

Tin Oxide Surfaces

Part 21.—Infrared Study of the Chemisorption of 2,2,2-Trifluoroethanol, 1,1,1,3,3,3-Hexafluoropropan-2-ol, 1,1,1-Trifluoropropan-2-one, 1,1,1,3,3,3-Hexafluoropropan-2-one and Trifluoroacetic Acid on Tin(IV) Oxide Gel

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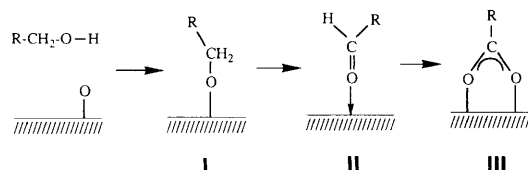
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The adsorption of trifluoroacetic acid, 1,1,1,3,3,3-hexafluoropropan-2-one, 1,1,1-trifluoropropan-2-one, 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol on tin(IV) oxide gel has been studied by infrared spectroscopy. Trifluoroacetic acid is adsorbed as both hydrogen-bonded molecular trifluoroacetic acid and surface trifluoroacetate, the former being totally converted into the latter by 533 K. The surface trifluoroacetate decarboxylates by 673 K to give surface trifluoromethoxide. Both of the ketones 1,1,1,3,3,3-hexafluoropropan-2-one and 1,1,1-trifluoropropan-2-one are chemisorbed as surface hemiacetal species by interaction with a surface hydroxyl group. These undergo subsequent thermal decomposition to give, respectively, surface trifluoroacetate and a mixture of surface trifluoroacetate and surface acetate. The two alcohols 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol are chemisorbed as surface alkoxy species which thermally decompose to surface formate and surface trifluoromethoxide in the case of the former and additionally in the case of the latter, surface trifluoroacetate. The thermal stability of the surface carboxylates is in the order: surface acetate > surface trifluoroacetate > surface formate.

Our previous studies have shown that the adsorption of a wide range of organic molecules including alkanes, alkenes, alcohols, aldehydes and ketones results in the facile formation of surface carboxylate species, which can also be generated by the adsorption of the appropriate carboxylic acid.^{1–3} Because of the extreme ease with which the surface carboxylate is formed, especially in the case of alcohols, aldehydes and ketones, we were able to gain little information concerning the mechanism of these surface oxidation reactions. Our available data are, however, consistent with a reaction scheme (Scheme 1) in which surface alkoxy species (I), formed by adsorption of alcohol molecules, are oxidised on the surface by hydrogen-abstraction involving surface oxide to transient surface-coordinated carbonyl species (II). These in turn are oxidised by a similar hydrogen-abstraction process to generate the surface carboxylate (III). In this paper we report our investigations on the chemisorption behaviour of some analogous perfluoro-substituted compounds, which undergo reaction much more slowly and allow identification of reaction intermediates in these cases.

Experimental

The preparation of self-supporting discs of tin(IV) oxide gel and the general methodology of the infrared experiments and vacuum-line techniques have been described previously.^{4,5} Infrared spectra were recorded using a Perkin-Elmer PE 683 spectrometer equipped with a PE 3600 Data Station. Abscissa scales for spectra within each figure are identical. The perfluoro-organic compounds were purified by trap-to-trap distillations and by several freeze-thaw cycles prior to use.



Results and Discussion

Trifluoroacetic Acid

Exposure of a tin(IV) oxide disc evacuated at 373 K to trifluoroacetic acid for 10 min at ambient beam temperature (abt) resulted in the appearance of new bands at 1715, 1602, 1467sh, 1416, 848, 789 and 747 cm^{-1} , and a broad envelope extending from ca. 1300 to 1100 cm^{-1} with maxima at 1250 and 1140 cm^{-1} due to $\nu(\text{C}-\text{F})$ stretching vibrations [Fig. 1(b)]. Very little change in the appearance of the spectra occurred on evacuation for 20 min at abt, although the band

