

## Fluoroalcohols. Part 24. Infrared, Matrix Infrared, and Raman Spectra of 1,1,1-Trichloro-3,3,3-trifluoro-2-propanol

JUHANI MURTO,<sup>a</sup> ANTTI KIVINEN<sup>b</sup> and PEKKA SAARINEN<sup>a</sup>

<sup>a</sup> Department of Physical Chemistry, University of Helsinki, Meritullinkatu 1, SF-00170 Helsinki 17, Finland and <sup>b</sup> Department of Pharmacy, University of Helsinki, Fabianinkatu 35, SF-00170 Helsinki 17, Finland

The alcohol 1,1,1-trichloro-3,3,3-trifluoro-2-propanol has been synthesized and its infrared spectra recorded in the gaseous and liquid phases and in argon and nitrogen matrices. In addition the Raman spectrum of the liquid alcohol was recorded. Assignments of the vibration bands are made. The discussion deals especially with vibrations related to the OH group. Two conformers are present in the gaseous and liquid phases. A reversible inter-conversion between two species of the alcohol occurs in nitrogen matrices when the temperature is varied.

We have previously studied the spectra of the hexahalogenated 2-propanols 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)<sup>2-4</sup> and 1,1,1,3,3,3-hexachloro-2-propanol (HCP)<sup>5</sup> and found significant differences in their behaviour in the OH stretching and torsion regions. Upon temperature variation, reversible changes were observed for these alcohols in nitrogen matrix medium, the most marked changes being in the case of HCP<sup>6</sup>. In the present paper we report results for an alcohol having both a CF<sub>3</sub> and a CCl<sub>3</sub> group, *viz.*, 1,1,1-trichloro-3,3,3-trifluoro-2-propanol (TCTFP). Spectral data for the corresponding ketone (CCl<sub>3</sub>COCF<sub>3</sub>) will be published elsewhere.<sup>7</sup>

### EXPERIMENTAL

1,1,1-Trichloro-3,3,3-trifluoro-2-propanol (a new compound) was synthesized from CCl<sub>3</sub>COCF<sub>3</sub> (obtained from PCR, Inc., Gainesville, Florida, U.S.A.) and LiAlH<sub>4</sub> (*cf.* HFP, Ref. 8). After several crystallizations (without solvent, or from pentane) the product melted at 29–30 °C (long, colourless needles). <sup>1</sup>H and

<sup>19</sup>F NMR spectra indicated the product to be at least 99 % pure.

The IR spectra were recorded with a Perkin-Elmer 621 spectrometer,<sup>9</sup> the matrix spectra as previously reported,<sup>5,10</sup> varying the matrix to absorber (M/Å) ratio between 1000 and 50. The Raman spectra were recorded with a Jarrell-Ash 25–305 spectrometer and argon ion laser<sup>8,10</sup> (488 nm exciting line; a slit servo system kept the spectral slit width constant at about 2 cm<sup>-1</sup>).

### RESULTS AND DISCUSSION

The alcohol molecule has 30 fundamental modes of vibration. The molecule has no symmetry, and thus all Raman bands are more or less polarized. The experimental results and assignments are given in Table 1.

*Bands related to the OH group. OH conformers.* The νOH band of TCTFP is a doublet in the IR spectra of the vapour (peaks at 3629 and 3599 cm<sup>-1</sup>) and CCl<sub>4</sub> solution (peaks at 3600 and 3560 cm<sup>-1</sup>). Two conformers are thus obviously present to an appreciable extent. Comparison with other alcohols having CF<sub>3</sub> and/or CCl<sub>3</sub> groups leads us to conclude that the higher-frequency peak is due to conformer II, the lower-frequency peak to conformer I (Fig. 1).

