Raman Spectroscopic Study of the Reaction of Oxygen with Polyacetylene Adsorbed on TiO₂ (Rutile) and of Benzene Adsorption on Rutile

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A Raman spectroscopic study of the reaction of oxygen with *trans*-polyacetylene adsorbed on rutile shows that the polymer breaks down. Benzene is obtained as a volatile reaction product and, particularly in the presence of the short-wavelength 457.9 nm Raman exciting line, this is converted to a different surface species of an aromatic nature. The adsorption of benzene itself on a bare TiO₂ surface gives a very closely similar spectrum from 457.9 nm excitation to that obtained from the O₂/polyacetylene reaction. The final aromatic surface product is tentatively identified as *para*-polyphenyl in type.

Longer-wavelength Raman excitation leads to less conversion of the polyacetylene to the final aromatic product; under these conditions benzene is also largely adsorbed intact on the TiO₂ surface.

In a previous paper[1] we have reported the formation of a *trans*-polyene from polymerisation of acetylene adsorbed at room temperature on a highly dehydroxylated TiO₂ (rutile) surface. The polymerisation led to different lengths of polymer chain with up to 20 conjugated double bonds. The intensities of skeletal fundamentals and overtones of the polymer were greatly enhanced by the Resonance Raman Effect.

In order to assess the characteristics of the polymers thus formed and to obtain more information about their chemical properties we have studied their interaction with oxygen by Raman spectroscopy.

The reaction of polyacetylene films with atmospheric oxygen has been previously reported[2] to produce an oxygenated material characterised by strong infrared bands at 1670 and 1720 cm⁻¹. These were assigned respectively to $v(\text{C}=\text{O})$ vibrations of α, β-unsaturated ketones and α diketones. Oxidation of the polymer by permanganate led to the identification of benzoic acid amongst the products. The production of this was indirectly attributed to the formation of phenyl groups through terminal cyclisation of growing chains.

EXPERIMENTAL

The TiO₂ sample was rutile obtained by hydrolysis of TiCl₄ and heating overnight at 400 K. It was kindly supplied by Dr T. A. Egerton of Tioxide International (sample code number CLD 1161/A). Acetylene was obtained from the National Physical Laboratories and oxygen from B.O.C.; both were used as purchased without any further purification, except that the oxygen was admitted to the Raman cell through a CO₂(s) + acetone cold trap (198 K) in order to remove water vapour. Benzene was obtained from B.D.H. and was subjected to several freeze–pump–thaw cycles before use.

A Spex 1401 double-monochromator Raman spectrometer coupled to a Coherent Radiation CR-MG 52 mixed gas Ar–Kr ion laser was used to record the Raman spectra using 90° optics.

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To avoid heating and decomposition of the sample the laser beam was used at very low power, *ca.* 20 mW, on the sample. This made necessary the use of wide slits.

In order to eliminate a fluorescence background the TiO$_2$ sample was pretreated at 723 K for 7 h with *ca.* 40 kN m^{-2} of oxygen and outgassed overnight at the same temperature. The sample was then left to cool down to room temperature while continuing to be outgassed. The specific surface area of the sample after this treatment was estimated by the B-point method to be 70 m^2 g^{-1}.

Once the TiO$_2$ sample had been given the above treatment and its Raman spectrum recorded in order to check the lack of impurities, a pressure of *ca.* 24 kN m^{-2} of acetylene was admitted to the cell at room temperature. After recording the Raman spectrum the gas phase was eliminated by outgassing for one minute at room temperature (this produced no change in the colour of the sample) and then *ca.* 11 kN m^{-2} of O$_2$ were admitted to the cell and the spectrum recorded once again.

