

Origin of prist-1-ene and prist-2-ene in kerogen pyrolysates

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Abstract

The principal isoprenoid hydrocarbons in flash pyrolysates from immature kerogens are prist-1-ene and, to a lesser extent, prist-2-ene. The precise origin of these compounds is still a matter of debate. Chemical degradation experiments performed on a sulfur-rich kerogen in this study show that at least two precursors can generate pristenes during pyrolysis of sulfur-rich kerogens: ether-bound precursors, probably tocopherols, and a sulfur-bound precursor. From pyrolysis experiments performed on mixtures of isolated kerogens with different clay minerals, it is concluded that prist-2-ene is likely formed by the double-bond isomerization of prist-1-ene. This isomerization of prist-1-ene into prist-2-ene depends on the amount of protons available for the formation of the intermediate carbonium ion. These protons can be derived from acidified aluminosilicates (e.g. the clay minerals montmorillonite or kaolinite) in the rock or from inorganic acids (e.g. HI, HCl). The degree of isomerization depends on the amount of protons available relative to the total organic carbon content. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Acyclic isoprenoid hydrocarbons have been identified in many pyrolysates of immature kerogens (e.g. Maters et al., 1977; Larter et al., 1979; van der Meent et al., 1980; Koopmans et al., 1999). The principal isoprenoid hydrocarbon is the C₁₉ component, prist-1-ene (Larter, 1984). The origin of this compound, i.e., its precursors and type of linkage, is

unclear (e.g. Sinninghe Damsté and de Leeuw, 1995). It is important to identify the origin of prist-1-ene in pyrolysates, since it is probably the source of pristane in more mature petroleum source rocks and crude oils (Goossens et al., 1984). For instance, a detailed study by van Graas et al. (1981) of a suite of Paris Basin rock samples of increasing maturity showed a good correlation between the disappearance of the pyrolysis product prist-1-ene and the appearance of pristane in the rock extract. A similar correlation was observed by Goossens et al. (1988) and Koopmans et al. (1999).

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Model compound pyrolysis studies (Larter et al., 1983 and references therein) indicate that prist-1-ene precursors are not ester-bound compounds, but probably C–C or C–O bound moieties that generate pristane during burial and prist-1-ene upon pyrolysis. Artificial maturation, flash pyrolysis, and chemical degradation experiments indicate that the precursor of pristane and prist-1-ene might occur in sulfur- or in oxygen-bound form (Koopmans et al., 1999). Kinetic studies suggest that a single-type kerogen-bound precursor is unlikely (Burnham, 1989; Tang and Stauffer, 1995).

Several studies suggest different precursors for prist-1-ene. Kerogen-bound diphytanyl ethers of archaeobacteria (e.g. Chappe et al., 1982) were proposed as precursors of prist-1-ene in kerogen pyrolysates. Goossens et al. (1984) showed that kerogen-bound tocopherols are also likely candidates for prist-1-ene precursors. Furthermore, Ishiwatari (1991) reported the formation of prist-1-ene upon pyrolysis of chlorophyll *a*. Recently, it was suggested that phenol–phytol condensation products (methyltri-methyltridecylchromans) bound into kerogens may also be a source of prist-1-ene upon pyrolysis (Li et al., 1995), although the geochemical significance of such condensation products was questioned (Sinninghe Damsté and de Leeuw, 1995).

Questions remain on the origin of both prist-1-ene and prist-2-ene in kerogen pyrolysates. Besides prist-1-ene, relatively high amounts of its isomer, prist-2-ene, sometimes occur in kerogen pyrolysates. It has been suggested that during pyrolysis, prist-2-ene is formed from prist-1-ene in the presence of clay minerals (Regtop et al., 1986). Clay minerals are

believed to catalyze the rearrangement of steroids (Sieskind et al., 1979; van Kaam-Peters et al., 1998) and to isomerise alkenes (Curtis, 1983; Regtop et al., 1985). In a study by Regtop et al. (1986), pyrolysis of demineralised kerogen of the Condor oil shale yielded predominantly prist-1-ene. However, the presence of prist-2-ene in kerogen/kaolinite pyrolysates demonstrated that kaolinite is able to act as a catalyst for prist-1-ene isomerization. Besides prist-2-ene, small amounts of prist-5-enes and prist-6-enes were detected as well. Prist-2-ene increased in abundance with increasing proportions of kaolinite. Therefore, Regtop et al. (1986) proposed that the principal source of prist-2-ene in pyrolysates of the Condor oil shale is prist-1-ene and that the double-bond isomerization is catalyzed by clay minerals such as kaolinite. The increasing proportion of kaolinite in the kerogen/mineral mixture was proposed to increase the opportunity for gaseous prist-1-ene to meet mineral surfaces, leading to increased isomerization of prist-1-ene. Other non-clay minerals such as quartz, feldspar, calcite and pyrite gave similar, but less striking, results (Regtop et al., 1986).

In contrast, a different behaviour of prist-2-ene and prist-1-ene in the flash pyrolysates of chemically degraded kerogen was observed by Koopmans et al. (1999). Upon HI/LiAlH₄ treatment of the desulfurized kerogen, prist-1-ene was no longer present in the kerogen pyrolysates but the relative amount of prist-2-ene remained unchanged and, therefore, different precursors were suggested.

In this study, flash pyrolysis was performed on extracted and decarbonated rocks and isolated kerogens. Chemical degradation techniques were used on

Table 1

TOC data and relative abundances of prist-1-ene (1P/(1P + 2P)) and 2,6,10-trimethyldec-1-ene (1TMD/(1TMD + 2TMD)) calculated from GC-FID peak areas n.d. = not determined.

