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INFRARED SPECTRA OF PENTAFLUOROPROPIONATE ESTERS

G. A. CROWDER

Department of Chemistry and Killgore Research Center, West Texas State University, Canyon, Texas 79015 (U.S.A.)

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SUMMARY

Infrared spectra obtained for seven alkyl esters of pentafluoropropionic acid show that six of the nine stretching vibrations of the CF_3CF_2COO group and the three CF_3 deformation vibrations have characteristic frequencies, with average deviations of 5 cm^{-1} or less. These frequencies are compared with the corresponding values in the acid and the trifluoroacetate esters.

INTRODUCTION

Infrared spectra have recently been presented for a number of esters of trifluoroacetic acid that show most of the vibrations of the trifluoroacetate group have characteristic frequencies[1–3]. Spectra have also been reported for pentafluoropropionic acid[4], and, in order to check for group frequencies of the CF_3CF_2-COO group in esters and to compare them with the acid and trifluoroacetate values, infrared spectra have now been obtained for seven pentafluoropropionate esters, including the methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl and n-pentyl esters.

EXPERIMENTAL

Infrared spectra were obtained with a Beckman IR-12 spectrophotometer. The esters were all prepared from pentafluoropropionic acid and the corresponding alcohol. No appreciable amounts of impurities were detected by gas chromatography.

RESULTS AND DISCUSSION

The CF_3CF_2COO group has 24 fundamental vibrations, including nine stretching, 13 bending and two torsional modes. Most of the bending and the torsional frequencies lie below the region investigated and were not observed, so the present work was limited to a study of the stretching frequencies and CF_3 deformation frequencies.

Liquid-state infrared spectra for the seven esters are shown for the 400–3200 cm^{-1} region in Figures 1–7, and the characteristic frequencies that were observed are listed in Table 1.

Carbonyl stretching frequency

The average C=O stretching frequency, 1784 cm^{-1}, is higher than the normal ester carbonyl frequency[5], *ca.* 1740 cm^{-1}, but lower than the average value for trifluoroacetate esters[3]. The CF_3COOX frequencies listed in the last column of Table 1 are vapor-state frequencies. For the carbonyl bands, the liquid-state frequencies are about 10 cm^{-1} lower than the vapor-state frequencies, so the difference between CF_3COOX and CF_3CF_2COOX carbonyl frequencies is not as large as indicated in Table 1. However, the propionate carbonyl frequencies are a little lower than for the acetates (*ca.* 10–15 cm^{-1}) because the CF_3CF_2 group electronegativity is less than that of the CF_3 group[4]. The carbonyl frequency for the methyl ester is significantly higher than for the other six esters, which show a range of only 5 cm^{-1}. Methyl trifluoroacetate showed the same behavior[3].

The C=O stretching frequency for the acid monomer is about 20 cm^{-1} higher than for the esters. The monomer does not exist in the neat liquid, but the C=O stretching frequency is 1802 cm^{-1} in CCl_4 solution.