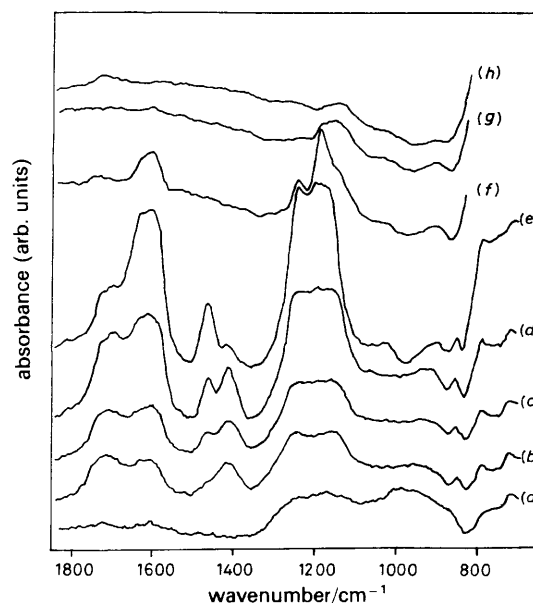


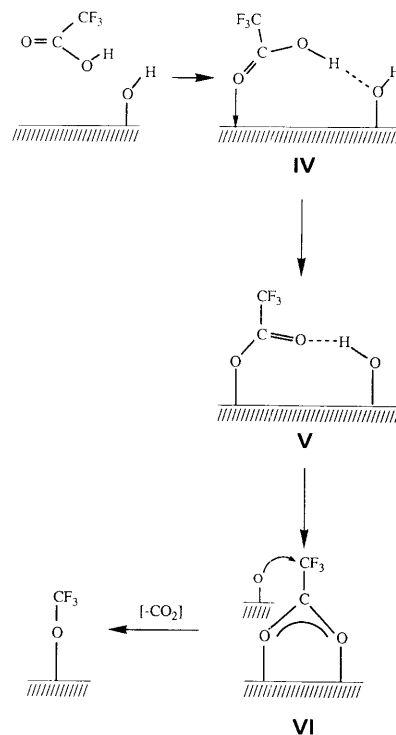
Fig. 1 Infrared spectra of a tin(IV) oxide disc exposed to trifluoroacetic acid followed by subsequent heating. (a) Initial disc after evacuation at 373 K, (b) after exposure to trifluoroacetic acid (1.5 Torr, 10 min, ambient beam temperature), (c) after evacuation (3×10^{-5} Torr) for 20 min at ambient beam temperature, after further evacuation at 373 K for 1.3 h (d), at 473 K for 3 h (e), at 523 K for 17 h (f), 3.5 h at 573 K (g) and 1.5 h at 623 K (h)

at 1467 cm^{-1} increased somewhat in intensity [Fig. 1(c)]. Evacuation at 373 K for 1.3 h resulted in a general increase in intensity of the bands at higher wavenumber [Fig. 1(d)], although the weak bands at 851, 789 and 747 cm^{-1} remain at approximately the same intensity and a new broad weak band appears at 909 cm^{-1} . The position of the 1602 cm^{-1} band moves slightly to 1613 cm^{-1} , and the 1715 cm^{-1} band also moves slightly to 1702 cm^{-1} with a shoulder appearing at 1722 cm^{-1} . Further evacuation at 473 K for 3 h results in significant changes, with the bands at 1613 and 1467 cm^{-1} increasing in intensity at the expense of the bands at 1702 and 1421 cm^{-1} , respectively, and the envelope due to the $\nu(\text{C}-\text{F})$ stretching vibrations now exhibits maxima at 1245, 1194 and 1181 sh cm^{-1} [Fig. 1(e)]. After evacuation of the sample at 523 K for 17 h the bands at *ca.* 1700, 1467 and 1421 cm^{-1} were removed completely, and the intensity of the band at 1610 cm^{-1} much lower [Fig. 1(f)]. In the C—F stretching region, well defined bands at 1245 and 1194 cm^{-1} are apparent, with a shoulder at 1152 cm^{-1} . The band at 909 cm^{-1} appears unchanged. The only features remaining after evacuation at 573 K for 3.5 h were broad weak bands at 1152 and 909 cm^{-1} [Fig. 1(g)] which were largely removed after evacuation at 623 K for 1.5 h [Fig. 1(h)].

The hydroxyl stretching region is typical for tin(IV) oxide gel, and comprises a very broad, featureless envelope stretching from *ca.* $3600\text{--}2000\text{ cm}^{-1}$, and is unchanged on adsorption of trifluoroacetic acid. The intensity of the envelope appears to increase after evacuation at 373 K for 1.3 h, but decreases on subsequent heat treatment. Significant intensity still remains, however, after evacuation at 523 K for 17 h.

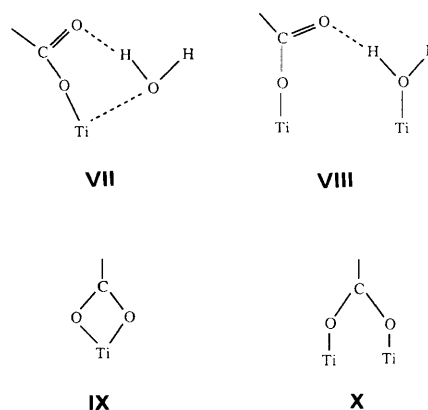
Adsorption of trifluoroacetic acid on to tin(IV) oxide discs evacuated at ambient temperature and at 473 K gave rise to very similar spectra although of lower intensity than those obtained when the oxide was pretreated by evacuation at 373 K.