	TOC		1P/(1P + 2P)			1TMD/(1TMD + 2TMD)		
	extracted rock (%)	decarbonated rock (%)	Extracted rock	Decarbonated rock	Kerogen	Extracted rock	Decarbonated rock	Kerogen
Monterey Formation	9.6	18	0.9	0.7	0.9	0.4	0.4	0.3
Mulhouse Basin (FMM)	1.2	1.5	0.8	0.3	0.6	0.9	0.6	0.8
Mulhouse Basin (S452)	3.0	6.5	0.7	0.4	n.d.	0.8	0.6	n.d.
Kimmeridge Clay	24	27	n.d.	0.5	1.0	n.d.	0.7	1.0
Vocontian Basin	3.0	4.6	≈ 0	≈ 0	n.d.	0.5	0.5	n.d.

kerogens to investigate the precursors of prist-1-ene and prist-2-ene, how these precursors are bound to the kerogen, and the influence of clay minerals on the formation of the pristenes.

2. Experimental

2.1. Rock samples

The rock samples were previously described by Höld et al. (1998a) and are listed in Table 1. The clay mineral samples used in the pyrolysis experiments include kaolinite from the Source Clay Minerals Repository (Kga-1), montmorillonite from Ward's (H-25 Upton Wyoming bentonite), and a fine-grained muscovite from the Van der Marel mineral collection (sericite 1398, Villar de Puerco). These clay mineral standard samples were used as received with no pretreatment.

2.2. Rock extraction, decarbonation and kerogen isolation

The different sequential isolation steps are depicted schematically in Fig. 1. The rocks were grounded and Soxhlet extracted with dichloromethane (DCM)/methanol (MeOH) (7.5/1, v/v) for 24 h. The residue was decarbonated by treatment with 4 N HCl at room temperature and ultrasonically re-extracted with water (3 ×), methanol (3 ×) and finally dichloromethane (3 ×). Kerogen isolation was performed by HCl/HF treatments of the solvent-extracted residue as described previously (Eglinton, 1988). The kerogen was ultrasonically extracted with methanol and DCM, respectively.

2.3. Sequential chemical degradation of kerogen

The different sequential chemical degradation steps are depicted schematically in Fig. 1. After each

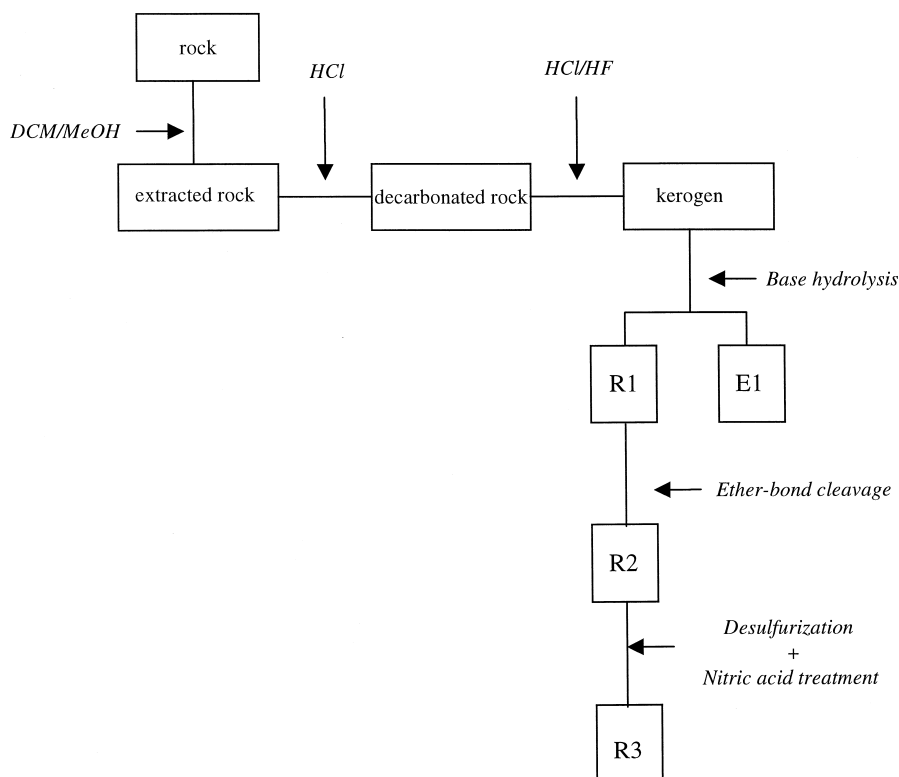


Fig. 1. Analytical flow diagram for kerogen isolation and sequential chemical degradation procedure.