RESULTS

RAMAN SPECTRA FROM THE PRODUCTS OF THE REACTION OF OXYGEN WITH POLYACETYLENE ADSORBED ON RUTILE

Fig. 1 shows the Raman spectra obtained with an exciting line wavelength, λ_{exc}, of 457.9 nm, of polyacetylene adsorbed on TiO$_2$ (*a*) before and (*b*) after admission of oxygen at room temperature. Interaction with oxygen is seen to have a drastic effect
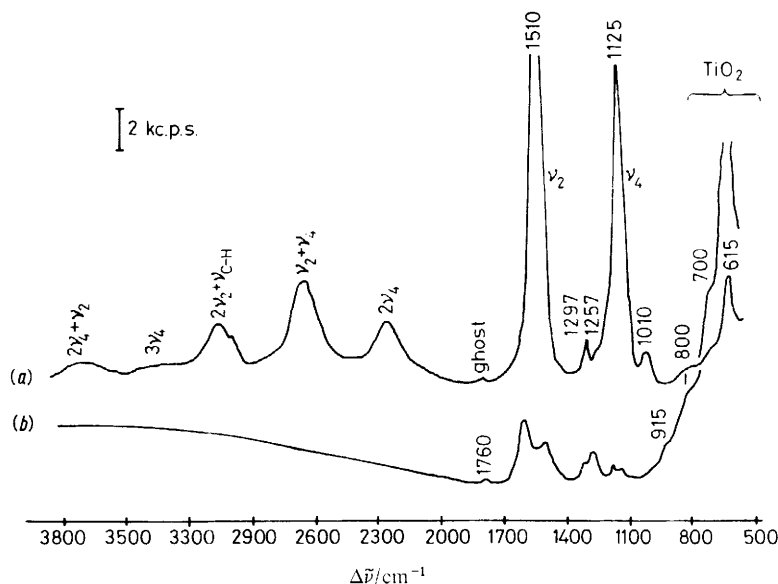

FIG. 1.—Raman spectrum of rutile-adsorbed *trans*-polyacetylene (*a*) before and (*b*) after admission of 11 kN m^{-2} O$_2$ at room temperature. Recording conditions: λ_{exc} = 457.9 nm, slits 13 cm^{-1}, scan speed 50 cm^{-1} min^{-1}, time constant 0.4 s, laser power 20 mW on the sample, 2×10^4 c.p.s. full scale.

on the spectrum of the original polyacetylene. However, no bands were observed in the *ca.* 1700 cm^{-1} region attributable to ν(C=O) vibrations; only a grating ghost appears at a $\Delta\tilde{\nu}$ position of 1760 cm^{-1}. Under these experimental conditions the skeletal modes ν_2[ν(C=C)] and ν_4[ν(C—C)] of the polymer and the overtone or combination bands $2\nu_4$, $\nu_2 + \nu_4$, $2\nu_2$, $3\nu_4$ and $\nu_2 + 2\nu_4$ (all enhanced in intensity by the Resonance Raman Effect) have been virtually completely removed by the oxygen treatment. A weak band at 1010 cm^{-1} attributed to an out-of-plane CH deformation mode of the polymer has also been eliminated. A band at 615 cm^{-1} and shoulders at

$ca.$ 700 and 800 cm^{-1} attributable to lattice modes of rutile[3, 4] are considerably enhanced in intensities in the spectra after the addition of oxygen. In the light of our previous results[1] the increase in intensities of these bands is probably caused by a thinning of the polyene coating on the TiO_2 particles which allows penetration by the exciting light and stronger Raman scattering by the oxide.

The spectrum of the product of oxygen treatment of the adsorbed polyacetylene is shown below 1700 cm^{-1} on a larger scale in fig. 2(a). It shows its strongest features at the $\Delta\tilde{\nu}$ values of 1595 (s), 1483 (m), 1300 (m), 1262 (vs), 1161 (m) and 915 cm^{-1} (ms). The first two bands at 1595 and 1483 cm^{-1} suggested that the product might be aromatic in nature; these two bands could then be assigned to skeletal modes of the aromatic ring. As we shall discuss below, the aromatic hypothesis was confirmed when we obtained a closely similar spectrum from benzene itself adsorbed on similarly prepared TiO_2. This spectrum is shown in fig. 2(b). The principal differences between
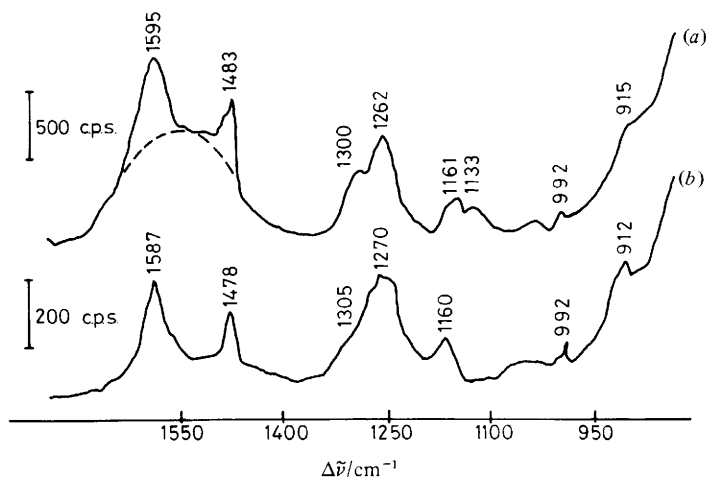