The observed bands are readily interpreted in terms of the species shown in Scheme 2 involving a physisorbed/hydrogen-bonded trifluoroacetic acid (IV), the hydrogen-bonded surface trifluoroacetate (V), and the surface trifluoroacetate (VI) {characteristic bands at 1610 cm^{-1} [$\nu_{\text{as}}(\text{CO})$], 1467 cm^{-1} [$\nu_{\text{s}}(\text{CO})$], 1245, 1194 and 1152 cm^{-1} [$\nu(\text{CF}_3)$]. Neither structure IV nor V would be inconsistent with the observed spectra, with the bands observed at 1702 and 1421 cm^{-1} being assigned to the $\nu_{\text{as}}(\text{CO})$ and $\nu_{\text{s}}(\text{CO})$ vibrations, respectively, of such structures. The separation of the $\nu_{\text{as}}(\text{CO})$ and $\nu_{\text{s}}(\text{CO})$ vibrations is a useful guide to the mode of bonding of carboxylate species. Large separations correspond to physisorbed acid or unidentate carboxylate due to the essentially single- and double-bond character of the two carbon–oxygen bonds, whilst hydrogen bonding would also be expected to reduce the magnitude of the separation. As the character of the two carbon–oxygen bonds becomes more similar, as in either chelating or bridging carboxylate, so the separation of the two vibrations becomes much smaller. Thus, the separation observed for matrix-isolated monomeric trifluoroacetic acid is 404 cm^{-1} , but that for the matrix-isolated hydrogen-bonded dimer is only 345 cm^{-1} .⁶ In contrast, the separations observed for the two surface trifluoroacetate species derived by adsorption of hexafluoroacetone on rutile are only 153 and 85 cm^{-1} , and have been ascribed to hydrogen-bonded unidentate surface trifluoroacetate species such as VII and VIII and chelating (IX) or bridging (X) bidentate surface trifluoroacetate, respectively.⁷ In the present case, the separation of the two C—O vibrations for the surface trifluoroacetate is 143 cm^{-1} , which would indicate a bidentate surface trifluoroacetate (VI) possibly perturbed by hydrogen bonding. The separation observed for the other surface species is 279 cm^{-1} , indicating



Scheme 2

either free physisorbed trifluoroacetic acid or unidentate surface carboxylate. The position of the $\nu_{\text{as}}(\text{CO})$ vibration is, however, significantly lower than that observed for physisorbed trifluoroacetic acid on rutile (1790 cm^{-1}),⁷ which is only slightly lowered from that in matrix-isolated (1819 cm^{-1}) trifluoroacetic acid.⁶ Hence the bands observed here are assigned to the hydrogen-bonded unidentate surface trifluoroacetate (V). The broad nature of the carbonyl stretching bands (which extend up to *ca.* 1790 cm^{-1}) on initial adsorption of trifluoroacetic acid would, however, not preclude the presence of adsorbed molecular trifluoroacetic acid species such as IV.

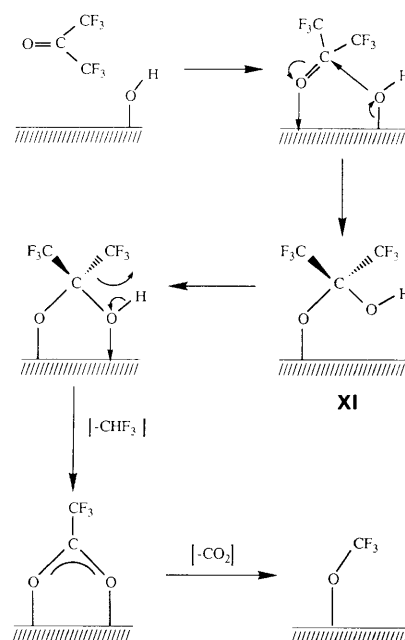


Heat treatment of the surface trifluoroacetate at 573 K results in decomposition to a surface species which exhibits only weak broad bands at 1152 and 909 cm^{-1} . Tin(IV) trifluoroacetate is known to decompose in a complex manner at 760 Torr evolving CO , CO_2 and CF_3COF leaving a residue of SnO_2 and SnF_4 ,⁸ whilst decarboxylation is a common thermal decomposition process for a number of per-

fluorocarboxylates of main-group metals including tin.⁹ It is highly likely, therefore, that the thermal decomposition of the surface trifluoroacetate involves decarboxylation to form either a surface (tin-bonded) trifluoromethyl or trifluoromethoxide species. Molecular analogues of the former species (*e.g.* $\text{Me}_3\text{SnCF}_3^{10}$) are, however, relatively unstable eliminating $[\text{CF}_2]$, and further, a reasonable mechanistic pathway for decarboxylation from a bidentate surface trifluoroacetate is difficult to envisage. The latter, on the other hand, could be formed in a relatively facile process by the participation of a neighbouring surface oxide (Scheme 2). The two bands observed at 1152 and 909 cm^{-1} are therefore assigned as $\nu_{\text{as}}(\text{CF}_3)$ and $\nu_{\text{s}}(\text{CF}_3)$, respectively, of a surface trifluoromethoxy species. The very weak band centred at *ca.* 1014 cm^{-1} is probably the corresponding $\nu(\text{CO})$ vibration of this species [doubtless the $\nu(\text{CF})$ and $\nu(\text{CO})$ vibrations are strongly coupled].