chemical degradation step, the residue was washed with H₂O/MeOH (1:1, v/v; 3 ×), with MeOH (3 ×) and with ethyl acetate (3 ×) and dried under nitrogen. Base hydrolysis, ether- and sulfur-bond cleavage were performed sequentially as described previously (Höld et al., 1998b) to obtain residues R₁, R₂ and R₃, respectively. Firstly, an alkaline hydrolysis was performed in order to hydrolyze ester bonds within the kerogen (Goossens et al., 1989). 1 N KOH in methanol (MeOH) was added to 400 mg kerogen, refluxed for 1 h at 65°C under a nitrogen atmosphere and then cooled to room temperature. The pH was adjusted to 3 by adding 4 N HCl(H₂O)/MeOH (1:1, v/v). During the second step, aliphatic ethers were cleaved by treatment with HI (March, 1985). A 56% HI solution (in H₂O) was added to residue R₁, refluxed for 1 h under a nitrogen atmosphere and then cooled to room temperature. In the third step, (poly)sulfide bonds in the kerogen were cleaved by treatment with Ni₂B (Schouten et al., 1993). In this step, MeOH/THF (1:1), NiCl₂ and NaBH₄ were added to residue R₂. The mixture was refluxed for 1 h under stirring and N₂ atmosphere and then cooled down to room temperature. The residue R₃ was obtained as described above. In order to remove the Ni salts present in the residue, concentrated HNO₃ was added and left to react for 12 h. The residue R₃ washed with H₂O/MeOH (1:1, v/v, 3 ×), with MeOH (3 ×) and with ethyl acetate (3 ×).

The residues were analyzed by flash pyrolysis gas chromatography mass spectrometry (Py-GC-MS).

2.4. Py-GC, Py-GC-MS and X-ray powder diffraction (XRD)

Py-GC and Py-GC-MS were carried out as described previously (Höld et al., 1998a). XRD was carried out with a Philips PW1050/25 goniometer, using CoK α radiation (40 kV, 40 mA) from a long fine focus tube, a graphite monochromator in the diffracted beam, and a vacuum/helium device to minimise the absorption of the X-rays by air (Van der Gaast and Vaars, 1981). The instrument was equipped with a variable divergence slit. The slit settings were: 12 mm irradiated specimen length; receiving slit, 0.1 mm; antiscatter slit, 0.5°; counting time, 2 s/0.02° 2 θ . Approximately 10 mg of sample

material was pressed into a 0.5-mm-deep depression in a low-background sample holder (Si wafer). The specimens were measured at 50% relative humidity. Patterns were corrected for the Lorentz and polarisation factor and for the irradiated specimen volume.

3. Results and discussion

3.1. Composition of flash pyrolysates

Several extracted rocks, decarbonated rocks and isolated kerogens (Table 1) were analyzed by Py-GC and Py-GC-MS as described previously (Höld et al., 1998a). The FID and TIC traces of the flash pyrolysates revealed significant differences in the composition of the pyrolysis products. Homologous series of *n*-alkanes and *n*-alkenes dominate the pyrolysates of most kerogens. Series of isoprenoid alkanes and alkenes were detected in all flash pyrolysates and consist of regular C₈–C₂₀ isoprenoids, which were especially abundant in the flash pyrolysates of the Kimmeridge Clay and the Vocontian Basin samples. Three irregular isoprenoid alkanes, 2,6,10,15,19-pentamethylcosane, 2,6,15,19-tetramethylcosane and 10-ethyl-2,6,15,19-tetramethylcosane were identified in the flash pyrolysate of the kerogen of the Vocontian Basin sample (Vink et al., 1998). Alkylated benzenes, naphthalenes and indenes were present in all flash pyrolysates, but are abundant in the Monterey Formation and Vocontian Basin pyrolysates. Kerogens from the Monterey Formation are organic-sulfur-rich and their flash pyrolysates contain high amounts of alkylated thiophenes, benzof[b]thiophenes and thiolanes. Thus, the samples investigated contain a wide range of kerogen compositions.

3.2. Ratio of prist-1-ene to prist-2-ene in flash pyrolysates

In most of the flash pyrolysates, both prist-1-ene and prist-2-ene are present in significant amounts. The relative abundance of prist-1-ene vs. prist-2-ene in the flash pyrolysates varies significantly (Table 1), which is significant since the reproducibility of the measurements is estimated to be approximately 10%. The prist-1-ene/(prist-1-ene + prist-2-ene)

[1P/(1P + 2P)] ratio varies strongly between the different fractions analyzed (extracted rock, decarbonated rock and isolated kerogen). For instance, the 1P/(1P + 2P) ratio in the pyrolysate of the extracted

rock from the Mulhouse Basin (FMM) is > 0.5 (predominantly prist-1-ene), whereas after decarbonation, the ratio is < 0.5, and after isolation with HCl/HF, the ratio is again > 0.5 (Fig. 2, Table 1).

