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Infrared Spectroscopic Comparison of the chemisorbed Species from Ethene, Propene, But-1-ene and *cis*- and *trans*-But-2-ene on Pt(111) and on a Platinum/Silica Catalyst

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The chemisorption of ethene, propene, but-1-ene, *cis*- and *trans*-but-2-ene and but-2-yne has been studied on a Pt(111) surface using reflection absorption infrared spectroscopy (RAIRS). The results have been compared with transmission infrared spectra of the alkenes adsorbed on a finely divided impregnated Pt/SiO_2 catalyst.

On the Pt(111) surface ethene, propene and but-1-ene are adsorbed in the corresponding n-alkylidyne form $CH_3(CH_2)_nCPt_3$ ($n = 0, 1, 2$) at room temperature. The *cis*- and *trans*-but-2-enes are adsorbed in the form of but-2-yne bonded to the surface in a di-σ/π fashion, as was confirmed by adsorption of but-2-yne itself.

The room-temperature spectra of ethene, propene and but-1-ene on Pt/SiO_2 all exhibited prominent absorptions from the n-alkylidyne, but other adsorbed species also contributed to the spectra, considered to be predominantly the appropriate di-σ species $PtCH_2CH(R)Pt$ (R = H, CH_3, C_2H_5) together with smaller amounts of the relevant π-complexes. In the case of the *cis*- and *trans*-but-2-enes, virtually identical spectra were obtained on Pt/SiO_2 but with many of the same prominent features as from but-1-ene. Clearly the finely divided catalyst had sites which led to double-bond isomerization. A smaller proportion of di-σ/π bonded but-2-yne was also present.

The infrared spectra proved to be very effective at delineating the similarities and differences between the species chemisorbed on Pt(111) and on the Pt/SiO_2 catalyst.

It has been possible to obtain transmission infrared spectra from alkenes chemisorbed on oxide-supported metal catalysts since the pioneering work of Pliskin and Eischens in the late 1950s.[1,2] However, it became apparent early that the interpretation of such spectra in terms of the structures of the chemisorbed species was complicated by the fact that a spectrum on a given metal catalyst had overlapping components from a number of different adsorbed species.[3,4]

This situation was somewhat relieved when in the 1970s and 1980s it became possible to measure spectra of single chemisorbed hydrocarbon species, one at a time, on particular surface planes of single crystals of the metals of interest. First of all vibrational electron energy-loss spectroscopy (VEELS) enabled such spectra to be obtained, literally from a single monolayer, with adequate sensitivity.[5,6] These spectra are of substantially lower resolution (>30 cm^{-1} for VEELS compared with 1–4 cm^{-1} for IR spectroscopy) but they have the advantage that they cover the whole wavenumber-equivalent range of energy losses. The oxide-supported metal catalysts give spectra of good sensitivity and resolution, but the available wavenumber ranges are limited by strong absorption by the oxide supports, *i.e.* to >1300 cm^{-1} for silica and >1000 cm^{-1} for alumina. The VEELS spectra are also, however, comparatively weak and poorly defined in the structurally important region of the ν(CH) bond-stretching modes.

The extra information provided by the VEEL spectra was nevertheless extremely useful and this stimulated renewed efforts to improve the sensitivity of infrared spectroscopy for this purpose. By using the higher sensitivity of Fourier-transform interferometer-based infrared spectrometers, which were also developed in the 1970s, and the recently developed mercury–cadmium telluride detectors, it was shown in this laboratory that good quality spectra from many hydrocarbon monolayers on metal single crystals could be obtained by reflection-absorption infrared spectroscopy (RAIRS) with adequate sensitivity and with a resolution equal to that of the transmission infrared studies on the finely divided catalysts.[7,8]

Optical considerations show that for RAIRS work on monolayers on flat metal surfaces there is a strict 'metal-surface selection rule' (MSSR) which determines that the intensity of an absorption depends only on the square of the vibrational dipole change (or partial dipole change) perpendicular to the metal surface.[9,10] The modes in question are always the completely symmetrical ones of the hydrocarbon/metal surface complex.[11] A similar selection rule applies to VEEL spectra when the most numerous specularly reflected (*i.e.* angle of reflection equal to the angle of incidence) electrons are measured, although 'parallel' modes with respect to the surface can also be detected due to non-dipole-scattering mechanisms.[12] A number of anomalies in the IR spectra from finely divided metal catalysts also found explanation when it was realised that the MSSR was relevant for spectra obtained on larger metal particles[13] ($>$*ca.* 2 nm in diameter[14]), causing increasing attenuation of the bands from the parallel modes with increasing metal particle size.

The overall result of these various developments is that within (but only within) the past five years, it has been possible to interpret in reliable detail the more complex spectra from a hydrocarbon such as ethene chemisorbed on oxide-supported metals.[15–19] Progress had previously been held up by the fact that some of the strongest absorptions turned out to be from an unexpected surface ethylidyne species (CH_3CM_3; M = metal). It was the simplified VEEL spectra[5,20] and comparison with the spectrum of a model compound,[21] that made possible the identification of this species.

Whereas the single-crystal work makes certain the identification of some of the surface species on metals, the spectra from finely divided metal catalysts often reveal additional ones which can be of catalytic importance. Not all such species necessarily occur on well defined crystalline facets of the metal particles.

