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INFRARED SPECTRA OF TRIFLUOROACETATE ESTERS

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SUMMARY

Infrared spectra obtained for seven trifluoroacetate esters show that most of the fundamental vibrations of the trifluoroacetate group have characteristic frequencies.

INTRODUCTION

A large number of hydrocarbon esters has been studied in the past by infrared spectroscopy, but infrared studies of fluorinated esters are rather limited. Recently, infrared and Raman spectra were presented for methyl trifluoroacetate[1] and vinyl trifluoroacetate[2], but prior to that, studies seemed to be limited to the carbon–hydrogen stretching region[3,4] or to studies of rotational isomerism in mono- and dihalogenated acetates[5–7]. Complete vibrational assignments were made for methyl and vinyl trifluoroacetates, but the most interesting vibrations of these compounds are those due to the trifluoroacetate group. It was found that most of the 15 fundamental frequencies of this group in the methyl and vinyl esters agreed very closely, so infrared spectra have been obtained for five additional trifluoroacetate esters in an attempt to determine characteristic vibrational frequencies of the trifluoroacetate group in these esters. The list includes ethyl, isopropyl, n-butyl, 2,2,2-trifluoroethyl, and phenyl trifluoroacetates. The methyl and vinyl esters are also included in the comparisons.

EXPERIMENTAL

Infrared spectra were obtained with a Beckman IR-12 spectrophotometer, which covers the region 200–4000 cm^{-1}. The samples were all obtained from PCR, Inc., and were used without further purification. No impurities were detected in any of the samples by gas chromatography.

RESULTS AND DISCUSSION

Infrared spectra for five of the seven esters are shown in Figs. 1–5. Spectra for the methyl and vinyl esters are shown elsewhere[1,2]. All spectra are for the vapor state except for the phenyl ester, which had insufficient vapor pressure to show all the bands.

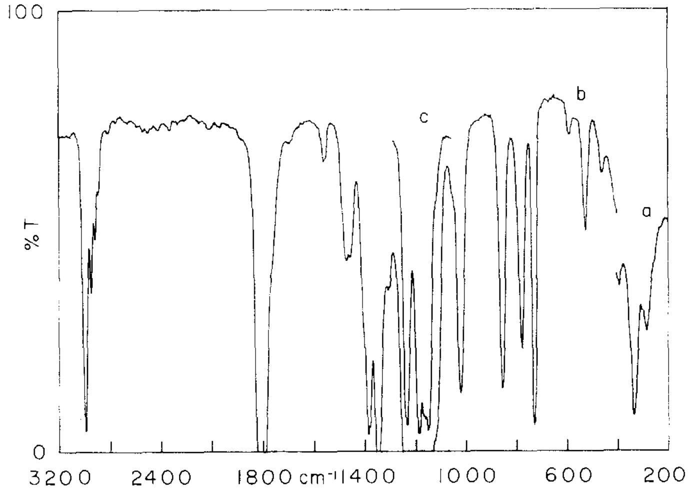

Fig. 1. Infrared spectrum of ethyl trifluoroacetate vapor, pathlength 9 cm. *a*, 80 Torr; *b*, 60 Torr; *c*, *ca.* 2 Torr.

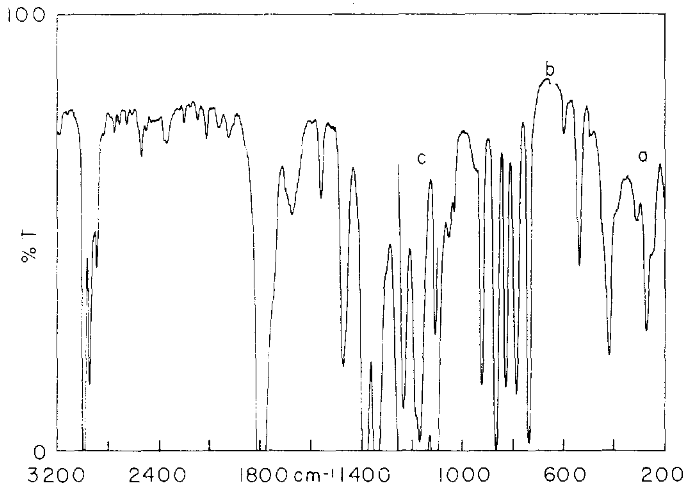

Fig. 2. Infrared spectrum of isopropyl trifluoroacetate vapor, pathlength 9 cm. *a*, 60 Torr; *b*, 50 Torr; *c*, *ca.* 1 Torr.