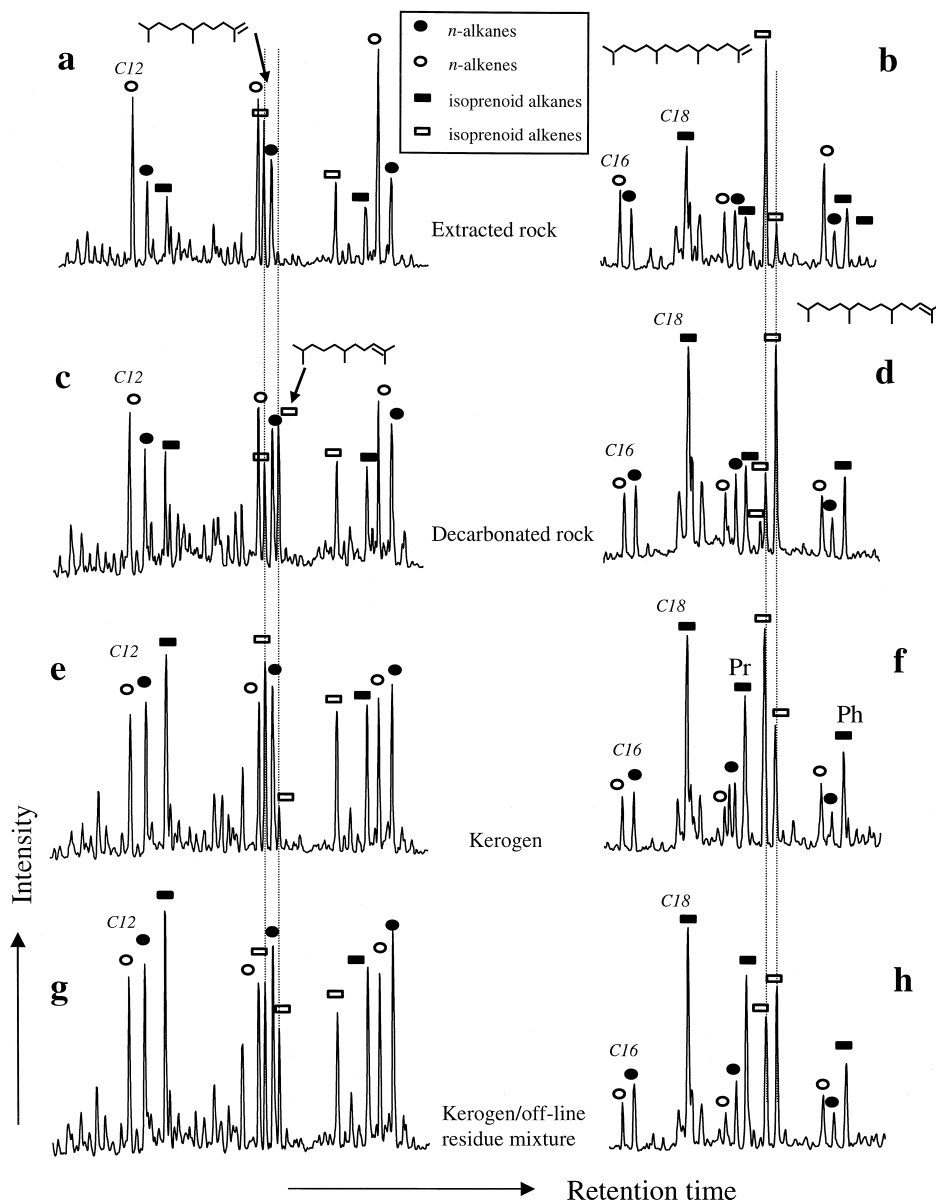


Fig. 2. Partial FID traces of the flash pyrolysates (Curie temperature 610°C) of (a and b) extracted rock, (c and d) decarbonated rock, (e and f) kerogen and (g and h) kerogen/off-line pyrolysis residue mixture from the Mulhouse (FMM) Basin. Filled and open circles indicate homologous series of *n*-alkanes and *n*-alk-1-enes, respectively, with the number of carbon atoms indicated. Filled and open rectangles indicate pseudo-homologous series of isoprenoid (*i*-)alkanes and *i*-alk-1-enes, respectively. Their number of carbon atoms is indicated with italic numbers.

Similar changes were noted in the relative abundance of 2,6,10-trimethylundec-1-ene compared to 2,6,10-trimethylundec-2-ene (Fig. 2, Table 1).

To investigate what causes these changes in the 1P/(1P + 2P) ratio, isolated kerogen from the Mulhouse Basin sample (FMM), which has abundant