In this paper our aim is to compare the RAIRS spectra from C_2–C_4 alkenes taken on a Pt(111) single-crystal face with the transmission spectra of the same hydrocarbons on a finely divided Pt/SiO_2 catalyst, in order to look for the

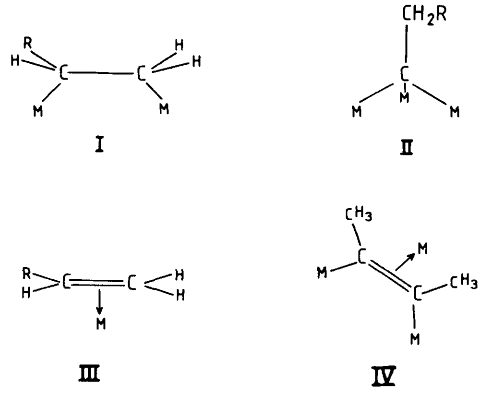

Fig. 1. The principal species from the chemisorption of alk-1-enes on Pt surfaces (R = H, CH_3 or C_2H_5); I, di-σ complex; II, alkylidyne complex; III, π-complex; IV, the surface complex from adsorbed but-2-enes or but-2-yne on Pt(111). The but-2-enes have R = CH_3 and additional CH_3 groups on the non-substituted carbon atoms in I and III.

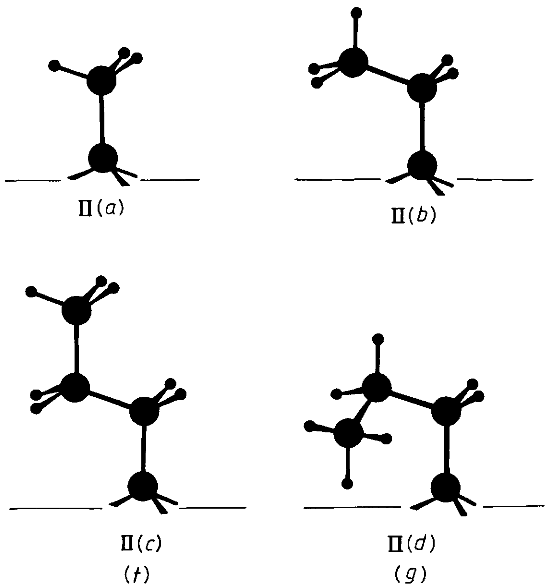

Fig. 2. The geometrical formulae for the alkylidynes: IIa, ethylidyne; IIb, propylidyne; IIc, *t*, *trans*-butylidyne; and IId, *g*, *gauche*-butylidyne.

common features and the significant differences. Comparison will also be made with the results of earlier VEELS studies of the same alkenes on Pt(111).[22-24] The various types of chemisorbed species involved are shown in fig. 1 and 2.

Experimental

The RAIRS experiments on the Pt(111) crystal were carried out in an oil diffusion pumped UHV chamber interfaced to a Mattson Cygnus 25 FTIR spectrometer which has been described previously.[7] A narrow-band mercury cadmium telluride detector was used which enabled spectra to be recorded in the range 4000–800 cm^{-1}. The Pt(111) crystal was kindly provided by Professor G. Comsa of KFA Jülich and had been prepared with a very low step-density. It was cleaned by heating in O_2 at 1×10^{-7} Torr,† 900 K, for 200 h followed by argon-ion sputtering at *ca.* 570 K and annealing at 1040 K.

The preparation of the impregnated Pt/SiO_2 catalysts has been described in detail elsewhere.[25] The pressed discs used for transmission IR work contained *ca.* 15% of Pt and had particle diameters mostly in the range 2–30 nm as shown by electron microscopy. The larger particles showed crystallite faces with rounded edges. IR spectra were recorded using a Digilab FTS-20V FTIR spectrometer and are presented as transmission ratios against the spectrum of a clean newly prepared disc and, where necessary, against the spectrum of any gas phase present. The latter was obtained by lifting the sample disc and its holder out of the IR beam.

Results and Discussion

Ethene Adsorption

The spectra from this system have been analysed in detail elsewhere,[17,19] and only an outline will be given here. However, it is necessary to review briefly these results from the parent alkene as they provide information about the types of surface species present that is very relevant for the subsequent discussion of the spectra of the higher alkenes.

Fig. 3(*a*) shows the RAIR spectrum of the ethylidyne species taken on the Pt(111) face at 360 K.[26,27] It is seen that the strongest absorptions at 2881 and 1342 cm^{-1} in the room-temperature (294 K) spectrum from ethene on Pt/SiO_2[17] [fig. 3(*b*)] clearly correspond to those of ethylidyne (IIa, fig. 2). Because of blackout absorption by the SiO_2 support below 1300 cm^{-1}, the 1100 cm^{-1} region is not accessible. Additional absorptions occur in the room-temperature spectrum on Pt/SiO_2 in both the $\nu(CH)$ and $\nu(C{=}C)/\delta(CH_2)$, $\delta(CH_3)$ regions which have been identified as those of the

