Journal of Organometallic Chemistry, 463 (1993) 85–90

JOM 23777

Tin oxide surfaces

XXII. Fourier transform infrared study of the thermal decomposition of organotin-substituted tin(IV) oxide gels

Edward N. Clark and Philip G. Harrison

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (UK)

(Received April 15, 1993)

Abstract

Organotin-substituted tin(IV) oxide gels have been obtained by the cohydrolysis of tin(IV) chloride with the appropriate organotin halide. On heating, reactions of the organic groups bonded directly to surface tin atoms have been shown to follow two pathways. One involves the conversion of the organic group to a surface carboxylate, and the other the release of both alkane and alkene hydrocarbons into the gas phase. Increasing the Bronsted acidity of the oxide by incorporation of –O–Si–O– linkages promotes butene isomerization in the thermal decomposition of the n-butyl-substituted gel.

1. Introduction

The zero-order kinetics and low activation energy observed in the oxidative thermolysis of tetramethyltin indicate that this process is kinetically controlled and surface-mediated [1]. In the proposed reaction scheme, the rate-determining step was postulated to be the dissociative chemisorption of an $Sn(CH_3)_4$ molecule with cleavage of the $(CH_3)_3Sn-CH_3$ bond, giving rise to $]-OSn(CH_3)_3$ and $]-OCH_3$ surface species. Subsequent Sn–C bond cleavage of the surface $]-OSnR_3$ groups was thought to occur in a stepwise fashion *via* surface $]-O_2SnR_2$ and $]-O_3SnR$ organotin species to give ultimately inorganic tin. This type of decomposition is in direct contrast to the pyrolysis of tetramethyltin in the absence of oxygen, which is generally accepted to proceed *via* a unimolecular gas-phase reaction in which stepwise Sn–C homolytic bond cleavage leads to the formation of methyl radicals [2]. In order to gain an understanding of the chemistry of organic groups linked to tin atoms in the surface layer of a tin(IV) oxide film, we have synthesised tin(IV) oxide gel materials in which are incorporated mono-organotin moieties, to serve as models for the surface intermediates which we have proposed, and we report below the results of a Fourier transform infrared study of their thermal reactions.

2. Experimental details

2.1. *Preparation of organotin-substituted tin(IV) oxide gels*

Ten gel materials were prepared by a method essentially the same as that previously employed for the preparation of mixed Sn–Si–O [3] and Sn–TM–O (TM = Fe, Co, Ni, Mn, Cu) [4] oxide gels. Redistilled anhydrous tin(IV) chloride and the appropriate mono-organotin trichloride or diorganotin dichloride were dissolved in triply distilled water and the resulting clear solution pH *ca.* 2) hydrolysed by the addition of 0.880 ammonia solution to pH 6 with vigorous agitation. The gelatinous white precipitates produced were separated by repeated centrifugation and washing (triply distilled water) cycles until the washings were free from chloride ion. Drying at 333 K afforded large particles of glassy gel. Moistening with triply distilled water caused the gels to shatter into smaller particles of *ca.* 0.5 mm

---

Correspondence to: Dr. P.G. Harrison.

diameter, which were washed as before and dried. The two gels containing silica were obtained by including the appropriate quantity of anhydrous silicon tetrachloride in the aqueous solution prior to hydrolysis. The analytical compositions of the gels are shown in Table 1. No incorporation of trimethyltin occurred when a mixture of tin(IV) chloride and trimethyltin chloride (molar ratio 10 : 1) was hydrolysed in a similar manner, and only tin(IV) oxide gel was obtained.

2.2. Infrared studies

Infrared spectra were recorded in transmission geometry by the "thin disc" method described previously [3,5] using a Nicolet 20SXC spectrometer. Discs were prepared by finely grinding 70 mg of the gel, drying at 373 K for 5 min, and pressing (20 tonnes) in a 25 mm die. The discs were held in a glass cradle at the centre of the infrared cell of path length 100 mm connected to a conventional vacuum line system operating at a backing pressure of 10^{-5} Pa. The discs could be heated to *ca.* 670 K by an externally wound resistance heater. Disc temperatures were recorded by a type K thermocouple at the centre of and in contact with the disc. Infrared spectra of the discs were recorded at the reaction temperatures indicated either under a dynamic vacuum or in the presence of a partial pressure (100 Torr) of oxygen. The gas phase was monitored by recording the spectra of a second (unheated) cell of identical dimensions connected in parallel to that containing the oxide disc, with the whole system sealed from the vacuum line. Although this arrangement permitted the simultaneous recording of both surface and gas phase spectra, the quality of the gas phase spectra were relatively poor owing to the large volume of the cell. Far better gas phase spectra (sufficient to allow full quantitative speciation) were obtained by using much large oxide samples (0.5 g) in separate experiments.