FIG. 2.—(a) Raman spectrum of O_2-treated, rutile-adsorbed $trans$-polyacetylene. Recording conditions: $\lambda_{exc} = 457.9$ nm, slits 13 cm^{-1}, scan speed 50 cm^{-1} min^{-1}, time constant 1 s, laser power 20 mW on the sample, 5×10^3 c.p.s., full scale. (b) The Raman spectrum of rutile-adsorbed benzene. Recording conditions: $\lambda_{exc} = 457.9$ nm, slits 10 cm^{-1}, scan speed 25 cm^{-1} min^{-1}, time constant 2 s, laser power 20 mW on the sample, 2×10^3 c.p.s. full scale.

fig. 2(a, b) is that the former shows additional features consisting of a broad background band centred near 1540 cm^{-1} and a weak band at 1133 cm^{-1}. We assign these additional bands to residual amounts of the polyacetylene remaining on the surface of the catalyst, $cf.$ fig. 1(a).

Confirmation that the spectrum in fig. 2(a) was also derived from benzene which had resulted from the reaction of polyacetylene with oxygen came from the following experiment. A fresh sample of powdered rutile was given the standard oxygen treatment, evacuated and had acetylene polymerised on it as checked by the Raman spectrum. Oxygen was then added to the cell and the Raman spectrum was recorded once again. The Raman cell was next attached to a greaseless vacuum line and the gas phase was trapped off at 77 K in a Pyrex cell suitable for recording Raman spectra of small liquid samples. After 30 min the cold trap was changed to solid CO_2 + acetone, thereby allowing any condensed oxygen to evaporate, and the cell was allowed to warm up to room temperature. The Raman bands observed from the residual liquid agreed in all respects with those from liquid benzene[5] except for two additional weak and broad bands of unknown origin near 804 and 2770 cm^{-1}.

Fig. 3 shows the Raman spectra of the O$_2$ + polyacetylene/TiO$_2$ system as a function of the wavelength of the exciting radiation. Only for excitation by the originally-used 457.9 nm line does the spectrum of the aromatic species completely dominate the spectrum. The very strong resonance-enhanced bands from the polyacetylene chains increasingly remain in the spectra as the wavelength of the exciting radiation increases. In these spectra the presence of the aromatic species is best identified through the *ca.* 1260 cm^{-1} band and its weaker companion near 1300 cm^{-1}. The 1483 and 1161 cm^{-1} bands from the aromatic species are obscured by the v_2 and v_4 bands of the polymer
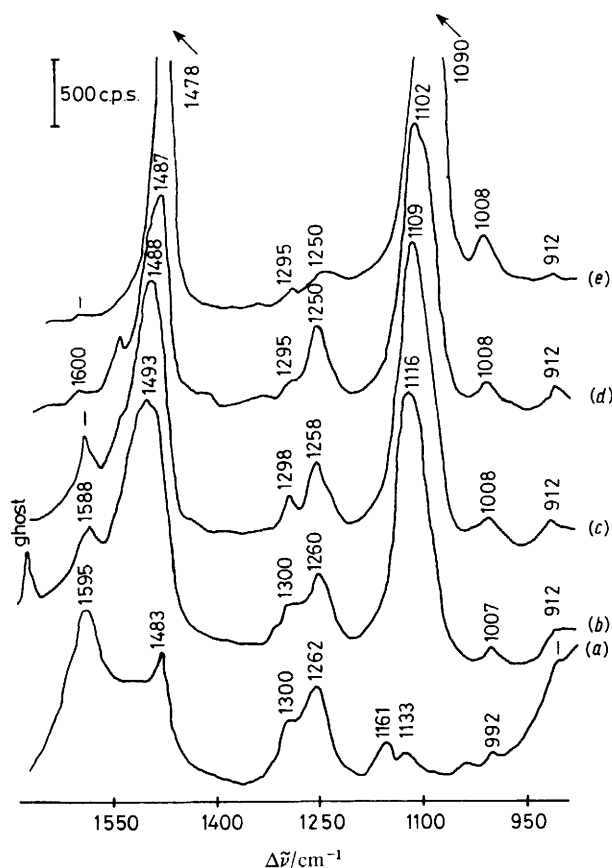

