# Infrared Study of the Adsorption of Ethyl Acetate on Rutile

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Infrared spectra of ethyl acetate adsorbed on rutile at the solid/vapour interface are reported. Dissociative chemisorption gave surface acetate and ethoxide ions. Reactions involving surface hydroxyl groups generated acetic acid which was weakly adsorbed and could be removed by evacuation at room temperature. The relative reactivities towards ethyl acetate of four types of hydroxyl group characterized by distinguishable infrared bands are discussed. Hydroxyl groups responsible for a maximum at 3410 cm<sup>-1</sup> are inaccessible to organic adsorbates and possibly exist at sub-surface lattice sites.

Spectra of acetic acid adsorbed on rutile are briefly reported.

Infrared studies of the adsorption of carbonyl compounds on rutile have shown that surface–adsorbate interactions involving different surface sites may lead to distinguishable surface species or chemisorption products.<sup>1-3</sup> Adsorbates may retain their molecular integrity in the adsorbed state either by acting as acceptors of hydrogen bonds from surface hydroxyl groups or by acting as electron donors to incompletely coordinated Lewis acid Ti<sup>4+</sup> ions. Hydroxyl groups, O<sup>2-</sup> ions or Ti<sup>4+</sup> ions in the exposed surface planes of rutile also act as potential sites for chemisorptive interactions. In continuation of our previous studies we here report infrared spectra of ethyl acetate adsorbed on rutile. The latter was preheated at 400 K in order to remove a high proportion of associatively adsorbed water whilst retaining appreciable populations of the two types of hydroxyl group characterized by infrared bands at 3655 and 3410 cm<sup>-1.4</sup> Because it was suspected that surface acetate ions were a product of chemisorption of ethyl acetate on rutile, the adsorption of acetic acid was also briefly investigated.

### EXPERIMENTAL

Rutile (code CL/D 338) prepared by the hydrolysis of titanium tetrachloride was supplied by Tioxide International and had a surface area of  $30.3 \text{ m}^2 \text{ g}^{-1}$ . In order to remove surface chloride ions<sup>5</sup> samples were subjected to alternate soxhlet extraction with water (24 h) and heat treatment in air (673 K, 24 h), repeated four times before a final soxhlet extraction with water and heat treatment (383 K, 24 h). The resulting material was compressed (84 MN m<sup>-2</sup>) under reduced pressure (500 N m<sup>-2</sup>) into discs of 2.5 cm diameter and *ca*. 150-170 mg weight which were mounted in a conventional infrared cell with an external furnace and fluorite optical windows. Before the admission of adsorbate vapour the disc was heated (673 K, 17 h) in oxygen (1.33 kN m<sup>-2</sup>), cooled in oxygen, exposed to saturated water vapour at room temperature (1 h) and finally evacuated (400 K, 1 h).

Acetic acid and ethyl acetate were shaken with calcium sulphate, distilled twice from calcium sulphate and stored over anhydrous copper sulphate. Vapours were admitted to the infrared cell by expansion from a comparatively small volume of vapour generated by the liquid adsorbates at 77 K.

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#### RESULTS

The spectrum of rutile exhibited infrared bands at 3725, 3680(sh), 3655, 3610, 3520 and 3410 cm<sup>-1</sup> [fig. 1(*a*)], the assignment of which to OH-stretching vibrations of different types of surface hydroxyl group has been discussed elsewhere.<sup>4</sup> A weak broad band at 1610 cm<sup>-1</sup> was due to the deformation vibration of a low residual concentration of molecular water.<sup>4</sup> The admission of ethyl acetate vapour at increasing pressures led to a sequence of spectroscopic changes which showed that distinguishable surface hydroxyl groups differed in their reactivities towards adsorbate molecules. Infrared bands characteristic of two types of surface organic species also appeared in the spectra.



FIG.1.—Spectra of rutile (a) after evacuation, (b)-(f) in contact with increasing pressures of ethyl acetate vapour.