TABLE 1. Composition of the organotin-substituted tin(IV) oxide gels of the form $(R_nSn_{2-n/2})_a(SnO_2)_b(H_2O)_d$ and $(R_nSn_{2-n/2})_a(SnO_2)_b(SiO_2)_c(H_2O)_d$

Organotin halide	"Target" atomic RSn/Sn(Si) ratio [a]	Observed composition			
		a	*b*	*c*	*d*
$MeSnCl_3$	1:10	0.90	10		14.4
Me_2SnCl_2	1:10	0.35	10		11.3
Me_3SnCl	1:10	0	10		11.0
Et_2SnCl_2	1:10	0.18	10		10.5
$^iPrSnBr_3$	1:10	0.98	10		13.8
$^nBuSnCl_3$	1:10	0.96	10		13.0
$^nBuSnCl_3$	1:2	3.53	10		16.7
$^nBuSnCl_3$	1:2:2	3.95	10	2.4	19.9
$PhSnCl_3$	1:10	0.16	10		11.0
$PhSnCl_3$	1:2:2	1.54	10	1.4	16.9

[a] The "target" RSn/Sn(Si) ratio is the molar ratio of organotin halide/tin(IV) chloride/silicon tetrachloride in the initial aqueous solution.

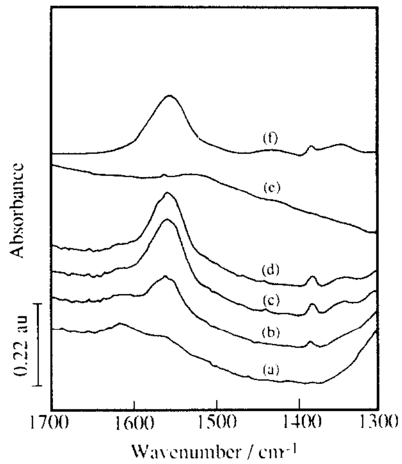


Fig. 1. Infrared spectra in the range 1700–1300 cm^{-1} of a pressed disc of the methyltin-substituted tin(IV) oxide gel heated *in vacuo* at 393 K (a), at 493 K after 5 min (b), 10 min (c), and 15 min (d), and at 573 K (e). The spectrum of authentic surface formate at 493 K (obtained by adsorption of formic acid) is shown in (f).

3. Results

All the organotin-substituted gels, like tin(IV) oxide gel itself, exhibited a strong, broad ν(OH) band extending over the range 3700–2000 cm^{-1} and a sharper δ(HOH) band at 1640 cm^{-1} due to physisorbed water and the high concentration of surface hydroxyl groups. The physisorbed water is readily removed by evacuation at 373 K for 2 h. The ν(CH) stretching modes characteristic of the organic residues are masked by the intense ν(OH) band, although with the exception of the methyltin gels characteristic deformation modes are observed.

Heating of the monomethyl-substituted gel *in vacuo* at 493 K resulted in the appearance of new bands in the infrared spectrum at 1558, 1382 and 1340 cm^{-1}, identified as the $\nu_{as}(COO)$, $\delta_{ip}(CH)$ and $\nu_s(COO)$ of surface formate species by comparison with the spectrum of an authentic surface formate produced by adsorption of formic acid (Fig. 1). The gel darkened in colour during heating, indicating increasing oxygen deficiency of the bulk oxide [6]. However, when the experiment was repeated under a partial pressure of oxygen (100 Torr) no darkening occurred, although the same surface formate species was again produced. Further heating of the disc to 573 K caused loss of the formate species, and only a weak, very broad band