FIG. 3.—Raman spectra of oxygen-treated, rutile-adsorbed *trans*-polyacetylene as recorded with different exciting lines. (a) 457.9 nm, slits 13 cm^{-1}; (b) 488.0 nm, slits 12 cm^{-1}; (c) 514.5 nm, slits 10 cm^{-1}; (d) 568.2 nm, slits 8 cm^{-1}; (e) 647.1 nm, slits 6 cm^{-1}. Recording conditions: laser power 20 mW on the sample, scan speed 50 cm^{-1} min^{-1}, time constant 1 s, 5 × 10^3 c.p.s. full scale.

when longer wavelength excitations are used. The *ca.* 912 cm^{-1} band is observable throughout, but in fig. 3(a) it is superimposed on a TiO$_2$ band. In fig. 3(d) the *ca.* 1600 cm^{-1} band of the aromatic species seems to be substantially weaker than the 1250 cm^{-1} band, and this raises the question whether these two bands arise from the same chemical species. However, spectra from the same species derived from adsorbed benzene (fig. 4 and 5, to be discussed below) consistently show the *ca.* 1600 and 1260 cm^{-1} bands to be increasing and decreasing simultaneously. Note that in fig. 3(a), the 1595 cm^{-1} band appears abnormally strong because of the very substantial

underlying *ca.* 1540 cm^{-1} band of the residual polymer. Fig. 2(*b*) probably gives a better measure of the relative strengths of the two bands in question.

In our earlier work on the polyacetylene polymer[1] we deduced from the dependence of the v_2 and v_4 frequencies on the wavelength of the exciting line that the 457.9 nm line excites the polymer of shortest chain lengths. It is not surprising that it is for the same exciting line that the polymer is most effectively removed by the action of oxygen.

RAMAN SPECTRA FROM BENZENE ADSORBED ON RUTILE

The discovery of benzene amongst the products of the O_2/polyacetylene reaction on TiO_2 led us to investigate the spectrum of the former compound itself on the TiO_2 surface. A fresh sample of rutile was given the standard oxygen and evacuation treatment at 723 K and cooled down to room temperature. Benzene vapour at a pressure of 2.7 kN m^{-2} was then added to the cell; it should be stressed that oxygen was not subsequently added to the adsorbed benzene.

The resulting Raman spectrum is shown in fig. 2(*b*). This is clearly not the spectrum of benzene itself adsorbed intact onto the oxide surface. Such spectra on oxides such as silica,[6,7] alumina[6] or porous glass[6,8-10] differ very substantially from that shown in fig. 2(*b*). In particular they show dominance of the spectrum by the strong and sharp band originating in the skeletal breathing vibration of benzene near 992 cm^{-1}.[5,11] Only a very weak sharp band occurs at this position in fig. 2(*b*) and the latter shows two features, at 1270 and 912 cm^{-1}, wavenumbers which have no counterparts amongst the Raman active or inactive fundamentals of benzene itself.[11]

Fig. 4 shows the spectrum obtained from benzene adsorbed on TiO_2 when different exciting lines are used on different locations of the same powdered sample of adsorbent. For 647.1 nm (red) excitation the spectrum is simply that of adsorbed benzene with the expected very strong band at 992 cm^{-1}. This band becomes progressively weaker, but always measurable, as the wavelength of the exciting line is decreased in sequence to 568.2 (yellow), 488.8 (blue) and 457.9 nm (indigo). At the same time the spectrum that we have previously discussed [fig. 2(*b*)] gradually strengthens.

Fig. 5 shows the results of a time-dependent Raman spectroscopic study using the 568.2 nm (yellow) exciting line, and taking spectral scans at *ca.* 15 min intervals. Here the spectrum is seen to change with time, with the 992 cm^{-1} band of benzene gradually decreasing and being replaced by the spectrum dominant in fig. 2(*b*). The rate of transformation of adsorbed benzene on the TiO_2 surface to form the new product increases both with the time of exposure and the decreasing wavelength of the exciting radiation.