There are 15 vibrations associated with the trifluoroacetate group, including six stretching, eight angle bending, and one torsion. The CF_3 torsion is expected to have a frequency around 50 cm^{-1}, which is the case for CF_3CHO[8] and CF_3CFO[9], and was therefore not observed for any of the compounds studied. In addition, one of the CF_3 rocking modes has a frequency around 200 cm^{-1}, and probably lies below 200 cm^{-1} for some of the other esters and was not observed. The C–O

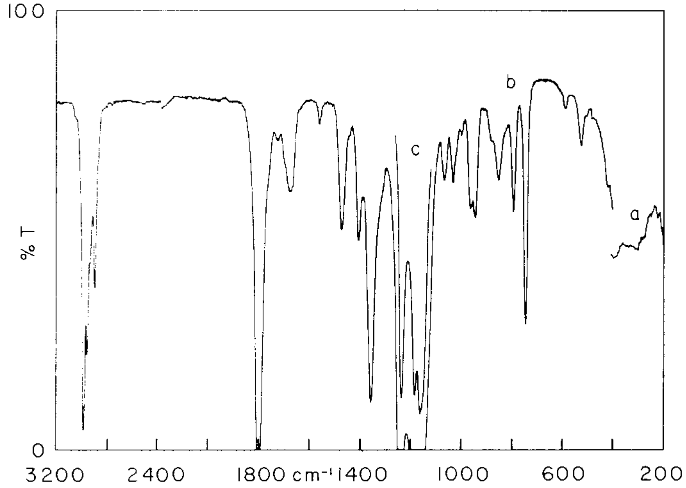

Fig. 3. Infrared spectrum of n-butyl trifluoroacetate vapor, pathlength 9 cm. *a*, 20 Torr; *b*, 30 Torr; *c*, *ca.* 2 Torr.

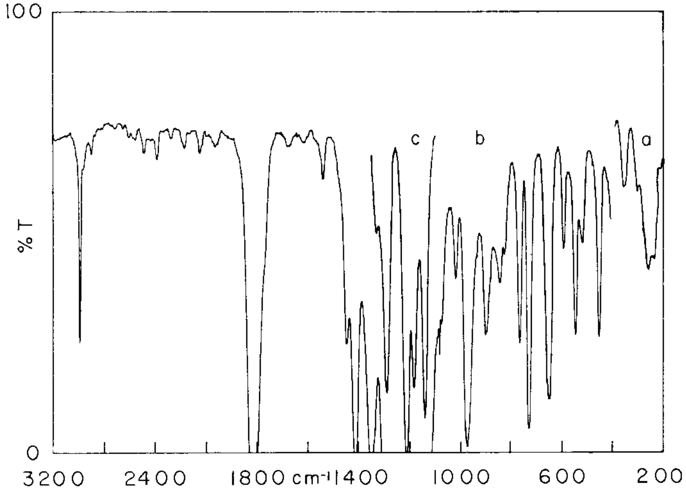

Fig. 4. Infrared spectrum of 2,2,2-trifluoroethyl trifluoroacetate vapor, pathlength 9 cm. *a*, 80 Torr; *b*, 40 Torr; *c*, *ca.* 1 Torr.

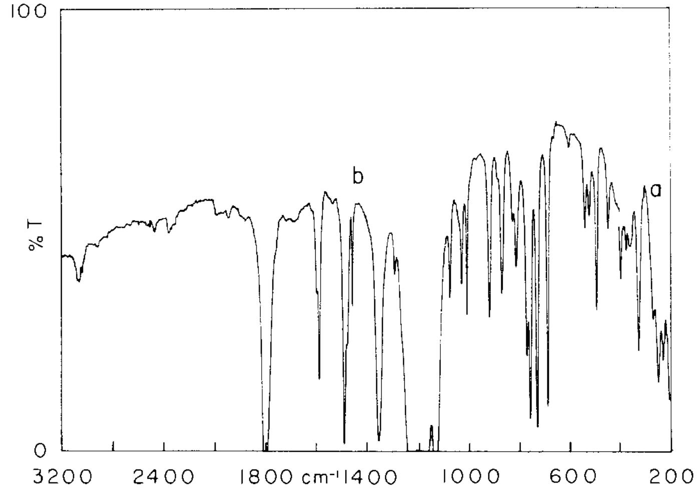

Fig. 5. Infrared spectrum of phenyl trifluoroacetate liquid, *a*, film; *b*, 0.007 mm.

stretching band could not be assigned for all esters, probably because it is overlapped by one of the more intense C–F stretching bands, and the C–C–O bending vibration could not be assigned with certainty for all the compounds. Therefore, only the 11 vibrations that could be confidently assigned in all seven compounds are included in the present assignment, and the frequencies of these vibrations are listed in Table 1.

TABLE 1

CHARACTERISTIC FREQUENCIES[a] OF THE TRIFLUOROACETATE GROUP IN CF_3 COOX

X =	CH_3	C_2H_5	$CH=CH_2$	CH_2CF_3	i-C_3H_7	n-C_4H_9	phenyl	average
ν(C=O)	1818	1804	1817	1808	1800	1803	1800(l)	1807 ± 7
$\nu(CF_3)$	1238	1233	1242	1248	1237	1238	1245	1240 ± 4
$\nu(CF_3)$	1193	1190	1192	1195	1173	1185	1196	1189 ± 6
$\nu(CF_3)$	1153	1155	1157	1142	1173	1166	1165	1159 ± 8
ν(C–C)	840	863	862	855	865	850	832	852 ± 10
δ(O = C–O)	783	782	775	776	782	783	770	779 ± 4
$\delta(CF_3)$	737	739	740	740	731	735	733	736 ± 3
$\delta(CF_3)$	591	593	597	602	590	590	607(l)	596 ± 5
$\delta(CF_3)$	525	526	525	528	527	525	528(l)	526 ± 1
$\gamma(CCO_2)$	420	460	407	458	420	451	497	445 ± 25
$\rho(CF_3)$	281	287	274	290	275	305(l)	267(l)	283 ± 10

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[a] All frequencies are in cm^{-1} and are for the vapor state except those indicated (l), which are for the liquid.

