Infrared Study of the Reactivity of Acetone and Hexachloroacetone Adsorbed on Haematite

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Infrared spectra of acetone adsorbed at beam temperature on α -Fe₂O₃ show that acetone can chemisorb on Lewis-acid sites and gives, at least partially, enolate anions; these, by aldolic condensation with molecules from the gas phase, produce a chemisorbed form of mesityl oxide. At 523 K acetate ions are formed.

Two different forms of trichloroacetate ions are formed on the surface at beam temperature by the adsorption of hexachloroacetone and trichloroacetic acid.

This behaviour indicates the presence of pairs of acid-base sites on the surface of haematite, and also shows that its surface hydroxy groups have a lower degree of nucleophilic character with respect to those of other oxides such as aluminas, SnO_2 and alkaline-earth oxides.

In recent years the interaction of several organic¹⁻⁴ and inorganic^{1, 5-8} compounds with the surface of haemative $(\alpha - Fe_2O_3)$ has been studied by infrared spectroscopy, showing the presence of different active sites and the possibility of several mechanisms

of adsorption. The present paper reports the results of an infrared spectroscopic study of the adsorption of acetone and hexachloroacetone, and of their transformation products, on the surface of α -Fe₂O₃, with the aim of identifying cooperative effects in connection with the surface sites.

Infrared studies of the interaction of acetone with various supports have shown that this molecule can both physisorb^{9, 10} and chemisorb⁹ on different adsorbants. On some oxide surfaces a number of transformation products, involving cooperative mechanisms, have been recently observed.¹¹⁻¹⁴

The use of ketones¹⁵ and perhalogenated acetones¹⁶ as probe molecules to study the surface Lewis acidity has also been discussed.

EXPERIMENTAL

The samples of α -Fe₂O₃ were obtained by vacuum decomposition of pressed discs of goethite (α -FeOOH) (3 × 10⁴ N cm⁻²; 30-50 mg cm⁻²) into the infrared cell. The B.E.T. surface area of the resulting haematite sample was 45.0 m² g⁻¹.

The samples were heated at 673 K in air for 1 h after decomposition and then evacuated for 1 h at beam temperature (b.t.). The resulting surfaces cannot be distinguished spectroscopically from the 'evacuated' surfaces of ref. (6) and (7). Adsorption experiments were also carried out on 'oxygen-rich' surfaces,^{6,7} but no difference in the infrared spectra of the adsorbed compounds was detected. Spectra were recorded with a Perkin-Elmer model 521 infrared spectrophotometer. The infrared cell was the same as in ref. (7).

The reference-beam attenuation was set up in order to obtain the best apparent transmission in each region for each sample. Real transmission values of the samples were a few percent in the 4000-3000 cm⁻¹ region, and *ca*. 10-15% in the 2000-1200 cm⁻¹ region.

Acetone, [2H6]acetone, mesityl oxide and trichloroacetic acid were reagent-grade products

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from Carlo Erba (Milano, Italy); hexachloroacetone was a pure product from Fluka (Buchs, Switzerland). Acetone was dried over calcium sulphate after the use. All liquid adsorbates were purified by freeze-pump-thaw cycles. Trichloroacetic acid was thoroughly degassed before use.

RESULTS AND DISCUSSION

Fig. 1 shows the spectra of acetone adsorbed on haematite at b.t. A species responsible for the bands at 2960, 2918, 1675, 1435, 1415, 1355 and 1240 cm⁻¹ is first formed on the surface [fig. 1(b)] and is slowly removed by degassing at b.t. [fig. 1(d)]. The frequencies of these adsorptions can be compared with those of acetone in the gas or liquid phase as reported by Dellepiane and Overend,¹⁷ and this comparison indicates that the species in question is a form of adsorbed acetone which is more perturbed than the purely physisorbed one.^{9, 10}



FIG. 1.—Infrared spectra of acetone adsorbed on haematite: (a) initial α -Fe₂O₃ surface; (b, c) after contact with acetone vapour (400 N m⁻²) at b.t. [(b) 10 min, (c) 30 min]; (d) evacuated for 4 h at b.t.