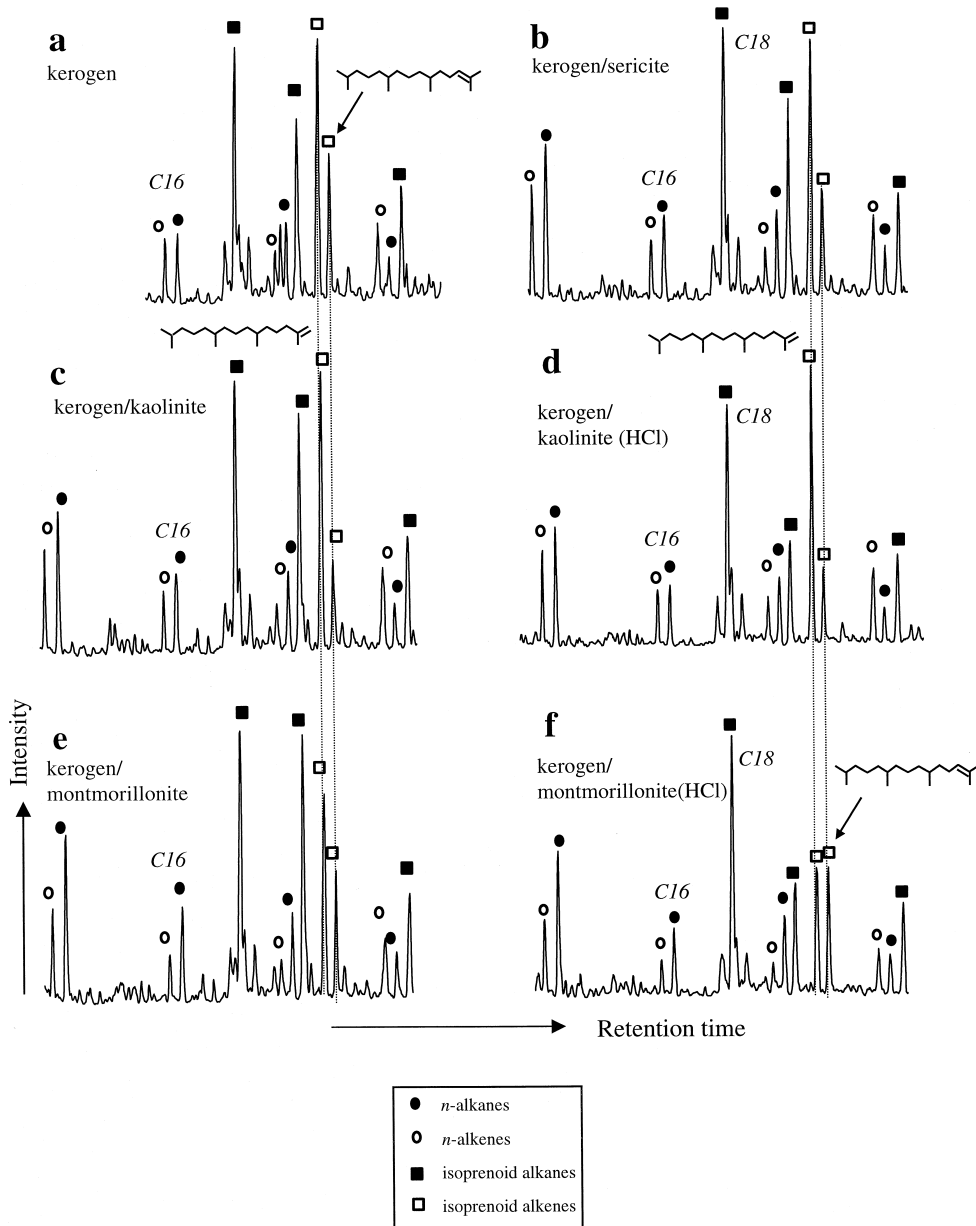


Fig. 3. Partial FID traces of the Mulhouse (FMM) pyrolysates (Curie temperature 610°C) of (a) kerogen, (b) kerogen/sericite mixture, (c) kerogen/kaolinite mixture, (d) kerogen/kaolinite mixture (activated by HCl), (e) kerogen/montmorillonite mixture and (f) (kerogen/montmorillonite mixture (activated by HCl)). Filled and open circles indicate homologous series of *n*-alkanes and *n*-alk-1-enes, respectively, with the number of carbon atoms indicated. Filled and open rectangles indicate pseudo-homologous series of isoprenoid (*i*-)alkanes and *i*-alk-1-enes, respectively. Their number of carbon atoms is indicated with italic numbers.

prist-1-ene in its flash pyrolysate (Fig. 2f), was mixed in a 1:3 ratio (w/w) with the residue of the decarbonated rock from the Mulhouse Basin after off-line pyrolysis. Flash pyrolysis of this residue indicated that no thermally releasable organic material was present and that it was mainly composed of inorganic minerals. The flash pyrolysate of the mixture of the off-line pyrolysis residue and the kerogen showed a much lower 1P/(1P + 2P) ratio compared to the isolated kerogen (Fig. 2h). Similar, but smaller, changes were found in the relative abundance of 2,6,10-trimethylundec-1-ene compared to 2,6,10-trimethylundec-2-ene (Fig. 2e and g). This experiment indicates that the inorganic matrix of the rock has a catalytic activity that results in the formation of prist-2-ene (cf. Regtop et al., 1986).

3.3. Influence of clay minerals on the 1P/(1P + 2P) ratio in rocks

Isolated kerogen from the Mulhouse Basin sample (FMM) was mixed in a 1:3 ratio (w/w) with three different clay minerals — sericite, kaolinite and montmorillonite — in order to investigate which clay minerals may cause changes in prist-1-ene and prist-2-ene concentrations during flash pyrolysis. These clay minerals are representatives of the three major clay mineral groups. The flash pyrolysate of the mixture of sericite and kerogen (Fig. 3b, Table 2) showed a similar 1P/(1P + 2P) ratio compared to that of the isolated kerogen (Fig. 3a, Table 2). A slight decrease in the 1P/(1P + 2P) ratio was detected in the case of kaolinite (Fig. 3c, Table 2). However, a significant decrease in the 1P/(1P + 2P)

ratio was detected in the montmorillonite experiment (Fig. 3e, Table 2). Similar changes were found in the relative abundance of 2,6,10-trimethylundec-1-ene compared to 2,6,10-trimethylundec-2-ene. However, none of the kerogen/clay mineral mixtures yielded a 1P/(1P + 2P) ratio < 0.5 as was found upon flash pyrolysis of the decarbonated Mulhouse rock (Table 2), suggesting that an additional catalyst or factor must operate in the decarbonated samples.

To investigate the influence of decarbonation of ground rocks on the 1P/(1P + 2P) ratio, the kerogen/clay mineral mixtures were treated with 4 N HCl and, subsequently, washed with water. The flash pyrolysates of the HCl-treated kerogen/sericite (Table 2) and kerogen/kaolinite mixtures (Fig. 3d, Table 2) showed only small differences in the 1P/(1P + 2P) ratios compared to the untreated mixtures. However, the ratio in the pyrolysate of the HCl-treated kerogen/montmorillonite mixture (Fig. 3f, Table 2) decreased substantially compared to the untreated mixture (Fig. 3e, Table 2). This indicates that HCl treatment of the montmorillonite increases its catalytic properties and relatively more prist-1-ene isomerize to prist-2-ene.