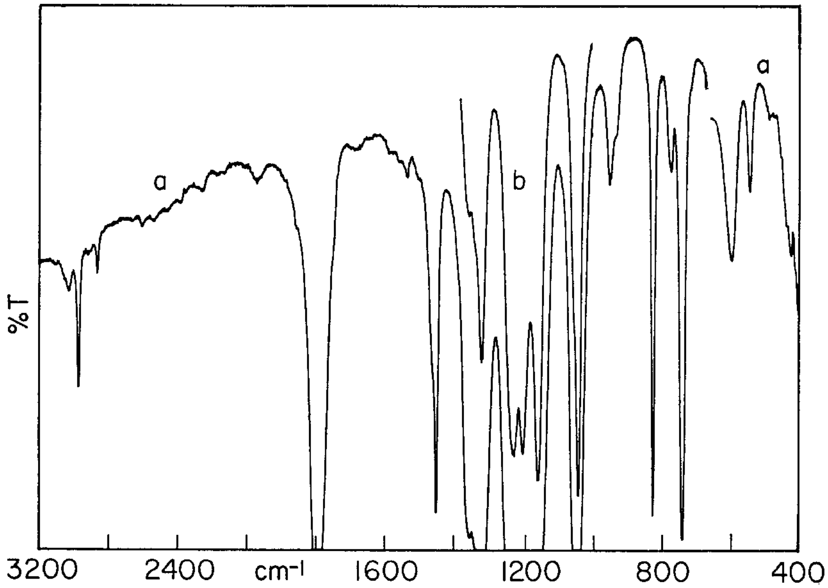

Fig. 1. Infrared spectrum of methyl pentafluoropropionate liquid. Path length: (a) 0.015 mm (b) film.

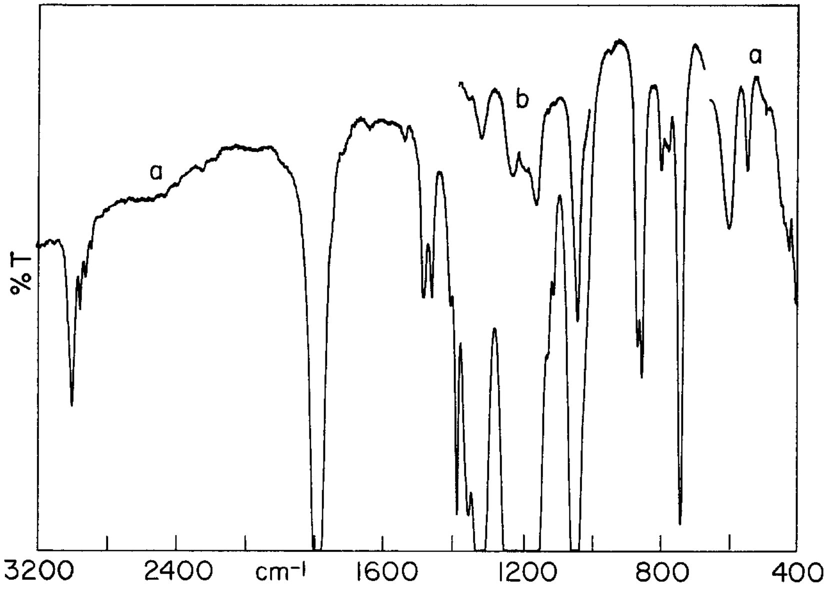

Fig. 2. Infrared spectrum of ethyl pentafluoropropionate liquid. Path length: (a) 0.015 mm; (b) film.

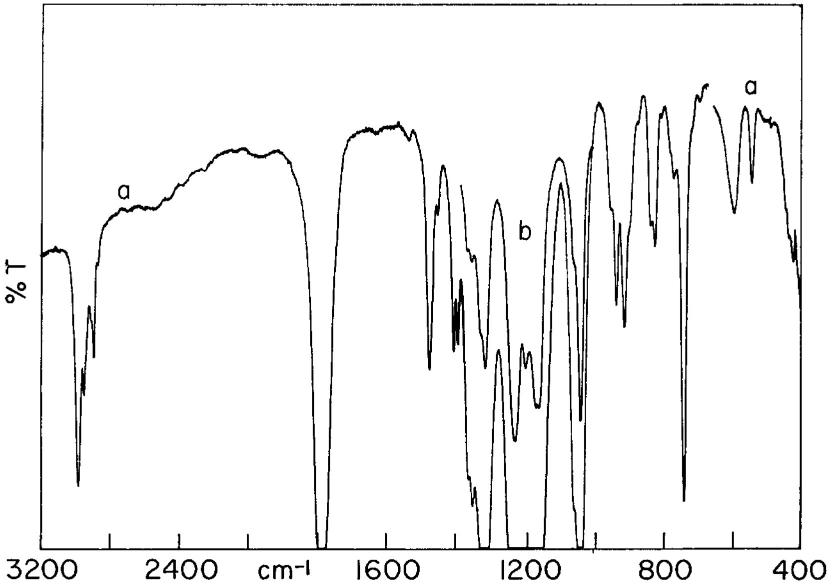

Fig. 3. Infrared spectrum of n-propyl pentafluoropropionate liquid. Path length: (a) 0.015 mm; (b) film.