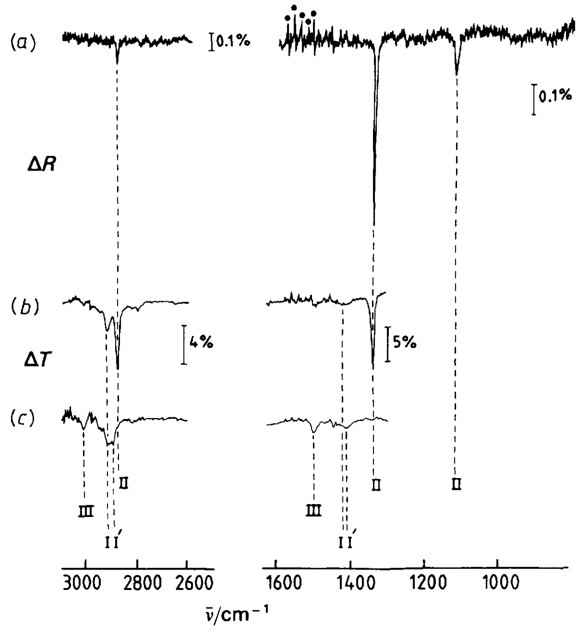

Fig. 3. (*a*) The RAIR spectrum from ethene adsorbed on Pt(111) at 360 K. ΔR = reflection loss through absorption by the adsorbed species. Resolution = 1 cm^{-1}. (*b*) The transmission IR spectrum of ethene adsorbed on a Pt/SiO_2 catalyst at 294 K (ΔT = loss of transmission through absorption by the adsorbed species). Resolution = 4 cm^{-1}. (*c*) As for (*b*) but at 189 K. (I, I′ di-σ species on different sites; II, ethylidyne; III, π-complex). (● indicates spectral features caused by inaccurate cancellation of water-vapour absorptions in the optical path of the spectrometer.)

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† 1 Torr = 101 325/760 Pa.

π-complex, (III, fig. 1, R = H) at 3016 and 1496 cm^{-1} and of the di-σ complex, (I, fig. 1, R = H) at 2922 and *ca.* 1428 cm^{-1}.[17]

Adsorption at the low temperature of 189 K, however [fig. 3(*c*)], shows no absorptions from ethylidyne but additional bands at 2905 and *ca.* 1419 cm^{-1}. The earlier VEELS work had shown that at low temperatures ethene is adsorbed on Pt(111) as the di-σ complex but that this is converted to the ethylidyne species near 300 K.[6,20] The transformation of the bands at 2905 and *ca.* 1419 cm^{-1} into those of ethylidyne implies therefore that the former absorptions are from the di-σ adsorbed species on the (111) plane. The wavenumbers observed make good sense on this assignment but unfortunately the spectrum of the di-σ adsorbed species has so far proved to be too weak for detection by RAIRS. The triangular groups of metal atoms on the (111) plane probably favour the ready transformation to ethylidyne. The companion bands in the low-temperature spectrum on Pt/SiO_2 (2922 and *ca.* 1428 cm^{-1}) to those assigned at 2905 and *ca.* 1419 cm^{-1} to the di-σ species have hence been assigned to the same type of di-σ species on another site, possibly a different surface plane such as (100).[17] In a related study of ethene on Pt/Al_2O_3,[28] the same conclusions were drawn on the di-σ to ethylidyne conversion, but the companion bands at 2922/1428 cm^{-1} were not observed. In that case only the π-complex and ethylidyne were found at room temperature. However, the lower-wavenumber transmission of Al_2O_3 also allowed the identification of the ν(C—C) mode of ethylidyne at 1128 cm^{-1} and an additional $\nu(C{=}C)/\delta(CH_2)$ mode of the π-complex at 1203 cm^{-1}.[28] The Pt/Al_2O_3 spectra had sufficiently small metal particles[14] (*ca.* 2 nm) that additional parallel modes of both the π-complex and ethylidyne were also observed. Possibly the continuing occurrence of the di-σ species at room temperature on our Pt/SiO_2 catalyst reflects the presence of more and larger crystalline facets on the larger metal particles. It is interesting to note that no π-complex has yet been found for ethene on any clean single-crystal planes, although it does occur on Pt(111) in the presence of oxygen co-adsorption.[20]

In terms of catalytic activity it is found, not surprisingly, that the absorptions from the non-dissociatively adsorbed species, the π- and di-σ complexes, are removed more rapidly than those of the dissociatively adsorbed ethylidyne species on addition of a dose of,[28] or in flowing,[29] hydrogen. It is not clear whether the labile π-complex, which is clearly very active in the hydrogenation reaction, is formed on amorphous areas of clean catalyst particles or whether it occurs on sites which are affected by proximity to the oxide substrate[28] or by contamination.

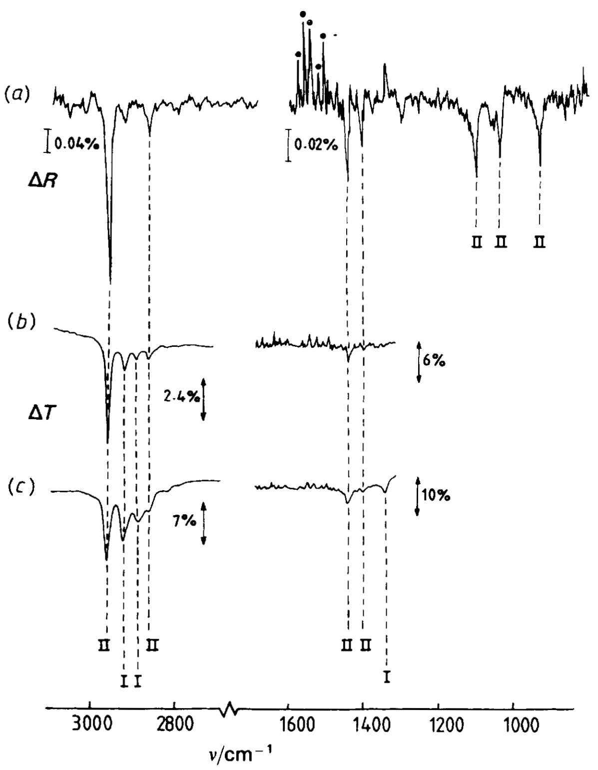

Fig. 4. (*a*) The RAIR spectrum from the adsorption of propene on Pt(111) at 340 K. Resolution = 2 cm^{-1}. (*b*) The transmission IR spectrum of propane adsorbed on Pt/SiO_2 at *ca.* 300 K. Resolution = 4 cm^{-1}. (*c*) As for (*b*) but with adsorption of propene. Structural symbols as in fig. 1. (I, di-σ species; II, propylidyne). (●, water-vapour miscancellation.)