Interestingly, the use of acidified clay minerals as catalysts was already disclosed in German patents in 1923. Most of these clay catalysts were prepared by the acid treatment of montmorillonite and halloysite (Rupert et al., 1987). Acidic aluminosilicates (e.g. montmorillonite) can cause migration of the double bond in olefins and thus cause isomerization of the double bond in prist-1-ene to form prist-2-ene (Rupert et al., 1987). This reaction probably proceeds via a carbonium ion intermediate, which arises by transfer of a proton from the catalyst surface to the reactant (prist-1-ene; Rupert et al., 1987). Hydrogen-rich clay minerals have acid strengths corresponding to sulfuric acid solutions between 71 wt.% and 90 wt.% H₂SO₄ (Rupert et al., 1987). Alumina is thought to be the source of the acidic nature of the surface. Isomorphous substitution of Al³⁺ for Si⁴⁺ in tetrahedral coordination in an aluminosilicate causes a net negative charge. A charge-balancing proton associated with this tetrahedral aluminum corresponds to a Brønsted, or protonic acid site (e.g. Rupert et al., 1987). The removal of one of a pair of octahedral aluminum ions from montmorillonite, for example, removes two hydroxyl groups and leaves the remain-

Table 2
Ratio of 1P/(1P+2P) in the flash pyrolysate (400°C) of the Mulhouse (FMM) kerogen calculated from GC-FID peak areas

	1P/(1P+2P)
Extracted rock	0.8
Decarbonated rock	0.3
Kerogen	0.6
Kerogen:sericite = 1:3	0.7
Kerogen:sericite = 1:3 (HCl)	0.8
Kerogen:kaolinite = 1:3	0.7
Kerogen:kaolinite = 1:3 (HCl)	0.7
Kerogen:montmorillonite = 1:3	0.6
Kerogen:montmorillonite = 1:3 (HCl)	0.5

ing aluminium in fourfold coordination. This tetrahedral aluminum, with its charge-balancing proton, forms an additional Brønsted, or protonic acid site, increasing the catalytic activity of the clay minerals (e.g. Rupert et al., 1987). Acid treatment of hydrogen-rich clays would therefore be expected to enhance the effect of these materials in promoting double-bond isomerization of prist-1-ene to form prist-2-ene. In order to minimize this extra catalytic effect, ground rocks must therefore be washed thoroughly after acid treatment.

The above experiments indicate that montmorillonite/smectite may also be an important isomerization catalyst in addition to the kaolinite suggested by Regtop et al. (1986). This is consistent with the fact that the acid strength of H-montmorillonite is even stronger than that of H-kaolinite (Rupert et al., 1987). In a sample from the Monterey Formation, where kaolinite is not present (Isaacs et al., personal communication), prist-2-ene occurs in the flash pyrolysate, indicating again that kaolinite cannot be the main catalyst (Table 1). However, kaolinite may still act in a number of rocks as the prime catalyst. For instance, XRD analysis indicated the presence of clay minerals in two decarbonated Mulhouse rocks (FMM and S452) and a decarbonated Vocontian Basin rock. In the S452 Mulhouse and in the Vocontian Basin rock, montmorillonite was present in much

higher abundance than kaolinite. However, in the FMM Mulhouse rock, montmorillonite is much less abundant and kaolinite is more abundant compared to the other two rocks. All three rocks have a relatively high amount of prist-2-ene in their pyrolysates. Since in the FMM Mulhouse rock little montmorillonite was present, kaolinite probably was the main catalyst, indicating that probably both montmorillonite and kaolinite can act as the isomerization catalyst.

Besides the acidic strength of clay minerals, the ratio of clay/TOC is another factor that determines the degree of isomerization of prist-1-ene to prist-2-ene. The diasterane/sterane ratios in samples from the Kimmeridge Clay and the Toarcian shale Formations strongly depend upon the ratio of clay to organic matter (van Kaam-Peters et al., 1998). Because isomerization is implicated in the origin of diasteranes, a similar phenomenon might occur for the isomerization of prist-1-ene. Thus, TOC values, clay/carbonate content and 1P/(1P + 2P) ratios in the pyrolysates were determined from 13 samples of the Kimmeridge Clay and are shown in Table 3 (van Kaam-Peters et al., 1998). No correlation between clay mineral concentration and 1P/(1P + 2P) ratio is observed (Table 3). However, samples with high clay/TOC ratios have relatively low 1P/(1P + 2P) ratios and vice versa (Table 3, Fig. 4). These results

Table 3
Data from the Kimmeridge Clay Formation samples (XRD and flash pyrolysis)

	TOC ^a (%)	Carbonate (w/w) (%)	1P/(1P + 2P) ^b	Clay ^c (w/w) (%)	Clay/TOC
KC1	7.0	85	0.9	3.4	0.5
KC2	6.2	10	0.4	70	11
KC3	10.7	71	0.9	11	1.0
KC4	18.2	0	0.7	57	3.1
KC5	2.1	86	0.5	10	4.5
KC6	4.8	22	0.3	53	11
KC7	52.1	17	0.9	3.1	0.06
KC8	3.7	25	0.3	56	15
KC9	10.8	25	0.4	47	4.4
KC10	0.6	76	0.01	21	33
KC11	24.1	10	0.7	43	1.8
KC12	4.5	93	1.0	0.3	0.06
KC13	7.4	30	0.4	44	5.9

^a In the extracted rock.

^b In the decarbonated rock.

^c $100 - (\% \text{ carbonate} + \% \text{ quartz} + \% \text{ pyrite} + (1.5 \times \text{TOC}))$.