The initial stage in the adsorption of ethyl acetate led to the disappearance of infrared bands at 3725 and 3680 cm<sup>-1</sup> [fig. 1(*b*) and (*c*)] due to isolated surface SiOH and TiOH groups, respectively. The former is attributed to the existence of a low (< 100 ppm) silica impurity content in the rutile. A simultaneous general increase in adsorption intensity occurred in the spectral range 3200–3640 cm<sup>-1</sup> although the bands at 3610, 3520 and 3410 cm<sup>-1</sup>, as individual components of the overall band envelope, were unchanged. Maxima at 2970, 2935 and 2875 cm<sup>-1</sup> [fig. 1(*c*)] may be assigned to CH-stretching vibrations of adsorbed species. Strong bands also appeared at 1515 and 1453 cm<sup>-1</sup> together with a weak band at 1650 cm<sup>-1</sup>.

The disappearance of the bands at 3725 and 3680 cm<sup>-1</sup> was accompanied by reductions in the intensity of the maximum at 3655 cm<sup>-1</sup> attributed to isolated hydroxyl groups on the {110} cleavage planes of rutile.<sup>4-6</sup> Increasing ethyl acetate

pressures caused further weakening of this band and the disappearance of the maxima at 3610 and 3520 cm<sup>-1</sup> [fig. 1(*d*)] which have been tentatively assigned to isolated hydroxyl groups on the exposed {100} planes of rutile.<sup>4</sup> The overall intensity of adsorption at 3410 cm<sup>-1</sup> reverted [fig. 1(*c*) and (*d*)] to its initial value for rutile alone [fig. 1(*a*)]. The bands at 1515 and 1453 cm<sup>-1</sup> attained their maximum intensities [fig. 1(*d*)].

Further increases in the vapour pressure of ethyl acetate caused the disappearance from spectra of the maximum at  $3655 \text{ cm}^{-1}$  [fig. 1(f)] which tended towards  $3640 \text{ cm}^{-1}$ [fig. 1(e)] with decreasing intensity. The band initially at  $1650 \text{ cm}^{-1}$  [fig. 1(b)] continued to grow and shifted with increasing intensity to become a maximum at  $1695 \text{ cm}^{-1}$  [fig. 1(f) and 2(a)]. The band at  $1515 \text{ cm}^{-1}$  remained unchanged but the band at  $1453 \text{ cm}^{-1}$ was slightly weakened in the presence of high vapour pressures of ethyl acetate. Surface hydroxyl groups responsible for the narrow maximum at  $3410 \text{ cm}^{-1}$  in spectra of rutile were apparently unaffected by the adsorption of ethyl acetate.



FIG. 2.—Spectra of rutile (a) in contact with ethyl acetate vapour, (b) after subsequent evacuation at ca. 306 K for 15 min or 17 h. (c) Spectrum of ethyl acetate vapour.

Bands at 2990, 2940, 1773, 1760 and 1380 cm<sup>-1</sup> in spectra of rutile in the presence of ethyl acetate [fig. 1(f) and 2(a)] were due to vibrations of ethyl acetate molecules in the vapour phase [fig. 2(c)] and disappeared when the infrared cell was evacuated. The removal of vapour caused the band at 1453 cm<sup>-1</sup> to revert to its maximum intensity [fig. 2(b)]. Species responsible for the maxima at 1515 and 1453 cm<sup>-1</sup> were not desorbed by evacuation with the rutile disc at the ambient temperature in the spectrometer beam. However, the maximum at 1695 cm<sup>-1</sup> was considerably weakened by the evacuation procedure. Only a weak maximum remained at 1660 cm<sup>-1</sup>. At the same time there was a general decrease in absorption intensity in the range 3200-3550 cm<sup>-1</sup> and a maximum reappeared at 3640 cm<sup>-1</sup> [fig. 2(*b*)]. However, prolonged evacuation failed to return this band to its original intensity at 3655 cm<sup>-1</sup> [fig. 1(*a*)]. Hydroxyl groups responsible for the maxima at 3725, 3680, 3610 and 3520 cm<sup>-1</sup> [fig. 1(*a*)] were not regenerated by evacuation although a shoulder appeared at 3580 cm<sup>-1</sup> [fig. 2*b*)].