Propene Adsorption

Fig. 4(*a*) shows the RAIR spectrum from propene on Pt(111) at 340 K. By analogy with the ethene case this might be expected to arise from the propylidyne species (IIb, fig. 2). In terms of a localised $CH_3CH_2CM_3$ complex this would have C_s symmetry with only the a′ modes allowed by the MSSR. These are, respectively, $\nu(CH_3)$as, $\nu(CH_3)$s, $\nu(CH_2)$s, $\delta(CH_3)$as, $\delta(CH_3)$s, $\delta(CH_2)$ (scissors), CH_2 wag, CH_3 rock and two ν(CC) modes. Other mode components of $\nu(CH_3)$as, $\delta(CH_3)$as and CH_3 rock, together with $\nu(CH_2)$as, CH_2 twist and CH_2 rock have a″ symmetry and are forbidden by the MSSR. The directions of the atomic motions imply that $\nu(CH_3)$as, $\delta(CH_3)$as, CH_3 rock and CH_2 wag amongst the a′ modes should give absorptions of full expected intensity (dipole changes more nearly perpendicular to the surface); $\nu(CH_3)$s, $\nu(CH_2)$s, $\delta(CH_3)$s and $\delta(CH_2)$ (scissors) should be weak (more nearly parallel) and the two ν(CC) modes may be of intermediate intensity. As shown in table 1, the spectrum lends itself to immediate and very convincing interpretation in these terms.[25,30,31] There can be no spectroscopic doubt that the structural assignment to propylidyne is correct, and this is in agreement with the conclusions from thermal desorption[22,32] and low-energy electron diffraction work.[33] Table 1 also summarises the corresponding features in the VEEL spectrum of propene on Pt(111) measured at 300 K.[22] With the exception of the much better quality of the RAIR spectra in the ν(CH) 3000 cm^{-1} region, the agreement is very good, and the previous structural and spectral assignments by Avery and Sheppard are confirmed. However, the higher resolution possible with RAIRS provides more reliable band positions. The RAIR spectrum does not extend beyond the effective limit of the HgCdTe detector near 800 cm^{-1}.

Fig. 4(*b*) and (*c*) show the room-temperature spectrum of propane and propene, respectively, chemisorbed on Pt/SiO_2.[25,30] That from propane is clearly the simpler spectrum and the majority of its features once again correlate extremely well with those of propylidyne on Pt(111), as shown in table 1. Only weak additional absorptions occur at 2895, 1365 and 1355 cm^{-1}, together with a relative intensification of the band at 2920 cm^{-1}. All these additional features are strengthened in the spectrum from the adsorption of propene [fig. 4(*c*)], and weak additional bands occur at 3020–2980, 2820 and 1465 cm^{-1}. By analogy with the ethene case on Pt/SiO_2, the most likely additional surface species are the di-σ one (I, fig. 1, R = CH_3) and the π-complex (III, fig. 1, R = CH_3). The 3020–2980 cm^{-1} absorptions clearly arise from ν(CH) modes of the C=C group in the π-complex, but their weakness suggests that relatively few of these species are present. Additionally no band assignable to the ν(C=C) mode of the π-complex has been observed in this case. It

Table 1. Assignment of the observed IR and VEELS bands (cm^{-1}) from propene adsorbed on Pt(111) and infrared bands from propene and propane adsorbed on a Pt/SiO_2 catalyst

Pt(111)[a] (VEELS) 300 K	Pt(111) (RAIRS) 340 K	propane on Pt/SiO_2 *ca.* 300 K	propene on Pt/SiO_2 *ca.* 300 K	assignments: vibration[b]	assignments: surface species[c]
			3020–2980 (w)	ν(HC═)	III
ca. 2980 (m)	2961 (vs)	2960 (vs)	2960 (s)	$\nu(CH_3)$as	II
ca. 2920 (m)	2921 (w)	2920 (mw)	2920 (ms)	$\nu(CH_2)$s[d]	I/II
		2895 (w)	2885 (m)	$\nu(CH_3)$s	I
	2865 (mw)	2870 (w)	2860 (w)	$\nu(CH_3)$s	II/I
			2820 (vw)	2 × 1410	I
			1465 (w)	$\delta(CH_3)$as	I
1465 (s)	1450 (s)	1450 (ms)	1450 (ms)	$\delta(CH_3)$as	II
	1407 (m)	1410 (w)	1410 (w)	$\delta(CH_2)$ (scissors)	II
		1365 (w)	1365 (w)	$\delta(CH_3)$s	II
		1355 (w)	1350 (ms)	$\delta(CH_3)$s	I
1295 (w)	1303 (w)	↑		CH_2 wag	II
1115 (s)	1103 (s)			ν(CC)	II
	1055 (w)			CH_3 rock (a″)	II
1055 (s)	1039 (s)	region obscured		CH_3 rock	II
940 (s)	929 (s)	↓		ν(CC)	II

(vs), very strong; (s), strong; (ms), medium strong; (m), medium; (mw), medium weak; (w), weak. [a] The lower resolution in VEELS leads to less precise band positions. [b] a′ modes only for propylidyne (see text). [c] I, the di-σ complex; II, propylidyne; III, the π complex. [d] This is a rather higher value than anticipated for propylidyne; it might alternatively be the overtone 2 $\delta(CH_3)$as for that species in Fermi resonance with $\nu(CH_3)$s, with $\nu(CH_2)$s coincident with $\nu(CH_3)$s at 2865 cm^{-1}.

therefore seems probable that the di-σ species is the most abundant additional one after propylidyne. This can have no symmetry elements so that all modes of vibration are MSSR-allowed. Successful schematic vibrational assignments of these extra spectral features in terms of the di-σ species have been given elsewhere.[25] However, the identification of the propylidyne species on the Pt/SiO_2 catalysts is clear-cut with the help of the RAIR spectrum although, as in the ethene case, this may not be the most catalytically active species for hydrogenation reactions. The spectra on the single-crystal face and on the finely divided catalysts provide complementary information.

