assigned, overlapping at 526 and 518 cm^{-1} (ref. 9). We believe from the matrix spectra that one of the *gauche* bands were rather situated at 583 cm^{-1} . It appears from Fig. 2 that (ClBr) has a prominent band at 583 cm^{-1} in the nitrogen matrix, obtained with a nozzle temperature of 450 K . This band is clearly a *gauche* band since it vanishes (or is rather strongly reduced in intensity) after annealing to 34 K . Thus, the matrix spectra can in some cases decide uncertain assignments regarding the *anti* and *gauche* fundamentals.

From our bulk of IR and Raman spectra fairly complete assignments of the *anti* and *gauche* bands have been made, deviating from those of Durig and coworkers (refs. 7-9) only in some instances.

Determination of the enthalpy difference (ΔH^0)

In Fig. 3 we present some characteristic Raman bands of (FBr) left and of (ClF) right obtained in the liquid state at various temperatures, of which the lowest may represent a supercooled liquid. It is easily seen from the curves that the intensities of the band pairs presented vary significantly with temperature. Since the band pairs represent an *anti* and a *gauche* component, the effect must be due to a considerable displacement of the conformational equilibria. For each of the 8 haloacetylhalides studied, some band pairs (at least 3 for each molecule) in which the bands were assumed to be "pure" were used

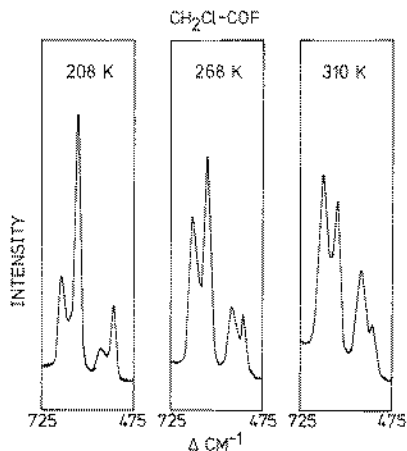


Fig. 3. Raman spectra of fluoroacetyl bromide (left) and chloroacetyl fluoride (right) as liquids at different temperatures.

for calculating ΔH^0 . The bands were in some cases treated first by a deconvolution procedure and the band areas used in the van't Hoff plots. A typical van't Hoff plot of (ClF) is shown in Fig. 4 and the ΔH^0 values were derived by a least squares procedure. In most cases the agreement between the ΔH^0 values obtained from different band pairs was quite satisfactory. Our results are presented in Table 1, for most of the compounds they appear to be somewhat higher than the recent values of Durig et al. (refs. 7-9).