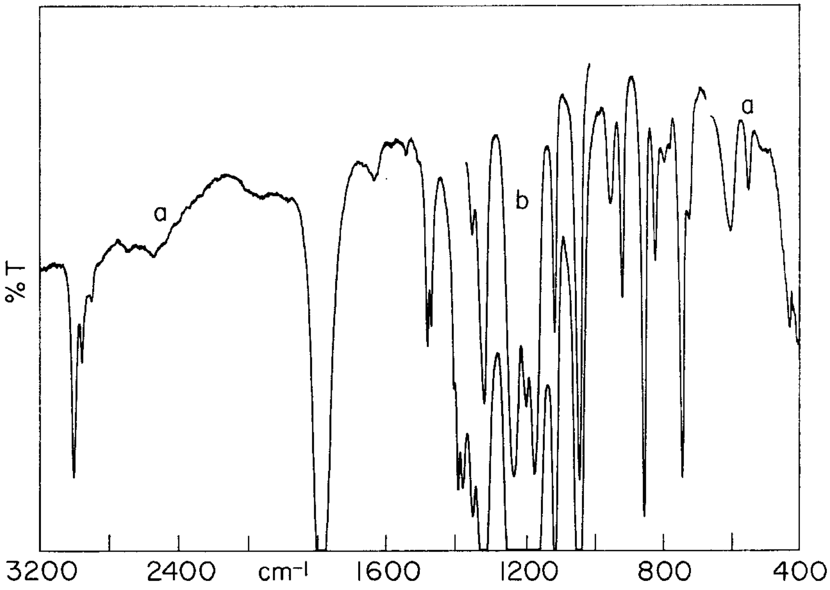

Fig. 4. Infrared spectrum of i-propyl pentafluoropropionate liquid. Path length: (a) 0.015 mm; (b) film.

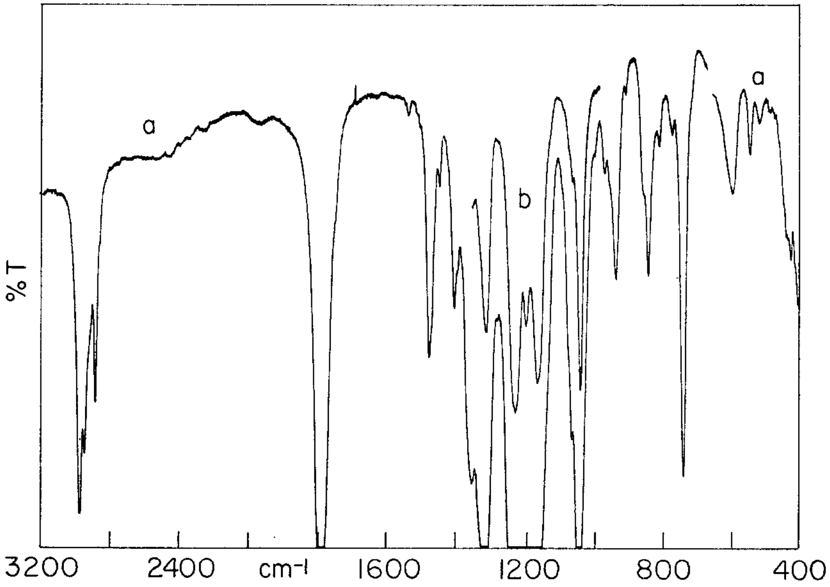

Fig. 5. Infrared spectrum of n-butyl pentafluoropropionate liquid. Path length: (a) 0.015 mm; (b) film.