But-1-ene Adsorption

If adsorption of but-1-ene follows the same pattern as is observed for ethene and propene, butylidyne (II, fig. 1, R = C_2H_5) should be the sole adsorbed species on Pt(111) at near room temperature. A more complex mixture of adsorbed species is to be expected on the Pt/SiO_2 catalyst. Butylidyne has a sufficiently long carbon chain to exist in two possible conformations, *trans* (*t*) and *gauche*, (*g*), (fig. 2, IIc and IId). Vibrational spectra recorded by VEELS have also been interpreted in terms of the butylidyne species[22] and the relative intensities of some bands suggested that the *trans* conformer predominates, although the poor resolution of VEELS and contributions from impact scattering makes such a conclusion uncertain.

The RAIR spectra of adsorbed layers resulting from exposure of Pt(111) to but-1-ene over a range of temperature (above 250 K) and pressure conditions have been interpreted in terms of mixtures of the *trans* and *gauche* conformers of butylidyne.[35] Here we present the spectrum of the butylidyne layer in the entirely *trans* form produced by rapid adsorption at 250 K, annealing to 270 K and cooling to 90 K [fig. 5(*b*)].

The C_s symmetry of the *trans* butylidyne surface complex leads to an expectation of a relatively simple spectrum (table 2). As with propene, it is the a′ (in-plane) modes that are allowed by the MSSR. In the ν(CH) region the $\nu(CH_3)$s mode, perpendicular to the surface, should be particularly strong, the $\nu(CH_3)$as correspondingly weak and at least one of the two $\nu(CH_2)$s modes could have intermediate intensity. On similar considerations $\delta(CH_3)$s, one of the CH_2 wags and at least one of the three ν(CC) bond-stretching modes should have full expected intensity. The a′ $\delta(CH_3)$as, $\delta(CH_2)$

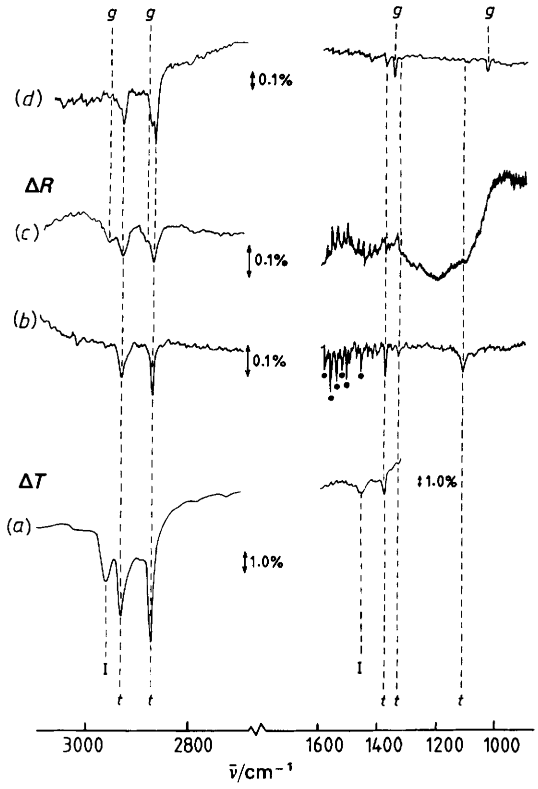

Fig. 5. (*a*) The transmission IR spectrum from but-1-ene adsorbed on a Pt/SiO_2 catalyst at *ca.* 300 K. Resolution = 4 cm^{-1}. (*b*) The RAIR spectrum from 5L but-1-ene adsorbed on Pt(111) at 270 K and then cooled to 90 K. Resolution = 4 cm^{-1} (*c*) As for (*b*) but the spectrum taken at 250 K after adsorption from 1 × 10^{-7} Torr but-1-ene. (*d*) As for (*b*) but the spectrum measured at 90 K after exposure to 10 L at 1 × 10^{-8} Torr of but-1-ene at *ca.* 300 K. (I, di-σ species; *t*, *trans*-butylidyne; *g*, *gauche*-butylidyne). (●, water-vapour miscancellation.)

(scissors) and CH_3 rocking modes should all be weak. The MSSR-forbidden a″ modes are one component of each of $\nu(CH_3)$as, $\delta(CH_3)$as and CH_3 rock, together with the pairs of $\nu(CH_2)$as, CH_2 twist and CH_2 rocking modes. The assignments given in table 2 are consistent with all these predictions.

The RAIR spectrum recorded at 250 K [fig. 5(*c*)] is more complex in the ν(CH) bond-stretching region, with extra bands at 2960 and *ca.* 2885 cm^{-1}, assigned to $\nu(CH_3)$as and $\nu(CH_3)$s [or $\nu(CH_2)$s] of the additional *gauche* isomer. Unfortunately this spectrum is poorly defined in the low wavenumber range. However, slower adsorption of but-1-ene at 300 K, followed by cooling to 90 K, gave a clearer spectrum in that region that also exhibits extra bands [fig. 5(*d*)]. The new bands at 1354 and 1035 cm^{-1} are also readily assigned to $\delta(CH_3)$s, and CH_3 rock or ν(CC) modes of the *gauche* isomer. It is not clear why in this spectrum the $\nu(CH_3)$as band has shifted to 2940 cm^{-1}.

