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Infrared Study of the Adsorption of Propan-2-ol on Rutile at the Solid/Vapour and Solid/Heptane Interfaces

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Infrared spectra of propan-2-ol adsorbed on rutile have shown that non-dissociatively adsorbed propan-2-ol is coordinatively liganded to Lewis-acidic surface sites. Dissociative chemisorption occurs at exposed Ti^{4+} cations, particularly for dehydroxylated rutile, and generates isopropoxide anions. Surface hydroxyl groups on rutile were replaced by isopropoxide anions with the concomitant formation of water. Hydroxyl groups at sub-surface lattice sites were unaffected by propanol adsorption. Multilayer adsorption of propan-2-ol at high surface coverages involved the formation of molecular aggregates which were weakly bound by hydrogen-bonding interactions and which contained water molecules resulting from the chemisorptive reactions. Heat treatment of adsorbed propan-2-ol resulted in the formation of adsorbed carboxylate and possibly carbonate species. The implications of the results with respect to the dehydration of propan-2-ol catalysed by rutile are briefly discussed.

Rutile catalyses the decomposition reaction of propan-2-ol to acetone, propene and di-isopropyl ether[1] and is also effective in the photocatalytic oxidation of propan-2-ol to acetone.[2] Interactions between the rutile surface and acetone,[3] propene[4] and di-isopropyl ether[4] have been characterized by infrared spectroscopy. The present paper reports infrared spectra of propan-2-ol adsorbed on an hydroxylated rutile surface.

Munuera and Stone[5] found no evidence for alcohol molecules coordinatively bound to exposed Ti^{4+} cation sites in spectra of propan-2-ol on partially hydroxylated rutile and concluded that propan-2-ol was adsorbed non-dissociatively through interactions involving an adjacent hydroxyl group and oxide ion sites or pairs of adjacent hydroxyl groups in the surface. A single spectrum of propan-2-ol adsorbed on titanium dioxide (of unspecified crystal structure) which had been preheated at 673 K suggested that a chemisorptive reaction had led to the formation of surface propan-2-oxide ions.[6] Alcohols are believed to adsorb on anatase to give alkoxide anions,[7] although one report suggested that the predominant interaction involved alcohol molecules coordinatively liganded to Lewis-acidic surface sites.[8]

The development of cells which enable infrared spectra of rutile immersed in liquid hydrocarbons to be recorded[9, 10] coupled with an interest in the photocatalytic oxidation of liquid propan-2-ol by rutile[2] prompted an infrared study, reported here, of rutile immersed in liquid propan-2-ol and solutions of propan-2-ol in heptane.

EXPERIMENTAL

Rutile (code CL/D 338, Tioxide International Ltd) with a surface area of 30.3 $m^2 g^{-1}$ was freed from surface impurities, pressed into self-supporting discs and pretreated as before,[10, 11] the final treatment involving heating in vacuum at 400 K for 1 h. A recently described cell[10] was used to record spectra of discs immersed in solutions of propan-2-ol and also served in the experiments involving the adsorption and desorption of propan-2-ol vapour. Discs were at *ca.* 306 K during spectroscopic examination.

AnalaR propan-2-ol was doubly distilled and stored over molecular sieve. Heptane was shaken with calcium sulphate for 24 h, triply distilled (twice from calcium sulphate, once from anhydrous copper sulphate) and stored in the vacuum apparatus where it was freed from permanent gases by cold pumping and finally vacuum distilled.

RESULTS

The adsorption of increasing amounts of propan-2-ol on rutile led to the progressive disappearance of infrared bands at 3725, 3680(sh) and 3655 cm^{-1} due to surface hydroxyl groups[12] and the growth of a broad absorption maximum centred at *ca.* 3350 cm^{-1} (fig. 1). The effects were time dependent [fig. 1(*b*) and (*c*)]. The appearance of a band at 1620 cm^{-1} showed that water was a product of the adsorption reaction, although water was apparently displaced from surface sites as the vapour pressure of propan-2-ol was increased [fig. 1(*d*)]. The growth of bands at 3610 and 3520 cm^{-1} for low coverages of the surface by propan-2-ol [fig. 1(*b*)] and the subsequent weakening of these bands at high coverages support this conclusion. The maxima at 3610 and 3520 cm^{-1} have been assigned to OH-stretching vibrations of surface hydroxyl groups which are formed on rutile in the presence of a high concentration of non-dissociatively adsorbed water molecules.[12] Maxima appearing in spectra at 2970, 2937, 2835, 1470, 1390(sh), 1383, 1368 and 1333 cm^{-1} could be ascribed to vibrations of isopropyl groups predominantly in adsorbed species but partly in gaseous propan-2-ol molecules [fig. 1(*e*) and (*f*)]. The shoulder at 1390 cm^{-1} could not be discerned for rutile in the presence of high pressures of propan-2-ol. Hydroxyl groups responsible for the absorption band at 3410 cm^{-1} [fig. 1(*a*)] probably exist at sub-surface lattice sites in rutile[9–11, 13] and were unaffected by the adsorption of propan-2-ol.