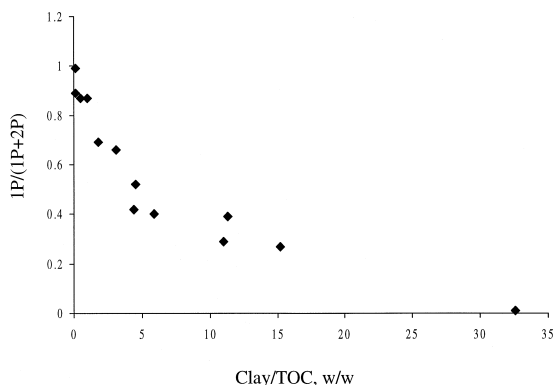


Fig. 4. Calculated IP/(IP+2P) ratios in samples from the Kimberley Clay Formation as a function of clay/TOC ratio.

support an origin of most prist-2-ene in pyrolysates from clay-catalyzed isomerization of prist-1-ene, as proposed by Regtop et al. (1986).

3.4. Sequential chemical degradation experiments

It is clear from the above results that prist-2-ene can be formed by isomerization of prist-1-ene, which contrasts with Höld et al. (1998b) and Koopmans et al. (1999), who proposed different precursors for prist-1-ene and prist-2-ene. How prist-1-ene is formed and from what precursor remains uncertain, although it has been proposed that tocopherol is the main precursor of prist-1-ene (Goossens et al., 1984, 1988).

In an attempt to resolve this issue, we performed flash pyrolysis on an isolated Monterey kerogen (KG-1) after saponification. The pyrolysate still contains prist-1-ene, small amounts of prist-2-ene and one of their alleged precursors, α - or γ -tocopherol (Fig. 5a and b; Goossens et al., 1984). Upon HI/LiAlH₄ treatment (which cleaves ether bonds) of saponified Monterey kerogen, prist-1-ene and 2,6,10-trimethylundec-1-ene as well as α - and γ -tocopherol nearly disappeared from the residue pyrolysate, while prist-2-ene and 2,6,10-trimethylundec-2-ene significantly increased (Fig. 5c; Höld et al., 1998b). Since bound tocopherols can thermally generate prist-1-ene via a Retro-Diels–Alder reaction (Goossens et al., 1984), ether-bound tocopherols are a likely major source of prist-1-ene in kerogen pyrolysates, at least in the Monterey Formation. However, tocopherols were not among the products re-

leased after HI treatment of the Monterey kerogen, possibly because the HI treatment effects the internal ether bond in the tocopherol molecule as well. Intriguingly, RuO₄ oxidation of a related Monterey kerogen (KG-2) released three isoprenoid compounds (Fig. 6). These three isoprenoid compounds

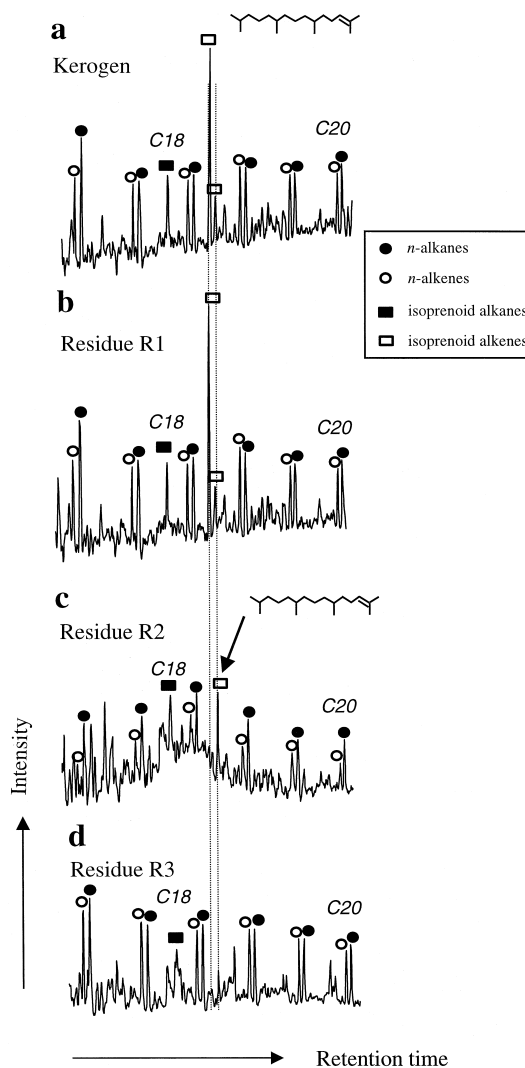


Fig. 5. Partial FID traces of the Monterey pyrolysate (Curie temperature 610°C) of (a) kerogen, (b) the residue R₁ after alkaline hydrolysis, (c) the residue R₂ after ether bond cleavage, (d) the residue R₃ after desulfurization. Filled and open circles indicate homologous series of *n*-alkanes and *n*-alk-1-enes, respectively. Their number of carbon atoms is indicated with italic numbers. Filled and open squares indicate pseudo-homologous series of isoprenoid alkanes and alk-1-enes, respectively.