In the VEEL spectrum[22] the strongest bands in the low-wavenumber region at 1400 and 1115 cm^{-1} are probably the counterparts of the absorptions from *trans*-butylidyne at 1377 and 1110 cm^{-1} more accurately located in fig. 5(*b*). The enhanced intensity in the VEEL spectrum at 1465 cm^{-1} and the different distribution of intensity in the poorly resolved ν(CH) region (which also contains impact contributions) probably denote the presence of a mixture of *trans* and *gauche* butylidyne isomers.

The transmission infrared spectrum of but-1-ene adsorbed on Pt/SiO_2 at room temperature is shown in fig. 5(*a*). It is closely similar to that reported earlier.[4] However, as in the case of ethene, the spectroscopic evidence from adsorption on Pt(111) requires substantial modifications of the earlier assignments of the structures of the chemisorbed species. The most intense band in the ν(CH) region at 2875 cm^{-1} absorption can clearly be assigned to *trans*-butylidyne by comparison with fig. 5(*b*) and the related entries in table 2. Although the prominent band at 2960 cm^{-1} could, on wavenumber grounds, be readily assigned to $\nu(CH_3)$as of the *gauche* butylidyne isomer, there is less intensity near 2885 cm^{-1} than would be expected through comparison with fig. 5(*c*) and (*d*). However, as in the propene case, it is very likely that there is also a di-σ species present (I, fig. 1, $R = C_2H_5$) which can contribute intensity to the 2960 cm^{-1} absorption and elsewhere in the ν(CH) region. The deformation region of the spectrum provides further confirmation. The bands at 1380 and 1330 cm^{-1} coincide in position and relative intensity with expectations for *trans*-butylidyne [fig. 5(*b*)] and there is only a weak feature at 1352 cm^{-1} for assignment to the *gauche* isomer. The broad band at 1450 cm^{-1} has no clear counterpart in the butylidyne spectra on Pt(111), but can readily be assigned to $\delta(CH_3)$as or $\delta(CH_2)$ (scissors) modes of the di-σ species.

In summary, the correlation between the infrared spectra of the adlayers on the single crystal and finely divided substrates indicates that butylidyne in its *trans* conformation is a major adsorbed species on the Pt/SiO_2 catalyst. The reason for the predominance of the *trans* conformer in the latter case even at room temperature may be that the high adsorption pressures used lead to a rather tightly packed monolayer, favouring the 'upright' conformer because of intermolecular repulsive interactions. We cannot be very specific about the other species present except that the band at 1450 cm^{-1} and at least part of the 2960 cm^{-1} band are likely to arise from the di-σ adsorbed species. The possibility of some isomerization to produce species arising from but-2-ene adsorption must also be considered, see below, and this leads to the possibility of adsorbed but-2-yne contributing to the weak bands at 2890 and 1352 cm^{-1} and to the 1450 cm^{-1} absorption.

But-2-ene Adsorption

Adsorption of both *cis*- and *trans*-but-2-ene at room temperature on the Pt(111) surface leads to an adsorbed layer with a very different IR spectrum to that produced by but-1-ene adsorption. The RAIR spectrum of the room-temperature adsorbed layer produced by *cis*-but-2-ene is shown in fig. 6(*a*); that of *trans*-but-2-ene was found to be essentially the same. The VEEL spectrum of this adsorbate had previously been assigned to adsorbed but-2-yne in a di-σ/π configuration on a three-fold surface site (IV, fig. 1).[23,24] The higher-resolution IR spectrum serves to confirm this assignment,

Table 2. Assignment of the IR and VEELS bands (cm^{-1}) for but-1-ene adsorbed on Pt(111) and on Pt/SiO_2

Pt(111)[a] (VEELS) 300 K	Pt(111) (RAIRS) *trans* 270 K[c]	Pt(111) (RAIRS) *trans* + *gauche* 250 K (300 K)[c]	Pt/SiO_2 *ca.* 300 K	assignment: vibration	assignment: surface species[b]
			3025 (w), 3005 (w)	ν(HC=)	III
		2960 (2940) (m)	2960 (m)	$\nu(CH_3)$as	I/*g*
ca. 2950 (m, bd)	2934 (ms)	2934 (2934) (ms)	2932 (s)	$\nu(CH_2)s^d$	*t*/I
	2924 (w, sh)		2920 (w, sh)	2 × 1408?	*t*
		2885 (2882) (m, sh)	2890 (vw)	$\nu(CH_3)$s	*g*
	2874 (s)	2874 (2874) (s)	2875 (vs)	$\nu(CH_3)$s	*t*
			1595 (w)	ν(C=C)?	III
			1480 (w)?		
1465 (m)			1450 (bd, m)	$\delta(CH_3)as/\delta(CH_2)$	I/*g*
			1408 (w)	$\delta(CH_2)$	I/*t* or *g*
1400 (vs)	1377 (ms)	(1377) (mw)	1380 (ms)	$\delta(CH_3)$s	*t*
		(1354) (m)	1352 (w)	$\delta(CH_3)$s	*g*
	1331 (w)	(1331) (w)	1330 (w)	CH_2 wag	*t*
1245 (w)			↑	CH_2 wag	*t* or *g*
1115 (vs)	1110 (m)	(1110) (w)	region	ν(CC)	*t*
		(1035) (mw)	obscured	CH_3 rock	*g*
900 (m)			|	ν(CC)	*t*
780 (m)		obscured	↓	CH_2 rock	*g*

(vs) *etc.* as in table 1; (sh), shoulder; (bd), broad. [a] The lower resolution of VEELS leads to less precise band positions. [b] I, di-σ complex; *t*/*g* *trans*/*gauche* butylidyne; III, π-complex. [c] Spectrum run at 90 K after warming to the stated temperature. [d] See comment (*d*) on table 1.

with excellent agreement in the positions of the major bands except in the 3000 cm^{-1} region, where probable additional impact scattering in the VEEL spectrum has modified the profile. The spectrum resulting from adsorption of but-2-yne itself is shown for comparison in fig. 6(*b*).