1,1,1,3,3,3-Hexafluoropropan-2-one

Exposure of a tin(IV) oxide disc previously evacuated at 473 K to 1,1,1,3,3,3-hexafluoropropan-2-one followed by evacuation at abt for 30 min resulted in the formation of new bands at 1300sh $[\delta(\text{COH})]$, 1280sh $[\delta(\text{COH})]$, 1222 $[\nu_{\text{as}}(\text{CF}_3)]$, 1144sh $[\nu_{\text{as}}(\text{CF}_3)]$, 1114 $[\nu_{\text{as}}(\text{CF}_3)]$, 954 $[\nu_{\text{s}}(\text{CF}_3)]$ and 897sh $[\nu(\text{CC})?]$ cm^{-1} [Fig. 2(c)]. These data are consistent with the formation of the surface hemiacetal species **XI** formed by nucleophilic attack of a surface hydroxyl group at the very electrophilic carbonyl carbon atom of the adsorbate (Scheme 3) similar to that formed by the adsorption of 1,1,1,3,3,3-hexafluoropropan-2-one on rutile.⁷ However, in contrast to the behaviour on rutile, no physisorbed 1,1,1,3,3,3-hexafluoropropan-2-one is observed on tin(IV) oxide. In addition



tion to the bands due to the hemiacetal species, a broad, very weak band is observed at 1616 cm^{-1} . Evacuation of the disk at 398 K for 30 min resulted in little change to the spectrum, although the band at 1616 cm^{-1} increased in intensity somewhat and a new weak band at 1540 cm^{-1} (unassigned) appeared [Fig. 2(c)], which persists even at 523 K. After 2 h at 433 K, however, the spectrum changed dramatically with little evidence of the hemiacetal bands and exhibiting bands at 1616, 1467, 1238 and 1199 cm^{-1} [Fig. 2(e)], characteristic of the formation of a bidentate surface trifluoroacetate (Scheme 3). This species is stable up to 523 K, but decomposes as before to a surface trifluoromethoxy species on evacuation of the sample at 573 K.

Tin(IV) oxide discs previously evacuated at temperatures lower than 473 K show similar adsorption behaviour towards 1,1,1,3,3,3-hexafluoropropan-2-one, although the spectra are generally weaker. Indeed, on a disc evacuated at ambient temperature the spectra of the initial adsorbate were very weak indeed, and only after evacuation at 473 K were spectra due to the surface trifluoroacetate fairly well developed.

1,1,1-Trifluoropropan-2-one

The adsorption of 1,1,1-trifluoropropan-2-one onto a tin(IV) oxide disc previously evacuated at 378 K also exhibited a spectrum consistent with the formation of a surface hemiacetal species **XII** (Scheme 4), with bands at 1460 and 1389 $[\delta(\text{CH}_3)]$, 1320 $[\delta(\text{COH})]$ and 1277 cm^{-1} $[\nu_{\text{as}}(\text{CF}_3)]$ [Fig. 3(b)]. Subsequent evacuation at 373 K for 1 h, 423 K for 1 h and 473 K for 1 h resulted in the loss of the bands due to the hemiacetal **XII** formed initially and the growth of new bands at 1720, 1609sh, 1530, 1423, 1390sh, 1346, 1320, 1277, 1233, 1194, 1157sh and 1010 cm^{-1} [Fig. 3(c)–(e)]. After further evacuation of the sample at 513 K for 2.75 h, the spectrum [Fig. 3(f)] was clearly a composite of the individual spectra of both surface trifluoroacetate (bands at 1609sh, 1233, 1194 and 1157sh cm^{-1}) and surface acetate (bands at 1520, 1423 and 1346 cm^{-1} , *cf.* bands observed by adsorption of acetic acid onto tin(IV) oxide: 1530, 1425 and 1347 cm^{-1}).¹ Clearly, both pathways for the conversion of the surface hemiacetal **XII** to surface carboxylate shown in Scheme 4 are available and proceed simultaneously. This behaviour is in sharp contrast to the adsorption of unsymmetrical organic ketones on