DISCUSSION

STRUCTURE OF THE AROMATIC PRODUCT

We next consider the evidence that the Raman spectra provide about the chemical structure of the unidentified final aromatic product from either the O_2/polyacetylene reaction or benzene. Its most clear-cut spectrum is shown in fig. 2(*b*). We shall assume that, apart from the presence of some traces of unreacted benzene, there is a single species present, although this is not certain. This species may or may not contain oxygen. Although no additional oxygen was added in its production from adsorbed benzene, it might have removed oxygen from the TiO_2 surface.

As noted earlier, the prominent bands near 1590 and 1480 cm^{-1} strongly suggest the presence of an aromatic ring.[5,12] Rather stronger Raman bands near 1260 cm^{-1} are not uncommon for aromatic rings with attached C—C bonds. We have taken
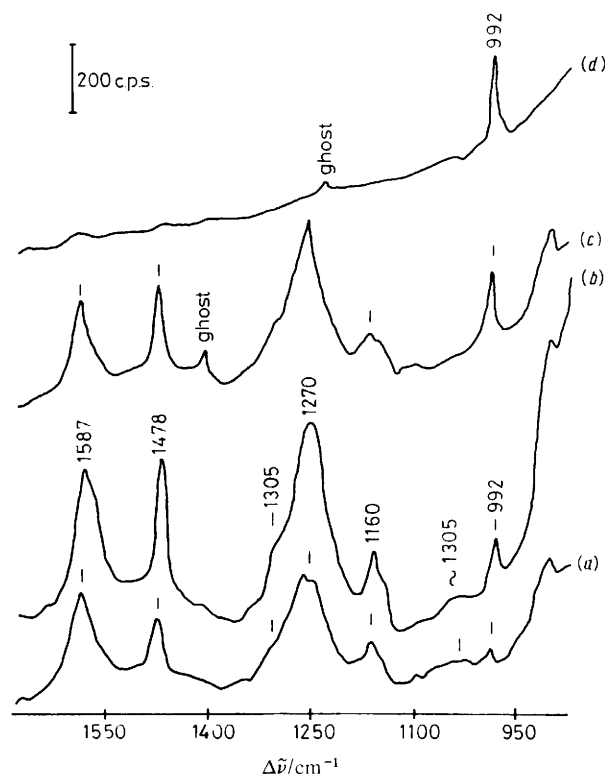
FIG. 4.—Raman spectra of rutile-adsorbed benzene recorded with different exciting lines. (a) 457.9 nm, slits 10 cm^{-1}, (b) 488.0 nm, slits 9 cm^{-1}, (c) 568.2 nm, slits 7 cm^{-1}, (d) 647.1 nm, slits 5 cm^{-1}. Recording conditions: laser power 20 mW on the sample, scan speed 25 cm^{-1} min^{-1} in (a) and (b) and 50 cm^{-1} min^{-1} in (c) and (d); time constant 2 s in (a), (b) and (c) and 1 s in (d); 2 × 10^3 c.p.s. full scale.

methyl substituted aromatic hydrocarbons as model compounds.[5] The absence of a strong 'ring-breathing' aromatic frequency in the 1100-980 cm^{-1} region makes it unlikely that monosubstituted, *ortho*- or *meta*-disubstituted, or 1,3,5-trisubstituted aromatic rings are present. *Para*-disubstituted rings as well as 1,2,4-trisubstituted and 1,2,4,5-tetrasubstituted rings all give prominent bands between 1200 and 1270 cm^{-1}. The simplest possibility would seem to be that the benzene rings have polymerised to give *para*-polyphenyls, possibly with transfer of hydrogen from benzene to form OH groups on the surface of TiO$_2$. Such compounds, including the first member of the series, biphenyl, give strong inter-ring C—C wavenumbers in the 1270-1300 cm^{-1} region. The Raman spectrum of biphenyl adsorbed on SiO$_2$ has been measured.[13]