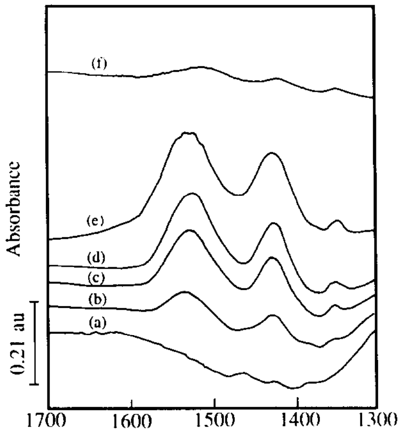


Fig. 2. Infrared spectra in the range 1700–1300 cm^{-1} of a pressed disc of the diethyltin-substituted tin(IV) oxide gel heated *in vacuo* at 393 K (a), at 493 K after 0 min (b), 5 min (c), and 10 min (d), and at 573 K (f). The spectrum of authentic surface authentic surface acetate at 493 K (obtained by adsorption of acetic acid) is shown in (e).

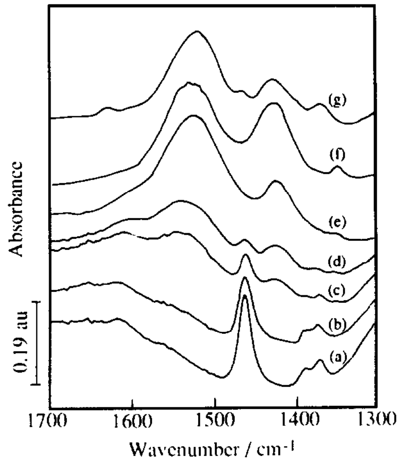


Fig. 3. Infrared spectra in the range 1700–1300 cm^{-1} of a pressed disc of the isopropyltin-substituted tin(IV) oxide gel heated *in vacuo* at 393 K (a), at 493 K after 0 min (b), 5 min (c), 10 min (d), and 60 min (e). Authentic spectra of surface acetate and propionate (obtained by adsorption of acetic acid and propionic acid, respectively) are shown in (f) and (g), respectively.

centred at *ca.* 1540 cm^{-1} remained in the spectrum. Monitoring of the gas phase showed that evolution of methane commenced at 423 K, with more methane together with carbon dioxide being produced at temperatures at which surface formate is observed. The behaviour of the dimethyltin-substituted gel was identical.

Figure 2 illustrates the changes which occur in the infrared spectrum of a diethyltin-substituted gel on heating at 493 K. The very weak bands due to the surface ethyl groups at 1459, 1426 and 1382 cm^{-1} are replaced by new bands at 1525 cm^{-1} (ν_{as}(COO)), 1424 cm^{-1} (ν_s(COO)) and 1349 cm^{-1} ($\delta_{ip}(CH_3)$ characteristic of surface acetate species. In contrast to the surface formate, the surface acetate species were stable at 573 K, but were lost on prolonged heating at 613 K. Heating a larger sample at 423 K resulted in the appearance in the gas phase of a mixture of ethane and ethene in a 3.7 : 1 molar ratio. Heating at higher temperatures (up to 600 K) with or without a partial pressure of oxygen gave only carbon dioxide and water as additional products.

Heating a disc of the isopropytin-substituted gel at 493 K also resulted in the formation of a surface acetate species, with bands observed at 1527, 1424 and 1349 cm^{-1}, rather than a surface propionate species (bands of an authentic surface propionate formed by adsorption of propionic acid at 1522 cm^{-1} (ν_{as}(COO)), 1428 cm^{-1} (ν_s(COO)), 1369 cm^{-1} ($\delta_{ip}(CH_3)$) and 1300 cm^{-1} (δ(CH)) (Fig. 3). Analysis of the gas phase of a sample heated at 423 K showed that propene was the major product together with propane and smaller amounts of isobutene and methane (Fig. 4).