Decreases in the intensities of the band at 2970, 2937, 2835, 1470, 1383, 1368 and 1333 cm^{-1} due to adsorbed species were caused by brief evacuation of the cell with the sample at ambient temperature [fig. 2(*a*)]. A concomitant decrease in intensity of the broad maximum centred at *ca.* 3350 cm^{-1} was not accompanied by the appearance of bands due to vibrations of unperturbed hydroxyl groups. The results suggest that hydrogen bonded aggregates of propan-2-ol molecules were weakly adsorbed in equilibrium with high vapour pressures of propan-2-ol and were easily desorbed by evacuation. A simultaneous decrease in absorption intensity at 1620 cm^{-1} suggests that water molecules were also present in the aggregates. Prolonging the evacuation time led to futher desorption of propan-2-ol and the growth of a doublet of bands at 3640 and 3620 cm^{-1} due to unperturbed or only very weakly perturbed hydroxyl groups. A maximum also appeared at 3530 cm^{-1} [fig. 2(*b*)]. Residual bands due to CH stretching and deformation vibrations of isopropyl groups showed that evacuation at *ca.* 306 K was insufficient to desorb completely the products of adsorption from the rutile surface. Subsequent evacuation at 373 K had little further effect but increasing the temperature to 423 K caused the disappearance of the weak band at 1390 cm^{-1}, the maximum at 3530 cm^{-1} and the broad band envelope centred at 3350 cm^{-1} [fig. 2(*c*)]. A maximum at 3640 cm^{-1} due to unperturbed surface hydroxyl

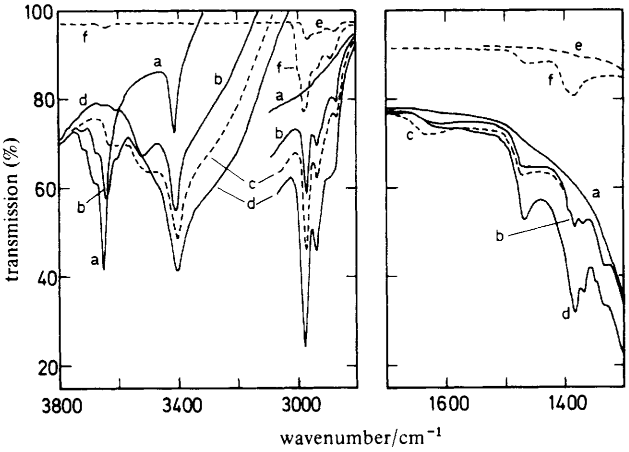


Fig. 1. Spectra of rutile (*a*) in vacuum, (*b*) and (*c*) in contact with propan-2-ol vapour at *ca.* 306 K for (*b*) 5 min and (*c*) 16 h and (*d*) exposed to s.v.p. of propan-2-ol at *ca.* 306 K. Spectra of propan-2-ol vapour at (*e*) a higher vapour pressure than that in the cell when spectra (*b*) and (*c*) were recorded and (*f*) s.v.p.