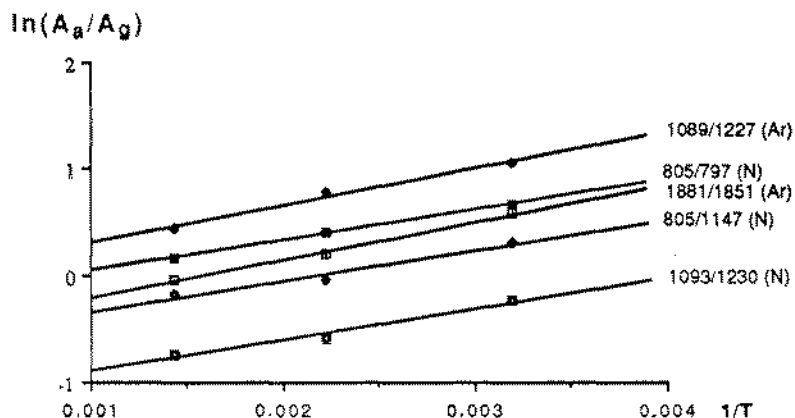


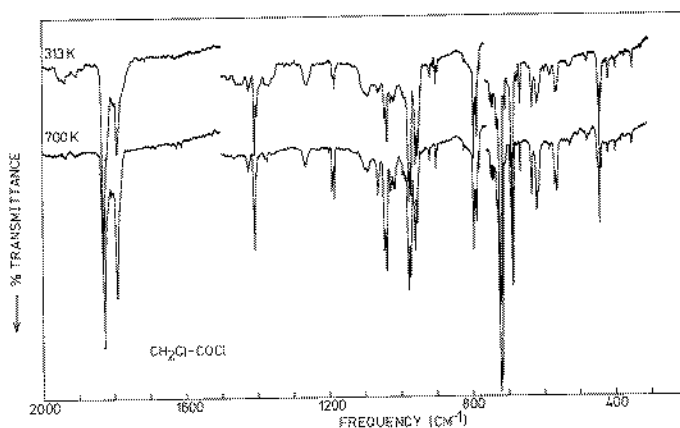
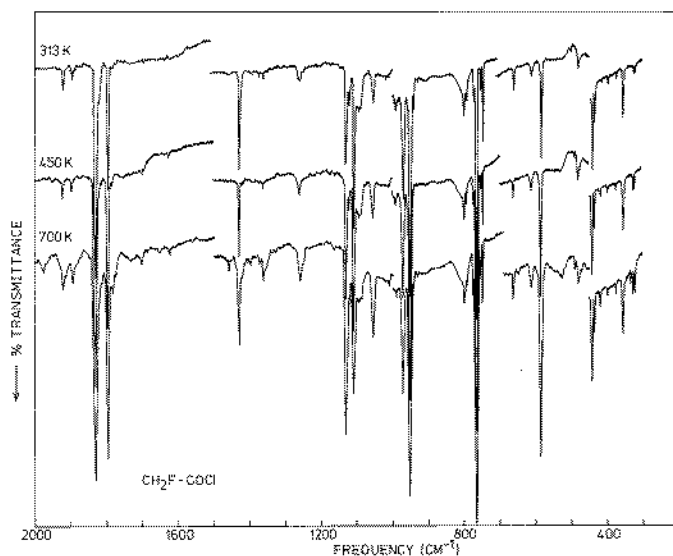
Fig. 4. The van't Hoff plots (*anti/gauche*) in chloroacetyl fluoride.

Table 1. The enthalpy difference ΔH^0 (*gauche-anti*), kJ mol^{-1} , obtained for the haloacetyl halides. ^a

Compound	Raman Liquid	IR matrix isolation (vapour)	
		Ar matrix	N ₂ matrix
CH ₂ F-COCl	6.40 ± 0.19	5.57 ± 0.30	4.92 ± 0.23
CH ₂ F-COBr	4.09 ± 0.05	{ 5.36 ± 0.63 ^b 5.11 ± 0.79	{ 5.55 ± 0.50 5.23 ± 0.61
CH ₂ Cl-COF	6.47 ± 0.10	2.63 ± 0.27	2.69 ± 0.38
CH ₂ Cl-COCl	8.39 ± 0.38	3.15 ± 0.37	4.32 ± 0.55
CH ₂ Cl-COBr	8.53 ± 0.21	5.10 ± 0.29	4.71 ± 0.30
CH ₂ Br-COF	4.88 ± 0.32	{ 0.61 ± 0.20 ^b 0.95 ± 0.26	{ 0.91 ± 0.22 0.69 ± 0.13
CH ₂ Br-COCl	4.75 ± 0.23	1.45 ± 0.22	1.82 ± 0.37
CH ₂ Br-COBr	7.39 ± 0.33	2.26 ± 0.15	2.50 ± 0.26

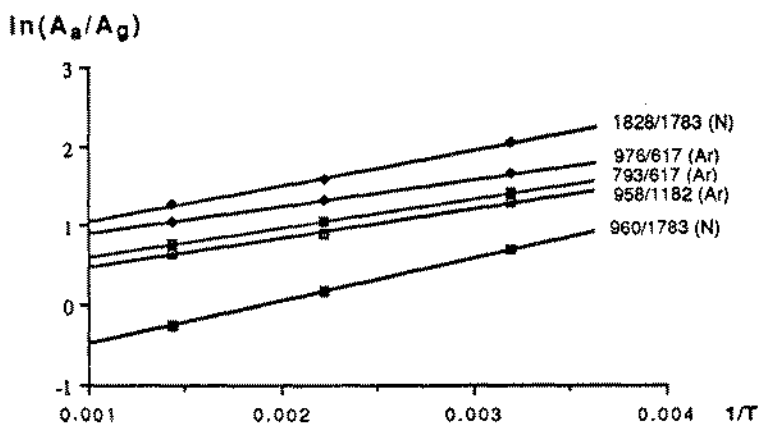
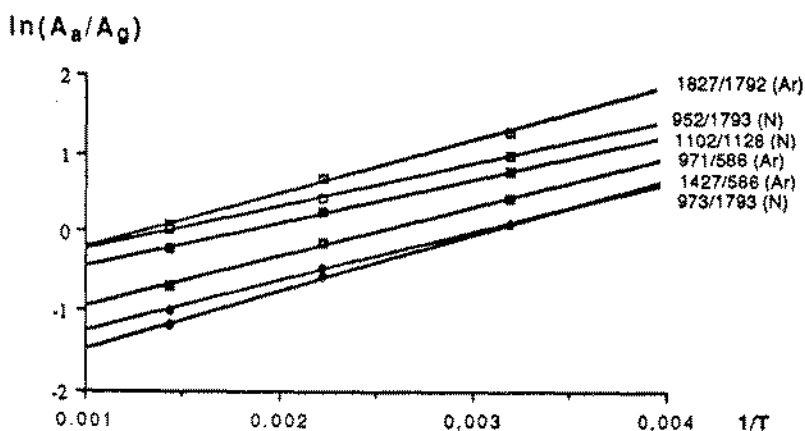
^a From peak heights. ^b From band area.