The spectra obtained by heating discs of the two n-butyltin-substituted gels and the n-butyltin-substituted mixed Sn–Si–O gel were very similar in form,

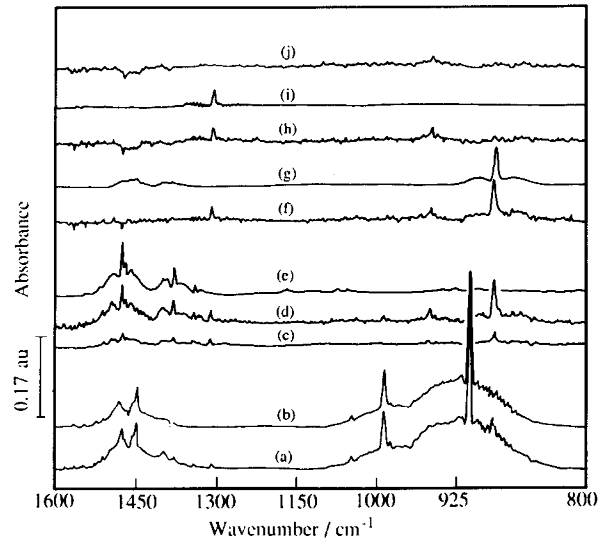


Fig. 4. Infrared spectra in the range 1800–800 cm^{-1} of (a) the gas phase after heating the isopropyltin-substituted tin (IV) oxide gel, (b) propene, (c) reaction mixture with propene spectrum subtracted, (d) spectrum (c) expanded, (e) propane, (f) spectrum (c) after subtraction of propane, (g) isobutene, (h) spectrum (f) after subtraction of isobutene, (i) methane, and (j) spectrum (h) after subtraction of methane.

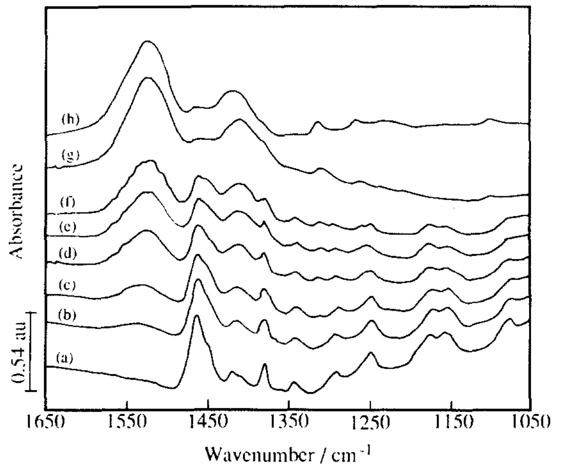


Fig. 5. Infrared spectra in the range 1650–1050 cm^{-1} of a pressed disc of the n-butyltin-substituted tin(IV) oxide gel ($BuSn/SnO_2$ 0.35:1) heated *in vacuo* at 393 K (a), at 493 K after 0 min (b), 5 min (c), 10 min (d), 15 min (e), 20 min (f), and 80 min (g). The spectrum of authentic surface butyrate at 493 K (obtained by adsorption of butyric acid) is shown in (h).

TABLE 2. Surface and gas phase products obtained by heating organotin-substituted tin(IV) oxide gels and 423 K

Gel	Surface species	Gas phase products [a,b]
Methyl	Formate	Methane
Dimethyl	Formate	Methane
Diethyl	Acetate	Ethane (1), ethene (0.27)
Isopropyl	Acetate	Propane (0.37), propene (1), methane (0.04) [c]
n-Butyl (1:10)	Butyrate	Butane (1), but-1-ene (0.15), butadiene (0.02), ethene (0.03)
n-Butyl (3.5:10)	Butyrate	Butane (1), but-1-ene (0.47), butadiene (0.03) ethene (0.04)
n-Butyl (Sn–Si–O)	Butyrate	Butane (0.85), but-1-ene (0.37), *cis*-but-2-ene (0.26), *trans*-but-2-ene (0.37), butadiene (0.02), ethene (0.03)
Phenyl (Sn–Si–O)	[d]	Benzene [e]

[a] Numbers in parentheses indicate the relative molar amounts of products (relative to major product = 1). [b] Carbon dioxide formed in all cases at 473 K. [c] Traces of isobutene and ethene also produced. [d] None observed. [e] Benzene only formed at 473 K.