The concomitant growth of the maxima at 1515 and 1453 cm<sup>-1</sup> due to vibrations of chemisorbed products of adsorption of ethyl acetate on rutile suggests that the two maxima could be ascribed to a single surface species. Analogous maxima at 1480 and 1440 cm<sup>-1</sup> in spectra of  $[{}^{2}H_{4}]$  acetic acid adsorbed onto a deuterated rutile surface were assigned to the asymmetric and symmetric (COO)-stretching vibrations, respectively, of surface  $[{}^{2}H_{3}]$  acetate ions.<sup>2</sup> Corresponding bands at 1545 and 1460 cm<sup>-1</sup> have been reported in spectra of acetic acid adsorbed on rutile.<sup>7</sup> The assignment of the present bands to acetate ions formed by the chemisorption of ethyl acetate was tested by adsorbing acetic acid on to a similarly pretreated sample of rutile (fig. 3).



FIG.3.—Spectra of rutile (a) after evacuation, (b) in contact with acetic acid vapour, (c) with a higher acetic acid pressure, (d) and (e) after subsequent evacuation at ca. 306 K for 5 min and 17 h, respectively. (f) Spectrum of acetic acid vapour.

The relative reactivities towards acetic acid of the hydroxyl groups giving infrared bands at 3725, 3680, 3655 and 3410 cm<sup>-1</sup> were similar to the corresponding relative reactivities towards ethyl acetate. The disappearance of the bands at 3725 and 3680 cm<sup>-1</sup> occurred first [fig. 3(*b*)] and was accompanied by a general increase in absorption intensity in the spectral range 3200-3600 cm<sup>-1</sup> and by the appearance of maxima at 1515 and 1453 cm<sup>-1</sup> due to surface acetate ions. A maximum also appeared at 1675 cm<sup>-1</sup> and may be assigned to the (C=O)-stretching vibrations of associatively adsorbed acetic acid molecules.<sup>2</sup> The band at 3655 cm<sup>-1</sup> was reduced to zero intensity at higher pressures of acetic acid vapour [fig. 3(*c*)] and was only slightly restored by

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evacuation of the rutile disc at ambient temperature [fig. 3(d)]. The bands at 3725 and 3680 cm<sup>-1</sup> did not reappear. The species responsible for the maximum at 1675 cm<sup>-1</sup> was partially desorbed by evacuation but adsorbed acetate ions remained on the surface [fig. 3(e)]. Hydroxyl groups giving the infrared band at 3410 cm<sup>-1</sup> retained their integrity in the presence of acetic acid vapour. In general the spectroscopic data for the adsorption of acetic acid on rutile were consistent with the results of the more detailed study of the adsorption of [<sup>2</sup>H<sub>4</sub>]acetic acid on deuterated rutile which had been pre-evacuated at either 673 K or room temperature.<sup>2</sup>

## DISCUSSION

The similar infrared spectroscopic results for the adsorption of ethyl acetate and acetic acid on rutile show that ethyl acetate is predominantly chemisorbed to give surface acetate ions. The maxima at 1515 and 1453 cm<sup>-1</sup>, characteristic of adsorbed acetate, compare with previous reports of corresponding bands at 1525 and 1440 cm<sup>-1</sup>, or 1400 and 1530 cm<sup>-1</sup>, or 1410 and 1555 cm<sup>-1</sup> in spectra of acetic acid adsorbed on anatase<sup>8-10</sup> and at 1460 and 1545 cm<sup>-1</sup> for acetic acid on rutile.<sup>7</sup> The disappearance of infrared bands at 3725 and 3680(sh) cm<sup>-1</sup> [fig. 1(c)] and the reductions in intensity of the maximum at 3655 cm<sup>-1</sup> [fig.1(a) and 2(b)] demonstrate the involvement of surface hydroxyl groups in the adsorption process. The reaction of a surface hydroxyl group with ethyl acetate to give an acetate ion at the same surface site may be represented by