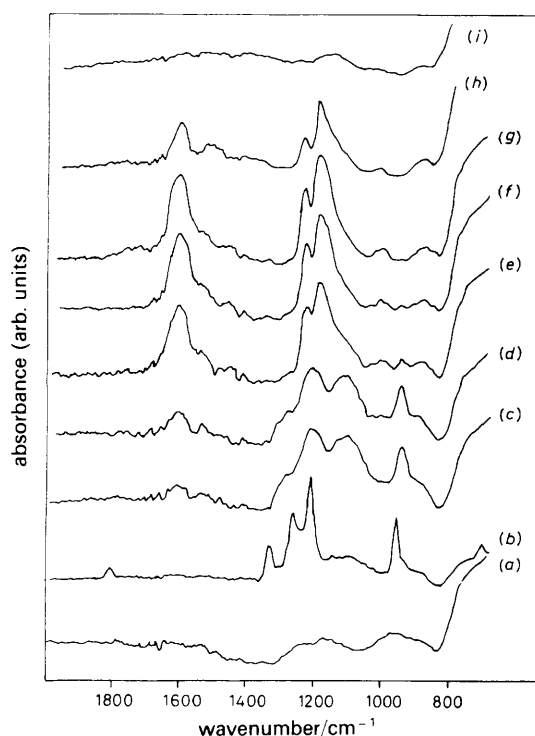
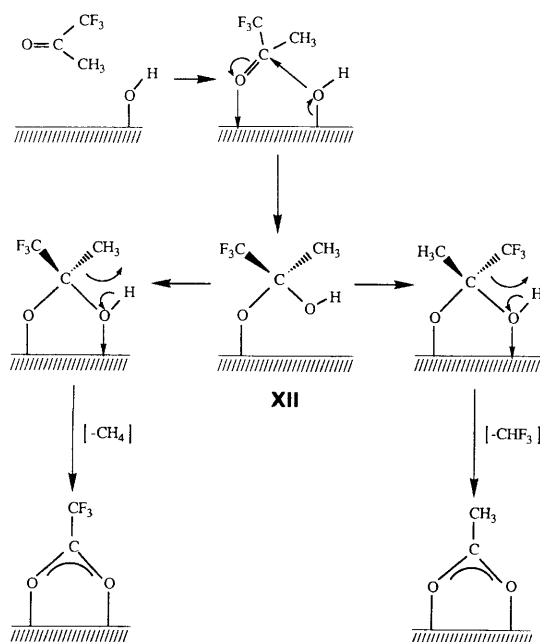


Fig. 2 Infrared spectra of a tin(IV) oxide disc exposed to 1,1,1,3,3,3-hexafluoropropan-2-one followed by subsequent heating. (a) Initial disc after evacuation at 473 K, (b) during exposure to 1,1,1,3,3,3-hexafluoropropan-2-one (4 Torr), and after evacuation at ambient beam temperature for 0.5 h (c), 398 K for 0.5 h (d), 433 K for 2 h (e), 453 K for 0.75 h (f), 473 K for 0.75 h (g), 523 K for 16.5 h (h) and 573 K for 5.5 h (i)



tin(IV) oxide, when only a single surface carboxylate is formed.² By 568 K, the surface trifluoroacetate is largely decomposed [Fig. 3(g), (h)], and by 618 K the spectrum comprises a superimposition of those of surface acetate and surface trifluoromethoxide [Fig. 3(i)]. Prolonged heating of the sample at this temperature causes the desorption of both of these surface species, and is complete after a further 6.5 h evacuation at 673 K [Fig. 3(j)–(l)]. Again, the adsorption behaviour on tin(IV) oxide discs pretreated by evacuation at

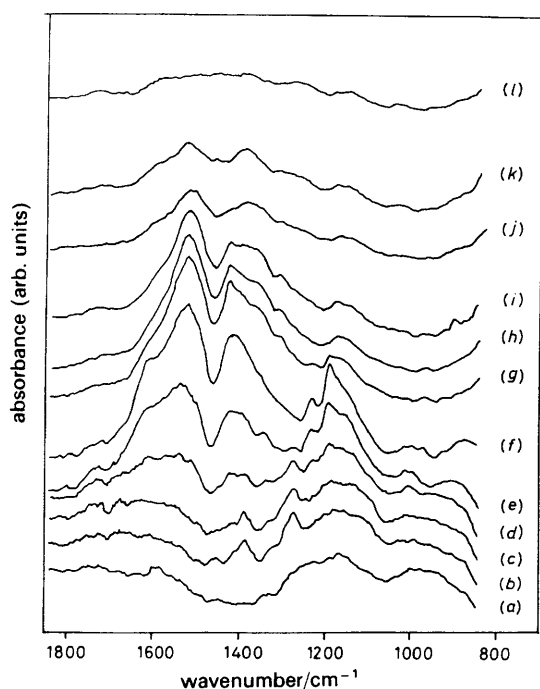


Fig. 3 Infrared spectra of a tin(IV) oxide disc exposed to 1,1,1-trifluoropropan-2-one followed by subsequent heating. (a) Initial disc after evacuation at 378 K, (b) after exposure to 1,1,1-trifluoropropan-2-one (5 Torr) followed by evacuation at ambient beam temperature, and subsequent evacuation at 373 K for 2 h (c), 423 K for 1 h (d), 473 K for 1 h (e), 513 K for 2.75 h (f), 568 K for 3.75 h (g), 568 K for 20 h (h), 618 K for 1.5 h (i), 618 K for 6 h (j), 618 K for 23 h (k) and 673 K for 6.5 h (l)

either ambient temperature or 473 K was similar, but the spectra differed somewhat in intensity.