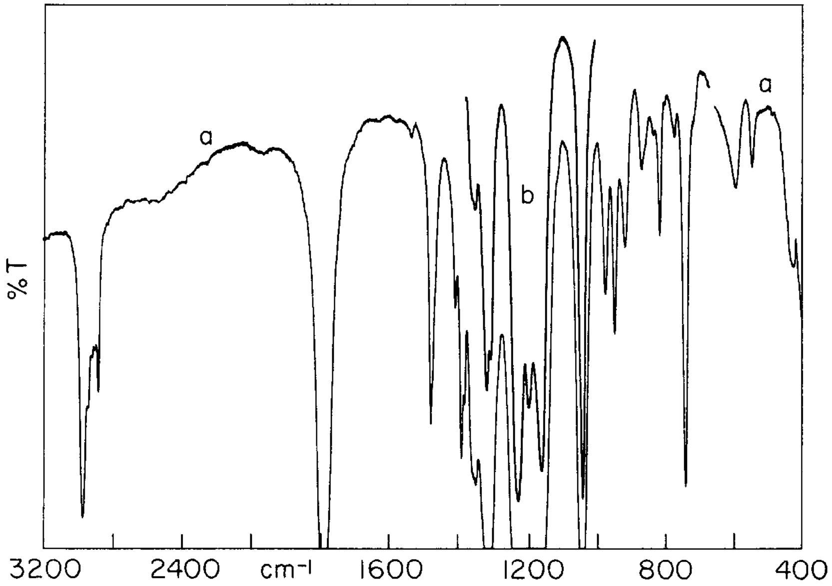

Fig. 6. Infrared spectrum of i-butyl pentafluoropropionate liquid. Path length: (a) 0.015 mm; (b) film.

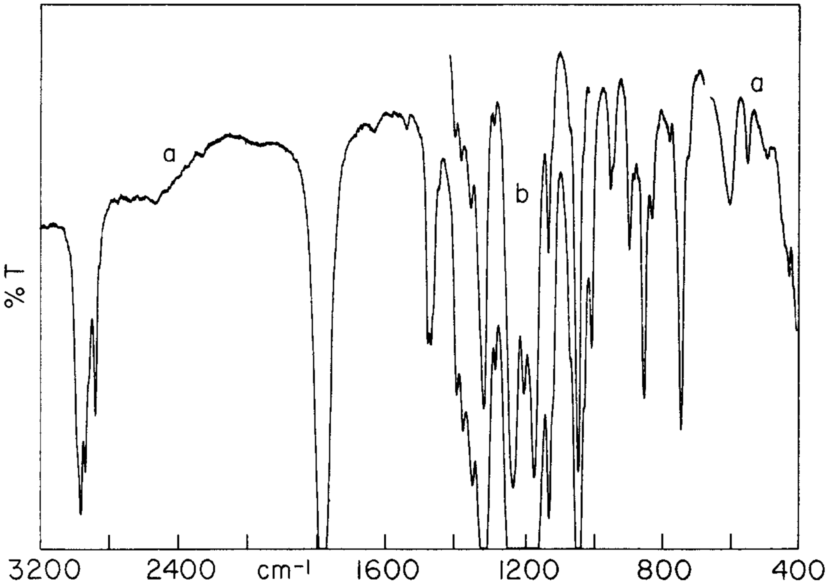

Fig. 7. Infrared spectrum of n-pentyl pentafluoropropionate liquid. Path length: (a) 0.015 mm; (b) film.

TABLE 1

CHARACTERISTIC WAVE NUMBERS (cm^{-1}) OF THE PENTAFLUOROPROPIONATE GROUP IN CF_3CF_2COOX

X =	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9	i-C_4H_9	n-C_5H_{11}	Average	H[b]	CF_3COOX (av.)[c]
ν(C=O)[a]	1794	1782	1784	1780	1783	1785	1780	1784±3	1822	1807
ν(C–F)	1319	1310	1309	1309	1306	1313	1310	1311±3	1340	—
ν(C–F)	1224	1217	1223	1223	1223	1226	1225	1223±2	1237	1240
ν(C–F)	1202	1180	1193	1188	1191	1192	1195	1191±5	1205	1189
ν(C–F)	1159	1155	1162	1162	1157	1155	1167	1160±4	1176	1159
ν(C–C)	1042	1035	1034	1033	1036	1036	1037	1036±2	1028	—
ν(C–C)	824	848	825	845	835	808	843	833±12	800	852
δ(CF_3)	741	736	736	734	734	735	737	736±2	716	736
δ(CF_3)	605	595	593	594	590	593	594	595±3	620	596
δ(CF_3)	547	544	544	542	544	544	543	544±1	545	526