A point of interest is that the ν(CH) stretching region in the spectrum of but-2-yne adsorbed on Pt(111) is similar to that for the same adsorbate on Cu(111),[34] but the 'fingerprint' regions of the spectrum are quite different for the two metals. On Cu(111) a single strong band at 1392 cm^{-1} is assigned to CC stretching of the central bond, implying a bond order between 1 and 2, but the methyl deformations are too weak to be detected. For the species on Pt(111) both the $\delta(CH_3)$as and $\delta(CH_3)$s deformations are seen, as is a ν(CC) or methyl rock, but the central CC stretch is expected (from VEELS results)[23,24] to be weak. These differences arise from substantial changes in the metal–adsorbate bonding in going from Pt(111) to Cu(111). The species on Cu(111) is believed to be bonded to 4 metal atoms with C_{2v} local symmetry in which the four carbon atoms lie in a plane at right angles to the surface. This is in contrast to the di-σ/π bonding on Pt(111) (IV, fig. 1) in which the plane of the carbon atoms is tilted with respect to the surface normal and the local symmetry is C_s. The interesting point is that all the characteristic group vibrations mentioned above belong to allowed vibrational modes for both types of adsorbate and so the differences between the spectra are not due to selection rules but rather to the differences in electronic structure affecting the intensities of bands in the two cases.

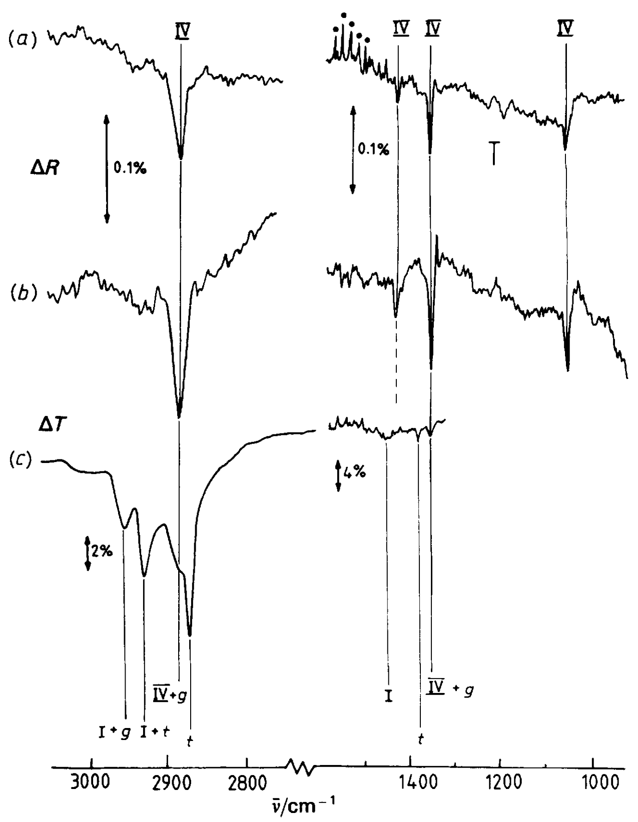

Fig. 6. (*a*) The RAIR spectrum from *cis*-but-2-ene adsorbed on Pt(111) at *ca.* 300 K. Resolution = 4 cm^{-1}. The spectrum from *trans*-but-2-ene shows the same features. (*b*) as for (*a*) but with the adsorption of but-2-yne instead of but-2-ene. (*c*) The transmission IR spectrum at *ca.* 300 K for the adsorption of *cis*-but-2-ene on Pt/SiO_2. Resolution = 4 cm^{-1}. (I, di-σ species from but-1-ene; *t*, *trans*-butylidyne; *g*, *gauche*-butylidyne; IV, adsorbed but-2-yne, fig. 1 IV). (●, water-vapour miscancellation.)

The spectrum shown in fig. 6(*c*) and listed in table 3 shows that the surface species generated by *cis*-but-2-ene adsorption on the Pt/SiO_2 catalyst are this time quite different to those produced on the (111) single-crystal surface. While it is possible that adsorbed but-2-yne may make some contribution to the spectrum (bands at 2890 and 1352 cm^{-1}) the major surface species are clearly similar to those produced by adsorption of but-1-ene at room temperature on Pt/SiO_2. It therefore appears that double-bond shift isomerization occurs in the adsorbed phase on the platinum particles but not on the (111) platinum single-crystal surface.

IR spectra of the gas phase above the Pt/SiO_2 sample over a period of several hours indicated that on this timescale no significant amount of but-1-ene or *trans*-but-2-ene is desorbed from the surface so it appears that the isomerization is confined to the adsorbed layer. However, it has previously been reported that, over a longer period of 20 h, but-1-ene can be converted to an equilibrium mixture of the linear butenes in the gas-phase over such Pt/SiO_2 catalysts.[4] *trans*-But-2-ene is the predominant species in the gas-phase equilibrium mixture, but it is clear from the present spectrum that adsorbed species from but-1-ene are substantially more abundant on the surface. This may be caused by the high stability of the butylidyne species on the (111) planes of the catalyst.