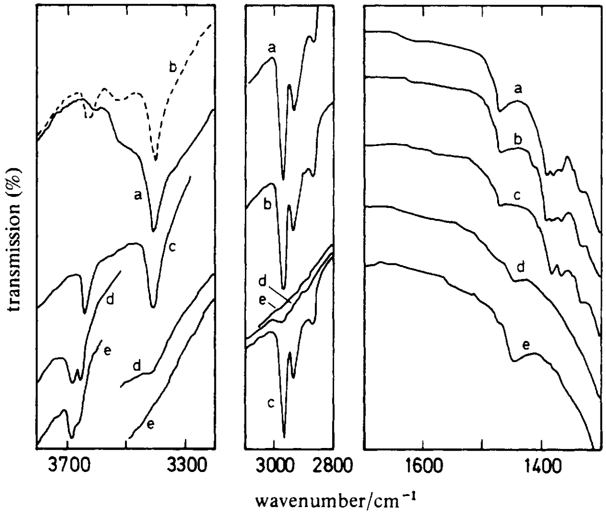


Fig. 2. Spectra of rutile after exposure to propan-2-ol (s.v.p., 16 h, *ca.* 306 K) and evacuation at (*a*) *ca.* 306 K (5 min), (*b*) *ca.* 306 K (1 h), (*c*) 423 K (30 min), (*d*) 523 K (30 min) and (*e*) 573 K (30 min).

groups was enhanced in intensity. Apart from the loss of a weak shoulder at 2895 cm^{-1} [fig. 2(*b*)], the bands due to CH-stretching vibrations of isopropyl groups were unchanged in intensity suggesting that evacuation at 423 K had led to a small amount of redistribution of surface species containing isopropyl groups but that negligible desorption had occurred. In contrast, surface species containing isopropyl groups were largely desorbed after evacuation at 523 K [fig. 2(*d*)]. An infrared band appearing at

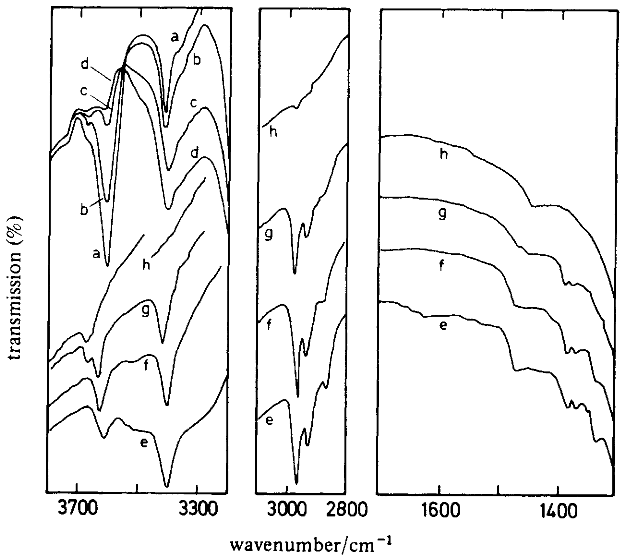


Fig. 3. Spectra of rutile (*a*) immersed in heptane, (*b*)–(*d*) immersed in solutions of propan-2-ol at mole fractions in heptane of (*b*) 10^{-3} (5 min), (*c*) 10^{-3} (16 h) and (*d*) 2.3×10^{-3} (5 min), (*e*)–(*h*) after subsequent evacuation for 30 min at (*e*) *ca.* 306, (*f*) 423, (*g*) 503 and (*h*) 563 K.

1445 cm^{-1} was enhanced in intensity after evacuation at 573 K [fig. 2(*e*)] and, together with a very weak maximum at *ca.* 1510–1560 cm^{-1}, suggested that adsorbed carboxylate anions had been formed.[4, 11]

Spectra of rutile immersed in solutions of propan-2-ol in heptane are shown in fig. 3. The maximum at 3605 cm^{-1} due to surface hydroxyl groups (band at 3655 cm^{-1} for rutile in vacuum) weakly perturbed by interaction with heptane molecules[9] decreased in intensity with increasing concentrations of propan-2-ol. The losses of intensity were time dependent [fig. 3(*b*) and (*c*)], suggesting that a slow chemisorption reaction involving the hydroxyl groups was taking place. The appearance of a weak band at 1600–1640 cm^{-1} showed that water was a reaction product. Increases in absorption intensity in the broad range 3000–3550 cm^{-1} were similar to corresponding increases for rutile in contact with propan-2-ol vapour. Unfortunately no bands due to vibrations of hydrocarbon groups in adsorbed species could be detected because of intense maxima in the same spectral regions due to vibrations of liquid heptane. Drainage of the liquid phase and subsequent evacuation at a series of increasing temperatures gave spectroscopic effects [fig. 3(*e*)–(*h*)] which were similar to those recorded after the adsorption of propan-2-ol vapour on rutile (fig. 2). Identical effects to those shown in fig. 2 were also recorded after immersion of rutile in pure liquid propan-2-ol, drainage and evacuation at increasing temperatures. The results showed that hydroxyl groups responsible for the band in spectra at 3410 cm^{-1} were completely unreactive, even towards liquid propan-2-ol.