The band at 1675 cm¹ which appears to be asymmetric (with a component at *ca*. 1685 cm⁻¹, probably caused by the heterogeneity of the Lewis-acid sites already discussed⁴), corresponds to the C=O stretching vibration of molecules chemisorbed on Lewis-acid sites and shows a shift in frequency $\Delta v = 46-56$ cm⁻¹ with respect to the gaseous molecule. This value, compared with the corresponding shifts of analogous species on magnesia (32 cm⁻¹),¹⁸ titania (51 cm⁻¹)¹² and AlCl₃ (81 cm⁻¹),⁹ defines the relative acidities of these adsorbants, which agree well with the data obtained using the shifts of the 8a band of chemisorbed pyridine.^{4, 19}

It is also interesting to compare the shift for chemisorbed acetone (46-56 cm⁻¹) with those previously reported for the C=O stretches of chemisorbed formaldehyde (113 cm⁻¹)³ and acetaldehyde (88 cm⁻¹)² on α -Fe₂O₃, as this reflects the electronic and steric effects of methyl groups on the acid-base interaction of such carbonylic compounds with iron ions.

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A further remark concerns the stretching vibrations of C—H, whose frequencies are lowered with respect to the liquid or gas phase (2960 and 2918 cm⁻¹) probably because of interactions with surface anions, as already noted for analogous species on magnesia¹⁴ and zeolites;²⁰ the bands at 1435, 1415 and 1355 cm⁻¹, assigned to CH₃ deformation vibrations, are only slightly perturbed.



FIG. 2.—Infrared spectra of acetone adsorbed on haematite: (a) initial α -Fe₂O₃ surface; (b) after contact with acetone vapour (133 N m⁻², 3 min) at b.t.; (c) evacuated for 1 h at b.t.

By increasing the time of contact at b.t. [fig. 1(c)], a new species is formed progressively which is more stable to degassing [fig. 1(d)] and which is characterized by bands at 2955, 2910, 1670(sh), 1590, 1570, 1445, 1385 and 1370 cm⁻¹. Another species, characterized by a broad absorption at 1540 cm⁻¹ and which is also resistant to degassing at b.t., can be identified by its very short time of contact [fig. 2(b) and (c)]; however, it also seems to be present under the conditions of fig. 1(b) and (c), but is partially masked by the more intense bands mentioned above.

These species cannot correspond to forms of acetone absorbed as such. At least two different transformation products are formed by the adsorption of acetone on haematite, one formed immediately and the second more slowly, and only in the presence of acetone vapour. Neither of these products is the acetate ion, as their infrared spectra and thermal behaviour clearly differ from those of the species detected after direct interaction of acetic acid on haematite.^{1, 2} These compounds can be eliminated from the surface by careful degassing at 423 K. However, higher temperACETONE ADSORBED ON α -Fe₂O₃

atures lead to the formation of a new species, probably acetate ions, with a pronounced change in the infrared spectrum.

In order to test if such transformation products can be obtained by the condensation of acetone on the surface, infrared spectra of mesityl oxide adsorbed on haematite were also studied.



FIG. 3.—Infrared spectra of mesityl oxide adsorbed on haematite: (a) initial α -Fe₂O₃ surface; (b) after contact with mesityl oxide vapour (133 N m⁻², 15 min) at b.t.; (c) evacuated for 4 h at b.t.; (d) spectrum of mesityl oxide (liquid film).

A comparison of fig. 3(c), which reports the infrared spectrum of haematite after contact with mesityl oxide vapour and thorough degassing at b.t., with fig. 3(d), which shows the spectrum of mesityl oxide in the pure liquid, indicates that the strong perturbation in the region of the double-bond stretching vibrations is caused by chemisorption; however, very small perturbations of the C-H stretching vibration (2950 and 2900 cm⁻¹ in the chemisorbed form) and C-H deformation (1465, 1450, 1420, 1380 and 1375 cm⁻¹, practically identical in both liquid and adsorbed species) are detected.

From these data it seems reasonable to conclude that mesityl oxide chemisorbs on haematite via coordination of the C=C-C=O conjugate system, probably on Lewis-acid sites, its spectrum being very similar to that of the same molecule chemisorbed on titania (rutile), as reported by Griffiths and Rochester.¹²

A comparison of fig. 1(c) with fig. 3(c) allows us to identify the main transformation product of acetone on haematite as an adsorbed form of mesityl oxide.

Mesityl oxide is produced industrially by the dehydration of diacetone alcohol, obtained by the base-catalysed liquid-phase aldol condensation of acetone.²¹ The mechanism of aldol condensation is well known, involving as its first step the formation of the enolate anion of acetone.²² It thus seems reasonable to postulate the same mechanism for the formation of mesityl oxide on haematite. On the basis



Fig. 4.—Infrared spectra of $[{}^{2}H_{s}]$ acetone adsorbed on haematite: (a) initial α -Fe₂O₃ surface; (b-e) after contact with $[{}^{2}H_{s}]$ acetone vapour (400 N m⁻²) at b.t. [(b) 1 min, (c) 5 min, (d) 10 min, (e) 40 min].