There are two νOH peaks in argon and nitrogen matrix spectra (Figs. 2, 4 and 5), similar to those of HCP. In argon the separation of these groups is only 14 cm<sup>-1</sup>, whereas in nitrogen it is 50 cm<sup>-1</sup>. In both matrices there are small irreversible changes in this region on warming the matrix (decrease of the 3586 cm<sup>-1</sup> band relative to the 3572 cm<sup>-1</sup> band in

Table 1. The observed frequencies (cm<sup>-1</sup>) for CCl<sub>3</sub>CHOHCF<sub>3</sub>.

Vapour IR <sup>a</sup>	Argon matrix IR <sup>b</sup>	Nitrogen matrix IR <sup>b,c</sup>	Liquid Raman <sup>d</sup>	Assignment Fundam.	Approximate description <sup>e</sup>
3629 w II		3619 } mw II 3614 } 3592 II	3605 <sup>f</sup> (4)	} $\nu_1$	$\nu$ OH $\nu_1$ , end group
3599 m I	3592 sh 3586 w 3578 sh 3572 m 3550	3574 sh I 3572 sh I 3568 } m Ia 3566 } 3546 I 3500 II 3465 I	3560 <sup>f</sup> (4)	} $\nu_1$	$\nu$ OH $\nu_1$ , end group $\nu_1$ , dimer
2965 vw I 2920 vw II	3450 br 3350 br 2960 br, vvw	3350 br 2960 br, vvw  1416 mw II	2960 <sup>f,s</sup> (10) 0.2 2926 <sup>f,s</sup> (8) 0.2	} $\nu_2$	$\nu_1$ , polymer $\nu$ CH
~ 1395 w	1399 sh 1396 w 1394 sh 1392 sh	1394 w I	1400 (1) > 0.5	} $\nu_3$	$\delta_a$ CH
1343	1348 sh 1344 sh 1342 m	1349 m 1346 sh	1343 (1)	} $\nu_4$	$\delta_s$ CH
1263 s	1256 s	1286 s II 1259 s Ia 1243 w II 1235 w II	1285 (2) > 0.5	} $\nu_5$	$\delta$ OH
	1270 vs	1274 m		$\nu_6$	$\nu$ CF <sub>3</sub>
1208 vs	1208 sh 1206 s 1196 vvs	1204 vs Ia 1187 vvs II	1185 (1)	} $\nu_7$	$\nu$ CF <sub>3</sub>
1160 vvs	1160 vvs 1155 vs	1154 vvs Ia 1145 vs II	1146 (2)	} $\nu_8$	$\nu$ CF <sub>3</sub>
1111 s	1112 } s 1110 }	1126 m II 1117 m I 1114 sh I	1110 (3) < 0.5	} $\nu_9$	$\nu_a$ CCC
1030 w	1033 } w 1031 }	1043 w II 1036 mw I 1030 sh I	1034 (5) 0.5	} $\nu_{10}$	$\nu$ CCO
860 sh	864 m 861 sh	864 } m 860 }	862 (13) 0.2	} $\nu_{11}$	$\nu$ CCl <sub>3</sub>
840 s	842 sh 839 s	839 sh 836 s Ia	835 (5) 0.7	} $\nu_{12}$	$\nu$ CCl <sub>3</sub>
790 m	793 sh 791 s	791 m I  785 m II	787 (6) 0.7	} $\nu_{13}$	$\nu_s$ CCC
690 s	691 m 687 s	688 vs	689 (6) 0.5	} $\nu_{14}$	$\delta_s$ CF <sub>3</sub> , ("umbrella")

Table 1. Continued.