2,2,2-Trifluoroethanol

Exposure of a tin(IV) oxide disc pretreated at 423 K to 2,2,2-trifluoroethanol at ambient temperature followed by evacuation at abt for 5 h resulted in new bands at 1460 [$\delta(\text{CH}_2)$], 1413 [$\omega(\text{CH}_2)$], 1290sh [$\nu(\text{CH}_2)$], 1276 [$\nu_{\text{as}}(\text{CF}_3)$], 1169 [$\nu_{\text{as}}(\text{CF}_3)$], 1100 [$\nu(\text{CO})$], 959 [$\delta(\text{CH})$] and 830 [$\nu_{\text{s}}(\text{CF}_3)$] cm^{-1} [Fig. 4(b)] owing to the formation of a surface 2,2,2-trifluoroethoxy species (Scheme 5). Physisorbed/hydrogen-bonded molecular 2,2,2-trifluoroethanol cannot, however, be

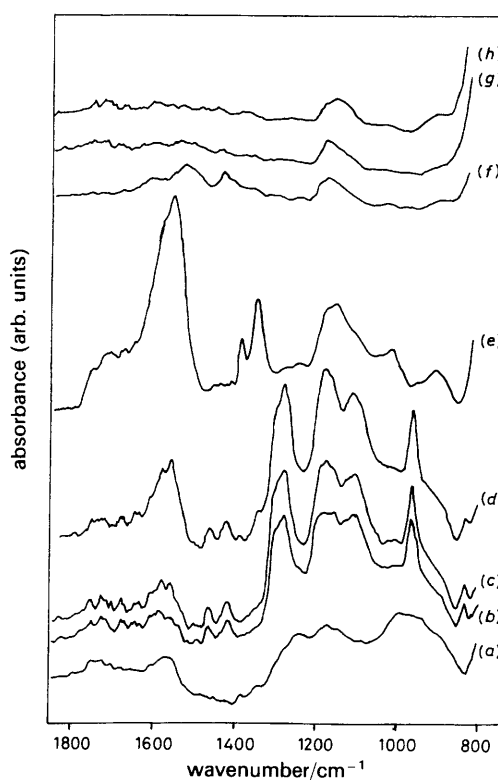
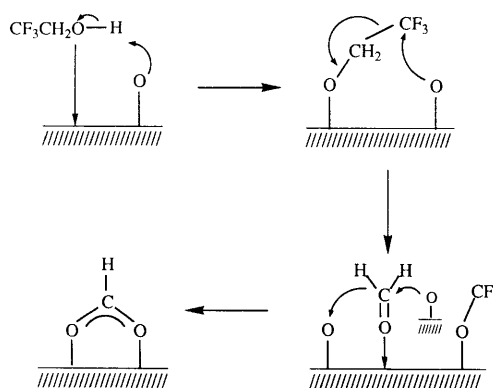


Fig. 4 Infrared spectra of a tin(IV) oxide disc exposed to 2,2,2-trifluoroethanol followed by subsequent heating. (a) Initial disc after evacuation at 423 K, (b) after exposure to 1,1,1-trifluoroethanol (10 Torr, 17 h, ambient beam temperature) followed by evacuation at ambient beam temperature for 5 h, and subsequent evacuation at 323 K for 1 h (c), 373 K for 13 h (d), 473 K for 4 h (e), 573 K for 3 h (f) and 661 K for 22 h (g) and after treatment in oxygen (18 Torr) at 661 K for 2 h (h)