[a] Abbreviations: ν = stretching vibration, δ = deformation vibration.

[b] Vapor-state values for the monomeric form of the acid[4].

[c] From ref. 3.

Carbon–fluorine stretching frequencies

The spectra of all seven esters are very similar in the region of the C–F stretching frequencies, and certainly the 1160, 1191 and 1223 cm^{-1} bands can easily be assigned to carbon–fluorine stretching modes. The 1311 cm^{-1} band is characteristic of the CF_3CF_2 group[5] and is usually assigned as a CF_3 stretch. However, normal-coordinate calculations for other fluorinated compounds may indicate that this band is due mainly to a mixture of C–C and C–F stretches[6]. Only four C–F stretch bands were observed for each of the esters, except for the n-propyl. Two bands were resolved slightly for that ester, at 1155 and 1162 cm^{-1}. The other esters probably have two accidentally degenerate C–F stretches. All four C–F stretching frequencies are slightly lower than for the acid, and three of them are in good agreement with the three frequencies for the trifluoroacetate esters. However, the 1311 cm^{-1} band in the propionates may correspond to the 1240 cm^{-1} band in the acetates.

It is not uncommon for C–F stretching frequencies of the CF_3CF_2 group to be accidentally degenerate. For CF_3CF_2CN and $CF_3CF_2CH{=}CH_2$, bands equivalent to the propionate 1311 and 1036 cm^{-1} bands were observed, but only two bands in between these were observed[7].

Carbon–carbon stretching frequencies

The two C–C stretching vibrations are assigned to the intense band at 1036 cm^{-1} and the weaker band at 833 cm^{-1}. As mentioned in the discussion of carbon–fluorine stretching frequencies, there is probably mixing among C–F and C–C stretching modes and these bands may actually have their greatest contributions from C–F stretches. The 1036 cm^{-1} band is absent in trifluoroacetates, but there is a band equivalent to the 833 cm^{-1} pentafluoropropionate band. This band frequency is the least constant of the 10 vibrations listed in Table 1 and the intensity of this band varies considerably among the different esters.

Carbon–fluorine bending frequencies

The assignments made here are limited to the CF_3 group because little work has been done relative to CF_2 frequencies and the CF_3 group seems to have relatively characteristic frequencies. The 736 and 595 cm^{-1} bands in the propionates are in excellent agreement with the acetate values, which indicates very little influence of the CF_2 group on these frequencies. The 736 cm^{-1} band has medium intensity in all the esters (both acetates and propionates), but the relative intensities of the two lower-frequency bands differ in the two ester families. The 596 cm^{-1} bands in the acetates are all very weak and the 526 cm^{-1} bands are several times more intense than this. In the propionates, the 595 cm^{-1} bands are more intense than the 544 cm^{-1} bands, with the intensities of both bands being relatively constant in all seven esters. The band-width/band-height ratio of the 595 cm^{-1} band is larger than for any of the other bands in the spectrum for all the esters.

CONCLUSIONS

Nine of the 10 vibrations listed in Table 1 seem to be good group frequencies, having average deviations of 5 cm^{-1} or less. Not only are these nine frequencies quite constant for all the compounds, but the intensities are approximately the same, being more constant than those for the trifluoroacetates. Most of the frequencies of CF_3CF_2COOH lie outside the average deviation range of the esters. In general, there is good agreement between frequencies of corresponding vibrations of trifluoroacetate and pentafluoropropionate esters.

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