DISCUSSION

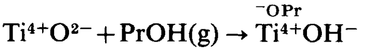
Bands at 1392, 1383 and 1368 cm^{-1} in spectra of propan-2-ol adsorbed on rutile may be compared with bands at 1390 and 1380 cm^{-1}, ascribed to non-dissociatively adsorbed di-isopropyl ether on rutile, and at 1383 and 1368 cm^{-1} in spectra of surface, isopropoxide ions on rutile formed by the chemisorption of di-isopropyl ether.[4] Isopropyl groups give two bands in this region of the spectrum because the maximum due to the symmetrical vibrations of methyl groups is split into a doublet. The bands were at 1393 and 1383 cm^{-1} for propan-2-ol vapour. The present results after adsorption of low vapour pressures of propan-2-ol [fig. 1(*b*)] or after adsorption and evacuation at ambient temperatures [fig. 2(*a*)] may be ascribed to two doublets, one at 1392 and 1383 cm^{-1} due to non-dissociatively adsorbed propan-2-ol molecules coordinatively liganded to Lewis-acidic surface sites,[14, 15] and the other at 1383 and 1368 cm^{-1} due to surface isopropoxide ions. Dissociative adsorption to give isopropoxide ions occurred more readily for propan-2-ol than for di-isopropyl ether.[4] The growth of absorption intensity at 1383 and 1368 cm^{-1} for high vapour pressures of propan-2-ol [fig. 1(*d*)] is, by comparison with corresponding maxima in spectra of liquid propan-2-ol, attributed to multilayer adsorption[16] involving the aggregation of propan-2-ol molecules through hydrogen-bonding interactions. The aggregated molecules were desorbed by evacuation at ambient temperature [fig. 2(*a*)].

Hydrogen-bonding interactions between surface hydroxyl groups on rutile and adsorbed molecules constituted a less significant mode of adsorption for propan-2-ol than for di-isopropyl ether[4] because propan-2-ol underwent a slow chemisorptive reaction which led to the replacement of hydroxyl groups by isopropoxide ions. Jackson and Parfitt[17] similarly observed that ethanol, butan-1-ol and hexan-1-ol reacted with surface hydroxyl groups to form adsorbed alkoxide ions on rutile. In contrast, surface hydroxyl groups formed hydrogen bonds with phenol molecules adsorbed from the vapour at pressures $< 133\ N\ m^{-2}$.[18] Reaction to adsorbed phenoxide ions was only observed for a dehydroxylated rutile surface. Primet *et al.*[18] reported a lack of reactivity between phenol and hydroxyl groups responsible for an infrared band at 3410 cm^{-1} in spectra of rutile. The lack of reactivity of these hydroxyl groups towards adsorbate molecules appears to be general[3, 4, 9–11, 13, 19, 20] and has been attributed to the existence of the groups at sub-surface lattice sites.[9, 11] The results for propan-2-ol conformed to the general pattern of behaviour, the only detectable effect being a reversible broadening of the band at 3410 cm^{-1} similar to that previously recognized from spectra of ethyl acetate[10] and triethylamine[13] on rutile.

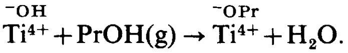
Water which is adsorbed through non-dissociative coordinative interactions with Lewis-acidic sites in the exposed {100} and {101} surface planes of rutile cannot be desorbed by evacuation at room temperature.[12] Water molecules formed by the chemisorption of propan-2-ol on rutile were desorbed by evacuation [fig. 2(*a*)], suggesting that the water was not adsorbed on Lewis-acidic sites but was involved in hydrogen bonding interactions with surface hydroxyl groups or with aggregates of propan-2-ol molecules. The adsorption of water on Lewis-acidic sites was precluded by the adsorption of propan-2-ol. Munuera and Stone[5] found that water was not able to displace propan-2-ol from the surface of rutile. Bickley *et al.*[21] reported that water was displaced by propan-2-ol. Similarly Jackson and Parfitt[17] observed, in accordance with the present results, that water was displaced from the rutile surface by the adsorption of alcohols. Alcohols also displace water from the surface of anatase.[22]