unequivocally excluded as the initial adsorbate, as has been observed on both silica (bands at 1460, 1416 and 1365 cm^{-1})¹¹ and alumina (bands at 1460, 1418, 1360, 1302, 1281, 1188 and 1160 cm^{-1}).¹² Little change occurred in the spectrum on evacuation at low temperatures (1 h at 323 K followed by 13 h at 373 K), except the very weak bands at 1552 and 1572 cm^{-1} increased in intensity. Evacuation at 473 K, however, resulted in dramatic changes with the bands due to the initial surface 2,2,2-trifluoroethoxide being replaced by bands at 1570sh, 1548, 1381, 1340, 1168sh, 1146, 1100sh, 1014 and 906 cm^{-1} . In addition, a weak, very broad band is apparent ranging from the high-wavenumber side of the shoulder at 1570 cm^{-1} to ca. 1780 cm^{-1} [Fig. 4(e)]. The bands at 1548, 1381 and 1340 are readily assigned as the $\nu_{\text{as}}(\text{CO}_2)$, $\delta(\text{CH})$ and $\nu_{\text{s}}(\text{CO}_2)$ of a surface formate (*cf.* bands observed for surface formate by adsorption of formic acid: 1550, 1382 and 1340 cm^{-1}).¹ The broad envelope of bands centred at 1146 cm^{-1} and the band at 906 cm^{-1} are the $\nu_{\text{as}}(\text{CF}_3)$ and $\nu_{\text{s}}(\text{CF}_3)$ vibrations, respectively, of a surface trifluoromethoxide (*vide supra*), for which the $\nu(\text{CO})$ vibration at 1014 cm^{-1} is much more intense than that observed from the adsorption of trifluoroacetic acid. Further heating at 573 K caused the surface formate to decompose, the bands due to the formate being replaced by new weak bands at 1606, 1522 and 1429 cm^{-1} . The nature of the surface species giving rise to these bands is not certain, but surface bidentate carbonate (bands at ca. 1600 and 1223 cm^{-1}), unidentate carbonate (bands at 1450 and 1380 cm^{-1}), or carboxylate (bands at 1540 and 1300 cm^{-1})¹³ may be excluded. The surface trifluoromethoxide appears to be fairly stable under these conditions as well as under a pressure of oxygen at 661 K.

1,1,1,3,3,3-Hexafluoropropan-2-ol

Dosing of a tin(IV) oxide disc previously evacuated at 473 K with 1,1,1,3,3,3-hexafluoropropan-2-ol at ambient temperature resulted in the appearance of new bands at 1368 [$\delta(\text{CH})$], 1287 [$\nu(\text{CF}_3)$], 1261sh [$\nu(\text{CF}_3)$], 1230 [$\nu(\text{CF}_3)$], 1194 [$\nu(\text{CF}_3)$], 1139 [$\nu(\text{CF}_3)$], 1095 [$\nu(\text{CF}_3)$], 891 [$\nu(\text{CO})$] and 862 [$\nu(\text{CO})$] cm^{-1} [Fig. 5(b), (c)] due to a surface 1,1,1,3,3,3-hexafluoropropoxide (Scheme 6) (*cf.* analogous bands observed for gaseous 1,1,1,3,3,3-hexafluoropropan-2-one: 1273, 1263, 1244, 1205, 1117, 894 and 833 cm^{-1}).¹⁴ The adsorption of 1,1,1,3,3,3-hexafluoropropan-2-one on silica has been shown to occur *via* hydrogen bonding to surface silanol groups, although few infrared data were reported.¹¹ In addition, a very weak, broad band is observed at ca. 1736 cm^{-1} which may be due to a small amount of adsorbed 1,1,1,3,3,3-hexafluoropropan-2-one produced by oxidation. Little change occurs in the spectrum on evacuation of the sample up to 413 K, although the band at 1736 cm^{-1} resolves into two maxima at 1722 and 1744 cm^{-1} and new bands begin to appear at 1599 and 1453 cm^{-1} [Fig. 5(c)–(f)]. In addition, the bands at 1230 and 1194 cm^{-1} are somewhat more intense than the other bands in the $\nu(\text{CF}_3)$ envelope. As the temperature of evacuation is increased, the bands due to the surface 1,1,1,3,3,3-hexafluoropropoxide decrease in intensity and the bands at 1601, 1557sh, 1458, 1434, 1350, 1194, 1020 and 900 cm^{-1} grow [Fig. 5(g), (h)]. By 473 K the spectrum comprised the composite spectra of surface formate (bands at 1557, 1379 and 1345 cm^{-1}), surface trifluoroacetate (bands at 1605, 1240, 1194 and 1154sh cm^{-1}), and surface trifluoromethoxide [bands at 1020 and 900 cm^{-1} , the $\nu_{\text{as}}(\text{CF}_3)$ band of this species is masked by the $\nu_{\text{as}}(\text{CF}_3)$ band of the surface trifluoroacetate] [Fig. 5(i)]. Further heating *in vacuo* results in the desorption of the surface formate, which is totally removed by 533 K, leaving the surface trifluoroacetate and surface trifluoromethoxide [Fig. 5(j)–(l)].