and Fig. 5 shows a typical series obtained during heating at 493 K. In every case, the bands characteristics of n-butyl groups attached to surface tin atoms at 1465, 1416, 1378, 1342, 1293, 1252, 1180, 1159 and 1076 cm^{-1} are observed to decrease in intensity whilst a new set of bands at 1525 (ν_{as}(COO)), 1410 (ν_s(COO)), 1310 (δ(CH)), 1263 and 1100 cm^{-1} grow. Again, corroboration of the new surface species as a surface butyrate was accomplished by comparison with an authentic spectrum produced by adsorption of butyric acid. The incorporation of silica appears to inhibit the oxidation

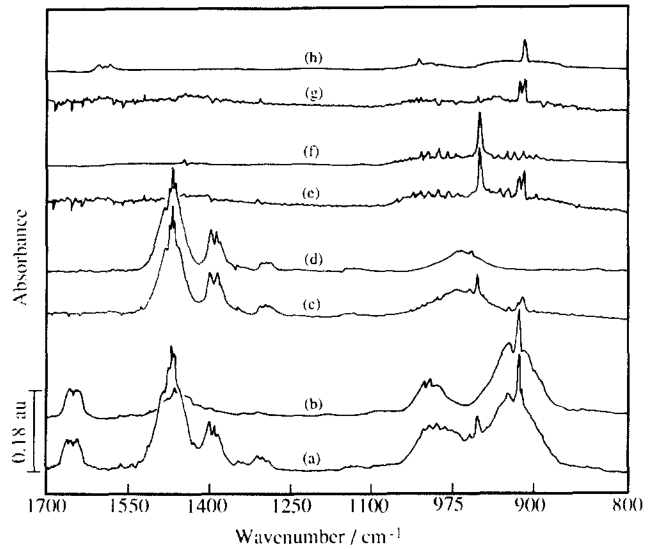


Fig. 6. Infrared spectra in the range 1700–800 cm^{-1} of (a) the gas phase after heating the n-butyltin-substituted tin(IV) oxide gel ($BuSn/SnO_2$ 0.35:1), (b) but-1-ene, (c) reaction mixture after subtraction of but-1-ene, (d) butane, (e) spectrum (c) after subtraction of butane, (f) ethene, (g) spectrum (e) after subtraction of ethene, (h) butadiene.

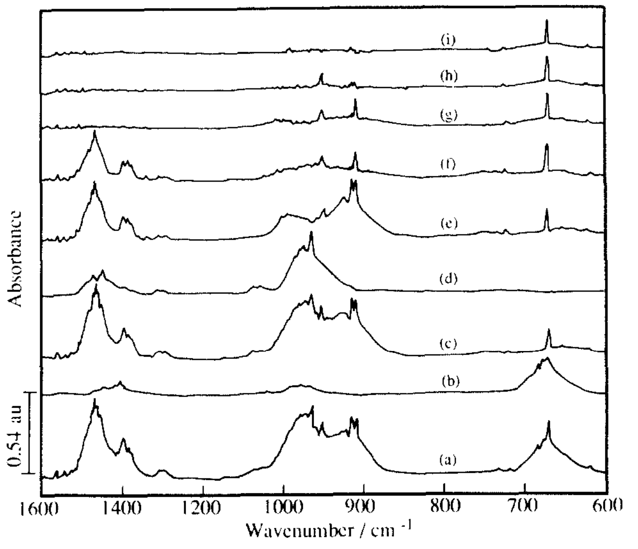


Fig. 7. Infrared spectra in the range 1600–600 cm^{-1} of (a) the gas phase after heating the n-butyltin-substituted Sn–Si–O gel in the presence of oxygen (100 Torr), (b) *cis*-but-2-ene, (c) reaction mixture after subtraction of *cis*-but-2-ene, (d) *trans*-but-2-ene, (e) spectrum (c) after subtraction of *trans*-but-2-ene, followed by subtraction of (f) but-1-ene, (h) butadiene, and (i) ethene. The residual spectrum (i) is that of carbon dioxide.