$$OH^{-} + CH_{3}COOC_{2}H_{5} \rightarrow CH_{3}COO^{-} + C_{2}H_{5}OH$$
(1)

in which an ethanol molecule is also generated as a product. An infrared study<sup>11</sup> has established that ethanol chemisorbs on rutile to give infrared bands at 2980, 2940 and 2885 cm<sup>-1</sup> due to CH-stretching vibrations of surface ethoxide ions. The maxima reported here at 2970, 2935 and 2875 cm<sup>-1</sup> were weak and their exact positions are less certain. Contributions to this spectral region also resulted from CH-stretching vibrations of acetate ions. However, the maxima were more intense after the chemisorption of ethyl acetate than after the chemisorption of acetic acid and therefore it must be concluded that surface ethoxide ions were present on rutile after exposure to ethyl acetate vapour. In accordance with

$$OH^{-} + CH_{3}COOC_{2}H_{5} \rightarrow C_{2}H_{5}O^{-} + CH_{3}COOH$$
(2)

it is possible that it is the ethoxide ion rather than the acetate ion which occupies the surface site initially occupied by the reactive hydroxyl group. The alternative reaction (2) generates acetic acid which would subsequently chemisorb to give acetate ions and hydroxyl groups or water.<sup>2</sup>

The disappearance of the bands at 3725 and 3680 (sh) cm<sup>-1</sup> due to surface hydroxyl groups was accompanied by the growth of maxima at 1515 and 1453 cm<sup>-1</sup> which were approximately half as intense for the adsorption of ethyl acetate [fig. 1(c)] than for the adsorption of acetic acid [fig. 3(b)]. During the adsorption of ethyl acetate ethoxide ions had replaced some of the OH-groups giving the infrared bands at 3725 and 3680(sh) cm<sup>-1</sup> and therefore fewer sites were available for occupancy by acetate ions. As the vapour pressure of ethyl acetate was further increased the bands associated with CH-stretching vibrations of adsorbed species decreased in intensity [fig. 1(c) and (d)] although the maxima at 1515 and 1453 cm<sup>-1</sup> continued to grow. The continued adsorption of ethyl acetate resulted in replacement of ethoxide ions by acetate ions. The adsorptive interactions also led to replacement of OH-groups responsible for the infrared band at 3655 cm<sup>-1</sup> by acetate or ethoxide ions.

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The interaction between surface OH-groups and ethyl acetate would be expected to lead to the formation of water *via* the adsorption of either ethanol<sup>11</sup> [eqn (1)] or acetic acid<sup>2</sup> [eqn (2)]. The general increase in adsorption intensity in the range 3200–3640 cm<sup>-1</sup> and the enhancement in the intensities of the bands at 3610 and 3520 cm<sup>-1</sup> [fig. 1(c)] can partially be attributed to the formation of water or surface hydroxyl groups resulting from the adsorption of water.<sup>4</sup> At higher surface coverages [fig. 1(d)] the surface population of molecular water apparently decreased.

With increasing surface coverage an increasing proportion of the hydrogen atoms remaining on the surface were present in associatively adsorbed acetic acid molecules formed by the hydrolysis of ethyl acetate. This conclusion is consistent with the identity of the spectra in the region  $1600-1700 \text{ cm}^{-1}$  following the adsorption of ethyl acetate or acetic acid. Bands at 1655, 1670 and 1690 cm<sup>-1</sup> in spectra of [<sup>2</sup>H<sub>4</sub>]acetic acid on rutile have been assigned to weakly adsorbed  $[{}^{2}H_{4}]$  acetic acid dimers.<sup>2</sup> The present maxima in the range 1650-1690 cm<sup>-1</sup> may be similarly assigned. An alternative assignment which would be consistent with the positions of the infrared bands would be that they are due to the (C=O)-stretching vibrations of ethyl acetate or acetic acid molecules associatively coordinated to Ti<sup>4+</sup> ions acting as Lewis acidic surface sites. However, the latter type of interaction would constitute a strong mode of adsorption; the bands would appear at low coverages of the surface by ethyl acetate and the species would not be desorbed by evacuation at ambient temperatures.<sup>2</sup> The present species were only formed at high coverages and were readily desorbed. The adsorptive interactions involved the formation of hydrogen bonds between surface hydroxyl groups and acid dimers. Desorption released unperturbed hydroxyl groups giving the band at 3640 cm<sup>-1</sup> at the expense of a broad band within the range 3200–3550 cm<sup>-1</sup> (fig. 2) due to the same hydroxyl groups perturbed by adsorbed dimers.