Table 3. Assignment of the IR and VEELS bands (cm^{-1}) for *cis*-but-2-ene and but-2-yne adsorbed on Pt(111) and *cis*-but-2-ene adsorbed on Pt/SiO_2

but-2-yne Pt(111) (VEELS)[a] 300 K	but-2-yne Pt(111) (RAIRS) *ca.* 300 K	but-2-ene Pt(111) (VEELS)[a] 300 K	but-2-ene Pt(111) (RAIRS) *ca.* 300 K	but-2-ene Pt/SiO_2 300 K	assignment	
					vibration	surface species[b]
				3020–2980 (w)	ν(HC=)	III
				2960 (m)	$\nu(CH_3)$as	I/*g*
ca. 2960 (m)	*ca.* 2930 (m, bd)	*ca.* 2960 (m)	*ca.* 2930 (m, bd)	2932 (s)	$\nu(CH_3)$as/$\nu(CH_2)$s	IV/*t*/I
ca. 2910 (m)	2886 (vs)	*ca.* 2910 (m)	2886 (vs)	2890 (ms, sh)	$\nu(CH_3)$s	IV/*g*
				2879 (vs)	$\nu(CH_3)$s	*t*
				1592 (w)	ν(C=C)	III
1435 (s)	1430 (m)	1435 (s)	1430 (m)	1450 (m, bd)	$\delta(CH_3)$as/$\delta(CH_2)$	IV/I/*g*
				1380 (m)	$\delta(CH_3)$s	*t*
1365 (s)	1354 (s)	1365 (s)	1354 (s)	1352 (m)	$\delta(CH_3)$s	IV/*g*
				1330 (w)	CH_2 wag	*t*
1045 (vs)	1036 (ms)	1045 (vs)	1036 (ms)	↑ obscured ↓	ν(CC)/CH_3 rock	IV

(vs) *etc.* as in footnotes to tables 1 and 2. [a] The lower resolution of VEELS leads to less precise band positions. [b] I, the di-σ species from but-1-ene; *t*/*g*, *trans*/*gauche* butylidyne; III, π-complex; IV, di-σ/π but-2-yne complex (fig. 1, IV).

The positions and relative intensities of the bands labelled 't' in fig. 6(*c*) are clearly indicative of the presence of the *trans* conformer of butylidyne (see also table 2). In addition contributions from *gauche*-butylidyne and di-σ adsorbed species may also be expected across the ν(CH) stretching and $\delta(CH_3)/\delta(CH_2)$ regions.

The adsorption of but-2-ene therefore appears to follow a substantially different path on the Pt/SiO_2 catalyst compared to the Pt(111) surface. This must be due to the presence of active sites on the catalyst surface which are capable of effecting the double-bond shift in the adsorbed species. The presence of the alkylidyne adsorbed species is normally associated with the (111) crystal facets of the catalyst particles, but the RAIRS and VEELS work shows that this plane does not bring about double-bond shifts from the *cis* or *trans* isomers. It seems necessary, therefore, to envisage that the adsorbed species are able to migrate, from the sites at which the double-bond shift occurs, onto the (111) faces where the butylidyne species is formed. The active sites may be steps or edges or other extended facets of the metal crystallite, such as (100) planes. It would therefore be instructive to investigate the adsorption of but-2-ene on stepped (111) crystal surfaces and on other planes.

Conclusions

The interpretation of the IR spectrum of ethene adsorbed on silica-supported platinum in terms of a number of different adsorbed species, which has been established over a number of years, has now been extended to adsorption of propene and but-1-ene. As in the ethene case the assignment was assisted by recording spectra of the alkylidyne species alone, produced by adsorption of the alkenes on Pt(111) near room temperature. The alkylidyne species generally produce relatively strong IR spectra and make major contributions to the spectra of the adsorbates on silica-supported platinum. There is clear evidence for the existence of another species, probably the di-σ adsorbed propene and butene species, and for traces of π-adsorbed species, on Pt/SiO_2. Both of these must be associated with planes other than (111) or with steps, edges or corners.

In the case of but-2-ene adsorption the correlation between the single-crystal and supported-metal results was not nearly so close. It is clear that double-bond shift isomerization to adsorbed but-1-ene occurs on the platinum particles, allowing the rather stable butylidyne species to form. The double-bond shift does not occur on the Pt(111) surface where the adsorbed but-2-ene dehydrogenates to adsorbed but-2-yne. This latter species contributes only to a limited extent to the infrared spectrum seen on the supported platinum samples.

The IR method is seen to provide much valuable information about the hydrocarbon species adsorbed on the surfaces of the Pt/SiO_2 catalyst, ranging from examples where the spectrum is closely similar to that on Pt(111) (propane) to examples where the adsorbed species are very, and unexpectedly, different (*cis*-but-2-ene).

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Note added in proof: We have belatedly found a detailed study and analysis of similar infrared spectra from the linear butenes adsorbed on Ni/SiO_2 in which the effects of the metal surface selection rule were also taken into account (T. J. Campione and J. G. Ekerdt, *J. Catal.*, 1986, **102**, 64). These authors also noted the unexpectedly high intensities of the *ca.* 2875 and 1380 cm^{-1} absorptions and interpreted these in the alternative terms of a 2,3-di-σ adsorbed butene species, with the C—C bonds of the terminal C—CH_3 groups near to perpendicular to the surface. However, such a species would not seem to account also for the marked differences in the $\nu(CH_3)as/\nu(CH_3)s$ and $\delta(CH_3)as/\delta(CH_3)s$ intensities between the spectra of the adsorbed butenes and propene. We therefore continue to prefer the interpretation in terms of alkylidyne species.

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