The adsorption of propan-2-ol on Lewis-acidic sites in the {100} and {101} planes of rutile is probably, as for water,[12] predominantly non-dissociative and involves coordinative interactions with exposed Ti^{4+} cations.[23] However, Jaycock and Waldsax[24] suggested that water could adsorb dissociatively on the {100} planes of rutile, and this led Griffiths and Rochester[12] tentatively to attribute bands at 3680, 3610 and 3520 cm^{-1} in infrared spectra of rutile to hydroxyl groups formed by this mode of adsorption. Evidence for a similar mode of adsorption for propan-2-ol was provided by the existence of bands at 3620 and 3530 cm^{-1} in spectra despite negligible evidence [fig. 2(*b*)] for non-dissociatively adsorbed water, which was a prerequisite for the appearance of the bands in the case of water adsorption. By analogy to the results for water, it is therefore proposed that a small proportion of the total number of adsorbed propan-2-ol molecules were dissociated on exposed Ti^{4+} cations to give adsorbed isopropoxide anions at the cationic sites. The proton from each dissociated molecule combined with an adjacent surface oxide anion to form a hydroxyl group. The suggestion that this mechanism occurs specifically on {100} planes remains tentative.[12] However, a similar mechanism must constitute the predominant mode of adsorption of alcohols on {110} planes of rutile which have been dehydroxylated by high temperature treatment before adsorption of an alcohol. The resulting alkoxide anions complete the coordination of row A Ti^{4+} cations in the {110} planes,[12, 23] and the hydroxyl ions exist at sub-surface sites,[9, 11] probably liganded to row B Ti^{4+} cations. This mechanism of chemisorption of alcohols on the {100} planes is analogous to the proposed mechanism for water adsorption,[9, 12] and is consistent with the observation[17] that the adsorption of alcohols on dehydroxylated rutile leads to the appearance of an infrared band at 3410 cm^{-1} but no band at 3655 cm^{-1} due to hydroxyl groups on row A sites. In the present study of alcohol adsorption on an hydroxylated rutile surface the final outcome was the same because row A hydroxyl groups (band at 3655 cm^{-1}) were replaced by isopropoxide ions and the sub surface hydroxyl groups were unaffected by the adsorption process.

Jackson and Parfitt[17] reported infrared spectra of ethanol, butan-1-ol and hexan-1-ol on rutile and concluded that chemisorptive reactions led to the formation of surface alkoxide species which were precursors of the appropriate alkenes generated by thermal activation. Two general mechanisms of chemisorption, represented by reactions (1) and (2), are consistent with the previous and present spectroscopic data:



$$\mathrm{Ti^{4+}O^{2-} + PrOH(g) \rightarrow \overset{^{-}OPr}{Ti^{4+}}OH^{-}} \qquad (1)$$



$$\mathrm{\overset{^{-}OH}{Ti^{4+}} + PrOH(g) \rightarrow \overset{^{-}OPr}{Ti^{4+}} + H_2O.} \qquad (2)$$

Reaction (1) occurs on dehydroxylated {110} planes, the product hydroxyl group giving an infrared band at 3410 cm^{-1}. Reaction (2) involves row A hydroxyl groups on hydroxylated {110} planes, and also hydroxyl groups giving bands at 3725 and 3700 cm^{-1} in spectra of rutile. Groups responsible for the latter two bands are particularly reactive towards a variety of adsorbates including acetone,[3] ethyl acetate[11] and hexafluoroacetone.[20] The weak band at 3725 cm^{-1} [fig. 1(*a*)] has been attributed to surface silanol groups resulting from a low silica impurity level in the rutile.[12] The extent to which reaction (1) goes to completion at equilibrium on surfaces other than {110} planes can only be conjectured. However, a stable intermediate in the reaction might involve each propan-2-ol molecule coordinatively liganded *via* its oxygen atom to a Ti^{4+} cationic site and with its hydrogen atom simultaneously linked by a hydrogen bond to a vicinal surface oxide ion. The geometry of the {100} planes is particularly favourable for this type of interaction,[23] which would explain why a broad infrared band at *ca.* 3400 cm^{-1} remained in spectra after weakly adsorbed water and propan-2-ol had been desorbed by evacuaton [fig. 2(*b*)]. The disappearance of this band after evacuation at 423 K [fig. 2(*c*)] was accompanied by the simultaneous disappearance of the maximum at 1390 cm^{-1} attributed to a vibration of propan-2-ol adsorbed on Lewis-acidic surface sites. The absence of change in the intensities of bands due to CH-stretching vibrations suggests that the thermal treatment had promoted the decomposition of propan-2-ol molecules on Lewis sites to give isopropoxide anions. No decomposition products other than water would have been expected to have been desorbed at this temperature.[5,17] At higher temperatures propene would be a significant product,[1,6,17] possibly formed by the decomposition of isopropoxide anions.[6,7,17,25]