Table 1 gives a comparison between the strongest Raman bands of biphenyl, C$_{12}$H$_{10}$, and its perdeuterated analogue[14] with those of the products from the adsorption of C$_6$H$_6$ and C$_6$D$_6$, respectively, adsorbed on TiO$_2$ as measured with 457.9 nm exciting radiation. The correspondence is sufficiently strong as to give good support to the identification of the aromatic product as biphenyl or its higher homologues. However, more work, using infrared spectroscopy and other techniques, is needed to confirm this structural assignment.
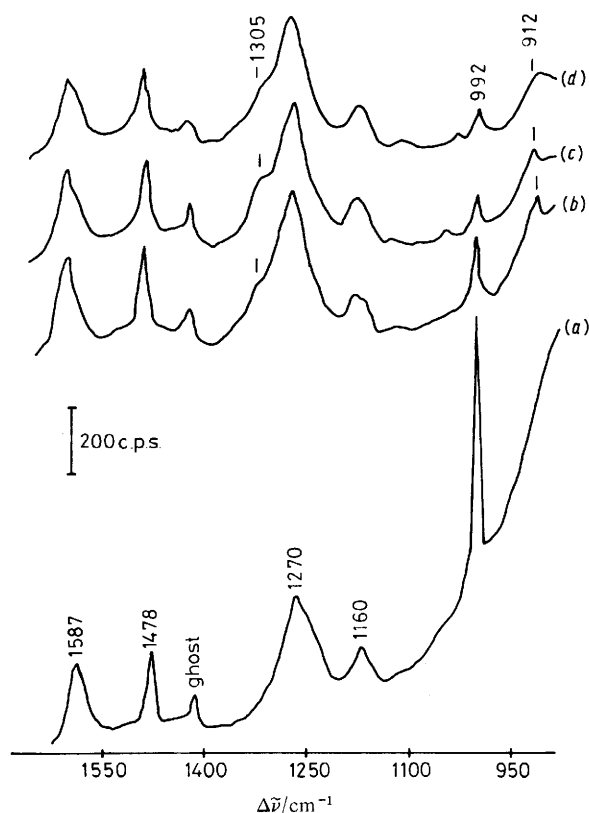
FIG. 5.—Raman spectra of rutile-adsorbed benzene showing the effect of the exposure time to the laser beam. (a) Spectrum recorded immediately after illumination; (b) 15 min later; (c) 30 min; (d) 45 min. Recording conditions: $\lambda_{exc} = 568.2$ nm, laser power 20 mW on the sample, slits 7 cm^{-1}, scan speed 50 cm^{-1} min^{-1}, time constant 1 s; 2×10^3 c.p.s. full scale.

TABLE 1.—MAIN RAMAN BANDS WITH $\Delta\tilde{\nu}$ (cm^{-1}) BETWEEN 1700 AND 950 cm^{-1} FOR LIQUID BIPHENYL AND PERDEUTEROBIPHENYL AND FOR C_6H_6 AND C_6D_6 ADSORBED ON TiO_2[a]

C_6H_6/TiO_2	$C_6H_5 \cdot C_6H_5$[14]	C_6D_6/TiO_2	$C_6D_5 \cdot C_6D_5$[14]
1587 (ms)	$\begin{Bmatrix} 1610\,(s) \\ 1591\,(s) \end{Bmatrix}$	1560 (vs)	1562 (vs)
1478 (ms)	1512 (m)	1405 (s)	1415 (s)
—	—	—	1401 (w)
—	1467 (vw)	1372 (w, sh)	$\begin{Bmatrix} 1376 \\ 1350 \end{Bmatrix}$ (vw)
1305 (w)	1335 (vw)	ca. 1270 (w, br)	1280 (w)
		—	1220 (w)
1270 (vs)	1277 (vs)	1200 (s)	1188 (vs)
	1209 (w)	—	—
1160 (m)	$\begin{Bmatrix} 1166 \\ 1150 \end{Bmatrix}$ (m)	1058 (w,br)	—
992 (w)[b]	—	945 (vw)[b]	—

[a] Raman spectra measured using the 457.9 nm exciting line. [b] Bands due to adsorbed C_6H_6 or C_6D_6. (vs) very strong; (s) strong; (ms) medium strong; (m) medium; (w) weak; (vw) very weak; (sh) shoulder; (br) broad.

POSSIBLE MECHANISMS FOR THE O$_2$/POLYACETYLENE REACTION ON THE RUTILE SURFACE

From the Raman results reported earlier it seems very probable that the reaction of O$_2$ with the adsorbed polyacetylene leads first to depolymerisation to give benzene, followed by interaction of the latter with the surface to give the final aromatic product. From fig. 4 it is seen that the benzene transformation reaction is speeded up by the use of short-wavelength radiation to excite the Raman spectrum. It seems probable that this reaction is photochemical in nature. This might be associated with the fact that the electronic band-gap for rutile is *ca.* 3.0 eV≡410 nm,[15] corresponding to a strong electronic absorption band which extends well beyond 400 nm to longer wavelengths.[16] It is therefore probable that photoactivation has occurred *via* the surface through the use of the shorter-wavelength exciting lines.