The difference between the positions of the infrared bands due to the symmetric and asymmetric (COO)-stretching vibrations of adsorbed acetate ions observed here was 62  $cm^{-1}$ . This difference is consistent with a mode of adsorption in which both oxygen atoms in an acetate ion are simultaneously liganded in a chelating bidentate configuration to a single exposed  $Ti^{4+}$  ion.<sup>2</sup> The requirement that two ligands are involved suggests that the Ti<sup>4+</sup> ions may possibly be those which are exposed at apex, step or edge sites where the completion of octahedral coordination around each Ti<sup>4+</sup> ion in the surface of pure rutile is less likely to be attained. Griffiths and Rochester<sup>4</sup> suggested that OH-groups responsible for the band at 3680(sh) cm<sup>-1</sup>, which becomes a distinct maximum at 3700 cm<sup>-1</sup> in spectra of rutile heated at > 455 K, may possibly exist at apex, step or edge sites in the exposed surface of the oxide. The ease of replacement of these hydroxyl groups by interaction with ethyl acetate vapour may therefore be related to the existence of a favourable stereochemical configuration for the formation of adsorbed acetate ions at the same sites. A plausible mechanism involving a Ti<sup>4+</sup> ion site liganded to one hydroxyl group in the surface, four O<sup>2-</sup> ions in the bulk oxide and having one vacant ligand would be as follows:

$$HO_{1}^{-1} (+MeCODEt) HO_{1}^{-1} (+V) + O_{1}^{-1} (+V) + O_{1$$

The relative reactivities towards ethyl acetate of surface hydroxyl groups responsible for four distinguishable infrared bands in spectra of rutile were in the sequence, in terms of band positions,  $3725 \approx 3680(\text{sh}) > 3655 > 3410 \text{ cm}^{-1}$ . Similar relative reactivities have been observed in studies of the adsorption of hexafluoroacetone<sup>1</sup> and acetone<sup>3</sup> on rutile. Griffiths and Rochester<sup>1</sup> concluded that deuteroxyl groups responsible for a band at 2720 cm<sup>-1</sup> in spectra of deuterated rutile resembled deuteroxide ions in metal deuteroxides in their nucleophilic reactivity towards electron deficient carbon atoms. The band at 2720 cm<sup>-1</sup> was equivalent to the present shoulder at 3680 cm<sup>-1.4</sup> Mechanism (3) is consistent with this suggestion. Associative adsorption of ethyl acetate by coordinative interaction at a vacant ligand site ( $\Box$ ) enhances electron deficiency at the carboxyl carbon atom which becomes active for attack by adjacent hydroxyl groups. The generation of acetate ions from ethyl acetate by catalysis involving hydroxyl groups responsible for the infrared band at 3680(sh) cm<sup>-1</sup> is probably base catalysed. A similar mechanism was proposed for the enolization of acetone on rutile<sup>3</sup> and kinetic results for the isotopic exchange reaction between acetone and deuterium oxide over rutile were also compatible with a base catalysed mechanism.<sup>12</sup>