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of these considerations, the band at 1540 cm⁻¹ (fig. 2) can be assigned to a chemisorbed form of the acetone enolate anion: also other enolate anions show characteristic bands, due to C—C—O stretchings, in this region.^{13, 23}

In order to confirm the formation of the acetone enolate anion, adsorption of $[{}^{2}H_{6}]$ acetone on haematite was also studied. After contact at b.t. new bands at 2950, 2550 (broad and very intense), 2220, 1435, 1415 and 1360 cm⁻¹ were detected, together with bands in the double-bond stretching region (1680, 1590 and 1540 cm⁻¹) corresponding to the vibrations previously assigned to chemisorbed acetone, chemisorbed mesityl oxide and chemisorbed enolate anion. The presence of the band at 2550 cm⁻¹, connected with O—D stretching vibrations, together with those detected at 2950, 1435, 1415 and 1360 cm⁻¹, the first due to C—H stretching and the others to C—H deformations of chemisorbed acetone (see above), indicates that a strong and fast isotopic exchange between acetone methyl groups and surface hydroxy groups takes place, producing undeuterated acetone and surface deuteroxy groups, the band at 2220 being due to C—D stretching vibration of chemisorbed [${}^{2}H_{6}$]acetone.

By increasing the time of contact [fig. 4(d) and (e)] the bands due to both $v_{\rm CH}$ and $\delta_{\rm CH}$ vibrations decrease in intensity, owing to further isotopic exchange, while the bands at 1590 and 1570 cm⁻¹, which can be assigned to perdeuteromesityl oxide, increase in intensity. Successive long periods of degassing at b.t. leave the bands at 2205, 1670(sh), 1590 and 1570 cm⁻¹ of perdeuteromesityl oxide.

The results obtained by adsorption of $[{}^{2}H_{6}]$ acetone therefore strongly support the previously discussed mechanism of formation of mesityl oxide on the haematite surface, confirming the deprotonating ability of the surface towards acetone, leading to the enolate anion.

In order to identify the surface sites where such chemisorptive activity takes place, the adsorption of acetone on surfaces with Lewis-acid sites previously poisoned with

acetone adsorption at b.t.				mesityl oxide	acetone adsorption	acetic acid	
		acetone		adsorption	at 523 K	adsorption	
physisorbed	chemisorbed	enolate	mesityl	mesityl	acetate	acetate	
acetone	acetone	ion	oxide	oxide	ions	ions	assignments
	2960		2955	2950	2940		
	2918		2910	2900	2880		V _{CH}
1(00	[1685]					-	
1690	1675						$v_{\rm CO}$
	C		1670sh	1665sh		٦	
			1590	1590			Vc-c-c-o
			1570	1560			0-0-0
_		1540					v_{c-c-0}
					1540	1540	Vas COE
					1440	1440	$v_{sym CO^{-}}$
				1465sh		ا	55m 602
			1445	1450			
1415	(1435			1420sh			δ_{CH}
	1415		1385	1380			on
1360	1355		1370	1375		j	ł
1240	—						v _{CC}

TABLE 1.—Infrared bands (cm⁻¹) and their assignments to adsorbed species on α -Fe₂O₃

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a stronger base (such as pyridine) has also been studied. No bands due to any form of acetone were detected on such surfaces at pressures of 1-5 Torr (133-665 N m⁻²), even after a long period of contact. At higher pressures (10 Torr = 1.33 kN m^{-2}) a broad band appears at 1690 cm⁻¹, together with a second band at 1360 cm⁻¹ and a shoulder on the lower-frequency side of the 19b band of chemisorbed pyridine (*i.e.* at *ca.* 1415 cm⁻¹). All these new features are very similar to those of acetone physisorbed on silica^{9, 10} and disappear on a short degassing at b.t., indicating the existence under these conditions of physisorbed acetone. [They are probably also present under the conditions of fig. 1(*b*), but are masked by the more intense bands of the previously identified species.]

The absence of chemisorbed acetone and of its transformation products on haematite poisoned by pyridine indicates that the formation of enolate anions needs the cooperative action of surface oxygen atoms or hydroxy groups on acetone previously chemisorbed on cationic sites. The fact that no mesityl oxide is formed on a surface where only chemisorbed acetone and enolate ion are present (*i.e.* with no gas-phase acetone), as shown in fig. 2(b) and (c), indicates that enolate ion should react with a molecule of gaseous acetone to give first the aldol condensation and then dehydration of the intermediate diacetone alcohol.