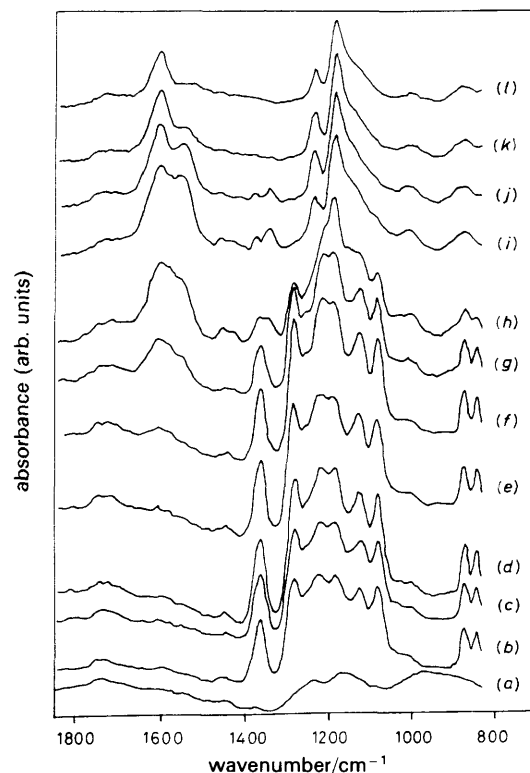
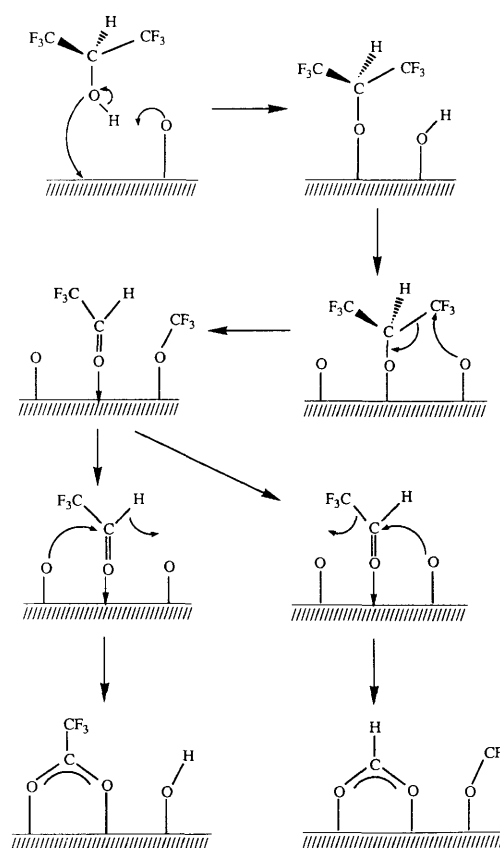


Fig. 5 Infrared spectra of a tin(IV) oxide disc exposed to 1,1,1,3,3,3-hexafluoropropan-2-ol followed by subsequent heating. (a) Initial disc after evacuation at 273 K, (b) after exposure to 1,1,1,3,3,3-hexafluoropropan-2-ol (1 Torr), followed by evacuation at ambient beam temperature for 5 min (c), 373 K for 10 min (d), 393 K for 2 h (e), 413 K for 2 h (f), 438 K for 2 h (g), 453 K for 2 h (h), 473 K for 2 h (i), 493 K for 2 h (j), 513 K for 2 h (k) and 533 K for 2 h (l).



Scheme 6

The mechanism of formation of these surface species is shown in Scheme 6. The surface 1,1,1,3,3,3-hexafluoropropoxide formed initially is first transformed *via* migration of a trifluoromethyl group from carbon to a neighbouring surface oxygen into surface trifluoromethoxide and transient surface-coordinated trifluoroacetaldehyde. This last species may then undergo further reaction involving surface oxygen to give the two surface carboxylate species observed.

Conclusions

Unlike organic alcohols, which undergo facile surface oxidation at temperatures <323 K to the corresponding surface carboxylate on tin(IV) oxide, the perfluoroalcohols, 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol, are chemisorbed to give stable surface alkoxy species. These do, however, convert on heating to 473 K to surface carboxylates, probably *via* transient surface-coordinated carbonyl intermediates, although some conversion is apparent at lower temperatures. The perfluoroketones, 1,1,1,3,3,3-hexafluoropropan-2-one and 1,1,1-trifluoropropan-2-one, are not adsorbed by coordination of the carbonyl oxygen to the surface as has been observed for organic ketones, but rather by interaction with surface hydroxyl groups, giving surface hemiacetal species. These in turn transform thermally to surface carboxylates at moderately low temperatures (completion by 473 K in the case of 1,1,1-trifluoropropan-2-one and by 433 K in the case of 1,1,1,3,3,3-hexafluoropropan-2-one, although again conversion starts at much lower temperatures). Adsorption of trifluoroacetic acid gives initially a mixture of physisorbed (hydrogen-bonded) trifluoroacetic acid and surface trifluoroacetate. On heating the sample only the latter is observed which decarboxylates giving surface trifluoromethoxy species which persist even after oxygen treatment at 661 K. A major factor in the reactivity of these perfluoromethyl adsorbates appears to be the susceptibility of the electrophilic trifluoromethyl carbon

centre to attack by surface oxide facilitating trifluoromethyl group transfer.

The thermal stability of the surface carboxylates varies significantly and follows the order (figures in parentheses indicate the highest temperature at which carboxylate is observed/temperature at which desorption is complete): surface acetate (618 K/673 K) > surface trifluoroacetate (523 K/573 K) > surface formate (473 K/533 K).

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