The temperature effect on the matrix spectra is demonstrated in Fig. 5 in which the unannealed IR curves of (ClCl) at 313 and 700 K are plotted and in Fig. 6 showing



Figs. 5 and 6. IR matrix isolation spectra in argon of chloroacetyl chloride (top) and fluoroacetyl chloride (bottom) recorded at various nozzle temperatures (unannealed).

spectra obtained at 313, 450 and 700 K for (FCI) all of these in argon matrices. As is apparent from Fig. 5, several pairs of *anti-gauche* bands having large intensity variations with temperature can be found for (ClCl). Among these the pairs at: 1825/1790, 1405/1790, 976/1036, 958/1182 and 793/617 cm^{-1} were employed for the determinations of ΔH° . Correspondingly, the band pairs at: 1827/1792, 1108/1129 and 971/586 cm^{-1} and some of their combinations were employed for (FCI). The ratios were correlated in van't Hoff plots (Figs. 6 and 7), and the results for all the eight compounds in both matrices are given in Table 1.



Figs. 7 and 8. The van't Hoff plots (*anti/gauche*) of fluoroacetyl chloride (top) and chloroacetyl chloride (bottom).

These data reveal that there is no systematic difference in the enthalpy values obtained in the argon and nitrogen matrices, and the values are mostly within the experimental uncertainties. Compared with the ΔH° values from the liquid, the vapour data obtained in the matrices are in most cases much lower. Also, they are generally lower than the recent values, obtained from the Raman vapour spectra (refs. 7-9).

In principle, the matrix hot nozzle method, using many bands and spanning a temperature range of typically 400 K should be superior to the IR or Raman temperature methods in which one band pair has been measured in a small temperature range of ca. 50 K. Unlike the spectral measurements carried out with a conventional isothermal cell, the matrix method assumes that the thermodynamic conformational equilibrium of the vapour is maintained in the matrices after deposition on the cold window. Thus, it is assumed that: (1) the vapour mixture attains the temperature of the nozzle and (2) the hot vapour mixture is quenched at the cold window and the high energy conformer is

prevented from passing the barrier and convert to the low energy conformer. Accordingly, the last assumption depends upon the conformational barriers.

Since the haloacetylhalides, with the exceptions of (FCI) and (FBr) relax within 15 minutes to the stable conformers (see Fig. 3) when annealed to ca. 34 K, their barriers are ca. 7 kJ mol⁻¹, while for (FCI) and (FBr) no conformational changes take place and the barriers must be higher than 10-11 kJ mol⁻¹. For the latter compounds we feel that the derived ΔH° values should be quite reliable, whereas they might be too low in the others due to a partial conversion in the matrices. Factors like the nozzle temperature, the deposition rate, and the thickness of the matrices are undoubtedly important in addition to the temperature of the cold window. Thus, in recent matrix spectra for halocyclobutanes the unstable axial conformer was not at all trapped in the matrices because of the low barriers in these molecules (ref. 10).

The conformational equilibria were studied qualitatively by Raman in solvents of varying polarity, selecting CCl₄ as the non-polar and CH₃CN as the most polar solvent. It was found from Raman intensities of a pair of C-hal stretching bands for the anti and gauche conformers that the three compounds studied, (ClCl), (BrBr) and (BrCl) all were displaced towards the anti conformer in the polar solvent, whereas the equilibria in CCl₄ was quite similar to that of the pure liquid.

Acknowledgement

The authors are grateful to Anne Horn for helpful assistance. AAEB acknowledges a stipend from the Egyptian government.

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