655 s	656 m 649 w 646 s	659 s 656 m 649 sh	658 (35) 0.10	} $\nu_{16}$	$\nu_s \text{CCl}_3$
~570 w	572 w	576 w	574 (2) 0.8		
~525	526 w 524 sh	524 w	525 (5) <0.1	} $\nu_{17}$	$\delta \text{CF}_3$
~455 vw	456 w	458 w	461 (39) 0.08		
	402 vw		404 (100) 0.04	$\nu_{19}$	$\delta_s \text{CCl}_3$ ("um- brella")
		420 sh 418 w 410 m 396 } 394 } <sup>w</sup>		} $\nu_{20}$	$\tau \text{OH}$
	333 m 326 ms 322 vs	Ia			
	346 s	325 br, w II			
	290 w 284 sh 261 vw	345 w 290 w 282 sh 269 vvw	343 (9) 0.5 295 (21) 0.75 287 sh 264 } (7) 0.6 256 } 215 (20) 0.6 190 (10) 0.8 154 (9) 0.7 N.O. N.O.		

<sup>a</sup> Incomplete data due to low vapour pressure. <sup>b</sup> Intensities refer to matrices with large M/A ratios (before warming). <sup>c</sup> The two species are designated by I and II (see text), Ia relating to the strongest  $\nu \text{OH}$  band of species I. <sup>d</sup> The relative intensities are given in parentheses. The figures after these are the depolarization ratios. N.O.=not observed. <sup>e</sup>  $\nu$ =stretching,  $\delta$ =bending,  $\rho$ =rocking,  $\tau$ =torsion; s=symmetric, a=asymmetric vibration (local symmetry). <sup>f</sup> 9.1 Wt. % in  $\text{CCl}_4$ . <sup>g</sup> Only one peak is seen in the neat liquid [2950 (16) 0.2].

argon, decrease of the shoulders at 3574 and 3568  $\text{cm}^{-1}$  in nitrogen).

In argon it is not clear, whether there are one or two OH conformers present (see Refs. 5 and 2). It seems possible that the conformer ratio changes during the deposition and that the  $\nu \text{OH}$  splitting is not due to OH conformers. No marked changes due to the IR beam occurred in the  $\nu \text{OH}$  region during the time interval 20 s to several hours (after opening the beam shutter) (cf. 2-fluoroethanol and 2-chloroethanol,<sup>11</sup> for which a change from the *gauche* conformer to the *trans* conformer was observed in the IR beam).

Marked reversible changes occur in the nitrogen matrix with changes in temperature:<sup>6</sup> with increasing temperature the peak at 3566  $\text{cm}^{-1}$  increases, while that at about 3617  $\text{cm}^{-1}$

decreases (Fig. 4). Similar, but still more marked changes have been observed for HCP.<sup>5,6</sup>

The energy difference of the two species was found to be about 150  $\text{J mol}^{-1}$ ,<sup>6</sup> with the species giving rise to the higher  $\nu \text{OH}$  frequency being that of the lower energy. Since the peak height ratios change fast in response to changes in temperature, the energy barrier between the two species is obviously low. We found<sup>6</sup> the

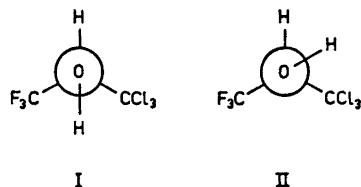


Fig. 1. The conformers of TCTFP.

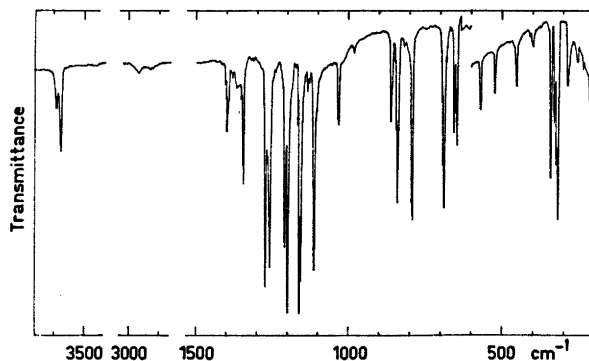


Fig. 2. IR spectrum of TCTFP in argon,  $M/A = 1000$ ,  $16 \mu\text{mol}$  TCTFP deposited during  $2\frac{1}{2}$  h at 13 K. The spectrum was recorded at 10 K.