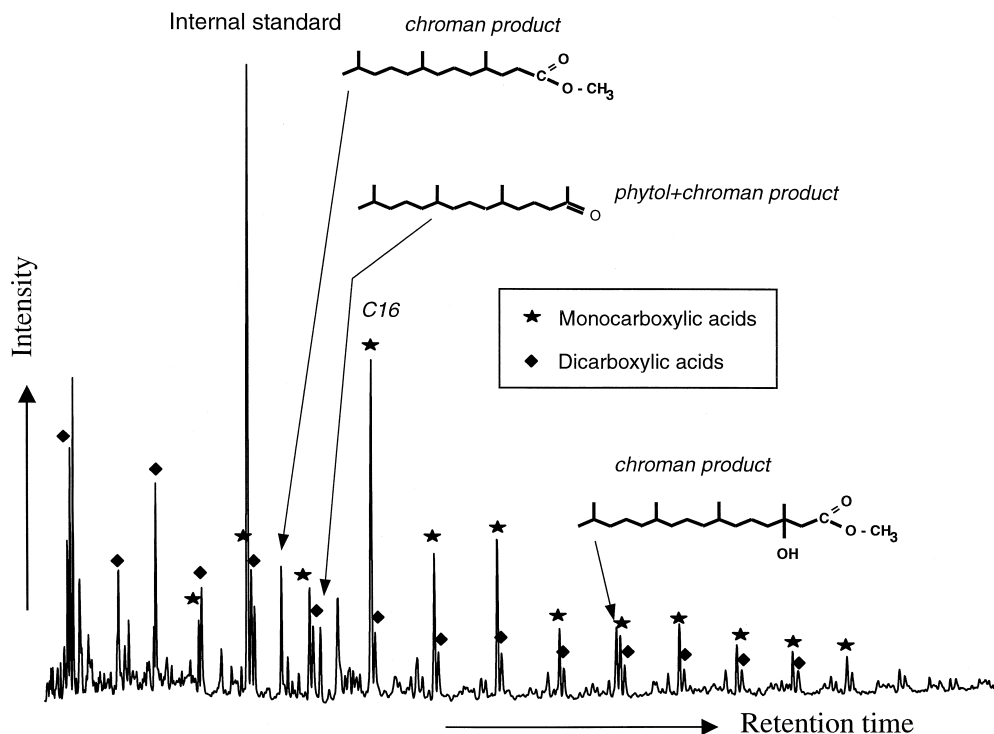


Fig. 6. FID trace of the extract released upon RuO_4 oxidation of a Monterey kerogen (KG-2). Stars indicate methylated derivatives of linear monocarboxylic acids. Diamonds indicate methylated derivatives of linear dicarboxylic acids. Their number of carbon atoms is indicated with italic numbers.

are also generated by oxidation of 2-methyl-2-(4,8,12-trimethyldecyl)chroman, whereas only 6,10,14-trimethylpentadecan-2-one is generated upon oxidation of phytol (Schouten et al., unpublished results). These results provide additional evidence for the presence of bound chromans/tocopherols in Monterey kerogen.

As described above, HI/LiAlH_4 treatment resulted in the disappearance of the O-bound precursor of prist-1-ene from the residue pyrolysate. However, an unknown precursor was still present because prist-2-ene was generated upon pyrolysis. Since clay minerals were no longer present, one would expect primarily prist-1-ene rather than the observed prist-2-ene. The same phenomenon was observed in samples from the Vena del Gesso (Gelin et al., personal communication) and the Green River Formation (Koopmans et al., 1999), i.e., large amounts of prist-2-ene compared to prist-1-ene occurred in the pyrolysate of the residue after HI treatment of the

kerogen. A likely explanation for this phenomenon is that an isomerization reaction takes place by the transfer of protons originating from incompletely removed HI, thereby generating prist-2-ene. A similar observation was made upon isolation of the Mulhouse kerogen with HCl/HF , where transfer of protons from incompletely removed acid probably caused a relatively low $1\text{P}/(1\text{P} + 2\text{P})$ ratio (Tables 1 and 2). This latter isomerization effect is probably smaller compared to the isomerization effect due to HI treatment, since HI is a much stronger acid than HCl and HF and may be more difficult to remove. After desulphurization of the kerogen with Ni_2B , no compounds with a pristane carbon skeleton were observed in the pyrolysate anymore (Fig. 5d). This indicates that the unknown precursor was probably removed and may have been bound by S- or S- and O linkages.

The chemical degradation experiments in this study, therefore, indicate the presence of at least two

different pristene precursors in sulfur-rich kerogens, an ether-bound precursor (probably tocopherol) and an unknown sulfur- or ether- and sulfur-bound precursor. However, in S-poor kerogens, tocopherols may be the predominant precursors. This is supported by the fact that the Pristane Formation Index, based upon the release of pristane from kerogen-bound tocopherols, is a reliable indicator for thermal maturity for most kerogens (Goossens et al., 1988).

4. Conclusions

(1) The double-bond isomerization of prist-1-ene to form prist-2-ene during pyrolysis depends on the amount of protons available for the formation of the intermediate carbonium ion which can originate from untreated aluminosilicates (e.g. montmorillonite, kaolinite), the acid used in decarbonation (HCl), or kerogen degradation (HI).

(2) The extent of isomerization depends on the amount of clay minerals vs. TOC and whether the clay minerals are activated by a proton donor (e.g. HCl).

(3) The clay minerals that act as isomerization catalysts are primarily montmorillonite and, to a lesser extent, kaolinite.

(4) At least two precursors in the S-rich kerogens investigated can generate pristenes during pyrolysis: an ether-bound precursor, probably tocopherols, and an unknown sulfur-bound precursor. In other (S-poor) kerogens, tocopherols are probably the only precursors for pristenes.

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