Gentry *et al.*[1] reported rates of decomposition of propan-2-ol to propene, acetone and di-isopropyl ether catalysed by rutile at 483–519 K. The infrared spectra show that under these conditions Lewis-acidic sites in the {100} and {101} surface planes are unlikely to be occupied by non-dissociatively adsorbed propan-2-ol molecules but that some sites might be occupied by isopropoxide anions, the population of which would become increasingly small with increasing temperature. Only a very small proportion of the available sites would be occupied at the upper end of the temperature range [fig. 2(*d*)]. The spectroscopic evidence would be consistent with a mechanism for propene formation in which propan-2-ol is decomposed at Lewis-acidic sites to give isopropoxide ions which subsequently break down to propene and a hydroxyl group. The latter can condense with a further hydroxyl group prior to desorption as water. Propene is readily desorbed as a reaction product.[4] The low yields of di-isopropyl ether as a product of propan-2-ol dehydration may be linked to the fact that di-isopropyl ether itself undergoes decomposition to isopropoxide ions on rutile at elevated temperatures.[4]

The possibility of a carbonium ion mechanism for the propan-2-ol dehydration reaction[1] prompted a search for infrared bands due to adsorbed propyl cations. The propyl cation in $(CH_3)_2CH^+SbF_6^-$ gives strong infrared bands at 2730, 1490 and 1260 cm^{-1}.[26] No similar bands were discernible in the present spectra, although a hint of a very weak band existed at 2720 cm^{-1} for rutile in the presence of propan-2-ol vapour. However, this band corresponds to shoulders at 2750 cm^{-1} reported[17] (but not interpreted) in spectra of primary alcohols on rutile where carbonium-ion formation is less likely than for propan-2-ol. No clear evidence for carbonium ions at ambient temperature was therefore detected, although this does not preclude their possible involvement in the mechanism of the catalytic dehydration reaction.

Jackson and Parfitt[17] reported that the thermal decomposition of ethanol adsorbed on rutile led to adsorbed carbonate species.[27] However, their figured spectra also resembled spectra of acetic acid on rutile[11] and therefore could at least partly be interpreted in terms of the formation of acetate species. The thermal decomposition of propan-2-ol on rutile [fig. 2(*e*)] gave weaker but similar infrared bands to those resulting from ethanol decomposition and can be attributed to the formation of surface carboxylate, possibly with some further oxidation to carbonate anions. Comparison of the spectra of adsorbed ethanol[17] and propan-2-ol [fig. 2(*d*)] after thermal activation at 523 K shows that surface isopropoxide ions on rutile are more readily decomposed than surface ethoxide ions. The lower extent of formation of adsorbed carboxylate or carbonate species after isopropoxide ion decomposition suggests that the hydrocarbon species were desorbed, predominantly as propene,[1,6,17] and supports the contention that at least one possible mechanism for propene formation may involve isopropoxide anions as intermediates in the reaction.[6,7,17,25]

The formation of carboxylate species by oxidation of propan-2-ol on rutile[21] may involve adsorbed acetone as a reaction intermediate.[6,21,28,29] Spectra of titanium dioxide exhibited a band at 1690 cm^{-1}, attributed to coordinatively adsorbed acetone, after the adsorption of propan-2-ol and subsequent heat treatment in oxygen at 423 K.[6] A similar band at 1700 cm^{-1} has been reported after the adsorption of propan-2-ol on anatase at 473–573 K.[7] No bands attributable to adsorbed acetone[3] were observed in the present work.

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