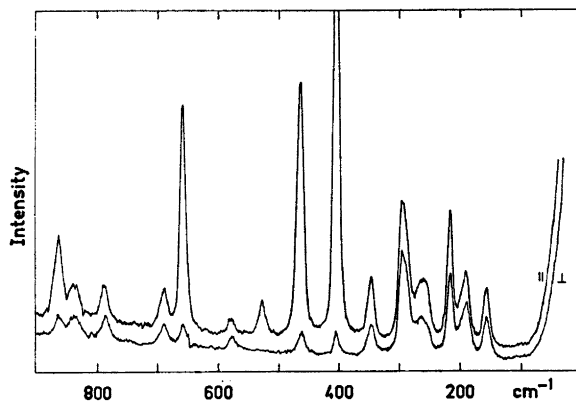


Fig. 3. Raman spectrum of liquid TCTFP in the region  $900-0 \text{ cm}^{-1}$ , single-pass cell.

formation of species II from species I to involve one nitrogen molecule in the cases of HCP and HFP, and the same is probably true also for TCTFP. Species I and II in nitrogen are probably related to the conformers I and II shown in Fig. 1, although the species in nitrogen may more properly be considered as nitrogen complexes of TCTCP.<sup>5</sup>

The changes in the  $\nu\text{OH}$  region of the nitrogen spectrum are paralleled by changes in the  $\delta\text{OH}$  and  $\tau\text{OH}$  regions (Fig. 4). The positions of the  $\nu\text{OH}$ ,  $\delta\text{OH}$  and  $\tau\text{OH}$  bands of species II indicate a more "free" OH group than in the case of species I.

TCTFP has less tendency to associate than HFP, but considerably more than HCP. In the IR spectrum of the pure liquid the monomer absorption band is at  $3550, 3600 \text{ sh cm}^{-1}$  and

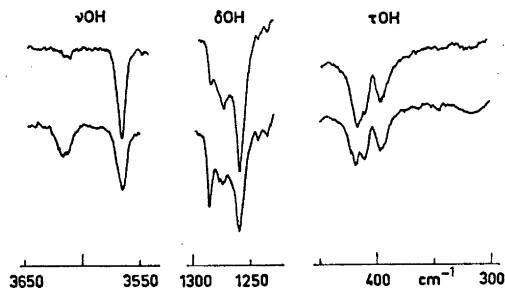


Fig. 4.  $\nu\text{OH}$ ,  $\delta\text{OH}$  and  $\tau\text{OH}$  regions of TCTFP in a nitrogen matrix ( $M/A = 500$ ,  $16 \mu\text{mol}$  TCTFP deposited during 1 h). The matrix was deposited at 13 K, annealed by warming to 27 K and the spectra were then recorded at 10 K (lower curves) and at 22 K (upper curves).

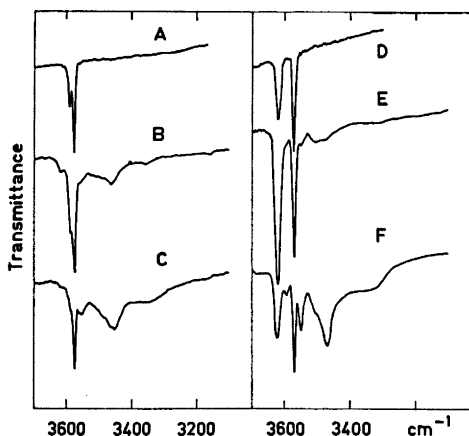


Fig. 5. IR spectra of the  $\nu\text{OH}$  region of TCTFP in argon (A, B and C) and nitrogen (D, E and F) matrices, recorded at 10 K. A, M/A=1000, 16  $\mu\text{mol}$  TCTFP deposited; B M/A=50, 45  $\mu\text{mol}$  deposited; C, the same as B, but after warming to 37 K; D, M/A=1000, 12  $\mu\text{mol}$  deposited; E, M/A=50, 45  $\mu\text{mol}$  deposited; F, the same as E, but after warming to 32 K.

the dimer absorption (equal in intensity to the monomer absorption but somewhat broader) at  $3470\text{ cm}^{-1}$ .