Carbonyl stretching frequency

The average carbonyl stretching frequency, 1807 cm^{-1}, is higher than the average ester carbonyl frequency (*ca.* 1740 cm^{-1})[10]. The introduction of the highly electronegative fluorine atoms increases the double-bond character of the carbonyl bond relative to the hydrogenated ester, and this increases the force constant of the bond. For example, the C=O force constant in CH_3CHO has been calculated[11] to be 10.77 mdyne Å^{-1}, whereas the value 11.89 mdyne Å^{-1} has been calculated for CF_3CHO[12].

Carbon–fluorine and carbon–carbon stretching frequencies

As expected, the C–F stretching bands are very intense in the infrared spectra, but they are very weak in the Raman spectra[1,2]. It has been popular in the past to assign the highest-frequency CF_3 stretching band to the symmetric stretch and the two lower-frequency bands to the two asymmetric stretches[8,13]. However, normal-coordinate calculations on CF_3CN[14], CF_3CCH[14], CF_3CCCH_3[15], CF_3CHO[12] and CF_3CH_3[16] show that the CF_3 symmetric stretching normal coordinate contributes about the same to the high-frequency band and to the band around 800^{-1} that has been assigned to the C–C stretch, and the C–C stretch contributes a significant amount to the band usually assigned as the CF_3 symmetric stretch. It is apparently this mixing of vibrations that causes the "CF_3 symmetric stretch" frequency to be higher than the asymmetric stretching frequencies, whereas the reverse is normally true for CX_3 groups. Calculations show that the asymmetric CF_3 stretching vibrations do not mix very much with other normal modes.

The bands assigned to the C–C stretching vibration, with an average frequency of 852 cm^{-1}, in some cases actually have the major contribution from the CF_3 symmetric stretch. This may also be the case for the esters under study here, but the 840 cm^{-1} Raman band of methyl trifluoroacetate is very strong, which is normally the case for C–C symmetric stretching vibrations. A normal-coordinate analysis of these esters is needed to determine the amount of mixing present.

Bending frequencies

The frequencies assigned to the O=C–O bending vibration (average 779 cm^{-1}) seem rather high for these relatively heavy atoms. However, there is some justification for making this assignment. The infrared bands for methyl (783 cm^{-1}) and vinyl trifluoroacetate (775 cm^{-1}) are moderately strong, but both are absent in the Raman spectra. This same behavior was observed for trifluoroacetic acid[17], for which the O=C–O bend was assigned to the band at 707 cm^{-1}. In addition, there is no corresponding band in the infrared spectrum of $CF_3C(=O)\text{–}S\text{–}C_2H_5$[18], which is to be expected if this assignment is correct.

The CF_3 deformation frequencies show the same pattern as the CF_3 stretches, with the higher-frequency band usually being assigned to the symmetric deformation[8]. This assignment is also in contrast to the normal case for CX_3 deformation frequencies. The normal-coordinate analyses previously discussed also show a considerable amount of mixing of the CF_3 symmetrical deformation mode with the C–C stretch, with the result that the deformation frequency is increased.

The CCO_2 out-of-plane bending frequency is the least constant of the 11 frequencies listed in Table 1, and it is perhaps surprising that the CO_2 in-plane bend has such a constant frequency. However, for some other types of molecules, the out-of-plane bending frequency is more dependent on conformation than is the in-plane bend, and that may be the case here. For example, the C–Cl out-of-plane wag in 2-chloro-1-butene has frequencies of 433 cm^{-1} (*trans* rotamer) and 560 cm^{-1} (*gauche* rotamer), but the in-plane wag frequency is 371 cm^{-1} for both rotamers[19]. 2-Bromo-1-butene shows the same behavior[19], and this variation in frequency in the trifluoroacetates may indicate different orientations of the group bonded to the oxygen relative the carbonyl oxygen.

The remaining vibration listed in Table 1 is the CF_3 rock, which shows the range 267–305 cm^{-1}. This is probably the out-of-plane rock and the one not observed for all the esters is the in-plane rock. For CF_3CHO, the a″ rock had the higher frequency[8].

Conclusions

Ten of the 11 vibrations of the CF_3COO group listed in Table 1 have average deviations of 10 cm^{-1} or less, indicating that these are good group frequencies. The CF_3 symmetrical stretch, C–C stretch, and CF_3 symmetrical deformation vibrations are rather highly mixed, but the mixing must be approximately the same in all the compounds or the frequencies would not be so constant.

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