This proposed mechanism involves the presence on the surface of pairs of acidic and basic sites, probably iron and oxygen ions, which interact at b.t. with the same acetone molecule.

On the basis of the results described above, the α -Fe₂O₃ surface shows behaviour with respect to the acetone molecule which is similar to that of rutile,¹² while on other oxides (Al₂O₃,¹¹ SnO₂,²⁴ alkaline-earth oxides²⁵ including MgO, where different results



FIG. 5.—Infrared spectrum of acetone adsorbed on haematite: (a) initial α -Fe₂O₃ surface; (b) after contact with acetone vapour (400 N m⁻², 15 min) at 523 K.

have been obtained with differently prepared samples^{14, 18, 25}) chemisorbed acetates are formed at room or beam temperature.

However, even on haematite, new features appear if the contact is made at 523 K (fig. 5). In this case the main product which resists degassing at 473 K shows two broad and very intense bands at 1540 and 1440 cm⁻¹ together with bands at 2940 and 2880 cm⁻¹, due to C—H stretching vibrations. Similar bands in the v_{CO} stretching region are also detected after adsorption of $[^{2}H_{6}]$ acetone at 523 K, together with a broad adsorption at 2550 cm⁻¹, due to surface deuteroxy groups formed under these conditions, and a band near 2200 cm⁻¹ with a shoulder near 2100 cm⁻¹, due to C—D stretching vibrations. Both their spectroscopic features and their stability on the surface indicate that these species are acetate ions (already observed on the same surface after the adsorption of acetic acid and other C₂ organic compounds²) and $[^{2}H_{3}]$ acetate ions, respectively.

From our data it is not possible to establish if acetate ions are obtained through an oxidation mechanism (also involving the formation of an oxidized C_1 species, probably formate or carbonate ions or CO_2) or through an acetal-like species (formed by nucleophilic attack of an OH species on the electrophilic carbonyl carbon of chemisorbed acetone, and production of methane); this has been shown to occur even under milder conditions on aluminas,¹¹ SnO₂^{24, 26} and MgO.¹⁴



FIG. 6.—Infrared spectra of hexachloroacetone and trichloroacetic acid adsorbed on haematite: (a) α-Fe₂O₃ surface; (b) after contact with hexachloroacetone vapour (133 N m⁻², 15 min) at b.t.; (c) another sample after contact with trichloroacetic acid vapour (66 N m⁻², 30 min) at b.t.

In order to confirm the behaviour of ketones on the haematite surface we have also studied the adsorption of hexachloroacetone; this cannot undergo enolization owing to the absence of active hydrogen atoms in the alpha position, but is more active towards nucleophilic attack, owing to the higher polarization of its C==O bond by the inductive effect of the chlorine atoms. The spectrum of hexachloroacetone adsorbed on α -Fe₂O₃ is shown in fig. 6(b). The two bands at 1770 and 1745 cm⁻¹,

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very similar to the C==O stretching vibrations of this molecule in the liquid phase or in solution,¹⁶ are due to weakly perturbed hexachloroacetone. The species responsible for the two intense bands at 1605 and 1385 cm⁻¹ is predominant at low pressures, while a new species, responsible for an analogous pair of bands centred at 1670 and 1360 cm⁻¹, is formed progressively at higher pressures. An analogous situation is detected after the adsorption of trichloroacetic acid [fig. 6(c)]. These species absorb in the same regions as the metal trichloroacetates²⁷ and can be identified as two different types of trichloroacetate ions. The species responsible for the lower frequencydifference bands, which is formed first and is more stable to degassing, is probably bidentate or bridged; the other is monodenate.²⁸ Trichloro- and trifluoro-acetate ions were also observed as the main product of hexachloro- and hexafluoro-acetone adsorption on alkaline-earth oxides,²⁵ TiO₂,²⁹ SnO₂²⁶ and alumina.^{11, 16}

The different behaviour of acetone and hexachloroacetone, which agrees with their differing abilities to undergo nucleophilic attack at a C=O bond, can be taken as an indication that, on haematite also, acetate and trichloroacetate ions are formed by a mechanism involving nucleophilic attack of the surface hydroxy groups. The difference in the behaviour of acetone on haematite with respect to that of the same molecule on other oxides (*e.g.* aluminas, SnO₂ and MgO) already remarked upon, indicates that the surface hydroxy groups have a smaller degree of nucleophilic character on this oxide.

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