Fig. 5 deals with the association in matrices. Separate "dimer end group" absorptions are observed for the two forms of TCTFP in nitrogen (Fig. 5F). Their intensity indicates a considerable fraction of "linear" dimers to be present.

Only one  $\delta\text{OH}$  peak is seen in the argon spectrum, although this region shows several bands in nitrogen (see Fig. 4).

The  $\tau\text{OH}$  band is the usual triplet in argon (Fig. 2), being much less intense than in the case of HCP. In nitrogen it consists of three relatively sharp peaks at 418, 410 and  $395\text{ cm}^{-1}$ , somewhat like those found for HFP (but differing from the spectrum of HCP), and of a broader absorption at about  $325\text{ cm}^{-1}$ , which obviously corresponds to species II. In  $\text{CCl}_4$  the broad  $\tau\text{OH}$  band is at about  $330\text{ cm}^{-1}$ , as in the case of HCP.<sup>5</sup>

**Other fundamentals.** The  $\nu\text{CH}$  absorption is a doublet in vapour and  $\text{CCl}_4$  spectra (in both cases the peaks are at  $2965$  and  $2920\text{ cm}^{-1}$ ).

The assignment of the other bands is indicated in Table 1. As is usual with polychloro compounds, the group frequency approxima-

tion is relatively poor. Some band splitting may occur in the matrix spectra because of the chlorine isotope effect.<sup>5</sup>

The most intense band of the Raman spectrum is that at  $404\text{ cm}^{-1}$ , which must thus refer to the  $\text{CCl}_3$  group.

Our assignment of the vibrations of the  $\text{CF}_3$  and  $\text{CCl}_3$  groups is similar to that given for 1,1,1-trichlorotrifluoroethane.<sup>12</sup>

**Acknowledgements.** Miss Tuula Suontausta is thanked for preliminary work on TCTFP. We gratefully acknowledge financial support from the Jenny and Antti Wihuri Foundation of the Finnish Academy of Science, and from the Science Research Council of Finland.

## REFERENCES

1. Part 23: Kivinen, A., Murto, J., Liljeqvist, S. and Vaara, S. *Acta Chem. Scand. A* 29 (1975) 911.
2. Barnes, A. J. and Murto, J. *J. Chem. Soc. Faraday Trans. 2* (1972) 1642.
3. Murto, J., Kivinen, A., Viitala, R. and Hyömäki, J. *Spectrochim. Acta* 29 A (1973) 1121.
4. Murto, J., Kivinen, A., Näsäkkälä, M., Viitala, R. and Hyömäki, J. *Suom. Kemistil. B* 46 (1973) 76.
5. Murto, J., Kivinen, A., Räsänen, M. and Perttilä, M. *Spectrochim. Acta. In press.*
6. Murto, J., Kivinen, A. and Mutikainen, I. *Chem. Phys. Lett.* 36 (1975) 369.
7. Murto, J., Kivinen, A. and Suontausta, T. *Finn. Chem. Lett.* (1976) 50.
8. Middleton, W. J. and Lindsey, R. V., Jr. *J. Am. Chem. Soc.* 86 (1964) 4948.
9. Murto, J., Kivinen, A., Kajander, K., Hyömäki, J. and Korppi-Tommola, J. *Acta Chem. Scand.* 27 (1973) 96.
10. Murto, J., Kivinen, A., Edelmann, K. and Hassinen, E. *Spectrochim. Acta* 31 A (1975) 479.
11. Murto, J., Kivinen, A., Halonen, L. and Perttilä, M. *Unpublished results.*
12. Laloraya, R. K. and Laloraya, K. *J. Chem. Phys.* 61 (1974) 1918.

Received February 26, 1976.