The possibility of acid catalysed reactions of ethyl acetate over rutile cannot be discounted. Brønsted acid sites on rutile have not been detected by infrared study of the adsorption of ammonia or pyridine.<sup>10, 13-15</sup> If Brønsted acid sites exist they are either at too low a surface concentration to be detected or too weak to cause protonation of ammonia or pyridine at the solid/vapour interface. Evidence for Brønsted acidity of rutile has, however, been provided by studies of alkene isomerization in the presence of adsorbed water or alcohol.<sup>16</sup> One possibility in the context of the present study would be that the silica content of the rutile gives a low concentration of surface silanol groups which exhibit Brønsted acidity. Silanol groups generated on rutile by treatment with silicon tetrachloride and subsequent hydrolysis exhibit Brønsted acidity towards adsorbed pyridine.<sup>17</sup> The band at 3725 cm<sup>-1</sup> in spectra of rutile has been tentatively ascribed to surface silanol groups.<sup>4</sup> If this assignment is correct then the disappearance of the band in the presence of ethyl acetate vapour may be related to the involvement of the hydroxyl groups in acid catalysed rather than base catalysed chemisorption of adsorbate molecules.

Hydroxyl groups in row A of the {110} surface planes of rutile<sup>4, 6</sup> (band at  $3655 \text{ cm}^{-1}$ ) formed hydrogen bonds with adsorbed hexafluoroacetone molecules<sup>1</sup> but were replaced by products of chemisorption in the presence of acetone vapour.<sup>3</sup> With ethyl acetate a proportion of the groups were replaced by acetate or ethoxide ions but some groups remained and formed hydrogen bonds with the weakly adsorbed acetic acid molecules responsible for the infrared bands at 1650-1690 cm<sup>-1</sup>.

Exposure of rutile to ethyl acetate, acetic acid, acetone<sup>3</sup> or hexafluoroacetone<sup>1</sup> failed to cause appreciable displacement, reaction or perturbation of the OH-groups responsible for the maximum at 3410 cm<sup>-1</sup>. A possible explanation would be that these groups are inaccessible to adsorbate molecules. However, the existence of these groups at the rutile surface has been rationalized by consideration of their thermal dehydration/rehydration behaviour and by their ease of replacement by isotopic exchange with deuterium oxide vapour.<sup>4, 15</sup> The infrared band at 3410 cm<sup>-1</sup> has been assigned to bridged hydroxyl groups in row B of the {110} surface planes of rutile.<sup>4, 6</sup> Models of the {110} planes<sup>4, 6</sup> of rutile suggest that the bridged hydroxyl groups should be accessible to adsorbate molecules. The dehydration of the {110} planes of rutile is thought to involve loss of hydroxyl groups from row A sites and of protons from bridging OH-groups which therefore become O<sup>2-</sup> ions at the bridging sites in row B.<sup>4</sup> Rehydration at room temperature reverses the reaction and regenerates both row A and row B hydroxyl groups. The lack of reactivity of the hydroxyl groups giving the band at  $3410 \text{ cm}^{-1}$  would be explained if the groups existed at equilibrium not at the bridging row B sites on the exposed {110} planes but at adjacent lattic sites in a sub-surface layer. The resulting sub-surface groups would be simultaneously liganded to two or possibly three Ti<sup>4+</sup> ions and therefore the assignment of the narrow band

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at 3410 cm<sup>-1</sup> to these groups is reasonable.<sup>4</sup> It is proposed that the hydration/dehydration behaviour at the exposed {110} planes of rutile proceeds as previously envisaged and involves bridging  $O^{2-}$  ions as sites for proton detachment (in dehydration) or proton attachment (in rehydration) at the surface. However proton transfer between the bridging  $O^{2-}$  ions and sub-surface sites occurs and the bridging  $O^{2-}$  ions therefore retain their integrity at equilibrium on both the dehydrated and hydrated {110} surface planes. Hydroxyl groups existing at sub-surface lattice sites will be inaccessible to adsorbate molecules. Isotopic exchange with deuterium oxide vapour rapidly takes place because of proton mobility between sub-surface hydroxyl groups and exposed surface sites.

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