Although the enhanced removal of the polyacetylene through interaction with oxygen is also observed when the shorter-wavelength exciting lines are used, it has to be borne in mind that the Resonance Raman Effect means that the shorter wavelengths excite the spectra of the shorter chain polyacetylenes. These are, of course, likely to be more rapidly removed in a depolymerisation reaction, so that photoactivation may or may not be occurring.

Boonstra and Mutsaers[17] reported that the interaction of acetylene with an anatase TiO$_2$ sample led to the formation of benzene rather than, as in our case with rutile, the long-chain polyacetylene. Apart from the different TiO$_2$ polymorph used by them, another significant experimental difference is that after outgassing and treating with O$_2$ at 773 K their sample was cooled in oxygen; in our case the oxide was outgassed at 723 K and cooled *in vacuo*. This can be a significant difference because oxygen-depletion of the surface by high-temperature evacuation may lead to electron transfer from O^{2-} to the surface to give Ti^{3+} as well as the more normal Ti^{4+} ions.[18] It is perhaps consistent with this idea that subsequent addition of oxygen to the depleted rutile surface causes conversion of the polyacetylene to the same product, benzene, obtained from acetylene on the non- or less-depleted anatase surface.[17]

A probable structure for the surface of rutile particles[19] approximates to the (110) plane of the single crystal. This has equal numbers of four-and five-coordinated metal cations which are represented in scheme 1. Further removal of oxygen will lead to more low-coordination cation sites, even down to three, some of which may have Ti^{3+} nature and will exhibit a tendency to complete their coordination spheres. We suggest that the polyene may originate at a Ti^{3+} site and grow until terminated by another Ti^{3+} low-coordination site, as represented in scheme 2.

C_{2v} site C_{4v} site
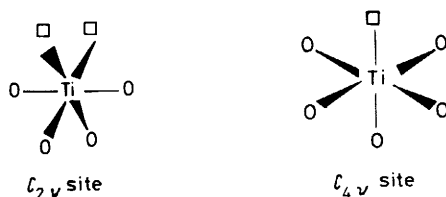
SCHEME 1.—Possible sites on TiO$_2$ surface.
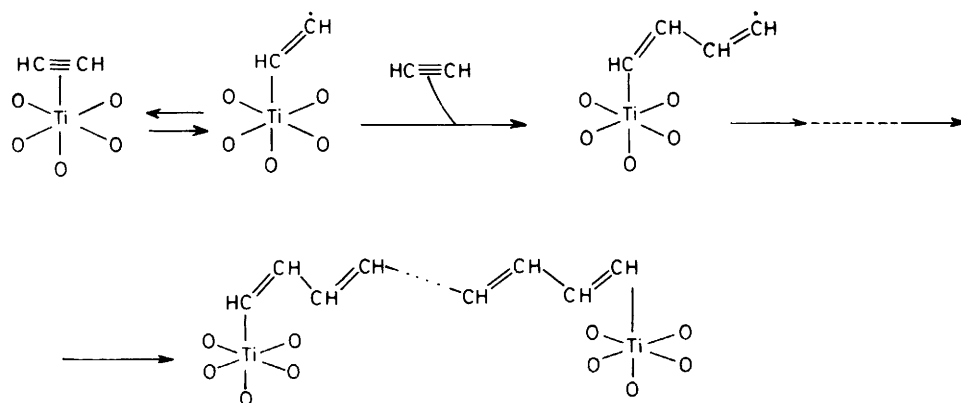
SCHEME 2.—Possible polymerization mechanism for acetylene on TiO_2.

Species with Ti—C bonds have previously been reported in the literature. Thus 25 years ago the compound $C_6H_5Ti(OC_3H_7)_3$ with a Ti—C σ-bond was reported[20] as was more recently the formation of Ti—CH_3 groups from mild decomposition of rutile- or anatase-adsorbed methanol.[21] π-type Ti–arene complexes have been reviewed by Silverthorn.[22]

When oxygen is brought into contact with the polyacetylene-covered TiO_2 it may displace the Ti—C bonds from the polymer, leading to the rapid degradation of the latter to form the more stable benzene product as in Boonstra's case.[17]

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