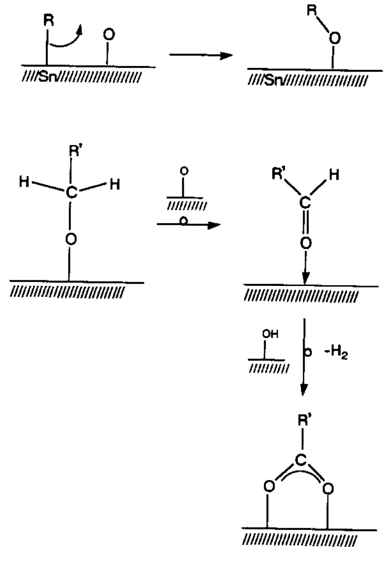
of the n-butyl group to surface butyrate, and the temperature required for reaction *in vacuo* increased from 493 K to 553 K. However, when the reaction was repeated in the presence of 100 Torr of oxygen, the reaction proceeded smoothly at 493 K. The major components of the gas phase produced from the n-butyl-substituted oxide gels are but-1-ene and butane together with small amounts of butadiene and ethene (Fig. 6). However, the gas phase product distribution obtained by heating the silica-containing gel (in the presence of 100 Torr of oxygen) were substantially different, comprising *cis*- and *trans*-but-2-ene, but-1-ene, butane, butadiene, ethene and carbon dioxide (Fig. 7).

Heating of a phenyltin-substituted oxide gel disc at 493 K resulted in the slow loss from the spectrum of bands at 1480 and 1431 cm^{-1} characteristic of the phenyl group, but no new features appeared and no products could be observed in the gas phase. Similar behaviour was observed for the phenyl-substituted Sn–Si–O gel, although heating at 473 K resulted in the formation of benzene, carbon dioxide, carbon monoxide and water in the gas phase.

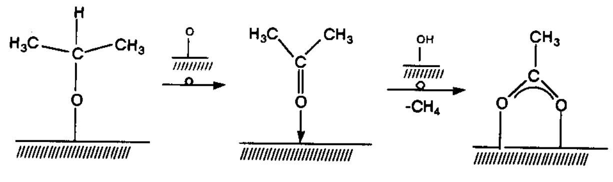
Reaction products are summarised in Table 2.

4. Discussion

It is apparent from the experimental observations that the reactions of the organic groups bonded directly to surface tin atoms follow two pathways. One involves the conversion of the organic group into a surface carboxylate, whilst the other involves the release of hydrocarbons to the gas phase. Our previous studies of the absorption of a wide range of organic molecules into tin(IV) oxide including hydrocarbons, alcohols, aldehydes and ketones, results in the formation of the corresponding surface carboxylate *via* intermediate surface alkoxy (]–OR) and surface-coordinated carbonyl (] ← O=CRR′) species [5,7]. In the present case, therefore, it would appear that the surface carboxylato species result from the oxidation of surface alkoxy groups formed by initial transfer of the organic group R from a surface tin to a surface oxygen atom (Scheme 1). Surface acetate is obtained together with gas phase methane during the thermolysis of the iso-propyl-substituted tin(IV) oxide gel (Scheme 2), consistent with previous observations of carbon–carbon bond fission during the adsorption of acetone onto tin(IV) oxide [5,8]. No surface carboxylate species was produced from the phenyl-substituted gels.

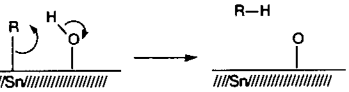


Scheme 1.

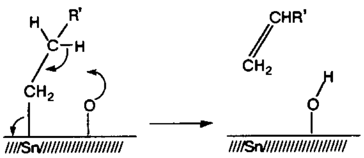


Scheme 2.

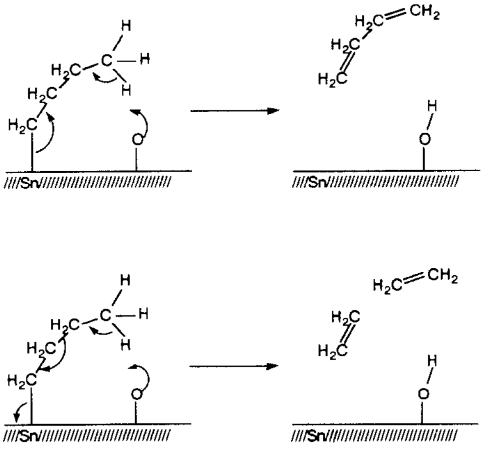
In all cases except that of the iso-propyl-substituted tin(IV) oxide gel, the principal gas phase product was the corresponding saturated hydrocarbon (or benzene in the case of the phenyl-substituted Sn–Si–O gel), most probably formed in a typical electrophilic cleavage of the organic group from tin involving surface hydroxyl groups:

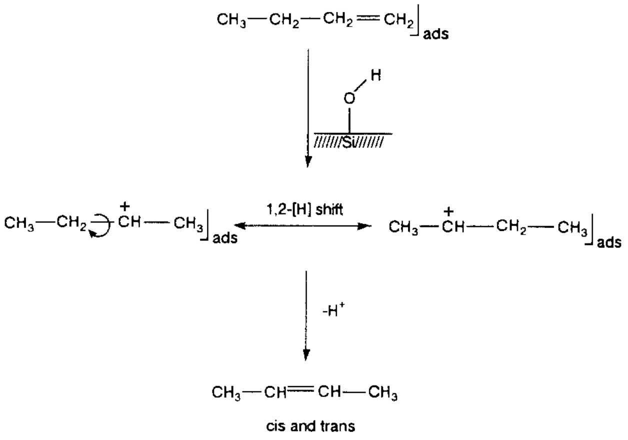


However, apart from the methyl- and phenyl-substituted gels, substantial quantities of alkenes are also formed probably by the surface oxygen-assisted abstraction of a hydrogen atom from the C(2)-carbon atom:



Both butadiene and ethene are also observed in the thermolysis of the n-butyl-substituted tin(IV) oxide gel, which would indicate that hydrogen atom abstraction from the C(4)-carbon atom is also possible, with the oxide bulk acting as either an electron donor or an electron sink:





Scheme 3.

Although not observed in the thermolysis of the n-butyltin-substituted tin(IV) oxide gel, substantial quantities of both *cis*- and *trans*-but-2-ene are formed in the thermolysis of the n-butyltin-substituted Sn–Si–O gel. Since but-2-enes cannot be formed directly *via* a surface oxide-assisted elimination process, these products must result from the isomerization of but-1-ene involving the participation of the more acidic surface silanol groups prior to its release into the gas phase (Scheme 3). Similar isomerization of butenes over Bronsted acidic Sn–Sb–O oxides is postulated to involve surface-adsorbed carbonium ions [9]. *cis-trans* But-2-ene isomerization occurs over tin(IV) oxide itself, but involves surface-adsorbed radical species and no double bond isomerization (*i.e.* but-1-ene/but-2-ene isomerization) occurs [10]. It appears therefore, the surface Bronsted acidity is a requirement for but-1-ene/but-2-ene isomerization to occur.

Acknowledgement

We thank the S.E.R.C. for a studentship (to E.N.C.).

References

1 P.G. Harrison, A. Ashworth, E.N. Clark and J. McManus, *J. Chem. Soc., Faraday Trans. 1, 86,* (1990) 4059.
2 R.P. Johnson and S.J. Price, *Can. J. Chem., 50* (1972) 50.
3 P.G. Harrison and B. Maunders, *J. Chem. Soc., Faraday Trans. 1, 80* (1984) 1341.
4 P.G. Harrison and E.W. Thornton, *J. Chem. Soc., Faraday Trans. 1, 75* (1979) 1487.
5 P.G. Harrison and E.W. Thornton, *J. Chem. Soc., Faraday Trans. 1, 71* (1975) 2468; *72* (1976) 2484.
6 A. Guest, Ph.D. Thesis, University of Nottingham, 1985.
7 P.G. Harrison and B. Maunders, *J. Chem. Soc., Faraday Trans. 1, 80* (1984) 1329; *81* (1985) 1311; *81* (1985) 1329.
8 J. Konstantatos and C.P. Quinn, *Trans. Farad. Soc., 65* (1969) 3349.
9 E.A. Irvine and K. Taylor, *J. Chem. Soc., Faraday Trans. 1, 74* (1978) 1590.
10 S. Kodama, M. Yabita, M. Anpo and Y. Kubokawa, *Bull. Chem. Soc. Jpn., 58* (1985) 2307.